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O⁽⁻⁾---C Interactions and Bond Formation in 1-Naphtholate Anions with *Peri*-Located Electrophilic Carbon Centres.

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Jonathan C. Bristow, Matthew A. Addicoat, John D. Wallis*

School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK.

Abstract.

The first *peri* interactions between naphtholate oxyanions and electrophilic double bonds are described. Tetramethylguanidine forms crystalline salts with 8-acetyl- and 8-benzoyl-naphthol which show O---C distances for the anions in the range 2.558-2.618 Å and small increases in carbonyl pyramidalities over the corresponding naphthols, whereas DMAP forms only hydrogen bonded complexes. Replacement of the acyl group with an alkene leads to intramolecular O-C bond formation for just the most electron deficient alkenes, with long *peri* O-C bonds (1.508 and 1.521 Å) observed in one case. However, both cyclised and uncyclised examples can be deprotonated to give cyclic structures according to NMR, and DFT calculations suggest very long *peri*- O-C bond lengths of 1.540 and 1.622 Å for two of these anions.

Introduction.

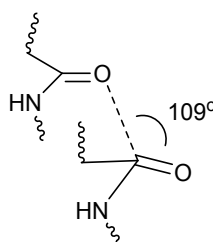


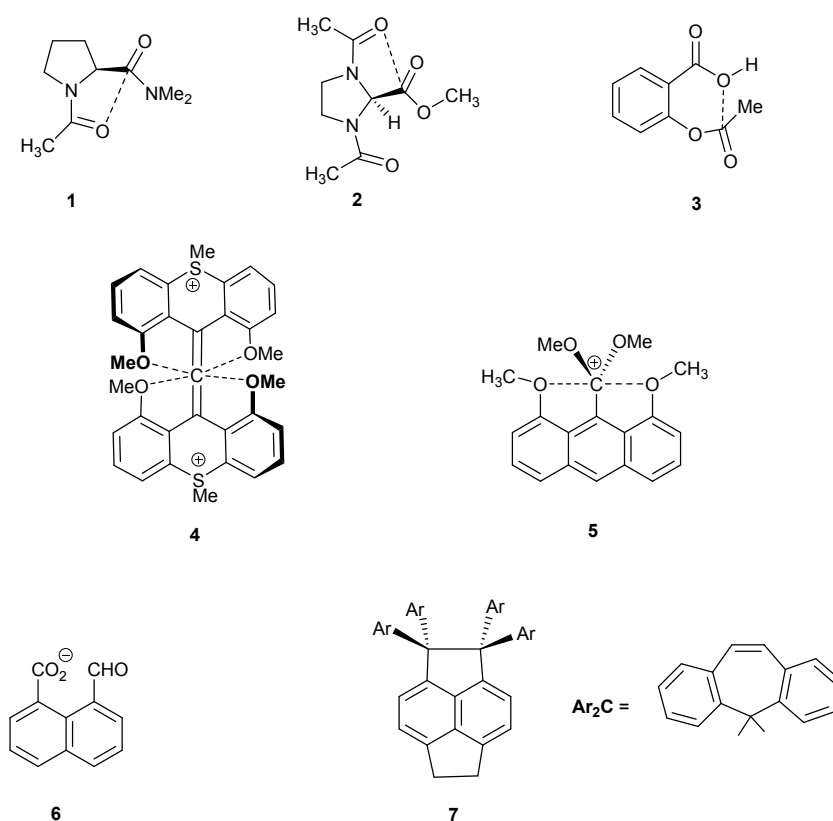
Figure 1. $n\text{-}\pi^*$ interaction between two amide carbonyl groups, with the acceptor carbon being slightly pyramidalised towards the approaching oxygen atom.

There is considerable current interest in molecular interactions between oxygen and carbon, from multipolar orthogonal interactions at longer separations ($> ca. 3.0 \text{ \AA}$)¹ to $n\text{-}\pi^*$ interactions at shorter distances.² $n\text{-}\pi^*$ interactions between carbonyl groups (Fig. 1) play an important role in stabilising the conformations of proteins³ and polymers such as poly-lactic acid.⁴ This is particularly clear in collagen which lacks hydrogen bonds.⁵ Such interactions, with energies in the range $0.3\text{-}0.7 \text{ kcal mol}^{-1}$, rank alongside hydrogen bonding in importance for the stabilisation of the conformations of most proteins, for example in the alpha helix. The angle of approach of the oxygen to the carbonyl bond, $ca. 109^\circ$ for optimisation of orbital overlap (known as the Bürgi-Dunitz angle), and a small pyramidalisation at the carbonyl carbon atom are signatures of this stereoelectronic interaction.⁶ Such interactions determine conformations of small molecules such as 1,⁷ are competitive with hydrogen bonds⁸ and affect the electrophilicity of the acceptor carbonyl, as in 2, where the ester group only forms one such interaction (Scheme 1).⁹ $\text{N}\cdots\text{C}=\text{O}$ $n\text{-}\pi^*$ interactions are also well known, as observed recently in the structure of the pyridine/formaldehyde adduct determined by rotational spectroscopy, with $\text{N}\cdots\text{C}$: 2.84 \AA and $\angle\text{N}\cdots\text{C}=\text{O}$ 102.8° , and a small pyramidalisation at the carbon atom predicted by calculation.¹⁰

Aspirin 3 and its anion are calculated to have a $\text{HO}\cdots\text{C}=\text{O}$ or $\text{O}\cdots\text{C}=\text{O}$ interaction between the carboxylic acid or carboxylate group and the ester group respectively, the latter being shorter (2.71 \AA) and more energetically favourable, and may account for aspirin's high acidity and its action as an acyl transfer agent.¹¹ $\text{O}\cdots\text{C}$ interactions occur too when oxygen lone pairs stabilise an electron-deficient alkene or a carbocation, with 4 and 5 being particular examples¹² and have been reported between an ether and a ketone¹³ and between an ester carbonyl and a nitrile.¹⁴

The *peri*-naphthalene scaffold's unique structure has been used considerably for studying molecular interactions especially those involving nitrogen,¹⁵⁻¹⁹ and has provided an

effective molecular environment for the observation of C-C bonds as long as 1.75 Å) in 720 and for the study of rare sulfur functionalities such as *vic*-disulfoxides and *bis*(sulfonyl)nitroxide radicals and for preparation of a source of S=O²¹ as well as S---C interactions.²² We recently reported two types of interaction between carboxylate and aldehyde groups in the anion 6 for a range of salts of naphthaldehydic acid (Fig. 2).²³ In most cases



Scheme 1.

a carboxylate oxygen atom was directed at the carbon of the aldehyde with $n\text{-}\pi^*$ interaction distances in the range 2.445-2.630 Å, but in two cases the aldehyde group directed its hydrogen atom at the face of the carboxylate group leading to short $(\text{O}_2\text{C}^{\ominus}\text{---H}(\text{C}=\text{O}))$ contacts of 2.29 and 2.42 Å, to provide the first known examples of this interaction. We now report our investigations of intramolecular 1,5 interactions between the more reactive 1-naphtholate anion and either a ketone or one of a range of electron deficient alkenes located at the other *peri*-position of the naphthalene system. It is of interest to compare the results to the corresponding interactions of a neutral hydroxyl group or a dimethylamino group with electrophiles. Such *peri*-interactions with a neutral methoxy oxygen, e.g. $\text{MeO}\text{---C}=\text{O}$ and

MeO---C=C are rather insensitive to the nature of the neighbouring group (O---C: 2.526 Å, 167.1(1)°; O---C: 2.672 Å, 167.1(1)°) while for dimethylamino groups the Me₂N---C separation is highly sensitive to the electrophile, and leads to N-C bond formation in the more reactive cases.¹⁵⁻¹⁷

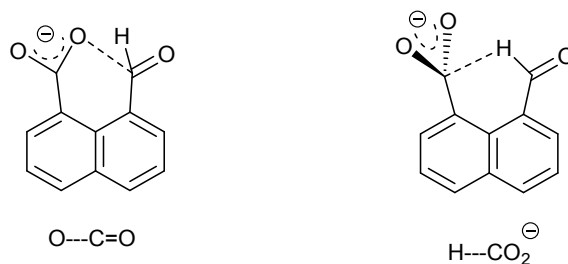
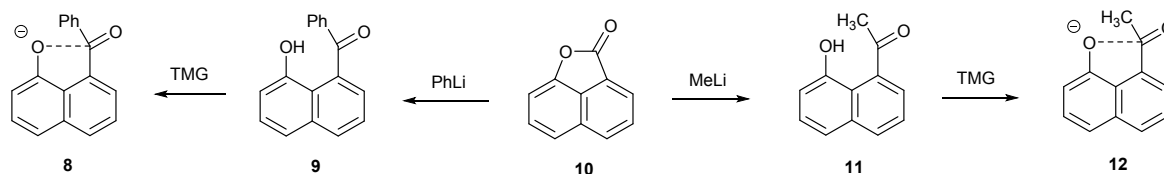


Figure 2. Two different types of interaction between functional groups in 6, the anion of naphthalaldehydic acid, observed in its salts with (a) metal ions or triphenylguanidinium (left) or (b) N,N,N',N'-tetramethylguanidinium or 4-dimethylaminopyridinium cations (right).

Results and Discussion.

Molecular structures of *peri*-hydroxy ketones and their anions.

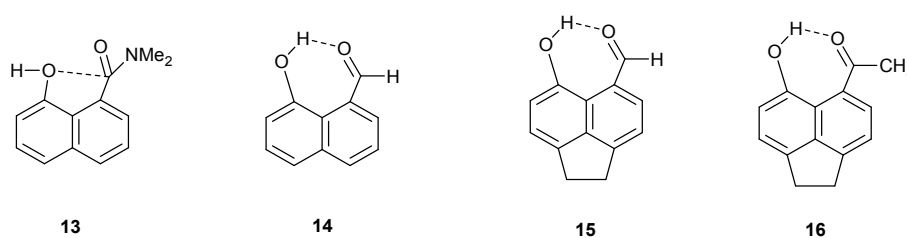


TMG = N,N,N',N'-tetramethylguanidine

Scheme 2: Syntheses of anions 8 and 12.

Peri-naphthalene hydroxyketones 9 and 11 were prepared by ring opening of the lactone 10 with organolithium reagents (Scheme 2). X-ray crystal structure determinations showed the presence of HO---C=O interactions in both cases (Fig. 3). The ketone group presents a face to the hydroxyl group. The hydroxyl group is bent towards the ketone, and the ketone bent away, such that the HO---C separations are 2.607(3) Å for the phenyl ketone and 2.621(3) and 2.623(3) Å for the two independent molecules of the methyl ketone. The HO---C=O angles are 115.82(14)° for the former and 108.3(2)° and 111.9(2)° for the latter, close to the optimal approach of a nucleophile to a carbonyl group. For all three molecules, the *peri* groups are displaced slightly to opposite sides of the naphthalene plane and there are small pyramidalisations at the carbonyl groups displacing the carbonyl carbon towards the hydroxyl

group by 0.051(2)-0.053(2) Å indicating that the interaction represents an early stage of the corresponding addition reaction. Similar interactions are seen between a hydroxyl and an amide group in *peri*-naphthalene 13,¹⁶ and in hydroxyl/aldehyde interactions in triptycenes (HO---C=O: 2.621-2.624 Å).¹³ However, in related naphthaldehydes 14 and 15, and also in the methyl ketone 16, an intramolecular O-H---O hydrogen bond is preferred.^{13,24} In the latter case, the effect of the ethylene bridge at the other set of *peri* positions, is to splay the two functional groups apart and this can now accommodate the hydrogen bond with an acetyl group lying coplanar with the naphthalene ring. In both 9 and 11, the molecules are linked together by hydrogen bonding between hydroxyl and carbonyl groups (ESI Fig. S1).



Scheme 3. O---C vs C=O---H interactions in selected naphthalene systems.

Treatment of these two ketones with N,N,N',N'-tetramethylguanidine (TMG) led to deprotonation of the hydroxyl groups to give TMG-H⁺ salts of the corresponding naphtholate anions 8 and 12. Crystals of the salts were grown by slow evaporation of solutions in dichloromethane under nitrogen and their crystal structures determined (Fig. 3). There are two crystallographically unique cations and anions for the TMG salt of the phenyl ketone, and four unique cations and anions for the salt of the methyl ketone. In both crystal structures pairs of anions and pairs of cations are linked together into approximate square motifs by hydrogen bonding (Fig. 3d and S2). The deprotonation of the hydroxyl group in the salt of the phenyl ketone is strongly supported by the shortening of the C-O bond from 1.346(2) to 1.299(2) and 1.306(2) Å, the lengthening of the two nearest aromatic C-C bonds from 1.379(3) and 1.432(2) Å to 1.385(3)/1.399(3) and 1.451(3)/1.445(3) Å, and the compression of the *ipso* bond angle from 120.54(17)° to 116.75(17) and 117.22(17)° in response to the presence of a more electron-rich substituent.²⁵ Furthermore, the two hydrogen atoms per TMG-H⁺ cation were located in difference Fourier maps and refined with reasonable positions, isotropic displacement parameters (0.020-0.044 Å²) and hydrogen bond distances to oxyanions (1.78-1.99 Å). Similar

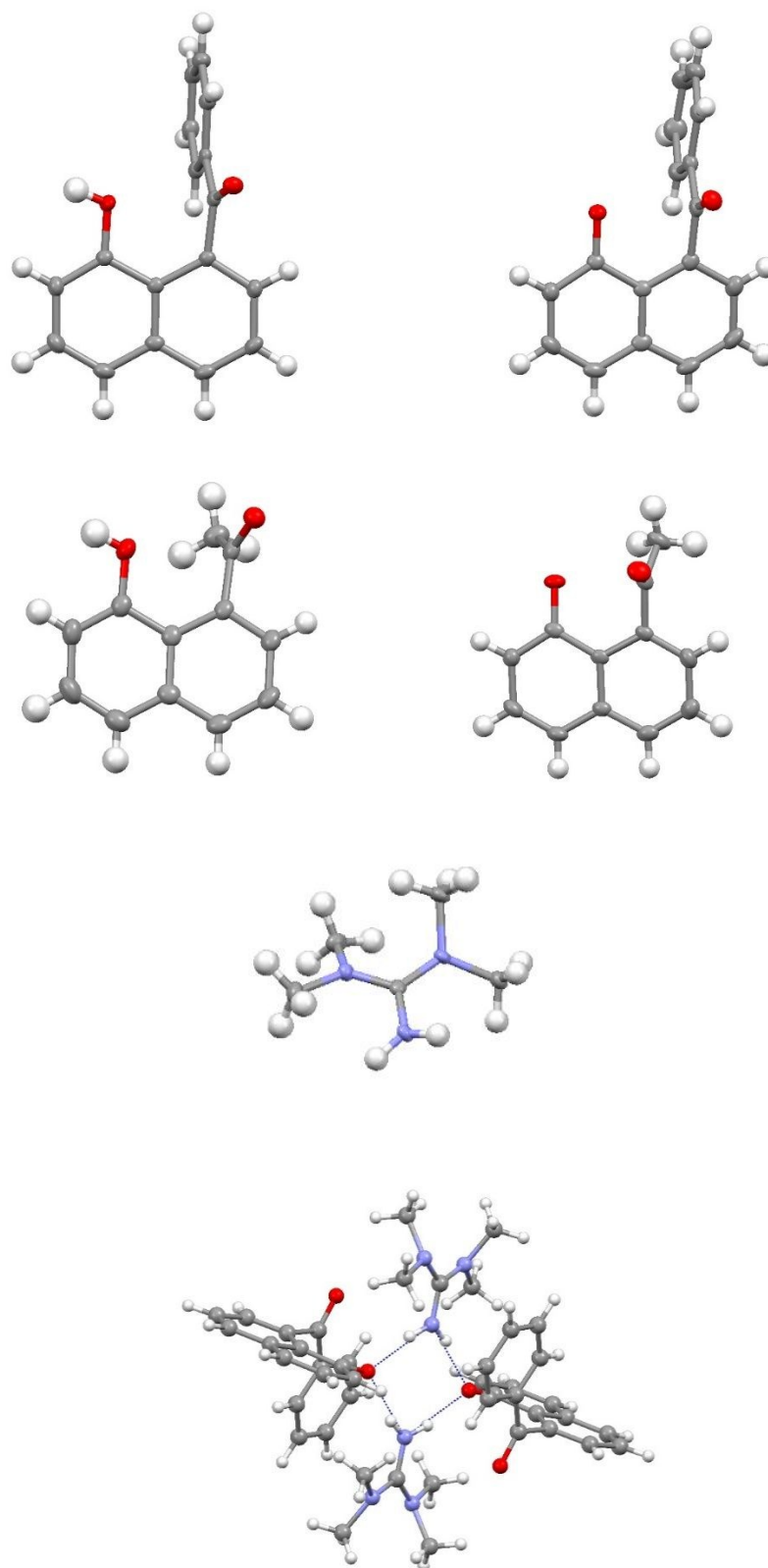
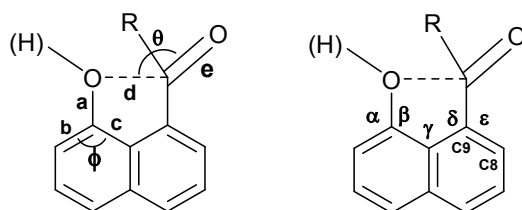


Figure 3. Molecular structures of (a) the *peri*-hydroxy phenyl ketone 9 (top left) and its anion 8 (top right), (b) the methyl ketone 11 (second row, left) and its anion 12 (second row, right), (c) one example of the twisted TMG-H⁺ cation showing the torsion (56-65°) between the two adjacent N-CH₃ bonds (centre) and (d) the hydrogen bonding arrangement of two TMG-H⁺ cations and two 8 anions in a square motif (bottom), a pattern also observed for the corresponding salt of anion 12.

Table 1. Selected geometric data for naphthols 9 and 11 and the TMG-H⁺ salts of their anions 8 and 12. View Article Online
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	a /Å	b /Å	c /Å	φ /°	d /Å	e /Å	θ /°	pyr ^a
9	1.346(2)	1.379(2)	1.432(2)	120.54(17)	2.607(3)	1.228(2)	115.82(14)	0.051(2)
11	1.367(3)	1.367(3)	1.422(3)	120.8(2)	2.621(3)	1.219(3)	108.25(15)	0.058(2)
	1.364(3)	1.367(3)	1.423(3)	121.28(19)	2.623(3)	1.219(3)	111.90(15)	0.063(2)
TMG-H ⁺ .8	1.306(2)	1.385(3)	1.451(3)	117.22(17)	2.571(2)	1.224(2)	109.29(14)	0.056(2)
	1.299(2)	1.399(3)	1.445(3)	116.75(17)	2.558(2)	1.222(2)	105.58(13)	0.060(2)
TMG-H ⁺ .12	1.306(2)	1.392(3)	1.449(3)	117.17(19)	2.574(3)	1.221(2)	108.38(16)	0.076(3)
	1.304(2)	1.395(3)	1.444(3)	116.98(15)	2.592(2)	1.218(3)	106.93(13)	0.070(2)
	1.293(3)	1.404(3)	1.454(3)	116.0(2)	2.618(2)	1.226(2)	112.50(16)	0.075(2)
	1.307(2)	1.392(3)	1.442(3)	117.24(19)	2.597(2)	1.211(3)	104.28(14)	0.068(2)

	α /°	β /°	γ /°	δ /°	ε /°	τ ^b /°	Δ ^c (O, C) \ Å
9	123.69(17)	115.76(15)	122.62(17)	124.80(17)	115.41(15)	62.6(2)	0.059(3), -0.073(3)
11	123.1(2)	116.07(19)	122.83(19)	123.52(18)	116.30(19)	65.2(3)	0.153(3), -0.342(3)
	122.70(19)	116.02(18)	123.54(18)	124.04(18)	115.81(2)	67.7(3)	0.104(3), -0.157(3)
TMG-H ⁺ .8	124.08(8)	118.69(17)	120.65(16)	123.20(16)	116.17(18)	73.4(2)	0.083(2), -0.161(3)
	124.14(17)	119.11(16)	120.41(16)	122.28(16)	116.80(17)	80.6(2)	0.099(2), -0.236(3)
TMG-H ⁺ .12	123.5(2)	119.36(18)	121.03(18)	122.4(2)	117.24(19)	75.3(3)	0.075(2), -0.030(3)
	123.55(19)	119.47(18)	121.30(19)	121.93(18)	117.16(19)	79.5(2)	0.202(2), -0.145(3)
	123.7(2)	120.31(18)	120.5(2)	123.3(2)	116.92(19)	69.7(3)	0.084(2), -0.041(3)
	123.44(19)	119.30(17)	121.55(19)	120.98(19)	117.97(18)	86.0(2)	0.298(2), -0.246(3)

^a pyr = pyramidal, deviation of the carbonyl carbon from the plane of its three neighbouring atoms towards the *peri* O atom; ^bτ = torsion angle: C8-C9-C=O; ^cΔ = deviation from best plane of the naphthalene skeleton.

features are seen in the four anions from the salt of the methyl ketone, for example the C-O bond and *ipso* angles lie in the ranges 1.293(3)-1.307(2) Å and 116.0(2)-117.24(19)° *cf.* 1.367(3)/1.364(3) Å and 120.8(2)/121.28(19)° in the parent ketone 11. The delocalisation of charge into the aromatic ring will reduce the negative charge at the naphtholate O atom. For comparison, the crystal structures of 2-dimethylamino- and 2,6-bis(dimethylamino)-phenolate show O⁽⁻⁾-C bonds in the range 1.300(5)-1.334(7) Å (average: 1.312 Å) and *ipso* bond angles in the range 116.1(4)-117.8(5)° (average: 116.8°).²⁶

For the TMG-H⁺ salt of the phenyl ketone the O⁽⁻⁾---C interaction distance is decreased on deprotonation from 2.607(3) to 2.571(2) / 2.558(2) Å. The pattern of in-plane displacements of the *peri*-groups in this naphtholate anion is the same as for the parent naphthol, but the displacements are less in the anion. Furthermore, the ketone group is twisted further out of the naphthalene plane. These two factors result in smaller, more favourable, Bürgi-Dunitz angles between the oxyanion and the carbonyl group of 109.29(14) and 105.58(13)° compared with 115.82(14)° in the corresponding naphthol. These trends are followed too for the four unique anions in the salt of the methyl ketone with O⁽⁻⁾---C interaction distances of 2.574(3)-2.618(2) Å, angles of attack of 104.28(14)-108.38(16)° and greater torsional twists of the ketone group (τ , Table 1) of 69.7-86.0° (average 77.6°) *cf.* 65.2-67.7°. For each anion of 8 and 12, the pyramidalisation at the carbonyl carbon has increased by 10-20% compared to the neutral species (Table 1). There is thus evidence for a closer O---C $n-\pi^*$ interaction in the anions than in the neutral naphthols. For the corresponding methyl and phenyl ketones in which a dimethylamino group replaces the oxyanion, the N---C contacts are 2.5290(13) and 2.5376(19) Å, very similar to those for the O⁽⁻⁾---C interactions, and the pyramidalisations 0.0942(10) and 0.0722(14) Å, just slightly larger than for those in the naphthoates.

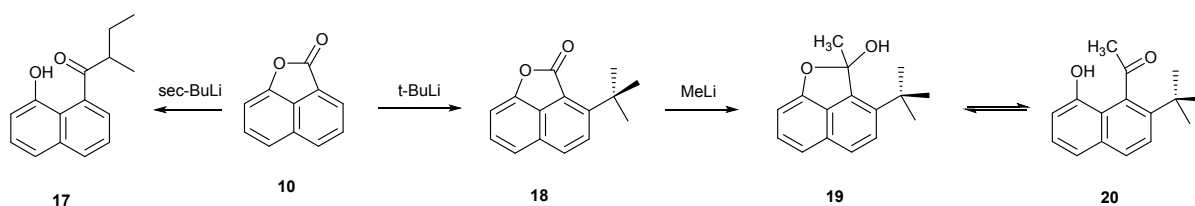
Comparison of the solution state ¹H and ¹³C NMR spectra of phenyl ketone 9 with those of its TMG-H⁺ and sodium salts in DMSO-d₆ suggest that, in contrast to the solid state, the naphthol is only partially deprotonated in the TMG-H⁺ salt in solution. In the fully deprotonated sodium salt the carbon *ipso* to the naphtholate oxygen resonates at δ_C : 168.1, compared to δ_C : 152.3 in the neutral compound. However, in the TMG-H⁺ salt this resonance occurs at 161.4 ppm, intermediate between these positions. The central carbon from TMG/TMG-H⁺ resonates at δ : 163.6 in this salt, which is in between δ : 166.1 for neutral TMG and δ : 161.0-162.3 for a series of TMG-H⁺ salts of triflate and carboxylate anions.²⁷ The TMG-H⁺ salt of the methyl ketone 11 showed similar results. In contrast, NMR studies on the sodium and TMG-H⁺ salts of naphth-1-ol in THF-d₆ suggest that the equilibrium with TMG lies strongly towards the deprotonated state, suggesting that the *peri*-ketone can stabilise the oxyanion.

Molecular complexes of *peri*-hydroxy ketones with DMAP.

In contrast to reaction with TMG, evaporation of solutions of the methyl and isobutyl ketones 11 and 17, and also the lactol 19, with 4-dimethylaminopyridine (DMAP) gave crystals of

molecular complexes in which DMAP was hydrogen bonded to the hydroxyl group but had not deprotonated it. The structures of the three substances were determined by X-ray crystallography. Selected molecular geometry information is summarised in Table 2, and the complexes are illustrated in Fig. 4 and the ESI. The assignment of the structures as hydrogen bonded complexes is supported by the lengths of the naphthol HO-C bonds (1.342(2)-1.356(3) Å) and the size of the corresponding *ipso* angles (120.0(2)-120.5(2)°). Furthermore, the size of the endocyclic angle at the pyridine N atom in DMAP (115.3-115.8°) is consistent with the neutral molecule but not the cation (*ca.* 120.2°).²³ The HO---C interaction distances lie in the range 2.508(3)-2.603(3) Å, which are a little shorter than in the methyl ketone 11 (2.621-2.623 Å). The O---N distances in the three hydrogen bonded complexes lie in the range 2.580(2)-2.627(3) Å, and the hydrogen bonding is close to linear at the hydrogen.

Of particular interest is the reaction of DMAP with the lactol 19. The latter is prepared in two steps by reaction of the lactone 10 with *t*-butyl lithium to give the *ortho*-substituted lactone 18, followed by reaction with methyl lithium to give 19 (Scheme 4). The steric compression between the *t*-butyl group and lactone or lactol groups in 18 and 19 is demonstrated in their crystal structures (ESI). In its DMAP complex, the lactol 19 has ring-opened to the ketone form 20 and shows the shortest O---C=O distance (2.508(3) Å) in a *peri*-naphthalene, due to the *ortho-t*-butyl group which pushes the ketone group back towards the hydroxyl group. Indeed, to the best of our knowledge, this is the first example of a *peri*-naphthalene with electrophilic and nucleophilic groups displaced *towards* each other, but without forming a bond.



Scheme 4: Synthesis of ketone 17 and lactol 19.

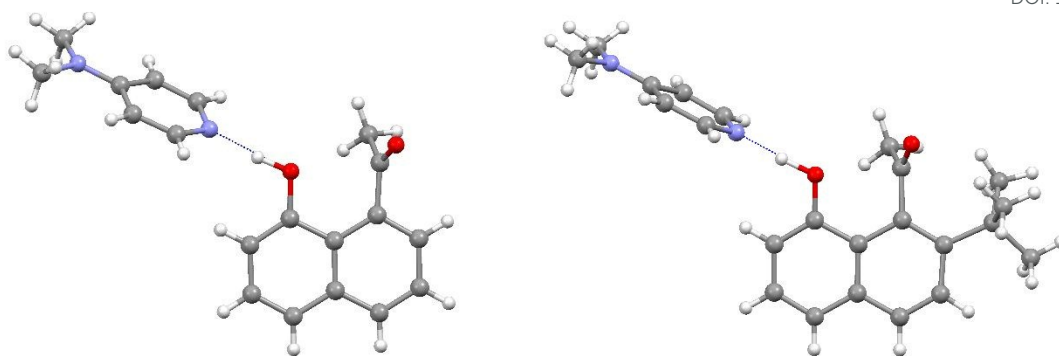
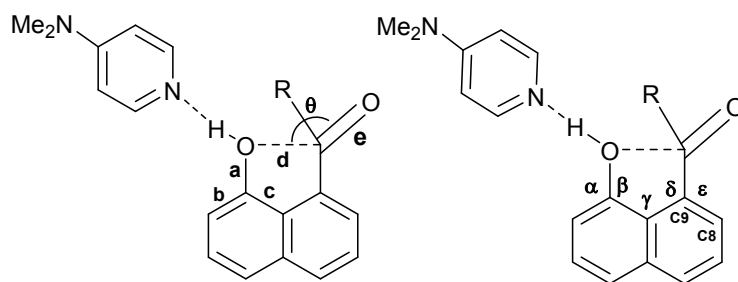


Figure 4. Molecular structures of the hydrogen bonded DMAP complexes of *peri*-hydroxy methyl ketone 11 (left) and its *ortho*-*t*-butyl substituted derivative 20 (right), showing how the ketone group is deflected away from the hydroxy group in the first case, but towards it in the second case.

Table 2. Selected geometric details for DMAP complexes of 11, 17 and 20.



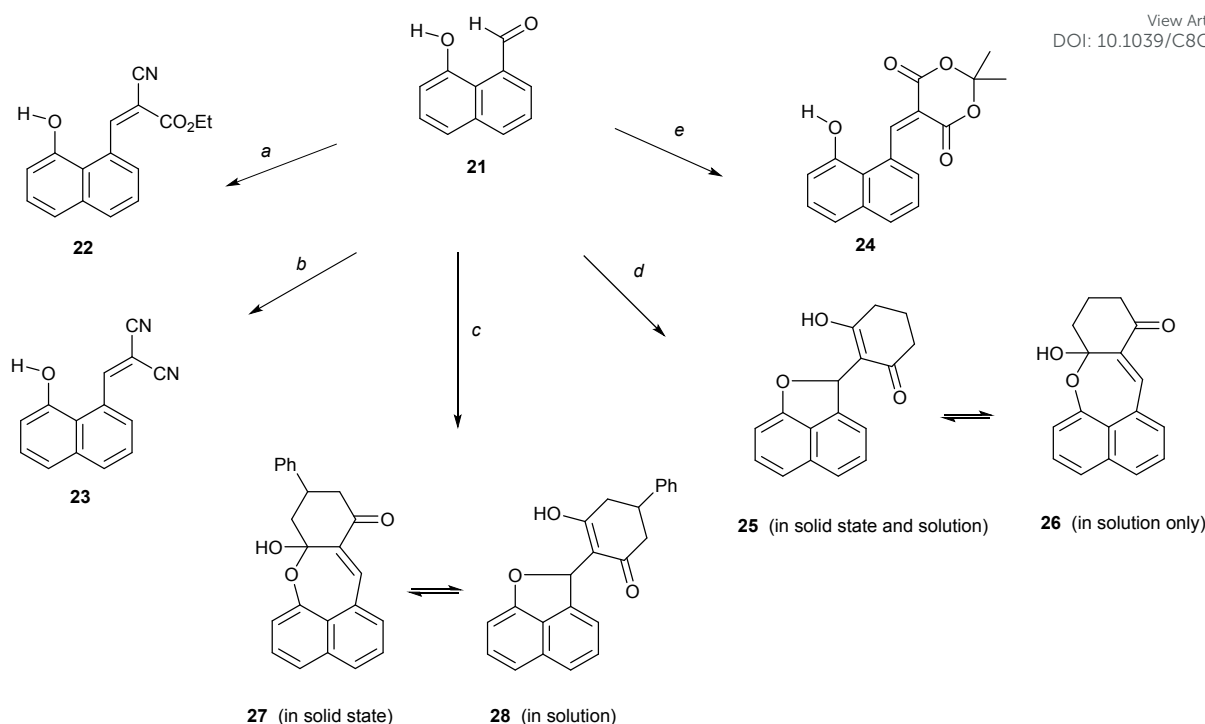
	N---O	a /Å	b /Å	c /Å	φ /°	d /Å	e /Å	θ /°
11. DMAP	2.616(2)	1.356(3)	1.367(3)	1.430(3)	120.1(2)	2.577(3)	1.218(2)	107.52(14)
17. DMAP	2.627(3)	1.352(3)	1.376(3)	1.425(3)	120.5(2)	2.603(3)	1.221(3)	111.97(15)
20. DMAP	2.580(2)	1.342(2)	1.366(3)	1.432(3)	120.00(19)	2.508(3)	1.206(3)	100.33(16)

	α /°	β /°	γ /°	δ /°	ϵ /°	τ^a /°	$\Delta(O, C) \backslash \text{Å}$
11.DMAP	123.7(2)	116.21(18)	122.5(2)	123.85(18)	116.57(19)	71.7(3)	0.067(3), -0.032(3)
17. DMAP	123.6(2)	115.9(2)	123.0(2)	123.22(19)	116.9(2)	62.7(3)	0.160(3), -0.263(3)
20. DMAP	122.51(19)	117.49(18)	122.85(18)	117.42(17)	121.71(18)	73.2(3)	0.260(2), -0.236(3)

^b τ = torsion angle: C8-C9-C=O.

Peri hydroxy alkenes and their salts.View Article Online
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Condensation of aldehyde 21²⁸ with active methylene compounds ethyl cyanoacetate, malononitrile and Meldrum's acid gave the expected Knoevenagel condensation products, alkenes 22-24. However, with cyclohexane-1,3-dione and 5-phenylcyclohexane-1,3-dione the reaction went a step further with the naphthalene's hydroxyl group adding to the electron-deficient alkene in the former case to give the fused furan derivative 25, or to a carbonyl group in the latter case to give the fused oxepine derivative 27 (Scheme 5). The structures were all determined by X-ray crystallography (Fig 4; 22-23: ESI; 24, 25, 27). For the uncyclised cases, 22-24, it is of particular note that the alkene groups are twisted rather less out of the naphthalene plane than are the carbonyl groups in ketones 9 and 11: (τ , Table 3) 41.1-48.8°, *cf.* 62.6-67.7°. This is indicative of weaker HO---C interactions for these alkenes, and greater preference for optimisation of conjugation of the alkene with the naphthalene ring which is limited only by a HO---H(alkene) contact of 2.22-2.26 Å between the *peri*-groups, and by a contact from an *ortho*-H atom of the naphthalene ring with a nitrile carbon (2.55-2.63 Å) for 22 and 23 or with the atoms of the carbonyl group (O: 2.70; C: 2.86 Å) for 24. The O---H contact between *peri*-groups may have an attractive component, given the polarisation of the alkene by two electron attracting groups, though the angle at hydrogen (HO---H-C = : 97.0-102.7°) is far from optimal for a hydrogen bond. This contrasts sharply with the corresponding series in which the more nucleophilic dimethylamino group replaces the OH group, which shows Me₂N---C distances of 2.531(2), 2.413(2) and 1.651(3) Å, with a long bond formed between the



Scheme 5. (a) $\text{NCCH}_2\text{CO}_2\text{Me}$, CH_3OH , $(^+\text{NH}_3\text{CH}_2)_2(\text{OAc})_2$ (cat.), $65\text{ }^\circ\text{C}$; (b) $\text{CH}_2(\text{CN})_2$, CH_3OH , $65\text{ }^\circ\text{C}$; (c) 5-phenylcyclohexa-1,3-dione, DMSO , $20\text{ }^\circ\text{C}$; (d) cyclohexa-1,3-dione, CH_3OH , $(^+\text{NH}_3\text{CH}_2)_2(\text{OAc})_2$ (cat.), $65\text{ }^\circ\text{C}$; (e) Meldrum's acid, DMSO , $20\text{ }^\circ\text{C}$.

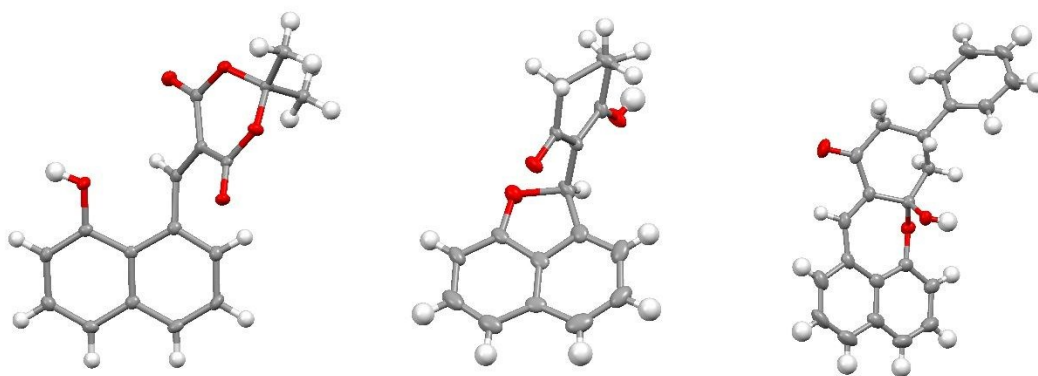


Figure 5. Molecular structures of Knoevenagel product 24, 25 (one of two unique molecules) and 27.

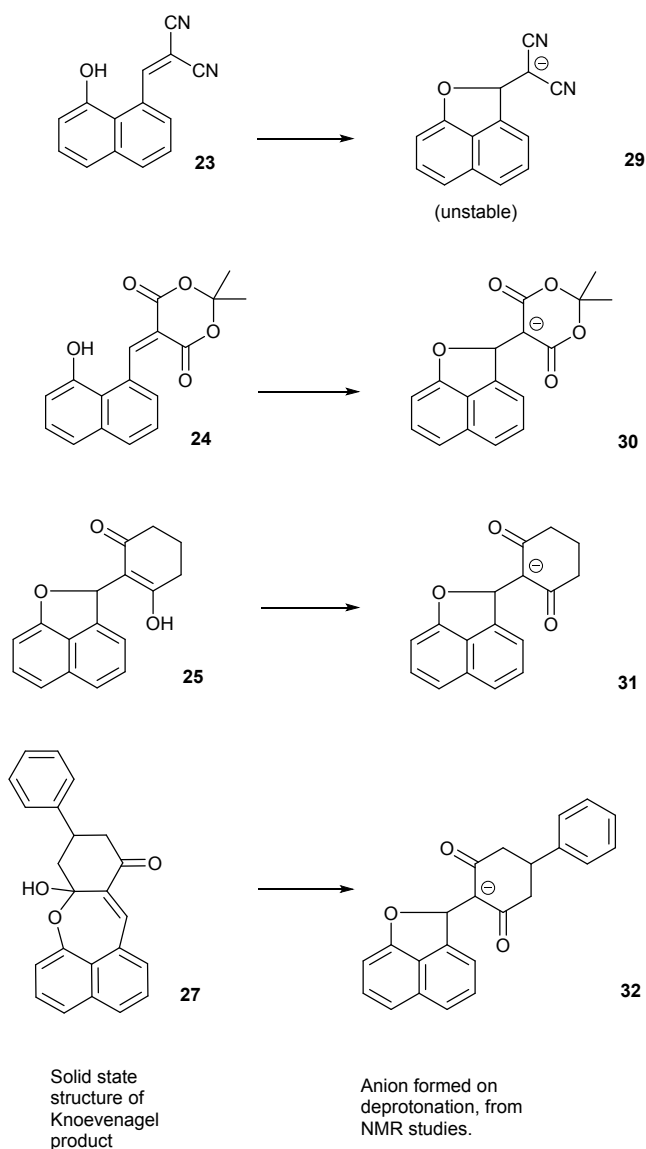
peri groups in the latter case.^{15,29} However, just a small further increase in the alkene's electron deficiency, by replacement of the cyclic diester group in 24 with a cyclic diketone, facilitates cyclisation in this hydroxyl series.

The X-ray crystal structure of the product from aldehyde 21 and cyclohexane-1,3-dione shows that it has ring closed structure 25 in which the hydroxyl group has added to the alkene and thus converted the dione to a β -hydroxy unsaturated ketone (Fig. 5 (middle)). The lengths

of the O-C bond formed between the *peri*-groups are 1.508(3) and 1.521(3) Å for the two independent molecules, which are surprisingly long for an Aryl-O-CHC₂ bond, for which the average value is 1.447 Å.³⁰ These bonds can be viewed as representing two points in the later stages of formation of an O-C bond.³¹ NMR studies show that in solution this cyclised structure is present as the main species along with a minor component 26 in a 17:3 ratio in CDCl₃. The product from 5-phenylcyclohexa-1,3-dione in DMSO-d₆ solution adopts the analogous fused furan structure 28 formed by addition to the alkene. However, the solid state crystallography shows that the *peri*-hydroxyl group has instead added to a carbonyl group to form a lactol and so completes a seven membered oxepine ring which is fused to both the naphthalene and cyclohexyl rings to give 27 (Fig. 5). The bonds from naphthalene to the *peri* atoms are necessarily splayed apart, and the lactol group shows the expected anomeric interaction with a short HO-C bond of 1.399(2) Å and the ring C-O bond lengthened to 1.457(2) Å.

Deprotonation of Knoevenagel products.

Knoevenagel products 23-25 and 27 were converted to salts using various organic bases and sodium hydride but we were unable to isolate any crystalline materials, despite exhaustive attempts, with “crispy foams” or gels being obtained instead, even though NMR evidence suggested pure materials had formed (Scheme 6). In summary, the Knoevenagel products 24, 25 and 27 in which the alkenes are activated by two in-plane carbonyl groups were deprotonated with mild bases such as DABCO or DMAP to give stable anions 30-32 respectively with an O-C bond between the *peri* groups and the negative charge stabilised by the two carbonyl groups. In contrast, the naphthol with the less electrophilic ethenedinitrile group 22, like the ketones 9 and 11, was not deprotonated with DABCO or DMAP, but was partially deprotonated by the stronger guanidine base TMG. It was completely deprotonated by sodium hydride, leading to the purple anion 29, formed by addition of the oxygen anion to the double bond, which decomposed after several hours. The reactivity of these products to base follows the trend in reactivity found in the series of corresponding *peri*-dimethylamino



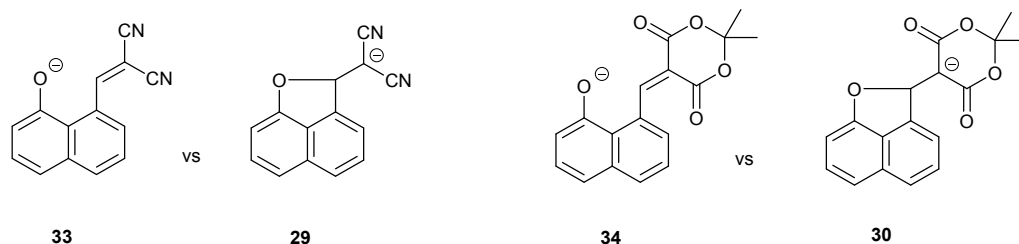
Scheme 6. Anions 29-32 produced by deprotonation of Knoevenagel products 23-25 and 27.

derivatives. As an example of the stable anions, uncyclised Knoevenagel product 24 derived from Meldrum's acid was treated with DABCO to give the cyclic anion 30. The new O-CH methine group shows chemical shifts of δ_H : 7.00 and δ_C : 89.7 ppm, the carbanionic centre shows a chemical shift of δ_C : 75.6 ppm and only one carbonyl carbon is observed (δ_C : 167.1 ppm) since the 1,3-dioxanedione ring now has rotational freedom. The naphthyl hydrogen *ortho* to the oxygen atom is shifted upfield by 0.38 ppm to δ_H : 6.50 ppm, the *ortho* carbon is shifted upfield by 10.8 ppm to 100.1 ppm, but the carbon *ipso* to the O atom is shifted downfield by 8.5 ppm to δ_C : 162.8 ppm, which all together suggest some delocalisation of charge into the aromatic ring despite formation of the *peri*-bond. The sodium salt of the less stable dinitrile anion 29, shows the O-CH methine group at δ_C : 101.8 and a $(^-)C(CN)_2$ carbanion at 23.2 ppm.³²

In contrast treatment of dinitrile 22 with TMG shows an equilibrium between the neutral dinitrile and its anion, in favour of the former, with two broad peaks in the ^{13}C NMR at 158.4 and 69.2 ppm for the alkene carbons.

Calculations.

In view of the lack of experimental structural data, the structures of the anions formed from *peri*-naphthols 23 and 24 were calculated by Density Functional Theory (DFT). 1D-Potential Energy Surfaces (PES), with different *peri* O---C separations were calculated using B3LYP/6-31++g(d,p) in order to identify the relative energies and structures of the open and closed forms: 33 vs 29, and 34 vs 30, for the two naphtholates (Scheme 7). For the anion of the Meldrum's acid derivative 24, the closed form 30, with a *peri* O-C bond length of 1.540 Å was the only minimum identified, consistent with NMR studies. In contrast, for the anion of dinitrile 23 both the open form 33 (O⁻---C: 2.362 Å) and the closed form 29 (O---C: 1.622 Å) were found to be of similar energy, $\Delta E = 0.33 \text{ kJ mol}^{-1}$, and separated by a low energy barrier of 2.35 kJ mol^{-1} . This is in contrast to the NMR studies of the sodium salt which support the short-lived closed structure. However, the calculations refer to the isolated anion *in vacuo*, and so do not include effects of cations or solvent. It is notable that the O-C bond length predicted for the closed form 29 is comparable to the longest O-C bond reported, which was observed in a strained oxonium system embedded in an oxatriquinane,³³ and so the low stability of this anion is not surprising. All calculations employed the Gaussian16 software package.³⁴



Scheme 7. Open and closed forms for the anions of naphthols 23 and 24 explored in the DFT calculations.

Conclusion.

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The first structures of 1-naphtholates in which the oxygen anion interacts with an electrophilic centre have been determined in the tetramethylguanidinium salts of *peri* acetyl- and benzoyl-naphthols and show O⁽⁻⁾---C=O distances of 2.558-2.618 Å. Small increases in the pyramidalities of the carbonyl groups compared to the neutral compounds are observed in accord with the greater nucleophilicity of the anion. The corresponding anions where a polarised alkene replaces the carbonyl could only be detected by NMR, but showed addition of the oxygen to the alkene. A dimethylamino group has a similar reactivity to the oxyanion according to the parallel series of *peri*-naphthalenes, for example when the electrophilic centre is an alkene activated by two coplanar carbonyls, the dimethylamino group adds to form a zwitterion, while the oxyanion adds to the alkene. When the alkene is activated, to a lesser extent, by two nitrile groups the dimethylamino group does not add, while the oxyanion does add but only to give a very unstable anion. When the electrophilic centre is a methyl or phenyl ketone, both the dimethylamino group and the oxyanion interact with the carbonyl with the former showing slightly larger pyramidalities at the carbonyl carbon. A long *peri* O-C bond was observed in the cyclised neutral compound 25 (1.508 and 1.521 Å), and remarkably longer bonds were calculated for the anions 29 and 30 (1.622 and 1.540 Å respectively), suggesting that very long bonds could be found and studied in similar derivatives but substituted sufficiently to increase their crystallinity.

Experimental.

All details of synthesis, crystallography and calculations are provided in the ESI. Crystallographic data are deposited at the Cambridge Crystallographic Data Centre with code numbers CCDC 1849340-1849345, 1849617-1849619, 1849628-1849632.

Conflicts of Interest.

There are no conflicts to declare.

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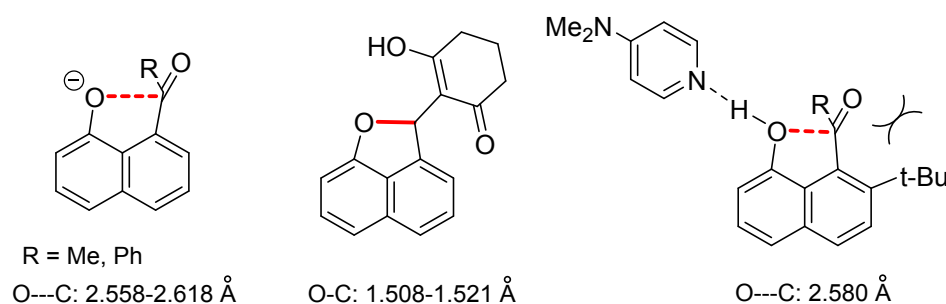
Graphical Abstract.

View Article Online
DOI: 10.1039/C8CE01872C**O⁽⁻⁾---C Interactions and Bond Formation in 1-Naphtholate Anions with *Peri*-Located Electrophilic Carbon Centres.**

Jonathan C. Bristow, Matthew A. Addicoat, John D. Wallis*

School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK.

Picture:



Text:

$n-\pi^*$ interactions between naphtholate O anions and carbonyl groups are determined to be shorter than in corresponding naphthols by X-ray crystallography, and lead to cyclisations with long O-C bonds when the carbonyl group is replaced by a strongly electron deficient alkene.