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Structural studies of *peri*-interactions and bond formation between electron-rich atomic centres and *N*-phenylcarboxamides or nitroalkenyl groups

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Structural studies of *peri*-interactions with dimethylamino groups in naphthalene systems indicate that the *N*-phenylcarboxamide group has a through-space electron attracting power closer to that of a carboxylic ester than a *N*,*N*-dialkylcarboxamide, while 2-nitroalkenyl groups have a lower through-space electron attracting power. However, addition of a benzoyl group to the 2-position of the nitroethenyl group leads to cyclisation to give a zwitterion, in which the carbanion is stabilised by full conjugation with the nitro group and partial conjugation with the carbonyl group. An interesting case where a steric interaction overrides an electrophile/nucleophile attraction is also described. The limitations to the interpretation of short contact distances from crystallographic measurements are discussed.

Introduction

Interactions between molecules underpin many chemical processes both in biological systems and in materials chemistry, and include effects such as hydrogen bonding, charge transfer interactions and π–π stacking. We have been interested in attractive interactions between electrophilic and nucleophilic groups. When pairs of such groups are forced close together, their interaction reveals the through-space electron-attracting power of the electrophilic group, and may model a stage in the chemical reaction between the two groups. These studies have built on pioneering work in which incipient bond formation was recognised in medium-ring compounds by Bürgi, Dunitz and Schefter[1] and the principles of structure correlation developed and applied.[2,3] The X-ray crystal structures of naphthalenes **1** bearing a dimethylamino group and an electron-deficient alkene or carbonyl substituent in the *peri*-positions show that the pyramidal dimethylamino group is oriented so that its lone pair lies in the space between the *peri* groups, and the electrophilic group presents a face to the dimethylamino group,[4–7] as originally demonstrated by Dunitz *et al.*[4] The 1,5 Me_2N–sp^2C separations decrease as the electron-deficient group is changed from a *N*,*N*-dialkylamide *e.g.* **2** or **3** (2.764 and 2.698 Å),[8] to a methyl ester **4** (2.594 Å),[4] to a methyl ketone **5** (2.557 Å)[4] to alkenes -CH=C(CN)CO_2Et **6** (2.531 Å)[7] and -CH=$C(CN)_2$ **7** (2.413 Å),[5] and culminates in almost complete bond formation in the zwitterionic structure **8**,[5] where this separation is only 1.651(3) Å (Table 1). In contrast, when the dimethylamino group is replaced by the much less nucleophilic methoxy group, the MeO–sp^2C separations vary over a much smaller range (2.55–2.62 Å), and any trend may be obscured by molecular distortions due to crystal packing. This led us to use the much more sensitive Me_2N–sp^2C separations to rank the unsaturated groups in an order of through-space accepting ability (Table 1). Other *peri*-interactions in naphthalene systems have been described, *e.g.* between electron-rich groups and alkynes[12] or nitriles[13] and between dimethylamino groups and selenium halides[14] or silicon-centred groups.[15] Of particular note is the use of the *peri*-arrangement to force hydrogen bonding to an amide N atom's lone pair as a model for amide cleavage by cysteine proteases,[16] as well as studies on proton sponges[17] including their dynamics[18] and the use of *peri*-naphthalenes as chiral auxiliaries.[8] Akiba has used 1,8,9-trisubstituted anthracenes to extend studies to interactions of two methoxy groups with a carbocation centre,[19] and interactions of two dimethylamino groups or two methoxy groups with a boron centre, including a measurement of the electron density distribution and topology for the latter case.[19,20] Recently, Kirby has shown how the interaction between an amino and a carbonyl group in the solid state is promoted by hydrogen bonding to the carbonyl oxygen atom.[21] Furthermore, he has studied this interaction type using an alicyclic system in which a high degree of bond formation between the groups is favoured by formation of an azaadamantane system.[21]

Determining the nature of the interaction between a particular pair of functional groups is not necessarily straightforward. However, as a rough guide, we proposed that the Me_2N–sp^2C interactions are attractive in nature if they are less than the corresponding MeO–sp^2C distance plus 0.15 Å.[6] The latter figure is the allowance for the larger size of the N atom over the O atom, and is estimated from the Me_2N---NMe_2 and MeO---OMe distances in *peri*-naphthalene derivatives containing fragments **9** and **10**. Thus, for the $CONMe_2$ group, the Me_2N–sp^2C distance is just 0.05 Å less than d(MeO–sp^2C) + 0.15 Å, and this interaction is interpreted as just having a very weak attractive component due to incipient addition to the carbonyl group, and that the separation is mainly determined by steric factors. In contrast, for the CH=$C(CN)_2$ group the Me_2N–sp^2C distance is 0.35 Å less than d(MeO–sp^2C) + 0.15 Å, and this indicates a more attractive interaction. The rapidly developing field of charge density determinations from accurate X-ray diffraction data should provide rather more insight into incipient bond formation than this rather superficial approach. Indeed, charge densities of the amide **3**[22] and the dicyanoethene **7**[23] show (3, −1) critical points in the charge density between the interacting groups, with electron densities at those points of 0.11(1) and 0.19(2) e $Å^{-3}$ respectively.

To expand the range of groups in this series we decided to investigate two areas. First, to examine the interaction with an *N*-phenylcarboxamide group, where the delocalisation of the nitrogen atom's lone pair into the carbonyl group is moderated by conjugation with a phenyl group, by study of the molecular structures of compounds **11–13**. Secondly, to examine interactions with a β-nitroethenyl group, since nitro-activated alkenes were not represented in the series so far, and to examine the effect of adding a further terminal substituent.

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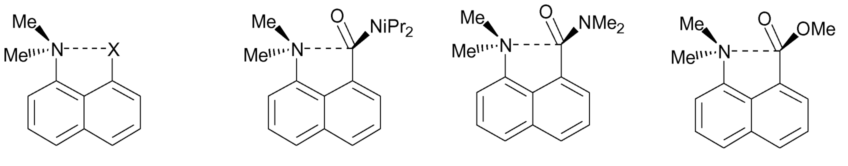
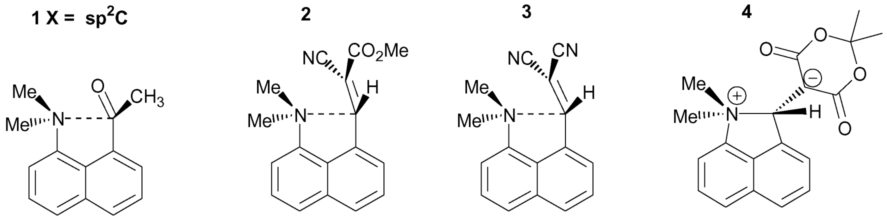
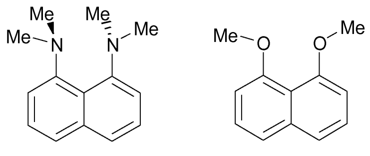
Table 1 Me_2N–sp^{2}C separations in *peri*-naphthalenes **1**



1 X = sp^{2}C **2** **3** **4**



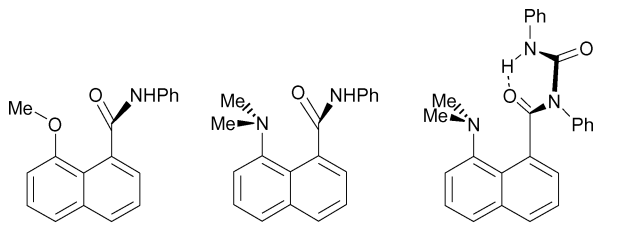
5 **6** **7** **8**



9 **10**

X	Compound	Me_2N–X distance/Å	MeO–X distance in corresponding methoxynaphthalene/Å
CON(iPr)$_2$	**2**	2.764(3)[8]	2.623(2)[8]
CH=CHBr		2.717(5)–2.758(2)[9]	—
CONMe$_2$	**3**	2.698(3)[8]	2.597(5)[4]
CH=C(COPh)$_2$		2.679(2)[5]	—
CO$_2$H		2.606(5)[4]	2.559(4)[4]
CO$_2$Me	**4**	2.594(4)[4]	2.588(3)[10,a]
COMe	**5**	2.557(3)[4]	2.606(9)[4]
CH=C(CN)CO$_2$Et	**6**	2.531(2)[7]	—
CHO		2.489(5)[9]	2.628(4)[11,b] and 2.644(4)[11,c]
CH=C(CN)$_2$	**7**	2.413(2)[5]	2.611(1)[6]
CH=C((C=O)O)CMe$_2$	**8**	1.651(3)[5]	2.550(2)[6]

[a] For methyl 5,8-dimethoxynaphthoate. [b] For 4,8-dimethoxy-5-(*p*-tosyloxy)-1-naphthaldehyde. [c] For 8-methoxy-5-(*p*-tosyloxy)-1-naphthaldehyde.



11 **12** **13**

Discussion

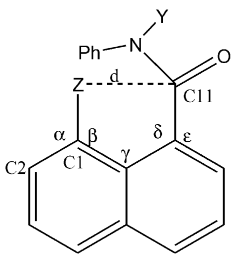
N-Phenylnaphthamides 11 and 12, and *N*,*N*′-diphenylnaphthoylurea 13

The *N*-phenylnaphthamides **11** and **12** containing *peri* methoxy or dimethylamino groups were prepared by *peri*-lithiation of the 1-methoxy- and 1-dimethylaminonaphthalenes followed by reaction with phenyl isocyanate. A further compound **13** was isolated from the latter reaction, arising by addition of phenyl isocyanate to the first-formed adduct to give an acyl urea group. This compound was included in the study because of the different electronic character of the amide carbonyl group presented to the dimethylamino group; this amide nitrogen atom shares its lone pair with a second carbonyl group. Molecular structures were measured by X-ray diffraction at low temperatures (mostly 100–120 K). Results are shown in Fig. 1–3, and relevant molecular geometries are presented in Table 2. Three polymorphs of the methoxy derivative **11** were measured, two triclinic (**11A**, measured at 100 K, and **11C**, measured at 150 K) and one monoclinic (**11B**, measured at 100 K). Each contained two independent molecules, and for **11C** one molecule was disordered between two orientations (85 : 15).

Molecules **11–13** show the distortion pattern characteristic of such compounds, in which both substituents are splayed in the same direction, with the carbonyl-containing group splayed outwards. The patterns of angles α–ε are similar for the three compounds and are comparable to the carbonyl derivatives discussed previously; in particular, they are closest to the carboxylic acid and ester derivatives.[1,3] In the *N*-phenylnaphthamides **11** and **12** the phenyl groups lie *syn* to the carbonyl and the angles between the amide group and phenyl ring planes are in the range 23.6(3)–37.43(15)° for **11** and 19.94(6)° for **12**, hence the amide N atom's lone pair can conjugate with the phenyl ring's π-system (Fig. 1). Thus, the amide C–N bond lengths (**11**: 1.352(2) Å (average over six molecules) and **12**: 1.3602(14) Å) are 0.02–0.03 Å longer than that for an *N*-methylamide derivative (1.329(10) Å for 19 measurements at $T \leq 150$ K).[24] The C(phenyl)–N bond lengths are 1.424(2) and 1.4145(14) Å for **11** and **12**, similar to acetanilide[25] (1.417 Å, angle between amide and phenyl planes: 16.1°).

The Me_2N---C distance in **12** is 2.6049(15) Å, which is similar to the corresponding separation for *peri*-interaction with a carboxylic ester or carboxylic acid, but considerably shorter than for the corresponding *N*,*N*-dimethylamide **3** (2.698(2) Å). The MeO---C distances in *N*-phenylnaphthamide **11** (2.574(2)–2.672(2) Å) have an average value of 2.637(2) Å, which is shorter than the Me_2N---C distance for **12**, and the value of the parameter [d(MeO–X) + 0.15 − d(Me_2N–X)] for the

Table 2 Selected geometric data for compounds **11–13**



Z = OMe (**11**), NMe_2 (**12**, **13**); Y = H (**11**, **12**), Y = CONHPh (**13**)

ΔC: deviation of C11 from the plane of its substituents towards the *peri* substituent.

T1 and T2: torsion angles of O-Me (**11**) or N-Me bonds (**12** & **13**) with the C1-C2 naphthyl bond.

	d/Å	*α* (°)	*β* (°)	*γ* (°)	*δ* (°)	*ε* (°)	Δ*C*/Å	*T*1 (°)	*T*2 (°)
11A	2.6715(17)	124.23(12)	114.89(11)	123.93(12)	122.68(11)	116.42(12)	0.0332(14)	0.4(2)	
	2.6708(18)	123.90(12)	115.10(11)	123.68(12)	122.68(11)	116.70(11)	0.0342(13)	1.5(2)	
11B	2.6540(16)	124.18(12)	114.68(11)	123.80(11)	123.24(11)	116.04(11)	0.0414(13)	1.63(18)	
	2.6588(15)	124.07(12)	114.93(11)	124.21(11)	123.99(11)	115.63(11)	0.0401(14)	0.30(18)	
11C	2.574(2)	124.4(2)	114.26(18)	123.93(18)	123.04(17)	117.2(2)	0.032(2)	8.2(3)	
	2.590(3)	123.7(2)	114.2(2)	123.4(2)	124.4(2)	115.7(2)	0.047(3)	8.8(5)	
12	2.6049(15)	122.95(11)	117.06(10)	123.36(10)	122.42(10)	117.16(10)	0.0555(12)	49.18(16)	−80.21(14)
13	2.6422(17)	123.60(14)	116.89(12)	123.09(12)	123.16(12)	116.56(12)	0.0502(15)	27.22(19)	−98.56(16)

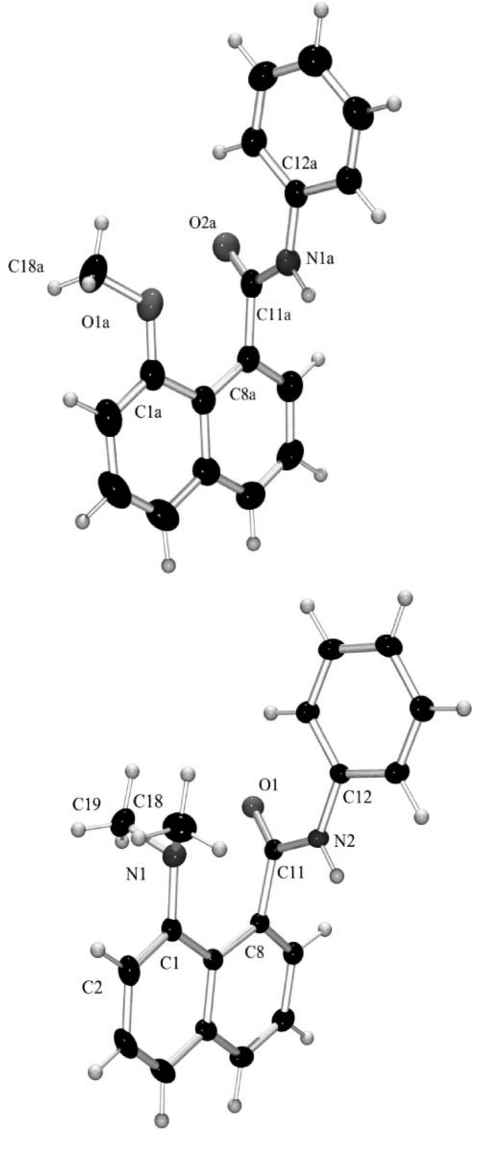


Fig. 1 Views of *N*-phenylcarboxamides **11** (above) and **12** (below).

N-phenylcarboxamide group is 0.18 Å. This suggests that the $Me_2N–sp^2C$ interaction in **12** involves a significant attractive component, and the value for this parameter is a little larger than that of carboxylic ester **4** (0.14 Å), but much larger than that for a *N*,*N*-dimethylcarboxamide (0.05 Å), consistent with the reduced electron donation from the N atom into the carbonyl group. Further evidence of an attractive interaction in **12** comes from the orientation of the dimethylamino group, so that the theoretical axis of the N atom's lone-pair axis lies at 15.1° to the vector between the *peri* nitrogen and carbonyl carbon atoms. The crystal packings in **11** and **12** involve hydrogen bonding linking the amide groupings into chains (Fig. 2), and for all polymorphs of **11** the hydrogen bonding links the two independent molecules in a A–B–A–B fashion.

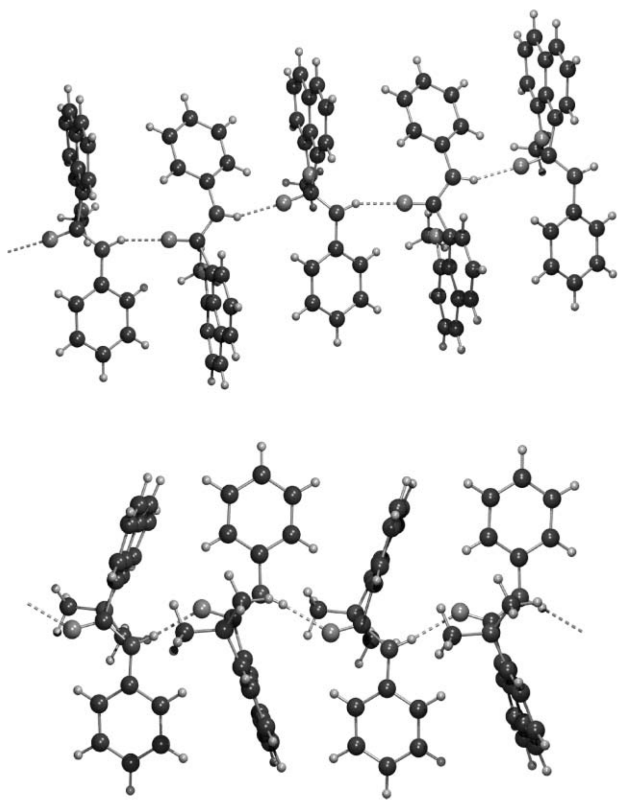


Fig. 2 Hydrogen bonding of molecules in chains in polymorph **11A** and **12**.

The structure of molecule **13** contains some very interesting features (Fig. 3 and 4). There is a hydrogen bond within the acyl urea grouping linking the terminal phenylamido group with the carbonyl group bonded to the naphthalene ring. The H–O distance is 1.901(19) Å, the N–H bond is 0.91(2) Å and the angles

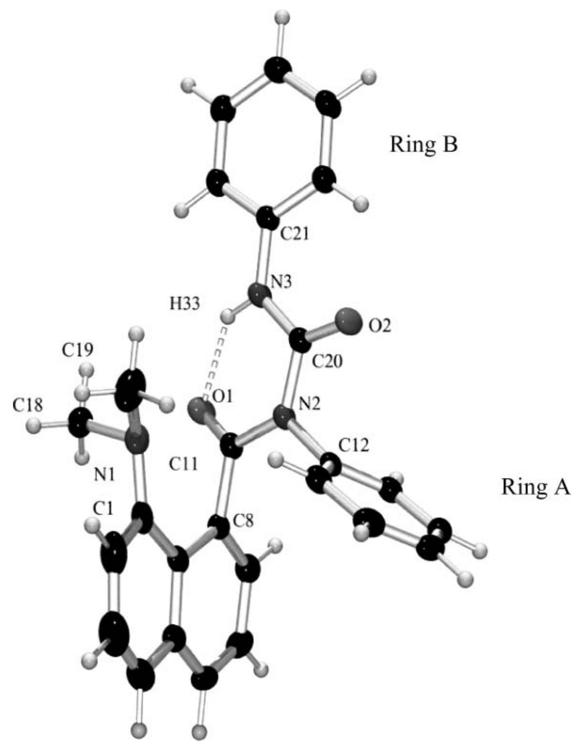


Fig. 3 View of the acyl urea **13** showing the internal hydrogen bonding.

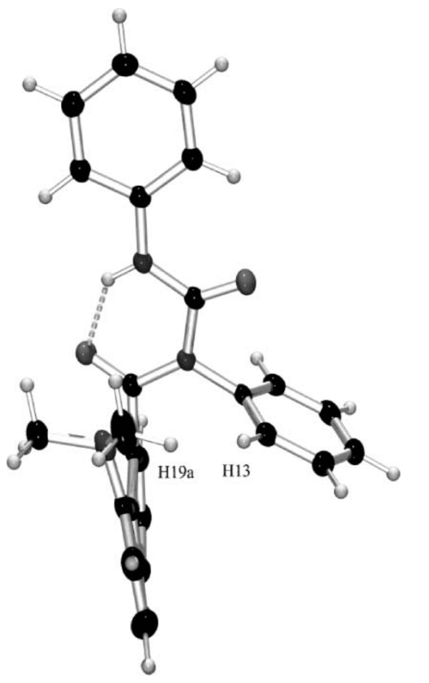
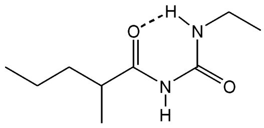


Fig. 4 View of **13** showing the steric interaction between hydrogen atoms H19a and H13, and the displacement of the *peri*-substituents from the naphthalene plane.

at the H and O atoms are 137.6(17)° and 99.5(6)° respectively. This completes a nearly planar six-membered ring system, which lies at 76.74(4)° to the naphthalene ring's best plane (Fig. 3). In fact, five atoms of this hydrogen-bonded ring lie close to a plane (rms deviation 0.015 Å) from which the hydrogen bonded oxygen atom is slightly displaced (by 0.212(12) Å) in a direction away from the *peri* dimethylamino group. The two phenyl rings lie at 85.36(4)° (ring A) and 13.21(8)° (ring B) to the best plane through the six-membered urea ring system. Thus, the terminal nitrogen, N3, is involved in conjugation with phenyl ring B, but the N atom located between two carbonyl groups, N2, is not conjugated with ring A.

This is consistent with the longer N–C(Ar) length to ring A than to ring B (1.4538(16) and 1.4205(17) Å respectively). The three N–C(carbonyl) bond lengths follow the expected pattern: the two bonds to N2 (N2–C11: 1.3890(16) and N2–C20: 1.4332(17) Å) are longer than the bond to N3 (N3–C20: 1.3530(17) Å). For the two amide bonds from N2, the bond to C20 is considerably longer (by 0.044 Å), since this carbonyl C atom is already receiving electron density from N3, being part of a urea grouping. The ^{1}H NMR solution spectrum shows a very deshielded amide H atom (δ_H: 11.60), and five shielded H atoms for phenyl ring A (δ_H: 6.84) which lies above the naphthalene ring system. The hydrogen bonded six-membered ring has been observed in many other acyl urea systems, *e.g.* **14**,[26] and included in rotaxanes,[27] biologically active materials like glimepiride[28] and as features within large ring systems.[29] Although no structures of acyl ureas with an *N*-aryl group between the two carbonyls are reported, the closely related triphenylbiuret **15**[30] and its tri(2-tolyl) analogue[31] have their central aryl ring at 70–71° to the plane of the hydrogen-bonded ring.



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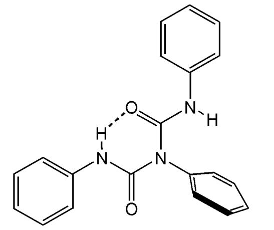


15

The Me_2N---C separation for the acyl urea **13** is 2.6422(17) Å, which is 0.037(3) Å longer than for the *N*-phenylcarboxamide **12**, suggesting a weaker interaction. We have no methoxy analogue for the acyl urea, but since the MeO–C separations are fairly insensitive to the nature of the electrophilic group, the methoxynaphthamide **11** can be used to estimate a value of 0.14 Å for the parameter [d(MeO–X) + 0.15 − d(Me_2N–X)] for the acyl urea grouping. Thus the Me_2N–sp^{2}C interaction in this compound also involves a small attractive component, but smaller than that observed in the *N*-phenylnaphthamide **12**. Furthermore, in acyl urea **13** the torsion angles between the N–Me bonds and the C1–C2 bond of the naphthalene ring are 27.22(19) and −98.56(16)°, and hence the theoretical axis of the nitrogen lone pair lies at 24.9° to the N1–C11 vector (*cf.* 15.1° for **12**). These results are rather surprising, considering the electronic structure of the carbonyl group under attack. Thus, compared to the *N*-phenylnaphthamide **12**, the *peri* carbonyl of the acyl urea might be expected to be *more* electron deficient, and thus make a *stronger* interaction with the dimethylamino group: N2 shares its lone pair electron density with a second carbonyl group, while in **12** the only alternative conjugating group is an in-plane phenyl group. This is reflected in the longer N–C(carbonyl) bond for **13** compared to **12**: N2–C11, 1.3890(16) Å *vs.* 1.3602(14) Å. However, in this case there is another factor to consider.

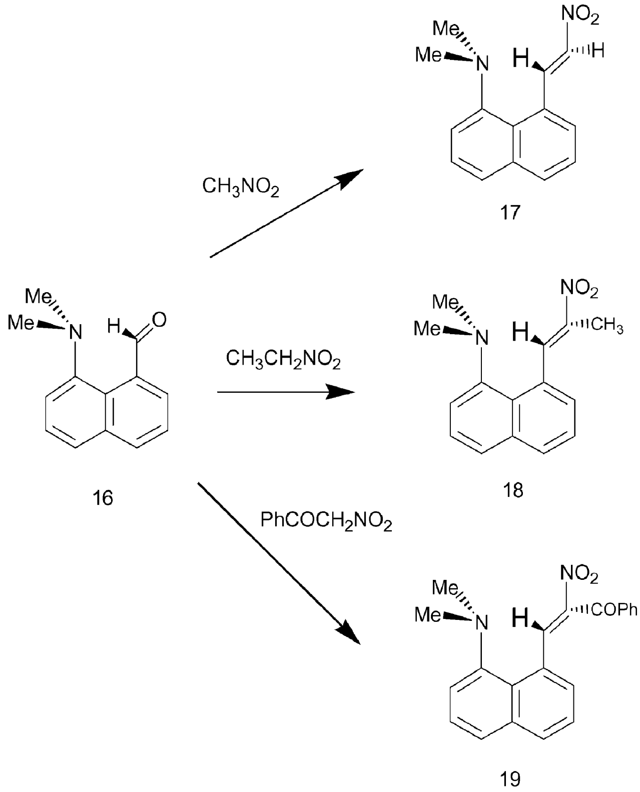
The phenyl ring A lies on the same side of the naphthalene plane as the dimethylamino methyl group (C19) and there is a short contact between an *ortho* hydrogen (H13) of the phenyl ring and a methyl hydrogen. The H–H separation is only *ca.* 2.28 Å, which corresponds to van der Waals contact. Indeed, it is a repulsion between the phenyl and methyl groups which has led to the *longer* N–sp^{2}C distance in **13** than that found in **12**, and this compound does not provide an adequate model for assessing the interaction of a dimethylamino group with this particular *peri* carbonyl group. Additionally, this steric effect also restricts the orientation of the dimethylamino group such that the N atom's lone pair cannot be directed towards the *peri* group. In an attempt to ease the repulsion, the *peri* groups are displaced to opposite sides of the naphthalene plane. The sizes of the displacements from the naphthalene ring's best plane are 0.3683(16) Å for the dimethylamino N atom and

−0.1919(17) Å for the carbonyl C atom, which are *larger* than the corresponding displacements in *N*-phenylnaphthamide **12** (0.2389(15) and −0.1529(15) for N1 and C11 respectively). The ^{1}H and ^{13}C NMR solution spectra of **13** show two distinct signals for the *N*-methyl groups (δ_H: 2.57, δ_C: 49.9 and δ_H: 2.98, δ_C: 43.7) due to the greater steric barrier for rotation of a *peri* group compared to the amide **12**, which shows just one signal (δ_H: 2.61, δ_C: 46.0). The methyl group involved in the steric interaction with the phenyl group is likely to have the more deshielded hydrogens. In solution it is much more difficult for the *peri* urea group of **13** to rotate about its bond to the naphthalene skeleton than for the amide group in **12**.

In summary, the structural measurements suggest that the *N*-phenylcarboxamide group has a through-space electron-attracting power significantly greater than a *N*,*N*-dialkylcarboxamide. The results for acyl urea **13** provide a cautionary tale about the need to carefully analyse a structure for all interactions, both steric and electronic. All three structures show small pyramidalisations of the carbonyl carbon towards the *peri*-substituent: 0.029(2) Å in **11**, 0.0555(12) Å in **12** and 0.0502(15) Å in **13**, the larger values for interaction with nitrogen, and the largest effect for the shorter contact to nitrogen. For **13** this contributes to the displacement of the carbonyl O atom out of the plane of the acyl urea. The Nu–C=O angles are 95.6(1)° in **11**, 97.35(7)° in **12** and 98.88(9)° in **13**, similar to those in related naphthalene systems.

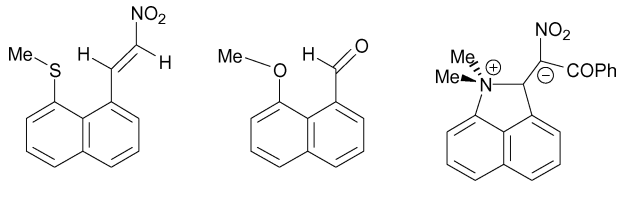
Nitroalkenes 17 and 18, and zwitterion 22

To investigate the electron-withdrawing effect of a nitro group on the through-space electron-attracting power of an alkene bond, three 1-(β-nitroalkenyl)naphthalene derivatives with *peri* dimethylamino groups were selected for study. The first one, **17**, contained the 2-nitroethenyl group and the second one, **18**, contained an additional methyl group at the terminus of the alkene. Although electronically very similar to **17** the terminal methyl group is included to modify the orientation of the alkene by steric interaction with the *ortho* naphthalene H atom (Fig. 4). It is already known that for cases where the *peri*-interaction is weak, and the electrophilic group is either an alkene with a H atom *cis* to the naphthalene ring, *e.g.* **20**, or an aldehyde such as **21**, then the dominating interaction is optimisation of the conjugation of the alkene or carbonyl group with the naphthalene, so the double bond does not present a face clearly to the *peri* group. We wanted to be sure to include a compound where this did not happen, given its occurrence in the nitroethenyl derivative **20**. The third compound **19** is selected since it is expected to have a more electron-deficient alkene due to the combination of terminal nitro and benzoyl groups. The compounds were prepared by Knoevenagel condensation on the aldehyde **16** (Scheme 1). It was notable that the crystals of **17** and **18** were dark orange in colour, but the crystals of the benzoyl



Scheme 1

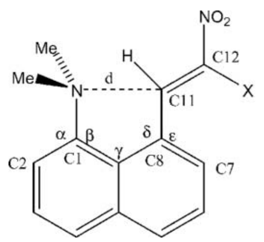
nitro compound **19** were pale yellow. Low temperature X-ray analysis revealed that the latter contained almost complete bond formation between the functional groups and had a zwitterionic structure **22**. Results are displayed in Fig. 5–7, and selected molecular geometries in Table 3.



20 21 22

The structures of the two molecules **17** and **18**, in which the *peri* alkene group contains only one electron-attracting substituent, adopt the *E* configuration and have very similar molecular conformations. The nitro and alkene groups are almost coplanar, and the alkene bond makes torsion angles with the C1–C2 aromatic bond of 50.52(19) and 53.50(19)°, and so presents a face to the dimethylamino group, in contrast to

Table 3 Selected geometric data for compounds **17**, **18** and **22**



ΔC: deviation of C11 from the plane of its substituents towards the *peri* substituent.

T1 and T2: torsion angles of N-Me bonds with the C1-C2 aryl bond.

T3 torsion angle of C11-C12 bond with C7-C8 aryl bond.

	X	d/Å	α (°)	β (°)	γ (°)	δ (°)	ε (°)	ΔC/Å	$T1$ (°)	$T2$ (°)	$T3$ (°)
17	H	2.6417(16)	123.44(12)	117.30(11)	122.95(12)	122.30(12)	118.39(12)	0.024(1)	−26.67(18)	103.13(15)	50.52(19)
18	CH_3	2.6744(17)	122.86(12)	117.47(11)	123.50(11)	121.98(12)	118.15(12)	0.042(1)	25.95(19)	−103.05(15)	53.50(19)
22	PhC=O	1.6397(17)	128.61(13)	109.43(11)	113.54(12)	109.99(12)	131.17(12)	0.370(1)	56.26(18)	−65.87(18)	50.8(2)

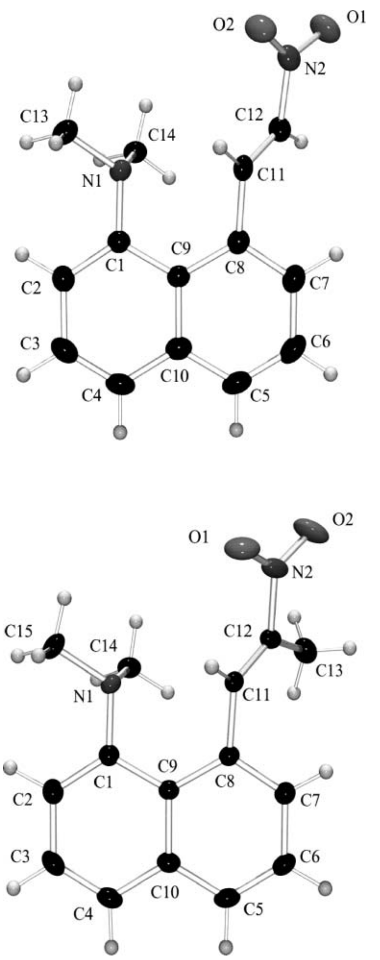


Fig. 5 Views of the nitroalkenes **17** (above) and **18** (below).

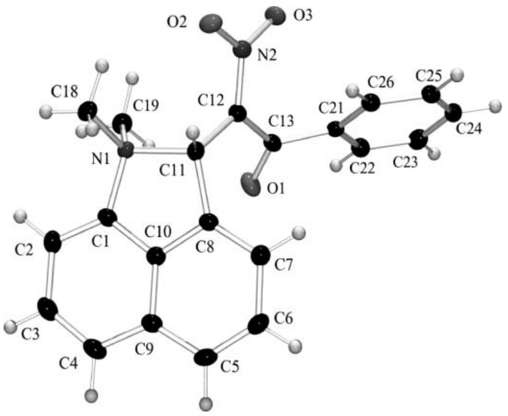


Fig. 6 View of the zwitterion **22** perpendicular to the naphthalene plane.

the methylthio analogue **20**. The Me_2N---C=CNO_2 separations of 2.6417(16) and 2.6744(17) Å place the β-nitroalkene group between the *N*-phenylcarboxamide group (N---C: 2.6049(15) Å) and the *N*,*N*-dimethylcarboxamide group (N---C: 2.698(3) Å) in power of "through-space" electron-attracting ability, and similar to the C=C$(COPh)_2$ group (N---C: 2.679(2) Å). (We were unable to obtain suitable crystals of the 8-methoxy analogue of **17** for a direct comparison of their *peri*-interactions and calculation of the parameter [d(MeO–X) + 0.15 − d(Me_2N–X)]). The dimethylamino groups in both nitroalkenes have similar orientations with the lone pair not well aligned with the Me_2N–C vector; the theoretical nitrogen lone pair axes lie at 27.6° (**17**) and 28.6° (**18**) to their N1–C11 vectors. A methyl group lies roughly perpendicular to the naphthalene plane. Similar orientations are observed in most cases with larger N–C

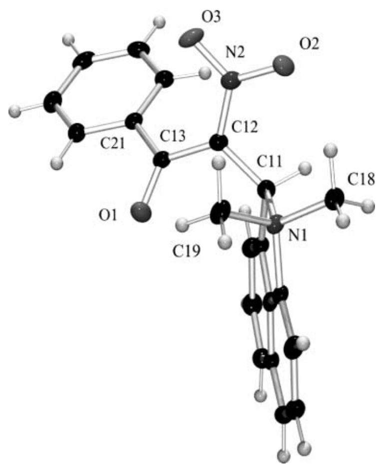
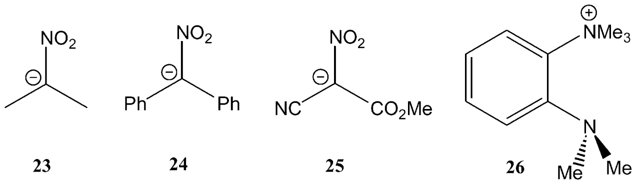


Fig. 7 View of zwitterion **22** approximately perpendicular to the plane of the carbanionic centre.

separations, but for shorter N–C separations, *e.g.* in the esters and carboxylic acids, the nitrogen lone pair approaches closer to the N–C vector. Compared to the *N*-phenylcarboxamide **12**, the increased Me_2N–sp^2 C separation is achieved by larger displacements of groups out of the naphthalene plane, rather than by in-plane displacements. There is always the question as to how much crystal-packing effects influence the molecular conformations observed, this being a more significant problem when intramolecular attractions are at their weakest. In this particular case, it is notable that these electronically similar molecules have taken almost the same conformation, but in different crystallographic environments ($C2/c$ *cf.* $P2_1/n$). The increase in the alkene bond length on addition of a methyl group (*cf.* **17**: 1.3237(19) Å *vs.* **18**: 1.3357(19) Å) is in line with the small amount of relevant data in the Cambridge Structural Database (CSD), which shows that nitroethenyl groups typically have short alkene bonds (1.303(35) Å for six structures) while additional of a sp^3 carbon atom at the α position increases the bond length (1.330(5) Å for six room temperature measurements.)[24]

In contrast, the addition of a benzoyl group to increase the electron-attracting power of the double bond has led to the formation of a very interesting zwitterionic structure **22** with a new N–C bond 1.6397(17) Å long. This is slightly shorter than in the zwitterion **8**, where the negatively charged centre is stabilised by two coplanar lactone groups (1.651(3) Å). The formal anionic centre at C12 has planar bonding geometry and is stabilised by the nitro and benzoyl substituents. The nitro group is better oriented for conjugation, lying almost coplanar with the carbanionic centre: the angle between nitro group and this plane [N2, C11, C12, C13] is only 2.02(14)° while the carbonyl group lies at 40.59(8)° to this plane. The benzene ring lies at 21.18(7)° to the carbonyl group. Thus, delocalisation of electron density into the nitro group leads to a shortened C12–N2 bond of 1.3744(17) Å and lengthened N=O bonds of 1.2623(15) and 1.2724(16) Å, compared to C–N bonds: (1.512(4) Å) and N=O bonds (1.220(1) Å) in neutral nitro groups.[24,32] In the tetrabutylammonium salt of 2-nitropropanate **23**,[33] where the nitro group is the sole stabilising group of the anionic charge, the C–N bond is shortened further to 1.311(7) Å and the N=O bonds are lengthened more to 1.299(5) and 1.303(5) Å, indicating that in zwitterion **22** the nitro group is not the only contributor to the stabilisation of the negative charge. Even in the diisopropylammonium salt of diphenylnitromethanide **24**,[34] the nitro group receives more electron density than in zwitterion **22**, judging from the lengths of the C–N (1.322(2) Å) and N=O bonds (1.302(2) and 1.308(2) Å). There is no direct analogy in the CSD for a carbanion stabilised by just a nitro group and one carbonyl group. In the potassium salt of carbanion **25**[35] in which three coplanar groups, nitro, cyano and a carboxylic ester, stabilise the negative charge, the bond lengths involving the nitro group are similar to those observed in the zwitterion **22**, *i.e.* C–N 1.371(3) Å and N=O 1.246(3) and 1.270(3) Å. The carbonyl group in zwitterion **22** is a long way from lying planar to the carbanionic centre, nevertheless there is evidence of some conjugation between them. The carbonyl bond is lengthened a little to 1.2355(17) Å compared to an unperturbed benzoyl carbonyl bond (1.221(1) Å).[24] The length of the C12–C13 bond connecting the carbonyl group to the carbanionic centre (1.4600(19) Å) is less than in a fully conjugated phenyl vinyl ketone (1.480(12) Å for eight structures at $T \leq 150$ K),[24] and substantially less than in an aliphatic α-nitroketone (1.544(6) Å for six structures at $T \leq 150$ K).[24] In contrast to the zwitterion **22**, for the uncoordinated enolate of acetophenone (as its potassium[12-crown-6] salt at 298 K),[36] the C=O bond is much longer (1.291(13) Å) and the C–C bond is considerably shortened (1.393(16) Å). The anion of nitroacetophenone is known in several transition metal complexes, where it binds through a carbonyl O atom and a nitro O atom. In the best determined structure,[37] a complex with zinc, the bonds from the carbanionic centre are 1.365(4) Å for the C–N bond (*cf.* 1.3744 Å in **22**) and 1.385 (4) Å for the C–C bond to the carbonyl group. The latter is much shorter than in the zwitterion **22**, where the carbonyl group lies out of the plane of the carbanionic centre, and there is no metal cation to enhance delocalisation of charge to the oxygen atoms.

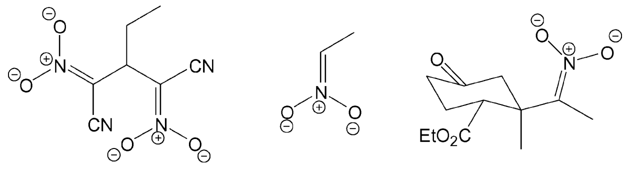


23 **24** **25** **26**

The five membered ring formed by cyclisation is close to planar, with no torsion angle around the ring greater than 6°. The new bond may not be fully formed, in part due to the strain in the fused five-membered ring. Furthermore, the alignment between the new σ bond and the π system at the carbanionic centre would permit some overlap of π electron density with the σ* orbital. Is there a way of determining if the new bond between the *peri* groups is indeed fully formed? If it is not fully formed then the formal positive and negative charges on the zwitterion will be reduced from +1 and −1. The N–Me bond lengths can provide a clue. The cation **26** contains a benzene ring *ortho*-substituted with a trimethylammonium group and a pyramidal dimethylamino group oriented so that its lone pair lies in the plane of the benzene ring.[38] These two groups provide models for the dimethylamino group in the *peri*-naphthalene in question in its fully cyclised and non cyclised forms **22** and **19**. In the tetraphenylborate salt of cation **26**[38] at 150 K the N–Me bonds in the trimethylammonium group lie in the range 1.503(2)–1.504(2) Å, which are considerably longer than the N–Me bonds from the dimethylamino group, 1.468(2)–1.470(2) Å. The N–Me bond lengths in the zwitterion **22** are 1.5022(18) and 1.5024(18) Å. Although the measurement temperatures differ by 30 K,[39] these results suggest that the bond formation in the zwitterion is at least close to completion. It is not so straightforward to make a similar analysis from the stabilisation of the carbanion, with no very close model for comparison.

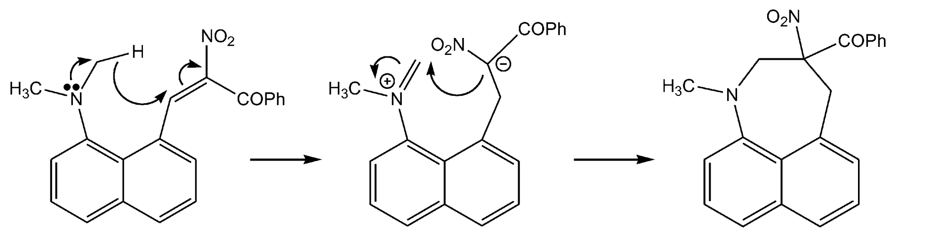
The delocalisation of negative charge to the oxygen atoms of the nitro and benzoyl groups in zwitterion **22** may be stabilised by formation of weak hydrogen bonds involving carbon-bound hydrogen atoms. The benzoyl oxygen makes a surprisingly short contact (2.235(16) Å) to H5 attached to the naphthalene ring of another molecule, with the four atoms involved not far from linear. Nitro oxygen atom O2 makes three contacts to hydrogens α to the cationic centre: two to methyl groups, one intermolecular (O2–H19B, 2.481(16) Å) and one intramolecular (O2–H18A, 2.548(16) Å), as well as a 1,5-intramolecular contact to the methine H (O2–H11, 2.345(14) Å). Similarly, O3 makes an intermolecular contact with a methyl group (O2–H18A, 2.457(17) Å).

NMR studies on **22** in DMSO-d_6 show the presence of two sets of resonances in the ratio 3 : 2, both of which correspond to ring-closed zwitterionic forms rather than the open-chain alkene form. In particular, the methine CH grouping bonded to the positively charged nitrogen gives signals at δ_C: 94.3 (major) and δ_C: 91.0 (minor), and the attached hydrogen atom has resonances at δ_H: 7.72 (major) and δ_H: 7.18 ppm. The corresponding atoms in the open-chain compound **7** resonate at δ_C: 165.7 ppm and δ_H: 8.75. Furthermore, the *N*-methyl groups of **22** show signals at δ_H: 3.60 and δ_C: 52.9 and 53.1, similar to those in zwitterion **8** (δ_H: 3.37 and δ_C: 51.8), but quite different from those of the uncharged dimethylamino group in **7** (δ_H: 2.69 and δ_C: 45.3). The two species present are likely to be rotamers arising from restricted rotation about the exocyclic C–C$^-$ bond. To interconvert while retaining the zwitterionic structure, either benzoyl O1 or nitro O2 must rotate past methyl group C19. In the solid-state conformation there are already short contacts involving these groups (O1–H19C: 2.519 Å; O2–H19B: 2.548 Å). The ^{13}C shifts of the carbanionic centres occur at δ_C: 116.5 and 116.7. In the pyrrolidinium salt of nitronate **27**, which has a cyano substituent to share the stabilisation of the negative charge, the corresponding carbon resonates at δ_C: 96.7,[40] while in the sodium salts of simple nitronates such as **28** or **29** it resonates at δ_C: 112.3 or 115.5.[41] The NMR spectra of zwitterion **22** in $CDCl_3$ show two sets of resonances in a 4 : 1 ratio, with the methine C and H resonances at lower field: δ_C 112.2 (major) and 104.5 (minor) and δ_H: 8.30 (major) and 7.51 (minor) than in DMSO-d_6. The difference in the shifts suggests that the precise degree of ring closure is affected by the solvent environment, with DMSO-d_6 being better able to stabilise two larger charges. Further differences in the spectra are in line with this: thus, using the data for the major isomer in each case, the shifts for the two methyl groups in DMSO-d_6 (δ_H: 3.58 and δ_C: 53.4) are further downfield than those in $CDCl_3$ (δ_H: 3.33 and δ_C: 51.7) and the ^{1}H shifts of the three hydrogens, *ortho*, *meta* and *para* to the positively charged N atom are also further downfield in DMSO-d_6 (8.06 d, 7.79 t, 8.02 d) than in $CDCl_3$ (7.82 d, 7.58 t, 7.41 d). The carbanionic centre in $CDCl_3$ occurs at δ_C: 125.8 for the main species.



27 **28** **29**

On heating a solution of **22** in DMSO-d_6 to 90 °C for 48 hours, an intramolecular reaction took place to give the fused azepine **30**. The structure shows two methylene groups with carbon shifts at δ_C: 41.6 and 63.3, assigned to the 4- and 2-C respectively. The methylene hydrogens appeared as two broad signals for 4-H_2, which sharpened to an AB system on heating to 90 °C, and a singlet for 2-H_2 which correlated to the carbon shift at δ_C: 63.3. (In contrast, in $CDCl_3$ at 24 °C the methylene hydrogens at position 2 appeared as an AB system which correlated to the carbon at δ_C 63.5, and the other methylene group gave a broad signal!) The structural assignment is further supported by a quaternary carbon at δ_C: 99.9 for 3-C and a molecular ion in the mass spectrum showing loss of a nitro group. A possible mechanism for this conversion is shown in Scheme 2. Opening of the zwitterion by reversal of the Michael reaction to give the disubstituted naphthalene **19** is followed by hydride donation from an *N*-methyl group to the electron-deficient alkene, producing an iminium cation and a stabilised carbanion which then react together. The initial donation of hydride is facilitated by the close proximity of the groups and the electron-rich character of the dimethylamino group. Intermediate NMR



30

Scheme 2

spectra taken during the first hours of the rearrangement at 90 °C show the presence of at least one intermediate species. Although the spectra are complex, the singlets at 8.21 and 3.05 (broad) may provide evidence for the alkenyl hydrogen and dimethylamino groups of one isomer of the open chain form **19**.

Finally, one should consider whether it is really valid to use *single* crystallographic measurements to characterise interactions between dimethylamino groups and electrophilic groups. Are our observations really accurate or not? As we have pointed out before,[6] crystal packing effects can provide small distortions to molecular structures which may compete with the effects of a weak interaction, and different crystalline environments in polymorphs may influence molecular geometry. Ideally, a number of different polymorphs or solvates should be measured (where they exist), or families of very closely related structures (*e.g.* bearing a small substituent remote from the groups involved in the interaction) should be measured. The existence of an interaction would be supported by the frequent occurrence of the feature, and the degree of accuracy of the method would be indicated by the spread of values for a particular interaction distance. We note the similarities of the interaction geometries in **17** and **18**. Nevertheless, in the three polymorphs of compound **11** there are small differences in the MeO–C=O distances (**11A**: 2.672(2) and 2.671(2), **11B**: 2.6540(16) and 2.6588(15), **11C**: 2.574(2) and 2.590(3) Å), even for the two which are measured at very similar temperatures (100 K for **11A** and **11B**, *cf.* 150 K for **11C**). The lack of any pronounced systematic variation in the MeO–sp^2C separations in a range of compounds (Table 1) suggests that any interaction is particularly weak, so it is perhaps not so surprising that this separation can be modified easily by external effects. This variability in the measured MeO–sp^2C separation for **11** also suggests that while comparison of the Me_2N–sp^2C separation with the MeO–sp^2C separation provides a useful qualitative comparison, the parameters deduced are subject to considerable error. While we could assign error bars to the parameter $d(\text{MeO–sp}^2\text{C}) + 0.15 - d(\text{Me}_2\text{N–sp}^2\text{C})$ derived from the e.s.d.s of the compared atomic separations, these would be very misleading, since the errors arising from crystal packing effects are considerably greater. The comparison of Me_2N–sp^2C separations in different *peri*-interactions is the simplest way of ranking interactions, though multiple measurements will provide a much sounder basis for identifying such trends. Thus, what we report here is more "the first indication" of interactions rather than the "last word". We may add that structures for comparison should be measured at low and similar temperatures to minimise the effects of thermal motion on the derived structural geometries. Indeed, some of the structures measured in the original pioneering work[4] should now be remeasured to put the data in Table 1 on a more closely comparable basis. Lloyd-Jones has reported interesting initial investigations of estimating distances between *peri*-substituents using ^{15}N,^{15}N coupling constants across hydrogen-bonded amino groups, but correlation of calculated coupling constants with N,N separation was better than for the observed data.[42]

While our measurements in most cases indicate a short contact between dimethylamino and electrophilic groups, they do not give direct insight into the mode of the interaction. Only in **22** is there clear evidence for bond formation. It will be studies on the topology of the total electron density, determined either by X-ray diffraction measurements or by *ab initio* calculations or both, which provide this, as in the alkynes studied earlier,[43] or the recent work of Akiba[19] or Lyssenko.[22] *Ab initio* calculations have the advantage of treating an isolated molecule without interactions with its crystalline environment. Thus, structural studies on the interactions of a carboxylic acid group or its anion with the α-nitrogen of a diazonium group in *ortho*-disubstituted aromatics[44,45] have led Glaser to propose that the short contacts between these groups (O–α-N: 2.517–2.621 Å) be described as 1,3-bridging interactions of the oxygen centre with the two atoms attached to the α-nitrogen, since it is these two atoms which bear partial positive charges, while the α-nitrogen bears a partial negative charge.[44] Nucleophilic addition is known to occur at the β-nitrogen but addition to the α-nitrogen would lead to the unstable 1,1-diazene system.[46] Orbital overlap is not the only aspect of an interaction that need to be considered, especially with charged groups. Indeed, any interaction is determined by a composition of different effects *e.g.* electrostatic, as is the process of developing a new bond between two groups.

It is sometimes commented that if there is an attraction between two *peri* groups then they should displaced *towards* each other; in **12**, **13**, **17** and **18** the dimethylamino group is displaced towards the electrophilic group which is displaced away. However, it is a matter of point of reference. The *peri* hydrogen atoms of naphthalene lie at a separation of 2.44 Å, reflecting the separation of the carbon atoms (2.48 Å) to which they are attached, and the H–H distance remains outside the sum of the van der Waals radii for two hydrogen atoms.[47] The *peri*-disubstituted naphthalenes described here are somewhat different. The constraint applied by bonding to the naphthalene system acts to hold the groups well within the sum of their van der Waals radii, so that separations slightly greater than 2.5 Å are still well within the van der Waals separation, and only indicate that at 2.5 Å the interaction would be repulsive. It is of note that in the dicyanoethenyl derivative **7** the electrophilic group is not displaced away from the dimethylamino group and the N–C separation is 2.413 Å. In summary, crystallographic studies are useful for identifying the existence of possible interactions, but these are only given credibility by multiple observations, and the underlying effects comprising the full interaction can only be more clearly unravelled by calculations and accurate electron density measurements. However, there is no substitute for experimental observations.

Experimental

General

NMR spectra were measured on a JEOL JNM-EX270 spectrometer at 270 MHz for ^{1}H and at 67.8 MHz for ^{13}C using $CDCl_3$ as solvent, and measured in ppm downfield from TMS, unless otherwise stated. IR spectra were recorded on a Perkin–Elmer Spectrum RX 1 FT-IR spectrometer. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre at Swansea University. X-Ray diffraction datasets were measured by the

EPSRC National Crystallography Service at Southampton University. Chemical analysis data were obtained from Mr T. Spencer, University of Nottingham. Flash chromatography was performed on 40–63 silica gel (Merck).

8-Methoxy-*N*-phenyl-1-naphthamide 11

t-Butyllithium (1.7 M solution in pentane, 20 ml, 33 mmol) was added to a stirred solution of 1-methoxynaphthalene (4.75 g, 30 mmol) in dry cyclohexane (60 ml) at room temperature, under nitrogen. After 48 h, the precipitated lithium salt was filtered under nitrogen and washed with dry ether. The lithium salt was suspended in dry ether and cooled to −78 °C. Phenyl isocyanate (3.57 g, 30 mmol) was added dropwise, the mixture allowed to warm to room temperature and stirred overnight. The resulting brown solution was poured on to aqueous NH_4Cl and the white solid product collected by vacuum filtration to yield **11** (6.0 g, 72%), mp 177–178 °C. ^{1}H NMR: 7.83 (1H, m, Ar-H_1), 7.59 (2H, d, J = 7.9 Hz, Ar-H_2), 7.47–7.38 (5H, m, Ar-H_4 + NH), 7.34 (2H, t, J = 7.8 Hz, ArH_2), 7.12 (1H, t, J = 7.3 Hz, Ar-H_1), 6.85 (1H, dd, J = 6.9, 1.5 Hz, Ar-H_1), 3.79 (3H, s, OCH_3); ^{13}C NMR: 170.0 (C=O), 155.1, 138.5, 135.0, 133.3, 129.3, 129.0, 126.6, 125.5, 125.1, 124.0, 121.4, 120.8, 119.8, 106.0 (Ar-C_{16}), 56.1 (OCH$_3$); ν_{max}/cm^{-1} (KBr): 3278, 1654, 1599, 1549, 1441, 1324, 1260, 1120, 1058, 768, 753; Found: C, 77.9; H, 5.4; N, 4.9%, $C_{18}H_{15}NO_2$ requires: C, 78.0; H, 5.5; N, 5.1%; HRMS (EI): Found: 277.1107, $C_{18}H_{15}NO_2$ requires: 277.1103.

8-(Dimethylamino)-*N*-phenyl-1-naphthamide 12 and *N*-(8-dimethylamino-1-naphthoyl)-*N*,*N*′-diphenylurea 13

n-Butyllithium (1.6 M solution in hexane, 26 ml, 41 mmol) was added to a stirred solution of the 1-dimethylaminonaphthalene (1.75 g, 10 mmol) in dry ether (35 ml) at room temperature under nitrogen. After 48 h the precipitated lithium salt was filtered under nitrogen and washed with dry ether. The lithium salt was then suspended in dry ether and cooled to −40 °C. Phenyl isocyanate (1.67 g, 14 mmol) was added dropwise, the mixture was allowed to warm to room temperature and stirred overnight. The resulting yellow solution was poured on to aqueous NH_4Cl and extracted with CH_2Cl_2. The organic solution was dried ($MgSO_4$), evaporated and the crude solid material separated on silica gel (hexane–ether, 2 : 1) to yield **12** (0.68 g, 23%) and **13** (1.92 g, 46%) as white solids.

8-(Dimethylamino)-*N*-phenyl-1-naphthamide 12

Mp 193 °C; ^{1}H NMR: 7.87 (1H, dd, J = 8.2 Hz, Ar-H_1), 7.66 (1H, dd, J = 8.1, 1.1 Hz, Ar-H_1), 7.57–7.29 (8H, m, Ar-H_8), 7.17 (1H, br.s, NH), 7.08 (1H, t, J = 7.3 Hz, Ar-H_1), 2.61 (6H, s, N(CH_3)$_2$); ^{13}C NMR: 169.8 (C=O), 150.9, 138.9 (Ar-C_2), 135.3, 134.5 (1′-C and Ar-C_1), 129.6 (Ar-C_1), 128.9 (3′-,5′-C), 127.5, 126.6, 126.1, 125.4, 124.9 (Ar-C_5), 123.5 (4′-C), 119.3 (2′-,6′-C and Ar-C_1)), 46.0 (N(CH$_3$)$_2$); ν_{max}/cm^{-1} (KBr): 3268, 1648, 1595, 1545, 1495, 1438, 1316, 778, 754, 712; HRMS (EI): Found: 290.1428, $C_{19}H_{18}N_2O$ requires: 290.1419.

N-(8-Dimethylamino-1-naphthoyl)-*N*,*N*′-diphenylurea 13

Mp 142 °C; ^{1}H NMR: 11.60 (1H, br.s, NH), 7.66 (2H, d, J = 8.1 Hz, Ar-H_2), 7.58 (1H, d, J = 7.7 Hz, Ar-H_1) 7.43–7.23 (7H, m, Ar-H_7), 7.12 (1H, t, J = 6.8 Hz, Ar-H_1), 6.84 (5H, br.s, N-C_6H_5), 2.98 (3H, s, (NCH_3), 2.57 (3H, s, NCH_3); ^{13}C NMR: 175.5 (N-C=O), 152.3 (N'-C=O), 150.6, 138.1, 137.7, 134.4, 132.1, 129.4, 129.3, 129.0, 127.6, 127.4, 127.2, 126.4, 126.3, 124.6, 124.5, 123.8, 120.1, 117.7 (Ar-C_{22}), 49.9 (N(CH$_3$)$_2$); ν_{max}/cm^{-1} (KBr): 3442, 3265, 1705, 1661, 1495, 1282, 1194, 1159, 789, 765; Found: C, 75.9; H, 5.7; N, 10.1%. $C_{26}H_{23}N_3O_2$ requires: C, 76.3; H, 5.7; N, 10.3%; HRMS (EI): Found: 409.1798, $C_{26}H_{23}N_3O_2$ requires: 409.1790.

E-1-(8′-Dimethylaminonaphth-1′-yl)-2-nitroethene 17

Nitromethane (0.3 ml, 5.50 mmol) and ethylenediamine diacetate (46 mg, 0.25 mmol) were added to a solution of aldehyde **16**[48] (0.50 g, 2.50 mmol) in dry methanol (5 ml) under a nitrogen atmosphere, and stirred together for 36 h at room temperature. The solvent was evaporated, and the residue purified by chromatography on silica, eluting with ether–hexane (1 : 2) to give **17** (0.22 g, 36%) as an orange solid, mp 139–140 °C. ^{1}H NMR: 9.31 (1H, d, J = 13.1 Hz, 1-H), 7.88 (1H, dd, J = 7.9, 1.5 Hz, Ar-H_1), 7.62 (1H, dd, J = 8.0, 1.2 Hz, Ar-H_1), 7.51–7.25 (4H, m, Ar-H_4), 7.32 (1H, d, J = 13.1 Hz, 2-H), 2.68 (6H, s, N(CH_3)$_2$; ^{13}C NMR: 151.1 (8′-C), 143.9 (1-C), 133.2 (2-C), 135.7, 131.2, 129.2, 128.4, 127.0, 126.7, 125.5, 124.9 (Ar-C_8), 118.9 (7′-C), 45.3 (N(CH$_3$)$_2$); ν_{max}/cm^{-1} (KBr): 1618, 1519, 1503, 1341, 970, 770, 762; m/z: (EI) 242 (M$^+$, 70), 196 ([M − NO_2]$^+$, 100), 181 (92), 166 (55); HRMS (EI) found 242.1060, $C_{14}H_{14}N_2O_2$ requires 242.1055.

E-1-(8′-Dimethylaminonaphth-1′-yl)-2-nitropropene 18

Nitroethane (0.01 ml, 0.14 mmol) and ethylenediamine diacetate (5 mg, 0.03 mmol) were added to a solution of aldehyde **16** (0.10 g, 0.50 mmol) in dry methanol (3 ml) under a nitrogen atmosphere, and stirred together for 48 h at room temperature. The solvent was evaporated, and the residue purified by chromatography on silica, eluting with cyclohexane–ethyl acetate (10 : 1) to give **18** (0.09 g, 68%) as an orange solid, mp 68–69 °C. ^{1}H NMR: 8.97 (1H, s, 1-H), 7.86 (1H, d, J = 8.1 Hz, Ar-H_1), 7.63 (1H, dd, J = 8.1, 1.2 Hz, Ar-H_1), 7.49–7.44 (2H, m, Ar-H2), 7.31 (1H, dd, J = 7.4, 1.3 Hz, Ar-H_1), 7.22 (1H, m, Ar-H_1), 2.63 (6H, s, N(CH_3)$_2$), 2.33 (3H, s, 3-H_3); ^{13}C NMR: 151.3 (8′-C), 141.3 (2-C), 139.5 (1-C), 135.6, 129.8, 129.5, 127.3, 126.5, 125.3, 124.8, (Ar-C_8, 1 degeneracy), 118.9 (7′-C), 45.5 (N(CH$_3$)$_2$), 13.3 (3-C); ν_{max}/cm^{-1}: 2856, 2827, 2787, 1653, 1516, 1455, 1426, 1387, 1321, 1025, 971, 775, 760; m/z: (EI) 256 (M$^+$, 20), 210 ([M − NO_2]$^+$, 70), 195 (100), 182 (43), 180 (45), 168 (35), 167 (30), 166 (38), 165 (30); HRMS (EI) found 256.1209, $C_{15}H_{16}N_2O_2$ requires 256.1212.

1,1-Dimethylbenzo[*cd*]indolium-2-benzoylnitromethide 22

Benzoylnitromethane (1.24 g, 7.50 mmol) and ethylenediamine diacetate (62 mg, 0.342 mmol) were added to a solution of aldehyde **16** (0.68 g, 3.42 mmol) in dry methanol (10 ml) under a nitrogen atmosphere, and stirred together for 28 h at room temperature. The resulting precipitate was filtered and washed with methanol to give **22** (0.89 g, 75%) as a yellow powder (from methanol), mp 161–162 °C. ν_{max}/cm^{-1} (KBr): 1610, 1577, 1450, 1408, 1321, 1309, 1190, 1176, 1106, 1083, 954, 812, 796, 777, 736, 710, 641; m/z (APCI): 347 ([M + H]$^+$, 100), 301 (22); HRMS (ES) found 347.1392 for [M + H]$^+$, $C_{21}H_{19}N_2O_3$ requires 347.1396. ^{1}H NMR (400 MHz, DMSO-d$_6$): 3 : 2 mixture of isomers, major component 8.06 (1H, d, J = 8 Hz, 8-H), 8.02 (1H, d, J = 8 Hz, 6-H), 7.88 (1H, d, J = 8.2 Hz, 5-H), 7.79 (1H, t, 7.8 Hz, 7-H), 7.72 (1H, s, 2-H), 7.61 (1H, dd, J = 8.2, 7.2 Hz, 4-H), 7.49 (2H, dm, J = 8.2 Hz, 2′-,6′-H), 7.32–7.40 (3H, m, 3′-,4′,-5′-H), 7.25 (1H, dd, J = 6.8, 1.2 Hz, 3-H), 3.58 (6H, s, N(CH_3)$_2$), minor component 8.06 (1H, d, J = 8 Hz, 8-H), 8.03 (1H, d, J = 7 Hz, 6-H), 7.92 (1H, d, J = 8.2 Hz, 5-H), 7.78 (1H, t, J = 7.9 Hz, 7-H), 7.72 (1H, t (partly obscured), J = 7.7 Hz, 4-H), 7.57 (2H, m, 2′-,6′-H), 7.32–7.40 (5H, m, 3′-,4′,-5′-H), 7.39 (1H, d (obscured), 3-H), 7.18 (1H, s, 2-H), 3.58 (6H, s, N(CH_3)$_2$); ^{13}C NMR (100 MHz, DMSO-d$_6$,): major component 188.8 (C=O), 147.4 (8a-C), 143.0 (1′-C), 135.0 (2a-C), 131.2 (5a-C), 130.1 & 130.0 (4-,4′-C), 128.7 (8b-C), 128.4 (7-C), 127.8 (2′-3′-,5′-,6′-C), 126.8 (6-C), 124.2 (5-C), 119.0 (3-C), 116.5 (^-C-NO_2), 114.5 (8-C), 94.3 (2-C), 53.4 (N-(CH$_3$)$_2$); minor component 189.2 (C=O), 147.7 (8a-C), 143.2 (1′C), 135.8 (2a-C), 131.3 (5a-C), 130.3 and 129.2 (4-,4′-C), 128.7 (8b-C), 128.3 (7-C), 127.7 (2′,-3′-,5′-,6′-C), 126.9 (6-*C*), 123.9 (5-*C*), 118.5 (3-*C*), 116.7 ($^-$*C*-NO_2), 114.2 (8-*C*), 91.0 (2-*C*), 52.9 (N-(CH_3)$_2$); ^{1}H NMR (400 MHz, $CDCl_3$): 4 : 1 mixture of isomers, main component 8.30 (1H, s, 2-*H*), 7.82 (1H, d, J = 8.3 Hz, 8-*H*), 7.78 (1H, d, J = 8.0 Hz, 5-H), 7.74 (2H, d, J = 8.0 Hz, 2′-,6′-*H*), 7.58 (1H, t, J = 7.7 Hz, 7-*H*), 7.46 (1H, t, J = 8.0 Hz, 4-*H*), 7.45 (1H, t, J = 7.4 Hz, 4′-*H*), 7.41 (1H, d, *J*-value obscured, 6-*H*), 7.37 (2H, t, J = 7.4 Hz, 3′-,5′-*H*), 7.20 (1H, br d, J = 7.0 Hz, 3-*H*), 3.33 (6H, s, N(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): main component 188.9 (C=O), 148.0 (8a-*C*), 140.4 (1′-*C*), 133.2 (2a-*C*), 130.8 (5a-*C*), 127.2–130.7, (4-,7-,8b, 2′,-3′-,4′-,5′-,6′-*C*), 126.8 (5-*C*), 123.7 ($^-$*C*-NO_2), 121.9 (3-*C*), 115.2 (6-*C*), 112.4 (2-*C*), 51.7 (N-(CH_3)$_2$).

Conversion of 22 to 30

On heating a solution of **22** for 48 h in DMSO-d_6, an intramolecular reaction yielded a single compound, whose structure is proposed as 3-benzoyl-*N*-methyl-3-nitro-1,2,3,4-tetrahydronaphth[1,8-*bc*]azepine **30**, ^{1}H NMR (400 MHz, DMSO-d_6): 7.83 (2H, d, J = 8.0 Hz, 2′-,6′-*H*), 7.73 (1H, dd, J = 8.3, 1.0 Hz, 7-*H*), 7.73 (1H, t, J = 7.4 Hz, 4′-*H*), 7.59 (2H, t, J = 7.8 Hz, 3′-,5′-*H*), 7.41 (1H, dd, J = 7.7, 0.8 Hz, 8-*H*), 7.34 (1H, t, J = 7.7 Hz, 9-*H*), 7.30 (1H, t, J = 7.6 Hz, 6-*H*), 7.13 (1H, br d, J = 6.8 Hz, 5-*H*), 6.90 (1H, d, J = 7.3 Hz, 10-*H*), 4.28 (1H, br) and 4.18 (1H, br) (at 90 °C, an AB system, J = 16 Hz, 4-H_2),† 4.15 (2H, s, 2-H_2), 3.03 (3H, s, N-CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): 191.2 (*C*=O), 151.1 (10a-*C*), 135.9 (4′-*C*), 134.2 (7-*C*), 134.1 (7a-*C*), 131.6 (4a-*C*), 129.5 (3′-,5′-*C*), 128.7 (2′-,6′-*C*), 128.3 (4′-*C*), 128.0 (5-*C*), 126.7 (10b-*C*), 126.2 (9-*C*), 125.8 (6-*C*), 121.1 (8-*C*), 110.2 (10-*C*), 99.9 (3-*C*), 63.3 (2-*C*), 41.6 (4-*C*), 41.4 (N-CH_3). Addition of water to the sample precipitated a small amount of **30**, ^{1}H NMR (270 HMz, $CDCl_3$): 7.77 (2H, d, J = 7.9 Hz, 2′-,6′-*H*), 7.60 (1H, dd, J = 8.3, 1.1 Hz, 7-*H*), 7.54 (1H, t, J = 7.4 Hz, 4′-*H*), 7.41 (2H, t, J = 7.4 Hz, 3′-,5′-*H*), 7.16–7.31 (3H, m, 6-,8-,9-*H*) 7.02 (1H, br d, J = 6.3 Hz, 5-*H*), 6.78 (1H, dd, J = 7.2, 1.5 Hz, 10-*H*), 4. 15 (2H, br, 4-*H*), 4.06 (2H, AB system, J = 15.3 Hz, 2-*H*),† 3.00 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$): 189.7 (*C*=O), 150.9 (10a-*C*), 135.9 (4′-*C*), 133.9 (7-*C*), 133.6 (7a-*C*) 131.3 (4a-*C*), 129.0 (3′-,5′-*C*), 128.5 (2′-,6′-*C*), 128.2 (4′-*C*), 128.0 (5-*C*), 126.4 (10b-*C*), 125.7 (9-*C*), 125.6 (6-*C*), 121.0 (8-*C*), 109.3 (10-*C*), 99.5 (3-*C*), 63.5 (2-*C*), 41.7 (4-*C*), 41.0 (N-CH_3); *m/z* (EI) 346 (M^+, 35), 301 (32), 300 ([M − NO_2]$^+$, 30), 285 (15), 196 (32), 195 ([M − NO_2 − PhCO]$^+$, 66), 194 (67), 181 (52), 180 (53), 168 (51), 152 (25), 105([PhCO]$^+$, 100).

X-Ray Crystallography

All structures were solved and refined with SHELX-97.[49] Non-hydrogen atoms were assigned anisotropic displacement parameters. H atom positions were located and refined with isotropic displacement parameters. Molecular geometry calculations were made with PLATON,[50] and illustrations were made with ORTEP-3[51] and POVRAY.[52] See http://dx.doi.org/10.1039/b506045a for crystallographic data in CIF or other electronic format.

Crystal data for 11A. $C_{18}H_{15}NO_2$, M_r = 277.32, triclinic, a = 10.153(3), b = 13.179(7), c = 13.179(7) Å, α = 77.35(2), β = 84.61(4), γ = 70.15(2)°, V = 1407.3 Å^3, Z = 4, $P\bar{1}$, D_c = 1.31 g cm^{-3}, μ(MoKα) = 0.08 mm^{-1}, T = 100 K, 6320 unique reflections, 5294 with $F_o > 4\sigma(F_o)$, R = 0.040, wR = 0.104. Crystals from methanol. CCDC reference number 279018.

Crystal data for 11B. $C_{18}H_{15}NO_2$, M_r = 277.32, monoclinic, a = 9.9997(2), b = 13.1284(2), c = 21.6474(3) Å, β = 95.7020(10)°, V = 2827.8 Å^3, Z = 8, $P2_1/n$, D_c = 1.30 g cm^{-3}, μ(MoKα) = 0.08 mm^{-1}, T = 100 K, 6211 unique reflections, 4157 with $F_o > 4\sigma(F_o)$, R = 0.037, wR = 0.080. Long rods from ethyl acetate. CCDC reference number 279018.

Crystal data for 11C. $C_{18}H_{15}NO_2$, M_r = 277.32, triclinic, a = 9.7709(4), b = 12.8905(5), c = 13.2494(6) Å, α = 70.822(2), β = 68.573(2), γ = 76.360(2)°, V = 1454.45 Å^3, Z = 4, $P\bar{1}$, D_c = 1.27 g cm^{-3}, μ(MoKα) = 0.08 mm^{-1}, T = 150 K, 6430 unique reflections, 3576 with $F_o > 4\sigma(F_o)$, R = 0.064, wR = 0.152. Crystals from acetone. One of the two independent molecules in the asymmetric unit is orientationally disordered over two positions, with relative populations 17 : 3. CCDC reference number 279018.

Crystal data for 12. $C_{19}H_{18}N_2O$, M_r = 290.36, monoclinic, a = 9.3770(2), b = 9.7055(2), c = 16.7953(3) Å, β = 91.3607(12)°, V = 1528.08 Å^3, Z = 4, $P2_1/c$, D_c = 1.26 g cm^{-3}, μ(MoKα) = 0.08 mm^{-1}, T = 120 K, 3504 unique reflections, 2884 with $F_o > 4\sigma(F_o)$, R = 0.045, wR = 0.119. Crystals from ethyl acetate. CCDC reference number 279019.

Crystal data for 13. $C_{26}H_{23}N_3O_2$, M_r = 409.48, triclinic, a = 9.8308(2), b = 9.6640(3), c = 12.0688(3) Å, α = 85.4547(15), β = 68.6506(14), γ = 78.8152(15)°, V = 1047.58 Å^3, Z = 2, $P\bar{1}$, D_c = 1.30 g cm^{-3}, μ(MoKα) = 0.08 mm^{-1}, T = 120 K, 4800 unique reflections, 3570 with $F_o > 4\sigma(F_o)$, R = 0.051, wR = 0.124. Crystals from ethanol. (It is interesting to note a short contact across the centre of symmetry between two *para* carbon atoms of ring A (C15–C15: 3.056(2) Å), which is accompanied by edge-to-face contacts between the attached H15 atoms which are directed to the centroids of the [C5–C10] naphthalene rings (H15 · · · centroid: 2.86 Å). CCDC reference number 279020.

Crystal data for 17. $C_{14}H_{14}N_2O_2$, M_r = 242.27, monoclinic, a = 15.8700(3), b = 5.4817(1), c = 28.7715(8) Å, β = 101.0295(8)°, V = 2456.7(1) Å^3, Z = 8, $C2/c$, D_c = 1.31 g cm^{-3}, μ(MoKα) = 0.09 mm^{-1}, T = 120 K, 2785 unique reflections, 2023 with $F_o > 4\sigma(F_o)$, R = 0.048, wR = 0.127. Crystals from ethyl acetate–hexane 1 : 2. CCDC reference number 279021.

Crystal data for 18. $C_{15}H_{16}N_2O_2$, M_r = 256.30, monoclinic, a = 10.3347(3), b = 7.0992(2), c = 18.2556(5) Å, β = 102.897(2)°, V = 1305.59(6) Å^3, Z = 4, $P2_1/n$, D_c = 1.30 g cm^{-3}, μ(MoKα) = 0.09 mm^{-1}, T = 120 K, 2981 unique reflections, 2600 with $F_o > 4\sigma(F_o)$, R = 0.055, wR = 0.163. Crystals from ether. CCDC reference number 279022.

Crystal data for 22. $C_{21}H_{18}N_2O_3$, M_r = 346.37, monoclinic, a = 7.7283(2), b = 13.6696(4), c = 15.7465(6)Å, β = 95.5779(12)°, V = 1655.63(9) Å^3, Z = 4, $P2_1/c$, D_c = 1.39 g cm^{-3}, μ(MoKα) = 0.09 mm^{-1}, T = 120 K, 3764 unique reflections, 2820 with $F_o > 4\sigma(F_o)$, R = 0.047, wR = 0.125. Crystals from acetonitrile. CCDC reference number 279023.

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