MNDO AND AM1 STUDIES ON THE RESONANCE STABILIZED ALLYL–TYPE RADICALS CONTAINING CC, CN AND NN BONDS

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THE HEATS OF FORMATION AND THE FULLY–OPTIMIZED GEOMETRIES OF 1–METHYLALLYL (1R), 1–METHYL–1–AZAALLYL (2R'), 1–METHYL–2–AZAALLYL (2R') AND 1–METHYL–1,2–DIAZAALLYL (3R) RADICALS WERE CALCULATED AT THE SEMIEMPIRICAL QUANTUM CHEMICAL LEVEL (MINDO/3––UHF, MNDO–HE AND AM1–HE). THE RESONANCE ENERGIES OF THE RADICALS WERE CALCULATED USING THE HEATS OF FORMATION OF THEIR PARENT COMPOUNDS (2–BUTENE (1), N–ETHYLIDENE––METHYLAMINE (2) AND AZOMETHANE (3)). THE RESONANCE ENERGIES OF 2R AND 3R WERE FOUND TO BE LESS THAN THOSE OF 1R, 2R'. ROTATIONAL AND INVERSIONAL MECHANISM OF THE ISOMERIZATION OF THE MOLECULES AND ALLYL–TYPE RADICALS CONTAINING ESSENTIAL DOUBLE BONDS AND PARTI–AL CC, CN AND NN DOUBLE BONDS WERE STUDIED. THE CALCULATED BARRIER HEIGHTS PREDICT TOO LOW ACTIVATION ENERGIES FOR THE ROTATION. THE REASON OF THE LOW BARRIERS CALCULATED IS THE UNDERESTIMATION OF THE LONE–PAIR AND THE DOUBLE LONE–PAIR REPULSION IN THE NDDO FORMALISM. ISOMERIZATION AT CC, NN AND CN DOUBLE BONDS AND PARTIAL DOUBLE BONDS BY INVERSION IS UNLIKELY.
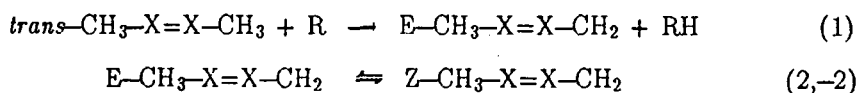
Introduction

The thermal decomposition of *cis*– and *trans*–diazenes can be described by comp–lex reaction schemes [1] involving the synchronous (a) or asynchronous (b) decompo–sition of these compounds. Much effort has been devoted to decide between mecha–nisms (a) and (b) [2]. Symmetrical dialkyldiazenes cleave by mechanism (a), whereas diazenes with different alkyl (or aryl) substituents do so by mechanism (b) [3,4]. MNDO calculations [5] on the thermal decompositions of *trans*– and *cis*–diethyldia–zene predict stepwise decomposition *via* synchronous bond fission and suggest a transi–tion state through *cis* isomers. Experimentally, the *cis*–diazenes are thermally less

stable than the *trans* isomers [1]. The role of the *cis* conformer in the photochemical deazatization of *trans*–1,3–dialkyl–1,2–diazenes has been confirmed experimentally [1,6]. In the thermolyses of *trans*– and *cis*–di(2–propyl)–diazene, FOGEL et al. [7] showed that the decomposition does not occur *via* the labile *cis* conformer, and suggested that the isomerization of the *cis* conformer proceeds with inversion.

For the *cis–trans* isomerization of alkyl–1,2–diazenes, three possible mechanisms have been suggested: rotation [2], inversion and dissociation/combination [8]. The electron configuration $(n_-)^2(\pi)^2(n_+)^2$ for the *trans* ground (π,π^*) state correlates with a doubly excited configuration of the *cis* isomer; rotation is symmetry–forbidden [9]. The rotation around the N=N bond is highly hindered (247–351.8 kJ mol^{-1}) [10], and the rotational barrier is significantly higher than those in the olefins [11]. A detailed INDO–SCF calculation, followed by CI calculations [10a] for the isomerization of azomethane in the ground and some low–lying excited states, showed that rotation of the methyl groups around the N=N double bond was more feasible than inversion.
The calculated relative stability of the *trans* and *cis* isomers, $\Delta\Delta_f H^o = \Delta_f H^o(trans) - \Delta_f H^o(cis)$, was found to be 14.2 kJ mol^{-1}, in contrast with the experimental data [12]. As products of radical H–abstractions from 2–butene, N–ethylidenemethylamine and azomethane (*Reaction 1*), resonance–stabilized allyl–type radicals are formed:

$$trans–CH_3–X=X–CH_3 + R \longrightarrow E–CH_3–X=X–CH_2 + RH \qquad (1)$$

$$E–CH_3–X=X–CH_2 \leftrightharpoons Z–CH_3–X=X–CH_2 \qquad (2,-2)$$

where X = CH, N.

Results on the reactions of 1–azaallyl and 2,3–diazaallyl radicals are scarce. The last reaction has been studied in the decompositions of dialkyldiazenes [13] and in the radical–initiated gas–phase reactions of dialkyl–diazenes [14]. In further reactions, the

radical can also isomerize (*Reaction 2*), similarly to the allyl radicals, and take part mostly in radical disproportionation and combination reactions forming stable products.

There is an equilibrium between the E and the Z isomer of 1—methylallyl radical at the temperature range 399—439 K [15].

Calculations for the compounds 1, 2 and 3 and the radicals 1R—3R were carried out by means of semiempirical quantum chemical methods (MINDO/3 [16], MINDO/3—UHF [17], MNDO—HE [18], AM1—HE [19,20] and AM1—UHF [21]).

Calculations

The heats of formation and the geometries of the molecules and radicals in the ground state were calculated with full geometrical optimization. In the calculations of the torsional profiles, the twist angle was fixed at different values as the reaction coordinate ($\Theta = 0^0$, 15^0, 30^0, 45^0, 60^0, 75^0, 90^0, 105^0, 120^0, 135^0, 150^0, 165^0 and 180^0), and an optimization was applied for the remainder geometrical parameters. In the calculation of the inversion profile (AM1—HE), the twist angle of $\Theta(C-N-N-C)$ was kept unchanged ($\Theta = 180^0$ and 0^0) and the bending—angle was kept fixed ($\phi = 110^0$, 120^0, 130^0, 140^0, 150^0, 160^0, 170^0, 180^0 and $360^0 - \phi$) values as reaction coordinates.

The resonance energies (RE) were defined similarly to the allyl resonance energies (ARE) [21] (ARE = $BDE(CH_3-H) - BDE((R_\pi CH_2-H))$, using the calculated data for dialkyl—diazenes, methane and methyl radical [19].

The stabilization energies (SE) were calculated by the method of LEROY [22]:

$$SE = \Delta H_a - \Sigma N_i E_i$$

where ΔH_a is the atomization energy and N_i the number of bond i.

The necessary bond terms to determine the atomization heats of radicals were unknown. By using the experimental and calculated heats of formation of dialkyldiazenes with low strain [23] (n—alkyl group substituted diazenes), for the bond energy terms (E) [22] $E(C-N=N-C) = 1105.5 \pm 0.8$ kJ mol^{-1} was obtained [24]. The $(E(C-H)_p^N$ and $E(C-H)_s^N$ were supposed to be equal to $E(C-H)_p^{C-N=N-C}$ and $E(C-H)_s^{C-N=N-C}$, respectively.

Results and Discussion

Resonance and stabilization energies of radicals 1R—3R

The heats of formation of compounds 1–3 calculated by means of MINDO/3, MNDO and AM1, are summarized and compared with the experiments in Table I–II. The best agreement with the experimental values was obtained by AM1. A dramatic improvement was observed at the N—containing compounds with changing the core—core repulsion function (CRF) in MNDO to result AM1 [19]. Table III contains the heats of formation of allyl—type radicals formed in reaction (1). Used the calculated data, the resonance energies were also calculated (Table IV) for the isomers of 1–3. The heats of formation for *cis* (Z) isomers of N—containing molecules suggest higher thermodynamic stability than for the *trans* ones in contradiction with the experimental results available in the literature [23]. (The only exception among the diazenes, the difluorodiimide, is more stable in the *cis* configuration [30].) MINDO/3 predicts an unrealistically small heats of formation for 1–3, because this method reduce the number of electron integrals to be considered using core approximation [25,18]. The lone—pair and double lone—pair interactions are underestimated not only in MINDO/3 [16], but in MNDO [18] and AM1 [25], too. An improvement was found for these compounds in MNDO which is probably due to the inclusion of directional

Table I

Calculated heats of formation of 2—butene and N—ethylidene—methylamine

| Method | $\Delta_f H^o$/kJ mol^{-1} | | | |
| | 1 | | 2 | |
	cis[a]	trans	cis[a]	trans
MINDO/3	−23.9 [25]	−26.4 [25]	47.6	40.2
MINDO	−16.7 [26]	−21.4 [25]	31.2	27.5
AM1	− 9.2	−14.0	33.6	42.7
exp.[b]	− 8.0	−12.6		

[a] The methyl groups have a staggered—staggered conformation in cis—1 and cis—2.
[b] See in [27]

Table II

Calculated heats of formation of azomethane

| Method | $\Delta_f H^o$/kJ mol^{-1} | |
	cis[a]	trans
MINDO/3	39.8	86.2 [28a]
MNDO	107.2	96.3
AM1	126.5	146.3
exp.		134.5 ± 3.8 [23a]
		148.8 ± 5.2 [23b]
		149.1 ± 6.2 [23c]

[a] The methyl groups have a staggered—staggered conformation in cis—dimethyldiazene; this was demonstrated by *ab initio* calculations to be the most stable geometry with C_{2v} [29a] symmetry.

effects in the two—center electron—electron repulsions and core—electron attractions [18b]. The further improvement in AM1 calculations is due to the modified CRF [19a]. Similar observation was made for the radicals 2R, 2R' and 3R. KAO et al. [31] completed by *ab initio* methods this effect with the strain among the large alkyl groups. The attraction between the alkyl H—atom and the lone—pair of electrons on N—atom can not be negligible either [30]. None of the methods applied in the calculations give good relative stability for the isomers of N—containing molecules.

The resonance energies in the radicals 1R and 3R are practically equal. In radicals 2R and 2R' the resonance energies are very different. In the radical, where the N—atom is in symmetrical position in the delocalized system, the stabilization through delocalization is greater than in the radicals 1R, 2R and 3R [35]. An N—atom in unsymmetrical position has an even lower delocalization effect. The stabilization energies of 1R and 3R calculated by LEROY [22] differ by circ. 10 kJ mol^{-1}. The UHF approximation [32b,33] (UHF—MINDO/3 and UHF—AM1) overestimates the thermodynamic stability of the radicals in each case considering the experimental data available in the literature and the half—electron (HE) approximation [34].

By means of the calculated heats of formation for dialkyl—diazenes the group increments of $\Delta_f H^{\circ}[C-(N_A)(H)_2] = 90.4$ kJ mol^{-1} and $\Delta_f H^{\circ}[C-(N_A)(C)(H)] = 94.8$ kJ mol^{-1} [24] were estimated using the group values for groups in molecules proposed by SCHERER et al. [23g].

The calculated geometries for 3 and 3R are summarized in Table V — VI. The difference between MINDO/3 and AM1 results is significant. As it can be seen in Table V, the geometry calculated by means of AM1 shows the best agreement with the experimental result. A similar observation was made for the allyl radicals [32].

The net atomic charges ($q_X = Z_X - \Sigma_\mu X_{P_{\mu\mu}}$, where Z_X is the core charge of

Table III

Calculated heats of formation of resonance stabilized radicals 1R–3R

Radical	$\Delta_f H^o$/kJ mol^{-1}			
	MINDO/3–UHF	MNDO–HE	AM1–HE	AM1–UHF
1R E	88.8	103.0	116.8	81.0
Z	91.8	105.5	119.5	84.0
2R E	163.9	166.9	196.4	161.2
Z	173.7	155.5	189.4	173.3
2R' E	139.7	132.9	147.1	120.3
Z	145.6	138.2	141.2	115.1
3R E	115.1 [28a]	214.4	275.4	245.4
Z	144.0	238.6	264.4	235.9

[a] The heats of formation of the radicals are calculated for the E and Z conformers.

Table IV

Calculated resonance (RE) and stabilization (SE) energies of radicals 1R–3R

Radical		RE/kJ mol^{-1}[a]	SE/kJ mol^{-1}
1R	E	41.7	77.3
	Z	34.2	75.1
2R	E	14.0	
	Z	11.9	
2R'	E	63.3	
	Z	60.1	
3	E	38.6	65.7
	Z	29.8	

[a] The resonance energies are calculated by means of the following expression: RE = $(\Delta_f H^o(CH_4) - \Delta_f H^o(CH_3)) - (\Delta_f H^o(\text{diazenes}) - \Delta_f H^o(\text{1,2–diazaallyls}))$ [21], supposed that 1R–3R to be carbon centered radicals.

atom X, $P_{\mu\mu}$ is a diagonal element of the bond order matrix) on the radicals in position 1 and 3 change slightly. The electron densities on the C— and N—atoms are very similar, while substantial deviation was found at the reactive centres (C— or/and N—atom). The π—spin density correlates with the reactivity of the radicals in combination reactions [17,36] and with the coupling constants of ESR measurements [37b]. A reactivity difference was proposed for the C— and N—atoms in radical 3R by means of UHF—AM1 and AM1/C1 3x3 calculations [24].

In radical combinations, the SOMOs (Singly Occupied MOs) interact with each other and correlate with the reactivity of the radicals [36]. The calculated SOMO energies show, that the nucleophilicity of alkyl radicals increases with the alkyl—substitution [28b,32]. In radicals 1R–3R, the nucleophilicity increases when one of the alkyl C—atoms is substituted for N in the order 2R'>2R>1R>3R.

Rotational and inversional barriers of 1–3 and 1R–3R

The (AM1—HE) calculated rotational profiles of 1 and radical 1R (around the C=C and C—C bonds), those of 2 and radical 2R and 2R' (around the C=N and C—N bonds) and those of 3 and radical 3R (around the N=N and N—N bonds) are depicted in Figs. 1–3. The characters of the rotation profiles of molecules are similar. The maxima of the rotational barriers are at $\Theta = 90^{\circ}$ in 1 and at $\Theta = 105^{\circ}$ in 3. The profile of 2 has a plateau in the range of 75–125°. This departure is due to lone—pair repulsions in molecules [18b].

The calculated height of the barrier of rotation around the N=N bond (182.3 kJ mol^{-1}) is considerably higher than those around the C=C bond (136.3 kJ mol^{-1}) in butene—2 (AM1—HE) and around the C=N bond (105.0 kJ mol^{-1}). A recent experimental value for 2—butene is 271.7 ± 8.8 kJ mol^{-1} [11a]. The calculated (AM1—HE)

Table V

The calculated and experimental geometries of *trans*– and *cis*–azomethane

	MINDO/3	MNDO	AM1	exp.[b]
r(N=N)/pm	119.2	122.2	122.5	124.7 [29a]
	(116.2)	(120.8)	(120.6)	(125.4) [29b]
r(C–N)/pm	140.0	147.5	145.5	148.2 [29a]
	(143.4)	(147.8)	(145.5)	(148.0) [29b]
< CNN/degree	127.6	116.6	119.5	112.0 [29a]
	(138.9)	(127.3)	(126.9)	(119.3) [29b]

[a] The geometrical parameters of the *cis* isomer are in parenthesis.

[b] The symmetries of the most stable *trans* and *cis* isomers are C_{2h} and C_{2v} [29], respectively.

Table VI

The calculated geometries of 1–methyl–1,2–diazaallyl radical[a]
$C^1H_3 - N^1 \cdots N^2 \cdots C^2H_2$

		MINDO/3–UHF	MNDO–HE	AM1–HE	AM1–UHF
r(N¹–N²)/pm	E	118.0	126.5	126.8	
	Z		(124.2)	(124.5)	(124.8)
r(C¹–N¹)/pm	E	127.0	135.5	134.0	
	Z		(136.3)	(134.9)	(135.6)
r(C²–N²)/pm	E	138.9	145.9	144.6	
	Z		(146.7)	(143.7)	(144.8)
<C¹N¹N²/	E	151.3	115.6	120.0	
degree	Z		(126.0)	(128.2)	(127.8)
<C²N²N¹/	E	133.1	117.3	118.0	
degree	Z		(128.8)	(126.4)	(125.6)

[a] The geometries of the E conformers are in parenthesis.

rotational barrier is significantly lower for the rotation around the N=N bonds than the barrier heights determined by other theoretical methods (*ab initio* with different
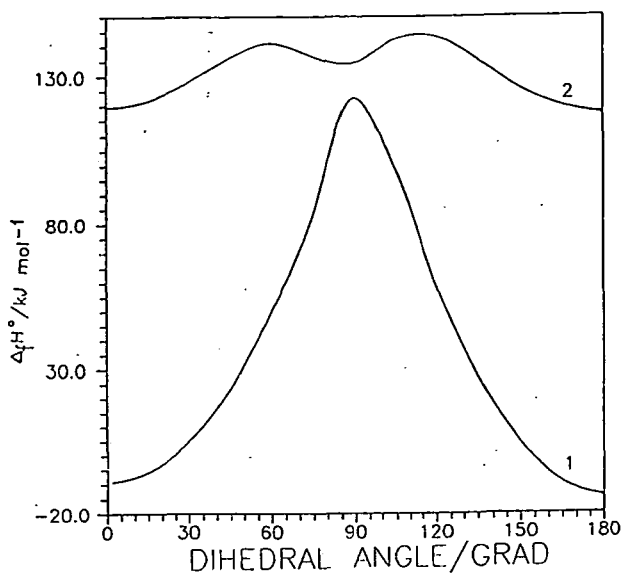
Figure 1:   Rotational barriers of the 2—butene and the 1—methylallyl radical,
            calculated by means of AM1—HE: 1: rotation around the C=C bond,
            2: rotation around the C—C bond.

basis sets, MNDO CI, *etc.*: 247.0—351.8 kJ mol^{-1}) [10], too.

The character of the rotational profiles of the radicals is similar: all have a valley —
a local minima at $\Theta = 90^{\circ}$, which is the less stable allenic form of the radical. The
heights of the barriers of radical 1R and 3R are 26.3 and 10.7 kJ mol^{-1}, respectively.
The barrier height around the N—N σ—bond in hydrazines, determined by means of
ESR—techniques, is 24 kJ mol^{-1} [38] (which is higher than the barrier for rotation
around the C—C σ—bond by circ. 4 kJ mol^{-1}). The allyl radical delocalization energies
(ADE) [37b] were calculated from the barrier heights of allyl—type radicals (determi—

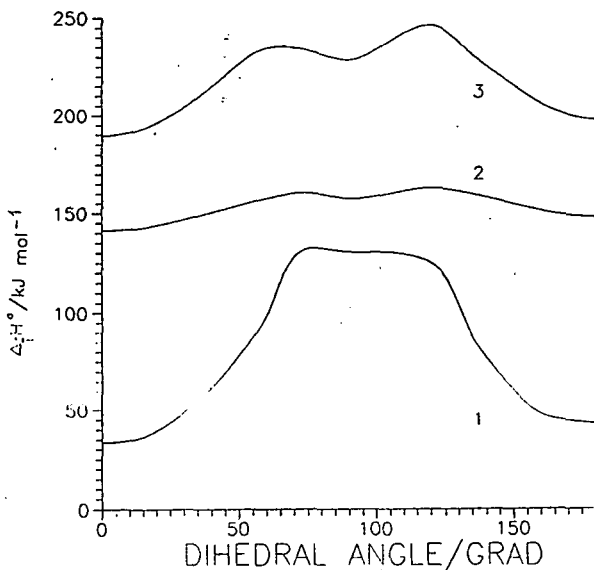*Figure 2:* Rotational barriers of N—ethylidenemethylamine around N=N double bond (1), 1—methyl—1—azaallyl (2R) around C—N (2) and 1—methyl—2—azaallyl (2R') radicals around C—N bonds (3), calculated by means of AM1—HE.

ned by ESR—technique) and from that of the σ—bond. The calculated ADE for the allyl radical was found to be circ. 48 kJ mol⁻¹ [37b]. Since the calculated values of the barrier heights are significantly lower than expected on the basis of the experimental data (for allyl—type radicals (see e.g.[37])), only a qualitative approximation can be made for the delocalization energy of 3R. (MNDO and AM1 underestimate the rotational barrier heights [20].) The rotational barrier in 3R is less than that in 1R. Thus,for ADE a smaller value is predicted than for the allyl—type radicals, considering the greater rotational barrier for the N—N σ—bond [38] than that for the C—C σ—bond.

The barrier heights of the radicals 2R and 2R' are also different — 2R' has a greater barrier (35 kJ mol⁻¹). We have found that 2R' is a more stable radical than 1R, 2R and 3R (see Table IV). On the basis of the calculations a qualitative conclusion was drawn to explain the possible mechanism of the isomerization and the experimental results [14b]. The barrier height of inversion in azomethane (Fig. 4) was found to be lower than the rotation barrier, 134.7 and 182.3 kJ mol⁻¹ (related to the *cis* isomer), respectively. The situation in radical 3 is reversed (Fig.4). The barrier height for inversion and rotation are 112.8 and 12.7 kJ mol⁻¹. Isomerization is preferable by a rotational mechanism. The rotational and inversional barriers at compound 2 are almost the same (Fig.5). At radical 2R and 2R' the rotation is more favourable than the inversion.

Under the experimental conditions (around 400 K) [14b], for which the reactions of alkyl— substituted 1,2–diazaallyl radicals were studied, an equilibrium is expected between Z and E radicals. The lack of *cis*—products can be attributed to the lower reactivity of Z than E radicals and the unstability of the products of Z radicals.

Conclusions

The AM1 method predicts greater stability for the *cis* and *syn* isomers of the compounds 2–3 and the radicals 2R, 2R' and 3R. The nucleophilicity increases in the order 2R' > 2R > 1R > 3R while the thermodynamic stability (RE and SE) decreases in the order 2R' > 1R > 3R > 2R. On the basis of the height of the barrier of rotation around the N–N and C–C bonds, the delocalization energy is lower in radical 3 than in 1R. On the basis of relative barrier heights of the rotation and inversion, an equilibrium was proposed between the E and Z conformers of the radicals at 400 K. The absolute values of the barrier heights are not acceptable because the semiempi-
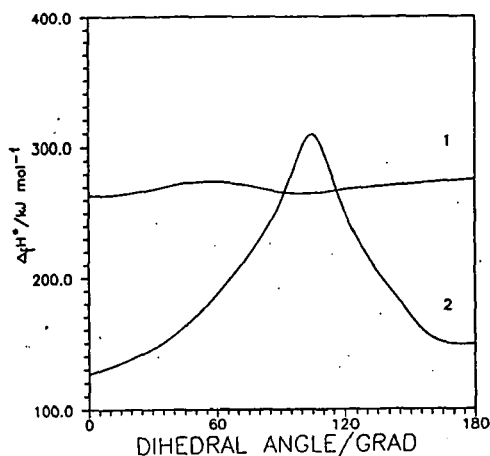
Figure 3: Rotational barriers of dimethyldiazene and the 1–methyl–1,2–diazaallyl radical, calculated by means of AM1–HE: 1: rotation around the N=N bond, 2: rotation around the N–N bond.
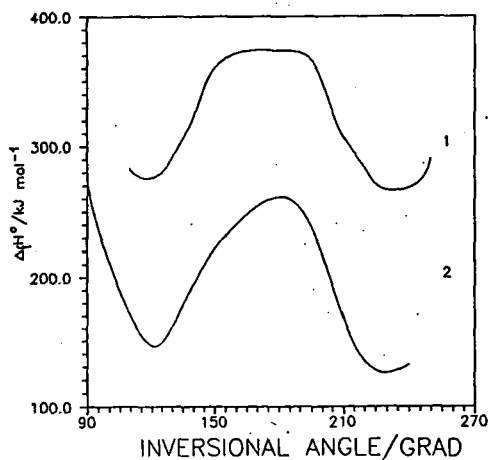

Figure 4: MEPs of inversion of the 1–methyl–1,2–diazaallyl radical (1) and azomethane (2), calculated by means of AM1–HE.
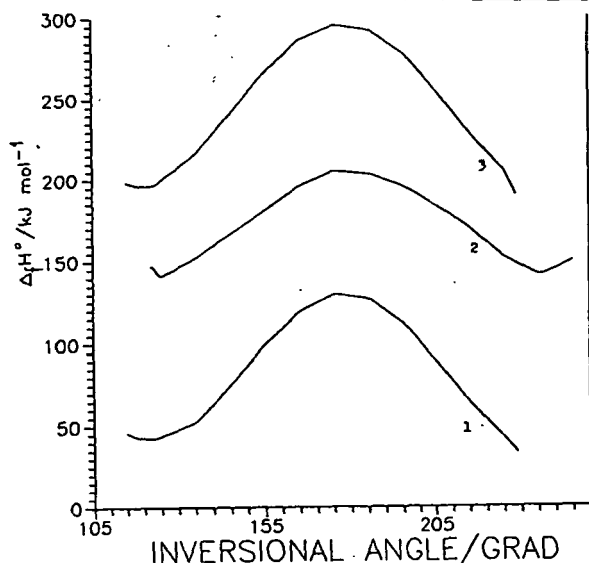
Figure 5: Inversional barriers of the N—ethylidene—methylamine and 1—methyl— —1—azaallyl and 1—methyl—3—azaallyl radical, calculated by means of AM1—HE. 2: 1; 2R: 2; 2R⁺: 3.

rical quantum chemical methods applied for the calculations handle the interactions of lone—pair and double lone—pairs of electrons with error.

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