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Desorption Electrospray Ionisation Mass Spectrometry of Stabilised Polyesters Reveals Activation of Hindered Amine Light Stabilisers

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Abstract

The use of hindered amine light stabilizers (HALS) to retard thermo- and photo-degradation of polymers has become increasingly common. Proposed mechanisms of polymer stabilisation involve significant changes to the HALS chemical structure; however, reports of the characterisation of these modified chemical species are limited. To better understand the fate of HALS and determine their *in situ* modifications, desorption electrospray ionisation mass spectrometry (DESI-MS) was employed to characterise ten commercially available HALS present in polyester-based coil coatings. TINUVIN® 770, 292, 144, 123, 152, and NOR371; HOSTAVIN® 3052, 3055, 3050, and 3058 were separately formulated with a pigmented, thermosetting polyester resin, cured on metal at 262 °C and analysed directly by DESI-MS. High-level *ab initio* molecular orbital theory calculations were also undertaken to aid the mechanistic interpretation of the results. For HALS containing *N*-substituted piperidines (*i.e.,* *N*-CH_3, *N*-C(O)CH_3, and *N*-OR) a secondary piperidine (*N*-H) analogue was detected in all cases. The formation of these intermediates can be explained either through hydrogen abstraction based mechanisms or direct *N*–OR homolysis with the former dominant under normal service temperatures (*ca*. 25-80 °C), and the latter potentially becoming competitive under the high temperatures associated with curing (*ca*. 230-260 °C).

Keywords

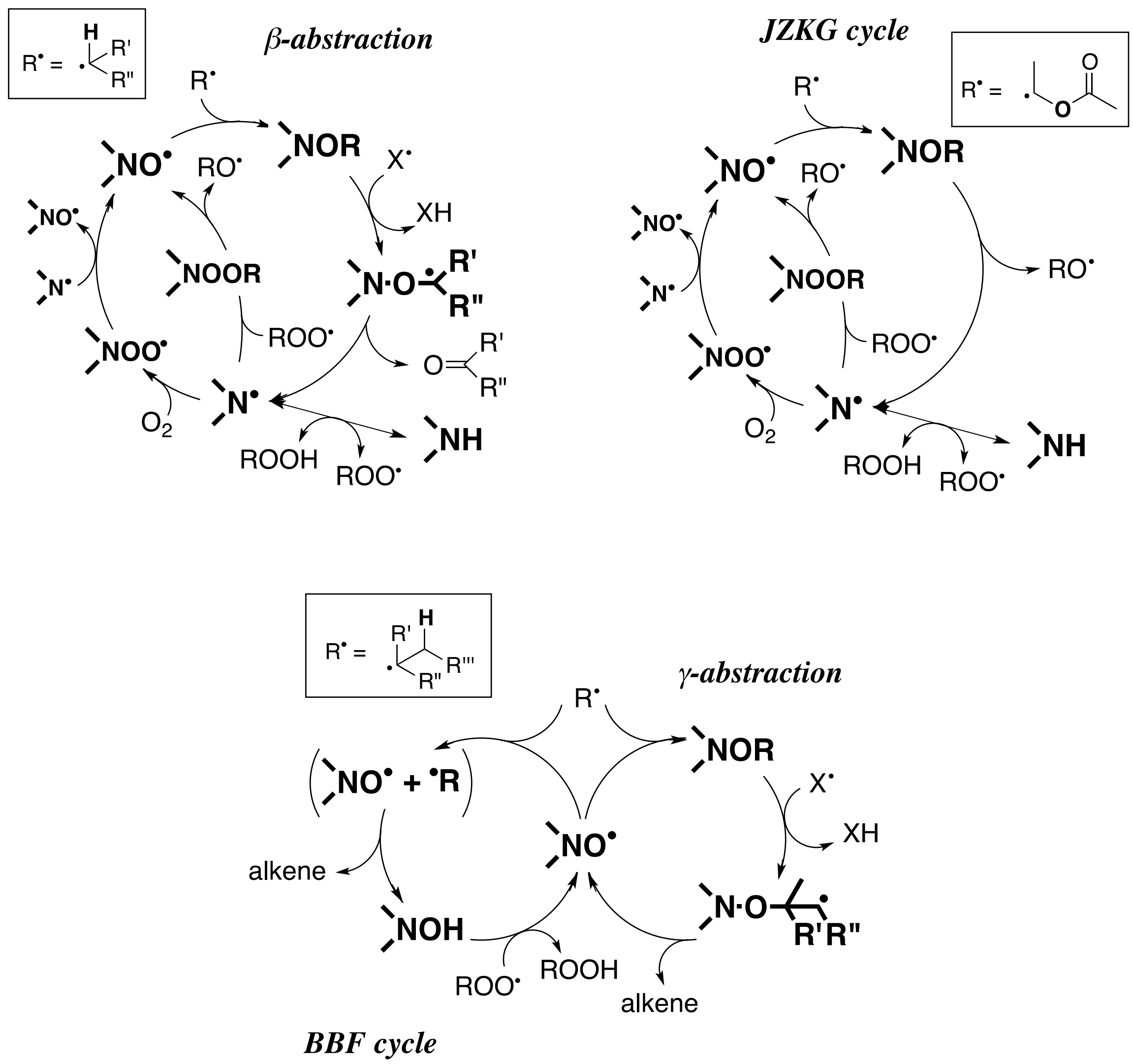
Mass spectrometry, polyester, hindered amine light stabiliser, mechanism

Introduction

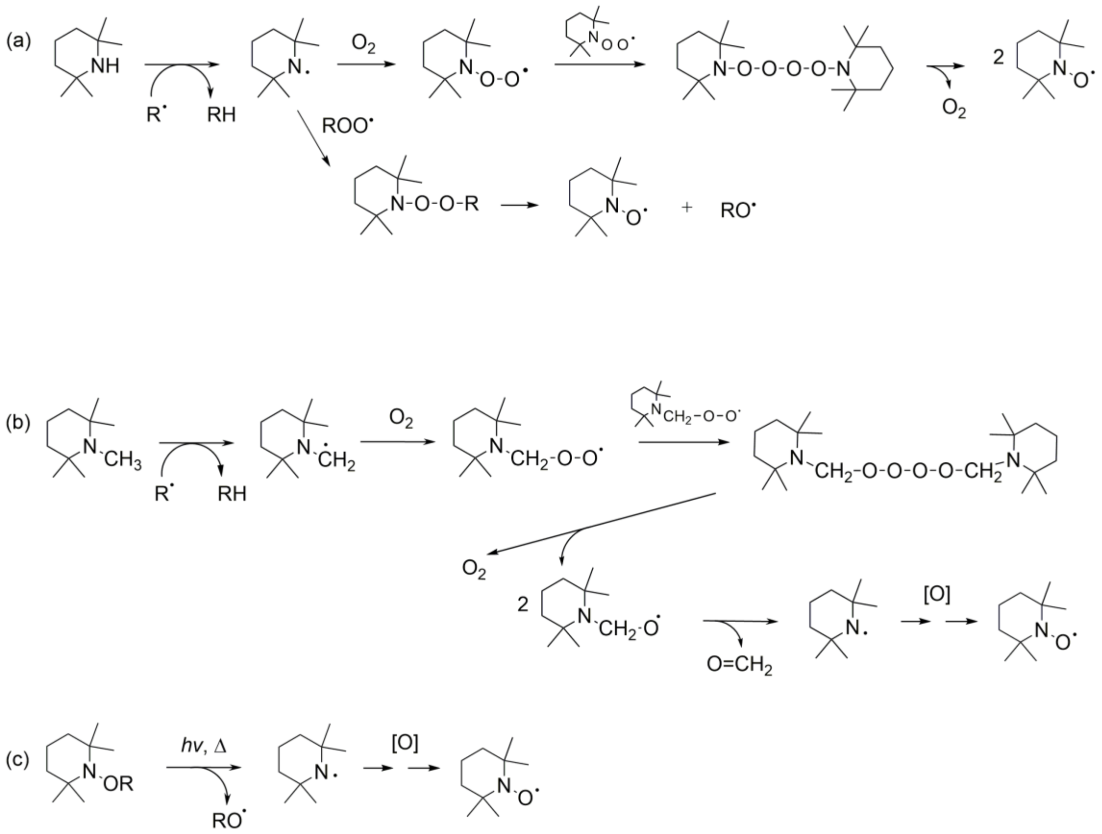
Many contemporary synthetic polymers require one or more chemical additives to enable them to carry out an intended function effectively. In the surface coatings sector, for example, the polymer provides the binder for a coating and the pigment the aesthetic, but several types of functional additive are also required for a successful formulation. Thus, additives for rheology control, pigment dispersion, wetting, levelling *etc*. are commonly found in a wide range of coating types. Many of these additives have performed the role for which they were designed after the coating has been applied and dried (or cured). However, additives such as UV-absorbers and the so-called hindered amine light stabilisers (HALS) function during the service lifetime of the coating, and their role is to retard the degradation of the coating caused by the continuous barrage of environmental insults which can lead to compromised performance. HALS have been commonly employed in automotive, wood and plastic coatings for decades [1-6], and the last 10 years has seen an increase in their use in coil coatings. Coil coating is a large-scale process for continuous painting of steel strip at speeds of up to 200 $m.min^{-1}$. The pre-painted steel strip thus produced is used in many different applications, the most severe of which is that employed in roofing, where the product needs to retain good appearance in service for 20 years or more. In turn, this places considerable emphasis on HALS to preserve the aesthetic and functional roles of the surface coating by protecting the polymer from degradation. Therefore, the optimisation of these compounds for such applications is of considerable interest; however, this first requires a thorough understanding of the chemistry associated with the protection of polymers by HALS. It is widely believed that HALS operate as chain-breaking antioxidants, undergoing oxidation of a heterocyclic amine to an aminoxyl radical, although the exact mechanisms by which this occurs is still the subject of investigation. It is this persistent aminoxyl radical that acts as a free radical scavenging intermediate and is thought to be involved in converting deleterious free radicals to less harmful even-electron species. As a result, regeneration of the aminoxyl radical occurs, theoretically allowing the process to repeat indefinitely [7-16]. However, empirical evidence suggests that the protective effects are finite and the use of HALS only delays the failure of polymers rather than denying it. Thus stabilisation *via* HALS must consist of a more complex mechanism.

Recently, Hodgson and Coote [17] deployed high-level quantum chemical calculations to compare the kinetics and thermodynamics of a dozen different reaction pathways comprising over 30 individual reactions. This allowed critical assessment of all the previously suggested mechanisms. Hodgson and Coote's analysis shows most of the mechanisms are kinetically and/or thermodynamically disfavoured with even the most favourable mechanism subject to a large activation barrier (~150 kJ mol^{-1}) for one of its key steps [17]. Furthermore, this mechanism does not account for previous experimental observations that suggest *in situ* conversion of an alkoxyamine functional group (*N*-OR) – analogous to an intermediate expected in an aminoxyl radical regenerative mechanism – to a secondary piperidine (*N*-H). This phenomenon was observed following high temperature curing of the polymer-based coating as well as subsequent exposure of the coating to accelerated weathering conditions [18]. Concordant results have also been reported in the literature for the decomposition of 2,2,6,6-tetramethylpiperidine-based HALS under thermo- and photo-oxidative conditions [19, 20].

The inability to account for these observations by any of the commonly accepted mechanisms sparked a follow-up computational study by Coote and co-workers in which a new mechanism was proposed to explain the catalytic free radical scavenging by HALS in organic materials [21]. In this proposed cycle, an aminoxyl radical traps a carbon-centred substrate radical to form an alkoxyamine, and is then regenerated in a cascade of reactions triggered by hydrogen atom abstraction at the β-position of the alkoxyamine via another substrate-derived radical. The resulting species rapidly undergoes β-scission to form a ketone and an aminyl radical, and the aminyl radical can then either be oxidised back to the aminoxyl or abstract a hydrogen atom to form a secondary amine (see Scheme 1) [21]. This secondary amine can re-enter the catalytic cycle *via* hydrogen abstraction with any number of substrate-derived radicals, depending on the relative concentrations. In species that degrade *via* tertiary substrate-derived radicals, for which *β*-hydrogen abstraction is not possible, alternative catalytic cycles were proposed depending on whether direct *N*–OR homolysis was possible or not (see Scheme 1) [21]. These were shown to be much less energetically favourable, thus providing an explanation for the lower catalytic efficiency of HALS in such cases. The activation of the HALS was also studied, and shown to vary depending on whether the starting material was a secondary amine, the *N*-methyl derivative or an alkoxyamine (see Scheme 2) [21].



Scheme 1. Regeneration mechanisms for the catalytic protection of organic materials against autooxidation, as identified in Ref [21]. The energetically preferred cycle for most combinations of aliphatic HALS is the *β*-abstraction. In cases where the degrading substrate radical does not contain an abstractable hydrogen, *γ*-abstraction or the JZKG cycle operate instead, the latter requiring preferred N–OR homolysis.



Scheme 2. HALS activation mechanisms for (a) secondary amines, (b) *N*-methyl amines, (c) alkoxyamines, as identified in Ref [21].

This recent computational study, supported by previous experimental observations, thus suggests there may be other major repositories for HALS outside of the traditional regenerative cycles. Therefore, the aim of this work is to investigate the changing functionalisation of the piperidine nitrogen by characterising the structural changes occurring to a range of HALS compounds in polymer-based coatings. In this study, the focus is on the changes that occur specifically during curing under typical curing conditions and what impact they have on the chemical structure of the HALS. This in turn has implications for its activation (and hence protective action) under subsequent in-service conditions.

We have employed desorption electrospray ionisation mass spectrometry (DESI-MS) for the analysis of ten polyester-based coil coatings each containing a different commercially available HALS compounds (Figure 1). The compounds selected are structurally diverse providing the four most common piperidinyl moieties (*i.e.*, *N*-H, *N*-CH_3, *N*-C(O)CH_3, and *N*-OR). It is noted that basic HALS (*N*-H, *N*-CH_3; pK_a 7.5-9.7) are not typically used in acid-catalysed, cross-linked polyesters as they interfere with the curing process. They are included here however, to provide insight into the changes in functionality of HALS that are associated with curing conditions. HALS compounds retained within the coating after cure are detected *in situ*, characterised by tandem mass spectrometry and the results are rationalised with the aid of high-level electronic structure calculations.

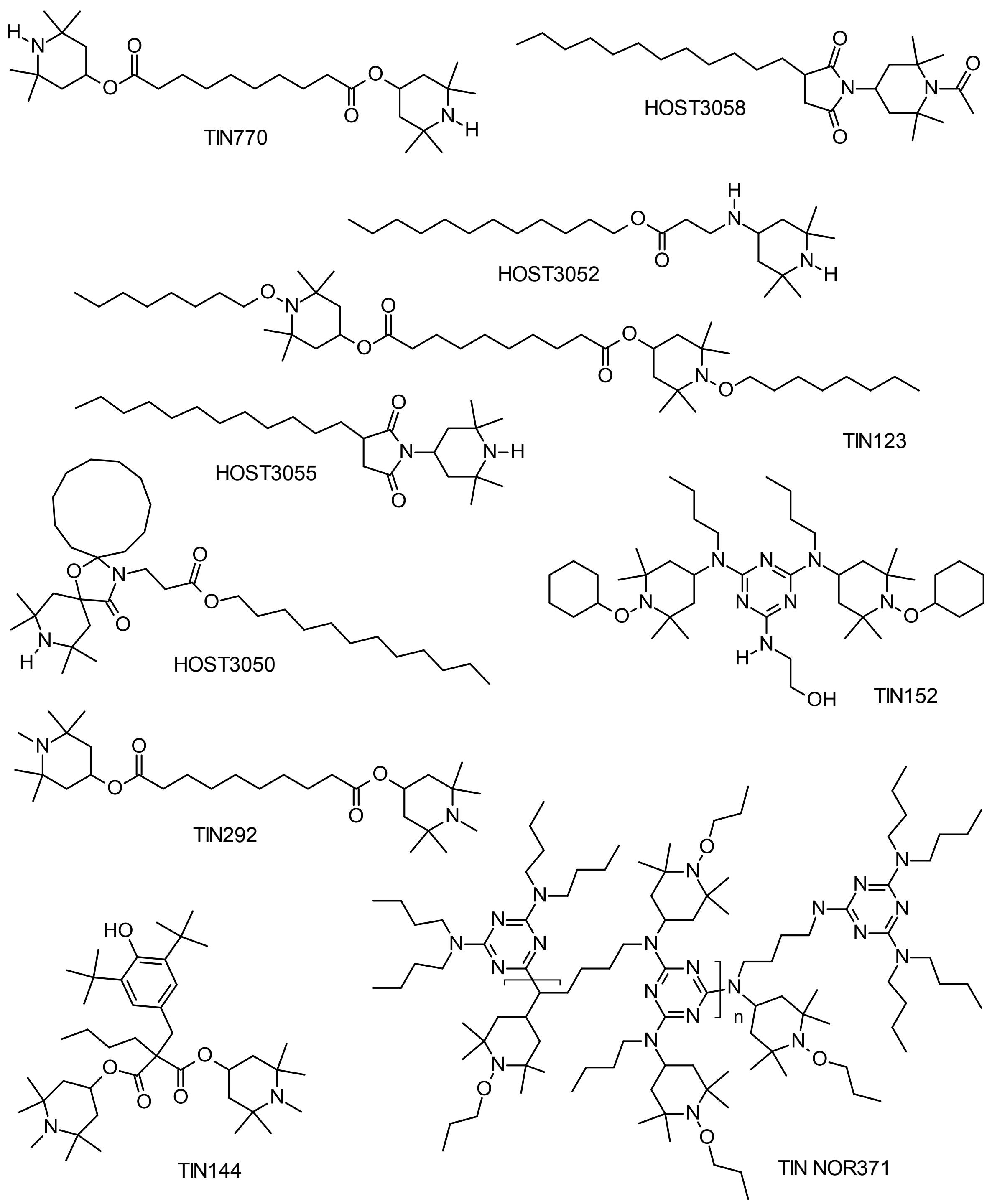


Figure 1. The structures of the ten commercially available hindered amine light stabilisers (HALS) used in this study.

Methods

Reagents

Methanol and formic acid were HPLC grade (Crown Scientific, Minto NSW, Australia). Chloroform and acetone were AR grade (Crown Scientific, Minto NSW, Australia). The hindered amine light stabilisers; bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (TIN770), bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate (TIN292), bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl)butylmalonate (TIN144), bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidinyl) sebacate (TIN123), 2,4-bis(*N*-butyl-*N*-(1-cyclohexyloxy-2,2,6,6-tetramethyl-4-piperidinyl)amino)-6-(2-hydroxyethylamine)-1,3,5-triazine (TIN152), and oligomers based on *N*-2-butyl-*N*-2-*N*-4-bis(2,2,6,6-tetramethyl-1-propoxy-4-piperidyl)-*N*4-[5-(2,2,6,6-tetramethyl-1-propoxy-4-piperidyl)pentyl]-1,3,5-triazine-2,4-diamine (TIN NOR371) were supplied by Ciba Specialty Chemicals (Basel, Switzerland) now BASF (Ludwigshafen, Germany) and were used without purification. The hindered amine light stabilisers; *β*-alanine-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-dodecyl ester and *β*-alanine-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-tetradecyl ester (HOST3052), 2-dodecyl-*N*-(2,2,6,6-tetramethyl-4-piperidinyl) succinimide (HOST3055), 7-oxa-3,20-diazadispiro[5.1.11.2]heneicosane-20-propanoic acid-2,2,4,4-tetramethyl-21-oxo-dodecyl ester (HOST3050), and 2-dodecyl-*N*-(1-acetyl-2,2,6,6-tetramethyl-4-piperidinyl) succinimide (HOST3058) were supplied by Clariant (Huningue, France) and were used without purification.

Preparation of coated steel panels

The topcoat paint system employed in these studies was a solvent-borne, polyester topcoat paint incorporating a melamine-formaldehyde cross-linker, acid catalysed and formulated for coil paint-line application. This sample was formulated as a wet paint mixture and found to be 45% w/w resin solids by thermogravimetry (Perkin-Elmer TGA 7). The bulk paint sample was sub-sampled and weighed into small containers providing an identical matrix for comparative HALS analysis. The paints were formulated to give a final concentration of each HALS that resulted in a molar equivalent of an aminoxyl radical precursor (*N*-R) to that of TIN123 added at 2% w/w of total resin solids. The coated samples that were used in this project were laboratory prepared upon a pre-primed (commercial chromated epoxy primer) panels of a 0.6 mm thick GALVALUME®-type steel substrate. Wet paint was applied using a #28 wire-wound draw-down bar then cured for 55 seconds in a fan forced oven set at 262 °C. Under these conditions, 55 seconds equates to a peak metal temperature of 232 °C.

Desorption electrospray ionisation-mass spectrometry (DESI-MS)

Metal panels with a thermosetting polyester-based coating were cut into small sections (7 × 25 mm) using hydraulic shears and affixed to a glass microscope slide. The samples were then placed in an enclosed atmosphere of acetone vapour for 5 minutes prior to DESI-MS analysis in order to swell the polymer, mobilising the HALS compounds to the surface of the substrate. Positive ion DESI-MS spectra were acquired using an Omni Spray® ion source (Prosolia Inc., Indianapolis, USA) coupled to a LTQ 2-dimensional (2-D) linear ion trap mass spectrometer (Thermo Fisher Scientific, San Jose, USA) with Xcalibur Tune Plus 2.0 software (Thermo Fisher Scientific, San Jose, USA) used for spectral acquisition. The DESI spray solvent, methanol acidified with 0.1 % formic acid (v/v), was delivered at a flow rate of 10 μL.min^{-1} with a 5 kV voltage applied to the spray emitter. MS instrument parameters were as follows: nebulizing gas pressure, 80 psi; capillary voltage, 30 V; capillary temperature, 200 °C; sample holder velocity, 200 μm.s^{-1}; ion injection time, 30 ms; microscans, 2; with automatic gain control switched off. DESI-MS/MS spectra were acquired on the LTQ by subjecting trapped ions to pulsed-Q dissociation (PQD) [22], allowing detection of subsequent product ions below the conventional low mass cut-off of the ion-trap mass spectrometer. Typical experimental parameters for PQD were: isolation width, 1.5 Da; ion injection time, 50 ms; microscans, 2; collision energy 25-37 arbitrary units (See Table 1). Baseline subtraction was not used and mass spectra were averaged over a minimum of fifty scans. All mass spectra were normalised to the most abundant ion in the spectrum.

Computational procedures

Standard ab initio molecular orbital theory and density functional theory calculations were carried out using Gaussian 09 [23] and Molpro 2009.1 [24]. Calculations on radicals were performed with an unrestricted wave function except in cases designated with an "R" prefix where a restricted open-shell wave function was used. For all species, either full systematic conformational searches (at a resolution of 120°) or, for more complex systems, energy-directed tree searches [25] were carried out to ensure global, and not merely local minima were located. Geometries of all species were fully optimized at the B3-LYP/6-31G(d) level of theory and frequencies were also calculated at this level and scaled by recommended scale factors [26]. Accurate energies for all species were then calculated using double-layer ONIOM-type method. The core layer was calculated using the high-level composite *ab initio* G3(MP2)-RAD [26] method, whereas either R(O)MP2/6-311+G(3df,2p) (in homolysis studies) or M06-2X/6-311+G(3df,2p) (in activation mechanism modelling) method was applied to the full system. Entropies and thermal corrections at 25, 80 and 260 °C were calculated using standard textbook formulae [27] for the statistical thermodynamics of an ideal gas under the harmonic oscillator approximation in conjunction with the optimized geometries and scaled frequencies. Reaction Gibbs free energies were computed using Gibbs fundamental equation.

Free energies of solvation in toluene were calculated using the polarized continuum model PCM-UAKS [28]at the B3LYP/6-31G(d) level of theory. Free energies of each species in solution at 298.15 K were calculated as the sum of the corresponding gas-phase free energy and the obtained free energy of solvation. The phase change correction term ΔnRT(lnV) was added to the resulting free energies for each species.

Results and Discussion

Positive ion DESI-MS of polyester-based coatings containing HALS

The ambient ionisation technique desorption electrospray ionisation-mass spectrometry (DESI-MS) has been employed herein for the detection of polymer additives in polyester-based coil coatings. To allow detection of HALS from thermoset coatings by DESI-MS a simple, non-destructive sample preparation method was developed by our research group that exposes the coatings to acetone vapour, partially swelling the coating and mobilising the additives to the surface for detection [18]. The samples were then positioned in a geometry that allowed a continuous flow of charged, pneumatically-assisted microdroplets from the DESI source to impact and wet the sample surface. HALS extracted into the localised solvent reservoir became entrained in secondary droplets released from the surface and upon drying resulted in gas phase ions that were detected by mass spectrometry. Positive ion DESI-MS spectra of polyester-based coatings containing each HALS separately, pre-treated in an acetone vapour bath for 5 mins were recorded using a linear ion-trap mass spectrometer and are shown in Figures 2-5. The spectra yield intense signals corresponding to the $[M+H]^+$ ion for each HALS resulting from protonation of the heterocyclic nitrogen or other basic sites present in the molecule. Structural confirmation of each HALS was achieved by tandem mass spectrometry – employing pulsed-Q dissociation (PQD) – of the $[M+H]^+$ ion with the resulting product ions reported in Table 1. PQD is a form of resonance excitation that allows ions of a selected *m/z* ratio to be isolated and activated to induce dissociation to product ions. The dissociation occurs as resonance activation of selected ions increases their kinetic energy, which is converted to internal energy through repeated collisions with buffer gas molecules present in the ion trap. PQD differs from conventional collision-induced dissociation (CID) methods as it allows the observation of low *m/z* fragments that are usually excluded from CID spectra and also helps to access higher energy dissociation channels [22]. Fragmentation mechanisms and resulting product ions of HOST3055, TIN292, HOST3058-TIN152 have been characterised previously using electrospray ionisation tandem mass spectrometry (ESI-MS/MS) and the product ions reported here are congruent with that study [29]. For those HALS not previously characterised by comparable mass spectrometric techniques (TIN770, HOST3052, HOST3050, TIN144 and TIN NOR371), structures were inferred by a comparative analysis of their product ions arising from PQD (Table 1).

Table 1. A summary of all DESI-MS/MS data acquired with a linear ion trap mass spectrometer following pulsed-Q dissociation (PQD) of selected precursor ions.

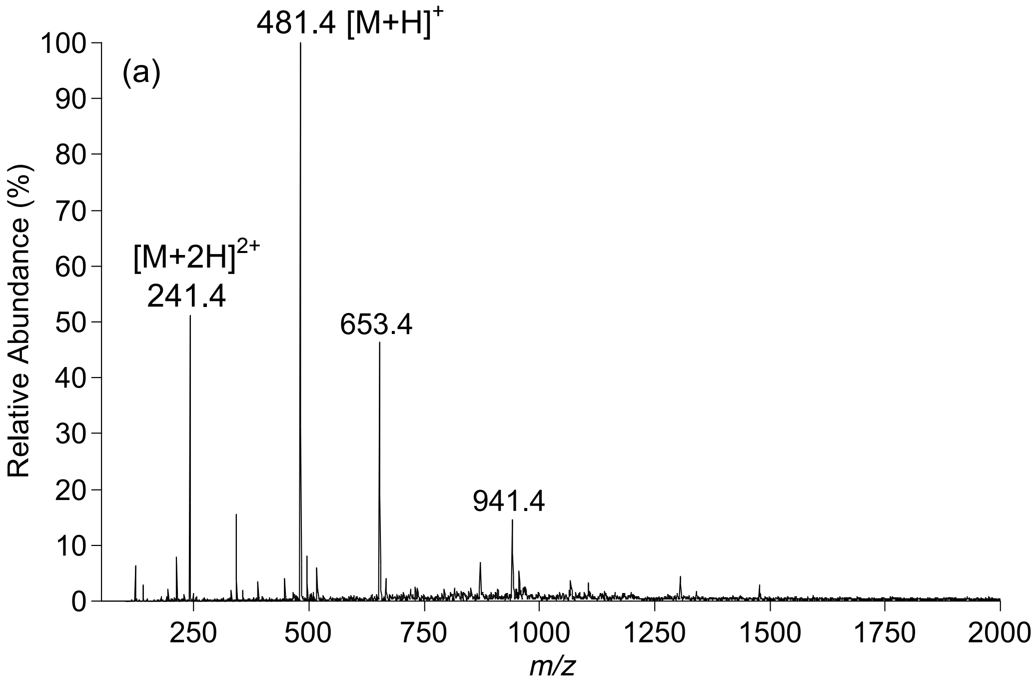
Formulated HALS	MS Acquisition Sequence[a]	Product ions *m/z* (% abundance of base peak)
TIN770	MS^2 481.4 (PQD @ 27)	464.6 (4.94), 463.6 (1.27), 399.1 (3.44), 342.3 (100.00), 317.4 (1.17), 140.0 (15.15)
HOST3052	MS^2 425.4 (PQD @ 35)	351.9 (4.47), 324.3 (15.34), 312.3 (33.23), 140.0 (8.32)
	MS^2 397.4 (PQD @ 35)	388.5 (1.60), 284.2 (8.82), 140.1 (11.18)
HOST3055	MS^2 407.4 (PQD @ 35)	334.3 (100.00), 316.3 (4.27), 306.3 (8.23), 288.3 (1.72), 268.2 (4.95), 123.1 (9.29)
HOST3050	MS^2 633.6 (PQD @ 37)	542.5 (2.11), 450.5 (55.03), 434.4 (4.02), 394.3 (18.45), 328.3 (1.72), 180.0 (6.06), 166.1 (2.23), 138.0 (3.07)
	MS^2 605.6 (PQD @ 37)	514.5 (2.29), 422.5 (38.49), 406.4 (3.84), 366.3 (15.56), 328.3 (1.60), 180.0 (4.40), 166.1 (2.23), 138.1 (2.31)
TIN292	MS^2 509.5 (PQD @ 27)	491.4 (1.04), 478.4 (23.88), 356.3 (100.00), 154.1 (8.04)
	MS^2 495.5 (PQD @ 30)	477.4 (4.14), 464.4 (36.55), 463.2 (4.45), 437.1 (2.72), 435.3 (2.96), 363.3 (2.52), 356.3 (100.00), 342.3 (83.49), 154.0 (9.43)

TIN144	MS^2 685.5 (PQD @ 27)	654.5 (1.92), 532.4 (100.00), 466.1 (1.66), 429.1 (3.34), 341.0 (1.90), 219.1 (1.41)
	MS^2 671.5 (PQD @ 26)	532.4 (41.78), 518.3 (1.66)
HOST3058	MS^2 449.4 (PQD @ 35)	389.4 (1.88), 334.3 (37.89), 235.1 (11.74)
	MS^2 407.4 (PQD @ 35)	334.3 (100.00), 316.3 (3.98), 306.3 (8.17), 288.3 (1.26), 268.2 (4.14), 123.1 (7.95)
TIN123	MS^2 737.5 (PQD @ 25)	625.4 (12.97), 624.4 (6.51), 607.5 (3.13), 593.4 (3.54), 496.4 (100.00), 470.3 (6.04), 342.3 (2.04), 268.1 (1.45)
	MS^2 609.5 (PQD @ 25)	573.2 (5.21), 496.5 (18.80), 496.1 (11.82), 481.5 (3.03), 477.5 (10.11), 470.0 (6.29), 342.1 (30.45), 243.0 (6.50)
TIN152	MS^2 769.5 (PQD @ 30)	686.5 (14.05), 655.4 (6.60), 588.4 (74.51), 558.4 (29.25), 532.4 (100.00), 449.4 (3.46), 295.2 (6.43), 238.1 (10.04)
	MS^2 757.5 (PQD @ 28)	725.0 (2.26), 674.6 (5.90), 576.4 (22.02), 546.5 (4.79), 520.4 (37.55), 283.2 (3.72), 238.0 (1.97)
	MS^2 671.5 (PQD @ 30)	588.6 (1.43), 558.2 (2.12), 532.4 (100.00), 472.4 (1.44), 460.3 (3.86), 434.4 (19.90), 376.2 (1.24), 295.3 (5.22), 238.1 (2.70)

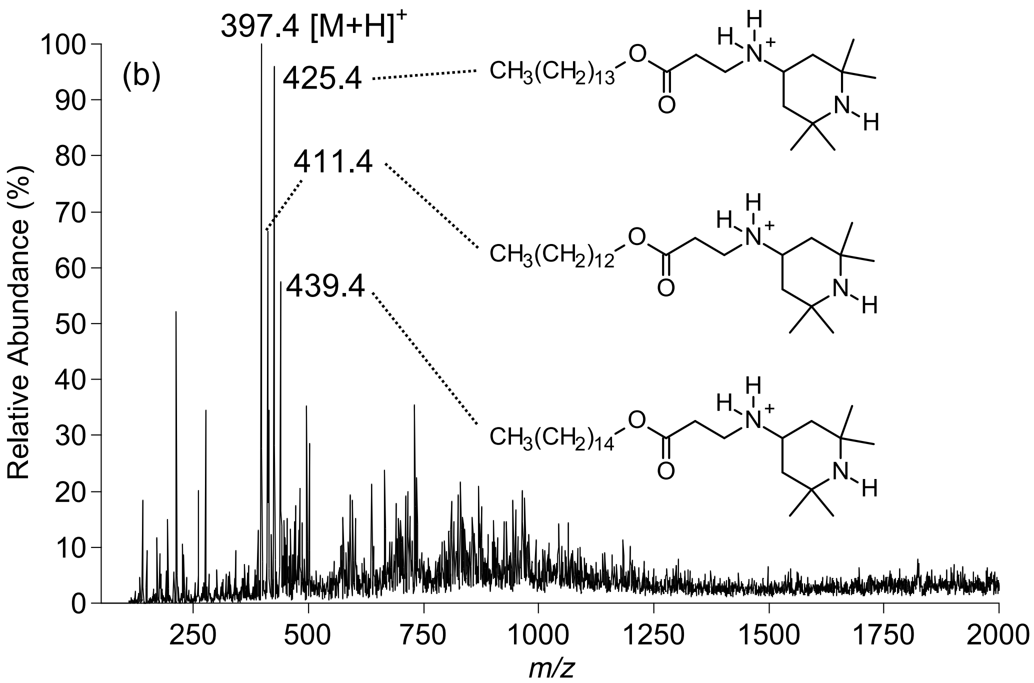
	MS^2 659.5 (PQD @ 26)	627.3 (7.52), 595.2 (9.54), 545.2 (7.81), 520.6 (31.01), 520.2 (18.62), 422.1 (11.83), 283.1 (10.17)
TIN NOR371	MS^2 1022.8 (PQD @ 35)	979.8 (78.26), 851.8 (12.59), 825.8 (100.00), 783.9 (1.56), 461.5 (1.63), 431.4 (1.49), 377.4 (1.88), 351.5 (1.26)
	MS^2 964.8 (PQD @ 35)	851.8 (7.30), 825.8 (100.00), 809.8 (1.35), 783.8 (12.22), 727.8 (2.09)

DESI-MS characterisation of TIN770, HOST3052, HOST3055, and HOST3050 (*N*-H)

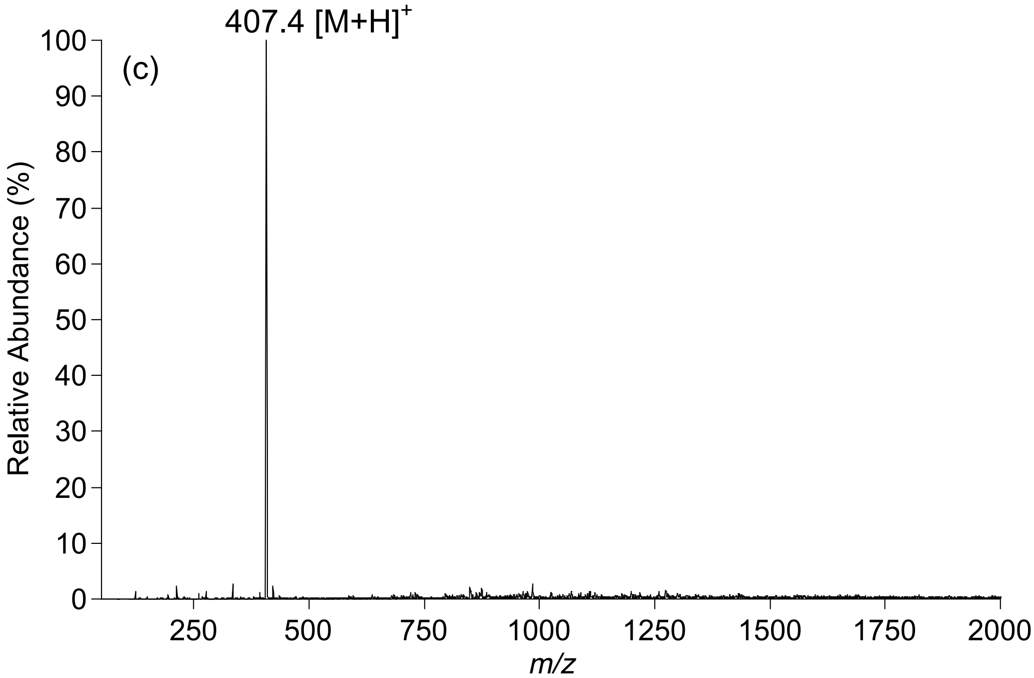
Figures 2(a-d) show DESI-MS spectra of four structurally diverse HALS (TIN770, HOST3052, HOST3055, and HOST3050) each containing 2,2,6,6-tetramethylpiperidine moieties unsubstituted at the nitrogen (*N*-H). All four spectra demonstrate an excellent signal-to-noise ratio for the peak corresponding to the $[M+H]^+$ ion except Figure 2(b). The poor signal-to-noise ratio in this spectrum is due to HOST3052 being supplied as a mixture of up to five different structural analogues of the compound listed by the manufacturer (Figure 2b). Spreading the peak intensity over four or more channels effectively reduces the signal-to-noise ratio and the contrast is easily observed by comparison with Figure 2(c) as HOST3055 is present as only one ionisable species. The remaining unassigned peaks in Figure 2(b) were confirmed to be chemical noise present in all ten DESI-MS spectra by comparison with the baseline of the spectrum in Figure 2(c) at 20 times magnification, *i.e*., the magnified baseline of Figure 2(c) was observed to be identical to the baseline of Figure 2(b).


481.4 [M+H]+
(a)
[M+2H]2+
241.4
653.4
941.4
Relative Abundance (%)
m/z

267


397.4 [M+H]+
(b)
425.4
411.4
439.4
CH3(CH2)13
CH3(CH2)12
CH3(CH2)14
Relative Abundance (%)
m/z

268


407.4 [M+H]+
(c)
Relative Abundance (%)
100
90
80
70
60
50
40
30
20
10
0
250
500
750
1000
1250
1500
1750
2000
m/z

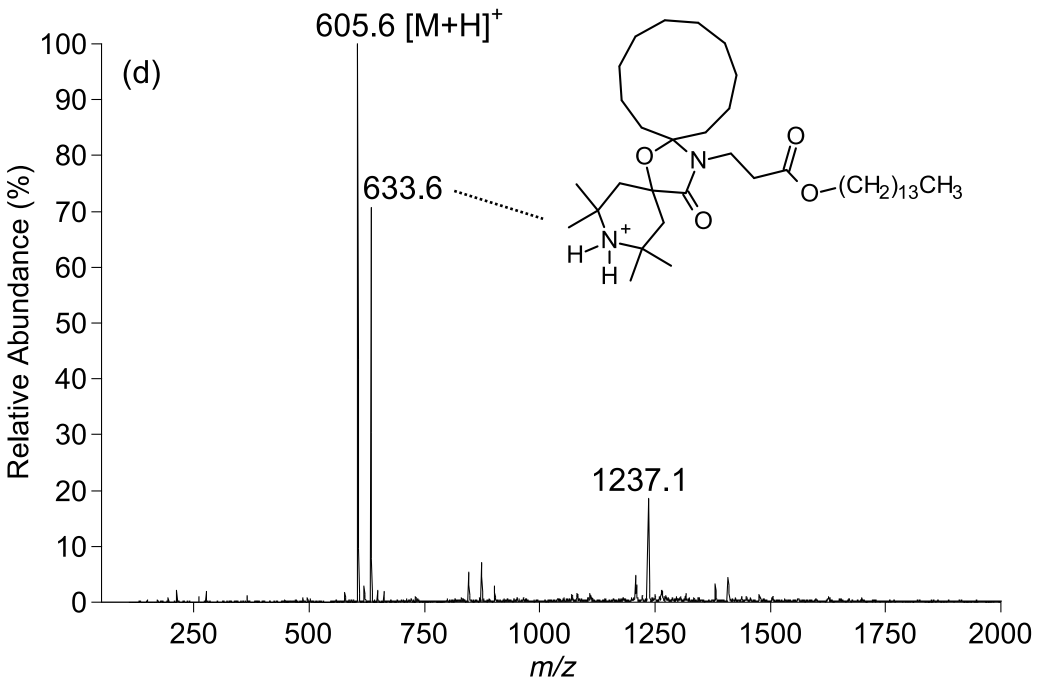
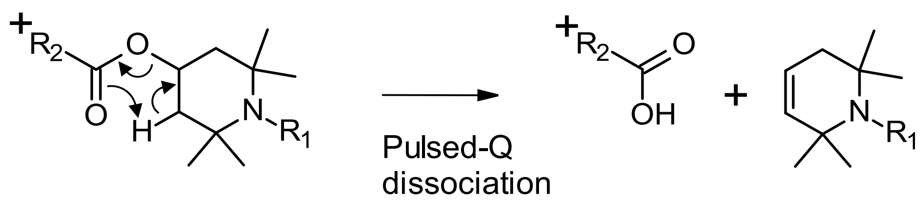

605.6 [M+H]+
(d)
633.6
1237.1
O
N
O
O
O–(CH2)13CH3
H
N+
H
Relative Abundance (%)
100
90
80
70
60
50
40
30
20
10
0
250
500
750
1000
1250
1500
1750
2000
m/z

Figure 2(a-d). Positive ion DESI-MS spectra of TIN770, HOST3052, HOST3055, and HOST3050 detected within polyester-based coil coatings after pre-treatment with acetone vapour. Inset – Putative structures for oligomers and synthetic by-products of the precursor HALS compounds present.

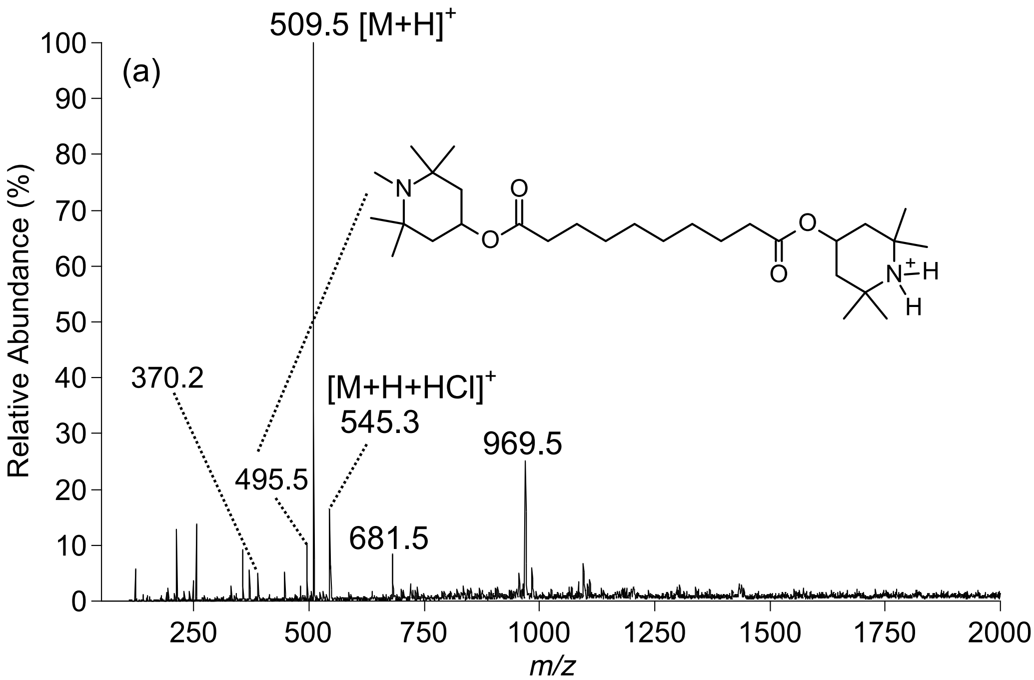
Structural modifications to HALS *in situ* detected by DESI-MS

HALS TIN292 and TIN144 (*N*-CH_3)

Positive ion DESI-MS spectra after pre-treatment of two cured polyester-based coil coatings each containing structurally distinct compounds with two 1,2,2,6,6-pentamethylpiperidine moieties, TIN292 and TIN144, show peaks that are indicative of their respective $[M+H]^+$ ions (Figure 3(a) *m/z* 509.5 and (b) *m/z* 685.5, respectively). These spectra also contain peaks at a mass-to-charge ratio 14 Da lower than the $[M+H]^+$ ions, *m/z* 495.5 and 671.5, respectively. Product ions arising from PQD activation of these species are listed in Table 1 and suggest a high degree of structural homology with their associated $[M+H]^+$ counterparts. The product ion spectra for both *m/z* 495.5 and 671.5 ions show a neutral loss of 153 Da from the precursor ion (Table 1; *m/z* 342.3 and 518.3, respectively); a loss also observed in the product ion spectra for TIN292 (*m/z* 356.3) and TIN144 (*m/z* 532.4). This neutral loss corresponds to the characteristic fragmentation product 1,2,2,6,6-pentamethyl-3*H*-pyridine that arises following elimination of the ester-bound substituent from the 4-position of the piperidine ring (Scheme 3) [29]. This unimolecular dissociation is driven by the non-bonding electron pairs on the ester moiety accepting a proton from the piperidine ring and forming a carbon-carbon double bond with loss of the substituent as a carboxylic acid [29-31]. Furthermore, the neutral loss of 139 Da is also observed from the *m/z* 495.5 and 671.5 precursor ions (Table 1; *m/z* 356.3 and 532.4, respectively) that, by the same rationale proposed for the above neutral loss, would correspond to the loss of 2,2,6,6-tetramethyl-1,3*H*-pyridine. This neutral loss is not observed in the product ion spectra for TIN292 and TIN144. The 14 Da mass difference and the PQD product ion spectra indicate that the ions at *m*/*z* 495.5 and 671.5 are protonated ions of TIN292 and TIN144 after conversion of one 1,2,2,6,6-pentamethylpiperidine moiety to a 2,2,6,6-tetramethylpiperidine (Figure 3a and b; inset). The ions attributed to these compounds are unlikely to be in-source fragments as they are not present in the MS/MS spectra of the $[M+H]^+$ ions for TIN292 and TIN144 and are not present in the authentic HALS samples. Therefore, these ions are proposed to be evidence for *in situ* modifications facilitated by the curing conditions experienced by the polyester-based coil coating.



Scheme 3. Fragmentation of ions derived from ester-linked HALS upon pulsed-Q-dissociation inside the mass spectrometer gives rise to characteristic neutral losses depending on the substitution of the piperidine nitrogen. For example, when $R_1 = CH_3$ a neutral loss of 153 Da is observed and where R1 = H a neutral loss of 19 Da is observed (see entries for TIN292 and TIN770, respectively in Table 1).


509.5 [M+H]+
(a)
Relative Abundance (%)
370.2
495.5
[M+H+HCl]+
545.3
681.5
969.5
m/z
O
N
H
0 10 20 30 40 50 60 70 80 90 100
250 500 750 1000 1250 1500 1750 2000

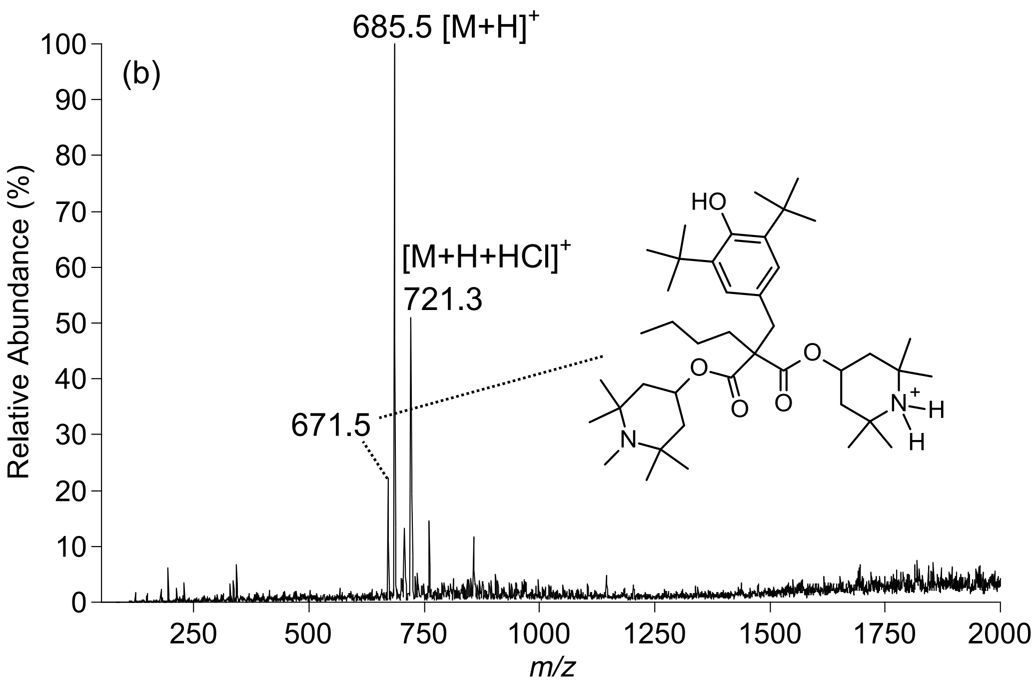

685.5 [M+H]+
(b)
Relative Abundance (%)
[M+H+HCl]+
721.3
671.5
HO
O
N
H
m/z
0 10 20 30 40 50 60 70 80 90 100
250 500 750 1000 1250 1500 1750 2000

Figure 3. (a and b) Positive ion DESI-MS spectra of TIN292 and TIN144 detected within polyester-based coil coatings after pre-treatment with acetone vapour. Inset – Putative structures for the *in situ* structural modifications to the precursor HALS compounds present. The ion at *m/z* 370 in the spectrum shown in (a) corresponds to a monofunctional derivative present in the TIN292 additive.

HALS HOST3058 (*N*-C(O)CH_3)

Positive ion DESI-MS spectrum of a cured polyester-based coil coating containing HOST3058 shows a peak that is indicative of the $[M+H]^+$ ion at *m/z* 449.4 (Figure 4). However, this is one of two cases where the base peak in the spectrum is not at the *m/z* associated with the $[M+H]^+$ ion. In this spectrum, the peak at *m/z* 407.4, 42 Da lower than the molecular mass of HOST3058 is the base peak and is more than 10 times the relative abundance of the ionised HOST3058. This ion represents protonated 2-dodecyl-*N*-(2,2,6,6-tetramethyl-4-piperidinyl) succinimide (Figure 4; inset) and is the synthetic precursor to HOST3058, being present at low levels in the authentic sample (data not shown). Product ions arising from PQD activation of *m/z* 407.4 (Figure 4) are shown in Table 1 with the peak distribution and ion abundances almost identical to the PQD spectrum reported for HOST3055 (Table 1) thus confirming the identity as the secondary piperidine of HOST3058. This ion at *m/z* 407.4 is not present in the MS/MS spectrum for the ion at *m/z* 449.4 and therefore is not attributed to in-source fragmentation caused by instrument conditions, and is detected in higher abundances compared to that found in the authentic sample. This phenomenon may be attributed to either selective depletion of HOST3058 over the secondary piperidine during cure or, as is more likely, an increase in abundance of the secondary piperidine compared to HOST3058 resulting from *in situ N*-deacetylation of the 1-acetyl-2,2,6,6-tetramethylpiperidine moiety to the 2,2,6,6-tetramethylpiperidine. This phenomenon has also been observed by ESI-MS and ESR analyses following solvent extraction of polyester-based coil coatings containing HOST3058 [29].

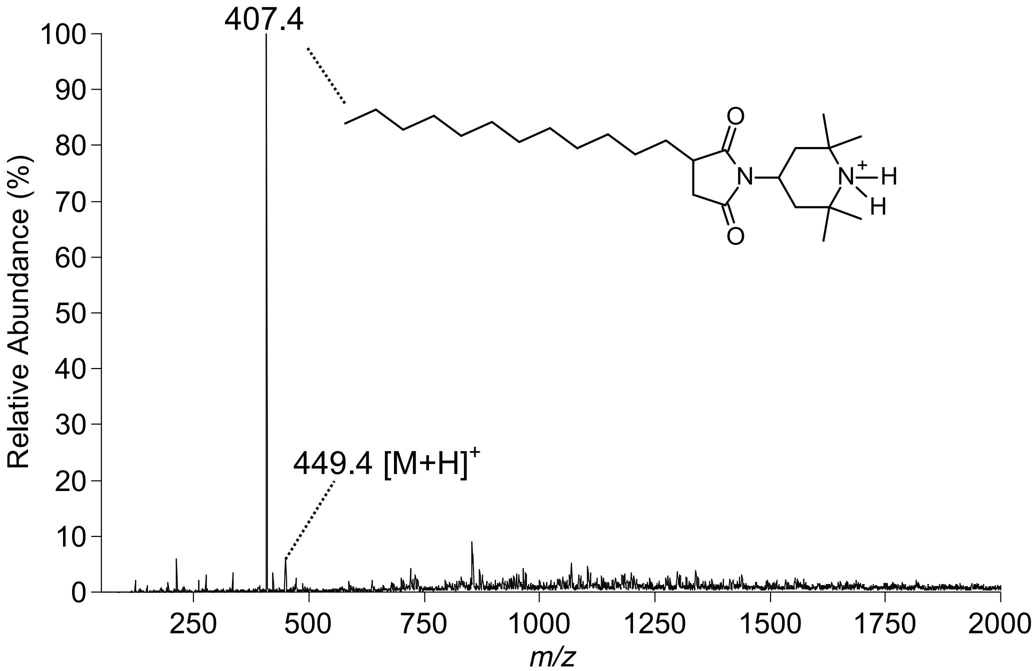


Figure 4. Positive ion DESI-MS spectra of HOST3058 detected within polyester-based coil coatings after pre-treatment with acetone vapour. Inset – Putative structures for the *in-situ* structural modification to the precursor HALS compounds present.

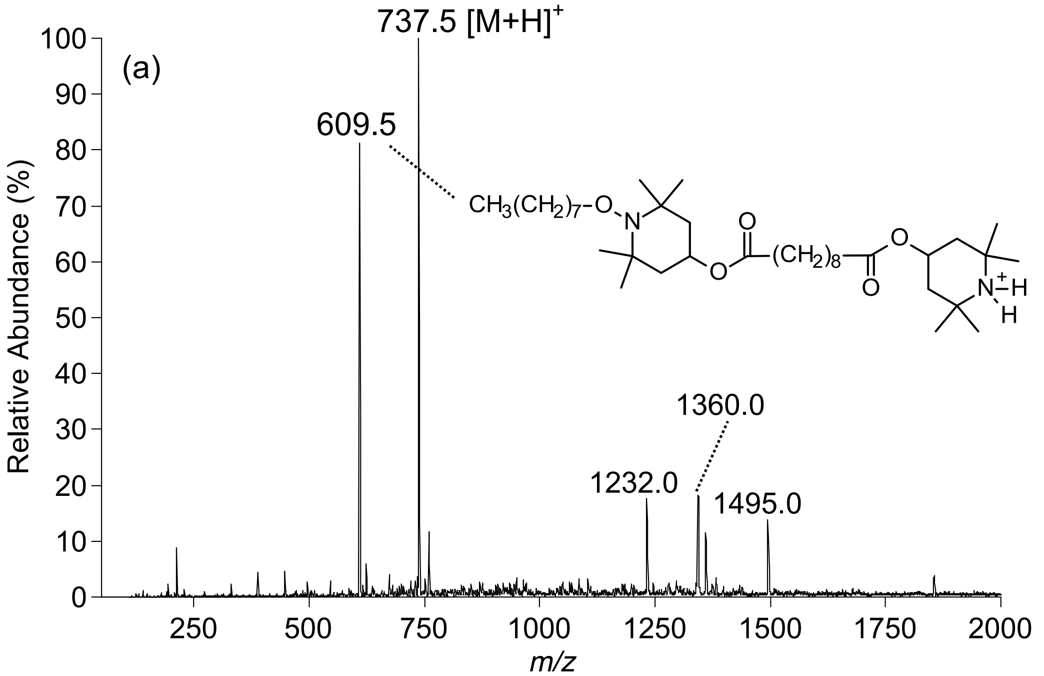
HALS TIN123, TIN152, and TIN NOR371 (*N*-OR)

Positive ion DESI-MS spectra of three polyester-based coil coatings each formulated with structurally distinct HALS compounds (TIN123, TIN152, and TIN NOR371) that contain two or more 2,2,6,6-tetramethylpiperidine moieties functionalised at the nitrogen with an alkoxyamine are shown in Figure 5(a-c). TIN123 and TIN152 show peaks that are indicative of their respective $[M+H]^+$ ions at *m/z* 737.5 (Figure 5a), and *m/z* 757.5 (Figure 5b), respectively) with a monomeric fragment of TIN NOR371 (*m/z* 1022.8) detected in Figure 5(c). Positive ion DESI-MS analysis of TIN123 present in polyester-based coil coatings has been well characterised previously [18] and structural modification of the alkoxyamine moiety to the secondary piperidine of TIN123 *in situ* (Figure 5a; inset).

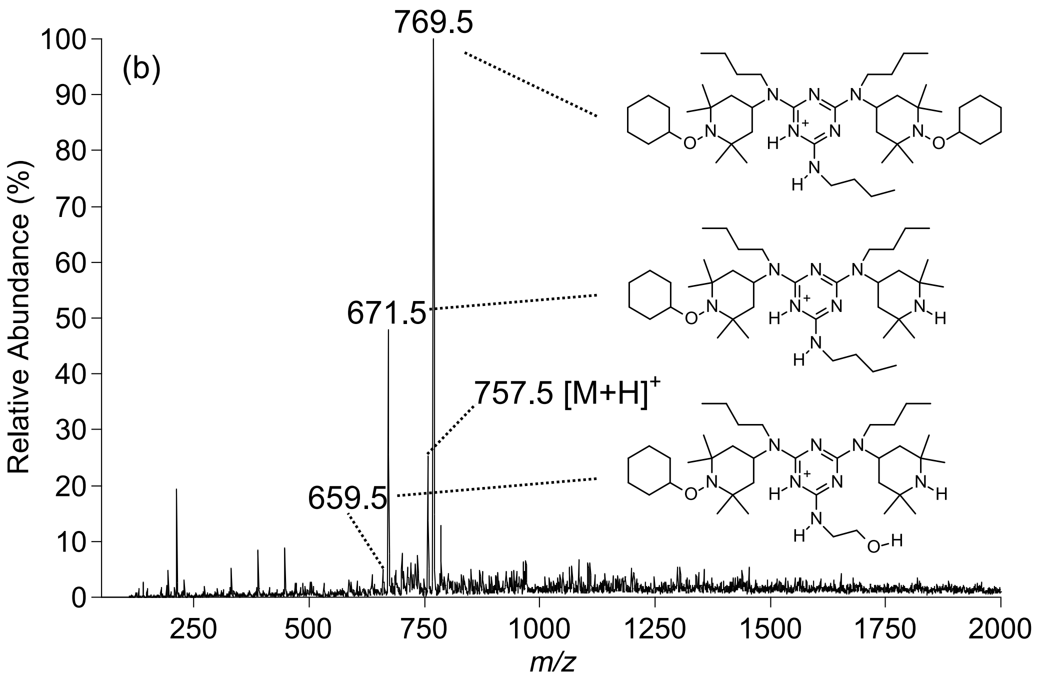
The DESI-MS spectrum for TIN152 is another case where the base peak in the spectrum is not at the *m/z* associated with the $[M+H]^+$ ion. Figure 5(b) shows the base peak at *m/z* 769.5, 12 Da higher than the protonated molecular mass of TIN152. The fragmentation pattern arising from the PQD of *m/z* 769.5 is shown in Table 1 and is similar to that of $[M+H]^+$ ion at *m/z* 757.5 suggesting a high degree of structural homology with TIN152. Tentative structural elucidation of the ion at *m/z* 769.5 using the PQD fragmentation pattern indicates that the aminoethanol group functionalised to the triazine is absent and an additional butyl group is present at this position (Figure 5b; inset). This is supported by the comparison between subsequent fragmentation of product ions generated by PQD of the ion at *m/z* 757.5 and 769.5 (Table 1) that show conservation of the 12 Da mass difference for the analogous ions all the way to the fragment corresponding to a substituted 1,3,5-triazine-2,4,6-triamine (*m/z* 283.2 and 295.2, respectively). Although this compound is not listed as a synthetic by-product by the supplier, analysis of an authentic sample of TIN152 under the same experimental conditions shows a very small relative abundance (< 1%; data not shown) at the same *m/z*. The difference in relative abundances of these two components when detected in a cured thermosetting coating can be rationalised by the propensity for TIN152 to be co-condensed to the polymer backbone through condensation of the primary alcohol substituent to melamine and isocyanate cross-linkers and therefore not able to be liberated from the coating using standard DESI techniques.

Figure 5(b) also exhibits peaks at *m/z* 659.5 and 671.5 corresponding to a mass loss of 98 Da from the $[M+H]^+$ ion of both TIN152 and the butylamino derivative (Figure 5b; inset). This mass difference equates to the substitution of one cyclohexyloxy group with hydrogen, consistent with the formation of a secondary piperidine for both TIN152 (Figure 5b; inset) and the butylamino derivative (Figure 5b; inset). These putative structures are supported by the detection of abundant product ions at *m/z* 520.2 and 532.4, respectively, corresponding to a 139 Da neutral loss from the precursor ions, which represents a loss of 2,2,6,6-tetramethyl-3*H*-pyridine and is indicative of the presence of a secondary piperidine moiety (*c.f.* Scheme 1). Again, these ions are not present in the analysis of authentic samples nor are they a result of in-source fragmentation caused by instrument conditions or listed as synthetic by-products listed by the supplier.

The positive ion DESI-MS spectrum of a cured polyester-based coil coating containing oligomeric TIN NOR371 after pre-treatment is shown in Figure 5(c). The spectrum contains a dominant base peak at *m/z* 1022.8 that corresponds to the monomeric structure of the oligomer minus an *N*,*N*-dibutyl amino group (Figure 1). The putative structure is supported by the MS/MS spectrum of ions at *m/z* 1022.8 (Table 1). PQD of the isolated ion yielded product ions at *m/z* 979.8 corresponding to the loss of a propyl radical from *N*O-C bond cleavage of the alkoxyamine and *m/z* 851 corresponding to the subsequent loss of an *N*,*N*-dibutylamino group. The major product ion at *m/z* 825 corresponds to the neutral loss of 197 Da (2,2,6,6-tetramethyl-1-propoxy-3*H*-pyridine) from the precursor resulting from elimination of 2,2,6,6-tetramethyl-1-propoxypiperidine following a highly characteristic fragmentation mechanism for HALS containing piperidine structures [29].


(a)
737.5 [M+H]+
609.5
1232.0
1360.0
1495.0
Relative Abundance (%)
m/z

394


(b)
769.5
671.5
757.5 [M+H]+
659.5
Relative Abundance (%)
m/z

395

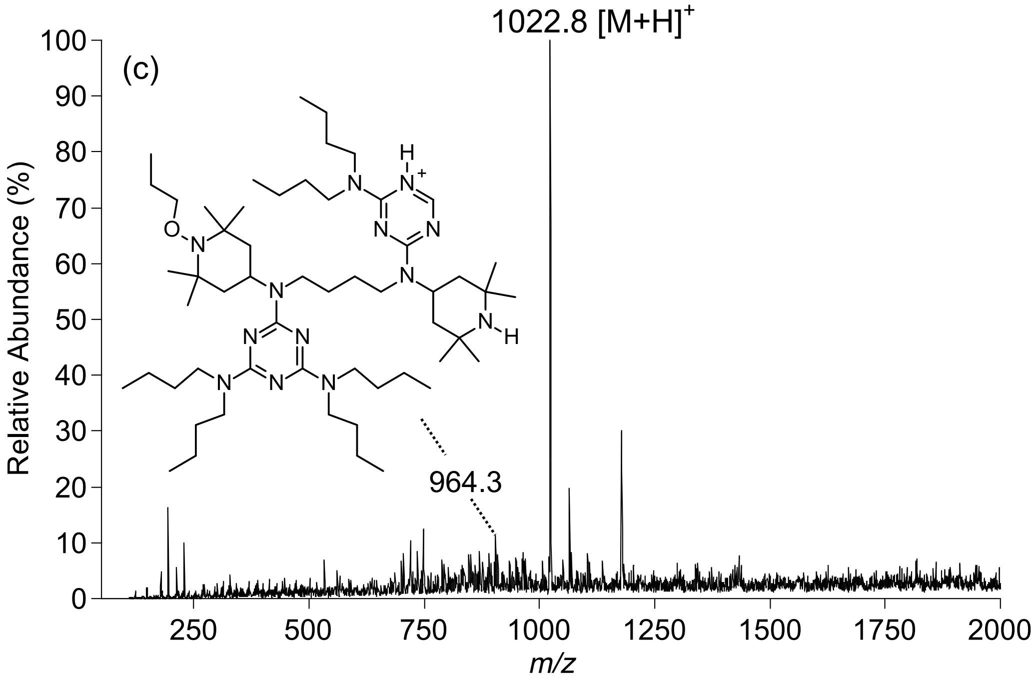


Figure 5. (a-d) Positive ion DESI-MS spectra of TIN123, TIN152, and TIN NOR371 detected within polyester-based coil coatings after pre-treatment with acetone vapour. Inset – Putative structures for synthetic by-products and *in-situ* structural modifications to precursor HALS compounds present.

Computational investigations of mechanisms for *N*-modifications

The above experimental analysis of the all the major classes of HALS (*N-OR*, *N*-R and *N*-C(O)R) indicates *in situ* conversion of the substituted piperidine moiety to a secondary amine within pigmented polyester-based coil coatings during curing. Below we discuss the mechanistic implications of these results with the aid of computational chemistry.

***N*-OR HALS**

The conversion of *N*–OR HALS to the corresponding secondary amine *N*–H under curing conditions (232 °C) echoes our earlier model spin-trapping ESR experiments for TIN123 at 80 °C (a typical service temperature), which detected the spin-trap adducts of an alkoxyl radical and α-phenyl-*N*-*tert*-butyl nitrone [18]. Collectively these experimental observations are equally consistent with both the *β*-hydrogen abstraction based regeneration mechanism and the direct *N*–OR homolysis mechanisms of Scheme 1 [21]. Previous computational studies concluded that, even for a model polyester-derived radical for which *N*–OR and *N*O–R homolysis is equally likely, the *β*-hydrogen abstraction based regeneration mechanism was still more energetically favourable, even at typical service temperatures of 80 °C [21]. Moreover, other computational studies have shown that *N*–OR homolysis is uncompetitive with *N*O–R homolysis for most other leaving groups [17, 32]. Nonetheless, in the present work we examine the *N*–OR and *N*O–R homolysis gas- and solution-phase enthalpies and Gibbs free energies (kJ mol^{-1}) for representative HALS from the present work (see Table 2) Table 2 shows results at 260 °C, which represents the upper end of typical curing temperatures; whilst the absolute Gibbs free energies are temperature dependent, the free energy differences themselves are relatively unaffected by temperature over the range studied (25 – 260 °C; see Table S1 of the Supporting Information).

Table 2. Gas- and solution-phase enthalpies and Gibbs free energies at 260 °C (kJ mol^{-1})[a] of *N*-OR and *N*O-R homolysis for TIN123, TIN152, and TIN NOR371.[a]

HALS	R	*N*-OR			*N*O-R		
		Gas phase		Solution	Gas phase		Solution
		ΔH	*ΔG*	*ΔG*	*ΔH*	*ΔG*	*ΔG*
TIN123	C_3H_7	233.90	118.13	123.49	219.61	109.19	114.77
TIN152	*c*-C_6H_{11}	228.13	113.77	115.00	216.27	101.46	103.02
TIN NOR371	C_3H_7	234.91	118.37	121.73	218.70	106.52	111.52

[a] Electronic energies of homolysis were calculated double-layer ONIOM approximation to G3(MP2)-RAD method at the R(O)MP2/6-311+G(3df,2p) level of theory in conjunction with B3LYP/6-31G(d) optimised geometries and scaled frequencies; Free energies of solvation in toluene were calculated using UAKS-PCM/B3LYP/6-31G(d) method. Results at 25 and 80 °C are given in Table S1 of the Supporting Information.

Comparison of the calculated gas and solution-phase Gibbs free energies of *N*-OR and *N*O-R homolysis for the three alkoxyamine HALS investigated (Table 2) indicates that *N*O-R homolysis would be thermodynamically favoured in each case. However, the Gibbs free energy differences between *N*-OR and *N*O-R homolysis in these examples are small (*ca*. 10 kJ mol^{-1}), suggesting that *N*–OR homolysis could be occurring once every ten or so *N*O–R reactions at 260 °C (or once every 60 at 80 °C). Whilst neither *N*–OR nor *N*O–R is competitive with β-hydrogen abstraction pathway at room temperature or service temperatures such as 80°C [21], homolysis *per se* becomes relatively more important at the high temperatures associated with curing (*e.g*., 260°C) due to its entropic favourability. Under those circumstances, it is conceivable that, for these simple alkyl leaving groups, *N*–OR homolysis may play a minor role. For example, in the TIN123 at 260 °C direct homolysis of the *N*–OR bond has a free energy change of ΔG = 123.5 kJ mol^{-1} and an approximate first order rate coefficient of k = 8.8 s^{-1}[33]. At the same temperature, based on previous calculations for similar systems [21], the second-order rate constants for *β*-hydrogen abstraction from the alkoxyamine range from 10^{-1} to 10^{5} M^{-1} s^{-1} depending on the abstracting radical. Depending on the steady state radical concentrations, it is conceivable that the unimolecular homolysis reaction could be competitive with the bimolecular abstraction reaction at this temperature. In contrast, at 80 °C the homolysis rate coefficient drops to 6.5×10^{-11} s^{-1}, and is uncompetitive with even the slowest abstraction rate coefficients, which in turn range from 10^{-4} to 10^{4} M^{-1} s^{-1}.

N-CH_3 and *N*-C(O)CH_3 HALS

In contrast to alkoxyamines, homolysis of the *N*-R bond is computed to be high in energy for R = H, CH_3 or C(O)CH_3 (Table 3). These bond energies are some 150 kJ mol^{-1} greater than those calculated for the alkoxyamine moiety (Table 2) and therefore direct homolysis seems an unlikely pathway to modification at the piperidinyl nitrogen. Indeed, for *N*-CH_3 HALS, activation pathways have been examined previously [21] with the most favoured pathway involving hydrogen abstraction from the *N*–CH_3 group, followed by addition of oxygen, coupling, decomposition to *N*–$CH_2O^•$ radical and *β*-scission to the aminyl radical, which then either convert to the secondary amine, or oxidise to the nitroxide (see Scheme 2).

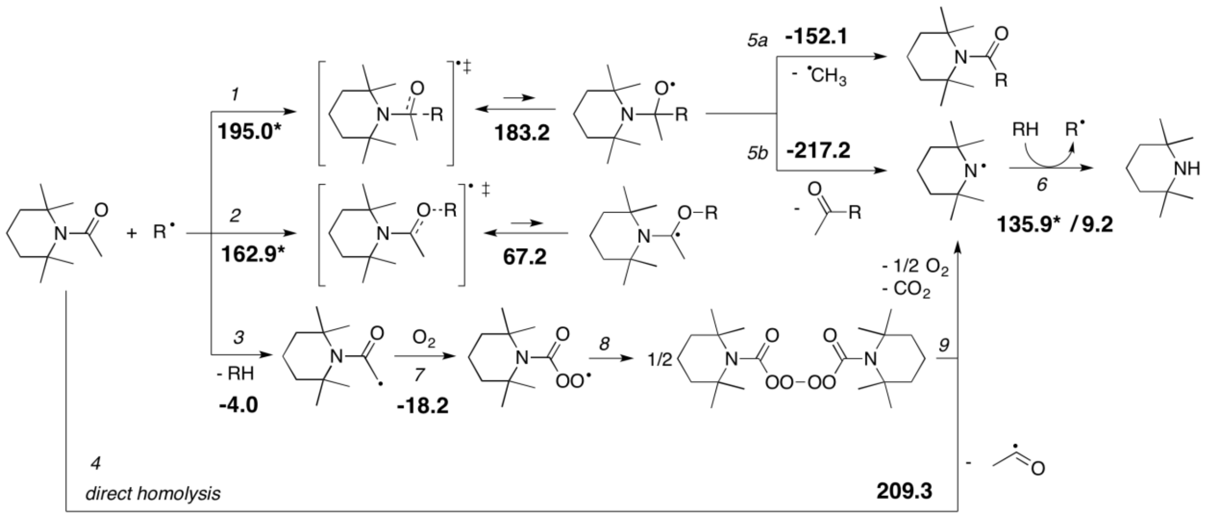
Table 3. Gas- and solution-phase enthalpies and Gibbs free energies at 260 °C (kJ mol^{-1})[a] of *N*-R homolysis for TIN770, HOST3052, HOST3055, HOST3050, TIN292, TIN144, and HOST3058.[a]

HALS	R	Gas phase		Solution
		ΔH	*ΔG*	*ΔG*
TIN770	H	407.48	335.77	362.02
HOST3052	H	406.60	334.31	360.14
HOST3055	H	406.83	334.69	360.90

HOST3050	H	406.58	334.21	360.25
TIN292, TIN144	CH_3	314.50	211.07	233.80
HOST3058	$C(O)CH_3$	326.25	208.16	226.62

[a] Electronic energies of homolysis were calculated double-layer ONIOM approximation to G3(MP2)-RAD method at the R(O)MP2/6-311+G(3df,2p) level of theory in conjunction with B3LYP/6-31G(d) optimised geometries and scaled frequencies; Free energies of solvation in toluene were calculated using UAKS-PCM/B3LYP/6-31G(d) method. Results at 25 and 80 °C are given in Table S2 of the Supporting Information.

For *N*-deacetylation, several mechanistic routes towards an aminyl radical can be suggested by analogy to the established chemistry of *N*–CH_3 and *N*–OR HALS (Scheme 4). Firstly, abundant reactive polymer radicals $R^•$ can attack the carbonyl bond [34] of an initial HALS, adding either to a carbon (Scheme 4, reaction *1*) or an oxygen atom (Scheme 4, reaction *2*). Addition to the carbon side of the carbonyl bond, followed by *β*-scission in the forming O-centred radical (Scheme 4, reaction *5*), ultimately leads to an aminyl radical, but is strongly disfavoured on both kinetic and thermodynamic grounds and thus is not likely to be responsible for the experimental observations. Addition to the oxygen side of the carbonyl moiety, likewise, appears to be energetically unfeasible, and, most importantly, does not provide a pathway to an aminyl radical. In contrast, hydrogen abstraction from the *N*-$C(O)CH_3$ group of the initial HALS (Scheme 4, reaction *3*) and subsequent oxidation (Scheme 4, reactions *7*-*9*) similar to that of the *N*-alkyl HALS adduct (Scheme 2b) [21] represents an energetically feasible route to the aminyl radical. As noted above, *N*–C homolysis (Scheme 4, reaction *4*), on the other hand, does not appear to be competitive with the aforementioned pathway. Once formed, the aminyl radical can abstract a hydrogen atom from, for example, polymer backbone to yield experimentally observed secondary amine or enter one of the regenerative cycles (*cf*. Scheme 1).



Scheme 4. Formation of aminyl radicals and secondary amines from the thermal decomposition of an *N*-acetyl-piperidine model for the HALS HOST3058: numbers in bold are the Gibbs free energies of reactions (activation*) in gas phase at 260 °C. Results at 25 and 80 °C are given in Table S3 of the Supporting Information.

Conclusion

The detection of ten hindered amine light stabilisers within polyester-based coil coatings by DESI-MS has proven to be rapid, straightforward and able to be performed under ambient conditions. DESI-MS/MS also provides enough qualitative information to enable the characterisation of structural changes occurring to HALS within polyester-based coil coatings. HALS containing a 2,2,6,6-tetramethylpiperidine moiety functionalised at the nitrogen (TIN292**,** TIN144, HOST3058, TIN123, TIN152, and TIN NOR371) all gave indications of undergoing *in situ* conversion to the corresponding secondary piperidine (*N*-H). These changes occurred under typical curing conditions implying that at least some portion of the initial HALS is actually converted to secondary amine even prior to service. This in turn has implications for their activation and performance under subsequent in-service conditions. Until recently [21] mechanisms for understanding aminoxyl radical regeneration of HALS (such as the Denisov cycle [7-16]) either did not account for a secondary piperidine intermediate or were deemed energetically unfeasible [17, 32] yet it is clear from these results that formation of this intermediate constitutes a major pathway in HALS protection of polymers. Recently, two possible mechanisms for the formation of the secondary piperidine *in situ* from alkoxyamines have been suggested [21]: (i) by direct *N*-OR bond homolysis or, (ii) *via* hydrogen abstraction and subsequent β-scission. In this work we show that both are consistent with the observed experimental data, though based on high-level quantum chemical calculations, pathway (ii) is dominant under normal service temperatures (25-80 °C), while pathway (i) may become competitive at low radical concentrations and the high temperatures associated with curing (260 °C). Thus both mechanisms warrant strong consideration for all future discussions involving the activation/regeneration of HALS in polymers.

The effectiveness of particular HALS as stabilising agents can be attributed to their ability to remain an active participant in the Denisov cycle, forming and reforming the aminoxyl radical intermediate. Concordantly, resistance to chemical deactivation and/or physical losses including leeching or volatilisation are paramount [35-38]. For these reasons, the stabilising efficacy of different HALS compounds may vary dramatically, being influenced by many factors such as diffusion and solubility coefficients as well as the properties of the coating itself including resin systems, pigment components, curing temperatures and the degree of degradation experienced [12, 36, 39-41]. In order to optimise HALS compounds, particularly for use in coil coatings, understanding the molecular changes that may occur *in situ* leading to activation or deactivation of HALS and affecting the total active content remaining in the coating after curing is vital.

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Desorption Electrospray Ionisation Mass Spectrometry of Stabilised Polyesters Reveals Activation of Hindered Amine Light Stabilisers

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Abstract

The use of hindered amine light stabilizers (HALS) to retard thermo- and photo-degradation of polymers has become increasingly common. Proposed mechanisms of polymer stabilisation involve significant changes to the HALS chemical structure; however, reports of the characterisation of these modified chemical species are limited. To better understand the fate of HALS and determine their *in situ* modifications, desorption electrospray ionisation mass spectrometry (DESI-MS) was employed to characterise ten commercially available HALS present in polyester-based coil coatings. TINUVIN® 770, 292, 144, 123, 152, and NOR371; HOSTAVIN® 3052, 3055, 3050, and 3058 were separately formulated with a pigmented, thermosetting polyester resin, cured on metal at 262 °C and analysed directly by DESI-MS. High-level *ab initio* molecular orbital theory calculations were also undertaken to aid the mechanistic interpretation of the results. For HALS containing *N*-substituted piperidines (*i.e., N*-CH_3, *N*-C(O)CH_3, and *N*-OR) a secondary piperidine (*N*-H) analogue was detected in all cases. The formation of these intermediates can be explained either through hydrogen abstraction based mechanisms or direct *N*–OR homolysis with the former dominant under normal service temperatures (*ca*. 25-80 °C), and the latter potentially becoming competitive under the high temperatures associated with curing (*ca*. 230-260 °C).

Keywords

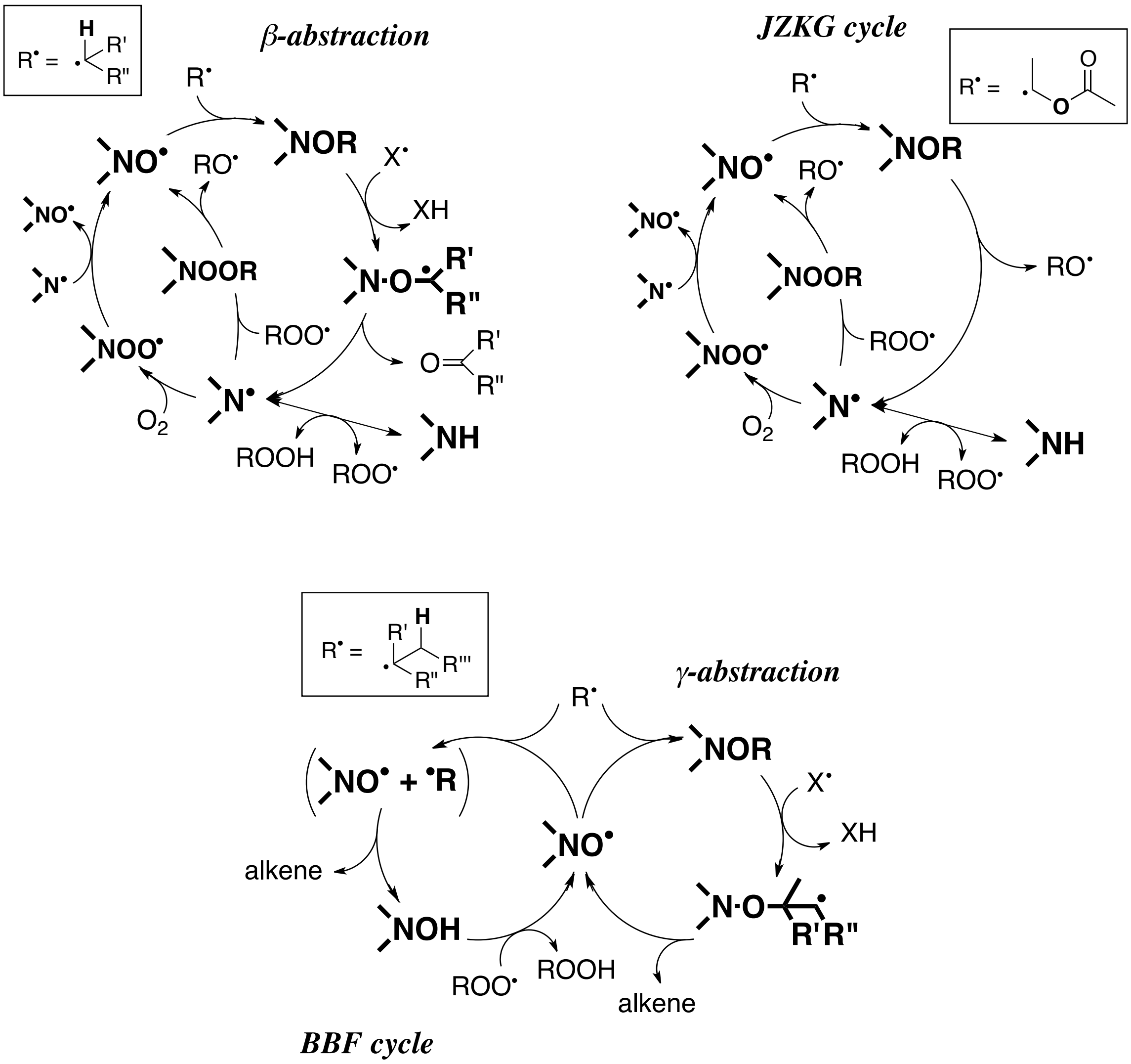
Mass spectrometry, polyester, hindered amine light stabiliser, mechanism

Introduction

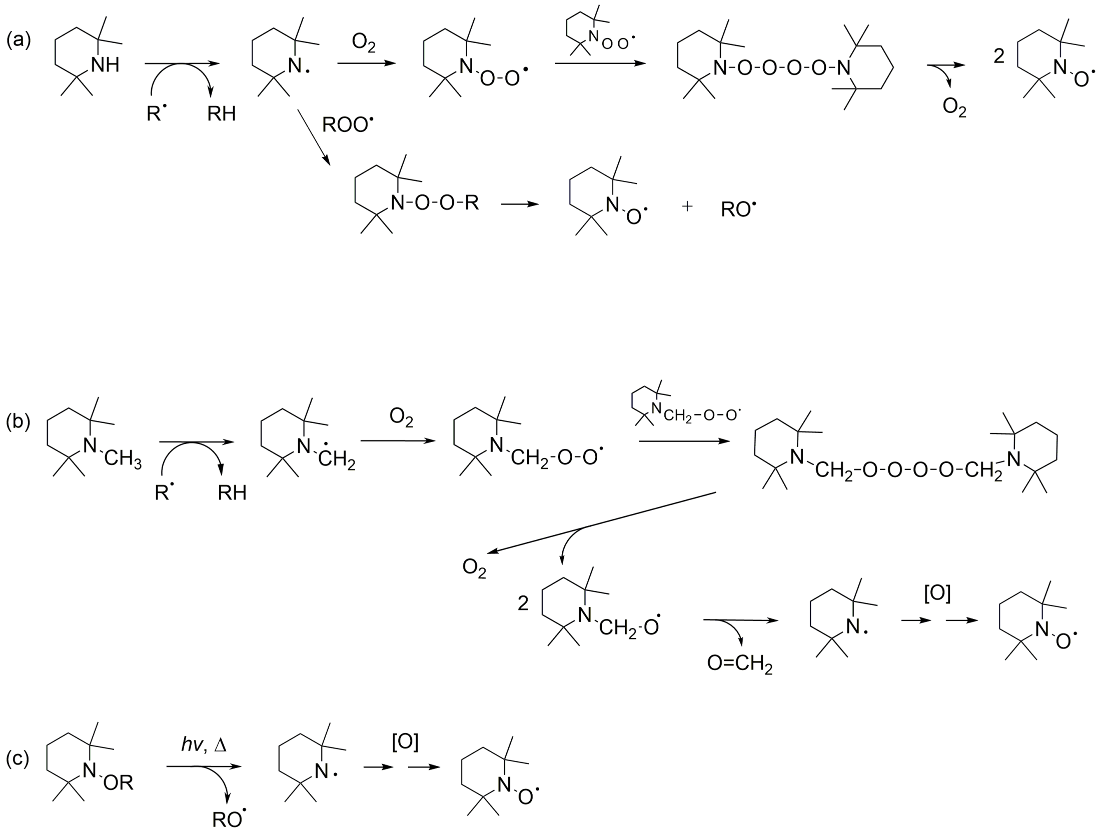
Many contemporary synthetic polymers require one or more chemical additives to enable them to carry out an intended function effectively. In the surface coatings sector, for example, the polymer provides the binder for a coating and the pigment the aesthetic, but several types of functional additive are also required for a successful formulation. Thus, additives for rheology control, pigment dispersion, wetting, levelling *etc*. are commonly found in a wide range of coating types. Many of these additives have performed the role for which they were designed after the coating has been applied and dried (or cured). However, additives such as UV-absorbers and the so-called hindered amine light stabilisers (HALS) function during the service lifetime of the coating, and their role is to retard the degradation of the coating caused by the continuous barrage of environmental insults which can lead to compromised performance. HALS have been commonly employed in automotive, wood and plastic coatings for decades [1-6], and the last 10 years has seen an increase in their use in coil coatings. Coil coating is a large-scale process for continuous painting of steel strip at speeds of up to 200 $m.min^{-1}$. The pre-painted steel strip thus produced is used in many different applications, the most severe of which is that employed in roofing, where the product needs to retain good appearance in service for 20 years or more. In turn, this places considerable emphasis on HALS to preserve the aesthetic and functional roles of the surface coating by protecting the polymer from degradation. Therefore, the optimisation of these compounds for such applications is of considerable interest; however, this first requires a thorough understanding of the chemistry associated with the protection of polymers by HALS. It is widely believed that HALS operate as chain-breaking antioxidants, undergoing oxidation of a heterocyclic amine to an aminoxyl radical, although the exact mechanisms by which this occurs is still the subject of investigation. It is this persistent aminoxyl radical that acts as a free radical scavenging intermediate and is thought to be involved in converting deleterious free radicals to less harmful even-electron species. As a result, regeneration of the aminoxyl radical occurs, theoretically allowing the process to repeat indefinitely [7-16]. However, empirical evidence suggests that the protective effects are finite and the use of HALS only delays the failure of polymers rather than denying it. Thus stabilisation *via* HALS must consist of a more complex mechanism.

Recently, Hodgson and Coote [17] deployed high-level quantum chemical calculations to compare the kinetics and thermodynamics of a dozen different reaction pathways comprising over 30 individual reactions. This allowed critical assessment of all the previously suggested mechanisms. Hodgson and Coote's analysis shows most of the mechanisms are kinetically and/or thermodynamically disfavoured with even the most favourable mechanism subject to a large activation barrier (~150 kJ mol^{-1}) for one of its key steps [17]. Furthermore, this mechanism does not account for previous experimental observations that suggest *in situ* conversion of an alkoxyamine functional group (*N*-OR) – analogous to an intermediate expected in an aminoxyl radical regenerative mechanism – to a secondary piperidine (*N*-H). This phenomenon was observed following high temperature curing of the polymer-based coating as well as subsequent exposure of the coating to accelerated weathering conditions [18]. Concordant results have also been reported in the literature for the decomposition of 2,2,6,6-tetramethylpiperidine-based HALS under thermo- and photo-oxidative conditions [19, 20].

The inability to account for these observations by any of the commonly accepted mechanisms sparked a follow-up computational study by Coote and co-workers in which a new mechanism was proposed to explain the catalytic free radical scavenging by HALS in organic materials [21]. In this proposed cycle, an aminoxyl radical traps a carbon-centred substrate radical to form an alkoxyamine, and is then regenerated in a cascade of reactions triggered by hydrogen atom abstraction at the β-position of the alkoxyamine via another substrate-derived radical. The resulting species rapidly undergoes β-scission to form a ketone and an aminyl radical, and the aminyl radical can then either be oxidised back to the aminoxyl or abstract a hydrogen atom to form a secondary amine (see Scheme 1) [21]. This secondary amine can re-enter the catalytic cycle *via* hydrogen abstraction with any number of substrate-derived radicals, depending on the relative concentrations. In species that degrade *via* tertiary substrate-derived radicals, for which *β*-hydrogen abstraction is not possible, alternative catalytic cycles were proposed depending on whether direct *N*–OR homolysis was possible or not (see Scheme 1) [21]. These were shown to be much less energetically favourable, thus providing an explanation for the lower catalytic efficiency of HALS in such cases. The activation of the HALS was also studied, and shown to vary depending on whether the starting material was a secondary amine, the *N*-methyl derivative or an alkoxyamine (see Scheme 2) [21].



Scheme 1. Regeneration mechanisms for the catalytic protection of organic materials against autooxidation, as identified in Ref [21]. The energetically preferred cycle for most combinations of aliphatic HALS is the *β*-abstraction. In cases where the degrading substrate radical does not contain an abstractable hydrogen, *γ*-abstraction or the JZKG cycle operate instead, the latter requiring preferred N–OR homolysis.



Scheme 2. HALS activation mechanisms for (a) secondary amines, (b) *N*-methyl amines, (c) alkoxyamines, as identified in Ref [21].

This recent computational study, supported by previous experimental observations, thus suggests there may be other major repositories for HALS outside of the traditional regenerative cycles. Therefore, the aim of this work is to investigate the changing functionalisation of the piperidine nitrogen by characterising the structural changes occurring to a range of HALS compounds in polymer-based coatings. In this study, the focus is on the changes that occur specifically during curing under typical curing conditions and what impact they have on the chemical structure of the HALS. This in turn has implications for its activation (and hence protective action) under subsequent in-service conditions.

We have employed desorption electrospray ionisation mass spectrometry (DESI-MS) for the analysis of ten polyester-based coil coatings each containing a different commercially available HALS compounds (Figure 1). The compounds selected are structurally diverse providing the four most common piperidinyl moieties (*i.e.*, *N*-H, *N*-CH_3, *N*-C(O)CH_3, and *N*-OR). It is noted that basic HALS (*N*-H, *N*-CH_3; pK_a 7.5-9.7) are not typically used in acid-catalysed, cross-linked polyesters as they interfere with the curing process. They are included here however, to provide insight into the changes in functionality of HALS that are associated with curing conditions. HALS compounds retained within the coating after cure are detected *in situ*, characterised by tandem mass spectrometry and the results are rationalised with the aid of high-level electronic structure calculations.

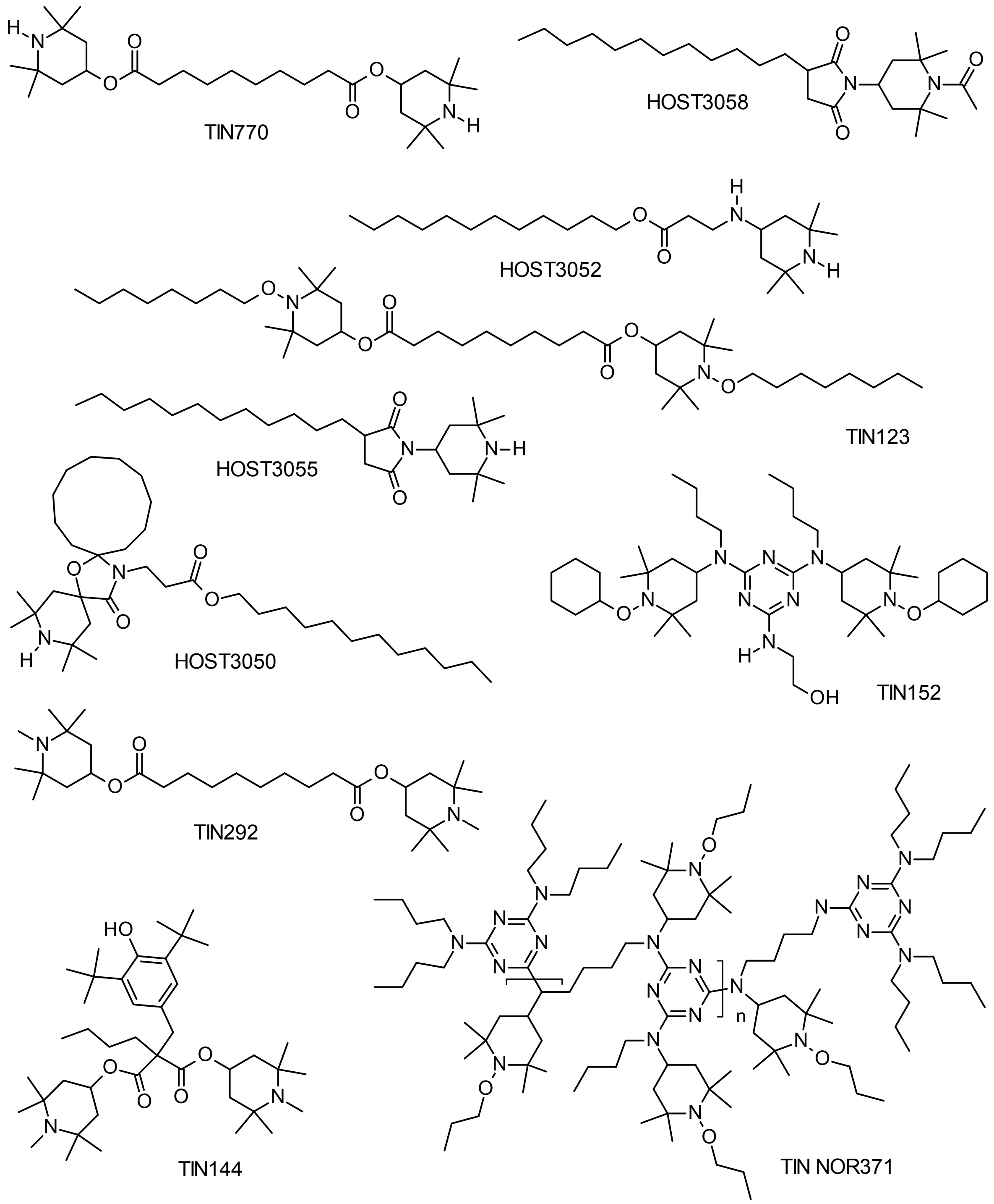


Figure 1. The structures of the ten commercially available hindered amine light stabilisers (HALS) used in this study.

Methods

Reagents

Methanol and formic acid were HPLC grade (Crown Scientific, Minto NSW, Australia). Chloroform and acetone were AR grade (Crown Scientific, Minto NSW, Australia). The hindered amine light stabilisers; bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (TIN770), bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate (TIN292), bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl)butylmalonate (TIN144), bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidinyl) sebacate (TIN123), 2,4-bis(*N*-butyl-*N*-(1-cyclohexyloxy-2,2,6,6-tetramethyl-4-piperidinyl)amino)-6-(2-hydroxyethylamine)-1,3,5-triazine (TIN152), and oligomers based on *N*-2-butyl-*N*-2-*N*-4-bis(2,2,6,6-tetramethyl-1-propoxy-4-piperidyl)-*N*4-[5-(2,2,6,6-tetramethyl-1-propoxy-4-piperidyl)pentyl]-1,3,5-triazine-2,4-diamine (TIN NOR371) were supplied by Ciba Specialty Chemicals (Basel, Switzerland) now BASF (Ludwigshafen, Germany) and were used without purification. The hindered amine light stabilisers; *β*-alanine-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-dodecyl ester and *β*-alanine-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-tetradecyl ester (HOST3052), 2-dodecyl-*N*-(2,2,6,6-tetramethyl-4-piperidinyl) succinimide (HOST3055), 7-oxa-3,20-diazadispiro[5.1.11.2]heneicosane-20-propanoic acid-2,2,4,4-tetramethyl-21-oxo-dodecyl ester (HOST3050), and 2-dodecyl-*N*-(1-acetyl-2,2,6,6-tetramethyl-4-piperidinyl) succinimide (HOST3058) were supplied by Clariant (Huningue, France) and were used without purification.

Preparation of coated steel panels

The topcoat paint system employed in these studies was a solvent-borne, polyester topcoat paint incorporating a melamine-formaldehyde cross-linker, acid catalysed and formulated for coil paint-line application. This sample was formulated as a wet paint mixture and found to be 45% w/w resin solids by thermogravimetry (Perkin-Elmer TGA 7). The bulk paint sample was sub-sampled and weighed into small containers providing an identical matrix for comparative HALS analysis. The paints were formulated to give a final concentration of each HALS that resulted in a molar equivalent of an aminoxyl radical precursor (*N*-R) to that of TIN123 added at 2% w/w of total resin solids. The coated samples that were used in this project were laboratory prepared upon a pre-primed (commercial chromated epoxy primer) panels of a 0.6 mm thick GALVALUME®-type steel substrate. Wet paint was applied using a #28 wire-wound draw-down bar then cured for 55 seconds in a fan forced oven set at 262 °C. Under these conditions, 55 seconds equates to a peak metal temperature of 232 °C.

Desorption electrospray ionisation-mass spectrometry (DESI-MS)

Metal panels with a thermosetting polyester-based coating were cut into small sections (7 × 25 mm) using hydraulic shears and affixed to a glass microscope slide. The samples were then placed in an enclosed atmosphere of acetone vapour for 5 minutes prior to DESI-MS analysis in order to swell the polymer, mobilising the HALS compounds to the surface of the substrate. Positive ion DESI-MS spectra were acquired using an Omni Spray® ion source (Prosolia Inc., Indianapolis, USA) coupled to a LTQ 2-dimensional (2-D) linear ion trap mass spectrometer (Thermo Fisher Scientific, San Jose, USA) with Xcalibur Tune Plus 2.0 software (Thermo Fisher Scientific, San Jose, USA) used for spectral acquisition. The DESI spray solvent, methanol acidified with 0.1 % formic acid (v/v), was delivered at a flow rate of 10 μL.min^{-1} with a 5 kV voltage applied to the spray emitter. MS instrument parameters were as follows: nebulizing gas pressure, 80 psi; capillary voltage, 30 V; capillary temperature, 200 °C; sample holder velocity, 200 μm.s^{-1}; ion injection time, 30 ms; microscans, 2; with automatic gain control switched off. DESI-MS/MS spectra were acquired on the LTQ by subjecting trapped ions to pulsed-Q dissociation (PQD) [22], allowing detection of subsequent product ions below the conventional low mass cut-off of the ion-trap mass spectrometer. Typical experimental parameters for PQD were: isolation width, 1.5 Da; ion injection time, 50 ms; microscans, 2; collision energy 25-37 arbitrary units (See Table 1). Baseline subtraction was not used and mass spectra were averaged over a minimum of fifty scans. All mass spectra were normalised to the most abundant ion in the spectrum.

Computational procedures

Standard ab initio molecular orbital theory and density functional theory calculations were carried out using Gaussian 09 [23] and Molpro 2009.1 [24]. Calculations on radicals were performed with an unrestricted wave function except in cases designated with an "R" prefix where a restricted open-shell wave function was used. For all species, either full systematic conformational searches (at a resolution of 120°) or, for more complex systems, energy-directed tree searches [25] were carried out to ensure global, and not merely local minima were located. Geometries of all species were fully optimized at the B3-LYP/6-31G(d) level of theory and frequencies were also calculated at this level and scaled by recommended scale factors [26]. Accurate energies for all species were then calculated using double-layer ONIOM-type method. The core layer was calculated using the high-level composite *ab initio* G3(MP2)-RAD [26] method, whereas either R(O)MP2/6-311+G(3df,2p) (in homolysis studies) or M06-2X/6-311+G(3df,2p) (in activation mechanism modelling) method was applied to the full system. Entropies and thermal corrections at 25, 80 and 260 °C were calculated using standard textbook formulae [27] for the statistical thermodynamics of an ideal gas under the harmonic oscillator approximation in conjunction with the optimized geometries and scaled frequencies. Reaction Gibbs free energies were computed using Gibbs fundamental equation.

Free energies of solvation in toluene were calculated using the polarized continuum model PCM-UAKS [28]at the B3LYP/6-31G(d) level of theory. Free energies of each species in solution at 298.15 K were calculated as the sum of the corresponding gas-phase free energy and the obtained free energy of solvation. The phase change correction term ΔnRT(lnV) was added to the resulting free energies for each species.

Results and Discussion

Positive ion DESI-MS of polyester-based coatings containing HALS

The ambient ionisation technique desorption electrospray ionisation-mass spectrometry (DESI-MS) has been employed herein for the detection of polymer additives in polyester-based coil coatings. To allow detection of HALS from thermoset coatings by DESI-MS a simple, non-destructive sample preparation method was developed by our research group that exposes the coatings to acetone vapour, partially swelling the coating and mobilising the additives to the surface for detection [18]. The samples were then positioned in a geometry that allowed a continuous flow of charged, pneumatically-assisted microdroplets from the DESI source to impact and wet the sample surface. HALS extracted into the localised solvent reservoir became entrained in secondary droplets released from the surface and upon drying resulted in gas phase ions that were detected by mass spectrometry. Positive ion DESI-MS spectra of polyester-based coatings containing each HALS separately**,** pre-treated in an acetone vapour bath for 5 mins were recorded using a linear ion-trap mass spectrometer and are shown in Figures 2-5. The spectra yield intense signals corresponding to the $[M+H]^+$ ion for each HALS resulting from protonation of the heterocyclic nitrogen or other basic sites present in the molecule. Structural confirmation of each HALS was achieved by tandem mass spectrometry – employing pulsed-Q dissociation (PQD) – of the $[M+H]^+$ ion with the resulting product ions reported in Table 1. PQD is a form of resonance excitation that allows ions of a selected *m/z* ratio to be isolated and activated to induce dissociation to product ions. The dissociation occurs as resonance activation of selected ions increases their kinetic energy, which is converted to internal energy through repeated collisions with buffer gas molecules present in the ion trap. PQD differs from conventional collision-induced dissociation (CID) methods as it allows the observation of low *m/z* fragments that are usually excluded from CID spectra and also helps to access higher energy dissociation channels [22]. Fragmentation mechanisms and resulting product ions of HOST3055, TIN292, HOST3058-TIN152 have been characterised previously using electrospray ionisation tandem mass spectrometry (ESI-MS/MS) and the product ions reported here are congruent with that study [29]. For those HALS not previously characterised by comparable mass spectrometric techniques (TIN770, HOST3052, HOST3050, TIN144 and TIN NOR371), structures were inferred by a comparative analysis of their product ions arising from PQD (Table 1).

Table 1. A summary of all DESI-MS/MS data acquired with a linear ion trap mass spectrometer following pulsed-Q dissociation (PQD) of selected precursor ions.

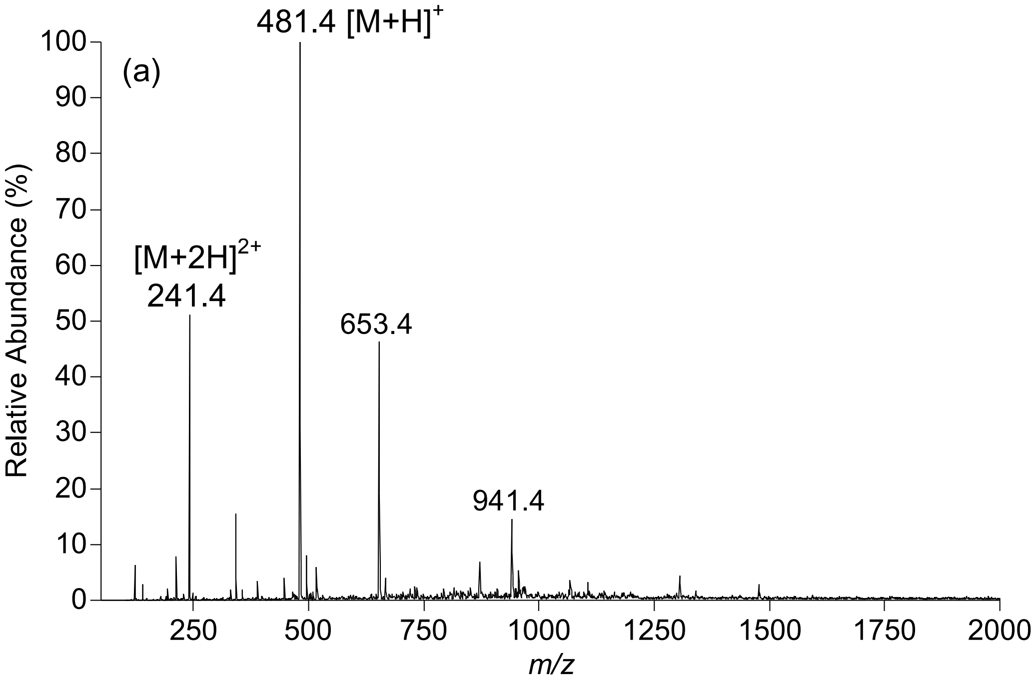
Formulated HALS	**MS Acquisition Sequence[a]**	**Product ions *m/z* (% abundance of base peak)**
TIN770	MS^2 481.4 (PQD @ 27)	464.6 (4.94), 463.6 (1.27), 399.1 (3.44), 342.3 (100.00), 317.4 (1.17), 140.0 (15.15)
HOST3052	MS^2 425.4 (PQD @ 35)	351.9 (4.47), 324.3 (15.34), 312.3 (33.23), 140.0 (8.32)
	MS^2 397.4 (PQD @ 35)	388.5 (1.60), 284.2 (8.82), 140.1 (11.18)
HOST3055	MS^2 407.4 (PQD @ 35)	334.3 (100.00), 316.3 (4.27), 306.3 (8.23), 288.3 (1.72), 268.2 (4.95), 123.1 (9.29)
HOST3050	MS^2 633.6 (PQD @ 37)	542.5 (2.11), 450.5 (55.03), 434.4 (4.02), 394.3 (18.45), 328.3 (1.72), 180.0 (6.06), 166.1 (2.23), 138.0 (3.07)
	MS^2 605.6 (PQD @ 37)	514.5 (2.29), 422.5 (38.49), 406.4 (3.84), 366.3 (15.56), 328.3 (1.60), 180.0 (4.40), 166.1 (2.23), 138.1 (2.31)
TIN292	MS^2 509.5 (PQD @ 27)	491.4 (1.04), 478.4 (23.88), 356.3 (100.00), 154.1 (8.04)
	MS^2 495.5 (PQD @ 30)	477.4 (4.14), 464.4 (36.55), 463.2 (4.45), 437.1 (2.72), 435.3 (2.96), 363.3 (2.52), 356.3 (100.00), 342.3 (83.49), 154.0 (9.43)

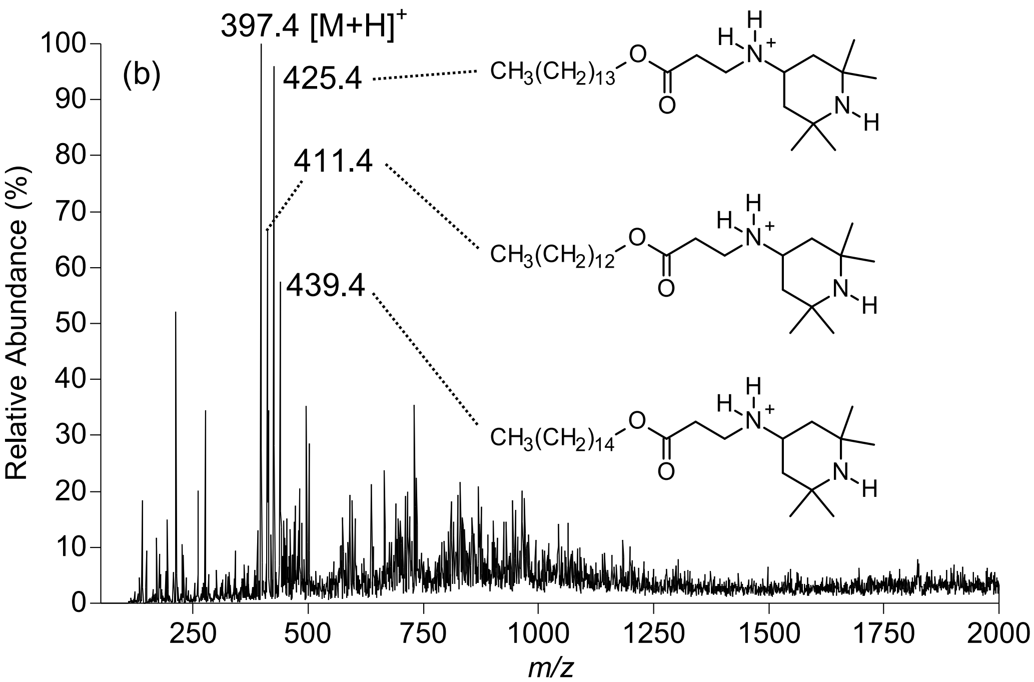
TIN144	MS^2 685.5 (PQD @ 27)	654.5 (1.92), 532.4 (100.00), 466.1 (1.66), 429.1 (3.34), 341.0 (1.90), 219.1 (1.41)
	MS^2 671.5 (PQD @ 26)	532.4 (41.78), 518.3 (1.66)
HOST3058	MS^2 449.4 (PQD @ 35)	389.4 (1.88), 334.3 (37.89), 235.1 (11.74)
	MS^2 407.4 (PQD @ 35)	334.3 (100.00), 316.3 (3.98), 306.3 (8.17), 288.3 (1.26), 268.2 (4.14), 123.1 (7.95)
TIN123	MS^2 737.5 (PQD @ 25)	625.4 (12.97), 624.4 (6.51), 607.5 (3.13), 593.4 (3.54), 496.4 (100.00), 470.3 (6.04), 342.3 (2.04), 268.1 (1.45)
	MS^2 609.5 (PQD @ 25)	573.2 (5.21), 496.5 (18.80), 496.1 (11.82), 481.5 (3.03), 477.5 (10.11), 470.0 (6.29), 342.1 (30.45), 243.0 (6.50)
TIN152	MS^2 769.5 (PQD @ 30)	686.5 (14.05), 655.4 (6.60), 588.4 (74.51), 558.4 (29.25), 532.4 (100.00), 449.4 (3.46), 295.2 (6.43), 238.1 (10.04)
	MS^2 757.5 (PQD @ 28)	725.0 (2.26), 674.6 (5.90), 576.4 (22.02), 546.5 (4.79), 520.4 (37.55), 283.2 (3.72), 238.0 (1.97)
	MS^2 671.5 (PQD @ 30)	588.6 (1.43), 558.2 (2.12), 532.4 (100.00), 472.4 (1.44), 460.3 (3.86), 434.4 (19.90), 376.2 (1.24), 295.3 (5.22), 238.1 (2.70)

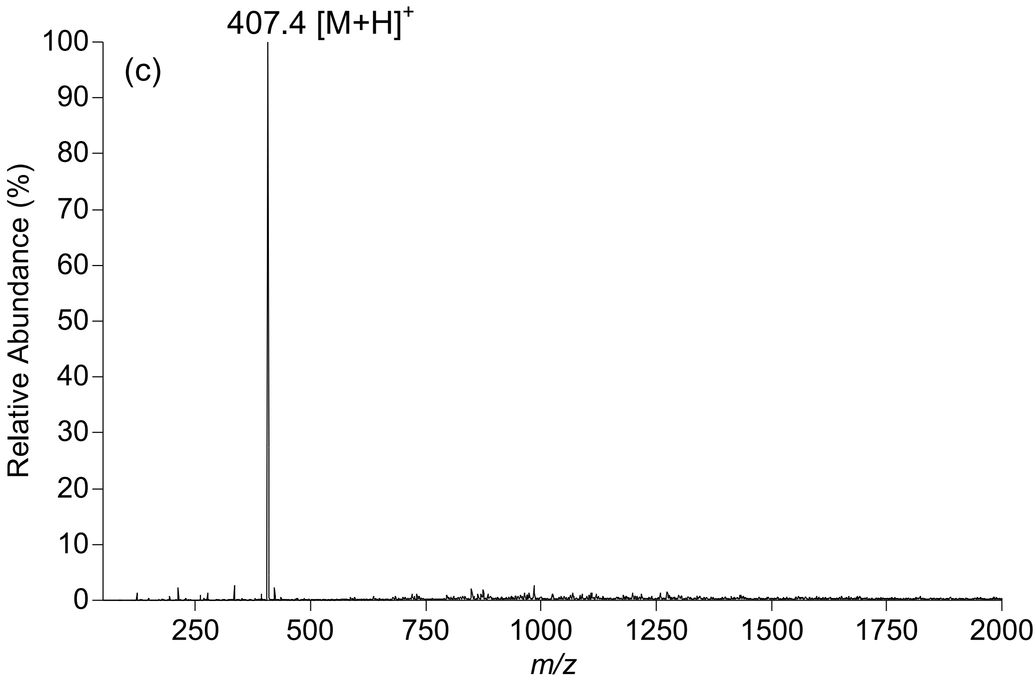
	MS^2 659.5 (PQD @ 26)	627.3 (7.52), 595.2 (9.54), 545.2 (7.81), 520.6 (31.01), 520.2 (18.62), 422.1 (11.83), 283.1 (10.17)
TIN NOR371	MS^2 1022.8 (PQD @ 35)	979.8 (78.26), 851.8 (12.59), 825.8 (100.00), 783.9 (1.56), 461.5 (1.63), 431.4 (1.49), 377.4 (1.88), 351.5 (1.26)
	MS^2 964.8 (PQD @ 35)	851.8 (7.30), 825.8 (100.00), 809.8 (1.35), 783.8 (12.22), 727.8 (2.09)

DESI-MS characterisation of TIN770, HOST3052, HOST3055, and HOST3050 (*N*-H)

Figures 2(a-d) show DESI-MS spectra of four structurally diverse HALS (TIN770, HOST3052, HOST3055, and HOST3050) each containing 2,2,6,6-tetramethylpiperidine moieties unsubstituted at the nitrogen (*N*-H). All four spectra demonstrate an excellent signal-to-noise ratio for the peak corresponding to the $[M+H]^+$ ion except Figure 2(b). The poor signal-to-noise ratio in this spectrum is due to HOST3052 being supplied as a mixture of up to five different structural analogues of the compound listed by the manufacturer (Figure 2b). Spreading the peak intensity over four or more channels effectively reduces the signal-to-noise ratio and the contrast is easily observed by comparison with Figure 2(c) as HOST3055 is present as only one ionisable species. The remaining unassigned peaks in Figure 2(b) were confirmed to be chemical noise present in all ten DESI-MS spectra by comparison with the baseline of the spectrum in Figure 2(c) at 20 times magnification, *i.e.*, the magnified baseline of Figure 2(c) was observed to be identical to the baseline of Figure 2(b).


481.4 [M+H]+
(a)
[M+2H]2+
241.4
653.4
941.4
Relative Abundance (%)
m/z


397.4 [M+H]+
(b)
425.4
411.4
439.4
CH3(CH2)13
CH3(CH2)12
CH3(CH2)14
Relative Abundance (%)
m/z


407.4 [M+H]+
(c)
Relative Abundance (%)
100
90
80
70
60
50
40
30
20
10
0
250
500
750
1000
1250
1500
1750
2000
m/z

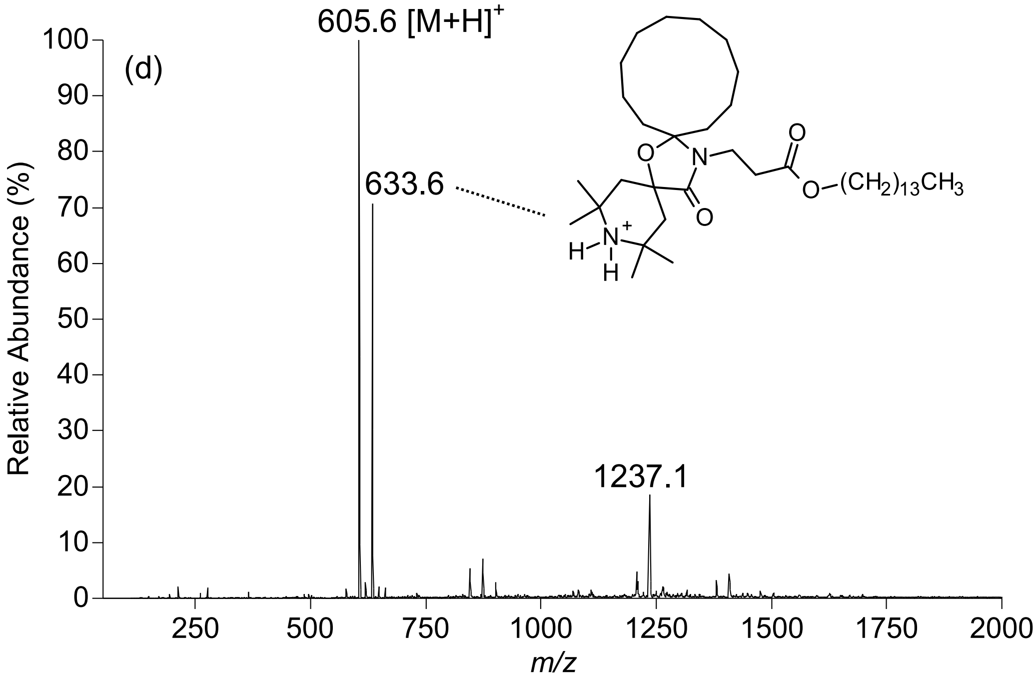
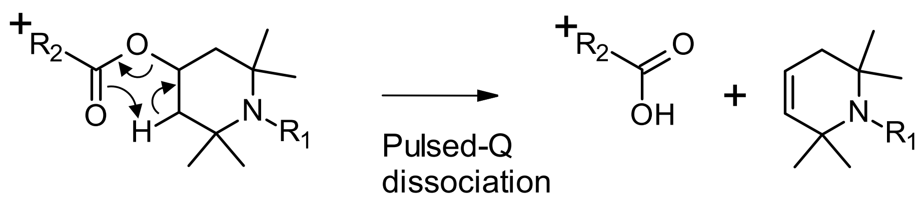

605.6 [M+H]+
(d)
633.6
1237.1
O
N
O
O
O–(CH2)13CH3
H
N+
H
Relative Abundance (%)
100
90
80
70
60
50
40
30
20
10
0
250
500
750
1000
1250
1500
1750
2000
m/z

Figure 2(a-d). Positive ion DESI-MS spectra of TIN770, HOST3052, HOST3055, and HOST3050 detected within polyester-based coil coatings after pre-treatment with acetone vapour. Inset – Putative structures for oligomers and synthetic by-products of the precursor HALS compounds present.

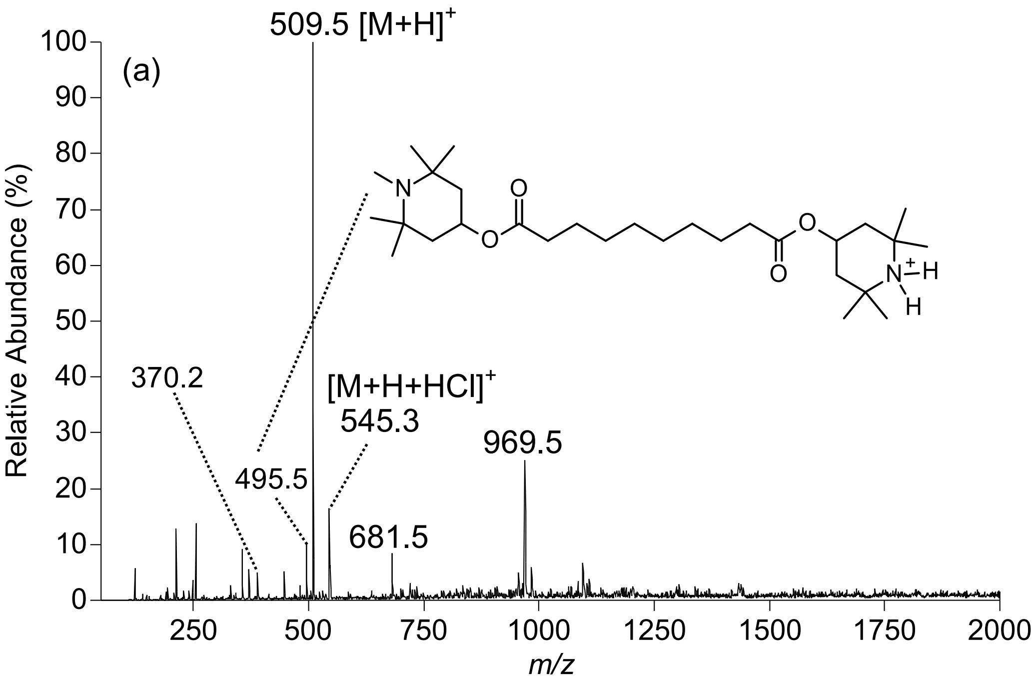
Structural modifications to HALS *in situ* detected by DESI-MS

HALS TIN292 and TIN144 (N-CH_3)

Positive ion DESI-MS spectra after pre-treatment of two cured polyester-based coil coatings each containing structurally distinct compounds with two 1,2,2,6,6-pentamethylpiperidine moieties, TIN292 and TIN144, show peaks that are indicative of their respective $[M+H]^+$ ions (Figure 3(a) *m/z* 509.5 and (b) *m/z* 685.5, respectively). These spectra also contain peaks at a mass-to-charge ratio 14 Da lower than the $[M+H]^+$ ions, *m/z* 495.5 and 671.5, respectively. Product ions arising from PQD activation of these species are listed in Table 1 and suggest a high degree of structural homology with their associated $[M+H]^+$ counterparts. The product ion spectra for both *m/z* 495.5 and 671.5 ions show a neutral loss of 153 Da from the precursor ion (Table 1; *m/z* 342.3 and 518.3, respectively); a loss also observed in the product ion spectra for TIN292 (*m/z* 356.3) and TIN144 (*m/z* 532.4). This neutral loss corresponds to the characteristic fragmentation product 1,2,2,6,6-pentamethyl-3*H*-pyridine that arises following elimination of the ester-bound substituent from the 4-position of the piperidine ring (Scheme 3) [29]. This unimolecular dissociation is driven by the non-bonding electron pairs on the ester moiety accepting a proton from the piperidine ring and forming a carbon-carbon double bond with loss of the substituent as a carboxylic acid [29-31]. Furthermore, the neutral loss of 139 Da is also observed from the *m/z* 495.5 and 671.5 precursor ions (Table 1; *m/z* 356.3 and 532.4, respectively) that, by the same rationale proposed for the above neutral loss, would correspond to the loss of 2,2,6,6-tetramethyl-1,3*H*-pyridine. This neutral loss is not observed in the product ion spectra for TIN292 and TIN144. The 14 Da mass difference and the PQD product ion spectra indicate that the ions at *m/z* 495.5 and 671.5 are protonated ions of TIN292 and TIN144 after conversion of one 1,2,2,6,6-pentamethylpiperidine moiety to a 2,2,6,6-tetramethylpiperidine (Figure 3a and b; inset). The ions attributed to these compounds are unlikely to be in-source fragments as they are not present in the MS/MS spectra of the $[M+H]^+$ ions for TIN292 and TIN144 and are not present in the authentic HALS samples. Therefore, these ions are proposed to be evidence for *in situ* modifications facilitated by the curing conditions experienced by the polyester-based coil coating.

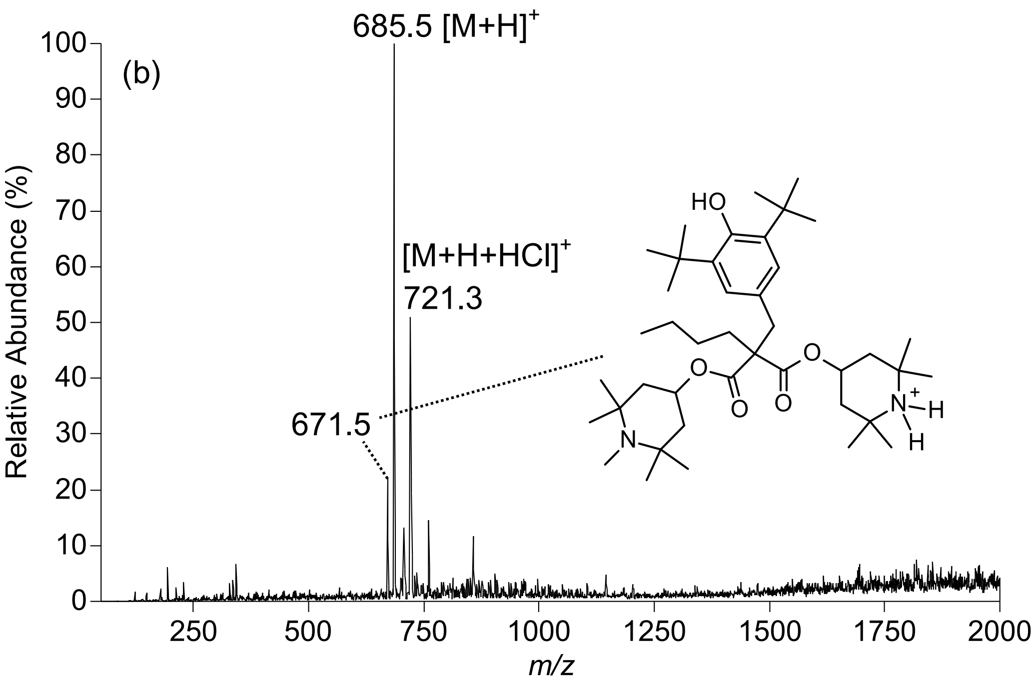


Scheme 3. Fragmentation of ions derived from ester-linked HALS upon pulsed-Q-dissociation inside the mass spectrometer gives rise to characteristic neutral losses depending on the substitution of the piperidine nitrogen. For example, when $R_1 = CH_3$ a neutral loss of 153 Da is observed and where R1 = H a neutral loss of 19 Da is observed (see entries for TIN292 and TIN770, respectively in Table 1).



509.5 [M+H]+
(a)
Relative Abundance (%)
370.2
495.5
[M+H+HCl]+
545.3
969.5
681.5
m/z

309



685.5 [M+H]+
(b)
Relative Abundance (%)
[M+H+HCl]+
721.3
671.5
HO
m/z

310

Figure 3. (a and b) Positive ion DESI-MS spectra of TIN292 and TIN144 detected within polyester-based coil coatings after pre-treatment with acetone vapour. Inset – Putative structures for the *in situ* structural modifications to the precursor HALS compounds present. The ion at *m/z* 370 in the spectrum shown in (a) corresponds to a monofunctional derivative present in the TIN292 additive.

HALS HOST3058 (*N*-C(O)CH_3)

Positive ion DESI-MS spectrum of a cured polyester-based coil coating containing HOST3058 shows a peak that is indicative of the $[M+H]^+$ ion at *m/z* 449.4 (Figure 4). However, this is one of two cases where the base peak in the spectrum is not at the *m/z* associated with the $[M+H]^+$ ion. In this spectrum, the peak at *m/z* 407.4, 42 Da lower than the molecular mass of HOST3058 is the base peak and is more than 10 times the relative abundance of the ionised HOST3058. This ion represents protonated 2-dodecyl-*N*-(2,2,6,6-tetramethyl-4-piperidinyl) succinimide (Figure 4; inset) and is the synthetic precursor to HOST3058, being present at low levels in the authentic sample (data not shown). Product ions arising from PQD activation of *m/z* 407.4 (Figure 4) are shown in Table 1 with the peak distribution and ion abundances almost identical to the PQD spectrum reported for HOST3055 (Table 1) thus confirming the identity as the secondary piperidine of HOST3058. This ion at *m/z* 407.4 is not present in the MS/MS spectrum for the ion at *m/z* 449.4 and therefore is not attributed to in-source fragmentation caused by instrument conditions, and is detected in higher abundances compared to that found in the authentic sample. This phenomenon may be attributed to either selective depletion of HOST3058 over the secondary piperidine during cure or, as is more likely, an increase in abundance of the secondary piperidine compared to HOST3058 resulting from *in situ* *N*-deacetylation of the 1-acetyl-2,2,6,6-tetramethylpiperidine moiety to the 2,2,6,6-tetramethylpiperidine. This phenomenon has also been observed by ESI-MS and ESR analyses following solvent extraction of polyester-based coil coatings containing HOST3058 [29].

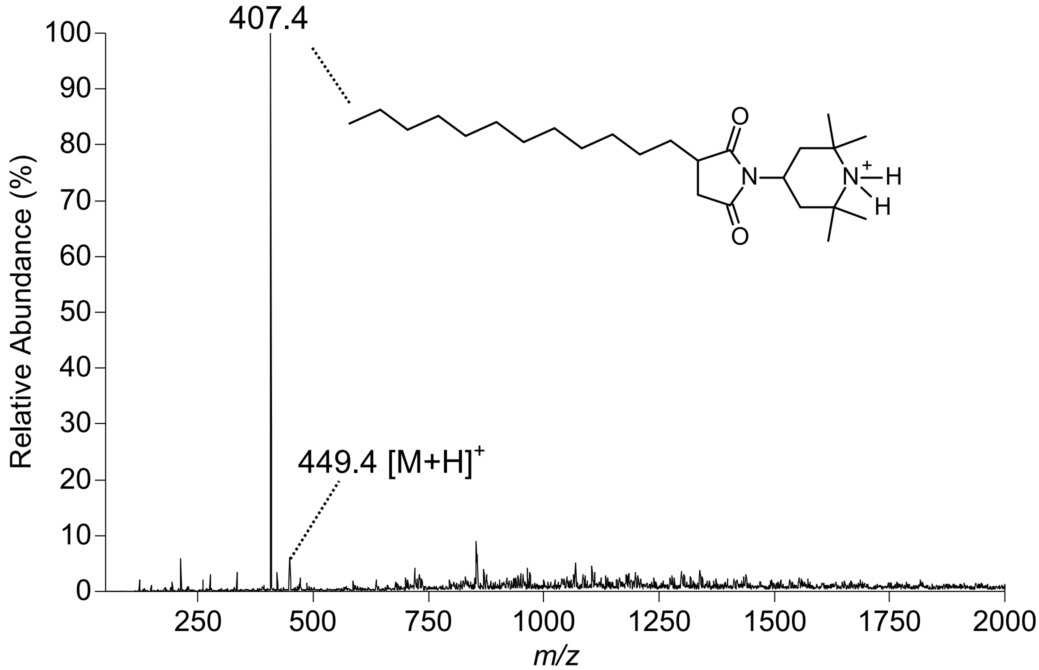


Figure 4. Positive ion DESI-MS spectra of HOST3058 detected within polyester-based coil coatings after pre-treatment with acetone vapour. Inset – Putative structures for the *in-situ* structural modification to the precursor HALS compounds present.

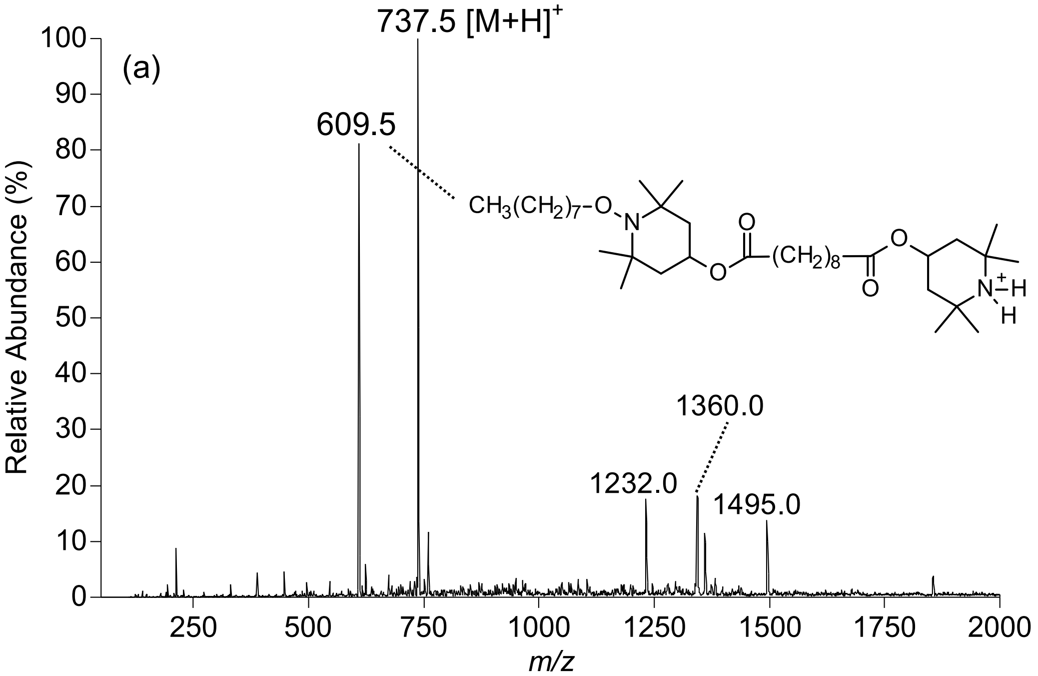
HALS TIN123, TIN152, and TIN NOR371 (*N*-OR)

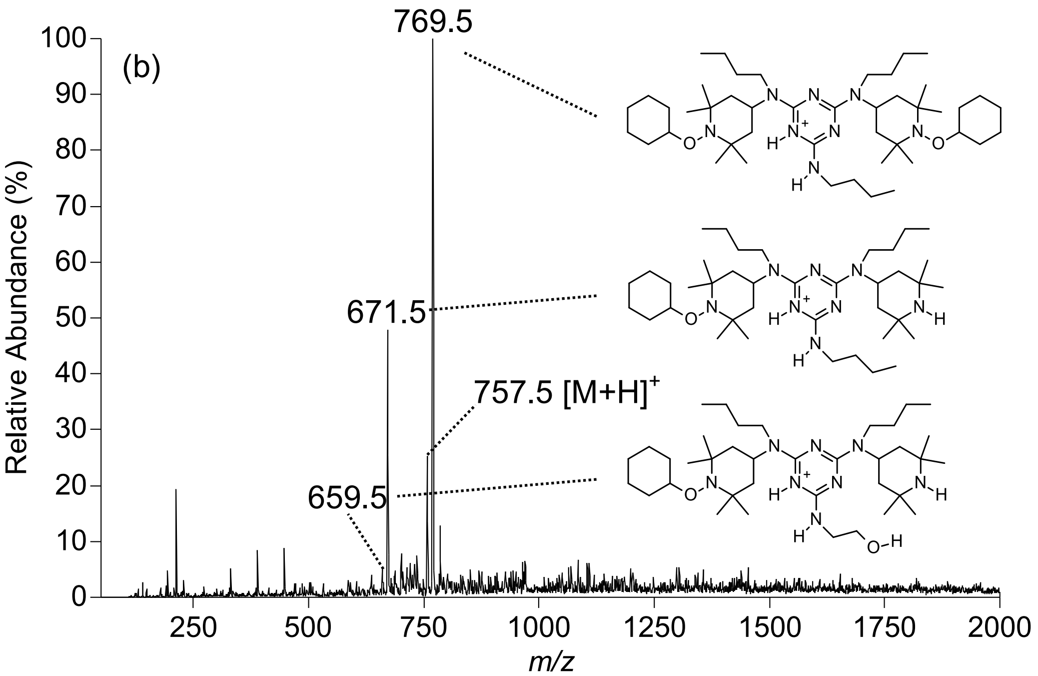
Positive ion DESI-MS spectra of three polyester-based coil coatings each formulated with structurally distinct HALS compounds (TIN123, TIN152, and TIN NOR371) that contain two or more 2,2,6,6-tetramethylpiperidine moieties functionalised at the nitrogen with an alkoxyamine are shown in Figure 5(a-c). TIN123 and TIN152 show peaks that are indicative of their respective $[M+H]^+$ ions at *m/z* 737.5 (Figure 5a), and *m/z* 757.5 (Figure 5b), respectively) with a monomeric fragment of TIN NOR371 (*m/z* 1022.8) detected in Figure 5(c). Positive ion DESI-MS analysis of TIN123 present in polyester-based coil coatings has been well characterised previously [18] and structural modification of the alkoxyamine moiety to the secondary piperidine of TIN123 *in situ* (Figure 5a; inset).

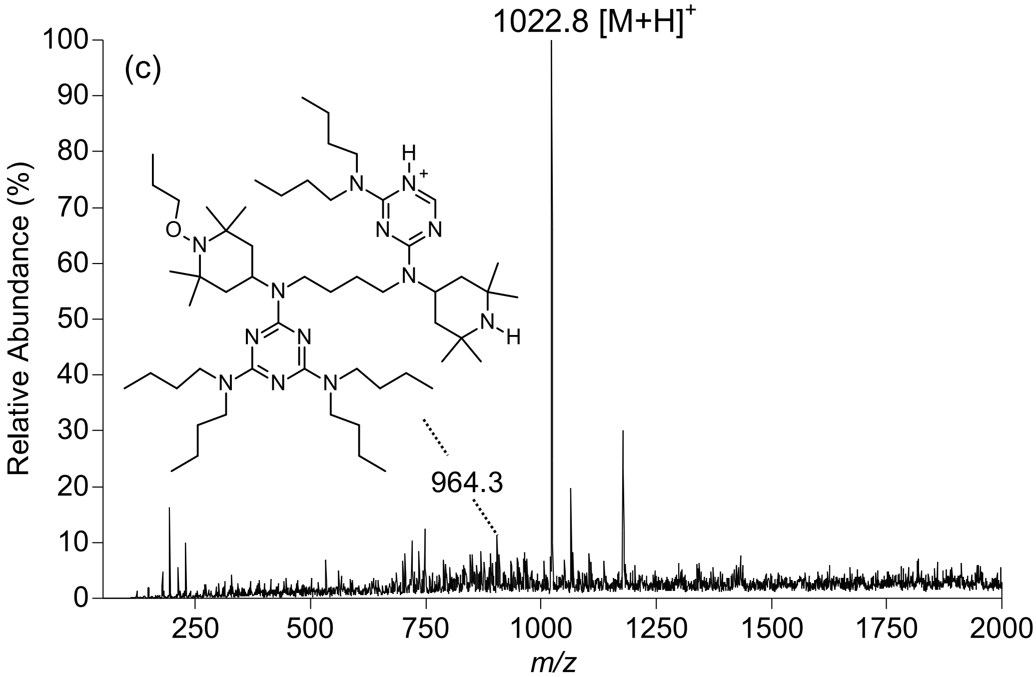
The DESI-MS spectrum for TIN152 is another case where the base peak in the spectrum is not at the *m/z* associated with the $[M+H]^+$ ion. Figure 5(b) shows the base peak at *m/z* 769.5, 12 Da higher than the protonated molecular mass of TIN152. The fragmentation pattern arising from the PQD of *m/z* 769.5 is shown in Table 1 and is similar to that of $[M+H]^+$ ion at *m/z* 757.5 suggesting a high degree of structural homology with TIN152. Tentative structural elucidation of the ion at *m/z* 769.5 using the PQD fragmentation pattern indicates that the aminoethanol group functionalised to the triazine is absent and an additional butyl group is present at this position (Figure 5b; inset). This is supported by the comparison between subsequent fragmentation of product ions generated by PQD of the ion at *m/z* 757.5 and 769.5 (Table 1) that show conservation of the 12 Da mass difference for the analogous ions all the way to the fragment corresponding to a substituted 1,3,5-triazine-2,4,6-triamine (*m/z* 283.2 and 295.2, respectively). Although this compound is not listed as a synthetic by-product by the supplier, analysis of an authentic sample of TIN152 under the same experimental conditions shows a very small relative abundance (< 1%; data not shown) at the same *m/z*. The difference in relative abundances of these two components when detected in a cured thermosetting coating can be rationalised by the propensity for TIN152 to be co-condensed to the polymer backbone through condensation of the primary alcohol substituent to melamine and isocyanate cross-linkers and therefore not able to be liberated from the coating using standard DESI techniques.

Figure 5(b) also exhibits peaks at *m/z* 659.5 and 671.5 corresponding to a mass loss of 98 Da from the $[M+H]^+$ ion of both TIN152 and the butylamino derivative (Figure 5b; inset). This mass difference equates to the substitution of one cyclohexyloxy group with hydrogen, consistent with the formation of a secondary piperidine for both TIN152 (Figure 5b; inset) and the butylamino derivative (Figure 5b; inset). These putative structures are supported by the detection of abundant product ions at *m/z* 520.2 and 532.4, respectively, corresponding to a 139 Da neutral loss from the precursor ions, which represents a loss of 2,2,6,6-tetramethyl-3*H*-pyridine and is indicative of the presence of a secondary piperidine moiety (*c.f.* Scheme 1). Again, these ions are not present in the analysis of authentic samples nor are they a result of in-source fragmentation caused by instrument conditions or listed as synthetic by-products listed by the supplier.

The positive ion DESI-MS spectrum of a cured polyester-based coil coating containing oligomeric TIN NOR371 after pre-treatment is shown in Figure 5(c). The spectrum contains a dominant base peak at *m/z* 1022.8 that corresponds to the monomeric structure of the oligomer minus an *N*,*N*-dibutyl amino group (Figure 1). The putative structure is supported by the MS/MS spectrum of ions at *m/z* 1022.8 (Table 1). PQD of the isolated ion yielded product ions at *m/z* 979.8 corresponding to the loss of a propyl radical from *N*O-C bond cleavage of the alkoxyamine and *m/z* 851 corresponding to the subsequent loss of an *N*,*N*-dibutylamino group. The major product ion at *m/z* 825 corresponds to the neutral loss of 197 Da (2,2,6,6-tetramethyl-1-propoxy-3*H*-pyridine) from the precursor resulting from elimination of 2,2,6,6-tetramethyl-1-propoxypiperidine following a highly characteristic fragmentation mechanism for HALS containing piperidine structures [29].


737.5 [M+H]+
(a)
609.5
1360.0
1232.0
1495.0
Relative Abundance (%)
m/z
CH3(CH2)7-O-N
(CH2)8


769.5
(b)
671.5
757.5 [M+H]+
659.5
Relative Abundance (%)
m/z



396

397 **Figure 5**. (a-d) Positive ion DESI-MS spectra of TIN123, TIN152, and TIN NOR371 detected within
398 polyester-based coil coatings after pre-treatment with acetone vapour. Inset – Putative structures for
399 synthetic by-products and *in-situ* structural modifications to precursor HALS compounds present.

400

Computational investigations of mechanisms for *N*-modifications

The above experimental analysis of the all the major classes of HALS (*N-OR*, *N*-R and *N*-C(O)R) indicates *in situ* conversion of the substituted piperidine moiety to a secondary amine within pigmented polyester-based coil coatings during curing. Below we discuss the mechanistic implications of these results with the aid of computational chemistry.

N-OR HALS

The conversion of *N*–OR HALS to the corresponding secondary amine *N*–H under curing conditions (232 °C) echoes our earlier model spin-trapping ESR experiments for TIN123 at 80 °C (a typical service temperature), which detected the spin-trap adducts of an alkoxyl radical and α-phenyl-*N*-*tert*-butyl nitrone [18]. Collectively these experimental observations are equally consistent with both the *β*-hydrogen abstraction based regeneration mechanism and the direct *N*–OR homolysis mechanisms of Scheme 1 [21]. Previous computational studies concluded that, even for a model polyester-derived radical for which *N*–OR and *N*O–R homolysis is equally likely, the *β*-hydrogen abstraction based regeneration mechanism was still more energetically favourable, even at typical service temperatures of 80 °C [21]. Moreover, other computational studies have shown that *N*–OR homolysis is uncompetitive with *N*O–R homolysis for most other leaving groups [17, 32]. Nonetheless, in the present work we examine the *N*–OR and *N*O–R homolysis gas- and solution-phase enthalpies and Gibbs free energies (kJ mol^{-1}) for representative HALS from the present work (see Table 2) Table 2 shows results at 260 °C, which represents the upper end of typical curing temperatures; whilst the absolute Gibbs free energies are temperature dependent, the free energy differences themselves are relatively unaffected by temperature over the range studied (25 – 260 °C; see Table S1 of the Supporting Information).

Table 2. Gas- and solution-phase enthalpies and Gibbs free energies at 260 °C (kJ mol^{-1})[a] of *N*-OR and *N*O-R homolysis for TIN123, TIN152, and TIN NOR371.[a]

HALS	R	*N*-OR			*N*O-R		
		Gas phase		Solution	Gas phase		Solution
		ΔH	*ΔG*	*ΔG*	*ΔH*	*ΔG*	*ΔG*
TIN123	C_3H_7	233.90	118.13	123.49	219.61	109.19	114.77
TIN152	*c*-C_6H_{11}	228.13	113.77	115.00	216.27	101.46	103.02
TIN NOR371	C_3H_7	234.91	118.37	121.73	218.70	106.52	111.52

[a] Electronic energies of homolysis were calculated double-layer ONIOM approximation to G3(MP2)-RAD method at the R(O)MP2/6-311+G(3df,2p) level of theory in conjunction with B3LYP/6-31G(d) optimised geometries and scaled frequencies; Free energies of solvation in toluene were calculated using UAKS-PCM/B3LYP/6-31G(d) method. Results at 25 and 80 °C are given in Table S1 of the Supporting Information.

Comparison of the calculated gas and solution-phase Gibbs free energies of *N*-OR and *N*O-R homolysis for the three alkoxyamine HALS investigated (Table 2) indicates that *N*O-R homolysis would be thermodynamically favoured in each case. However, the Gibbs free energy differences between *N*-OR and *N*O-R homolysis in these examples are small (*ca*. 10 kJ mol^{-1}), suggesting that *N*–OR homolysis could be occurring once every ten or so *N*O–R reactions at 260 °C (or once every 60 at 80 °C). Whilst neither *N*–OR nor *N*O–R is competitive with β-hydrogen abstraction pathway at room temperature or service temperatures such as 80°C [21], homolysis *per se* becomes relatively more important at the high temperatures associated with curing (*e.g.*, 260°C) due to its entropic favourability. Under those circumstances, it is conceivable that, for these simple alkyl leaving groups, *N*–OR homolysis may play a minor role. For example, in the TIN123 at 260 °C direct homolysis of the *N*–OR bond has a free energy change of ΔG = 123.5 kJ mol^{-1} and an approximate first order rate coefficient of k = 8.8 s^{-1}[33]. At the same temperature, based on previous calculations for similar systems [21], the second-order rate constants for *β*-hydrogen abstraction from the alkoxyamine range from 10^{-1} to 10^{5} M^{-1} s^{-1} depending on the abstracting radical. Depending on the steady state radical concentrations, it is conceivable that the unimolecular homolysis reaction could be competitive with the bimolecular abstraction reaction at this temperature. In contrast, at 80 °C the homolysis rate coefficient drops to 6.5×10^{-11} s^{-1}, and is uncompetitive with even the slowest abstraction rate coefficients, which in turn range from 10^{-4} to 10^{4} M^{-1} s^{-1}.

N-CH_3 and *N*-C(O)CH_3 HALS

In contrast to alkoxyamines, homolysis of the *N*-R bond is computed to be high in energy for R = H, CH_3 or C(O)CH_3 (Table 3). These bond energies are some 150 kJ mol^{-1} greater than those calculated for the alkoxyamine moiety (Table 2) and therefore direct homolysis seems an unlikely pathway to modification at the piperidinyl nitrogen. Indeed, for *N*-CH_3 HALS, activation pathways have been examined previously [21] with the most favoured pathway involving hydrogen abstraction from the *N*–CH_3 group, followed by addition of oxygen, coupling, decomposition to *N*–$CH_2O^{\bullet}$ radical and *β*-scission to the aminyl radical, which then either convert to the secondary amine, or oxidise to the nitroxide (see Scheme 2).

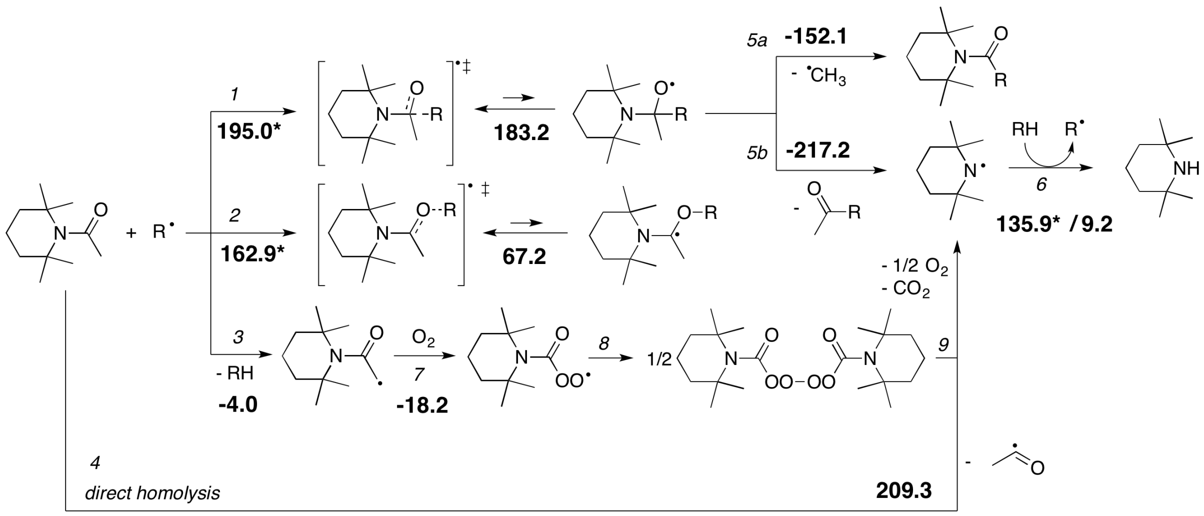
Table 3. Gas- and solution-phase enthalpies and Gibbs free energies at 260 °C (kJ mol^{-1})[a] of *N*-R homolysis for TIN770, HOST3052, HOST3055, HOST3050, TIN292, TIN144, and HOST3058.[a]

HALS	R	Gas phase		Solution
		ΔH	*ΔG*	*ΔG*
TIN770	H	407.48	335.77	362.02
HOST3052	H	406.60	334.31	360.14
HOST3055	H	406.83	334.69	360.90

HOST3050	H	406.58	334.21	360.25
TIN292, TIN144	CH_3	314.50	211.07	233.80
HOST3058	$C(O)CH_3$	326.25	208.16	226.62

[a] Electronic energies of homolysis were calculated double-layer ONIOM approximation to G3(MP2)-RAD method at the R(O)MP2/6-311+G(3df,2p) level of theory in conjunction with B3LYP/6-31G(d) optimised geometries and scaled frequencies; Free energies of solvation in toluene were calculated using UAKS-PCM/B3LYP/6-31G(d) method. Results at 25 and 80 °C are given in Table S2 of the Supporting Information.

For *N*-deacetylation, several mechanistic routes towards an aminyl radical can be suggested by analogy to the established chemistry of *N*–CH_3 and *N*–OR HALS (Scheme 4). Firstly, abundant reactive polymer radicals $R^•$ can attack the carbonyl bond [34] of an initial HALS, adding either to a carbon (Scheme 4, reaction *1*) or an oxygen atom (Scheme 4, reaction *2*). Addition to the carbon side of the carbonyl bond, followed by β-scission in the forming O-centred radical (Scheme 4, reaction *5*), ultimately leads to an aminyl radical, but is strongly disfavoured on both kinetic and thermodynamic grounds and thus is not likely to be responsible for the experimental observations. Addition to the oxygen side of the carbonyl moiety, likewise, appears to be energetically unfeasible, and, most importantly, does not provide a pathway to an aminyl radical. In contrast, hydrogen abstraction from the *N*-$C(O)CH_3$ group of the initial HALS (Scheme 4, reaction *3*) and subsequent oxidation (Scheme 4, reactions *7*-*9*) similar to that of the *N*-alkyl HALS adduct (Scheme 2b) [21] represents an energetically feasible route to the aminyl radical. As noted above, *N*–C homolysis (Scheme 4, reaction *4*), on the other hand, does not appear to be competitive with the aforementioned pathway. Once formed, the aminyl radical can abstract a hydrogen atom from, for example, polymer backbone to yield experimentally observed secondary amine or enter one of the regenerative cycles (*cf.* Scheme 1).



Scheme 4. Formation of aminyl radicals and secondary amines from the thermal decomposition of an *N*-acetyl-piperidine model for the HALS HOST3058: numbers in bold are the Gibbs free energies of reactions (activation*) in gas phase at 260 °C. Results at 25 and 80 °C are given in Table S3 of the Supporting Information.

Conclusion

The detection of ten hindered amine light stabilisers within polyester-based coil coatings by DESI-MS has proven to be rapid, straightforward and able to be performed under ambient conditions. DESI-MS/MS also provides enough qualitative information to enable the characterisation of structural changes occurring to HALS within polyester-based coil coatings. HALS containing a 2,2,6,6-tetramethylpiperidine moiety functionalised at the nitrogen (TIN292, TIN144, HOST3058, TIN123, TIN152, and TIN NOR371) all gave indications of undergoing *in situ* conversion to the corresponding secondary piperidine (*N*-H). These changes occurred under typical curing conditions implying that at least some portion of the initial HALS is actually converted to secondary amine even prior to service. This in turn has implications for their activation and performance under subsequent in-service conditions. Until recently [21] mechanisms for understanding aminoxyl radical regeneration of HALS (such as the Denisov cycle [7-16]) either did not account for a secondary piperidine intermediate or were deemed energetically unfeasible [17, 32] yet it is clear from these results that formation of this intermediate constitutes a major pathway in HALS protection of polymers. Recently, two possible mechanisms for the formation of the secondary piperidine *in situ* from alkoxyamines have been suggested [21]: (i) by direct *N*-OR bond homolysis or, (ii) *via* hydrogen abstraction and subsequent β-scission. In this work we show that both are consistent with the observed experimental data, though based on high-level quantum chemical calculations, pathway (ii) is dominant under normal service temperatures (25-80 °C), while pathway (i) may become competitive at low radical concentrations and the high temperatures associated with curing (260 °C). Thus both mechanisms warrant strong consideration for all future discussions involving the activation/regeneration of HALS in polymers.

The effectiveness of particular HALS as stabilising agents can be attributed to their ability to remain an active participant in the Denisov cycle, forming and reforming the aminoxyl radical intermediate. Concordantly, resistance to chemical deactivation and/or physical losses including leeching or volatilisation are paramount [35-38]. For these reasons, the stabilising efficacy of different HALS compounds may vary dramatically, being influenced by many factors such as diffusion and solubility coefficients as well as the properties of the coating itself including resin systems, pigment components, curing temperatures and the degree of degradation experienced [12, 36, 39-41]. In order to optimise HALS compounds, particularly for use in coil coatings, understanding the molecular changes that may occur *in situ* leading to activation or deactivation of HALS and affecting the total active content remaining in the coating after curing is vital.

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Supporting Information: Computational Section

Desorption Electrospray Ionisation Mass Spectrometry of Stabilised Polyesters Reveals Activation of Hindered Amine Light Stabilisers

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Table S1. Calculated gas-phase enthalpies and Gibbs free energies (kJ mol^{-1}) of *N*-OR and *N*O-R homolysis for TIN123, TIN152, and TIN NOR371.

HALS	R	*N*-OR			*N*O-R			ΔΔ*G*
		Gas phase		Solution	Gas phase		Solution	
		Δ*H*	Δ*G*	Δ*G*	Δ*H*	Δ*G*	Δ*G*	
25 °C								
TIN123	C_3H_7	233.93	169.26	170.61	219.15	157.85	158.57	12.04
TIN152	*c*-C_6H_{11}	228.78	164.43	161.80	216.93	152.34	150.01	11.79
TIN NOR371	C_3H_7	234.93	169.84	171.03	218.21	155.95	156.17	14.86
80 °C								
TIN123	C_3H_7	234.10	157.29	155.79	219.46	146.48	145.20	10.59
TIN152	*c*-C_6H_{11}	228.75	152.53	146.89	216.96	140.39	135.09	11.80
TIN NOR371	C_3H_7	235.10	157.79	154.28	218.53	144.41	142.53	11.75
260 °C								
TIN123	C_3H_7	233.90	118.13	123.49	219.61	109.19	114.77	8.72
TIN152	*c*-C_6H_{11}	228.13	113.77	115.00	216.27	101.46	103.02	11.98
TIN NOR371	C_3H_7	234.91	118.37	121.73	218.70	106.52	111.52	10.21

Table S2. Calculated gas-phase enthalpies and Gibbs free energies (kJ mol^{-1}) of *N*-R homolysis for TIN770, HOST3052, HOST3055, HOST3050, TIN292, TIN144, and HOST3058.

HALS	R	Gas phase		Solution
		Δ*H*	Δ*G*	Δ*G*
25 °C				
TIN770	H	403.72	366.46	383.71
HOST3052	H	402.83	365.25	382.08
HOST3055	H	403.06	365.56	382.77
HOST3050	H	402.80	365.19	382.23
TIN292, TIN144	CH_3	311.99	256.13	269.87
HOST3058	$C(O)CH_3$	326.34	260.34	269.80
80 °C				
TIN770	H	404.69	359.47	378.85
HOST3052	H	403.80	358.20	377.17

HOST3055	H	404.03	358.53	377.87
HOST3050	H	403.77	358.13	377.30
TIN292, TIN144	CH_3	312.82	245.72	261.59
HOST3058	$C(O)CH_3$	356.51	248.11	259.71
		260 °C		
TIN770	H	407.48	335.77	362.02
HOST3052	H	406.60	334.31	360.14
HOST3055	H	406.83	334.69	360.90
HOST3050	H	406.58	334.21	360.25
TIN292, TIN144	CH_3	314.50	211.07	233.80
HOST3058	$C(O)CH_3$	326.25	208.16	226.62

Table S3. Calculated kinetic and thermodynamic parameters (in the gas phase) for studied reactions of N-acetyl HALS activation in Scheme 4 of the manuscript.

Reaction	Kinetics		Thermodynamics		
	$\Delta G^{\neq}$, kJ mol^{-1}	ln k	ΔS, J mol^{-1} K^{-1}	ΔH, kJ mol^{-1}	ΔG, kJ mol^{-1}
25 °C					
1	145.292	-25.955	-216.098	68.465	132.894
2	119.203	-15.431	-172.412	-24.155	27.250
3			-2.951	-5.656	-4.776
4			222.018	327.812	261.617
5a			168.832	-61.844	-112.181
5b			241.357	-88.958	-160.918
6	101.553	-3.708	-1.799	8.598	9.135
7			-156.724	-102.111	-55.384
80 °C					
1	156.978	-20.468	-215.381	68.704	144.765
2	129.511	-11.114	-171.361	-23.810	36.706
3			-3.289	-5.764	-4.603
4			222.641	328.010	249.384
5a			169.934	-61.493	-121.505
5b			240.656	-89.191	-174.179
6	111.098	-1.688	-0.973	8.867	9.210
7			-157.665	-102.414	-46.734
260 °C					
1	195.022	-10.177	-211.450	70.468	183.203
2	162.918	-2.935	-167.495	-22.088	67.212
3			-3.577	-5.879	-3.972
4			222.255	327.795	209.300
5a			169.599	-61.710	-152.131
5b			236.852	-90.898	-217.175
6	141.702	3.158	0.874	9.666	9.200
7			-158.408	-102.697	-18.241

Table S4. Contributions to the gas and solution-phase free energies (at 298.15 K) of species in homolysis reactions.

Species	Raw E^0_{gas} RMP2[a] (Hartrees)	Raw E^0_{gas} G3(MP2)-RAD (Hartrees)	E^0_{gas} [b] (Hartrees)	T_c (Hartrees)	$ZPVE$ (Hartrees)	S_{gas} (J mol K^{-1})	G_{gas} (Hartrees)	ΔG_{solv} (toluene) (kJ mol^{-1})
•H	-0.49981	-0.50171	-0.50171	0.00236	0.00000	114.61	-0.51236	8.16
•CH_3	-39.73168	-39.78519	-39.78519	0.00405	0.02925	201.12	-39.77473	4.44
•C_3H_7	-	-118.30909	-118.30909	0.00593	0.08723	289.68	-118.21594	-1.88
•OC_2H_5	-154.05369	-154.18727	-154.18727	0.00547	0.06355	281.79	-154.15025	-4.06
•cyclo-C_6H_{13}	-	-234.89564	-234.89564	0.00699	0.15324	323.39	-234.73541	-7.28
•O-cyclo-C_6H_{13}	-309.74935	-310.03707	-310.03707	0.00756	0.15797	338.14	-309.90993	-7.74
•C(O)CH_3	-152.89296	-152.99942	-152.99942	0.00490	0.04257	268.88	-152.98249	-0.04
•R1 (full)	-306.46556	-	-306.60575	0.00830	0.10327	354.21	-306.53441	-4.10
•iPr (R1 core)	-118.17367	-118.31386	-	-	-	-	-	-
•O-R1 (full)	-381.55224	-	-381.72871	0.00914	0.10724	379.71	-381.65545	-4.10
•O-iPr (O-R1 core)	-193.27734	-193.45382	-	-	-	-	-	-
•R2 (full)	-345.69158	-	-345.87428	0.00999	0.13088	395.55	-345.77833	-3.81
•tBu (R2 core)	-157.39814	-157.58085	-	-	-	-	-	-
•O-R2 (full)	-420.77967	-	-420.99841	0.01051	0.13536	404.57	-420.89848	-3.60
•O-tBu (O-R2 core)	-232.50351	-232.72225[c]	-	-	-	-	-	-
•R3	-306.46217	-306.68555	-306.68555	0.00865	0.10194	365.82	-306.61650	-3.89
•O-R3	-381.57225	-381.83217	-381.83217	0.00907	0.10690	380.81	-381.75944	-3.22
Piperidine	-251.33730	-251.58766	-	-	-	-	-	-
•Piperidinyl	-250.67354	-250.92251	-	-	-	-	-	-
N-methylpiperidine	-290.55252	-290.84510	-	-	-	-	-	-
N-ethoxypiperidine	-404.84120	-405.20849	-	-	-	-	-	-

piperidine								
N-acetylpiperidine	-403.72957	-404.07589	-	-	-	-	-	-
Tinuvin770	-635.74325	-	-635.99360	0.01680	0.30754	519.93	-635.72831	-4.44
•Tinuvin770	-635.07815	-	-635.32712	0.01689	0.29407	530.32	-635.07638	-3.10
Tinuvin292	-674.94803	-	-675.24062	0.01809	0.33566	544.07	-674.94866	-4.64
Tinuvin123	-789.24406	-	-789.61135	0.02051	0.36734	595.21	-789.29110	-0.75
Tinuvin123-1	-828.46268	-	-828.87281	0.02193	0.39536	628.18	-828.52685	1.46
Tinuvin152	-1201.14364	-	-1201.66452	0.02862	0.54190	758.15	-1201.18009	-5.98
•Tinuvin152	-891.28406	-	-891.53303	0.02211	0.37559	635.85	-891.20753	-8.62
TinuvinNOR371	-1045.45038	-	-1045.81767	0.02570	0.44891	699.34	-1045.42248	-6.11
TinuvinNOR371-1	-1084.66893	-	-1085.07906	0.02713	0.47692	732.27	-1084.65817	-3.14
Hostavin3052	-769.42397	-	-769.67433	0.02043	0.38132	601.37	-769.34088	-4.98
•Hostavin3052	-768.75921	-	-769.00818	0.02055	0.36782	612.80	-768.68940	-4.06
Hostavin3055	-767.08131	-	-767.33167	0.01826	0.33760	547.70	-767.03801	-5.98
•Hostavin3055	-766.41645[d]	-	-766.66542	0.01838	0.32409	558.86	-766.38641	-4.69
Hostavin3050	-1074.20359	-	-1074.45394	0.02591	0.45721	694.65	-1074.04971	7.82
•Hostavin3050	-1073.53883	-	-1073.78780	0.02603	0.44371	706.21	-1073.39825	8.95
Hostavin3058	-919.45010	-	-919.79642	0.02120	0.37602	606.37	-919.46806	-6.44
N(i-propyloxy)-piperidine	-444.06716	-444.47698	-	-	-	-	-	-
N(t-butyloxy)-piperidine	-483.29322	-483.74502	-	-	-	-	-	-
N(1-ethoxyacetyl)-piperidine	-632.36176	-632.85495	-	-	-	-	-	-
•N-oxypiperidine	-325.78849	-326.06353	-	-	-	-	-	-
•O-Tinuvin770	-710.19849	-	-710.47353	0.01766	0.29976	544.11	-710.21790	-3.68
Tinuvin770-R1	-1016.74477	-	-1017.15458	0.02490	0.40945	690.18	-1016.79861	3.72
Tinuvin770-R2	-1055.96549	-	-1056.41729	0.02641	0.43634	710.59	-1056.03524	5.56
Tinuvin770-R3	-1016.76198	-	-1017.25517	0.02500	0.40876	696.95	-1016.90056	4.56
•O-TinuvinNOR371	-966.40508	-	-966.68013	0.02292	0.38125	651.40	-966.34994	-8.79
TinuvinNOR371-R1	-1272.95114	-	-1273.36095	0.03012	0.49098	794.64	-1272.93009	-2.01

TinuvinNOR371-R2	-1312.17178	-	-1312.62358	0.03164	0.51786	815.80	-1312.16672	-0.67
TinuvinNOR371-R3	-1272.96836	-	-1273.46155	0.03018	0.49035	800.23	-1273.03190	-1.67
•O-Hostavin3052	-843.88085	-	-844.15589	0.02132	0.37355	626.84	-843.83220	-4.60
Hostavin3052-R1	-1150.42606	-	-1150.83587	0.02855	0.48321	771.46	-1150.41171	3.35
Hostavin3052-R2	-1189.64673	-	-1190.09853	0.03010	0.51001	793.95	-1189.64858	5.27
Hostavin3052-R3	-1150.44325	-	-1150.93644	0.02864	0.48251	778.40	-1150.51368	3.43
•O-Hostavin3055	-841.53683	-	-841.81187	0.01915	0.32979	572.79	-841.52798	-5.48
Hostavin3055-R1	-1148.08308	-	-1148.49289	0.02640	0.43940	719.21	-1148.10875	1.34
Hostavin3055-R2	-1187.30379	-	-1187.75559	0.02789	0.46639	738.39	-1187.34516	4.06
Hostavin3055-R3	-1148.10013	-	-1148.59331	0.02644	0.43884	723.35	-1148.21017	1.30
•Hostavin3050_1	-806.81044	-	-807.05941	0.02087	0.37212	597.83	-806.73431	0.04
•O-Hostavin3050	-881.93082	-	-882.20586	0.02166	0.37782	611.80	-881.87587	-0.63
Hostavin3050-R1	-1188.47691	-	-1188.88672	0.02891	0.48740	757.86	-1188.45648	6.95
Hostavin3050-R2	-1227.69748	-	-1228.14928	0.03040	0.51435	777.93	-1227.69287	9.16
Hostavin3050-R3	-1188.49400	-	-1188.98719	0.02894	0.48684	761.67	-1188.55789	7.61

[a] Found with a 6-311++G(3df,2p) basis set except where noted; [b] Value used in the determination of G_{gas}, based on the G3(MP2)-RAD or ONIOM E^{o}_{gas} value of the species; [c] UCCSD calculated with Gaussian 09; [d] Calculated with Gaussian 03.

Table S5. Contributions to the gas and solution-phase free energies (at 533.15 K) of species in N-acetyl HALS activation reactions sequence (1)-(7).

Species[a]	Raw E^{0}_{gas}		E^{0}_{gas}[c] (Hartrees)	S_{gas} (J mol K^{-1})	T_c (Hartrees)	$ZPVE$ (Hartrees)	G_{gas} (Hartrees)
	M06-2X[b] (Hartrees)	G3(MP2)-RAD (Hartrees)					
$(CH_3)_2NC(O)CH_3$	-287.79850	-287.48753	0.31097	440.0223	0.02179	0.12856	
TEMP-$C(O)CH_3$	-561.73256		-561.42158	654.8125	0.04433	0.30487	-561.20534
TEMP-$C(O)CH_3$ (no core)	-561.73256	-561.11452	-561.11452	654.8125	0.04433	0.30487	-560.89828
TS1 (core)	-594.79174	-594.14916	0.64258	679.3580	0.04191	0.23303	
TS1	-868.72015		-868.07757	890.0320	0.06454	0.40988	-867.78389
R•	-307.01821	-306.68555	-306.68555	445.4854	0.02117	0.10201	-306.65282
$(CH_3)_2NC(CH_3)(O•)C(CH_3)$ $OC(O)CH_3$	-594.79292	-594.15196	0.64095	680.8120	0.04222	0.23466	
TEMP-$C(CH_3)(O•)$-$C(CH_3)OC(O)CH_3$	-868.72549		-868.08454	888.8475	0.06486	0.41179	-867.78839
$•CH_3$	-39.82312	-39.78519	-39.78519	220.1523	0.00790	0.02927	-39.79272
$CH_3C(O)$-R	-460.31680	-459.82150	-459.82150	553.8248	0.03002	0.15283	-459.75111
$(CH_3)_2NC(O)$-R	-554.98355	-554.38401	0.59954	630.3916	0.03691	0.19879	
TEMP-C(O)-R	-828.91736		-828.31782	838.2944	0.05966	0.37478	-828.05361
RH	-307.68173	-307.35567	-307.35567	436.1049	0.02090	0.11656	-307.30676
$(CH_3)_2NH$	-135.13826	-134.99992	0.13834	318.8637	0.01294	0.09128	
TEMPH	-409.09690		-408.95856	563.3681	0.03618	0.26626	-408.77052
TEMPH (core)	-409.09690	-408.64882	-408.64882	563.3681	0.03618	0.26626	-408.46079
$(CH_3)_2N•$	-134.47923	-134.33626	0.14297	330.0176	0.01315	0.07615	
TEMP•	-408.43548		-408.29250	571.8743	0.03590	0.25274	-408.11999
TEMP• (no core)	-408.43548	-407.98286	-407.98286	571.8743	0.03590	0.25274	-407.81035
TS6 (core)	-442.13898	-441.66964	0.46934	612.4480	0.03449	0.19009	
TS6	-716.09486		-715.62552	840.4219	0.05780	0.36559	-715.37279
TS2 (core)	-594.78856	-594.14603	0.64253	689.7528	0.04238	0.23234	
TS2	-868.72579		-868.08326	916.1177	0.06557	0.40760	-867.79612
$(CH_3)_2NC•(CH_3)OR$	-594.81291	-594.16842	0.64449	696.2255	0.04235	0.23541	

TEMP-C•(CH_3)OR	-868.76345		-868.11896	932.8033	0.06603	0.40978	-867.83257
O_2	-150.31772	-150.17181	-150.17181	222.4622	0.00600	0.00371	-150.20728
$(CH_3)_2$NC(O)CH_2•	-287.13227	-286.81653	0.31574	442.5173	0.02168	0.11469	
TEMP-C(O)CH_2•	-561.07002		-560.75428	660.6157	0.04424	0.29059	-560.55360
TEMP-C(O)CH_2• (no core)	-561.07002	-560.44654	-560.44654	660.6157	0.04424	0.29059	-560.24586
$(CH_3)_2$NC(O)CH_2OO•	-437.49806	-437.03301	0.46505	512.8648	0.02595	0.12498	
TEMP-C(O)CH_2OO•	-711.43433		-710.96928	724.6696	0.04862	0.30116	-710.76665
TEMP-C(O)CH_2OO• (no core)	-711.43433	-710.66271	-710.66271	724.6696	0.04862	0.30116	-710.46008
•C(O)CH_3	-153.16507	-152.99942	-152.99942	305.1934	0.01059	0.04260	-153.00821

[a] •R = •CH(CH_3)OC(O)CH_3; [b] Found with a 6-311++G(3df,2p) basis set except where noted; [c] Value used in the determination of G_{gas}, based on the G3(MP2)-RAD or ONIOM E^o_{gas} value of the species;.

APPENDIX 2: Geometries of the species in this study

NOTE: All species had zero imaginary frequencies, as determined from frequency calculations at the B3-LYP/6-31G(d) level.

•H

```
1\1\GINC-V1257\FOpt\UB3LYP\Gen\H1(2)\GXG501\19-Jul-2010\0\\#B3LYP/gen
6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\
\h.freq\\0,2\H,0.,0.,0.741\\Version=EM64L-G09RevA.02\State=2-A1G\HF=-0
.5002728\S2=0.75\S2-1=0.\S2A=0.75\RMSD=7.184e-12\RMSF=0.000e+00\Dipole
=0.,0.,0.\Quadrupole=0.,0.,0.,0.,0.,0.\PG=OH [O(H1)]\\@
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•CH$_3$

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1\1\GINC-V1261\FOpt\UB3LYP\Gen\C1H3(2)\GXG501\21-Jul-2010\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843545
6\\ch3r.freq\\0,2\C,0.,0.,1.3624813574\H,1.0827958978,-0.0000001934,1.
3621061251\H,-0.5413981164,-0.9377286579,1.3621061251\H,-0.5413977814,
0.9377288513,1.3621061251\\Version=EM64L-G09RevA.02\State=2-A1\HF=-39.
8382919\S2=0.753765\S2-1=0.\S2A=0.750007\RMSD=1.738e-09\RMSF=1.802e-05
\Dipole=0.,0.,-0.0003342\Quadrupole=0.4052027,0.4052027,-0.8104053,0.,
0.,0.\PG=C03V [C3(C1),3SGV(H1)]\\@
```

•C$_3$H$_7$

```
1\1\GINC-V1250\FOpt\UB3LYP\Gen\C3H7(2)\GXG501\21-Oct-2010\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843545
6\\prop.freq\\0,2\C,0.1647780965,0.0000000757,0.0116168345\C,0.0685201
884,-0.0000001167,1.501324309\C,1.4466219378,0.0000001561,2.2064001204
\H,-0.4945095712,0.8805605508,1.8403221659\H,2.0296234207,0.8850521718
,1.9282678628\H,1.3261041329,0.0000000025,3.2966121429\H,2.029623873,-
0.8850514991,1.9282676635\H,-0.4945091212,-0.8805611482,1.8403219676\H
,0.298331835,0.9273258601,-0.5381300047\H,0.2983323089,-0.9273255167,-
0.5381302136\\Version=EM64L-G09RevA.02\State=2-A'\HF=-118.4711129\S2=0
.753855\S2-1=0.\S2A=0.750009\RMSD=3.016e-09\RMSF=1.521e-05\Dipole=0.04
91446,0.,0.0766628\Quadrupole=-0.7208283,0.6967959,0.0240324,-0.000000
3,-0.4269637,0.\PG=CS [SG(C3H1),X(H6)]\\@
```

•OC$_2$H$_5$

```
1\1\GINC-V1274\FOpt\UB3LYP\Gen\C2H5O1(2)\GXG501\26-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\oetr1.freq\\0,2\C,2.0237955308,-0.6188973789,-1.2594651264\C,1.43
72172039,0.0226406536,-0.0023922362\O,0.1739974544,0.5378054988,-0.138
```

```
4639416\H,2.0974384465,0.8171273717,0.4012042827\H,1.3802926606,-0.709
1694037,0.8316010524\H,2.1021711372,0.1203455482,-2.0636114498\H,1.381
114937,-1.434118359,-1.6074947891\H,3.0241496297,-1.0230399307,-1.0643
697919\\Version=EM64L-G09RevA.02\State=2-A\HF=-154.3704911\S2=0.75302\
S2-1=0.\S2A=0.750007\RMSD=9.673e-09\RMSF=5.301e-05\Dipole=0.7047509,-0
.3041536,0.0943465\Quadrupole=-1.1345337,0.4673455,0.6671882,1.1230422
,0.4912559,-0.4836376\PG=C01 [X(C2H5O1)]\\@
```

•cyclo-C_6H_{13}

```
1\1\GINC-V1250\FOpt\UB3LYP\Gen\C6H11(2)\GXG501\21-Oct-2010\0\\#B3LYP/g
en 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=2684354
56\\chex.freq\\0,2\C,0.0664538163,0.0014238557,0.1163507693\C,0.046472
2387,0.0117189303,2.637692549\C,2.2483888054,0.0117198237,1.3799659473
\C,1.4852276754,-0.5249634501,2.6002142658\C,1.5234351707,-0.339780982
7,0.0630869232\C,-0.7195631524,-0.3397818927,1.3442792723\H,0.07491651
36,1.1043733693,2.7517752613\H,2.3322049695,1.1043742852,1.4624204413\
H,1.463352221,-1.6248758009,2.5619158726\H,1.6485485868,-1.4269636892,
-0.1151151084\H,-0.9366155624,-1.4269647381,1.3615210954\H,-0.45928743
8,0.2444112333,-0.8040703769\H,-0.4891323339,-0.3849814146,3.509560909
4\H,3.271466018,-0.3849798888,1.3615210349\H,2.0130085185,-0.255627835
4,3.524206508\H,2.0096279873,0.1566168427,-0.7864375476\H,-1.698293403
9,0.1566153383,1.3315134416\\Version=EM64L-G09RevA.02\State=2-A'\HF=-2
35.2138993\S2=0.753951\S2-1=0.\S2A=0.750011\RMSD=3.503e-09\RMSF=2.012e
-06\Dipole=0.0102256,-0.0599868,0.017902\Quadrupole=0.1629528,-0.24877
84,0.0858256,-0.0078342,-0.0653889,-0.0137158\PG=CS [SG(C2H3),X(C4H8)]
\\@
```

•O-cyclo-C_6H_{13}

```
1\1\GINC-V1254\FOpt\UB3LYP\Gen\C6H11O1(2)\GXG501\21-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\ochexr.freq\\0,2\C,0.0117198281,-0.0659718621,0.0205272438\C,0.0
050181057,0.0032516957,2.5682083446\C,2.2095960891,0.0032528901,1.3089
618288\C,1.4736465586,-0.4483510803,2.5799395482\C,1.4973954132,-0.484
8927563,0.0372043637\C,-0.7286293562,-0.4848939623,1.3087012016\H,-0.0
348628814,1.1022539025,2.6079602138\H,2.2640951905,1.1022551481,1.2948
041523\H,1.5146265069,-1.5452264563,2.651682595\H,1.5371875101,-1.5820
187475,-0.0136460739\H,-0.7926431718,-1.5820200098,1.3171443044\H,-0.0
223267003,1.0480915861,-0.039077365\H,-0.5134989708,-0.3575788421,3.46
5176288\H,3.2456127985,-0.3575768054,1.3179860169\H,1.9822118073,-0.05
77734801,3.4702912013\H,1.9869688605,-0.1052327295,-0.8666892914\H,-1.
7559084205,-0.1052347574,1.2712279021\O,-0.6429775233,-0.4414081188,-1
.1256596202\\Version=EM64L-G09RevA.02\State=2-A'\HF=-310.4259829\S2=0.
753067\S2-1=0.\S2A=0.750007\RMSD=2.980e-09\RMSF=1.946e-05\Dipole=0.411
0066,0.2182126,0.7195544\Quadrupole=0.2426776,2.3577656,-2.6004432,-0.
5294502,-2.4104124,-0.9269141\PG=CS [SG(C2H3O1),X(C4H8)]\\@
```

•C(O)CH_3

1\1\GINC-V1254\FOpt\UB3LYP\Gen\C2H3O1(2)\GXG501\21-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\rh3058.freq\\0,2\H,0.0125353036,0.0511276585,-0.0323469471\C,0.00
59662917,-0.0025001208,1.063040887\H,1.0282685413,0.0545716495,1.45136
23958\H,-0.5462781186,0.8458936563,1.4806612661\C,-0.6314249886,-1.288
9243438,1.5536224735\O,-1.0877088406,-2.1726909097,0.9018470809\\Versi
on=EM64L-G09RevA.02\State=2-A'\HF=-153.1798349\S2=0.752253\S2-1=0.\S2A
=0.750003\RMSD=3.829e-09\RMSF=1.098e-07\Dipole=0.4289621,0.853632,-0.0
026276\Quadrupole=0.5831531,-0.310411,-0.2727421,-0.603143,-0.054379,-
0.0652512\PG=CS [SG(C2H1O1),X(H2)]\\@

•R1 (full)

1\1\GINC-V1257\FOpt\UB3LYP\Gen\C4H7O2(2)\GXG501\22-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\rad1.freq\\0,2\H,-0.3100475901,0.0770742013,0.0203002908\C,-0.143
9714168,0.0436315212,1.099541357\H,0.8668800844,0.420280288,1.31606401
86\H,-0.8398279791,0.7415644114,1.588666736\C,-0.3220754374,-1.3378535
859,1.6126837277\H,-0.1947869646,-1.5568031784,2.6685960585\C,-0.66927
2791,-2.4335885177,0.729149009\O,-0.8444225155,-2.3397168499,-0.479186
4114\O,-0.7822549198,-3.609717272,1.4082052382\C,-1.1242197508,-4.7430
863654,0.6018462293\H,-2.089724062,-4.5925325963,0.109784805\H,-1.1737
466022,-5.5888428231,1.2889319286\H,-0.3641724304,-4.9172809019,-0.165
5949246\\Version=EM64L-G09RevA.02\State=2-A\HF=-307.0484424\S2=0.75668
6\S2-1=0.\S2A=0.750029\RMSD=5.999e-09\RMSF=1.452e-05\Dipole=0.0999382,
-0.0111591,0.6393926\Quadrupole=-0.6937178,4.2242459,-3.5305282,1.2828
211,-0.0459464,1.9627779\PG=C01 [X(C4H7O2)]\\@

•iPr (R1 core)

1\1\GINC-X95\FOpt\UB3LYP\Gen\C3H7(2)\GXG501\28-Jul-2010\0\\#B3LYP/gen
6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=1342177280
\\rad1_c.freq\\0,2\H,0.0736592556,0.278803746,-0.011710523\C,-0.014825
7838,0.0506066829,1.0669560947\H,1.0111617892,0.0457522972,1.461731045
8\H,-0.5499410299,0.8906604451,1.5243337633\C,-0.7031136213,-1.2506252
395,1.3146587496\H,-1.7846605222,-1.2507577064,1.4310829649\C,-0.01454
40338,-2.5516426569,1.0666126428\H,1.0114424752,-2.5466703076,1.461388
8908\H,0.0739903873,-2.7795358151,-0.012114171\H,-0.5494773462,-3.3919
329777,1.523768535\\Version=EM64L-G09RevA.02\State=2-A'\HF=-118.478156
\S2=0.754002\S2-1=0.\S2A=0.750011\RMSD=2.904e-09\RMSF=6.340e-07\Dipole
=0.0164894,0.0000121,-0.0783758\Quadrupole=0.3007783,0.2162605,-0.5170
388,0.0000144,-0.0395218,0.0000925\PG=CS [SG(C1H1),X(C2H6)]\\@

•O-R1 (full)

1\1\GINC-V1387\FOpt\UB3LYP\Gen\C4H7O3(2)\GXG501\22-Jul-2010\0\\#B3LYP/

gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\rad2.freq\\0,2\H,0.5941806174,-0.2533731532,0.0939821153\C,0.0627
155874,-0.0394658541,1.0257387888\H,0.7340160343,0.4833415714,1.712753
1772\H,-0.7825511944,0.6135199219,0.7917170218\C,-0.431425938,-1.32457
57948,1.6930622349\C,-1.3667442034,-2.1523156973,0.7641248692\O,-1.688
3969602,-1.7985776011,-0.3466631122\O,-1.7558180943,-3.2896576989,1.35
30274912\C,-2.650392165,-4.1111297713,0.5792015581\H,-3.5707463921,-3.
5652301244,0.3570015461\H,-2.8594485875,-4.9795252043,1.2035393435\H,-
2.1770404931,-4.4133253463,-0.3586972596\H,0.4239595709,-2.011842582,1
.8816022508\O,-1.0002794608,-1.1546415293,2.9209140175\\Version=EM64L-
G09RevA.02\State=2-A\HF=-382.2412986\S2=0.753451\S2-1=0.\S2A=0.750009\
RMSD=1.021e-09\RMSF=3.416e-05\Dipole=0.2157196,-0.6499517,-0.2539752\Q
uadrupole=3.2303638,2.8033519,-6.0337157,2.5027079,0.3021679,0.7896993
\PG=C01 [X(C4H7O3)]\\@

•O-iPr (O-R1 core)

1\1\GINC-X95\FOpt\UB3LYP\Gen\C3H7O1(2)\GXG501\28-Jul-2010\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=13421772
80\\rad2_c.freq\\0,2\H,-0.007917582,0.0743173418,-0.0035857196\C,0.000
7420605,0.0380365406,1.091389632\H,1.0434633544,0.084975255,1.42551640
68\H,-0.5246490066,0.91501203,1.4804280943\C,-0.6599079814,-1.25059423
6,1.6097455061\C,0.001084482,-2.5390083702,1.0912305873\H,1.0437511708
,-2.5857935518,1.4255783918\H,-0.0073712752,-2.5750287306,-0.003765539
4\H,-0.5242645974,-3.4161332023,1.4800246795\H,-1.7199103123,-1.250713
3595,1.2634550724\O,-0.8130183051,-1.2507215271,2.9769839057\\Version=
EM64L-G09RevA.02\State=2-A\HF=-193.6887883\S2=0.753054\S2-1=0.\S2A=0.7
50007\RMSD=5.534e-09\RMSF=1.173e-04\Dipole=0.0635933,-0.0008473,-0.768
9933\Quadrupole=1.2206412,0.5534143,-1.7740555,0.0009642,0.9767983,-0.
0024479\PG=C01 [X(C3H7O1)]\\@

•R2 (full)

1\1\GINC-V1262\FOpt\UB3LYP\Gen\C5H9O2(2)\GXG501\22-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\rad3.freq\\0,2\H,-0.3259488426,-0.0083344858,0.0209887997\C,-0.15
38765185,-0.0081459393,1.0985444195\H,0.8566397128,0.3796856346,1.2978
242054\H,-0.8506582577,0.7011417718,1.5704253594\C,-0.3205238122,-1.37
76902779,1.6697480661\C,-0.6692282168,-2.4609763034,0.7618878702\O,-0.
8375604296,-2.331700444,-0.4459130722\O,-0.7959345658,-3.6662150624,1.
3896177446\C,-1.138634329,-4.7599494939,0.5317284331\H,-2.0987139769,-
4.5812980572,0.0387206186\H,-1.1996574807,-5.634527937,1.1810817989\H,
-0.3735880182,-4.9059623053,-0.236479733\C,-0.1252786559,-1.5838793264
,3.1370145149\H,-0.2735024517,-2.6225761439,3.4333510912\H,0.886253801
1,-1.2737840496,3.4407529155\H,-0.8194644869,-0.9529239522,3.712847225
3\\Version=EM64L-G09RevA.02\State=2-A\HF=-346.3696468\S2=0.756647\S2-1
=0.\S2A=0.750029\RMSD=7.835e-09\RMSF=4.387e-05\Dipole=0.1107111,-0.059

2881,0.7640873\Quadrupole=-0.3443712,3.9070795,-3.5627083,1.1834532,-0
.0744238,2.153437\PG=C01 [X(C5H9O2)]\\@

•tBu (R2 core)

1\1\GINC-X97\FOpt\UB3LYP\Gen\C4H9(2)\GXG501\28-Jul-2010\0\\#B3LYP/gen
6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=1342177280
\\rad3_c.freq\\0,2\H,0.1763563342,0.3055419215,0.0056616431\C,0.022696
3384,0.0393133838,1.0690310443\H,1.0208798187,-0.0090895408,1.52283474
95\H,-0.5182961547,0.8795443654,1.5228879011\C,-0.7219345099,-1.250431
615,1.2274081482\C,0.0227244959,-2.5401744478,1.0687759399\H,1.0207846
462,-2.4920357573,1.5228853058\H,0.1767725805,-2.8060821014,0.00535761
3\H,-0.5184038184,-3.3805953651,1.5221202932\C,-2.2112083345,-1.250421
3071,1.0688232834\H,-2.5186122025,-1.2503341722,0.0054260636\H,-2.6684
89164,-0.3618215857,1.5226396242\H,-2.6685111296,-2.1390728755,1.52249
23908\\Version=EM64L-G09RevA.02\State=2-A\HF=-157.7983172\S2=0.754019\
S2-1=0.\S2A=0.750012\RMSD=7.519e-09\RMSF=1.719e-05\Dipole=0.0001113,-0
.000109,-0.0759207\Quadrupole=0.1745263,0.1743177,-0.348844,-0.0001027
,0.0000847,0.0001004\PG=C01 [X(C4H9)]\\@

•O-R2 (full)

1\1\GINC-V1252\FOpt\UB3LYP\Gen\C5H9O3(2)\GXG501\23-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\rad4.freq\\0,2\H,-0.1233268105,0.0808565484,-0.0154350799\C,-0.08
16621693,0.0229925206,1.074866899\H,0.9601116664,0.0648882449,1.405567
4184\H,-0.6123313848,0.8891206098,1.4806336587\C,-0.7166798077,-1.2781
297486,1.5935823934\C,-2.1873479267,-1.4031623976,1.1041465568\O,-2.65
67649986,-0.7323384421,0.2112369571\O,-2.8590421122,-2.3530626336,1.77
20680442\C,-4.2266608613,-2.5393003469,1.3663966073\H,-4.7938218392,-1
.6151282987,1.5036544308\H,-4.6156831672,-3.3285050075,2.0097491409\H,
-4.2785680596,-2.8363954833,0.3154060724\O,-0.6311405318,-1.4001775391
,2.9514856912\C,0.0504819067,-2.5306638215,1.0425051352\H,1.0930456699
,-2.481231195,1.3663157464\H,-0.4072039042,-3.4480519787,1.4166531407\
H,0.007557029,-2.510764147,-0.0509868745\\Version=EM64L-G09RevA.02\Sta
te=2-A\HF=-421.5593366\S2=0.753222\S2-1=0.\S2A=0.750008\RMSD=9.027e-09
\RMSF=6.025e-06\Dipole=-0.0694863,-0.5712874,-0.3552931\Quadrupole=4.6
555668,0.2217841,-4.8773509,1.9405588,-2.87459,1.9562617\PG=C01 [X(C5H
9O3)]\\@

•O-tBu (O-R2 core)

1\1\GINC-X97\FOpt\UB3LYP\Gen\C4H9O1(2)\GXG501\28-Jul-2010\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=13421772
80\\rad4_c.freq\\0,2\C,2.0074679113,-0.5878385831,-1.2569805241\C,1.47
31711234,0.0269496588,0.0521246177\O,0.1652084539,0.4445044936,-0.0997
455779\H,2.033390682,0.1714635778,-2.0461512004\H,1.3545966183,-1.4018
089232,-1.5869926828\H,3.0231418644,-0.9786644746,-1.1263327795\C,2.36

25928071,1.1839129603,0.5497966567\C,1.3640954228,-1.0741056321,1.1535
121296\H,2.3966338144,1.9817774005,-0.2000415215\H,3.3885132097,0.8447
206419,0.7336939166\H,1.9564622247,1.6021324727,1.4759822538\H,0.96182
75012,-0.6522744041,2.0783955144\H,2.3667019895,-1.471098791,1.3459468
702\H,0.7145443773,-1.8873943976,0.8191103271\\Version=EM64L-G09RevA.0
2\State=2-A\HF=-233.0061609\S2=0.752892\S2-1=0.\S2A=0.750006\RMSD=6.84
3e-09\RMSF=2.673e-05\Dipole=0.6954117,-0.3107252,0.1680292\Quadrupole=
-1.7622148,0.7592219,1.0029929,0.8878146,-0.4179701,-0.3913985\PG=C01
[X(C4H9O1)]\\@

•R3

1\1\GINC-V1250\FOpt\UB3LYP\Gen\C4H7O2(2)\GXG501\22-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\rad5.freq\\0,2\H,-0.8104817274,-0.1829595055,0.0143788352\C,-0.28
24136547,0.1615156814,0.9127719641\H,0.6154869541,0.7038722432,0.56833
41473\H,-0.9221158533,0.8807067781,1.4339372417\C,0.0461254073,-0.9697
876457,1.8133112484\H,0.1893151753,-0.8909627133,2.8835346046\O,0.6716
132594,-2.0358147087,1.1998012982\C,1.2171108414,-3.0173957146,1.98665
03348\O,1.2099908551,-2.9828550138,3.1948166358\C,1.7978003095,-4.1122
25574,1.1277108694\H,1.0008070482,-4.605377824,0.5601045396\H,2.298865
6889,-4.8424808663,1.7638872272\H,2.5053028373,-3.6970364893,0.4028620
564\\Version=EM64L-G09RevA.02\State=2-A\HF=-307.0439999\S2=0.753621\S2
-1=0.\S2A=0.750009\RMSD=2.926e-09\RMSF=1.178e-05\Dipole=0.0287663,0.14
06237,-0.780083\Quadrupole=0.2827745,3.0772734,-3.3600479,-1.4036509,-
0.9229834,2.0033167\PG=C01 [X(C4H7O2)]\\@

•O-R3

1\1\GINC-V1249\FOpt\UB3LYP\Gen\C4H7O3(2)\GXG501\22-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\rad6.freq\\0,2\H,0.439454935,-0.1021465587,0.2948481109\C,0.04107
79957,-0.1998603704,1.3079948943\H,0.7722121008,-0.7049688699,1.943906
2342\H,-0.1762295202,0.7914763728,1.7123036659\C,-1.2538997239,-1.0367
732037,1.2715496861\H,-1.6049554419,-1.1905530472,2.313273378\O,-0.947
4996047,-2.3610152619,0.7287690845\C,-0.6653626006,-3.3243112703,1.634
3666609\O,-0.6344810402,-3.1289749099,2.833333359\C,-0.4030743934,-4.6
489501379,0.9604131134\H,-1.2865546841,-4.9580703518,0.3921675161\H,-0
.1625526461,-5.4001692242,1.7132967451\H,0.4238735696,-4.552092808,0.2
495097182\O,-2.2238201716,-0.4533305805,0.584165895\\Version=EM64L-G09
RevA.02\State=2-A\HF=-382.2612259\S2=0.753425\S2-1=0.\S2A=0.750009\RMS
D=1.536e-09\RMSF=7.690e-06\Dipole=0.5837395,-0.1623612,-0.2487185\Quad
rupole=-0.1863152,3.5602696,-3.3739544,1.9395887,-2.0493082,3.1901562\
PG=C01 [X(C4H7O3)]\\@

Piperidine

1\1\GINC-V1284\FOpt\RB3LYP\Gen\C5H11N1\GXG501\21-Jul-2010\0\\#B3LYP/ge

n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843545
6\\nh6.freq\\0,1\H,-0.0258218042,-0.025468577,-0.0029054737\C,0.007689
0976,-0.0061169007,1.0941374337\H,1.0639903329,-0.0120397321,1.3916377
019\C,-0.6932495174,1.2607321818,1.6096809786\H,-0.2430082653,2.157881
9153,1.166522607\H,-0.5433688821,1.3383464879,2.6970113944\C,-2.200064
6208,1.2093321484,1.3116547676\C,-0.6892023819,-1.2635793169,1.6254402
042\H,-0.2320673458,-2.1633767486,1.1968945172\H,-0.5447758948,-1.3144
272439,2.7246007221\N,-2.1042389419,-1.2380511829,1.2473689061\H,-2.55
22523473,-2.1041024798,1.5390509105\C,-2.8102938073,-0.0963191078,1.83
38259938\H,-2.7133339915,2.0673212443,1.764104004\H,-2.3632915003,1.26
19567212,0.2273990596\H,-3.8683674909,-0.1619356652,1.5537786072\H,-2.
7644843763,-0.0935010681,2.9426576963\\Version=EM64L-G09RevA.02\State=
1-A\HF=-251.9043757\RMSD=4.208e-09\RMSF=2.216e-05\Dipole=-0.0173925,-0
.089506,0.3248056\Quadrupole=0.4359886,1.026499,-1.4624876,0.268392,-0
.7290807,-0.9993967\PG=C01 [X(C5H11N1)]\\@

•Piperidinyl

1\1\GINC-V1251\FOpt\UB3LYP\Gen\C5H10N1(2)\GXG501\21-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\nr6.freq\\0,2\H,-0.0089919358,-0.0129244341,-0.0025580843\C,0.00
80622774,0.0039402326,1.0948861405\H,1.0607200524,-0.026113241,1.40189
70695\C,-0.6873280493,1.2722471771,1.606313641\H,-0.2410256535,2.16472
00912,1.1494571002\H,-0.5319861565,1.3605181313,2.6912974785\C,-2.1917
944832,1.2148311854,1.3113349069\C,-0.7156206278,-1.2617659098,1.61928
10509\H,-0.2407002327,-2.1652432187,1.2201068959\H,-0.6149863778,-1.28
75135079,2.7206738721\N,-2.1139983851,-1.2543952271,1.2414145648\C,-2.
7957470861,-0.1167794024,1.8239492884\H,-2.7221637006,2.056140383,1.77
41033588\H,-2.3615284187,1.2820076698,0.2289131773\H,-3.8619753423,-0.
1719455884,1.5764121538\H,-2.7049223468,-0.1371274454,2.926307289\\Ver
sion=EM64L-G09RevA.02\State=2-A'\HF=-251.2503017\S2=0.753606\S2-1=0.\S
2A=0.75001\RMSD=6.537e-09\RMSF=4.150e-05\Dipole=0.3592277,0.5956929,0.
3184602\Quadrupole=0.8662502,-1.3681969,0.5019467,-1.9778037,-0.753447
8,-1.0958362\PG=CS [SG(C1H2N1),X(C4H8)]\\@

1-Methylpiperidine

1\1\GINC-V1254\FOpt\RB3LYP\Gen\C6H13N1\GXG501\21-Jul-2010\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843545
6\\nme6.freq\\0,1\H,0.0662379314,-0.0130110566,0.067295165\C,0.0143733
379,0.0130837663,1.163594672\H,1.0452240007,0.0212425095,1.5395702086\
C,-0.7401096237,1.2712509549,1.6135802314\H,-0.2731628896,2.1728196381
,1.1979090242\H,-0.6784674645,1.35924508,2.7084462173\C,-2.2135801739,
1.1817261906,1.1951251156\C,-0.6971461951,-1.2530090824,1.6511248906\H
,-0.1893308867,-2.1444257647,1.2625948225\H,-0.6347330626,-1.306198293
7,2.759966738\N,-2.0874286217,-1.2865119221,1.1968786779\C,-2.83988113
46,-0.1291014773,1.6814173981\H,-2.7842743562,2.0299473019,1.593763422

1\H,-2.2888420169,1.2222792468,0.1006279509\H,-3.8703027638,-0.2136401
125,1.3146268874\H,-2.8945235206,-0.1208862707,2.7919122669\C,-2.73791
22299,-2.5364698204,1.554344001\H,-3.754993128,-2.5546638293,1.1464487
948\H,-2.1840151638,-3.3785990746,1.1244071722\H,-2.807304819,-2.69785
41375,2.6492782002\\Version=EM64L-G09RevA.02\State=1-A\HF=-291.2163649
\RMSD=2.968e-09\RMSF=1.681e-05\Dipole=0.0125771,0.0188586,0.1755033\Qu
adrupole=0.7101495,0.6413274,-1.3514769,-0.0581709,-0.1487135,-0.22707
27\PG=C01 [X(C6H13N1)]\\@

1-Ethoxypiperidine

1\1\GINC-V1267\FOpt\RB3LYP\Gen\C7H15N1O1\GXG501\21-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\nac6.freq\\0,1\H,-0.2454508518,0.0380915261,-0.1290188839\C,-0.13
71142414,-0.0689232947,0.9581658229\H,0.9229260011,-0.2643781618,1.161
3078494\C,-0.5989717081,1.2202411311,1.6528571653\H,-0.0575099688,2.08
76957787,1.2558782357\H,-0.3595372387,1.1601578201,2.724416161\C,-2.11
3929137,1.4048314738,1.4824914294\C,-0.9712603792,-1.268804525,1.42317
06294\H,-0.6924557142,-2.1751195171,0.8758545911\H,-0.7997547068,-1.46
11562744,2.4978592022\N,-2.3907883706,-1.0084815929,1.1623179107\C,-2.
8706580064,0.1472328673,1.9269687321\H,-2.4705802192,2.265543857,2.061
3925617\H,-2.3455561977,1.6037578243,0.4280072765\H,-3.9443175578,0.24
92577575,1.7384115203\H,-2.7358779887,-0.0176874604,3.0114123718\O,-3.
110931557,-2.1548460408,1.6696428455\C,-3.8427932637,-2.7576722395,0.6
049744483\C,-4.5806798596,-3.9541208965,1.1861864752\H,-4.5468296648,-
2.0318874041,0.1728327152\H,-3.1563850635,-3.0686826268,-0.1959784199\
H,-5.1623373271,-4.4564776045,0.4053845874\H,-5.2658754687,-3.63841349
07,1.9798472993\H,-3.8749460048,-4.6755895852,1.6109132543\\Version=EM
64L-G09RevA.02\State=1-A\HF=-405.7034822\RMSD=5.814e-09\RMSF=1.586e-05
\Dipole=0.1073004,0.1956313,-0.1461637\Quadrupole=1.0107371,0.6526124,
-1.6633495,0.6298777,0.6475551,1.5924254\PG=C01 [X(C7H15N1O1)]\\@

1-Propyloxypiperidine

1\1\GINC-V1257\FOpt\RB3LYP\Gen\C8H17N1O1\GXG501\21-Oct-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\nop6.freq\\0,1\H,-0.007267091,0.0154839335,-0.0265618611\C,0.0089
409318,0.0184985216,1.0711055795\H,1.0612898866,0.0246070768,1.3804084
143\C,-0.7230120398,1.2623318243,1.5955149805\H,-0.2932673727,2.173969
8002,1.1625634386\H,-0.5843331973,1.3323638168,2.6841146\C,-2.22324640
83,1.1705748457,1.2812533148\C,-0.6605466463,-1.2640436392,1.579661182
1\H,-0.1852329987,-2.1512209461,1.1488131631\H,-0.5672959737,-1.335092
8844,2.6785920524\N,-2.070648056,-1.2724597848,1.1764341644\C,-2.80563
84817,-0.1568798272,1.7814818489\H,-2.770741403,2.0023460324,1.7412078
358\H,-2.3785434583,1.2394079596,0.1966883682\H,-3.8574912951,-0.25609
3855,1.494436176\H,-2.7537814242,-0.2065800757,2.8843571686\O,-2.64100
3056,-2.4795720686,1.7305349237\C,-3.1599390424,-3.2848769394,0.674068

5619\C,-3.7868196308,-4.5263766997,1.3011646579\H,-3.9082662937,-2.716
6321256,0.1011396907\H,-2.351697781,-3.5628908297,-0.0181159347\H,-3.0
136183358,-5.0587142968,1.8701047714\H,-4.0936338744,-5.1950596316,0.4
856410688\C,-4.983237576,-4.2168544086,2.2068890465\H,-4.6879588337,-3
.5572601379,3.0282233444\H,-5.4012005989,-5.1339579692,2.6369514463\H,
-5.7824689655,-3.716459184,1.6457005797\\Version=EM64L-G09RevA.02\Stat
e=1-A\HF=-445.017191\RMSD=2.713e-09\RMSF=4.038e-06\Dipole=0.1128468,0.
2146433,-0.1358178\Quadrupole=0.4634332,1.3086394,-1.7720726,0.6487363
,0.5251759,1.2585096\PG=C01 [X(C8H17N1O1)]\\@

1-Cyclohexyloxypiperidine

1\1\GINC-V1259\FOpt\RB3LYP\Gen\C11H21N1O1\GXG501\21-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\noc6.freq\\0,1\H,-0.4944058161,-0.5467692712,-0.2029324147\C,-0.
2347953286,-0.4924175173,0.8624500749\H,0.7911738386,-0.8665827542,0.9
655793689\C,-0.3381943501,0.9612850841,1.3454930302\H,0.2793939455,1.6
199188743,0.7225504545\H,0.0558947185,1.0320483496,2.3696341772\C,-1.8
025178081,1.4225990392,1.3337723877\C,-1.1853019852,-1.4020083183,1.65
0429843\H,-1.1642844961,-2.4235017522,1.2593023711\H,-0.8808676451,-1.
4448318469,2.7120801188\N,-2.5587780454,-0.9032850174,1.5244865493\C,-
2.6896082452,0.4385326669,2.1057027913\H,-1.9016616202,2.4221428682,1.
7745624622\H,-2.1616189154,1.4870140524,0.2983099679\H,-3.7430736149,0
.7300966601,2.0395823834\H,-2.4122740513,0.4279654171,3.1751399061\O,-
3.378169499,-1.7765495273,2.3371110326\C,-4.5062821727,-2.2414745417,1
.5853084136\C,-5.3545159446,-3.8072861535,-0.2158727417\C,-6.703074257
5,-3.4591944062,1.9048867329\C,-6.3228643549,-4.4474719743,0.790971186
9\C,-5.45976976,-2.8784353524,2.5988726618\C,-4.1123996675,-3.23602399
56,0.4878497034\H,-4.920178469,-3.6766803801,3.1275536148\H,-5.7430658
773,-2.1338018225,3.3522245904\H,-7.3483204254,-3.9476236405,2.6457597
414\H,-5.8448678844,-5.3309386815,1.2393558705\H,-7.2248580576,-4.8058
560563,0.2785462179\H,-5.05276527,-4.5394152202,-0.9754016428\H,-3.449
7699655,-2.7395694237,-0.2295227521\H,-3.5409220679,-4.052230995,0.953
0672396\H,-4.9999514711,-1.3734445902,1.1195698177\H,-5.8730781919,-2.
9994270697,-0.7534922064\H,-7.2938382763,-2.6382120053,1.472258461\\Ve
rsion=EM64L-G09RevA.02\State=1-A\HF=-561.7581983\RMSD=7.124e-09\RMSF=5
.929e-06\Dipole=0.073533,0.1786356,-0.1976288\Quadrupole=1.6804445,0.9
577685,-2.638213,1.2041096,-0.1502892,0.5090922\PG=C01 [X(C11H21N1O1)]
\\@

1-Acetylpiperidine

1\1\GINC-V1253\FOpt\RB3LYP\Gen\C7H13N1O1\GXG501\21-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\h3058_c.freq\\0,1\H,0.6617293324,0.5449240019,0.594388264\C,0.294
4620487,0.1342232456,1.5443602397\H,1.168959955,-0.2277849943,2.099395
3672\C,-0.4332269409,1.2303624582,2.3371133002\H,0.2206034813,2.097973

0462,2.4872098524\H,-0.683803366,0.8483973946,3.3381377652\C,-1.725059
2704,1.6519472639,1.6214653637\C,-0.6411345135,-1.0443022338,1.2458579
795\H,-0.1761001425,-1.7790910264,0.5889266658\H,-0.9129270127,-1.5487
820594,2.1871681552\N,-1.865663519,-0.5871719344,0.5852202387\C,-2.610
3941082,0.4325645547,1.3188879498\H,-2.2913864743,2.3680504689,2.23037
50994\H,-1.4778843716,2.1526415414,0.6755462057\H,-3.4903116459,0.7315
159443,0.7490604937\H,-2.969767149,0.0003648551,2.2675235557\C,-2.2367
093733,-1.1512792413,-0.6143071684\O,-1.5629829762,-2.0206165013,-1.15
95991859\C,-3.5266608158,-0.6550846839,-1.2605591235\H,-4.4006098465,-
0.8328028934,-0.6235392078\H,-3.6512039911,-1.2076721016,-2.1923029825
\H,-3.4888636371,0.4166055846,-1.4869781024\\Version=EM64L-G09RevA.02\
State=1-A\HF=-404.5718202\RMSD=6.155e-09\RMSF=3.996e-06\Dipole=-0.4412
28,1.0794217,0.9046256\Quadrupole=3.669768,-2.6231998,-1.0465682,0.309
2363,1.929706,-3.8884546\PG=C01 [X(C7H13N1O1)]\\@

Tinuvin770

1\1\GINC-V1443\FOpt\RB3LYP\Gen\C11H21N1O2\GXG501\22-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t770.freq\\0,1\H,-0.0965974919,-0.2890474813,-0.1929863267\C,0.0
148232524,-0.2192537967,0.8962946717\H,1.0826208692,-0.2799815643,1.13
15376936\C,-0.537611376,1.1344916017,1.3369710569\H,-0.3249498421,1.31
23106645,2.3937462977\C,-2.0283727441,1.2320702523,1.0364684305\C,-0.7
328874315,-1.4003108578,1.5550044158\N,-2.1821191204,-1.1844357575,1.3
67467885\H,-2.7005538801,-1.9542991922,1.7871686251\C,-2.8343619274,0.
0962246151,1.70530674\H,-2.4158197867,2.2047837947,1.3614876146\H,-2.1
611539585,1.1713644278,-0.0506742531\C,-4.2379757155,0.0411779341,1.07
2908331\H,-4.1646727066,-0.1750063734,0.0029262045\H,-4.7696595133,0.9
900719531,1.2091071382\H,-4.8429780309,-0.7475770785,1.5387475174\C,-3
.0077493823,0.3633122694,3.2228537339\H,-2.0603667671,0.5399789165,3.7
379076977\H,-3.4956150057,-0.4919863108,3.7063174765\H,-3.6413444913,1
.2432112884,3.3892215971\C,-0.392395157,-2.6946032371,0.792081353\H,0.
6858243142,-2.890823855,0.811179692\H,-0.7222684862,-2.6208281487,-0.2
485157464\H,-0.8946266952,-3.5579092993,1.2479566679\C,-0.2831194704,-
1.5846542543,3.0271017025\H,0.76380316,-1.907942974,3.0714049645\H,-0.
8904202477,-2.3562666558,3.5164421591\H,-0.3647961422,-0.669809894,3.6
188589939\O,0.1077394158,2.2003208912,0.5842124362\C,1.2781878079,2.67
70694774,1.0673210301\O,1.8141479552,2.2753071831,2.0780305544\C,1.814
8655186,3.7725989097,0.1738098025\H,2.0035884001,3.3779555042,-0.83020
03507\H,2.740225583,4.1656372153,0.5962418153\H,1.0774331161,4.5756363
073,0.0744223099\\Version=EM64L-G09RevA.02\State=1-A\HF=-637.0409768\R
MSD=2.928e-09\RMSF=9.646e-07\Dipole=-0.5127537,-0.053047,-0.2420161\Qu
adrupole=-2.0989978,3.5942313,-1.4952335,0.2546198,-5.1828266,-3.71269
76\PG=C01 [X(C11H21N1O2)]\\@

•Tinuvin770

1\1\GINC-V1295\FOpt\UB3LYP\Gen\C11H20N1O2(2)\GXG501\22-Jul-2010\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\t770r.freq\\0,2\H,-0.1125643601,-0.2663551332,-0.187938887\C,
0.0082304784,-0.2011854619,0.9016998292\H,1.0792228704,-0.2761641426,1
.1179880304\C,-0.52817072,1.1526025205,1.3479909079\H,-0.3185301107,1.
324869831,2.4066529443\C,-2.0146542483,1.2329442627,1.0419259507\C,-0.
7438871496,-1.3802426595,1.5750659244\N,-2.1962847643,-1.2333261889,1.
6625963359\C,-2.8135755622,0.0910638347,1.7242387716\H,-2.4194576439,2
.2040461418,1.3507002475\H,-2.1407419919,1.1665009457,-0.046757739\C,-
4.1887201883,-0.0461028814,1.0383651061\H,-4.0684699967,-0.3381100463,
-0.0104334903\H,-4.7348722675,0.9043487319,1.071117001\H,-4.7864857646
,-0.8147337208,1.5376686038\C,-3.0523693591,0.4170164722,3.2247008414\
H,-2.1200804428,0.6255017817,3.7574605195\H,-3.5470516362,-0.424668371
1,3.7183084877\H,-3.69691266,1.2996629395,3.3100796633\C,-0.4935717329
,-2.6701484084,0.7663267771\H,0.5811514883,-2.8706850806,0.6811456634\
H,-0.9080027494,-2.5785325574,-0.2434788305\H,-0.9747948058,-3.5234033
948,1.2541234852\C,-0.2164715753,-1.6057264324,3.0194403735\H,0.830522
7953,-1.9271898742,2.9800730594\H,-0.8030315646,-2.3839329217,3.516805
6544\H,-0.2656622868,-0.69720157,3.626225587\O,0.1157742284,2.22059709
98,0.5998934576\C,1.2930766891,2.6860160705,1.0800650197\O,1.831428965
6,2.2705564477,2.083676404\C,1.8315833657,3.7855343565,0.1931467347\H,
2.0254551269,3.3942285138,-0.8112707493\H,2.7550090168,4.1776664599,0.
6205670689\H,1.0937125564,4.5879524354,0.0930402463\\Version=EM64L-G09
RevA.02\State=2-A\HF=-636.3869068\S2=0.753646\S2-1=0.\S2A=0.75001\RMSD
=6.827e-09\RMSF=6.735e-06\Dipole=-0.2222035,0.3752538,-0.445151\Quadru
pole=-2.2374491,1.5741195,0.6633296,-2.5183909,-4.1544632,-2.360657\PG
=C01 [X(C11H20N1O2)]\\@

Tinuvin292

1\1\GINC-V1270\FOpt\RB3LYP\Gen\C12H23N1O2\GXG501\22-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t292.freq\\0,1\H,-0.0165343285,-0.0295650979,0.0310402867\C,-0.0
188260994,-0.014056754,1.1284689499\H,1.0225479771,-0.0173097846,1.466
8393127\C,-0.7076313708,1.2649979883,1.5742454231\H,-0.6276347166,1.39
72325195,2.6555653365\C,-2.149770505,1.2496949176,1.1054973175\C,-0.71
99227872,-1.2916242904,1.6473114783\N,-2.1782047055,-1.2194738877,1.32
87653794\C,-2.941012914,0.0287373075,1.6300337617\H,-2.6603476611,2.16
84483248,1.4168973796\H,-2.1512035082,1.2301675661,0.0084276065\C,-4.2
667899788,0.0083389984,0.8321628743\H,-4.0842141219,-0.3086103742,-0.1
998097022\H,-4.6993208091,1.0148552627,0.8142892522\H,-5.017670645,-0.
6533509509,1.2749413391\C,-3.2983119821,0.2316471085,3.1269137267\H,-2
.4250150762,0.4385938205,3.7504343809\H,-3.7993599264,-0.6516211101,3.
5366128393\H,-3.9874312089,1.0775976678,3.2363397279\C,-0.0953667882,-
2.467424561,0.8585177711\H,0.9954558397,-2.3654616524,0.8528618298\H,-
0.449591869,-2.4609628565,-0.1775100683\H,-0.3217767224,-3.4425832953,

1.3009201035\C,-0.388627845,-1.5054477278,3.1482148029\H,0.6820835718,
-1.7066697346,3.2697518652\H,-0.931400992,-2.3658180637,3.553832353\H,
-0.6265017155,-0.6368407832,3.767016966\O,-0.0751016485,2.4191386086,0
.9514279814\C,1.0027402702,2.9447044447,1.5777451301\O,1.4660508651,2.
5177037069,2.6137394621\C,1.5409784169,4.1287742563,0.806351265\H,1.86
93375802,3.8088195759,-0.1883262392\H,2.3802852415,4.5650425487,1.3490
043476\H,0.7555349698,4.877973871,0.6643516156\C,-2.9081987086,-2.4429
973589,1.6494715817\H,-2.3985264882,-3.3069235341,1.2192300363\H,-3.03
66871656,-2.638409328,2.7289146438\H,-3.902868062,-2.415381726,1.20079
86981\\Version=EM64L-G09RevA.02\State=1-A\HF=-676.338425\RMSD=3.148e-0
9\RMSF=7.948e-06\Dipole=-0.471734,-0.0610547,-0.4151419\Quadrupole=-1.
1385529,3.906927,-2.7683742,-0.0034951,-4.4359258,-3.1605515\PG=C01 [X
(C12H23N1O2)]\\@

Tinuvin123

1\1\GINC-V1257\FOpt\RB3LYP\Gen\C13H25N1O3\GXG501\22-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t123.freq\\0,1\H,-0.1251535839,0.0501479474,-0.0353917487\C,-0.1
120339049,0.0171316483,1.0614323569\H,0.9311359217,-0.0718568977,1.382
3370533\C,-0.7077546246,1.32186744,1.5772094307\H,-0.5834041423,1.4033
728277,2.6590774837\C,-2.1676619138,1.4272486371,1.1643245565\C,-0.890
3026576,-1.2294238002,1.5403664795\N,-2.3296448286,-1.0150638569,1.187
0604891\C,-3.0156141566,0.2310982746,1.6526290698\H,-2.6062314549,2.35
55499894,1.5487866009\H,-2.2107307621,1.4748498098,0.0691281941\C,-4.3
788040904,0.3013427992,0.9369662195\H,-4.2558169906,0.1710506365,-0.14
28716852\H,-4.844829611,1.2767942995,1.1174584313\H,-5.0605407695,-0.4
681612172,1.3103465936\C,-3.2792218043,0.3109522146,3.1753882696\H,-2.
3809813417,0.5164544951,3.7612956471\H,-3.7131830106,-0.6278940705,3.5
282635343\H,-3.9938404119,1.1160662048,3.3822802124\C,-0.3908722944,-2
.4357256675,0.7214294806\H,0.6971584742,-2.525361699,0.8172389521\H,-0
.6362647554,-2.3124688752,-0.3382220035\H,-0.8351387118,-3.3684682451,
1.0809458459\C,-0.6130553834,-1.5269038065,3.0333595782\H,0.4045050503
,-1.9180434622,3.1455238624\H,-1.3116852374,-2.2836349349,3.3989687483
\H,-0.6898601485,-0.6458894032,3.6736717089\O,-0.022146247,2.456099299
5,0.9774569757\C,1.1106979408,2.8824129033,1.5834429199\O,1.5811548068
,2.3786881633,2.580720681\C,1.6958130166,4.0648566006,0.8449499671\H,1
.9431124646,3.7799028187,-0.1831119224\H,2.5939056084,4.4069028468,1.3
603123733\H,0.9634139407,4.8768189307,0.7903797103\O,-3.0777836236,-2.
1406357461,1.6951561776\C,-3.6576627962,-2.9057387847,0.6329962133\C,-
4.4135528542,-4.0538205968,1.2847750786\H,-3.7367786337,-4.6798764617,
1.8757788801\H,-2.8747324422,-3.2812110725,-0.0362649853\H,-4.33248043
52,-2.2793120655,0.0377683151\H,-5.1972748353,-3.6763473822,1.95006334
54\H,-4.8828245962,-4.6799851517,0.5179661947\\Version=EM64L-G09RevA.0
2\State=1-A\HF=-790.8318255\RMSD=6.172e-09\RMSF=4.820e-06\Dipole=-0.45
67561,0.0577575,-0.6768354\Quadrupole=-1.8206179,4.8161283,-2.9955104,

0.7108105,-3.770727,-1.292623\PG=C01 [X(C13H25N1O3)]\\@

Tinuvin123-1

1\1\GINC-V1303\FOpt\RB3LYP\Gen\C14H27N1O3\GXG501\21-Oct-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t123i.freq\\0,1\H,0.0053666386,0.0044776354,0.0027615379\C,0.002
9587609,0.0033759974,1.1001500253\H,1.0444882998,0.0024534333,1.438295
046\C,-0.6973248886,1.2734201959,1.5690877877\H,-0.596673638,1.3948383
593,2.6496961813\C,-2.1542551269,1.2568058627,1.1331007453\C,-0.687389
778,-1.2845440397,1.6039717206\N,-2.1324828739,-1.1890791165,1.2234489
049\C,-2.9177442944,0.0137979052,1.6435206624\H,-2.6674214546,2.159517
1353,1.4847759349\H,-2.1832343443,1.2709277261,0.0364953156\C,-4.27042
9449,-0.0389593552,0.906701033\H,-4.1202857069,-0.1912366814,-0.166794
0629\H,-4.8105230951,0.903792851,1.0509248318\H,-4.8991761068,-0.84604
91478,1.2934701351\C,-3.2115632876,0.1153264627,3.1594602739\H,-2.3417
323665,0.4069898699,3.7516378361\H,-3.5766241668,-0.8444859343,3.53323
56253\H,-3.9900586153,0.867382783,3.3327812757\C,-0.0853681129,-2.4722
161737,0.8278881125\H,1.0046097322,-2.4766945399,0.9418327707\H,-0.321
9468147,-2.3976931052,-0.2382885971\H,-0.4642507772,-3.4253127107,1.20
82113915\C,-0.4135271558,-1.5184684172,3.1087849758\H,0.628593747,-1.8
280970669,3.2470523532\H,-1.0592081796,-2.3154805266,3.4859662791\H,-0
.5672516687,-0.6284033983,3.7220908829\O,-0.0891071511,2.4386544602,0.
9456384212\C,0.9984739548,2.9664995024,1.5545284267\O,1.4888461255,2.5
289364189,2.5732158988\C,1.5057127319,4.167502616,0.7888602686\H,1.794
2707043,3.8710148944,-0.2251147287\H,2.3648780652,4.5931876564,1.30827
73188\H,0.7146417873,4.9185879196,0.6956003297\O,-2.8025672286,-2.3538
455677,1.7526928527\C,-3.3061414654,-3.1899105673,0.7065649837\C,-3.98
54362363,-4.3800106165,1.3754110534\H,-3.2542667263,-4.8916381792,2.01
40904117\H,-2.4876442143,-3.5243653238,0.0569718929\H,-4.0191609067,-2
.6354214627,0.083514139\H,-4.7750010645,-4.0086275085,2.0410100133\C,-
4.5731083361,-5.3607885379,0.355232235\H,-5.326310535,-4.8762332975,-0
.277893732\H,-3.7959893866,-5.7656329391,-0.3043911823\H,-5.0557517479
,-6.206207483,0.8569988463\\Version=EM64L-G09RevA.02\State=1-A\HF=-830
.145289\RMSD=8.484e-09\RMSF=3.145e-06\Dipole=-0.461472,-0.0205478,-0.6
700415\Quadrupole=-1.8681779,5.1746829,-3.306505,0.026326,-4.1001087,-
2.421718\PG=C01 [X(C14H27N1O3)]\\@

Tinuvin152

1\1\GINC-V1301\FOpt\RB3LYP\Gen\C19H35N7O1\GXG501\27-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t152.freq\\0,1\H,-0.5908797801,-1.5788651513,1.7755944911\C,-0.4
318948007,-0.5238063897,1.5170187631\H,0.1936479049,-0.088948725,2.305
4596348\C,0.2863350624,-0.4261924669,0.1687234188\H,0.4979186848,0.619
3279849,-0.0482843786\C,-0.6277038811,-0.9952267183,-0.919608772\C,-1.
8051228462,0.1884259564,1.5340038249\N,-2.6149208737,-0.3503747274,0.3

875337725\C,-2.0037751871,-0.292042575,-0.9882099382\H,-0.1453677999,-
0.9067216484,-1.9005868385\H,-0.7964465204,-2.0644616998,-0.7369644332
\C,-2.8823316945,-1.12897838,-1.9407793733\H,-3.0864652199,-2.11749417
17,-1.5169564828\H,-2.3572075203,-1.2664240839,-2.8930697855\H,-3.8318
778497,-0.6334471204,-2.1606492843\C,-1.8783203614,1.1245794858,-1.597
3767306\H,-1.0482155553,1.701970663,-1.1861563726\H,-2.8032821101,1.68
35408506,-1.4370408739\H,-1.7104651595,1.0440633314,-2.6776261522\C,-2
.5031019495,-0.2145042013,2.8450550755\H,-1.8464969702,0.0108031443,3.
693330603\H,-2.719658764,-1.2872115836,2.8542632197\H,-3.435754389,0.3
351224315,2.9867252488\C,-1.6360291861,1.7273405584,1.5532940815\H,-1.
2702012361,2.0397845222,2.53825066\H,-2.5993846933,2.2123449541,1.3787
884451\H,-0.9234183596,2.096120445,0.8133268044\O,-3.8511949726,0.4067
830978,0.3531088528\N,1.6081625818,-1.0708182569,0.1866383337\C,1.7193
816545,-2.5155823369,0.3625903952\H,2.4865458843,-2.7529481023,1.10316
97646\H,0.760913569,-2.9076009534,0.7062296202\H,1.9920209014,-3.02055
01302,-0.5722130046\C,2.7467386977,-0.3529429081,-0.0452607405\N,5.022
2701661,1.0340402444,-0.4888212077\N,2.641069254,0.9829163658,-0.20890
95352\N,3.9007206777,-1.0490177706,-0.0881050074\C,4.9894359959,-0.294
838305,-0.2999511829\C,3.8063118784,1.6031838536,-0.4345049426\N,3.752
9363006,2.949389192,-0.6619191046\N,6.1918449814,-0.9418487948,-0.2972
522088\H,6.1675810497,-1.9458013306,-0.3962395732\H,6.9759789396,-0.44
50403092,-0.6932204663\H,4.6226518078,3.4552937205,-0.582399882\H,2.90
53623693,3.4229561154,-0.3866408063\C,-5.0467929842,-0.4020024408,0.30
18501248\C,-6.9455847051,-1.515480499,1.5606818951\C,-7.4312811065,-0.
2651151419,-0.5825305958\C,-7.9739874082,-0.6719831713,0.7946967651\C,
-6.0710359916,0.4416423489,-0.467949452\C,-5.5915876117,-0.7930133753,
1.681145303\H,-6.8014107369,-2.4724605737,1.0369712719\H,-7.3219572627
,-1.1641750931,-1.2070503254\H,-8.2054945547,0.2329381896,1.3756459731
\H,-6.1919873691,1.3985735744,0.0592242507\H,-5.7124221147,0.117654345
7,2.2846618606\H,-4.8287063593,-1.3176687525,-0.2567628829\H,-7.321777
8401,-1.765283651,2.5606964718\H,-8.1457948366,0.3867140447,-1.1007472
974\H,-8.9161889429,-1.2239943468,0.6851419589\H,-5.6743912558,0.68021
42733,-1.4619942929\H,-4.8722646004,-1.4334328079,2.1989570396\\Versio
n=EM64L-G09RevA.02\State=1-A\HF=-1203.5934407\RMSD=3.450e-09\RMSF=3.06
6e-06\Dipole=-0.1254271,-0.1878329,-0.0715057\Quadrupole=3.700459,2.42
26775,-6.1231365,0.2148785,-2.1250183,1.8382085\PG=C01 [X(C19H35N7O1)]
\\@

• **Tinuvin152**

1\1\GINC-V1260\FOpt\UB3LYP\Gen\C13H24N7(2)\GXG501\27-Jul-2010\0\\#B3LY
P/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=2684
35456\\t152r.freq\\0,2\H,-0.8396868035,-1.5559227222,1.5868782437\C,-0
.6180830726,-0.503562529,1.3618394924\H,-0.0494464337,-0.1106777033,2.
2131916863\C,0.2218813395,-0.4194223464,0.0822827404\H,0.4682896754,0.
6235772879,-0.1137112369\C,-0.6061084307,-0.9727907597,-1.0830385667\C

,-1.9596128619,0.2658910525,1.2353752758\N,-2.6724515148,0.0880313722,
-0.0293441018\C,-1.9470481086,-0.2126088175,-1.2631427532\H,-0.0313177
269,-0.9229006307,-2.0160039421\H,-0.8266570019,-2.03368448,-0.9022504
728\C,-2.9058666865,-1.0631526214,-2.1225649665\H,-3.1531896898,-1.999
90424,-1.6112122857\H,-2.4467016977,-1.3084618078,-3.0878721962\H,-3.8
38816977,-0.5201190891,-2.3029394023\C,-1.7100847197,1.135872729,-1.99
80337741\H,-0.9515347992,1.7493983216,-1.5038268802\H,-2.6409374134,1.
7092180937,-2.042927686\H,-1.3711107608,0.9396808667,-3.0219040693\C,-
2.928728023,-0.208884531,2.3384904807\H,-2.4796582016,-0.0798585881,3.
1.4002973817,1.9875464484,2.4499715333\H,-2.659079026,2.338052755,1.24
33258062\H,-0.964363085,2.1805575967,0.7440551807\N,1.5255296251,-1.08
60011574,0.2156254216\C,1.5920842887,-2.5353478641,0.3729150271\H,2.33
64753261,-2.8002581454,1.126099296\H,0.6161416412,-2.9050361121,0.6921
610046\H,1.8697562262,-3.0376806699,-0.5624376069\C,2.6918399697,-0.38
6082149,0.0880950129\N,5.018296646,0.9675613216,-0.1452919879\N,2.6216
625078,0.9540764909,-0.0601212197\N,3.8339232269,-1.1014081265,0.12644
56512\C,4.948636196,-0.3634157865,0.0177274538\C,3.8116212236,1.557023
6357,-0.1802224318\N,3.7991632608,2.90744718,-0.388206438\N,6.13577111
97,-1.0312938261,0.1075088257\H,6.1040918828,-2.0332417844,-0.00802066
06\H,6.9585184587,-0.5421120176,-0.2121912019\H,4.6681080412,3.3959982
918,-0.2301074284\H,2.9406569495,3.3920983843,-0.1727255527\\Version=E
M64L-G09RevA.02\State=2-A\HF=-893.0997543\S2=0.753647\S2-1=0.\S2A=0.75
001\RMSD=4.657e-09\RMSF=6.691e-06\Dipole=0.4197612,-0.0061056,-0.01209
11\Quadrupole=-2.6865044,6.1526784,-3.466174,-0.8021496,-1.7241366,1.7
890271\PG=C01 [X(C13H24N7)]\\@

Tinuvin NOR371

1\1\GINC-V1301\FOpt\RB3LYP\Gen\C15H29N7O1\GXG501\27-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t371.freq\\0,1\H,-0.5886688511,0.2830233639,-0.1920164466\C,-0.5
728078821,0.4217444629,0.8968305195\H,0.4385520253,0.7476546137,1.1672
387284\C,-1.5901874357,1.4975910554,1.2955849252\H,-1.5191373763,1.672
7282146,2.3677023002\C,-3.0035404442,1.0090565694,0.9560303806\C,-0.84
66893,-0.9469255773,1.5620468027\N,-2.2687360649,-1.3067876785,1.26525
70179\C,-3.3537260899,-0.3405085068,1.6246919066\H,-3.7435252491,1.756
1755129,1.267655012\H,-3.1008363943,0.8891961657,-0.1306295777\C,-4.65
84042719,-0.8569248673,0.986302739\H,-4.5100785779,-1.0738256862,-0.07
64797997\H,-5.4433383165,-0.0975062006,1.0782993885\H,-5.0119289652,-1
.7639544258,1.4853327704\C,-3.6102008019,-0.1685134371,3.1408457327\H,
-2.8489967481,0.4308188087,3.6441228808\H,-3.6576387743,-1.1471801651,
3.6251048415\H,-4.5717813433,0.3348373584,3.294583985\C,0.0464052329,-
1.9945783264,0.8684222703\H,1.0947465985,-1.6780052081,0.9138858633\H,
-0.2350932358,-2.1076540125,-0.1834816024\H,-0.0294843466,-2.968756967
8,1.3603500122\C,-0.4690247935,-0.9290417653,3.0626124687\H,0.62240902
99,-0.9241835448,3.1649689704\H,-0.8527134608,-1.826089089,3.555199148

2\H,-0.8467328399,-0.0531798491,3.5938982796\O,-2.5535955916,-2.553613
4741,1.9379892397\C,-2.8304727693,-3.6008352598,1.0029039822\C,-3.1137
676303,-4.8523931244,1.8202499448\H,-2.249979609,-5.1171207333,2.43923
4563\H,-1.9727315004,-3.7532881002,0.3371477926\H,-3.6928653118,-3.336
381298,0.3795821714\H,-3.9730499897,-4.69922618,2.4817050975\H,-3.3345
290025,-5.6952305491,1.1559542238\N,-1.2893890405,2.8037983254,0.69049
72715\C,-1.3907952409,2.9837120085,-0.7544316971\H,-0.5241289026,3.530
5031175,-1.1320950535\H,-1.4295686848,2.0042544098,-1.2337744129\H,-2.
2887489777,3.5485558444,-1.0341329998\C,-0.9979372307,3.8903352,1.4652
540588\N,-0.4056347504,6.0590120408,2.9634891714\N,-0.9037016511,3.718
7829052,2.8009685186\N,-0.8212070068,5.0615538494,0.8210863779\C,-0.51
81742203,6.0907884536,1.6259492973\C,-0.6180806331,4.8370681941,3.4802
544461\N,-0.5646097568,4.7334186535,4.8415261033\N,-0.2732608625,7.289
6908377,1.0200957421\H,-0.5823629444,7.3870486713,0.0644237458\H,-0.29
0530083,8.1085316292,1.6097539575\H,-0.1130504878,5.4895784944,5.33444
33681\H,-0.4771820435,3.8032347037,5.2229864248\\Version=EM64L-G09RevA
.02\State=1-A\HF=-1047.5448583\RMSD=3.017e-09\RMSF=1.863e-06\Dipole=-0
.0323731,-0.0510875,-0.1722384\Quadrupole=-5.4481174,4.0884344,1.35968
29,0.2149944,3.6142106,0.2507208\PG=C01 [X(C15H29N7O1)]\\@

Tinuvin NOR371-1

1\1\GINC-V1399\FOpt\RB3LYP\Gen\C16H31N7O1\GXG501\21-Oct-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t371i.freq\\0,1\H,-0.8274334944,-1.5314781689,1.6244323542\C,-0.
6235417972,-0.4833986351,1.3693814259\H,-0.0539225529,-0.052345645,2.2
011943841\C,0.2057396398,-0.4167007322,0.0811799417\H,0.4563315479,0.6
223447461,-0.1255174256\C,-0.6199598305,-0.9782894999,-1.0825717294\C,
-1.9756314614,0.2583203706,1.2578687919\N,-2.6760121486,-0.2777224353,
0.0488096721\C,-1.9714083583,-0.2508480032,-1.2713426988\H,-0.04987499
35,-0.9049022053,-2.0166584318\H,-0.8243132267,-2.0426960094,-0.909576
1644\C,-2.8166526017,-1.0785445977,-2.2597139333\H,-3.056751053,-2.059
3816718,-1.8368348389\H,-2.2579905491,-1.2300873737,-3.1904454522\H,-3
.7493532467,-0.5648746863,-2.5105493752\C,-1.7737272243,1.1548799539,-
1.8869060663\H,-0.983425686,1.7326651715,-1.4036798719\H,-2.705344529,
1.7232548559,-1.8270365119\H,-1.5018176394,1.0564202445,-2.9442657805\
C,-2.8244571316,-0.1229009826,2.4868726426\H,-2.268389142,0.0971064866
,3.405411238\H,-3.0641758485,-1.1910285599,2.4753813413\H,-3.757484007
,0.4474598179,2.5170368255\C,-1.7791418111,1.7930847101,1.2817602205\H
,-1.5131125273,2.1119057169,2.2963157977\H,-2.7095052026,2.2933084931,
1.0011603633\H,-0.985246338,2.1385016829,0.6165413544\O,-3.9124843439,
0.4557200579,-0.1009855058\C,-5.0498675343,-0.3943841844,0.0681177025\
C,-6.2884721101,0.4774190625,-0.1088317979\H,-6.2545635141,1.293242228
2,0.6244106573\H,-5.0387918235,-0.8552626235,1.0638961738\H,-5.0363808
074,-1.2040144674,-0.6724653675\H,-6.2516024643,0.9473083031,-1.099892
0033\N,1.507486843,-1.0871130017,0.2182091124\C,1.5715825767,-2.534117

0539,0.3983227986\H,2.2870560713,-2.7887146463,1.1830797685\H,0.584772
8791,-2.9018707194,0.6839860629\H,1.8866115887,-3.047058196,-0.5189418
505\C,2.6763200743,-0.3918785183,0.0908496657\N,5.0087238026,0.9513408
405,-0.1428414035\N,2.6115695415,0.9464495281,-0.0738858251\N,3.815842
807,-1.1105257363,0.1457417281\C,4.9334843637,-0.3773114037,0.03528164
42\C,3.8040435289,1.5442617594,-0.1929314194\N,3.7970640063,2.89204119
67,-0.416872146\N,6.1181297806,-1.0480720208,0.1407662475\H,6.08313334
43,-2.0509426344,0.0341919165\H,6.9436355322,-0.565504914,-0.181978384
2\H,4.6660428865,3.3804087758,-0.2586729806\H,2.9378060035,3.381343859
2,-0.2152251942\C,-7.5870415739,-0.3205905456,0.0490469712\H,-7.654402
8291,-1.1260778682,-0.6923157485\H,-8.4624797845,0.3244570352,-0.08158
6531\H,-7.6571386317,-0.7782881567,1.0433194808\\Version=EM64L-G09RevA
.02\State=1-A\HF=-1086.8583153\RMSD=8.464e-09\RMSF=2.217e-06\Dipole=-0
.089102,-0.1494171,0.0141036\Quadrupole=3.9737503,2.3010376,-6.274788,
0.0228378,-1.8522602,1.9187719\PG=C01 [X(C16H31N7O1)]\\@

Hostavin3052

1\1\GINC-V1255\FOpt\RB3LYP\Gen\C13H26N2O2\GXG501\25-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3052.freq\\0,1\H,-0.2764405606,-1.0440656467,0.122392296\C,-0.2
116316901,-0.511926401,1.0822949318\H,0.8199145862,-0.1561026002,1.183
9055954\C,-1.1623622302,0.6901609207,1.0223871484\H,-1.0599661951,1.27
48968197,1.9473605714\C,-2.6113501804,0.1767655877,0.9050784636\C,-0.5
40422538,-1.508081612,2.2139735332\N,-1.9765408717,-1.8413871249,2.132
1844189\H,-2.2191919693,-2.4992040112,2.8714303073\C,-3.0159442533,-0.
7984469845,2.0327110839\H,-3.32080224,1.0132742489,0.8874740349\H,-2.7
045831243,-0.3446395735,-0.0581177682\C,-4.3127724921,-1.5269680559,1.
6303428755\H,-4.1539091603,-2.1072290572,0.716461277\H,-5.1294270844,-
0.8150845439,1.4619683506\H,-4.6337470158,-2.2188045892,2.4205739951\C
,-3.2960891061,-0.0301681925,3.3505094367\H,-2.467851512,0.6154778961,
3.6528946954\H,-3.4860251065,-0.7344588214,4.1701509683\H,-4.185905709
,0.6032491225,3.246245344\C,0.2171617814,-2.8259360075,1.9619370749\H,
1.3001187121,-2.6583405955,1.9303330826\H,-0.1008639266,-3.2712363565,
1.0144161245\H,0.0167398633,-3.5508805719,2.7620731571\C,-0.0780888621
,-0.9532003489,3.5860980123\H,1.0164784698,-0.8933812813,3.6282491274\
H,-0.4052626885,-1.6163733841,4.3967342752\H,-0.468066951,0.0459753094
,3.7956811713\N,-0.7319955227,1.5769710494,-0.0650685341\H,-0.85376526
58,1.1024453823,-0.959497709\C,-1.4208573693,2.8619224528,-0.141533133
\C,-0.7306175078,3.7910612013,-1.1430969234\C,-0.848188003,3.315257110
9,-2.5774068846\O,-1.2939574763,2.2430805511,-2.9359145658\O,-0.379982
0701,4.2441586946,-3.4381965304\C,-0.4198118109,3.8770592892,-4.827411
7067\H,-2.4904561874,2.7862718152,-0.4052829403\H,-1.3722341359,3.3316
221541,0.8491754003\H,0.3371181859,3.8672079017,-0.9020542422\H,-1.140
5647302,4.8068192072,-1.0865642157\H,-1.4483872401,3.6877163176,-5.145
7979679\H,-0.0021404758,4.7278957769,-5.3664212935\H,0.1772199481,2.97

85756398,-5.0049160541\\Version=EM64L-G09RevA.02\State=1-A\HF=-771.001
1785\RMSD=3.085e-09\RMSF=1.081e-05\Dipole=-0.0154097,0.6225317,-0.0134
728\Quadrupole=-3.9935503,-0.3705885,4.3641388,-0.206303,-2.6655329,-6
.1470918\PG=C01 [X(C13H26N2O2)]\\@

•Hostavin3052

1\1\GINC-V1258\FOpt\UB3LYP\Gen\C13H25N2O2(2)\GXG501\25-Jul-2010\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\h3052r.freq\\0,2\H,-0.287875082,-1.0371093855,0.1285450012\C,
-0.2163361721,-0.5043687501,1.0888887546\H,0.823020119,-0.1687998001,1
.1822957394\C,-1.1494069062,0.7062892343,1.0258434667\H,-1.052973504,1
.2861551864,1.9549472916\C,-2.5888037163,0.1798239997,0.9008358012\C,-
0.5576048308,-1.4905863351,2.2339200526\N,-1.9805933025,-1.7722974003,
2.4242733742\C,-2.9927729016,-0.7879994479,2.0436598\H,-3.312249119,1.
0037615118,0.8630210198\H,-2.6681308954,-0.3491520559,-0.06065119\C,-4
.233998968,-1.5996089482,1.6159998518\H,-4.0028315637,-2.2266028236,0.
7480464616\H,-5.0604795287,-0.9307920138,1.3465066066\H,-4.5605335622,
-2.2550172061,2.4296372094\C,-3.3598320206,0.0093544262,3.3259735896\H
,-2.5574742078,0.6847799391,3.6369636892\H,-3.5668399083,-0.6779192361
,4.1518756272\H,-4.2573091777,0.6111006826,3.1397944847\C,0.1109750409
,-2.8532461207,1.954780008\H,1.1945750193,-2.7351642301,1.8332546647\H
,-0.2909807991,-3.2979627412,1.0378827781\H,-0.0789770015,-3.547736651
5,2.7791656829\C,-0.0129959489,-0.9576723284,3.5881466651\H,1.08263674
41,-0.933646307,3.5585605028\H,-0.3256629697,-1.6139355791,4.406019615
5\H,-0.3673306321,0.0539990201,3.80658923\N,-0.7115720092,1.5951301554
,-0.0555544766\H,-0.8253046664,1.1228438326,-0.9522882123\C,-1.4040867
531,2.8783384012,-0.1346106403\C,-0.7190143544,3.8056730705,-1.1413649
533\C,-0.8417187081,3.3258219449,-2.5739742296\O,-1.2683899384,2.24355
69168,-2.9260243014\O,-0.4009084307,4.2620525851,-3.4404728178\C,-0.44
50735001,3.8915889373,-4.8288883239\H,-2.4741628598,2.7985148859,-0.39
52749901\H,-1.3543279069,3.3514590301,0.8544069932\H,0.3497794153,3.88
26246096,-0.9048171885\H,-1.1290637829,4.8211863187,-1.0850543474\H,-1
.4722517066,3.6803568389,-5.1377488901\H,-0.0499731723,4.7500186096,-5
.3727630686\H,0.1690971686,3.005482224,-5.0099393322\\Version=EM64L-G0
9RevA.02\State=2-A\HF=-770.3474397\S2=0.753642\S2-1=0.\S2A=0.75001\RMS
D=4.855e-09\RMSF=1.521e-06\Dipole=0.1064901,0.9999465,-0.4108106\Quadr
upole=-1.7339835,-2.1251132,3.8590967,-1.6741306,-1.2425909,-1.8485337
\PG=C01 [X(C13H25N2O2)]\\@

Hostavin3055

1\1\GINC-V1255\FOpt\RB3LYP\Gen\C13H22N2O2\GXG501\22-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3055.freq\\0,1\H,-0.2692983962,0.237157849,-0.0764339707\C,-0.1
924233152,0.2030088274,1.0144886653\H,0.8666286324,0.3058856364,1.2812
08229\C,-0.9962736365,1.3733852091,1.5979588558\H,-0.8746895066,1.4028

821737,2.6839358268\C,-2.4823885437,1.2267472793,1.2429117886\C,-0.716
6709109,-1.1618304936,1.5147187627\N,-2.1761863016,-1.1987434457,1.296
4139103\H,-2.5465373103,-2.0961031338,1.6048428121\C,-3.0661907046,-0.
1114700618,1.749086704\H,-3.0541579089,2.0586537819,1.6722564089\H,-2.
5868458212,1.2731882216,0.1547379267\C,-4.4209505511,-0.3536806244,1.0
566228027\H,-4.286469062,-0.4219446118,-0.0268558299\H,-5.1272290705,0
.4550103061,1.2778882891\H,-4.8725652321,-1.2920781293,1.4042256957\C,
-3.3159629672,-0.0644998902,3.278501671\H,-2.432661145,0.2307556332,3.
8503002224\H,-3.6341440808,-1.0493181157,3.6422074108\H,-4.1137073392,
0.649769932,3.5166161154\C,-0.1250102315,-2.27421549,0.6281025841\H,0.
9704496038,-2.2710116572,0.6696436938\H,-0.4419654411,-2.1406629171,-0
.4103455016\H,-0.466247239,-3.2619585394,0.9646983666\C,-0.2666145477,
-1.4277215369,2.9743257188\H,0.8215811507,-1.5565906712,3.0243142308\H
,-0.7266626074,-2.3491125976,3.3521922762\H,-0.5310285684,-0.619355136
3,3.6606067479\N,-0.4573754683,2.6757983609,1.1625257985\C,-0.38940594
73,3.1228404698,-0.1583721529\C,0.234255622,4.5179742212,-0.1571681673
\C,0.5219578951,4.8311528331,1.31663097\C,0.047990982,3.6005693525,2.0
834049309\O,0.0908872076,3.4285976373,3.28402531\O,-0.7637426632,2.502
8944602,-1.1333639629\H,1.1306025084,4.5005895776,-0.7848388977\H,1.58
28719272,4.9918575457,1.5324069286\H,-0.0154972544,5.7073704463,1.6925
113331\H,-0.4682357909,5.215045824,-0.6244256474\\Version=EM64L-G09Rev
A.02\State=1-A\HF=-768.629038\RMSD=2.771e-09\RMSF=6.648e-06\Dipole=0.1
672676,0.3573792,0.074901\Quadrupole=2.5118413,8.9564525,-11.4682939,2
.6778651,-3.8526551,-5.6804303\PG=C01 [X(C13H22N2O2)]\\@

- **Hostavin3055**

1\1\GINC-V1255\FOpt\UB3LYP\Gen\C13H21N2O2(2)\GXG501\22-Jul-2010\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\h3055r.freq\\0,2\H,-0.2835445991,0.2532396493,-0.0666869611\C
,-0.1999871444,0.2149729388,1.0244228256\H,0.8645469403,0.3058209024,1
.2736037848\C,-0.9880239575,1.3884993739,1.6125792204\H,-0.8674066066,
1.4157236727,2.6991516346\C,-2.4670537128,1.2284850484,1.2506911419\C,
-0.7310077293,-1.1499277465,1.5366686673\N,-2.1862614716,-1.2850535751
,1.5825279093\C,-3.0444332307,-0.1156858211,1.7675796268\H,-3.05408156
56,2.0576807642,1.6647087134\H,-2.5642325729,1.2728366338,0.1609428697
\C,-4.3541807509,-0.4250514388,1.0126502418\H,-4.1587979393,-0.5604632
225,-0.056393544\H,-5.0722537523,0.3954697691,1.1304886385\H,-4.804359
8296,-1.3462188239,1.395272705\C,-3.3707191212,-0.0222168114,3.2839301
242\H,-2.5089804202,0.2990739132,3.8763132286\H,-3.6990485138,-0.99609
42819,3.6589877561\H,-4.1782935174,0.7023337227,3.4408447032\C,-0.2287
804536,-2.2693477999,0.6008638804\H,0.8660644435,-2.2593143906,0.53774
60927\H,-0.6328665578,-2.1367478658,-0.4083424096\H,-0.552411394,-3.24
70946027,0.9708430296\C,-0.1986113852,-1.4403575901,2.9673062177\H,0.8
902086058,-1.5636229654,2.9349259913\H,-0.6420342753,-2.3627839676,3.3
538433945\H,-0.4262286957,-0.6320585317,3.6684352385\N,-0.4498383865,2

.6897249724,1.1761229865\C,-0.3829022704,3.1341914101,-0.1453144888\C,
0.2406273235,4.5290419222,-0.147167037\C,0.5288497383,4.8452821063,1.3
261123573\C,0.0560548224,3.6161593489,2.0956927735\O,0.0988778903,3.44
50190115,3.2962205672\O,-0.7579793476,2.511114409,-1.1184433886\H,1.13
6817005,4.5104665218,-0.7750290535\H,1.5897579273,5.0071181843,1.54095
08938\H,-0.0089315847,5.7219939353,1.7003217704\H,-0.4619334372,5.2252
22322,-0.6156282494\\Version=EM64L-G09RevA.02\State=2-A\HF=-767.975271
\S2=0.753653\S2-1=0.\S2A=0.75001\RMSD=4.540e-09\RMSF=1.431e-05\Dipole=
0.377317,0.8600509,-0.0714753\Quadrupole=3.6409335,5.1469914,-8.787924
9,0.0849775,-3.320059,-4.5947182\PG=C01 [X(C13H21N2O2)]\\@

Hostavin3050

1\1\GINC-V1268\FOpt\RB3LYP\Gen\C17H30N2O4\GXG501\24-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3050.freq\\0,1\H,0.8934842767,0.1412229676,0.8020450772\C,0.487
350157,0.065320893,1.8173288333\H,1.3385334948,0.0442193813,2.50627312
37\C,-0.3261020198,1.3507603981,2.0472978253\C,-1.5762451396,1.3507543
548,1.1527262219\C,-0.3251490453,-1.2423135157,1.9277179681\N,-1.54234
45295,-1.0930445574,1.1052102893\H,-2.0910371369,-1.9503067244,1.15083
7345\C,-2.4377454071,0.0717160214,1.2420915334\H,-2.1917848323,2.22779
96947,1.3853216314\H,-1.2165091927,1.4648108544,0.1236552241\C,-3.3738
580137,0.031202344,0.0177481671\H,-2.7912361046,-0.0080067502,-0.90756
64406\H,-4.0274088951,0.9111414,-0.0094081731\H,-4.0173499415,-0.85772
92324,0.0529070395\C,-3.3222888479,0.0725509886,2.5145736842\H,-2.7454
496678,0.2333487245,3.4251852587\H,-3.8580907812,-0.881239523,2.601817
7316\H,-4.075199297,0.8690718606,2.4561927979\C,0.489980096,-2.3753490
936,1.273213729\H,1.4581751273,-2.5024723152,1.7712585557\H,0.66039615
08,-2.1607649727,0.213877626\H,-0.0480466768,-3.3298528938,1.345147062
1\C,-0.5770103419,-1.6335004096,3.4055424042\H,0.3697660332,-1.8858271
319,3.8996087477\H,-1.2225002683,-2.5197762506,3.4566163114\H,-1.04080
42432,-0.8305183463,3.9781246058\O,-0.6705222903,1.5299525866,3.437268
8636\C,-0.069448836,2.7001073616,4.0091169554\N,0.6594424509,3.2952970
791,2.8803995859\C,0.5458991473,2.5654523411,1.7342168505\O,1.05497148
36,2.8368098459,0.6539081573\C,-1.1894305944,3.6206871775,4.5085250699
\C,0.8571442935,2.2628748377,5.1500294969\C,1.4772263234,4.4953777696,
2.925969328\C,2.9501494254,4.2624450779,3.3518413512\C,3.596510975,3.1
887385118,2.5010608414\O,3.6027557984,2.0060684669,2.7795411558\O,4.11
36851942,3.7034801689,1.3722465606\C,4.5413125613,2.7399636885,0.39195
35633\H,3.006455724,3.9456264272,4.3950209432\H,1.4644118552,4.9141335
227,1.9159403356\H,1.0180935726,5.2212084059,3.6046333616\H,3.48815599
75,5.2090332849,3.2383913308\H,5.2776889946,2.0555023137,0.8199181203\
H,3.673953142,2.1791247605,0.0359162111\H,4.9806697566,3.323804357,-0.
4172536744\H,-0.7893717354,4.5308395364,4.9692091887\H,-1.8447840392,3
.9013083623,3.679064701\H,-1.7838524614,3.09374734,5.2612311638\H,1.24
2190082,3.1254502208,5.7058607182\H,1.6998738048,1.6891625053,4.756203

7474\H,0.2899632416,1.6385153266,5.8472639608\\Version=EM64L-G09RevA.0
2\State=1-A\HF=-1076.3131777\RMSD=6.192e-09\RMSF=5.432e-06\Dipole=-0.1
251117,0.7657523,0.849894\Quadrupole=-0.368807,3.3471939,-2.978387,2.7
506783,-1.860349,5.1633792\PG=C01 [X(C17H30N2O4)]\\@

• **Hostavin3050**

1\1\GINC-V1279\FOpt\UB3LYP\Gen\C17H29N2O4(2)\GXG501\24-Jul-2010\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\h3050r.freq\\0,2\H,-0.6602958397,-1.9599027462,-0.2768847614\
C,-0.8876183795,-1.1593055187,0.4378678119\H,-0.1602496814,-1.25039235
5,1.2519548465\C,-0.6616880428,0.1577823817,-0.3160629585\C,-1.7332724
294,0.2958421172,-1.4035031794\C,-2.3263098375,-1.3535211952,0.9798620
503\N,-3.4021581916,-0.9343434906,0.0845945571\C,-3.1904138288,0.12338
10601,-0.9001406004\H,-1.6301552596,1.2644373685,-1.9073046467\H,-1.51
222722,-0.4762864643,-2.1506288784\C,-4.0908938723,-0.2326629382,-2.10
29396699\H,-3.7944697581,-1.1937599876,-2.537113202\H,-4.0177417971,0.
5349611862,-2.883054557\H,-5.1343991034,-0.3123316279,-1.7829004776\C,
-3.7205346259,1.4433016364,-0.2744745478\H,-3.0662145644,1.8033462634,
0.5209601039\H,-4.7253104759,1.2874573736,0.1300586013\H,-3.7739508478
,2.2174665476,-1.0497849942\C,-2.5571988534,-2.857638538,1.2422485193\
H,-1.8042887946,-3.2490649169,1.9369430661\H,-2.4935310274,-3.42756930
89,0.3088100575\H,-3.5513972391,-3.0182747344,1.6707422619\C,-2.524105
5654,-0.5951185054,2.3216199752\H,-1.862949536,-1.0270829053,3.0825486
416\H,-3.5594815898,-0.6990547583,2.6606667393\H,-2.2836329922,0.46469
86034,2.225286247\O,-0.6513523619,1.2957792733,0.5696283456\C,0.613913
0891,1.9733784022,0.5809891866\N,1.4165597152,1.2128131623,-0.38751860
13\C,0.7346663522,0.1659024632,-0.9326597408\O,1.1670997022,-0.6249279
322,-1.7619394281\C,0.3901547784,3.4182016452,0.1193170088\C,1.1841344
129,1.9126534984,2.0028076846\C,2.8071004318,1.4602140726,-0.729370026
1\C,3.8373931347,0.7676102407,0.2001124437\C,3.5519068148,-0.715596240
1,0.3149093509\O,2.835678865,-1.211144324,1.1622295466\O,4.146723876,-
1.4070254664,-0.6721936235\C,3.7532393651,-2.7870947136,-0.7855117545\
H,3.8033591175,1.1962715183,1.2035248573\H,2.9438438978,1.0866091326,-
1.7478839888\H,2.9934645146,2.5388252468,-0.7313190926\H,4.8345871438,
0.9289573702,-0.2215303766\H,3.9316779281,-3.3170217585,0.1532116095\H
,2.6937997285,-2.8395683912,-1.0472100764\H,4.3681347416,-3.2000586109
,-1.5855156897\H,1.3243523051,3.9907677199,0.117498804\H,-0.0353546362
,3.4306063651,-0.8881780152\H,-0.3085720858,3.9133443203,0.8006179898\
H,2.088666945,2.5241996922,2.0974079426\H,1.4228151606,0.8807865785,2.
2724267472\H,0.438041417,2.3049071881,2.7007538908\\Version=EM64L-G09R
evA.02\State=2-A\HF=-1075.6597343\S2=0.753651\S2-1=0.\S2A=0.75001\RMSD
=5.787e-09\RMSF=4.328e-06\Dipole=1.0299846,1.1160691,0.0644305\Quadrup
ole=-1.3016681,5.5949455,-4.2932774,0.7851258,0.4830375,0.6858353\PG=C
01 [X(C17H29N2O4)]\\@

Hostavin3058

1\1\GINC-V1270\FOpt\RB3LYP\Gen\C15H24N2O3\GXG501\22-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3058.freq\\0,1\H,-0.2556788114,0.0804232467,-0.137740283\C,-0.1
837333819,-0.0155062385,0.9500664901\H,0.8797719003,-0.1090587586,1.19
80520679\C,-0.7706581883,1.2403437466,1.5742421711\H,-0.6997107142,1.2
080776715,2.6642702468\C,-2.2211947917,1.3110512101,1.1254220699\C,-0.
8676009473,-1.333648753,1.3995554819\N,-2.3829120598,-1.2147681477,1.3
962929056\C,-3.0782503801,0.1274555546,1.6312360557\H,-2.6952227099,2.
2282034905,1.4924107062\H,-2.2436483958,1.3486375301,0.0316278991\C,-4
.3778450765,0.2135714565,0.7933002377\H,-4.1785404115,-0.0936246704,-0
.239359968\H,-4.7125542012,1.2575492111,0.7728027428\H,-5.1759635511,-
0.4035611436,1.1965879188\C,-3.3941223913,0.3365437651,3.1298748922\H,
-2.4851745272,0.4160749048,3.7355904054\H,-4.0000990983,-0.4844338314,
3.5115133286\H,-3.957202727,1.2687316339,3.257624117\C,-0.3412301404,-
2.3652761293,0.3667973536\H,0.7106750137,-2.1417172599,0.159128337\H,-
0.8913748957,-2.2809311892,-0.5756121172\H,-0.3783296553,-3.3977499493
,0.7088405566\C,-0.3642281027,-1.6984177976,2.8156164236\H,0.719823566
9,-1.8620425422,2.8017079261\H,-0.8342746808,-2.6121691337,3.189241223
6\H,-0.5738287836,-0.9038386692,3.5376523502\N,-0.0066796867,2.4474825
176,1.2123029748\C,0.1918285076,2.923171618,-0.0850911308\C,1.02430403
27,4.2012340486,-0.000872265\C,1.2988278449,4.4080446216,1.4943458107\
C,0.6038063187,3.2427583773,2.1907220593\O,0.5697309908,3.0177893309,3
.3822187977\O,-0.2283117052,2.4014471888,-1.0986373184\H,1.9306826597,
4.0689822355,-0.5996641981\H,2.3623075335,4.3867937199,1.7520952195\H,
0.8942967101,5.3449412888,1.8897446611\H,0.456859976,5.0175333786,-0.4
585873361\C,-3.1855341447,-2.3271668079,1.6601715997\O,-4.3377288744,-
2.2148084441,2.0738839524\C,-2.7150473778,-3.7568984012,1.3873361739\H
,-2.4685797818,-3.9145239442,0.3345179708\H,-1.8556428626,-4.061656348
5,1.9890698032\H,-3.561770415,-4.3917727596,1.6502991424\\Version=EM64
L-G09RevA.02\State=1-A\HF=-921.267444\RMSD=3.741e-09\RMSF=1.032e-05\Di
pole=1.5157614,0.6215456,-0.4419342\Quadrupole=-2.5492266,11.7286577,-
9.1794312,-2.4317992,-0.8838991,-1.3552065\PG=C01 [X(C15H24N2O3)]\\@

N(i-propyloxy)piperidine

1\1\GINC-V1252\FOpt\RB3LYP\Gen\C8H17N1O1\GXG501\22-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\nor12.freq\\0,1\H,-0.0163821408,-0.0355000539,0.0026404723\C,-0.0
081460594,-0.0599356988,1.1001836189\H,1.0392371688,-0.1431999007,1.41
52430857\C,-0.6455959664,1.2236523833,1.6509082994\H,-0.1442536393,2.1
098407412,1.2427902469\H,-0.5098112995,1.2564956856,2.741612887\C,-2.1
45951749,1.2542141281,1.3261420346\C,-0.7795785361,-1.297382442,1.5742
161865\H,-0.3667949553,-2.2079068789,1.1273066887\H,-0.7048705451,-1.4
001497767,2.6717124491\N,-2.1840229839,-1.1911468684,1.1594484951\C,-2
.8344242164,-0.0361795756,1.7871731568\H,-2.6319885595,2.1133740212,1.

8044913516\H,-2.2868612661,1.3635141938,0.2428093661\H,-3.8878988612,-
0.0457519912,1.4921377799\H,-2.7960812813,-0.1174078368,2.8887781839\O
,-2.8515905841,-2.3603977987,1.6865274938\C,-3.2362600452,-3.240408483
3,0.6174359653\C,-3.6465389452,-4.5414423839,1.3005246615\H,-2.3550688
243,-3.4211454358,-0.0165023643\H,-3.9310465291,-5.2920338994,0.555107
6135\H,-4.5031128494,-4.3719185117,1.9627145688\H,-2.8227875723,-4.939
5530365,1.9014195414\C,-4.3503533652,-2.639385387,-0.2374697328\H,-4.0
253326124,-1.6863546142,-0.6645330634\H,-4.6127335174,-3.3139237896,-1
.0612523137\H,-5.2488511759,-2.4680685838,0.3673379596\\Version=EM64L-
G09RevA.02\State=1-A\HF=-445.0217728\RMSD=9.782e-09\RMSF=2.233e-06\Dip
ole=0.1866083,0.1795901,-0.1550739\Quadrupole=0.4018129,1.3333805,-1.7
351934,0.4064262,0.5382882,1.5379233\PG=C01 [X(C8H17N1O1)]\\@

N(t-butyloxy)piperidine

1\1\GINC-V1297\FOpt\RB3LYP\Gen\C9H19N1O1\GXG501\22-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\nor34.freq\\0,1\H,0.0455290288,0.1113105817,0.0927820088\C,0.0059
523853,0.0600592628,1.188883496\H,1.0417551111,0.0467304223,1.54986048
19\C,-0.7493152912,1.2790440774,1.7356165819\H,-0.2997294968,2.2097158
004,1.3681519861\H,-0.6644474335,1.2967392875,2.8317936107\C,-2.231081
2286,1.2018226653,1.3436413521\C,-0.6873327328,-1.2445580394,1.5994281
254\H,-0.1833627488,-2.1078913064,1.1563771114\H,-0.6545280709,-1.3667
313194,2.6970805137\N,-2.0774582227,-1.2401853423,1.1230593472\C,-2.83
61330414,-0.1478370567,1.7480677776\H,-2.8038178483,2.0094770598,1.815
9088239\H,-2.3325816738,1.3250842734,0.2573006008\H,-3.8737253278,-0.2
243674373,1.4116678604\H,-2.8337167765,-0.2545023629,2.8478234791\O,-2
.669853922,-2.4666234984,1.6077862613\C,-3.1710368594,-3.3050848964,0.
5344189646\C,-2.0308920703,-3.728777247,-0.4004871879\H,-2.4032655781,
-4.4013540747,-1.1818458547\H,-1.2492513258,-4.2550598114,0.1585758822
\H,-1.588544684,-2.8532968908,-0.8847979014\C,-3.7348567436,-4.5119466
745,1.2913819012\C,-4.2765807216,-2.5832703495,-0.2467881857\H,-5.0947
795892,-2.2933904897,0.4217969624\H,-4.5248943886,-4.1972054285,1.9811
230994\H,-4.1549851122,-5.2417128911,0.5907726553\H,-4.6872553138,-3.2
363798991,-1.0254637726\H,-3.879957468,-1.684514971,-0.7280573665\H,-2
.9472139384,-5.0019806386,1.8731521316\\Version=EM64L-G09RevA.02\State
=1-A\HF=-484.3369548\RMSD=2.241e-09\RMSF=1.293e-05\Dipole=0.0987449,0.
2139431,-0.1508364\Quadrupole=0.5163968,1.1533076,-1.6697043,0.6168126
,0.6672508,1.5548284\PG=C01 [X(C9H19N1O1)]\\@

N(1-ethoxyacetyl)piperidine

1\1\GINC-V1250\FOpt\RB3LYP\Gen\C9H17N1O3\GXG501\19-Aug-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\nor56.freq\\0,1\H,-0.1788585806,1.3168537282,0.958819078\C,-0.211
6020165,0.316289129,1.40924004\H,-0.4738281517,0.444729931,2.466418325
2\C,-1.2582496616,-0.542850195,0.6855518579\H,-1.3858379935,-1.4916584

575,1.2264029695\C,-0.8047980691,-0.8353662703,-0.7519109172\C,1.18106
79908,-0.3178246569,1.3106390529\N,1.5313779964,-0.4962481874,-0.10448
87543\C,0.6108086852,-1.4248700849,-0.771241703\H,-1.4914103878,-1.533
9995211,-1.2450851744\H,-0.8096072664,0.0927870083,-1.3377966072\O,2.8
307474039,-1.1502022511,-0.1211277285\C,3.766726493,-0.3408736842,-0.7
596426411\C,4.998206505,-1.1778552711,-1.0460992671\H,3.3483004287,0.1
174431376,-1.6579557766\H,4.7394537399,-2.0074439113,-1.7107825942\H,5
.7565449058,-0.5575034628,-1.5306917306\H,5.4016180445,-1.5833307615,-
0.1134523489\O,4.1088959291,0.7409334575,0.1579259121\C,4.5163851062,1
.9078803065,-0.3910174455\C,4.7216584703,2.9596652328,0.6754540221\O,4
.6903551935,2.0762883796,-1.5795604011\H,5.3867164995,2.5832084226,1.4
589704378\H,5.1441589135,3.8578062767,0.2235214466\H,3.7633651689,3.20
15179085,1.1479863682\H,-2.2349817398,-0.04401173,0.6867301066\H,0.623
4333917,-2.4118991416,-0.2755097342\H,0.9615952283,-1.5632513082,-1.79
89751827\H,1.9432776016,0.3244179808,1.7585561121\H,1.198542171,-1.286
2320042,1.8417012776\\Version=EM64L-G09RevA.02\State=1-A\HF=-633.59281
14\RMSD=6.060e-09\RMSF=1.855e-06\Dipole=-0.5654234,-0.2033723,0.632346
6\Quadrupole=2.3155212,-0.3748998,-1.9406214,-0.1103156,2.6137675,5.33
16726\PG=C01 [X(C9H17N1O3)]\\@

•N-oxypiperidine

1\1\GINC-V1297\FOpt\UB3LYP\Gen\C5H10N1O1(2)\GXG501\22-Jul-2010\0\\#B3L
YP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268
435456\\nor6.freq\\0,2\H,-0.0350766521,-0.0072619408,-0.0040257139\C,-
0.0042343181,-0.000930994,1.0935279452\H,1.0525812656,0.0125957307,1.3
860165822\C,-0.7328855005,1.2445694424,1.619202394\H,-0.2801559067,2.1
531929986,1.2051149238\H,-0.6177341265,1.3031041784,2.7116002766\C,-2.
2258137638,1.1837829471,1.2642267453\C,-0.6547646621,-1.2847620025,1.6
198552743\H,-0.2606726675,-2.1811315609,1.1355806459\H,-0.4819335465,-
1.3835213875,2.7052580247\N,-2.1017781929,-1.2863311728,1.3689919266\C
,-2.8665231297,-0.1052853487,1.789799463\H,-2.7610912976,2.0463339618,
1.6790465397\H,-2.3448011458,1.2244575969,0.1734458595\H,-3.8819070683
,-0.2500158915,1.4138242928\H,-2.9139505559,-0.0865862445,2.8921261495
\O,-2.7073533932,-2.4176535706,1.3394662283\\Version=EM64L-G09RevA.02\
State=2-A'\HF=-326.4609425\S2=0.753323\S2-1=0.\S2A=0.750007\RMSD=9.296
e-09\RMSF=1.839e-05\Dipole=0.641217,1.1740122,0.1971066\Quadrupole=1.5
417282,-3.2081138,1.6663856,-3.6126283,-0.3921255,-0.4713526\PG=CS [SG
(C1H2N1O1),X(C4H8)]\\@

•O-Tinuvin770

1\1\GINC-V1260\FOpt\UB3LYP\Gen\C11H20N1O3(2)\GXG501\24-Jul-2010\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\t770o.freq\\0,2\H,-0.1419897544,-0.2887078728,-0.1964167753\C
,-0.001966073,-0.2185302141,0.890039562\H,1.0729116301,-0.275722275,1.
0894013228\C,-0.5470331352,1.13120492,1.3443515184\H,-0.3421520293,1.2

970132883,2.4046755711\C,-2.0329324855,1.217572942,1.0297801629\C,-0.6
945634495,-1.4128608394,1.577557736\N,-2.183811005,-1.2098014476,1.590
3763234\C,-2.8622741969,0.1233107652,1.7318087677\H,-2.4266208357,2.19
86669134,1.3189646667\H,-2.1560353399,1.1301598921,-0.0572035748\C,-4.
2341906785,0.0078213857,1.0471309843\H,-4.1186694848,-0.2704377686,-0.
0056499786\H,-4.7532291644,0.9713301417,1.0966945393\H,-4.8447137719,-
0.7522267245,1.5376272847\C,-3.0667914533,0.4340100616,3.2303817921\H,
-2.1245260219,0.6306513443,3.7505301442\H,-3.5559183276,-0.4166137728,
3.7129697362\H,-3.7051625758,1.3170671979,3.3465020528\C,-0.4209229091
,-2.6930527502,0.7710439658\H,0.6593185216,-2.8627141175,0.7054845665\
H,-0.8206509907,-2.6034386497,-0.2445691322\H,-0.8892539413,-3.5552124
283,1.2491374295\C,-0.1936223214,-1.6066185609,3.0251117398\H,0.855445
8767,-1.9220256295,3.0182887205\H,-0.7899253434,-2.3817937149,3.514400
8716\H,-0.2602122574,-0.6902049735,3.6188118045\O,0.0951424661,2.20200
67891,0.6031956036\C,1.2807626056,2.6543378298,1.0804946142\O,1.822909
3597,2.2175073236,2.0723309359\C,1.8164731571,3.7653206611,0.207589486
2\H,1.9822857972,3.3955070526,-0.8097964094\H,2.7542071256,4.134229360
4,0.6242179068\H,1.0886161393,4.5805307862,0.1430837635\O,-2.881132133
1,-2.2277859158,1.9487542977\\Version=EM64L-G09RevA.02\State=2-A\HF=-7
11.5998463\S2=0.753679\S2-1=0.\S2A=0.750009\RMSD=9.767e-09\RMSF=6.738e
-06\Dipole=0.1450933,0.9153524,-0.6036921\Quadrupole=-2.12714,0.346116
5,1.7810235,-5.1462486,-3.666576,-1.6575311\PG=C01 [X(C11H20N1O3)]\\@

Tinuvin770-R1

1\1\GINC-V1306\FOpt\RB3LYP\Gen\C15H27N1O5\GXG501\24-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t770x1.freq\\0,1\H,0.9271067051,-1.5556014654,0.0394073637\C,1.0
135120869,-0.7642059518,0.7948777369\H,1.4523421243,-1.2068032794,1.69
49971611\C,1.9336007399,0.3151776949,0.2413581291\H,2.1701194573,1.055
7839054,1.008227098\C,1.299648194,0.9474463371,-0.9859287578\C,-0.3987
72296,-0.2403985514,1.1436005704\N,-0.9289792429,0.4575577965,-0.07597
50878\C,-0.0994859242,1.5413172854,-0.7044937778\H,1.9442257709,1.7393
081436,-1.3849018759\H,1.2138052826,0.175837379,-1.7611256114\C,-0.725
0307117,1.8817006212,-2.0720942524\H,-0.8915841083,0.9738765731,-2.660
6958011\H,-0.0480407549,2.5352140703,-2.6338534872\H,-1.6743296789,2.4
123719596,-1.9613590188\C,-0.0002365108,2.8523173189,0.1100598133\H,0.
6561763435,2.7733935291,0.9788120912\H,-0.9914411408,3.1554496257,0.45
55534378\H,0.3979352065,3.6501039358,-0.5275850887\C,-1.2895679863,-1.
4692228438,1.4043590308\H,-0.7940616608,-2.1365453348,2.11876651\H,-1.
4610105691,-2.0226768608,0.4751732968\H,-2.2515521025,-1.1800407098,1.
8317456469\C,-0.3800817666,0.6102859453,2.4349903485\H,-0.2126542062,-
0.0453896494,3.2968841429\H,-1.3437526145,1.1074786304,2.5695432653\H,
0.4076391955,1.3663232897,2.4488486957\O,-2.2083919716,1.0438603746,0.
2764262966\C,-3.2788744798,0.6043471623,-0.5708545054\C,-4.2602756905,
1.7709876366,-0.6823789446\C,-4.0259016674,-0.5903671755,0.0352616918\

O,-4.5611937721,-0.5931375653,1.122140824\O,-4.0567664858,-1.634378008
3,-0.8206467731\C,-4.7861362957,-2.7859260809,-0.3602296364\H,-5.82276
09375,-2.519248276,-0.1383903236\H,-4.7390297121,-3.5077812134,-1.1759
110091\H,-4.32328034,-3.1936795785,0.5421665667\H,-5.1151362739,1.4972
611925,-1.3108713928\H,-4.6316926144,2.0324400941,0.312427679\H,-3.767
7121761,2.643224738,-1.1208216361\H,-2.8798839557,0.3127538278,-1.5428
973677\O,3.1904722088,-0.2719633334,-0.1953222807\C,4.1547570693,-0.43
07418992,0.7418124047\O,4.0308793209,-0.1175077082,1.9062159172\C,5.39
30755874,-1.0465895023,0.1311644689\H,5.155866741,-2.0315718776,-0.284
5822827\H,6.1650064092,-1.1437686352,0.8952392281\H,5.7580132038,-0.42
48235668,-0.6927795042\\Version=EM64L-G09RevA.02\State=1-A\HF=-1018.69
89602\RMSD=6.385e-09\RMSF=5.350e-06\Dipole=-0.0224116,-0.3890083,-1.33
41758\Quadrupole=1.1278009,5.2406157,-6.3684167,1.5719286,-0.4673731,-
1.1724216\PG=C01 [X(C15H27N1O5)]\\@

Tinuvin770-R2

1\1\GINC-V1280\FOpt\RB3LYP\Gen\C16H29N1O5\GXG501\25-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t770x2.freq\\0,1\H,-0.103757389,-0.2367121625,-0.2017104347\C,-0
.0007487659,-0.1855115387,0.8897352895\H,1.0599214794,-0.3080774529,1.
1319620794\C,-0.4874754949,1.1829798333,1.3417455579\H,-0.2786750866,1
.3421720654,2.4016508351\C,-1.9648268588,1.321759102,1.0230886877\C,-0
.7890404595,-1.3498157404,1.5314573995\N,-2.2565031162,-1.113801924,1.
2764055382\C,-2.8372298024,0.219880129,1.6691955386\H,-2.337032813,2.2
9839273,1.3533267295\H,-2.0832677119,1.2813048627,-0.0670360466\C,-4.2
345526544,0.3465680831,1.032070201\H,-4.2121025932,0.0796072216,-0.028
3048729\H,-4.5793553205,1.383753666,1.1142447975\H,-4.9707119724,-0.27
669268,1.5408447622\C,-2.9926748631,0.444439929,3.1910569887\H,-2.0448
319638,0.6220258358,3.7030891969\H,-3.4766172629,-0.4223099496,3.64658
20963\H,-3.6259513772,1.3222969337,3.3654170403\C,-0.3744965061,-2.631
385815,0.7860988096\H,0.7124123263,-2.7556291093,0.8481927827\H,-0.651
7885188,-2.5750047036,-0.2704063258\H,-0.8356914499,-3.5175876177,1.22
84323048\C,-0.402017196,-1.5249295989,3.0200421814\H,0.61608684,-1.924
8123218,3.0852160413\H,-1.0788929411,-2.2311619827,3.5056696098\H,-0.4
149645166,-0.5908335758,3.5846263464\O,0.1995683055,2.2305694837,0.602
9938521\C,1.3989887022,2.6365626532,1.0820311746\O,1.9253518907,2.1809
854402,2.0744614866\C,1.9777780029,3.727832109,0.2104297979\H,2.125456
6136,3.3549660919,-0.8086142777\H,2.9308333786,4.0572540584,0.62553279
81\H,1.2835928722,4.5723136924,0.1505097621\O,-2.9558418135,-2.1489923
252,2.0072473978\C,-3.8447649653,-3.0290562884,1.2663925888\C,-3.65637
36569,-3.0438006586,-0.2476776238\H,-3.758258758,-2.0474334377,-0.6778
205775\H,-4.4212523221,-3.6874008002,-0.6881972077\H,-2.6713530739,-3.
4347151782,-0.5058832829\C,-3.5983984576,-4.4241190312,1.8742198018\H,
-2.6041329876,-4.7843030952,1.5951782713\H,-4.3418498227,-5.1408663928
,1.5079947706\H,-3.6641829591,-4.3750797967,2.9642649517\C,-5.31465173

9,-2.6763647256,1.5971556267\O,-6.2344159597,-2.7299116458,0.809030795
7\O,-5.4785845096,-2.3803612132,2.9045746171\C,-6.8334187115,-2.123477
5374,3.3097311258\H,-7.234146081,-1.2533089833,2.7825878873\H,-6.78554
47623,-1.9325296561,4.3820990883\H,-7.4683261974,-2.9880119818,3.09855
9041\\Version=EM64L-G09RevA.02\State=1-A\HF=-1058.0081453\RMSD=6.490e-
09\RMSF=2.884e-06\Dipole=-0.2398166,0.148458,-0.0355663\Quadrupole=-4.
8783931,5.8027697,-0.9243766,-2.0244998,-12.2469385,-4.6708409\PG=C01
[X(C16H29N1O5)]\\@

Tinuvin770-R3

1\1\GINC-V1283\FOpt\RB3LYP\Gen\C15H27N1O5\GXG501\25-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\t770x3.freq\\0,1\H,-0.1920422599,-0.2995239114,-0.2219704783\C,-
0.0658738904,-0.2469413495,0.8668086804\H,1.0009546957,-0.3587223114,1
.0857416394\C,-0.5540304333,1.1194679518,1.3285670963\H,-0.3150936492,
1.2835840029,2.381461341\C,-2.0428214089,1.249512356,1.0545846314\C,-0
.8267166951,-1.4233208519,1.5218346359\N,-2.2938964131,-1.1797622021,1
.3052620474\C,-2.8775191414,0.1390034201,1.7317726533\H,-2.4114015474,
2.22375769,1.3958806202\H,-2.1966438852,1.2047350947,-0.0306790138\C,-
4.305041034,0.231443349,1.1560252489\H,-4.3112651875,-0.0025183942,0.0
868584148\H,-4.6881057683,1.2497258168,1.2868836837\H,-4.9942246712,-0
.44396525,1.6708831117\C,-2.969341366,0.360022431,3.2599731612\H,-2.00
51799199,0.570593048,3.726412688\H,-3.3997414623,-0.5197610265,3.74434
50362\H,-3.6235716098,1.2151596487,3.4649636187\C,-0.4397305673,-2.698
299871,0.7508432018\H,0.6517315389,-2.7977915101,0.7371386988\H,-0.798
1076228,-2.6435842396,-0.2819757066\H,-0.8638852997,-3.5891378323,1.21
60043741\C,-0.4014682032,-1.6135134309,2.9969730822\H,0.6182786987,-2.
0129009696,3.0296019687\H,-1.0621589572,-2.3298809853,3.491236848\H,-0
.4013565975,-0.6869438328,3.5743131728\O,0.102973471,2.1695508801,0.56
74652626\C,1.3100788046,2.590506472,1.0145192633\O,1.8646693418,2.1457
545966,1.9963159596\C,1.8560987425,3.6820298275,0.1226793099\H,1.98280
55278,3.3042498241,-0.8973674328\H,2.8154914445,4.0236901585,0.5124826
752\H,1.1519540869,4.5189813562,0.0745977756\O,-3.0180272644,-2.216601
4346,2.0267104126\C,-3.8956293748,-2.9466951139,1.2175084186\H,-4.2669
374868,-2.3450767139,0.3904414845\C,-5.0041179843,-3.4888046233,2.1024
603647\H,-4.5767216253,-4.1028827138,2.9009473663\H,-5.685830357,-4.09
86441133,1.5035275613\H,-5.5687007693,-2.6675544419,2.5535543567\O,-3.
1721003959,-4.0723196159,0.6425715465\C,-3.598784051,-4.5292248333,-0.
5586409817\O,-4.5662876443,-4.0934327454,-1.1458489987\C,-2.7106023323
,-5.6476575561,-1.0525656282\H,-1.6926898885,-5.2750252739,-1.20927230
61\H,-3.1083807868,-6.0404408524,-1.988931125\H,-2.6542888012,-6.44507
29236,-0.304711741\\Version=EM64L-G09RevA.02\State=1-A\HF=-1018.717610
5\RMSD=4.327e-09\RMSF=1.584e-06\Dipole=0.0010891,0.1503986,-0.0811232\
Quadrupole=-5.8626342,9.3105342,-3.4479,-3.6482979,-10.6577392,-3.8832
899\PG=C01 [X(C15H27N1O5)]\\@

•O-Tinuvin NOR371

1\1\GINC-V1485\FOpt\UB3LYP\Gen\C13H24N7O1(2)\GXG501\27-Jul-2010\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\t371o.freq\\0,2\H,-0.8766469873,-1.5685302612,1.5758779767\C,
-0.6352111012,-0.5177574736,1.3672555731\H,-0.0521983485,-0.1488657532
,2.2189197225\C,0.2004510148,-0.4280521781,0.0837274624\H,0.4439458924
,0.61540172,-0.1117290458\C,-0.6231318522,-0.986935875,-1.0838000331\C
,-1.9512357434,0.283650662,1.291676079\N,-2.642593519,0.0242675147,-0.
016593308\C,-1.9384631048,-0.2161895542,-1.3216803408\H,-0.0341799208,
-0.9581166902,-2.0081479339\H,-0.8631119898,-2.040684723,-0.8898930554
\C,-2.8797836659,-1.0662754982,-2.1914219988\H,-3.1246211437,-2.008368
8214,-1.689395371\H,-2.3913468491,-1.2977593852,-3.1443863145\H,-3.810
666094,-0.5314429685,-2.3880509393\C,-1.6865927411,1.1372565549,-2.020
6821268\H,-0.9307034175,1.7393510789,-1.5079084189\H,-2.6195940386,1.7
066923245,-2.0559699183\H,-1.3397411582,0.9692426559,-3.0464561857\C,-
2.9025639114,-0.1865346097,2.4047957173\H,-2.4231261386,-0.0501267322,
3.3804145629\H,-3.1453743307,-1.2475562077,2.2832192669\H,-3.833840489
2,0.3822177595,2.38190805\C,-1.7037411718,1.8001312256,1.4439917384\H,
-1.3671545219,2.0229976095,2.4627412307\H,-2.6360989595,2.3404814853,1
.2575742135\H,-0.9419685256,2.1715556051,0.7522157449\O,-3.8448303268,
0.4698065105,-0.1077995201\N,1.5035888817,-1.0918171279,0.216769101 7\C
,1.574976938,-2.5414747167,0.3721249041\H,2.3204927468,-2.8044685579,1
.124782859\H,0.6005994037,-2.9155879041,0.691381921\H,1.8544727223,-3.
0416898547,-0.5637646805\C,2.6683707602,-0.3865763329,0.0884241206\N,4
.9877717259,0.9758975444,-0.1460573646\N,2.5914037392,0.9524810491,-0.
0598068315\N,3.8117961601,-1.0978821792,0.1262842693\C,4.9242114101,-0
.355215937,0.017060295\C,3.7792361933,1.5611170625,-0.1806778476\N,3.7
608002052,2.9104418209,-0.3887623542\N,6.1131984143,-1.0182184716,0.10
58441219\H,6.0868895159,-2.020774278,-0.0052090504\H,6.9356692971,-0.5
254916929,-0.2089662914\H,4.6281766248,3.4040109698,-0.2382612816\H,2.
8998204048,3.3931776313,-0.1792897187\\Version=EM64L-G09RevA.02\State=
2-A\HF=-968.3132213\S2=0.753687\S2-1=0.\S2A=0.750009\RMSD=8.548e-09\RM
SF=1.192e-05\Dipole=1.0931334,-0.1986746,0.0251686\Quadrupole=-7.67960
02,8.1989215,-0.5193213,0.9246046,-2.0907965,1.9149844\PG=C01 [X(C13H2
4N7O1)]\\@

Tinuvin NOR371-R1

1\1\GINC-X152\FOpt\RB3LYP\Gen\C17H31N7O3\GXG501\27-Jul-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=134217
7280\\t371x1.freq\\0,1\H,-0.8185342156,-1.570904312,1.5921200047\C,-0.
6154483119,-0.5174338042,1.3594096796\H,-0.0541092221,-0.1020221447,2.
2044516861\C,0.2208425928,-0.4211017693,0.0799625098\H,0.4655000027,0.
622954584,-0.1079663408\C,-0.5999505201,-0.9683148443,-1.0918165156\C,
-1.9693484634,0.2243019538,1.262743158\N,-2.6731335051,-0.2902417747,0

.0411302091\C,-1.954353326,-0.2444999376,-1.2773715246\H,-0.0305075548
,-0.8793113269,-2.0247726257\H,-0.7990635905,-2.0361955623,-0.93419066
79\C,-2.7728891449,-1.0721392184,-2.2889737601\H,-3.012930691,-2.05952
25286,-1.8813085128\H,-2.1888277624,-1.2128682635,-3.2055319177\H,-3.7
022786085,-0.5683802284,-2.5680368172\C,-1.7579078133,1.1690981819,-1.
8730471398\H,-0.9706448555,1.7405804359,-1.3779245007\H,-2.6895004407,
1.7367956758,-1.8102481009\H,-1.480281478,1.0845570303,-2.930057967\C,
-2.8053848549,-0.1827400554,2.4906477791\H,-2.2079695872,-0.0531389579
,3.4004720774\H,-3.1037098462,-1.2340574368,2.4199862705\H,-3.69927577
86,0.4363273287,2.5886986774\C,-1.7751799058,1.7578129727,1.315537705\
H,-1.4894595744,2.0505659805,2.332485357\H,-2.712391239,2.2630497997,1
.0695512117\H,-0.9955813799,2.121726598,0.6431704304\O,-3.900617252,0.
4711433376,-0.1089576771\C,-5.0715731004,-0.3550725099,-0.1476399489\C
,-6.0742081536,0.3423481844,-1.0669470418\H,-6.3086336632,1.3329111198
,-0.6672140391\H,-4.8068963968,-1.3481796196,-0.5119953256\H,-5.657681
0231,0.4516043631,-2.0719938139\H,-7.0039017873,-0.2340393358,-1.13237
29087\N,1.5262171299,-1.0853264805,0.2085503924\C,1.6013976062,-2.5319
269666,0.3887213766\H,2.2942916371,-2.7818545935,1.19549474\H,0.610368
6323,-2.9116263574,0.6418621323\H,1.9516961087,-3.0381288287,-0.519095
8821\C,2.6908770858,-0.3834531266,0.0767672209\N,5.0152486732,0.971051
6284,-0.1662128411\N,2.6183197278,0.9535862343,-0.0935910803\N,3.83389
98142,-1.0960299084,0.1327859088\C,4.9475876145,-0.3572806995,0.016895
5615\C,3.8074531897,1.5575930623,-0.216268092\N,3.7928850254,2.9043305
804,-0.4449664893\N,6.1357514159,-1.0212763992,0.1222512782\H,6.106485
5636,-2.0249105964,0.0217538224\H,6.9588041139,-0.5353440784,-0.201594
4093\H,4.6596842439,3.3979253555,-0.2910826761\H,2.9315421006,3.390141
072,-0.2437435786\C,-5.712971847,-0.4929106568,1.2389835793\O,-6.10058
5593,0.4325203013,1.9182010979\O,-5.8392145493,-1.7898600196,1.5945034
297\C,-6.481015336,-2.0203729289,2.8611344952\H,-5.8959213708,-1.57634
33636,3.670687196\H,-7.4837223257,-1.5850355045,2.8675398584\H,-6.5297
562102,-3.1039096411,2.972026349\\Version=EM64L-G09RevA.02\State=1-A\H
F=-1275.4121134\RMSD=5.213e-09\RMSF=2.901e-06\Dipole=0.0866095,-0.7547
646,-0.1843885\Quadrupole=2.5732739,1.9501439,-4.5234178,7.2959657,-0.
7296276,-2.139764\PG=C01 [X(C17H31N7O3)]\\@

Tinuvin NOR371-R2

1\1\GINC-X90\FOpt\RB3LYP\Gen\C18H33N7O3\GXG501\27-Jul-2010\0\\#B3LYP/g
en 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=1342177
280\\t371x2.freq\\0,1\H,-0.7906470773,-1.5639752742,1.5970766507\C,-0.
5997726216,-0.5139070494,1.3397451863\H,-0.0535587398,-0.0696416966,2.
1800505703\C,0.2481465929,-0.4415054336,0.0678353049\H,0.480608016,0.5
99576782,-0.1490974138\C,-0.5576832364,-1.0350852687,-1.089494412\C,-1
.9604303588,0.2086749665,1.2070128404\N,-2.6633551687,-0.34241113,-0.0
066980196\C,-1.9198419506,-0.3358825831,-1.3170051062\H,0.0176700404,-
0.9717717522,-2.0208320471\H,-0.745790734,-2.0995240708,-0.897996493\C

,-2.6967301794,-1.2131600134,-2.3180438916\H,-2.9700021326,-2.17490747
88,-1.8743779984\H,-2.0668943499,-1.4096871488,-3.1933144624\H,-3.5994
223028,-0.718209194,-2.6783694829\C,-1.7368281286,1.0578835993,-1.9604
906524\H,-0.9826865131,1.6703544959,-1.4626300659\H,-2.6863714727,1.59
78993323,-1.9546622181\H,-1.417809528,0.9364184222,-3.0023522297\C,-2.
7889069189,-0.1653965515,2.4498758767\H,-2.2351264118,0.1087252453,3.3
549239602\H,-2.9809444992,-1.2418043919,2.4812332976\H,-3.7431711974,0
.3663669127,2.4708120083\C,-1.7733215323,1.7453958427,1.213926122\H,-1
.4937885832,2.0719032017,2.2222301552\H,-2.707663568,2.2411941801,0.94
17033023\H,-0.9899053575,2.0887617635,0.5359149849\O,-3.8666361707,0.4
499878306,-0.1594071403\C,-5.1450471023,-0.2404961029,-0.1654991969\C,
-5.1353508072,-1.6641947012,0.3835374726\H,-4.4256369231,-2.2976661319
,-0.1484879035\H,-4.8739302666,-1.662807635,1.4425099784\H,-6.13355847
21,-2.0915677505,0.2638725542\N,1.5604117741,-1.0853351135,0.228199204
9\C,1.6506178392,-2.5295553044,0.4196238771\H,2.3716935889,-2.76397634
09,1.2052719853\H,0.6712321458,-2.9133013756,0.7100784162\H,1.97355322
2,-3.0446025068,-0.4938081006\C,2.7168938613,-0.3674157094,0.110628180
5\N,5.0241370067,1.0215911,-0.1026192072\N,2.6269203695,0.9681436106,-
0.0636801719\N,3.8697785578,-1.0622935246,0.1844732194\C,4.973766533,-
0.3071575074,0.0834886916\C,3.8084922123,1.589478958,-0.1718921465\N,3
.7769053375,2.9352591511,-0.4050061691\N,6.1700949992,-0.9528647176,0.
2084942922\H,6.1572656683,-1.9570513831,0.1098289323\H,6.990297181,-0.
4555719771,-0.1052216546\H,4.6338348022,3.4423226953,-0.240042986\H,2.
9054545492,3.4084229194,-0.2177447412\C,-6.0782519639,0.6693563263,0.6
580901759\H,-5.7901575388,0.6453073812,1.7128762189\H,-6.012650805,1.6
988397694,0.296415996\H,-7.1174863974,0.3320526436,0.575127276\C,-5.72
2106777,-0.2486428681,-1.6012626325\O,-6.3611524116,-1.1575911725,-2.0
866580198\O,-5.5069686369,0.9238948301,-2.2358231152\C,-6.0850372331,1
.0259531594,-3.547453896\H,-5.6591756554,0.2720894858,-4.2152826034\H,
-7.1684446555,0.8865627219,-3.5022493791\H,-5.8392529176,2.0290565329,
-3.8969711742\\Version=EM64L-G09RevA.02\State=1-A\HF=-1314.7211495\RMS
D=3.130e-09\RMSF=2.484e-06\Dipole=0.2454967,0.4363223,0.0065965\Quadru
pole=0.0036581,1.9161709,-1.9198289,-7.6691084,-2.0422165,-1.9703312\P
G=C01 [X(C18H33N7O3)]\\@

Tinuvin NOR371-R3

1\1\GINC-X90\FOpt\RB3LYP\Gen\C17H31N7O3\GXG501\27-Jul-2010\0\\#B3LYP/g
en 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=1342177
280\\t371x3.freq\\0,1\H,-0.8829629244,-1.5883245414,1.5557174623\C,-0.
6762074615,-0.533619808,1.3330232755\H,-0.1254366858,-0.125219188,2.18
83109833\C,0.1783347573,-0.4315379603,0.0659112813\H,0.4319261909,0.61
23719841,-0.1104608963\C,-0.6289390841,-0.9652565333,-1.1216886788\C,-
2.0287932268,0.2101807626,1.2259596536\N,-2.7141337909,-0.2898466109,-
0.0133952764\C,-1.9741912879,-0.2288930559,-1.3210327885\H,-0.04569059
44,-0.8733562547,-2.0457100198\H,-0.8388491111,-2.0325553849,-0.975461

0986\C,-2.7838190486,-1.0340942595,-2.3578398552\H,-3.0456193453,-2.02
28830145,-1.9679394172\H,-2.1833969725,-1.1709485089,-3.2642352759\H,-
3.70098157,-0.5148813483,-2.650861994\C,-1.755772989,1.1910174439,-1.8
938776539\H,-0.9732210734,1.750438047,-1.3781560663\H,-2.6831094556,1.
7669776182,-1.8436821369\H,-1.4590946977,1.1158199768,-2.9462838058\C,
-2.8783952347,-0.2106643757,2.4390814394\H,-2.3134252408,-0.0258650714
,3.3601199958\H,-3.1183871589,-1.2773723988,2.3858051404\H,-3.81309404
19,0.3498115689,2.4867684454\C,-1.8321280564,1.7430562055,1.2962929163
\H,-1.5593681555,2.024809247,2.3197119472\H,-2.7626760601,2.2561596195
,1.0413364168\H,-1.0420754623,2.1110505399,0.6388632068\O,-3.934756409
8,0.4892089704,-0.1790134133\C,-5.0878477927,-0.2974071538,-0.26186594
75\C,-6.1265388867,0.4765492355,-1.0543865944\H,-6.3215590112,1.439318
901,-0.5722689372\H,-4.8718757794,-1.2762689317,-0.6848662107\H,-5.771
6613452,0.6582858822,-2.0730274519\H,-7.0552982266,-0.0984604539,-1.10
13276764\N,1.477323592,-1.1045889168,0.2084994928\C,1.5408160468,-2.55
4473848,0.366646711\H,2.2336678848,-2.8208821455,1.1678073662\H,0.5474
394701,-2.9300250604,0.6170571483\H,1.8845357513,-3.0505211401,-0.5493
736133\C,2.6477982566,-0.4070144047,0.1056224445\N,4.9822562404,0.9388
620211,-0.0804042953\N,2.5844364324,0.9331304347,-0.0430478006\N,3.785
9575367,-1.1264606146,0.1664548545\C,4.9052242066,-0.3920172345,0.0796
024238\C,3.7785351147,1.5326048755,-0.1384579478\N,3.7743954009,2.8829
865415,-0.3449455676\N,6.0879108148,-1.0639943489,0.1913849138\H,6.055
4118894,-2.065892556,0.0758556728\H,6.9189165911,-0.5772543386,-0.1100
751159\H,4.6416668532,3.3691241665,-0.1712556015\H,2.9129473013,3.3704
286018,-0.1483916305\O,-5.6034141744,-0.5131338211,1.0842426615\C,-6.2
926929302,-1.6571279296,1.3037625932\O,-6.5459647614,-2.473800948,0.44
34945446\C,-6.7002492991,-1.7666564266,2.7550790048\H,-5.8097229547,-1
.8124174144,3.3909940656\H,-7.3020578166,-2.6650808942,2.8964672361\H,
-7.2704262134,-0.8819137477,3.0559604698\\Version=EM64L-G09RevA.02\Sta
te=1-A\HF=-1275.4308128\RMSD=7.801e-09\RMSF=2.227e-06\Dipole=0.410221,
0.4316135,0.2128784\Quadrupole=0.3986483,0.4534835,-0.8521318,-6.96281
56,-5.4858413,-0.2935257\PG=C01 [X(C17H31N7O3)]\\@

- **O-Hostavin3052**

1\1\GINC-V1255\FOpt\UB3LYP\Gen\C13H25N2O3(2)\GXG501\25-Jul-2010\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\h3052o.freq\\0,2\H,-0.2993984477,-1.0700930478,0.1366377433\C
,-0.2135404076,-0.5277929491,1.0896382365\H,0.8246686443,-0.1858413003
,1.1641327263\C,-1.1498874811,0.6817621298,1.0315042208\H,-1.059644337
2,1.2558881065,1.96381379\C,-2.5910038609,0.1596983064,0.8885245044\C,
-0.5021970224,-1.5028505413,2.2470805231\N,-1.9764981399,-1.7699029709
,2.3494012988\C,-3.0486752321,-0.7678334598,2.032135067\H,-3.305202140
3,0.9892477261,0.823369359\H,-2.6555616188,-0.3855397267,-0.0642004534
\C,-4.2893181265,-1.5609574344,1.5877680055\H,-4.0592278806,-2.1786807
342,0.7132268196\H,-5.0938793274,-0.8672844459,1.3195024974\H,-4.63529

38525,-2.2166015697,2.3890865304\C,-3.3886163361,0.028705958,3.3106542
663\H,-2.5746265329,0.692494468,3.6177642272\H,-3.5932169821,-0.667238
5601,4.1290491513\H,-4.2797054392,0.6445138119,3.1434828587\C,0.181883
5453,-2.8513542266,1.9656727562\H,1.2611035732,-2.7001647569,1.8527022
987\H,-0.2041669112,-3.2942507913,1.0414162715\H,0.0028916772,-3.55282
18734,2.7825901982\C,0.0051130858,-0.9500739254,3.5965747481\H,1.10019
64324,-0.9096169689,3.5969696191\H,-0.3214199185,-1.6092014545,4.40583
97854\H,-0.3670304986,0.0586125718,3.8006063836\N,-0.7061271102,1.5736
68735,-0.0432867332\H,-0.8242126719,1.1113685502,-0.94466606\C,-1.3844
085594,2.8652552957,-0.1104527548\C,-0.7003291646,3.7872068207,-1.1227
893876\C,-0.8434721317,3.3104131597,-2.5546932578\O,-1.2701245465,2.22
60622379,-2.9011896411\O,-0.4209583883,4.2497691396,-3.4255052443\C,-0
.4833325815,3.8819230422,-4.8143552783\H,-2.4581540828,2.7979153675,-0
.3598625424\H,-1.3184613157,3.3347194272,0.8792535145\H,0.3717252354,3
.8522592539,-0.8974806891\H,-1.0990025652,4.8065929552,-1.059449088\H,
-1.5138889893,3.6663973824,-5.1084131761\H,-0.1004009793,4.7435637912,
-5.3616927261\H,0.1326540854,2.9993493933,-5.0058515398\O,-2.317551699
2,-2.7168058931,3.1491691714\\Version=EM64L-G09RevA.02\State=2-A\HF=-8
45.561318\S2=0.753697\S2-1=0.\S2A=0.750009\RMSD=4.467e-09\RMSF=3.309e-
06\Dipole=0.2792657,1.5102213,-0.8404422\Quadrupole=0.649025,-3.734511
1,3.085486,-3.1635614,-0.0088569,1.2679125\PG=C01 [X(C13H25N2O3)]\\@

Hostavin3052-R1

1\1\GINC-V1281\FOpt\RB3LYP\Gen\C17H32N2O5\GXG501\25-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3052x1.freq\\0,1\H,-0.3094650613,-1.0334978054,0.1113044798\C,-
0.2428134772,-0.5093023392,1.0757154731\H,0.796757241,-0.1820198321,1.
1888898004\C,-1.1633203869,0.7094257069,1.0209211469\H,-1.054014983,1.
287261433,1.948459916\C,-2.6100284095,0.2049832251,0.901529202\C,-0.57
29607643,-1.5129478048,2.2025157405\N,-2.0228575063,-1.8752009622,2.07
0209691\C,-3.0394925031,-0.7714122033,2.0208307117\H,-3.3200566031,1.0
410134074,0.8963230185\H,-2.710118159,-0.3039935225,-0.0678279722\C,-4
.3856143373,-1.3906905868,1.5931431468\H,-4.2643155346,-1.997953595,0.
6903545747\H,-5.1044835317,-0.5927583522,1.3745631356\H,-4.8173360707,
-2.0118318058,2.3828952791\C,-3.2665358188,-0.0264182178,3.3573288245\
H,-2.4529582609,0.6547875781,3.6146616034\H,-3.384720554,-0.7433149964
,4.173554344\H,-4.1836441353,0.5708215174,3.292212036\C,0.2530045542,-
2.7869192379,1.9415864022\H,1.3026582321,-2.5164233385,1.7786056857\H,
-0.1129554659,-3.3040077897,1.0483598705\H,0.2140872295,-3.4705771933,
2.791984636\C,-0.15707165,-0.9610805517,3.586119557\H,0.9365681553,-0.
9587530487,3.6607208366\H,-0.5487274792,-1.6020535899,4.3797931708\H,-
0.4961273256,0.0613731119,3.7661595402\N,-0.7224215759,1.5935820949,-0
.063068735\H,-0.8510252037,1.1255186664,-0.9599481908\C,-1.3953151361,
2.8875325795,-0.1319865968\C,-0.7035200667,3.8083595834,-1.140030327\C
,-0.8426239185,3.335352038,-2.5733899158\O,-1.2938030986,2.2634610892,

-2.9266054692\O,-0.3859781089,4.2646269998,-3.4392142005\C,-0.44415626
12,3.8993151952,-4.8284236481\H,-2.4684677811,2.8249747453,-0.38530423
42\H,-1.3311723346,3.3557750769,0.8584449017\H,0.3677178585,3.86926409
18,-0.9101577425\H,-1.098590289,4.8294810921,-1.0776232473\H,-1.476923
0788,3.710738776,-5.133320103\H,-0.0333895512,4.7507921014,-5.37162939
27\H,0.1503445763,3.0009707781,-5.0147916823\O,-2.3663785634,-2.732068
5157,3.1917295272\C,-2.9027525201,-3.9973554049,2.7852058511\H,-3.3584
594128,-3.9018470643,1.7991148516\C,-3.9214591349,-4.4090024215,3.8482
838748\H,-4.3638978609,-5.3812548201,3.6036014338\H,-3.4241079536,-4.4
894730926,4.8189625918\H,-4.7214278891,-3.6667607145,3.9168634962\C,-1
.8162654311,-5.0784700152,2.7243930548\O,-1.1089496849,-5.4032505058,3
.6530507742\O,-1.7763846816,-5.666010518,1.5088470614\C,-0.8198914483,
-6.7314330157,1.372029691\H,0.194981271,-6.353049254,1.5195402582\H,-1
.0153973604,-7.5187067411,2.1048734939\H,-0.9450745376,-7.1090284149,0
.3568948298\\Version=EM64L-G09RevA.02\State=1-A\HF=-1152.6598707\RMSD=
4.324e-09\RMSF=2.173e-06\Dipole=-0.280427,0.5743347,-1.0123676\Quadrup
ole=-3.3975696,8.0597315,-4.6621619,1.3881902,-5.2624222,0.0298092\PG=
C01 [X(C17H32N2O5)]\\@

Hostavin3052-R2

1\1\GINC-V1281\FOpt\RB3LYP\Gen\C18H34N2O5\GXG501\25-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3052x2.freq\\0,1\H,-0.323711393,-1.0248058662,0.0880610041\C,-0
.2560318748,-0.5044800388,1.054479745\H,0.7889084156,-0.1985107974,1.1
782639828\C,-1.1524333472,0.7301739097,0.9929431392\H,-1.0467474761,1.
3031235754,1.9238236875\C,-2.6021623171,0.2453938535,0.8517418414\C,-0
.6186038902,-1.5006435952,2.1774043296\N,-2.0764352191,-1.8534976588,2
.0366997213\C,-3.0716743689,-0.7261522934,1.9607179941\H,-3.3004817802
,1.0909415852,0.8361745486\H,-2.693824077,-0.2594410719,-0.1208103142\
C,-4.421444368,-1.3053473469,1.4936439097\H,-4.295005841,-1.9404941495
,0.6121982318\H,-5.0963941872,-0.4842545336,1.2255719324\H,-4.91405052
07,-1.8809543096,2.2786341237\C,-3.3176484951,0.0191476769,3.293107776
6\H,-2.4917728981,0.672258527,3.5824741182\H,-3.4901076403,-0.70016667
93,4.0968698803\H,-4.2111424306,0.6476975264,3.1976669991\C,0.20750709
,-2.7764619383,1.9300155303\H,1.273245975,-2.5227837048,1.9011641311\H
,-0.0594069912,-3.2334373138,0.9726941585\H,0.062249244,-3.5100947725,
2.7267066318\C,-0.2130206107,-0.9417075669,3.5627793012\H,0.8797765442
,-0.9414708236,3.64846846\H,-0.6178236363,-1.5702834209,4.3589992678\H
,-0.5498621752,0.0833105078,3.7296673762\N,-0.6831813315,1.6106592786,
-0.0823050098\H,-0.8117336684,1.149023513,-0.9825892517\C,-1.332683442
7,2.9165896471,-0.1524719756\C,-0.6178347901,3.8278050137,-1.153232497
7\C,-0.7564668363,3.3618623478,-2.5889521441\O,-1.2173167013,2.2960086
263,-2.9478480725\O,-0.2867502247,4.2894749183,-3.449512584\C,-0.34337
30784,3.9297783852,-4.8403201935\H,-2.4049102636,2.8735049324,-0.41348
83309\H,-1.2673923147,3.3811000118,0.8396561582\H,0.452927672,3.868066

6991,-0.9164766569\H,-0.9943932744,4.8557700033,-1.0897528512\H,-1.376
881932,3.7531355283,-5.1497661239\H,0.0783571422,4.7788787388,-5.37882
01407\H,0.2423767281,3.0259166623,-5.0276628654\O,-2.3984559866,-2.674
2689262,3.1870356232\C,-2.9357557209,-4.002508937,2.9505786921\C,-2.74
33603001,-4.5572800713,1.5420732144\C,-2.2414516275,-4.8924756718,4.00
09899145\H,-2.3275946801,-4.4390290176,4.9919785108\H,-2.6995402495,-5
.8875271013,4.0273107422\H,-1.1819674371,-5.005655656,3.7543336002\H,-
1.6822699334,-4.6871263488,1.3254177267\H,-3.2416464639,-5.5273309438,
1.4774334811\H,-3.1735075308,-3.8998125418,0.7866458198\C,-4.440951943
4,-4.0238675902,3.3088248444\O,-5.2829604698,-4.6751533335,2.728194553
6\O,-4.7057051268,-3.2934835444,4.4138633244\C,-6.0711896984,-3.329911
2417,4.8591216937\H,-6.3776207182,-4.3563853566,5.0776676608\H,-6.1000
455214,-2.7183483261,5.7613725247\H,-6.736218007,-2.917766978,4.095174
1048\\Version=EM64L-G09RevA.02\State=1-A\HF=-1191.9689305\RMSD=8.985e-
09\RMSF=3.003e-06\Dipole=0.2117591,0.9770603,0.0312958\Quadrupole=-4.6
881577,-0.7836608,5.4718185,-3.5627046,-6.9220379,-9.0454068\PG=C01 [X
(C18H34N2O5)]\\@

Hostavin3052-R3

1\1\GINC-V1282\FOpt\RB3LYP\Gen\C17H32N2O5\GXG501\25-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3052x3.freq\\0,1\H,-0.3814421576,-1.1514128084,0.1805589669\C,-
0.2937422646,-0.6122740545,1.1347611705\H,0.7558623062,-0.3146357648,1
.2360727019\C,-1.1772713873,0.6327129097,1.0598484884\H,-1.0438378806,
1.2277503692,1.9733357551\C,-2.6396882958,0.1700699133,0.9609566246\C,
-0.6457677511,-1.5864172433,2.2814377526\N,-2.1094560792,-1.9018210028
,2.1672953315\C,-3.0895004187,-0.7640649793,2.1073767483\H,-3.32389620
93,1.0269949396,0.9400637553\H,-2.7627833689,-0.3594776731,0.005520034
5\C,-4.4621579667,-1.3469393789,1.7134596096\H,-4.3752662462,-1.986000
6247,0.8290921667\H,-5.1536040972,-0.529705461,1.478835371\H,-4.908529
379,-1.9268086708,2.5269001791\C,-3.2732793379,0.0201497238,3.42809501
08\H,-2.4353673863,0.6808521805,3.6587629992\H,-3.4061302983,-0.670337
3172,4.2646118706\H,-4.171013558,0.6453316073,3.3577303477\C,0.1390358
544,-2.8879193172,2.0337772941\H,1.2050673692,-2.6551985742,1.92837201
19\H,-0.2041868662,-3.3707553441,1.1132247009\H,0.0169686326,-3.592319
1222,2.857831382\C,-0.2018056832,-1.0215111879,3.6513756733\H,0.892009
6177,-1.0477917173,3.7155500043\H,-0.6030536559,-1.6338270872,4.462714
6496\H,-0.5106690108,0.012968041,3.8148494512\N,-0.7168291678,1.478128
14,-0.0463007422\H,-0.8688533419,0.9959404103,-0.9319913194\C,-1.34658
65042,2.7923608159,-0.1377821785\C,-0.6375081957,3.6649825303,-1.17632
42041\C,-0.8111780166,3.1625164366,-2.5958810728\O,-1.2964654045,2.095
1812124,-2.9161896431\O,-0.3425709142,4.0579007704,-3.4901678239\C,-0.
4311221007,3.6612695852,-4.869351606\H,-2.4244358325,2.7601631466,-0.3
76363562\H,-1.253738879,3.2814444735,0.8402542149\H,0.4381229822,3.694
8437601,-0.9611583074\H,-0.9971702364,4.7000307189,-1.133626947\H,-1.4

730228339,3.4939622627,-5.1548461626\H,-0.0054576357,4.4879953183,-5.4
386526683\H,0.1359692427,2.7427449957,-5.0421322906\O,-2.4721953457,-2
.7168899136,3.3205636706\C,-3.0585729038,-3.9374424571,2.9743569445\C,
-3.9546577243,-4.369342674,4.1218820967\H,-3.5854358616,-3.870507795,2
.0246757337\H,-4.7590421442,-3.6431935145,4.2713989506\H,-4.3959642104
,-5.3437877418,3.8959878229\H,-3.3698632264,-4.4419946724,5.0439402773
\O,-2.0044952326,-4.9319575343,2.8137314709\C,-2.2476097605,-5.9539519
658,1.9608824444\C,-1.038880535,-6.8540361202,1.8446022072\O,-3.298211
5613,-6.1167310441,1.3768055904\H,-0.7275952214,-7.2010195996,2.835051
0505\H,-1.2805178012,-7.706076051,1.2082029112\H,-0.199173115,-6.29707
3849,1.4152860906\\Version=EM64L-G09RevA.02\State=1-A\HF=-1152.678558\
RMSD=5.820e-09\RMSF=3.343e-06\Dipole=0.4413835,1.0451672,-0.069654\Qua
drupole=-4.8450531,1.5730581,3.2719951,-6.3313896,-4.240499,-9.1715232
\PG=C01 [X(C17H32N2O5)]\\@

•O-Hostavin3055

1\1\GINC-V1270\FOpt\UB3LYP\Gen\C13H21N2O3(2)\GXG501\23-Jul-2010\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\h3055o.freq\\0,2\H,-0.3103569573,0.227356881,-0.0811580876\C,
-0.2064760991,0.1973800696,1.0080416424\H,0.8600267625,0.3057946851,1.
2388688097\C,-0.9990689271,1.3654910415,1.6041931544\H,-0.8813039457,1
.3865288059,2.690873502\C,-2.4783334339,1.2130702741,1.234588603\C,-0.
677544025,-1.1733787881,1.5358412334\N,-2.1775777369,-1.2506185681,1.5
147575527\C,-3.0967422642,-0.0918123012,1.777086099\H,-3.0567335525,2.
0568785981,1.6294361952\H,-2.5678791283,1.236624675,0.1439563779\C,-4.
4085142054,-0.3774677441,1.0270544765\H,-4.2212682286,-0.5007591655,-0
.0446415253\H,-5.1012808211,0.460119457,1.1642288507\H,-4.874035754,-1
.2905253168,1.4022314813\C,-3.3846593205,-0.004366851,3.2914032268\H,-
2.509350879,0.307294823,3.8694385503\H,-3.7077706592,-0.9833631617,3.6
559659609\H,-4.1847384999,0.7204763784,3.4791174823\C,-0.1555445583,-2
.27886683,0.6029403886\H,0.9385820746,-2.240151906,0.5619190223\H,-0.5
45639962,-2.1440429034,-0.4111808329\H,-0.4644608393,-3.2619387813,0.9
624996378\C,-0.1752328149,-1.4392387654,2.9713548815\H,0.9139904156,-1
.5590452419,2.9706703921\H,-0.6276439426,-2.3604332751,3.3488014357\H,
-0.4213091887,-0.6262483486,3.6612209364\N,-0.4600275415,2.667047814,1
.1746077516\C,-0.3906118068,3.1172462505,-0.1452799275\C,0.2330142074,
4.5115357946,-0.1392332247\C,0.5193490595,4.820982556,1.3362169222\C,0
.0447294444,3.5894457168,2.1001572824\O,0.0850377645,3.410668334,3.299
2734381\O,-0.7657425572,2.4970875211,-1.1200421662\H,1.1301072644,4.49
58293516,-0.7658445664\H,1.5800542919,4.981251403,1.5531098009\H,-0.01
82580292,5.6965282502,1.7133127186\H,-0.4685625295,5.2102260387,-0.605
3831245\O,-2.6761698098,-2.414589042,1.7333124982\\Version=EM64L-G09Re
vA.02\State=2-A\HF=-843.1881877\S2=0.753685\S2-1=0.\S2A=0.750009\RMSD=
4.407e-09\RMSF=1.602e-05\Dipole=0.6400259,1.4698825,-0.1719929\Quadrup
ole=5.0802185,2.3229744,-7.4031929,-2.1955012,-3.0998449,-3.8509632\PG

=C01 [X(C13H21N2O3)]\\@

Hostavin3055-R1

1\1\GINC-V1268\FOpt\RB3LYP\Gen\C17H28N2O5\GXG501\24-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3055x1.freq\\0,1\H,0.0396708402,-0.2112676161,0.1236992061\C,-0
.0369019748,-0.1103081601,1.2107510994\H,0.98043535,-0.1250974653,1.61
99793136\C,-0.7170969603,1.2212649147,1.5340293629\H,-0.733107726,1.38
23871002,2.6146218393\C,-2.1438930479,1.2044351191,0.9823712671\C,-0.8
023537538,-1.3271986504,1.7810000604\N,-2.2183143054,-1.2328545542,1.2
924685282\C,-2.9855936533,0.0341643993,1.5426729767\H,-2.6568155109,2.
1428585992,1.2257580885\H,-2.0961846721,1.1236641751,-0.1079285715\C,-
4.2776542099,-0.0241403478,0.7029377149\H,-4.0533044196,-0.2763422741,
-0.3382686319\H,-4.7716422946,0.9540137183,0.7199561613\H,-4.986566899
5,-0.7546045614,1.1017334438\C,-3.387777108,0.2816682281,3.0153417419\
H,-2.5557831342,0.6042606214,3.6445349783\H,-3.8115111657,-0.628155429
8,3.4471777916\H,-4.1507501256,1.0674822699,3.0589051466\C,-0.17472000
4,-2.5878366253,1.157270155\H,0.9138735427,-2.556731398,1.2820003212\H
,-0.3985784183,-2.636911474,0.0866735631\H,-0.5388356315,-3.4953525669
,1.6424319495\C,-0.6403323478,-1.4304177169,3.3154482246\H,0.385563608
4,-1.7359583828,3.5513420275\H,-1.3182693943,-2.1896166719,3.712779081
5\H,-0.8269080968,-0.4909020343,3.840127662\N,0.0541524783,2.371988323
4,1.0289469857\C,0.3535093839,2.6206888317,-0.3117370643\C,1.168270082
3,3.9111125038,-0.3860333834\C,1.3070671456,4.3862842265,1.0659481247\
C,0.5657302673,3.3441875275,1.8971750759\O,0.427801066,3.3353290444,3.
1025352271\O,0.0190069474,1.9250203253,-1.2496509268\H,2.1256277799,3.
6924622601,-0.8691488316\H,2.3435714128,4.4394929518,1.4133519615\H,0.
8584466163,5.3671479331,1.2517009679\H,0.6408983038,4.6206682569,-1.03
11112243\O,-2.9642975491,-2.3171800057,1.9033405918\C,-3.6031724752,-3
.1687734848,0.9421746571\C,-4.8982802496,-3.6654489565,1.5847040313\C,
-2.7390817691,-4.3908567941,0.6066151005\O,-2.3337262543,-5.1959964168
,1.416375598\O,-2.5243325065,-4.4881859785,-0.7226581875\C,-1.76647540
28,-5.6368931242,-1.141770936\H,-2.2635300148,-6.5588557894,-0.8288112
751\H,-1.7172582053,-5.574289468,-2.229072649\H,-0.7632127594,-5.60941
65828,-0.7087208322\H,-5.4341862216,-4.3362495746,0.9038392051\H,-4.66
43136117,-4.2160566732,2.5001894041\H,-5.5495200293,-2.8223615085,1.83
10760948\H,-3.7909098898,-2.6090259755,0.0254695658\\Version=EM64L-G09
RevA.02\State=1-A\HF=-1150.2872403\RMSD=3.476e-09\RMSF=5.483e-06\Dipol
e=0.1688249,0.688361,-0.9100784\Quadrupole=5.9683357,5.7806055,-11.748
9412,4.6528947,-1.9443612,2.2434073\PG=C01 [X(C17H28N2O5)]\\@

Hostavin3055-R2

1\1\GINC-V1279\FOpt\RB3LYP\Gen\C18H30N2O5\GXG501\25-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3055x2.freq\\0,1\H,-0.2062148878,0.2660168286,-0.2385210347\C,-

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0.0285616558,0.0996694451,0.8284028251\H,1.0546346402,0.1378428235,0.9
959197729\C,-0.7271475247,1.2056967023,1.6188728269\H,-0.5043561374,1.
1081026049,2.6840616101\C,-2.2338249138,1.1058158911,1.3826583484\C,-0
.525585223,-1.3123588425,1.2149436221\N,-2.0255245116,-1.3335014728,1.
0716695082\C,-2.8199219912,-0.269495539,1.7830848893\H,-2.7601125101,1
.8780877079,1.9564909696\H,-2.4334662105,1.286842567,0.3218972639\C,-4
.2603032051,-0.2946919651,1.2355958393\H,-4.2674395515,-0.3027031226,0
.1420941404\H,-4.7932352969,0.602072971,1.5721868384\H,-4.8199648289,-
1.1557087663,1.6028072179\C,-2.8970232631,-0.4269606174,3.3190070434\H
,-1.9671110822,-0.1709736221,3.8309304835\H,-3.1621999173,-1.455320163
8,3.5740908806\H,-3.6763506918,0.2360758492,3.7128080603\C,0.066586398
9,-2.2856833776,0.1792104471\H,1.1588398793,-2.1963180855,0.1740005142
\H,-0.2994090399,-2.054846197,-0.8251090349\H,-0.179966959,-3.32252197
88,0.4193584955\C,0.0050307388,-1.7276658982,2.6085028954\H,1.08278782
94,-1.916921625,2.5451581973\H,-0.4833719524,-2.6465444538,2.939827373
1\H,-0.143343687,-0.9654059723,3.3759287924\N,-0.203344209,2.542044571
4,1.2812394582\C,-0.2475156289,3.1338627979,0.0175431166\C,0.403376810
9,4.5127447225,0.114713374\C,0.8302291937,4.656285694,1.5811737203\C,0
.4039351767,3.3524660837,2.2481370049\O,0.5532221002,3.0452494421,3.41
2374762\O,-0.7233559367,2.63058472,-0.9803522511\H,1.2387176914,4.5551
525361,-0.5910848496\H,1.9092463862,4.7822211808,1.7142384988\H,0.3462
50549,5.4899112349,2.099561663\H,-0.3231602682,5.2655783832,-0.2063358
685\O,-2.4496586726,-2.6270022214,1.5642258194\C,-3.2105050814,-3.4839
899808,0.6699879744\C,-3.1507172395,-3.120224246,-0.8106996072\C,-4.68
75120165,-3.5291396199,1.1291131807\O,-5.6420578555,-3.6073032007,0.38
57033638\O,-4.7952427237,-3.5619720931,2.4750285743\C,-6.1347534976,-3
.690500465,2.9794662472\H,-6.6013384266,-4.6047643834,2.6031397302\H,-
6.0352234294,-3.7265012303,4.0646271105\H,-6.7432264284,-2.8333556673,
2.678269267\H,-3.8116490112,-3.7928170097,-1.3621761556\H,-3.477437054
9,-2.0959107372,-0.9896158214\H,-2.134125856,-3.2310222195,-1.19028619
91\C,-2.6493372065,-4.8977086597,0.9217781209\H,-1.631492286,-4.972598
6408,0.5286763254\H,-3.2689276426,-5.6522707865,0.4245165415\H,-2.6312
079089,-5.1084535265,1.9943129942\\Version=EM64L-G09RevA.02\State=1-A\
HF=-1189.5963549\RMSD=6.300e-09\RMSF=5.256e-06\Dipole=0.4415123,0.5407
504,0.3091321\Quadrupole=0.2990716,12.128272,-12.4273436,3.2019656,-11
.0194593,-5.0161423\PG=C01 [X(C18H30N2O5)]\\@
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Hostavin3055-R3

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1\1\GINC-V1279\FOpt\RB3LYP\Gen\C17H28N2O5\GXG501\25-Jul-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3055x3.freq\\0,1\H,0.2119406897,0.2294326181,0.1889291104\C,0.1
207878873,0.226994854,1.2793645987\H,1.1331874618,0.2671447465,1.69886
02293\C,-0.6778415376,1.4601460901,1.7063568838\H,-0.7133783325,1.5270
8723,2.7964149149\C,-2.0948066442,1.3629826025,1.1374788651\C,-0.53358
84372,-1.1001948021,1.7306747395\N,-1.95246779,-1.0875817132,1.2377783
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809\C,-2.8300610105,0.0809642734,1.5919270352\H,-2.6908418905,2.228558
5424,1.450973387\H,-2.0359181242,1.3769470167,0.044848209\C,-4.1147830
892,-0.0217378934,0.7448401097\H,-3.8741714138,-0.1727838509,-0.312000
7546\H,-4.689575592,0.9067280066,0.836686228\H,-4.759902169,-0.8377643
214,1.0829873103\C,-3.2492815128,0.1684211535,3.0780652494\H,-2.448308
9012,0.5078958167,3.7376936373\H,-3.5946360158,-0.8059400558,3.4318777
301\H,-4.0766447161,0.8798920337,3.1807307963\C,0.209783227,-2.2362437
191,1.004589742\H,1.2842641214,-2.155801481,1.2064895486\H,0.051985948
9,-2.1654936251,-0.0760407716\H,-0.1339447275,-3.2154849347,1.34022595
21\C,-0.3684894104,-1.3216637333,3.2526788686\H,0.6802749945,-1.551500
8459,3.4726663106\H,-0.9755061347,-2.1695526129,3.5789668642\H,-0.6414
180766,-0.4519068339,3.8539740672\N,-0.0104759719,2.7132081866,1.30970
32901\C,0.2703775116,3.1009419758,-0.0020266187\C,0.9653740548,4.46076
4881,0.0425067699\C,1.0560021021,4.8205282344,1.5311296738\C,0.4090885
339,3.6490983727,2.2629148128\O,0.2689351352,3.5241393238,3.4616163103
\O,0.0031750115,2.4598826746,-0.998415408\H,1.9401052054,4.3711627284,
-0.446963359\H,2.0823439356,4.9366655963,1.8930498008\H,0.5200568181,5
.737745394,1.7944427246\H,0.378121523,5.1727152464,-0.5456708222\O,-2.
6035120988,-2.2807480664,1.7603772078\C,-3.1722861537,-3.0842419154,0.
7660362121\C,-4.3145889343,-3.8635350555,1.3934936198\H,-4.7542433245,
-4.5321065599,0.6486324899\H,-3.943472526,-4.4545836169,2.2363181873\H
,-5.088457547,-3.180573715,1.7559844579\H,-3.4815471446,-2.4931685885,
-0.0935641436\O,-2.1665618034,-4.029585174,0.3006554772\C,-2.290564659
8,-4.482111991,-0.9694842245\O,-3.2103563112,-4.1939261578,-1.70546097
49\C,-1.1358971615,-5.3874666009,-1.3312941471\H,-1.2952810225,-5.7975
946768,-2.3291344461\H,-0.1979451718,-4.8222909627,-1.309010313\H,-1.0
459183192,-6.1982127874,-0.6013524196\\Version=EM64L-G09RevA.02\State=
1-A\HF=-1150.3057807\RMSD=3.754e-09\RMSF=3.546e-06\Dipole=0.6393869,0.
6344331,0.3109864\Quadrupole=3.6252715,12.9136319,-16.5389034,0.627476
4,-6.2456231,-6.2849312\PG=C01 [X(C17H28N2O5)]\\@

- **Hostavin3050_1**

1\1\GINC-X138\FOpt\UB3LYP\Gen\C14H25N2O2(2)\GXG501\01-Sep-2010\0\\#B3L
YP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=134
2177280\\h3050rr.freq\\0,2\H,-0.6680522849,-1.9927996855,-0.2765438709
\C,-0.9092716906,-1.1951522502,0.4367168583\H,-0.1967567122,-1.2845374
612,1.2654714357\C,-0.677466646,0.1257021012,-0.3068148536\C,-1.746990
2535,0.273694154,-1.3957126068\C,-2.3523857055,-1.3977128469,0.9667620
496\N,-3.4228814016,-0.9696061545,0.0702053075\C,-3.2062230718,0.09951
83729,-0.9009520087\H,-1.63987679,1.2459763504,-1.8913887342\H,-1.5237
695122,-0.4924560373,-2.1482701261\C,-4.1027414963,-0.2409656369,-2.11
11511651\H,-3.8062779576,-1.1973389978,-2.5554662739\H,-4.0250844763,0
.5356131567,-2.8818385137\H,-5.1476513028,-0.3223365212,-1.7961308331\
C,-3.7364622762,1.4130211358,-0.2618387075\H,-3.0839453909,1.763812147
3,0.5392162081\H,-4.7427223153,1.2544222761,0.137936814\H,-3.786561866

,2.1955061352,-1.0289001269\C,-2.583652732,-2.9046384593,1.2115882271\
H,-1.8355291835,-3.3036697591,1.9073956543\H,-2.5132899783,-3.46451518
6,0.272682178\H,-3.5804308667,-3.0704300133,1.631876396\C,-2.558597302
2,-0.6524748543,2.3147391047\H,-1.9088589041,-1.0971525169,3.078463063
\H,-3.5978865413,-0.7531816152,2.6422587893\H,-2.3100923237,0.40674033
,2.2321037944\O,-0.6655084249,1.25399421,0.5921871154\C,0.5896046941,1
.9492042114,0.5750475232\N,1.3888667619,1.1964562287,-0.3938265086\C,0
.7183959867,0.1398564084,-0.9338523487\O,1.1444849339,-0.6513804982,-1
.762795617\C,0.3442780953,3.3919791157,0.1173033123\C,1.1972823725,1.8
980730297,1.9817923061\C,2.7527364961,1.5201321077,-0.7588355457\H,3.0
678726594,0.7791347609,-1.4965803296\H,2.8224206614,2.5203725907,-1.20
21849674\H,1.270963099,3.9762307091,0.1149969851\H,-0.0826283899,3.400
4483845,-0.8898379975\H,-0.3615168752,3.8752449782,0.7997052028\H,2.14
69311369,2.4421165512,2.029674494\H,1.3680675247,0.859818552,2.2809634
601\H,0.5052067972,2.3573497409,2.6941556243\H,3.4221155428,1.47086155
88,0.108083396\\Version=EM64L-G09RevA.02\State=2-A\HF=-808.4722398\S2=
0.753653\S2-1=0.\S2A=0.75001\RMSD=4.682e-09\RMSF=6.307e-06\Dipole=0.74
10828,1.236927,0.654218\Quadrupole=-0.0510365,1.5645416,-1.5135051,3.9
629813,4.4202862,-2.6825707\PG=C01 [X(C14H25N2O2)]\\@

•O-Hostavin3050

1\1\GINC-X135\FOpt\UB3LYP\Gen\C14H25N2O3(2)\GXG501\01-Sep-2010\0\\#B3L
YP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=134
2177280\\h3050oo.freq\\0,2\H,-0.5660668371,-1.9091258628,-0.2922762626
\C,-0.7600145528,-1.1064083396,0.4289264873\H,-0.0392166073,-1.2305794
697,1.2454577874\C,-0.4803293888,0.2079546539,-0.3117347848\C,-1.53561
31253,0.4012056977,-1.4088096625\C,-2.1828686977,-1.2657232101,1.00345
7185\N,-3.2006580827,-0.8093991207,0.0018120273\C,-3.0062277616,0.3346
973743,-0.9474590221\H,-1.3722764109,1.3607033821,-1.9131629525\H,-1.3
50388441,-0.3844987433,-2.1507363594\C,-3.8950468503,0.0581391681,-2.1
732494575\H,-3.6362609707,-0.9020155932,-2.6318992326\H,-3.7508177622,
0.8485601426,-2.9181763432\H,-4.9471882828,0.0283268347,-1.8849120192\
C,-3.4670232904,1.6448232932,-0.2728951837\H,-2.7978630617,1.946042633
7,0.5347336469\H,-4.4770472352,1.5095735156,0.1244480617\H,-3.48953385
97,2.4542658956,-1.012131999\C,-2.445156249,-2.760131017,1.2622936871\
H,-1.6933210145,-3.1507307698,1.9570307588\H,-2.3862311796,-3.33189832
24,0.3301792922\H,-3.4374402024,-2.9062453091,1.6924690474\C,-2.372457
1885,-0.4826168509,2.3204991522\H,-1.750782939,-0.9253701065,3.1076870
399\H,-3.4198872047,-0.5450899777,2.6292185394\H,-2.0876026461,0.56571
18529,2.2173427568\O,-0.4174587471,1.3328237772,0.5845925869\C,0.86832
28465,1.9726612477,0.5664115431\N,1.6320926403,1.1841240322,-0.4028304
234\C,0.9156628447,0.158542577,-0.9415838932\O,1.3027410436,-0.6523985
491,-1.7701627019\C,0.6859410463,3.4241523233,0.108168708\C,1.47325911
7,1.8949539543,1.972774397\C,3.0092719507,1.446795284,-0.7689302039\H,
3.2911848581,0.6926488905,-1.5066834345\H,3.122135163,2.4429567797,-1.

2125098623\H,1.6373268771,3.9670808025,0.1062494171\H,0.2602751705,3.4
51734767,-0.8991602859\H,0.0019042863,3.9378750611,0.7903649333\H,2.44
53274301,2.3977141163,2.0200313834\H,1.5996490916,0.8505205674,2.27250
88121\H,0.8019027721,2.3837990291,2.6851789096\O,-4.4213755219,-1.1070
000524,0.2727429993\H,3.675571317,1.3682684795,0.0978565693\\Version=E
M64L-G09RevA.02\State=2-A\HF=-883.6848718\S2=0.753682\S2-1=0.\S2A=0.75
0009\RMSD=3.092e-09\RMSF=1.465e-05\Dipole=1.436412,1.4016719,0.5403539
\Quadrupole=-3.1321253,2.7487232,0.3834021,2.4039926,5.4136698,-2.8926
093\PG=C01 [X(C14H25N2O3)]\\@

Hostavin3050-R1

1\1\GINC-V1435\FOpt\RB3LYP\Gen\C18H32N2O5\GXG501\31-Aug-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3050x1.freq\\0,1\H,-0.1133478865,1.2991435894,-0.2983742055\C,-
0.1824377079,0.4764585684,0.4230062477\H,-0.7772076264,0.8361836436,1.
2706477126\C,-0.9306535879,-0.6568149369,-0.2879006766\C,-0.0262154503
,-1.2428305457,-1.3771773996\C,1.2373892483,0.1355817691,0.9320677458\
N,1.9902984765,-0.4560439125,-0.2212422391\C,1.3991948653,-1.640290569
3,-0.9281259507\H,-0.5077816684,-2.1203516261,-1.824224071\H,0.0462741
672,-0.4773757425,-2.1585735107\C,2.2119977546,-1.870798233,-2.2193697
884\H,2.3148035354,-0.9413594498,-2.7886463332\H,1.697928233,-2.604032
4497,-2.851329077\H,3.2073686243,-2.2679826915,-2.0031438207\C,1.40204
71945,-2.9615338886,-0.1247916551\H,0.6423222494,-2.9822212177,0.65504
99336\H,2.3849941065,-3.1241411412,0.3243763507\H,1.1966331752,-3.7981
452523,-0.8036394945\C,1.9111285834,1.474483629,1.2909382766\H,1.25093
66956,2.0546211459,1.9462066725\H,2.1045152484,2.0625387127,0.38765881
35\H,2.8506089446,1.3151097751,1.8235446594\C,1.1999283303,-0.72932178
02,2.2132866897\H,0.8459982442,-0.1146788226,3.0498493593\H,2.20670200
78,-1.0783757054,2.456070683\H,0.5294840589,-1.583623327,2.1314611445\
O,-1.3923609716,-1.6662716718,0.6320000735\C,-2.8225605279,-1.77623555
53,0.6483048997\N,-3.2563787916,-0.7919584765,-0.3450488946\C,-2.21985
45144,-0.1166632133,-0.9161099823\O,-2.2962193252,0.7565343476,-1.7683
514883\C,-3.2058378036,-3.2048108579,0.2450459254\C,-3.3268387218,-1.4
314089098,2.0549256956\C,-4.6381590063,-0.5365021218,-0.6964039474\H,-
4.6325481114,0.2468445635,-1.4572925557\H,-5.1192887871,-1.432222209,-
1.1064192465\H,-4.2908650857,-3.353235113,0.2725549835\H,-2.8435123715
,-3.4215073744,-0.7641417044\H,-2.7467882367,-3.9140734456,0.940371939
2\H,-4.4153290593,-1.5317611318,2.1278208965\H,-3.0474811651,-0.406332
9251,2.3153869482\H,-2.8720383568,-2.1118225386,2.7811688122\O,3.29838
02539,-0.8525063362,0.2679894976\C,4.3746300793,-0.2510830695,-0.46342
02517\H,4.041012367,-0.008694917,-1.4728384416\C,5.5231532735,-1.25995
00005,-0.4677744221\H,5.2117157465,-2.1895213653,-0.9519927724\H,5.823
4681079,-1.4759806154,0.5613732348\H,6.3892485625,-0.8567724105,-1.004
5839626\C,4.8713621882,1.0329597926,0.2130873754\O,5.2877634629,1.1016
903743,1.3489346728\O,4.8337675478,2.0809650844,-0.6377877398\C,5.3314

141198,3.3221507914,-0.1079228646\H,4.7240799036,3.6438742432,0.742077
5301\H,6.3687941701,3.2109854054,0.2185395041\H,5.2584668354,4.0398055
037,-0.9254232545\H,-5.2146895984,-0.1914923889,0.169968473\\Version=E
M64L-G09RevA.02\State=1-A\HF=-1190.7837077\RMSD=9.208e-09\RMSF=4.727e-
06\Dipole=-0.9216604,-0.4756054,-0.0223186\Quadrupole=8.8328454,0.7392
39,-9.5720844,9.7763265,-11.722724,2.967217\PG=C01 [X(C18H32N2O5)]\\@

Hostavin3050-R2

1\1\GINC-V1383\FOpt\RB3LYP\Gen\C19H34N2O5\GXG501\31-Aug-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3050x2.freq\\0,1\H,0.7055072862,-1.6612861369,-0.1599005927\C,0
.6331836524,-0.8355050935,0.5575514049\H,1.3539379376,-1.0371888724,1.
3585467981\C,1.0458981718,0.4277191059,-0.2032658521\C,-0.0471870689,0
.7650868156,-1.2209296043\C,-0.7862396185,-0.8210164792,1.169795397\N,
-1.7537793041,-0.4417366379,0.0809855077\C,-1.4929849269,0.8332601629,
-0.6738265984\H,0.1825636131,1.7210062128,-1.7057523776\H,0.0048861755
,-0.0110538941,-1.9935602957\C,-2.4088901151,0.8547273943,-1.914345992
9\H,-2.3744409861,-0.0970560513,-2.4520831674\H,-2.0760156697,1.643489
2227,-2.5989841991\H,-3.4427754454,1.078325851,-1.648545151\C,-1.75004
98727,2.1345880746,0.1199385556\H,-0.9781009401,2.3406657624,0.8598414
944\H,-2.7232966842,2.0802454696,0.6132217739\H,-1.7678326666,2.981865
1182,-0.5766754271\C,-1.0872627034,-2.2722718813,1.590777545\H,-0.3136
797449,-2.6207230045,2.2845719289\H,-1.0923686584,-2.9389112389,0.7237
757364\H,-2.0491675142,-2.3461685011,2.103526734\C,-0.8479550641,0.058
8333943,2.4416028771\H,-0.2947819944,-0.4368277742,3.2485465408\H,-1.8
843041141,0.1785351622,2.7655050814\H,-0.3997353792,1.0406247845,2.298
5669661\O,1.3251124761,1.5311865736,0.6812893283\C,2.6804440747,1.9882
428795,0.5722011694\N,3.2619247995,1.1077993635,-0.4427764897\C,2.3765
908264,0.1914288021,-0.9255313994\O,2.5952186069,-0.6610453183,-1.7740
712046\C,2.668022522,3.4536402991,0.1210558178\C,3.3644094805,1.822120
7891,1.9344906178\C,4.6333976452,1.1810116858,-0.9029991084\H,4.757741
7193,0.3994306326,-1.6555101156\H,4.8521653559,2.1547481131,-1.3568095
904\H,3.6821561774,3.8623299732,0.0530858766\H,2.183388882,3.543560584
3,-0.8555264698\H,2.1068660578,4.0519627205,0.8451896244\H,4.396988796
9,2.1874806122,1.9134860063\H,3.3671621307,0.7685872651,2.2290087232\H
,2.8155018955,2.3937384682,2.6889559444\O,-3.0487704019,-0.3381919111,
0.7212148665\C,-4.1304232159,-1.1643481179,0.2124315634\C,-3.714195434
6,-2.3406541847,-0.6660080444\C,-4.8728863334,-1.6454086644,1.47510780
23\C,-5.1386223389,-0.2797009462,-0.5593400919\O,-5.7472956756,-0.6237
007896,-1.5499315223\H,-3.1268687135,-3.0574275657,-0.0906350467\H,-4.
2528596906,-2.3590741613,2.0250215625\H,-5.8130044873,-2.1393330329,1.
2050930676\H,-5.0959320339,-0.7954444775,2.1253175656\H,-4.6147770524,
-2.8352339174,-1.0371242522\H,-3.1233783129,-2.0166744768,-1.522729995
8\O,-5.3357095638,0.9083772105,0.0522546787\C,-6.3212863742,1.75604104
43,-0.5596251168\H,-6.0241594586,2.01819661,-1.578796607\H,-7.29258620

27,1.255220679,-0.5926819819\H,-6.3680098154,2.6475724162,0.066356159\
H,5.3407672936,1.0065698761,-0.0837414198\\Version=EM64L-G09RevA.02\St
ate=1-A\HF=-1230.0926607\RMSD=8.002e-09\RMSF=6.585e-06\Dipole=0.784598
1,1.2485162,0.9749512\Quadrupole=8.0043151,0.4730372,-8.4773523,4.2208
676,0.7902925,-6.286784\PG=C01 [X(C19H34N2O5)]\\@

Hostavin3050-R3

1\1\GINC-V1311\FOpt\RB3LYP\Gen\C18H32N2O5\GXG501\31-Aug-2010\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\h3050x3.freq\\0,1\H,-0.116211572,1.3136692513,-0.1455802156\C,-0
.2209348207,0.454973255,0.5276942602\H,-0.8466257277,0.7757357079,1.36
85818397\C,-0.9495773429,-0.6301716708,-0.2726450956\C,-0.0058342542,-
1.167725062,-1.3541517964\C,1.1747969188,0.0747153451,1.0754401383\N,1
.9676265918,-0.4674624031,-0.0769391303\C,1.3932813115,-1.6089380788,-
0.8661704054\H,-0.4768918522,-2.0131574885,-1.8689015983\H,0.109503037
3,-0.362321342,-2.088793751\C,2.2608579251,-1.7885606201,-2.1298330776
\H,2.4088689799,-0.8338542522,-2.6443084832\H,1.7624662208,-2.47701300
37,-2.8217011111\H,3.237648058,-2.2192709819,-1.8913375597\C,1.3431604
277,-2.9684866151,-0.1310796214\H,0.547883047,-3.0188512248,0.61073968
69\H,2.3020495278,-3.1705838843,0.3527711116\H,1.1589435868,-3.7653874
464,-0.8616411072\C,1.8401560959,1.387912284,1.5298596489\H,1.18183455
35,1.903415084,2.2389577236\H,2.0136843862,2.0468956077,0.6733392972\H
,2.7965364193,1.1995695765,2.0194617493\C,1.0757687067,-0.8563009441,2
.3065196166\H,0.6897159444,-0.2831861707,3.1580075069\H,2.0669478441,-
1.2300382124,2.5754228222\H,0.4028715673,-1.6982438042,2.1508053993\O,
-1.4589493423,-1.6804259996,0.5732496262\C,-2.8888704361,-1.7844083096
,0.5128965099\N,-3.2714824468,-0.7393705958,-0.4382838002\C,-2.2061704
138,-0.0422876523,-0.9238138624\O,-2.2382788569,0.8789584879,-1.726561
1291\C,-3.2558977802,-3.1839486835,0.0056983088\C,-3.4590808678,-1.522
6791238,1.9120340696\C,-4.6343267448,-0.453673053,-0.8376557797\H,-4.5
895576526,0.3723921169,-1.5505316289\H,-5.099937117,-1.3204600099,-1.3
211058961\H,-4.3413741864,-3.3274120717,-0.0287753034\H,-2.8454888731,
-3.3417802595,-0.9959614747\H,-2.8336633294,-3.9366263523,0.6783636362
\H,-4.5500695059,-1.6208932425,1.9264323158\H,-3.1895159292,-0.5168752
418,2.2471807139\H,-3.0419666288,-2.248642446,2.6164923862\O,3.2487095
556,-0.9176260789,0.4512688856\C,4.3473950247,-0.3330985537,-0.1858446
462\H,4.1192014472,-0.0775853079,-1.2186135196\C,5.5232976395,-1.28512
37049,-0.0554010137\H,5.721580883,-1.4891103854,1.0012472522\H,5.30616
61376,-2.2302361115,-0.5616542309\H,6.4104700437,-0.8363397685,-0.5100
224061\O,4.6784056217,0.9084053923,0.5023872344\C,5.2829207464,1.87375
18267,-0.2286185498\O,5.6118114252,1.7416159631,-1.3885981134\C,5.4891
083449,3.1223431053,0.5977991823\H,6.0350810543,2.8840165271,1.5161326
821\H,4.5197588563,3.5382609722,0.8928609234\H,6.0427819007,3.85750775
71,0.0127149425\H,-5.2488231498,-0.1552681032,0.0198118371\\Version=EM
64L-G09RevA.02\State=1-A\HF=-1190.8023181\RMSD=7.476e-09\RMSF=6.643e-0

6\Dipole=-1.2268064,-0.935598,1.0675216\Quadrupole=8.3734671,-1.144452
3,-7.2290148,5.502463,1.7219463,8.1278107\PG=C01 [X(C18H32N2O5)]\\@

$(CH_3)_2NC(O)CH_3$

1\1\GINC-V1367\FOpt\RB3LYP\Gen\C4H9N1O1\GXG501\30-Jun-2011\0\\#B3LYP/g
en 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=2684354
56\\tempac_core.freq\\0,1\N,0.6543160426,0.0312301013,0.3637619141\C,-
0.0922579422,0.0074269784,1.6076871893\H,0.4167527603,-0.6193658998,2.
3537609191\H,-0.2027006588,1.0079255599,2.0228759607\H,-1.0965075494,-
0.410917849,1.4493373034\C,0.8533849814,-1.2630388035,-0.2700728738\H,
1.404348555,-1.9392205296,0.3977285617\H,-0.1125356967,-1.7285067515,-
0.5089591511\H,1.422088886,-1.1113811566,-1.1862890848\C,1.1703644703,
1.1580753005,-0.238080052\O,1.792875759,1.1018157972,-1.2937412711\C,0
.9423514836,2.4974905673,0.455553999\H,1.3860869303,2.5241780821,1.457
2679385\H,1.4178739855,3.261158172,-0.1604786667\H,-0.1231642635,2.734
8176273,0.553020269\\Version=EM64L-G09RevB.01\State=1-A\HF=-287.830206
1\RMSD=4.426e-09\RMSF=1.858e-05\Dipole=-0.7522357,-0.2742884,1.1963357
\Quadrupole=-0.7078166,2.6435928,-1.9357762,-0.5000742,1.502245,1.3912
866\PG=C01 [X(C4H9N1O1)]\\@

TEMP-C(O)CH_3

1\1\GINC-V1344\FOpt\RB3LYP\Gen\C11H21N1O1\GXG501\30-Jun-2011\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\tempac.freq\\0,1\N,0.4772855522,0.0261166285,0.3183817765\C,-0.8
727290445,0.0074936241,2.9470178818\H,-0.9624152574,-0.0001202624,4.04
03874752\H,-1.8950155011,-0.0061045749,2.5494851583\C,-0.0749433804,-1
.1967220229,2.4809549766\C,-0.1092368517,1.2350029605,2.4825435476\C,0
.114460602,-1.3117393659,0.9452257415\C,0.0400521864,1.3520652669,0.94
86965303\C,1.2410269403,-2.3685541923,0.8015006947\C,1.1313400101,2.43
0009708,0.740173899\C,-1.198478291,-1.847258731,0.3287503533\C,-1.3038
839384,1.8283833733,0.3525563729\H,-0.5343250642,-2.1359289977,2.81129
20734\H,-0.5879321011,2.1595954492,2.8251222332\H,0.9158463988,-1.1518
772928,2.9537792317\H,0.8894204543,1.2124666315,2.9410252971\H,2.22041
1294,-1.913306104,0.9806162079\H,2.1131056583,2.0267033433,1.013571183
1\H,1.0890201491,-3.1416447922,1.5626229036\H,0.9198594792,3.274661804
3,1.407021311\H,1.2594400274,-2.8781959357,-0.1600843655\H,1.174035427
7,2.7920201531,-0.2834700991\H,-1.4205943256,-2.8472031863,0.720334789
4\H,-1.5549744299,2.8150286117,0.760324734\H,-2.0458039814,-1.19717069
31,0.5658769262\H,-2.1245446603,1.1483287717,0.6051010091\H,-1.1375677
604,-1.9218408512,-0.7603547287\H,-1.2365509511,1.9129632328,-0.731534
0682\C,0.793504381,0.1158177166,-1.0377014104\O,0.6993219018,1.1717445
019,-1.6616112878\C,1.34654498,-1.0715523261,-1.8292354665\H,2.2971964
932,-1.4267704225,-1.4236262004\H,0.6632895175,-1.9215471097,-1.891201
2388\H,1.514791528,-0.68993546,-2.8368336779\\Version=EM64L-G09RevB.01
\State=1-A\HF=-561.7987025\RMSD=4.856e-09\RMSF=7.379e-06\Dipole=-0.157

5452,-0.9876736,0.928507\Quadrupole=1.0559781,0.9564993,-2.0124774,-1.
1472916,0.0649563,4.0797453\PG=C01 [X(C11H21N1O1)]\\@

R•

1\1\GINC-V1422\FOpt\UB3LYP\Gen\C4H7O2(2)\GXG501\26-Aug-2011\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\pe_r.freq\\0,2\C,0.0525637755,0.1021307886,-0.3327505698\O,1.1955
174838,-0.0949075831,0.4147971158\C,-0.6941236708,1.3427568098,-0.0132
385301\H,-0.0318866156,2.2179974273,-0.0086203595\H,-1.4793379265,1.50
87530836,-0.7575174805\H,-1.1787725577,1.3025566782,0.9779732807\H,-0.
3784662916,-0.7853170655,-0.7785556761\C,1.8170239344,-1.3156329178,0.
3532523188\O,1.3974472586,-2.2442733592,-0.2967348038\C,3.0700643292,-
1.3061414477,1.1919644034\H,3.5071192535,-2.3051431246,1.1989587886\H,
3.7917537496,-0.5926087498,0.7789276871\H,2.8450672775,-0.9872305398,2
.2147138253\\Version=EM64L-G09RevB.01\State=2-A\HF=-307.0439999\S2=0.7
53621\S2-1=0.\S2A=0.750009\RMSD=5.533e-09\RMSF=9.537e-06\Dipole=0.1151
044,0.6385543,0.4561405\Quadrupole=3.2984159,-2.9459016,-0.3525144,-1.
3792482,1.3847368,-1.8959329\PG=C01 [X(C4H7O2)]\\@

TS1 (core)

1\1\GINC-V1251\FTS\UB3LYP\Gen\C8H16N1O3(2)\GXG501\11-Aug-2011\0\\#B3LY
P/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IO
P(2/17=4) Freq=noraman maxdisk=268435456\\tsac1_core.freq\\0,2\N,-1.17
47429362,-0.1468814032,0.3162964828\C,-2.4840146069,0.3815267833,0.002
8135486\C,-2.5744793419,0.2944089664,-1.8579687277\O,-3.9102879842,0.4
943726067,-2.240768118\C,-4.6559701651,-0.5931871403,-2.614317265\O,-4
.2276475455,-1.7228832888,-2.6548938538\C,-6.0582246504,-0.163803414,-
2.9610344217\C,-1.7046051333,1.3672754675,-2.4565141647\O,-2.680149089
7,1.6260611717,0.2140970989\C,-3.6252135606,-0.5595633192,0.4662618411
\C,-0.748693258,-1.4689209512,-0.0911311413\H,-1.6000215566,-2.1433791
606,-0.1940269162\H,-0.0760056629,-1.8903583418,0.6673458986\H,-0.1978
423732,-1.4638133061,-1.0492472276\C,-0.1033556268,0.7849594679,0.6031
723713\H,0.5419118091,0.3683006056,1.3877175334\H,-0.5394849454,1.7241
539717,0.9427495787\H,0.5354586141,0.9918457881,-0.2734154639\H,-3.601
9576609,-1.5583172097,0.0259768353\H,-3.5557381088,-0.6493399204,1.554
5984269\H,-4.572593494,-0.0788756908,0.218189609\H,-2.2709645393,-0.73
23520998,-2.0579624684\H,-6.5494424672,0.2481964739,-2.0728181932\H,-6
.0366535964,0.6283513766,-3.7159446143\H,-6.6207205496,-1.0218190402,-
3.3301673729\H,-1.7438987904,1.2972878103,-3.5513206501\H,-2.049927303
9,2.3555040674,-2.1478030963\H,-0.665309476,1.2427837289,-2.1435485295
\\Version=EM64L-G09RevB.01\State=2-A\HF=-594.84201\S2=0.758791\S2-1=0.
\S2A=0.750032\RMSD=7.986e-09\RMSF=1.233e-06\Dipole=0.195472,-0.3749731
,-0.4800162\Quadrupole=7.1882126,-6.8482021,-0.3400105,-1.2109031,2.55
71841,-5.3478185\PG=C01 [X(C8H16N1O3)]\\@

TS1

```
1\1\GINC-V1278\FTS\UB3LYP\Gen\C15H28N1O3(2)\GXG501\06-Jul-2011\0\\#B3L
YP/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) I
OP(2/17=4) Freq=noraman maxdisk=268435456\\tsac1.2.freq\\0,2\N,-0.9338
708122,-0.0496232887,0.0188977269\C,-3.768248005,0.7244060488,-0.45891
77291\H,-4.6654059872,0.8954964413,-1.0671728103\H,-4.0293684094,1.005
796994,0.5685593639\C,-2.6034974852,1.5488264968,-0.9768297343\C,-3.34
13264487,-0.7286149999,-0.5572975815\C,-1.3252747185,1.4125939825,-0.1
114196221\C,-2.028079465,-1.1127688543,0.1777077583\C,-0.2690130359,2.
2387922826,-0.8812998665\C,-1.6612714663,-2.4751204645,-0.4690274841\C
,-1.6103015146,2.1241895868,1.2435356483\C,-2.3285233361,-1.346768725,
1.6777653392\H,-2.8559343881,2.6142251873,-1.0262390557\H,-4.121332135
4,-1.4008379362,-0.1804101494\H,-2.3747412991,1.2298178514,-2.00327700
34\H,-3.2208475676,-0.9641519797,-1.6236714593\H,-0.0931984432,1.81646
7737,-1.876158533\H,-1.3452671262,-2.337749421,-1.506825972\H,-0.66360
58567,3.2513236487,-1.0229627663\H,-2.5681383146,-3.092946364,-0.48584
33635\H,0.6896007525,2.3475035707,-0.3734589332\H,-0.8835822547,-3.006
62152,0.0697489623\H,-0.7027939933,2.3339333834,1.8087123056\H,-3.0161
984895,-2.1937745134,1.7904439325\H,-2.0969074628,3.0878341483,1.05146
49608\H,-2.7987903902,-0.475770183,2.1448659069\H,-2.2749232756,1.5418
341266,1.8849026105\H,-1.4137947164,-1.5901729413,2.2234528596\C,0.362
8943591,-0.4263613362,0.5847281763\O,0.5361174547,-1.6526089681,0.9251
507417\C,1.0148117502,0.52004063,1.6338081544\H,1.2160550531,1.5387964
637,1.3100098829\H,0.3587381151,0.5414489954,2.5082948492\H,1.94904437
63,0.0461535504,1.9346928632\C,1.6169313515,-0.3607614549,-0.832862518
2\O,2.8748710391,-0.6885100478,-0.2994480999\C,1.253466194,-1.33494348
52,-1.9180205197\H,1.5889926762,0.6839500373,-1.1182111724\C,3.7705696
855,0.3204175742,-0.0741530635\O,3.5510472739,1.4865717404,-0.30924477
72\C,5.0477076552,-0.2399529282,0.4978615855\H,5.4483362335,-1.0168795
455,-0.1609507359\H,5.775603387,0.5627011152,0.6194874608\H,4.84532008
21,-0.7098452634,1.4663955267\H,1.991665129,-1.2583580712,-2.727267891
6\H,1.2522077732,-2.3598541641,-1.5420100505\H,0.2691850563,-1.0952641
371,-2.3229887231\\Version=EM64L-G09RevB.01\State=2-A\HF=-868.801377\S
2=0.759781\S2-1=0.\S2A=0.750034\RMSD=8.119e-09\RMSF=7.055e-07\Dipole=-
0.0834049,0.3055107,-0.2757394\Quadrupole=6.4066782,-6.4040013,-0.0026
769,-4.2863624,1.0968867,2.5542257\PG=C01 [X(C15H28N1O3)]\\@
```

$(CH_3)_2NC(CH_3)(O\bullet)C(CH_3)OC(O)CH_3$

```
1\1\GINC-V1259\FOpt\UB3LYP\Gen\C8H16N1O3(2)\GXG501\07-Jul-2011\0\\#B3L
YP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268
435456\\ac_r1core.freq\\0,2\N,-0.2401414777,-0.4356706695,0.0174082362
\C,-0.0189562023,-0.299024031,1.4773831248\C,1.4945630435,-0.654832749
2,1.7709003775\C,1.868454975,-0.6168956699,3.244981805\C,-1.2822525486
,-1.3739445977,-0.3495991161\H,-1.1455551178,-2.3093736298,0.200353676
7\H,-2.2970814245,-1.0114298935,-0.1098995971\H,-1.2245329868,-1.56405
```

13321,-1.4264136412\C,-0.1121959662,0.708282247,-0.8676847752\H,-0.978
3469956,1.3934823333,-0.8308835842\H,-0.0240782813,0.3468763343,-1.898
8136072\H,0.7897102099,1.2723037944,-0.6284373748\O,-0.7862380135,-1.1
133493583,2.1991274801\C,-0.3573574321,1.1591201235,1.9629542553\O,2.3
24110259,0.278364452,1.0332560529\C,3.4911104582,-0.1957827637,0.52543
77037\C,4.2153514169,0.8858848176,-0.2430557061\O,3.8833992466,-1.3312
133433,0.6714631832\H,0.3234947865,1.8797820678,1.5061688833\H,-1.3891
20497,1.3903825659,1.6899177803\H,-0.261144587,1.2023135185,3.04784635
64\H,1.6626858181,-1.6525670157,1.3623172085\H,3.6512201729,1.14192942
31,-1.1469444869\H,4.2998297121,1.7947200267,0.3604979183\H,5.20615399
2,0.5280103883,-0.5250003062\H,2.8762756842,-1.0238974049,3.3728941348
\H,1.8578587742,0.4057748877,3.635865051\H,1.163477981,-1.2235795214,3
.817523967\\Version=EM64L-G09RevB.01\State=2-A\HF=-594.8462003\S2=0.75
5019\S2-1=0.\S2A=0.750016\RMSD=8.509e-09\RMSF=5.984e-06\Dipole=-0.1095
545,1.2768723,-0.6961771\Quadrupole=-2.0975609,-0.392665,2.4902259,2.6
863931,2.6386809,0.4467963\PG=C01 [X(C8H16N1O3)]\\@

TEMP-C(CH$_3$)(O•)-C(CH$_3$)OC(O)CH$_3$

1\1\GINC-V1271\FOpt\UB3LYP\Gen\C15H28N1O3(2)\GXG501\07-Jul-2011\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\ac_r1.freq\\0,2\N,-0.2088254057,-0.2389001678,0.0134456196\C,
0.1444615475,-0.0217073905,2.9464450707\H,0.76777495,-0.1232511974,3.8
439697556\H,-0.8376577902,0.32331231,3.2930566368\C,0.0351294356,-1.36
11292664,2.2355037758\C,0.7662816228,0.9742705629,1.9809969356\C,-0.76
20343077,-1.3348426273,0.9003018861\C,-0.0081461075,1.1306307023,0.647
2941852\C,-0.5501018751,-2.7571779495,0.3138618036\C,0.8923990972,2.05
32669824,-0.2056455253\C,-2.2763893543,-1.1947045173,1.2321504285\C,-1
.3370170422,1.8948049205,0.8916097945\H,-0.4402873593,-2.1080272153,2.
8835493796\H,0.8446298817,1.9675540518,2.4393566749\H,1.0482589536,-1.
7274416734,2.0189109257\H,1.7878851613,0.6475670511,1.7465853225\H,0.3
891165506,-2.833309367,-0.2340443631\H,1.8929496863,1.6321970873,-0.32
96710385\H,-0.5202858324,-3.4677583103,1.1469926129\H,0.9975645634,3.0
015778334,0.3326801008\H,-1.3627452039,-3.0815409933,-0.3360041955\H,0
.4642232873,2.2856841276,-1.1851125169\H,-2.6538838483,-2.1531159852,1
.6086270906\H,-1.1109264443,2.9087944303,1.2433594068\H,-2.4740999445,
-0.4475344985,2.0023544166\H,-1.9698554658,1.4281778938,1.6478315961\H
,-2.8675004814,-0.9232596162,0.354352307\H,-1.9006950319,1.9687610567,
-0.039114882\C,-0.3867936169,-0.224831921,-1.4780909809\O,-0.936277390
5,0.9310675276,-1.9184947426\C,-1.3552189877,-1.2950092874,-2.09451827
37\H,-0.8722004466,-2.2686369939,-2.1623078869\H,-2.2804539588,-1.3641
046954,-1.5270098733\H,-1.6029015674,-0.9606193981,-3.1025146023\C,1.0
298121615,-0.3894836823,-2.1863586819\O,1.6687142645,-1.6250022487,-1.
7797022843\C,0.9658629299,-0.38576948,-3.7093450449\H,1.6565739022,0.4
268979582,-1.8479138345\C,2.8345304353,-1.541881132,-1.0915684205\O,3.
3811191536,-0.5054891772,-0.7814478478\C,3.3593400515,-2.9204361198,-0

.7604717182\H,2.782007453,-3.34342456,0.0698375668\H,3.2529074257,-3.5
944335441,-1.6148130277\H,4.4054651381,-2.8459068949,-0.4604372895\H,1
.979218741,-0.3041301512,-4.1167959668\H,0.5188174993,-1.3037617258,-4
.1027813405\H,0.3824523694,0.4722868546,-4.0518334983\\Version=EM64L-G
09RevB.01\State=2-A\HF=-868.8077245\S2=0.754791\S2-1=0.\S2A=0.750015\R
MSD=9.816e-09\RMSF=3.173e-06\Dipole=-0.2471663,-1.0989146,0.3011558\Qu
adrupole=-3.4859558,1.3162815,2.1696743,-1.1791259,-1.3942069,2.261631
9\PG=C01 [X(C15H28N1O3)]\\@

$(CH_3)_2NC(O)$-R

1\1\GINC-V1273\FOpt\RB3LYP\Gen\C7H13N1O3\GXG501\08-Jul-2011\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\tempcope_core.freq\\0,1\N,-0.4254051598,0.1910603807,0.3893901307
\C,0.2751241098,0.3101412454,1.5581602175\O,1.4944975007,0.4384095143,
1.6054294848\C,-0.5293465274,0.3817227469,2.8743738277\H,-1.5513795995
,0.0191484245,2.7597933119\O,0.1235848626,-0.4431388309,3.8650396351\C
,-0.5079619765,1.8032666805,3.42261175\C,-1.8303178128,-0.2155272711,0
.3320856852\H,-1.9886378338,-1.1673427503,0.8497510569\H,-2.4953025258
,0.5456832785,0.7562777523\H,-2.1062243755,-0.3407083753,-0.7171634261
\C,0.3283868271,0.1547785066,-0.8597973957\H,0.4073957959,-0.870613252
6,-1.2457486003\H,-0.1673926389,0.7772439542,-1.6130019184\H,1.3306034
007,0.5351033232,-0.6674866668\C,0.1006511644,-1.7728747056,3.62885244
17\C,0.8850696759,-2.5230233577,4.676546737\O,-0.4727240878,-2.2764170
727,2.684216567\H,1.9525755909,-2.316937375,4.5407005716\H,0.610358806
5,-2.186848336,5.6805989066\H,0.7050381626,-3.5933822092,4.5706216199\
H,-1.0014720694,1.8427064603,4.3984618321\H,0.5268037037,2.1398505915,
3.5272524476\H,-1.0301029937,2.4806204299,2.7380170319\\Version=EM64L-
G09RevB.01\State=1-A\HF=-555.0197207\RMSD=6.161e-09\RMSF=4.020e-06\Dip
ole=-0.9839097,0.188651,-0.0456174\Quadrupole=-2.983242,-2.411691,5.39
49331,-4.0691765,2.4711777,-2.3095409\PG=C01 [X(C7H13N1O3)]\\@

TEMP-C(O)-R

1\1\GINC-V1251\FOpt\RB3LYP\Gen\C14H25N1O3\GXG501\08-Jul-2011\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\tempcope.freq\\0,1\N,-0.5003649403,0.2745969238,0.311209801\C,0.
8392183532,-0.1625720545,2.9108979844\H,1.6530877455,-0.3582763612,3.6
19945179\H,-0.078010494,-0.0671254674,3.5042301212\C,0.7432920706,-1.2
937531339,1.9049161608\C,1.1196079539,1.0947118105,2.1079297417\C,-0.3
827863864,-1.1546152798,0.8433815958\C,-0.006713981,1.4827153914,1.124
6254454\C,0.0545225318,-2.1654061455,-0.2469560808\C,0.6290146171,2.53
60234729,0.1863136418\C,-1.7165463179,-1.5842874971,1.492683996\C,-1.1
688604486,2.1026609508,1.9333050974\H,0.581848445,-2.2593261002,2.3982
202015\H,1.2798114481,1.9617923204,2.7587901331\H,1.7112380401,-1.3663
273642,1.3901255928\H,2.0550921754,0.9468671312,1.5500126368\H,0.91096
24466,-1.7765652143,-0.8067287766\H,1.3460326154,2.0534543066,-0.48787

66006\H,0.3761851523,-3.0866860237,0.2509499742\H,1.1818684797,3.25954
87028,0.7973818205\H,-0.7236093312,-2.4548126771,-0.9510903281\H,-0.10
7526796,3.0704771658,-0.4077803485\H,-1.6727044316,-2.6456716644,1.766
0032113\H,-0.8086021397,2.9947035233,2.4598521288\H,-1.9044462575,-1.0
126826874,2.407538521\H,-1.5535864485,1.4051590292,2.6844222148\H,-2.5
74957225,-1.4286847422,0.8367579868\H,-1.9882044003,2.3968720933,1.279
4921407\C,-1.4206190828,0.6138264273,-0.6729046251\O,-1.7926846516,1.7
680330323,-0.866364981\C,-1.9653697703,-0.4096778456,-1.7148763365\O,-
3.2030717394,0.1037252921,-2.2480616564\C,-1.0348350925,-0.4792767886,
-2.9262518882\H,-2.1765182918,-1.3876143509,-1.2921994383\C,-4.2738438
038,0.1093959325,-1.4277752477\O,-4.2819325249,-0.3828212817,-0.318519
3223\C,-5.4404036486,0.8138890169,-2.0747750247\H,-5.2363760308,1.8903
76702,-2.0899535299\H,-5.5668382647,0.4871916633,-3.1109026278\H,-6.34
79655793,0.6240288714,-1.5004659261\H,-1.4560391918,-1.1449797455,-3.6
860283908\H,-0.9360463744,0.5222542276,-3.3548620299\H,-0.0425028177,-
0.8407653402,-2.6510319368\\Version=EM64L-G09RevB.01\State=1-A\HF=-828
.9877686\RMSD=6.696e-09\RMSF=8.795e-06\Dipole=0.7161362,-0.7195334,-0.
017613\Quadrupole=0.7942559,-2.2521457,1.4578898,-2.0984931,4.6769892,
1.9857405\PG=C01 [X(C14H25N1O3)]\\@

•CH$_3$

1\1\GINC-V1403\FOpt\UB3LYP\Gen\C1H3(2)\GXG501\28-Jun-2011\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843545
6\\ch3_r.freq\\0,2\C,0.3855126697,0.2225708049,0.0935096787\H,-0.08567
01997,-0.0494789562,1.0296181659\H,1.0899342163,-0.4534639967,-0.37456
15769\H,0.1522739924,1.1706553676,-0.3745275529\\Version=EM64L-G09RevB
.01\State=2-A1\HF=-39.8382919\S2=0.753764\S2-1=0.\S2A=0.750007\RMSD=4.
159e-10\RMSF=3.137e-06\Dipole=-0.0003971,-0.0002292,-0.0002665\Quadrup
ole=-0.2762816,0.1780416,0.0982401,-0.3934148,-0.4573357,-0.2640293\PG
=C03V [C3(C1),3SGV(H1)]\\@

(CH$_3$)$_2$N•

1\1\GINC-V1307\FOpt\UB3LYP\Gen\C2H6N1(2)\GXG501\01-Dec-2010\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435
456\\nch32_r.freq\\0,2\N,-0.0043137033,-0.0199999238,1.0092779562\C,-0
.0030871928,0.0116207134,-0.4330888731\C,0.6842112151,-1.1824596505,1.
5152861179\H,-0.5297103462,0.9001252907,-0.7939402984\H,1.025440021,0.
0236766561,-0.8362075233\H,-0.4913751729,-0.8839557866,-0.8573951334\H
,1.7351681777,-1.2093721126,1.1757520199\H,0.2183529837,-2.1170045553,
1.1545644097\H,0.6707873098,-1.1855636349,2.6092679481\\Version=EM64L-
G03RevE.01\State=2-B1\HF=-134.5094891\S2=0.753609\S2-1=0.\S2A=0.75001\
RMSD=8.094e-09\RMSF=1.224e-04\Thermal=0.\Dipole=0.2942216,-0.4823727,-
0.3994148\PG=C02V [C2(N1),SGV(C2H2),X(H4)]\\@

TEMP•

```
1\1\GINC-V1399\FOpt\UB3LYP\Gen\C9H18N1(2)\GXG501\27-Aug-2011\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843
5456\\temp_r.freq\\0,2\N,0.9910490242,0.0873568842,0.\C,-1.9510904757,
0.1336940901,0.\H,-2.9537396208,0.5790438432,0.\H,-2.0989178487,-0.954
3898755,0.\C,-1.1778999032,0.5734749207,1.2446784057\C,-1.1778999032,0
.5734749207,-1.2446784057\C,0.2712750496,0.0237469743,1.2736871002\C,0
.2712750496,0.0237469743,-1.2736871002\C,1.1141031726,0.8393953702,2.2
758070441\C,1.1141031726,0.8393953702,-2.2758070441\C,0.2785997659,-1.
4597303578,1.7339569476\C,0.2785997659,-1.4597303578,-1.7339569476\H,-
1.696461981,0.2697576182,2.1631393949\H,-1.696461981,0.2697576182,-2.1
631393949\H,-1.1378295687,1.6720644253,1.2589382193\H,-1.1378295687,1.
6720644253,-1.2589382193\H,1.189128966,1.8839107523,1.9541320617\H,1.1
89128966,1.8839107523,-1.9541320617\H,0.6585057229,0.8185951916,3.2734
436644\H,0.6585057229,0.8185951916,-3.2734436644\H,2.1282506914,0.4330
136721,2.3424574997\H,2.1282506914,0.4330136721,-2.3424574997\H,-0.046
9892419,-1.5206218896,2.7791678789\H,-0.0469892419,-1.5206218896,-2.77
91678789\H,-0.3914168446,-2.0820938293,1.13378229\H,-0.3914168446,-2.0
820938293,-1.13378229\H,1.2885533712,-1.8743718303,1.6598609932\H,1.28
85533712,-1.8743718303,-1.6598609932\\Version=EM64L-G09RevB.01\State=2
-A'\HF=-408.5056918\S2=0.753638\S2-1=0.\S2A=0.75001\RMSD=7.022e-09\RMS
F=7.707e-06\Dipole=-0.5366635,-0.1009999,0.\Quadrupole=-1.7483573,0.42
35938,1.3247635,-0.3859685,0.,0.\PG=CS [SG(C1H2N1),X(C8H16)]\\@
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$CH_3C(O)$-R

```
1\1\GINC-V1405\FOpt\RB3LYP\Gen\C6H10O3\GXG501\30-Jun-2011\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843545
6\\acpe.freq\\0,1\C,0.0047068375,-0.0164184966,-0.1176849063\C,-0.3316
508599,0.4277649987,1.2856003178\O,-0.3821397697,1.5745786143,1.668650
0653\O,-0.5768967164,-0.6480469737,2.0810006218\C,-0.8805993252,-0.380
3689264,3.4720648826\C,-1.9466946751,-1.3855176764,3.9301806544\H,-1.3
286929451,0.6203076496,3.5265833455\H,0.1720347175,0.8592645255,-0.745
3741163\H,0.9026642089,-0.6429933215,-0.1063551776\H,-0.8098682907,-0.
6214139929,-0.5290033859\C,0.3872171588,-0.4256720667,4.3136933711\H,0
.1288708645,-0.3069486748,5.3684429691\H,0.8965337173,-1.3867803534,4.
1904610904\H,1.0642255227,0.3795955134,4.0156100882\O,-2.0248942362,-1
.6844041757,5.1058071417\C,-2.9035282828,-1.9287498789,2.889166783\H,-
2.364276084,-2.5647300072,2.1782685693\H,-3.6834050265,-2.5081431696,3
.3868270186\H,-3.3523913582,-1.1153972054,2.3066023319\\Version=EM64L-
G09RevB.01\State=1-A\HF=-460.3470326\RMSD=8.480e-09\RMSF=3.340e-05\Dip
ole=0.1047232,-0.4103377,-1.0501581\Quadrupole=3.4291125,-3.4607022,0.
0315896,-1.0175743,1.6080393,3.8800959\PG=C01 [X(C6H10O3)]\\@
```

TS2 (core)

```
1\1\GINC-V1265\FTS\UB3LYP\Gen\C8H16N1O3(2)\GXG501\07-Jul-2011\0\\#B3LY
P/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IO
```

P(2/17=4) Freq=noraman maxdisk=268435456\\tsac2_core.freq\\0,2\N,-0.08
37762653,-0.1827707095,0.2812250792\C,-0.1737203327,0.0946828956,1.643
543763\O,0.9125562454,0.3010237465,2.329545752\C,-1.5072888756,0.08665
52391,2.3329548884\C,1.2326655572,-0.1502086395,-0.333574051\H,1.11848
93623,0.0024483958,-1.4125342565\H,1.8113914728,0.6726170089,0.0873165
005\H,1.7966095557,-1.0831888428,-0.1708263468\C,-1.0361255883,-1.0681
458243,-0.3685812186\H,-1.1049979038,-0.8187901652,-1.4336494306\H,-2.
0283894635,-0.9581893945,0.0711421465\H,-0.7433316264,-2.1309255699,-0
.2860067563\C,1.6200259667,-1.0126825291,3.2666448472\O,1.5991130818,-
2.1648335154,2.4992088902\C,0.5243296809,-3.0113357744,2.6070201585\C,
0.6962645065,-4.207159359,1.7029176829\C,3.0087273381,-0.5149448596,3.
4985136664\O,-0.3904255071,-2.8416720113,3.3867452422\H,-2.3066566818,
0.4918907004,1.7029214174\H,-1.8026855067,-0.9223135451,2.6624452904\H
,-1.429912997,0.7082542467,3.2297399774\H,0.9456349032,-1.0684645632,4
.1155670739\H,3.5622405296,-1.1679037077,4.1864567901\H,3.5566960075,-
0.4628740951,2.5525407632\H,2.9633483912,0.4888792947,3.9304379727\H,1
.2608435171,-4.9837653489,2.2351408499\H,-0.2847572431,-4.6156918209,1
.4524992103\H,1.2481958754,-3.9517992521,0.7958110975\\Version=EM64L-G
09RevB.01\State=2-A\HF=-594.8440591\S2=0.760905\S2-1=0.\S2A=0.750056\R
MSD=9.609e-09\RMSF=1.072e-06\Dipole=0.327739,-0.4952857,-0.7313369\Qua
drupole=0.2790129,-1.0769212,0.7979083,-1.6803279,3.4187283,2.015103\P
G=C01 [X(C8H16N1O3)]\\@

TS2

1\1\GINC-V1258\FTS\UB3LYP\Gen\C15H28N1O3(2)\GXG501\07-Jul-2011\0\\#B3L
YP/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) I
OP(2/17=4) Freq=noraman maxdisk=268435456\\tsac2.freq\\0,2\N,-0.002013
3943,-0.0026331538,-0.0011815182\C,-0.009760423,0.007305851,2.91806990
88\H,0.5082951506,0.0066563622,3.8855213433\H,-1.0829451297,0.02527235
64,3.146792342\C,0.356050961,-1.2483218691,2.1304420325\C,0.392164116,
1.2381434621,2.1095546491\C,-0.2672095404,-1.2986442258,0.7171195255\C
,-0.251429441,1.3062400457,0.7034058097\C,0.3937723415,-2.4820886992,-
0.0162630512\C,0.4879640192,2.424449951,-0.0632461686\C,-1.7851864181,
-1.6017120873,0.8091258992\C,-1.7416491316,1.7116477841,0.8182033044\H
,0.0533657001,-2.1528168398,2.6739795183\H,0.1328136792,2.1585221385,2
.648158921\H,1.4489541245,-1.2900250244,2.0255266145\H,1.4843650835,1.
2359254648,1.9896108794\H,1.4724278006,-2.338105778,-0.1217265185\H,1.
5315453754,2.1428578591,-0.2420662859\H,0.2357215595,-3.3898865276,0.5
766638367\H,0.4812633737,3.3390892948,0.5406698234\H,-0.0303680297,-2.
6597742568,-1.0082888334\H,0.0161316862,2.6478893939,-1.0221359757\H,-
1.9466546659,-2.6408716988,1.1241510379\H,-1.8135755931,2.7417410047,1
.189363166\H,-2.300760237,-0.962757102,1.5289696636\H,-2.3035398427,1.
0799072868,1.5106229782\H,-2.2617072706,-1.4536960406,-0.1638725715\H,
-2.2182697321,1.6628250195,-0.1618351922\C,-0.0559470471,0.0390874945,
-1.4086393126\O,-0.9674681382,0.7262135159,-2.018720754\C,1.0438572914

,-0.5486508103,-2.2610882514\H,1.907254013,-0.8583612762,-1.6715819623
\H,0.6938779007,-1.4002578731,-2.8607848424\H,1.3678195886,0.221873678
7,-2.9738940204\C,-2.1419174544,-0.0205288312,-3.2384374698\C,-3.07335
46174,1.1295145193,-3.420608306\H,-1.4467936726,-0.2663400757,-4.03357
15762\O,-2.7755990377,-1.1339608587,-2.719667642\H,-3.7604206078,0.957
7963852,-4.2610888712\H,-3.6689524867,1.2889622933,-2.5164574077\H,-2.
4936975434,2.0340750973,-3.6225025682\C,-2.2692787876,-2.3807398778,-2
.9973010637\O,-1.2820909519,-2.564267418,-3.6764658884\C,-3.114590131,
-3.4515001962,-2.356991989\H,-2.950243323,-3.463683972,-1.2738474659\H
,-4.1781279067,-3.2584689415,-2.525658161\H,-2.8354504109,-4.421003579
,-2.7717016073\\Version=EM64L-G09RevB.01\State=2-A\HF=-868.8157495\S2=
0.765136\S2-1=0.\S2A=0.75008\RMSD=6.473e-09\RMSF=3.110e-07\Dipole=-0.5
826721,-0.2246323,0.4042695\Quadrupole=1.5135183,-0.0125963,-1.500922,
2.5555653,3.8602129,-2.8099352\PG=C01 [X(C15H28N1O3)]\\@

$(CH_3)_2$NC•(CH_3)OR

1\1\GINC-V1368\FOpt\UB3LYP\Gen\C8H16N1O3(2)\GXG501\08-Aug-2011\0\\#B3L
YP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268
435456\\ac_r2core.freq\\0,2\N,0.1936629485,0.3032341439,0.5733397319\C
,0.0433595684,0.0782837677,1.936014204\C,1.1797115209,-0.4993365745,2.
7232573238\O,-1.2428775954,-0.3963712229,2.3019674576\C,-1.8137291573,
0.1811939588,3.43311495\C,-2.9710245921,-0.6809501938,3.8944216432\O,-
2.3086518423,1.4987259133,3.0419126786\C,-2.3468100042,2.4547449555,3.
9989102841\O,-2.0652952312,2.2624956314,5.1629319227\C,-2.7830761488,3
.7793233753,3.4160171069\C,1.0147116463,-0.5858147245,-0.2452964912\H,
0.4789221436,-1.5051940121,-0.5405780854\H,1.9207847437,-0.8738566922,
0.2917628018\H,1.3161437004,-0.0612210469,-1.1590922703\C,-0.950211764
1,0.8593682469,-0.1353179524\H,-0.5964503987,1.3927082549,-1.026128080
8\H,-1.4755508841,1.5600480665,0.5149147568\H,-1.6658841638,0.08626491
63,-0.4576292024\H,2.1150846054,0.0190734323,2.4899940362\H,0.99958770
66,-0.3834623409,3.797837079\H,1.3302459077,-1.5779018244,2.5412142725
\H,-1.081298955,0.341832818,4.2287214706\H,-3.4467731549,-0.2288376757
,4.7687385074\H,-3.704887368,-0.7794266643,3.0888891276\H,-2.606773756
6,-1.6771335054,4.1631950611\H,-2.0402463844,4.1286057853,2.690637055\
H,-3.7326082317,3.6662375722,2.8833998022\H,-2.887320859,4.5120906394,
4.2169628096\\Version=EM64L-G09RevB.01\State=2-A\HF=-594.8616013\S2=0.
752932\S2-1=0.\S2A=0.750006\RMSD=6.266e-09\RMSF=2.112e-06\Dipole=0.091
8789,-0.1052628,-0.8080427\Quadrupole=2.3084289,1.9201131,-4.228542,-2
.69155,-0.7663368,-2.4874701\PG=C01 [X(C8H16N1O3)]\\@

TEMP-C•(CH_3)OR

1\1\GINC-V1405\FOpt\UB3LYP\Gen\C15H28N1O3(2)\GXG501\08-Aug-2011\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\ac_r2.freq\\0,2\N,0.1857523554,0.0007242658,0.2976157296\C,-0
.3207017078,0.4153734987,3.125945157\H,0.0046685401,0.6808967436,4.139

8874334\H,-1.3909957054,0.1840529088,3.199533237\C,0.4616618668,-0.800
3331308,2.6294840524\C,-0.0872144451,1.5917922009,2.1779780332\C,0.114
6544107,-1.2145357786,1.1817949861\C,-0.4760395086,1.286174404,0.71410
44806\C,1.1937360519,-2.2108033393,0.7123277634\C,0.0790800445,2.42231
25313,-0.1659605729\C,-1.2491439231,-1.9465046205,1.1340817153\C,-2.01
79755719,1.2869191122,0.5584356207\H,0.2983791403,-1.663329828,3.28792
44187\H,-0.6455749894,2.4764355535,2.5108206063\H,1.5341338525,-0.5646
575062,2.6722052053\H,0.9788382292,1.8569487449,2.204714596\H,2.175040
4902,-1.7270864852,0.6611668938\H,1.173238224,2.4441907196,-0.13735998
14\H,1.2587117056,-3.043121824,1.4229640271\H,-0.2917654998,3.38541445
75,0.2024466697\H,0.95772942,-2.6265639976,-0.2723551638\H,-0.24151048
59,2.3236706107,-1.2084360199\H,-1.180764155,-2.8994867832,1.673938115
8\H,-2.4093917476,2.295097357,0.7450067579\H,-2.0552861256,-1.36923566
18,1.5933933811\H,-2.5129494673,0.6113939794,1.259927659\H,-1.53149170
89,-2.1580192985,0.0997203861\H,-2.3024930793,0.9883908413,-0.45294578
7\C,0.3231594127,-0.2488062817,-1.0656940385\O,-0.877369063,-0.5063742
994,-1.7586632688\C,1.5517682666,0.0768218022,-1.8576901127\H,2.361541
226,0.3050569928,-1.162329473\H,1.8844633428,-0.75556512,-2.495325072\
H,1.4242596395,0.9493549669,-2.5215812409\C,-0.8292234816,-1.096454519
7,-3.0212392928\C,-2.2123836894,-1.0376600586,-3.6372597654\H,-0.07945
74727,-0.6362520635,-3.6684983328\O,-0.4315139274,-2.4873866342,-2.821
238538\H,-2.1996905362,-1.5118861888,-4.6220231439\H,-2.9301658318,-1.
551746607,-2.9913463666\H,-2.5227040245,0.0054476337,-3.750865648\C,0.
1787714482,-3.1113086399,-3.858166515\O,0.3780950133,-2.5935480389,-4.
9364751252\C,0.5681098271,-4.5218396361,-3.4811735755\H,1.2879032561,-
4.5045923098,-2.6558812002\H,-0.3101118579,-5.0765546243,-3.1358320423
\H,1.0090825417,-5.0195565152,-4.3455246483\\Version=EM64L-G09RevB.01\
State=2-A\HF=-868.8453419\S2=0.754012\S2-1=0.\S2A=0.750011\RMSD=4.702e
-09\RMSF=9.578e-07\Dipole=-0.0267215,-0.152981,0.4626171\Quadrupole=0.
8904879,5.5473431,-6.437831,-0.4310535,2.4271998,-0.2446892\PG=C01 [X(
C15H28N1O3)]\\@

$(CH_3)_2NC(O)CH_2•$

1\1\GINC-V1349\FOpt\UB3LYP\Gen\C4H8N1O1(2)\GXG501\11-Aug-2011\0\\#B3LY
P/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=2684
35456\\tempac_rcore.freq\\0,2\C,0.1113534054,-0.2644419009,0.089735965
4\C,0.2064229062,0.3630064645,1.4024278373\N,1.2605980058,0.0209579878
,2.2321705541\C,2.3005812188,-0.933306365,1.890130861\C,1.2561186798,0
.5089905455,3.6019523714\O,-0.6631854058,1.1732715383,1.7525498424\H,-
0.6580443006,0.1222467015,-0.5665164294\H,0.6744035451,-1.1345783682,-
0.225283259\H,2.5050436993,-0.9248729308,0.8181204678\H,2.0506189889,-
1.9607288555,2.1968582407\H,3.2265745273,-0.6473644934,2.4009623682\H,
1.1030659307,-0.3140850734,4.3151218151\H,2.2120047287,0.9941517623,3.
8372960837\H,0.4450420703,1.2283849873,3.7054292811\\Version=EM64L-G09
RevB.01\State=2-A\HF=-287.164222\S2=0.75708\S2-1=0.\S2A=0.750031\RMSD=

9.479e-09\RMSF=6.344e-06\Dipole=1.1034622,-0.9267219,-0.0845345\Quadru
pole=-1.8297956,-1.1610144,2.99081,1.4863531,0.9539485,1.0314126\PG=C0
1 [X(C4H8N1O1)]\\@

TEMP-C(O)CH$_2$•

1\1\GINC-V1260\FOpt\UB3LYP\Gen\C11H20N1O1(2)\GXG501\11-Aug-2011\0\\#B3
LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26
8435456\\tempac_r.freq\\0,2\N,0.1288543465,-0.0103970166,0.0270543674\
C,0.1334027462,0.0051946676,2.9604986463\H,0.6348183596,0.0115303555,3
.9363729101\H,-0.9438803627,0.0074137958,3.1675640962\C,0.5374060856,-
1.2383504631,2.1787685691\C,0.5371814914,1.2307893394,2.1501900434\C,-
0.0571615364,-1.326244012,0.7531471662\C,-0.1182106617,1.2981805917,0.
7524712657\C,0.6903891318,-2.4943271276,0.0754449848\C,0.6127780586,2.
4261801691,-0.0106329477\C,-1.5554619398,-1.7130148209,0.8084679853\C,
-1.6112924933,1.6818623539,0.8939755877\H,0.2497152801,-2.1509662574,2
.7152860932\H,0.2806889414,2.1554341713,2.6812762381\H,1.6329222438,-1
.2534152255,2.0948294691\H,1.6294713869,1.226870197,2.0286836602\H,1.7
506597045,-2.2641982041,-0.0673937519\H,1.649513322,2.1365886457,-0.21
62265469\H,0.6254295487,-3.3657391367,0.736724597\H,0.6299542954,3.325
6764474,0.6150417241\H,0.2554554453,-2.784962965,-0.88458787\H,0.12280
31787,2.6740209598,-0.9521746657\H,-1.6712769178,-2.714832647,1.239299
206\H,-1.6825332269,2.704968883,1.2832718578\H,-2.1462845402,-1.021268
215,1.4117631466\H,-2.1499945874,1.0341777822,1.5908720111\H,-1.985475
7134,-1.727262889,-0.1988797751\H,-2.1060529525,1.6456048893,-0.076307
4795\C,-0.1388560818,0.0258111562,-1.3592790966\O,-0.9169952615,0.8435
710268,-1.8771649973\C,0.6251980176,-0.8110747391,-2.2665326978\H,1.57
64892063,-1.2569389463,-2.0103367272\H,0.2898293814,-0.8404662971,-3.2
968773177\\Version=EM64L-G09RevB.01\State=2-A\HF=-561.1362073\S2=0.759
967\S2-1=0.\S2A=0.750048\RMSD=7.611e-09\RMSF=4.654e-06\Dipole=0.547776
9,-0.7662428,0.7219117\Quadrupole=-0.4074146,1.3058666,-0.898452,0.480
716,-2.8551274,3.3413436\PG=C01 [X(C11H20N1O1)]\\@

RH

1\1\GINC-V1425\FOpt\RB3LYP\Gen\C4H8O2\GXG501\26-Aug-2011\0\\#B3LYP/gen
 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456
\\pe.freq\\0,1\C,2.6358584364,-0.380079926,0.\C,1.3732920556,0.4613054
906,0.\O,0.2470171825,-0.4461418115,0.\C,-0.976101523,0.1320688178,0.\
C,-2.0659519248,-0.9155202383,0.\O,-1.1516641253,1.3309541595,0.\H,3.5
169782249,0.2709206774,0.\H,-3.0401159882,-0.4254962585,0.\H,-1.972189
345,-1.5575968147,-0.8821101991\H,-1.972189345,-1.5575968147,0.8821101
991\H,2.6797633678,-1.0193709359,-0.8876092949\H,2.6797633678,-1.01937
09359,0.8876092949\H,1.3075828079,1.1054632941,-0.8829242523\H,1.30758
28079,1.1054632941,0.8829242523\\Version=EM64L-G09RevB.01\State=1-A'\H
F=-307.7074375\RMSD=2.778e-09\RMSF=4.952e-05\Dipole=0.4057331,-0.65700
22,0.\Quadrupole=2.3263895,-2.845561,0.5191716,3.6170265,0.,0.\PG=CS [

SG(C4H2O2),X(H6)]\\@

O_2

1\1\GINC-V1358\FOpt\UB3LYP\Gen\O2(3)\GXG501\24-Aug-2011\0\\#B3LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\ \o2.freq\\0,3\O,0.,0.,-0.0022684066\O,0.,0.,1.2122684066\\Version=EM64 L-G09RevB.01\State=3-SGG\HF=-150.3200401\S2=2.006604\S2-1=0.\S2A=2.000 023\RMSD=4.107e-09\RMSF=2.702e-08\Dipole=0.,0.,0.\Quadrupole=0.1136871 ,0.1136871,-0.2273743,0.,0.,0.\PG=D*H [C*(O1.O1)]\\@

$(CH_3)_2NC(O)CH_2OO\bullet$

1\1\GINC-V1260\FOpt\UB3LYP\Gen\C4H8N1O3(2)\GXG501\11-Aug-2011\0\\#B3LY P/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=2684 35456\\tempac_oocore.freq\\0,2\N,-0.3343742208,-0.2845263362,0.2041052 093\C,-0.0387559734,0.0326691417,1.50571976\C,1.4614781518,0.106299291 3,1.8629937796\O,1.6259822446,0.5011478331,3.235506474\O,1.4080572774, -0.5219798241,4.0498497098\H,1.9777904396,0.8822080155,1.2890874682\H, 1.9627654369,-0.8557604161,1.725546575\O,-0.8867904201,0.2514907132,2. 3549880706\C,-1.7323292912,-0.3643549777,-0.1989386182\C,0.63617556,-0 .5561999071,-0.842864412\H,-1.9433182297,0.3613571613,-0.9951420361\H, -2.3538065864,-0.1459473524,0.6682498149\H,-1.964825371,-1.3693649722, -0.574110976\H,0.484150839,-1.5629395184,-1.2546992931\H,1.6589626841, -0.4969010291,-0.4716719674\H,0.5300994591,0.1649721772,-1.6647495585\ \Version=EM64L-G09RevB.01\State=2-A\HF=-437.5250988\S2=0.752919\S2-1=0 .\S2A=0.750006\RMSD=3.526e-09\RMSF=4.753e-06\Dipole=0.4738249,-0.27568 99,-2.2906629\Quadrupole=1.7953716,0.6889196,-2.4842912,0.7045254,0.07 50026,0.008443\PG=C01 [X(C4H8N1O3)]\\@

TEMP-C(O)$CH_2OO\bullet$

1\1\GINC-V1374\FOpt\UB3LYP\Gen\C11H20N1O3(2)\GXG501\11-Aug-2011\0\\#B3 LYP/gen 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26 8435456\\tempac_oo.freq\\0,2\N,-0.3184023499,-0.1156142267,0.108681008 4\C,0.3387983329,0.0282090567,2.9815997017\H,0.9682867934,0.1289137087 ,3.874111351\H,-0.6927172888,-0.0820203632,3.3376262749\C,0.7753591644 ,-1.1679677004,2.1539865582\C,0.4981543808,1.2492425338,2.0938157644\C ,-0.0777807693,-1.4156526267,0.8901868939\C,-0.3543718858,1.2420359241 ,0.7977796085\C,0.7491556635,-2.4055965121,0.0358039977\C,0.2894530074 ,2.3624171509,-0.0615275517\C,-1.4203986347,-2.055305483,1.3079065588\ C,-1.8100712011,1.6112245468,1.1649909387\H,0.7463142756,-2.0936887239 ,2.7397752545\H,0.2442742557,2.17202525,2.6286391444\H,1.823236711,-1. 0186622132,1.8583141017\H,1.5579211802,1.3316794906,1.8163289863\H,1.6 207510087,-1.8969012636,-0.391595065\H,1.2037124558,2.0015882703,-0.54 39975439\H,1.1172111835,-3.2051027387,0.6896159517\H,0.5690201889,3.18 86040221,0.6006503328\H,0.1725018481,-2.8514320146,-0.7704474012\H,-0. 3672681287,2.790675099,-0.8179660722\H,-1.2271897453,-3.0158648492,1.8

000083449\H,-1.8495008944,2.6270289679,1.5755227503\H,-1.9677173393,-1
.4248718152,2.0165666482\H,-2.2149865199,0.9285286468,1.9175364969\H,-
2.0525499218,-2.2378936521,0.4394111463\H,-2.4792303425,1.573884893,0.
3008246348\C,-0.9367962668,-0.3088407426,-1.1193301215\O,-1.2782174077
,-1.4047586358,-1.5408118088\C,-1.1609460132,0.8802694357,-2.090239967
9\H,-1.7916562197,1.6689035908,-1.6843107842\H,-0.2112804324,1.2927184
537,-2.4371264502\O,-1.8049355485,0.4081274876,-3.2905541664\O,-3.1090
814868,0.2728523644,-3.1016807612\\Version=EM64L-G09RevB.01\State=2-A\
HF=-711.4955154\S2=0.75294\S2-1=0.\S2A=0.750006\RMSD=7.437e-09\RMSF=3.
725e-06\Dipole=1.1350573,1.1651865,1.6953542\Quadrupole=-0.6139005,4.3
920435,-3.778143,-1.069557,-5.4594971,-3.5639724\PG=C01 [X(C11H20N1O3)
]\\@

RH

1\1\GINC-V1425\FOpt\RB3LYP\Gen\C4H8O2\GXG501\26-Aug-2011\0\\#B3LYP/gen
6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456
\\pe.freq\\0,1\C,2.6358584364,-0.380079926,0.\C,1.3732920556,0.4613054
906,0.\O,0.2470171825,-0.4461418115,0.\C,-0.976101523,0.1320688178,0.\
C,-2.0659519248,-0.9155202383,0.\O,-1.1516641253,1.3309541595,0.\H,3.5
169782249,0.2709206774,0.\H,-3.0401159882,-0.4254962585,0.\H,-1.972189
345,-1.5575968147,-0.8821101991\H,-1.972189345,-1.5575968147,0.8821101
991\H,2.6797633678,-1.0193709359,-0.8876092949\H,2.6797633678,-1.01937
09359,0.8876092949\H,1.3075828079,1.1054632941,-0.8829242523\H,1.30758
28079,1.1054632941,0.8829242523\\Version=EM64L-G09RevB.01\State=1-A'\H
F=-307.7074375\RMSD=2.778e-09\RMSF=4.952e-05\Dipole=0.4057331,-0.65700
22,0.\Quadrupole=2.3263895,-2.845561,0.5191716,3.6170265,0.,0.\PG=CS [
SG(C4H2O2),X(H6)]\\@

TS6 (core)

1\1\GINC-V1410\Freq\UB3LYP\Gen\C6H14N1O2(2)\GXG501\27-Aug-2011\0\\#B3L
YP/gen 6D SCF=Tight INT(grid=ultrafine) IOP(2/17=4) Freq=noraman maxdi
sk=268435456\\tsj_core.freq\\0,2\N,-2.5909473173,1.3989008443,-0.58835
47786\C,-2.9644147556,1.8682288589,0.7383938675\C,-1.6029411294,0.3276
401594,-0.5202643049\C,-1.3100739481,3.415078793,-1.6549835888\C,-2.17
07771011,4.0225575657,-2.728600465\O,-1.0886557032,4.3542213991,-0.616
1664992\H,-0.3732664898,2.9569103536,-1.9791404284\H,-2.0329452832,2.3
535702463,-1.1503946677\H,-1.6711534784,4.8713073414,-3.2171883793\H,-
3.1201015812,4.3815855962,-2.3163844696\H,-2.3932334857,3.2703458324,-
3.4923075322\C,-0.0988183413,4.086251617,0.2768629982\O,0.5760367655,3
.0807445052,0.2515101066\C,0.030546315,5.2096724999,1.2775028045\H,0.2
939882737,6.1416114321,0.7659821128\H,0.8013707039,4.9587891451,2.0068
479045\H,-0.9252493597,5.3757841911,1.7849780975\H,-3.5791945166,2.770
3212288,0.651949488\H,-3.5716994806,1.0948996732,1.23176087\H,-2.10739
7834,2.0820304005,1.4010995621\H,-1.2856690851,0.0570799451,-1.5330555
545\H,-0.710717777,0.5800843969,0.0744995281\H,-2.0712593909,-0.558873

0251,-0.0682806716\\Version=EM64L-G09RevB.01\State=2-A\HF=-442.1920253
\S2=0.757041\S2-1=0.\S2A=0.750024\RMSD=7.777e-09\RMSF=2.309e-05\ZeroPo
int=0.1937122\Thermal=0.2063714\Dipole=-0.1352778,0.614029,0.1358028\P
G=C01 [X(C6H14N1O2)]\\@

TS6

1\1\GINC-V1410\FOpt\UB3LYP\Gen\C13H26N1O2(2)\GXG501\27-Aug-2011\0\\#B3
LYP/gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman
maxdisk=268435456\\tsj.freq\\0,2\C,-2.5889642891,1.3622042326,-0.52628
89996\C,-3.2033551194,1.6567256983,0.845276233\C,-2.9018504608,0.55384
02433,1.8996003081\N,-3.2899692768,-0.7360720043,1.2911943193\C,-2.707
1971191,-1.1496575455,-0.0015698551\C,-3.0303741229,-0.0196747001,-1.0
182546008\C,-3.8406052541,0.7714566939,3.1033098601\C,-1.4403199298,0.
6675644858,2.404476201\C,-3.4556768734,-2.4286320404,-0.425349917\C,-1
.1871591241,-1.4560854651,-0.0174788415\C,-3.1006004421,-2.6318827891,
3.1242329216\C,-4.5303929759,-3.0879484929,3.2507275354\O,-2.278907246
8,-3.7183059802,2.7249338902\C,-0.956194596,-3.6690301268,3.0352008001
\C,-0.2506124612,-4.9129966271,2.5510596859\O,-0.4327000852,-2.7428261
481,3.615121675\H,-4.115730982,-0.0087517987,-1.1837553267\H,-2.559755
6973,-0.2641104819,-1.979711991\H,-2.9013934609,2.1304632251,-1.245304
1049\H,-1.4942707919,1.4211423707,-0.4773061921\H,-2.8511059836,2.6208
194466,1.2347437675\H,-4.2931827442,1.7330336603,0.7345504454\H,-3.735
3853632,1.7900532625,3.4948741584\H,-4.8823757071,0.6162679398,2.80515
04708\H,-3.6088146262,0.0807561739,3.9221201553\H,-1.3395910032,1.5535
788056,3.0434842085\H,-1.1576495828,-0.2099507166,2.9945535674\H,-0.71
62312695,0.7712058715,1.5933180585\H,-4.5372609221,-2.270339033,-0.367
9201656\H,-3.1945246442,-3.2708492628,0.2252170131\H,-3.1959601935,-2.
7065662404,-1.4537890005\H,-0.9052333494,-2.0935468139,0.8247780525\H,
-0.5682269504,-0.5579732065,0.028942961\H,-0.9273985487,-1.9840063714,
-0.9433071545\H,-3.1480279873,-1.6656530973,2.1483248229\H,-2.67795104
29,-2.1304275066,3.9960004764\H,-5.168813004,-2.2331945145,3.494265165
9\H,-4.6425878293,-3.8411686104,4.0430648235\H,-4.8897322962,-3.524230
5217,2.3128439274\H,0.7898810967,-4.8890881455,2.8764446182\H,-0.29307
7258,-4.9627394177,1.4575506961\H,-0.7460284822,-5.8089794508,2.938080
3306\\Version=EM64L-G09RevB.01\State=2-A\HF=-716.1823867\S2=0.757253\S
2-1=0.\S2A=0.750025\RMSD=5.535e-09\RMSF=7.972e-06\Dipole=-0.1610741,-0
.371705,-0.3398711\Quadrupole=-3.1712473,4.8650138,-1.6937664,-2.05041
19,-3.679288,-1.3330265\PG=C01 [X(C13H26N1O2)]\\@

$(CH_3)_2NH$

1\1\GINC-V1467\FOpt\RB3LYP\Gen\C2H7N1\GXG501\29-Nov-2010\0\\#B3LYP/gen
 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456
\\nhch32.freq\\0,1\N,0.0304150124,-0.0178934253,0.9982891432\C,-0.0198
146806,0.0019817004,-0.4578184968\C,0.6807108866,-1.2113623143,1.52356
50601\H,-0.5684389773,0.8877755904,-0.7952233076\H,1.0007224344,0.0715

340028,-0.8541069882\H,-0.4905064039,-0.8916739784,-0.9120905677\H,1.7
380485503,-1.2055503344,1.2313641359\H,0.2446377742,-2.1649790942,1.16
72091105\H,0.6382853023,-1.2023289692,2.6179050024\H,-0.9177766654,0.0
333515881,1.3649068738\\Version=EM64L-G03RevE.01\State=1-A'\HF=-135.16
2856\RMSD=5.280e-09\RMSF=1.973e-05\Thermal=0.\Dipole=-0.2806955,-0.281
6242,-0.0732178\PG=CS [SG(H1N1),X(C2H6)]\\@

TEMPH

1\1\GINC-V1285\FOpt\RB3LYP\Gen\C9H19N1\GXG501\29-Nov-2010\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=26843545
6\\temph.freq\\0,1\N,0.9003536946,0.3397574,0.\C,-1.9504833027,0.12995
89059,0.\H,-2.9511512165,0.5804794052,0.\H,-2.1066836064,-0.95673877,0
.\C,-1.1858578853,0.5617500666,1.2569955404\C,-1.1858578853,0.56175006
66,-1.2569955404\C,0.2606656893,0.0221203388,1.2937489423\C,0.26066568
93,0.0221203388,-1.2937489423\C,1.0616758843,0.7889656734,2.3627593358
\C,1.0616758843,0.7889656734,-2.3627593358\C,0.2771961313,-1.480109656
9,1.6758523514\C,0.2771961313,-1.4801096569,-1.6758523514\H,-1.7141916
175,0.2412619676,2.1639635449\H,-1.7141916175,0.2412619676,-2.16396354
49\H,-1.1441540148,1.6590481969,1.2802098659\H,-1.1441540148,1.6590481
969,-1.2802098659\H,1.1016776698,1.8541865822,2.1156499941\H,1.1016776
698,1.8541865822,-2.1156499941\H,0.609431944,0.6707964574,3.354600621\
H,0.609431944,0.6707964574,-3.354600621\H,2.0927004075,0.4156150845,2.
4223608656\H,2.0927004075,0.4156150845,-2.4223608656\H,-0.0481844181,-
1.6174539504,2.7146503866\H,-0.0481844181,-1.6174539504,-2.7146503866\
H,-0.3768657314,-2.0871160688,1.044840905\H,-0.3768657314,-2.087116068
8,-1.044840905\H,1.2931300415,-1.8857372116,1.5910046479\H,1.293130041
5,-1.8857372116,-1.5910046479\H,1.8595664847,-0.0040446076,0.\\Version
=EM64L-G03RevE.01\State=1-A'\HF=-409.1596489\RMSD=6.377e-09\RMSF=3.331
e-06\Thermal=0.\Dipole=-0.0261937,-0.2508807,0.\PG=CS [SG(C1H3N1),X(C8
H16)]\\@

•C(O)CH_3

1\1\GINC-V1456\FOpt\UB3LYP\Gen\C2H3O1(2)\GXG501\05-Oct-2011\0\\#B3LYP/
gen 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxd
isk=268435456\\coch3_r.freq\\0,2\C,-0.0313903853,0.0543697422,-0.03104
03192\C,-0.0096737827,0.0167554832,1.4851596261\H,1.0317215869,-0.0245
319861,1.8212592988\H,-0.5136522634,0.8896718177,1.9172493271\H,-0.494
6154703,-0.9057630969,1.8212592988\O,-0.5106651791,0.8844980359,-0.734
887231\\Version=EM64L-G09RevB.01\State=2-A'\HF=-153.1798348\S2=0.75225
3\S2-1=0.\S2A=0.750003\RMSD=4.158e-09\RMSF=6.649e-05\Dipole=0.1661442,
-0.2877703,0.8962225\Quadrupole=0.573612,-0.0544694,-0.5191426,0.54393
44,-0.0873561,0.1513053\PG=CS [SG(C2H1O1),X(H2)]\\@