

Interactions between alkynes and methoxy or dimethylamino groups in *peri*-naphthalene systems

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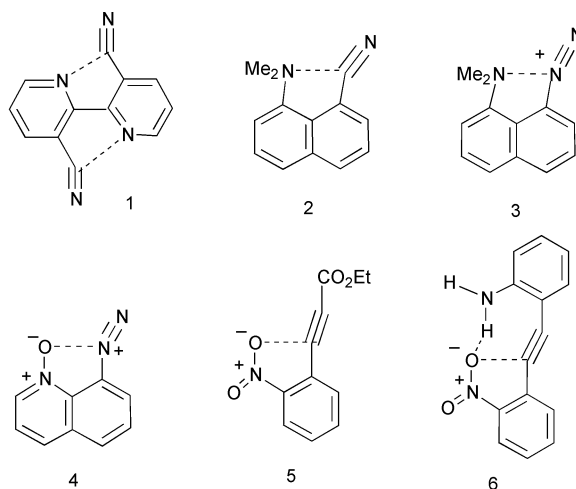
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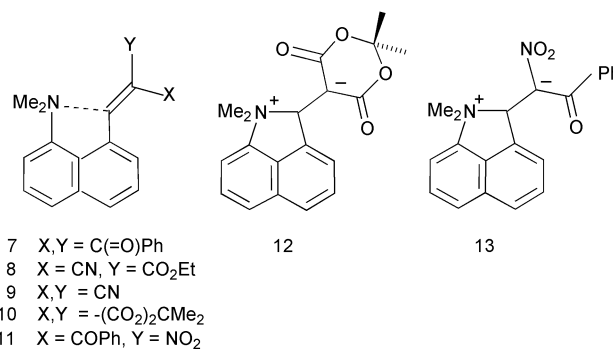
X-Ray studies of a series of 1-ethynyl-8-methoxynaphthalenes with varying functional groups at the alkyne terminus show only small changes in the 1,5 MeO \cdots spC contact distances (2.593–2.663 Å) despite the different through-bond electron-attracting powers of the terminal substituents. Replacement of methoxy with dimethylamino led to a chemical reaction when the alkyne's activating group was a carboxylic ester. The 1,5 N \cdots spC interaction between a dimethylamino group and a triphenylsilylethyne group has a 1,5 Me₂N \cdots spC contact distance *ca.* 0.12 Å longer than for the corresponding methoxy case, indicative of a primarily steric interaction.

Introduction

The progress of a chemical reaction between two functional groups has been modelled by examining the structures of families of compounds containing those groups in close proximity, for example a dialkylamino and a carbonyl group,¹ resulting in the construction of a reaction coordinate. A similar approach has been used to follow the decomposition of acetals, and has been developed to relate the sensitivity of bond length changes in a particular system to its rate of reaction.^{2–4} There have been considerably fewer structural studies on the incipient nucleophilic addition to triply bonded systems, especially alkynes. Interactions between nitriles or diazonium cations with electron-rich functional groups in *peri*-naphthalene and other systems have been observed, for example in 1–4.^{5–8} Typically the triply bonded functional group shows a bend of *ca.* 10° from linearity at the α -atom. More recently, short O \cdots spC contacts [2.642(2) to 2.672(4) Å] were observed between *ortho* nitro and alkyne groups in 5 and 6,^{9,10} and in each case the triple bond shows a *trans* bend. However, the nitro group is a very poor nucleophile.



The *peri*-naphthalene system has been used to investigate interactions between functional groups^{8,11} and recently was used to construct models for different stages of the Michael reaction of electron-deficient alkenes with dimethylamino groups using molecules 7–11.¹² Indeed, compounds 10 and 11 shows almost complete bond formation between the groups, so the structures are better represented as zwitterions 12 and 13. When combined with data for *peri*-interactions with less activated alkenes¹³ and with carbonyl derivatives, the considerable variation in the Me₂N \cdots sp²C separation [1.639(2)–2.758(2) Å] allowed an order of through-space electron accepting power to be constructed.¹⁴ We now report on the synthesis and molecular geometries of naphthalene derivatives containing a methoxy or a dimethylamino group and an alkyne group in the *peri* positions.

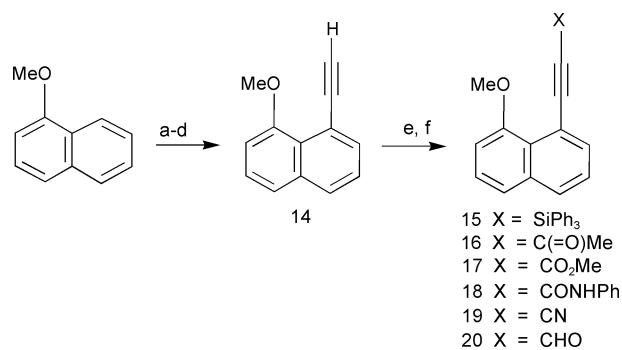


- 7 X, Y = C(=O)Ph
8 X = CN, Y = CO₂Et
9 X, Y = CN
10 X, Y = -(CO₂)₂CMe₂
11 X = COPh, Y = NO₂

Discussion

A series of crystalline 8-methoxy-1-ethynyl-naphthalene derivatives 14–20 was prepared from 1-methoxynaphthalene (Scheme 1). *peri*-Lithiation and reaction with iodine gave 8-iodo-1-methoxynaphthalene which underwent Sonogashira coupling with trimethylsilylethyne or 2-methylbut-3-yn-2-ol and subsequent hydrolysis to give the unsubstituted ethyne 14. Deprotonation of 14 with methylolithium and treatment with a range of electrophilic reagents gave the substituted alkynes 15–19 as crystalline materials. Reaction of lithiated 14 with DMF gave the propynal derivative 20 but only as an oily solid. The molecular structures of 14–19 were measured by X-ray diffraction at low temperature. The molecular structures are

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Scheme 1 Reagents and conditions: a, *t*-BuLi 48 h; b, I₂; c, HCCSiMe₃ (or HCCC(Me)₂OH), PdCl₂(PPh₃)₂, CuI, Et₃N; d, NaOH, MeOH; e, MeLi; f, Ph₃SiCl or Ac₂O or ClCO₂Me or PhNCO or PhOCN or DMF.

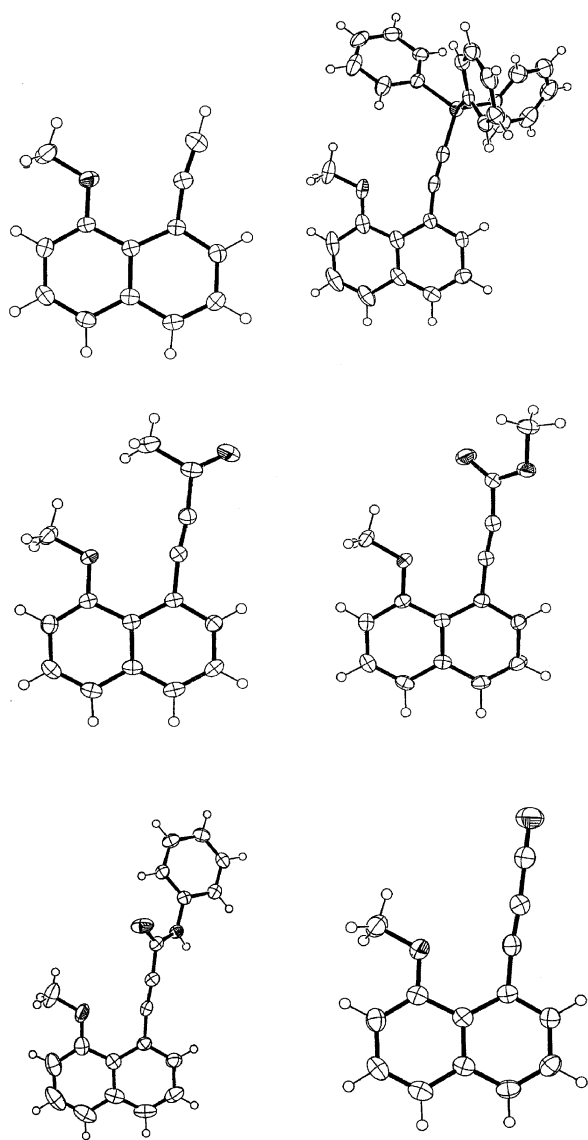


Fig. 1 Molecular structures of **14** and **15** (top), **16** and **17** (middle) and **18** and **19** (bottom) with anisotropic displacement parameters drawn at the 50% level.³⁴

shown in Figs. 1 and 2. Each molecule contains an in-plane methoxy group with the methyl group directed towards the *ortho* hydrogen atom. In all cases the geometry of the alkyne group has been influenced by the presence of a neighbouring methoxy group. There is a short 1,5 O...spC contact with the *peri*-alkyne group lying in the range 2.593(2)–2.664(2) Å. Each triple bond shows a *trans* bend, with angles at the spC atoms in the

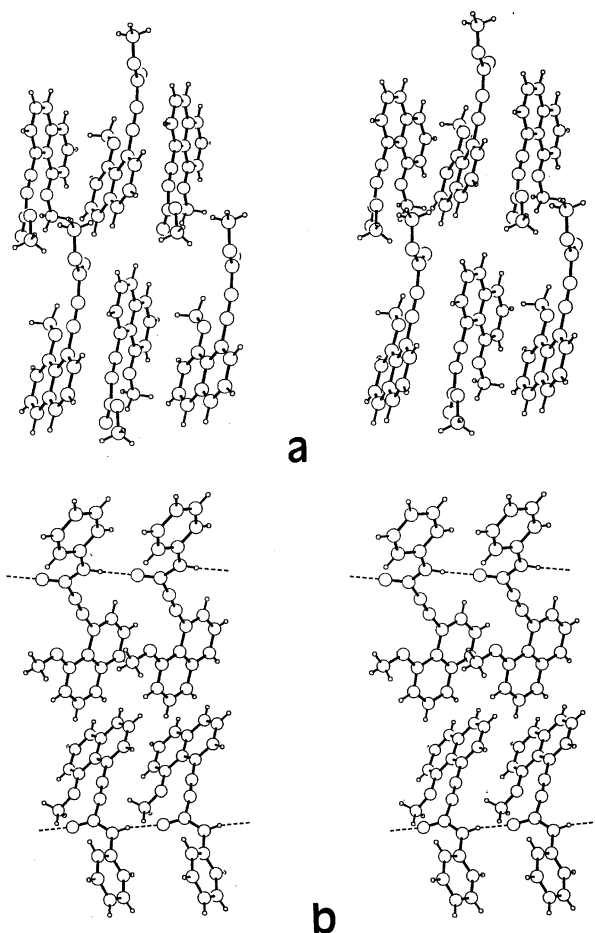
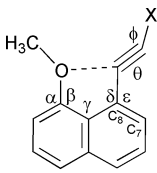


Fig. 2 Stereo-diagrams³⁵ of the crystal packing in **17** (a) and **18** (b), which show the carbonyl groups lying out of the naphthalene plane, and hydrogen bonding of molecules of **18** into stacks along the *b* axis.

range 169.2(2) to 176(1)°, such that the carbon atom involved in the short contact is displaced towards the methoxy O atom from the vector connecting its bonded neighbouring atoms. Selected geometric details for **14** to **19** are given in Table 1.

The longer O...C contacts are for the unsubstituted alkyne **14** [2.663(2) Å], the triphenylsilylalkyne **15** [2.664(4) and 2.623(4) Å] and the butynone **16** [2.645(2) Å], but are significantly shorter than van der Waals separation (*ca.* 3.2 Å). The acetyl group in **16** is almost exactly coplanar with the naphthalene ring system, so that this group does not exert a mesomeric electron withdrawing effect on the component of the alkyne's π orbitals lying in the molecular plane. The O...C contact distances in these three cases are similar to those in **5** and **6**. In contrast, in the alkyne nitrile **19** where the nitrile group can activate the alkyne's in-plane π orbitals the O...C distance is 2.593(2) Å, 0.048 Å shorter than in ketone **16**. The nitrile group has linear geometry [C–C \equiv N angle: 179.5(2)°]. Furthermore, the two crystallographically independent molecules of the amide **18** and the molecule of the methyl ester **17** also show shorter O...C distances than in the ketone **16** by virtue of their conformations in the solid state. Thus, they contain groups which can partially activate the in-plane component of the alkyne's π system since their carbonyl groups have rotated out of the molecule plane by 35–48° (Fig. 2). Of the two independent molecules of **18** the one with the greater angular displacement of the carbonyl out of the naphthalene plane [48.4(2) *cf.* 43.0(2)°] shows the shorter O...C distance [2.598(4) *cf.* 2.621(4) Å]. In this case the molecules are packed in stacks, neighbours related to each other by one unit cell translation along the *b* axis, and are held in the stacks by the formation of N–H...O=C hydrogen bonds (H...O 1.96 and 1.97 Å, N–H...O 168 and 167°) (Fig. 2). Alignment of groups

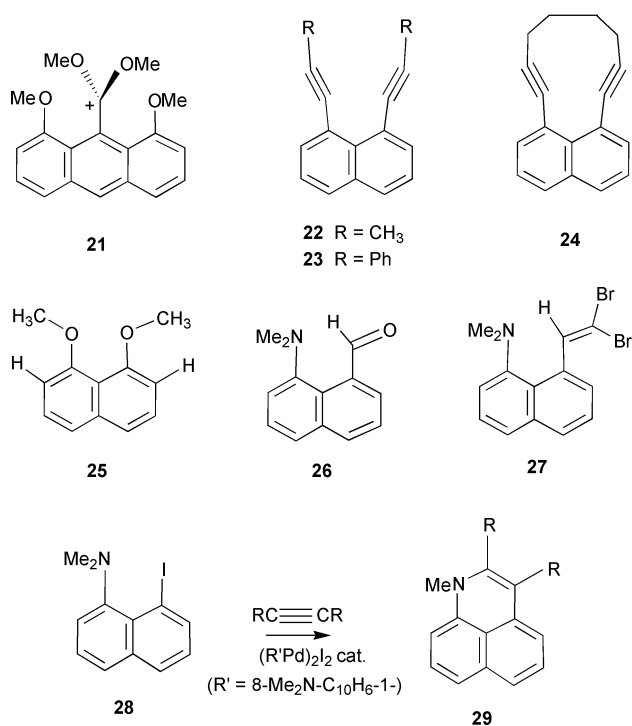
Table 1 Selected molecular geometry for **14–19**, with distances in Å and angles in degrees


X	O...C	C≡C	α	β	γ	δ	ϵ	θ	ϕ	Torsion angle between C7–C8 and the C=O
14 , H	2.663(2)	1.191(2)	123.5(2)	115.8(1)	124.7(1)	124.4(1)	115.9(1)	169.2(2)	176(1)	—
15 , SiPh ₃	2.664(4)	1.216(4)	124.4(4)	115.5(3)	124.5(3)	125.0(3)	115.5(3)	169.8(3)	174.1(3)	—
15 , SiPh ₃	2.623(4)	1.207(4)	124.1(3)	115.2(3)	123.9(3)	124.0(3)	116.1(3)	173.2(3)	173.3(3)	—
16 , COMe	2.645(1)	1.206(2)	123.6(1)	115.5(1)	124.5(1)	124.0(1)	116.4(1)	173.0(1)	172.8(1)	0.87(9)
17 , CO ₂ Me	2.606(3)	1.202(4)	124.2(2)	114.9(2)	124.1(2)	123.5(2)	116.5(2)	174.6(3)	169.0(3)	35.03(6)
18 , CONHPh	2.621(5)	1.192(4)	123.0(3)	115.4(3)	124.7(3)	123.3(3)	116.8(3)	175.2(4)	170.4(3)	43.0(2)
18 , CONHPh	2.598(4)	1.197(4)	124.8(3)	115.0(3)	123.7(3)	123.9(3)	116.0(3)	172.6(3)	174.9(3)	48.4(2)
19 , CN	2.593(2)	1.203(3)	124.2(2)	115.0(2)	124.0(2)	123.3(2)	116.4(2)	173.7(2)	175.4(2)	—

to make these intermolecular attractions necessitate a displacement of the amide group out of the naphthalene plane. Larger angular displacements of the amide groups to form the hydrogen bond could be produced by small changes to the molecular structure designed to increase the separation between neighbours in the stack.

The narrow range (0.073 Å) of MeO...spC contacts indicate that this interaction is rather insensitive to the electronic character of the alkyne. Similar results were found for the *peri* interactions of methoxy groups with sp² C atoms of carbonyl groups and electron deficient alkenes [2.526(3)–2.623(2) Å for 10 structures].¹⁴ Even when the interaction is with a carbocation in **21** the MeO...C⁺ separations are quite long [2.43(1) and 2.45(1) Å].¹⁵ In the interaction with alkynes there does indeed appear to be a relationship between a shortening MeO...spC distance and an increasing electron attracting effect of the alkyne's substituent working on the component of the π bond "facing" the methoxy group. However, it needs to be noted that optimisation of the way the molecules pack together can make small perturbations to a molecular structure, and this can be a complicating factor if the interactions under investigation vary only over a small range. Furthermore, any disorder in the structure may have a similar effect. Thus, for the two independent molecules of **15** the MeO...spC distance in molecule **A** is *ca.* 0.04 Å longer than in molecule **B**. However, the latter has some disorder at the triphenylsilyl group; two of these groups lie close together across a centre of symmetry. In some parts of the crystal there is a molecule of methanol located at this centre, which causes a perturbation to the orientation of one of the phenyl groups. This is the only structural change which was modelled, but it should be borne in mind that there are likely to be small differences in the rest of the structure, and these will be absorbed in the observed molecular geometry which is a weighted average of the perturbed and unperturbed **B** molecules.

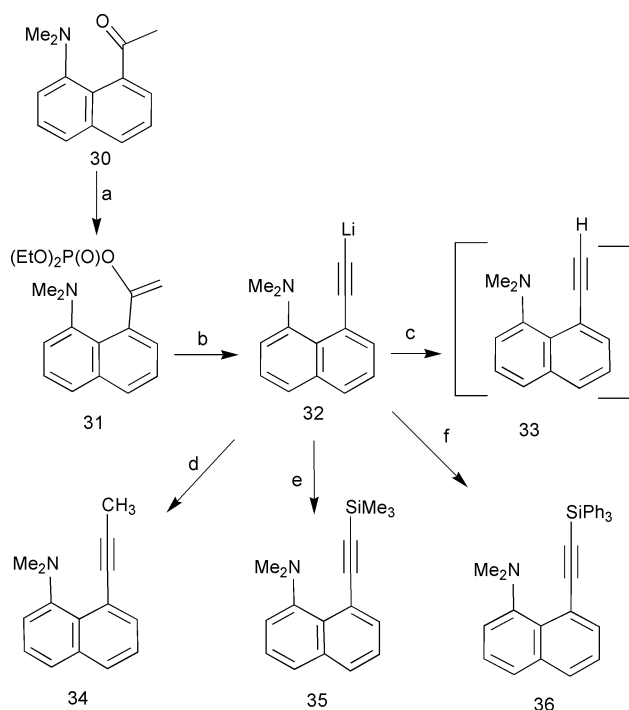
Molecular packings in these substances can also be optimised by small angular changes at the alkyne C atoms. Thus, although all the materials show a *trans* distortion in the same sense, there is no strong relationship between the degree of the *trans* distortion and the MeO...spC distance. The deviation of sterically unencumbered alkynes from linearity in the solid state is on average *ca.* 3°, but only rarely more than 4°. It is important to note that in *peri*-naphthalenedialkynes such as **22** and **23** although the two alkyne groups are splayed apart with shortest spC...spC separations of *ca.* 2.85 Å, the triple bonds still retain a *trans* bend,¹⁶ and this is so even when the triple bonds are joined by a -(CH₂)₄- link forming an eleven-membered ring system in **24**.¹⁷ Thus, a *trans* bend is not necessarily an indicator for an attractive interaction with a neighbouring group.



The Cambridge Structural Database¹⁸ contains eight naphthalenes which contain the fragment **25**, *i.e.* 1,8 *peri* methoxy groups with no *ortho* substituents, with in-plane conformations similar to those observed for **14–19** and an average O...O separation of just 2.51 Å.¹⁹ From these data and the spC...spC separations in **22** and **23** one could predict a O...spC separation between *peri*-groups of *ca.* 2.68 Å, close to that observed in **14**. Thus, the MeO...spC separation and the *trans* bend of the alkyne in **14** do not necessarily imply an attractive interaction. The reduction in the separation with more electron deficient alkynes indicates some form of weak interaction which could be ascribed to either covalency or a closed shell interaction, the latter arising from the contraction in the alkyne π electron cloud when an electron withdrawing substituent is present. No distinction can be made from these studies.

Since in earlier work the *peri* interactions of dimethylamino groups with electron deficient alkenes were found to be much more sensitive to the electronic character of the alkene than were the interactions of methoxy groups, the 8-dimethylamino-1-naphthylethyne was an obvious next step for investigation of interactions with carbon–carbon triple bonds. However, the synthesis of this group of molecules was not straightforward.

Reaction of the *peri*-dimethylamino aldehyde **26** with triphenylphosphine and tetrabromomethane using the Corey–Fuchs procedure²⁰ gave the dibromoethene derivative **27** as an unstable solid which decomposed over three hours. An attempt to eliminate hydrogen bromide with *n*-BuLi gave no identifiable products. Palladium-catalysed couplings of the *peri*-iodo compound **28** with terminal alkynes were unsuccessful, and others have reported the isolation of the cyclised products of type **29** which have lost one methyl group from reaction with various di-substituted alkynes.²¹ Nevertheless, success was achieved using a three-step ‘one pot’ procedure²² starting from the methyl ketone **30** (Scheme 2). The ketone was converted into its



Scheme 2 Reagents and conditions: a, LDA, (EtO)₂POCl; b, 2.15 eq. LDA; c, H₂O; d, CH₃I; e, Me₃SiCl; f, Ph₃SiCl.

enol diethyl phosphate **31** with LDA and diethyl chlorophosphate, which was then added to two further equivalents of LDA leading to production of a solution of the lithiated ethyne **32** by elimination of lithium diethyl phosphate and deprotonation. The anion **32** could be converted *in situ* to its methyl, trimethylsilyl and triphenylsilyl derivatives **34–36** by reaction with appropriate electrophile. Of these alkynes only **36** was a solid at room temperature, and its structure was measured by X-ray crystallography.

The molecular structure of **36** determined at 150 K is illustrated in Fig. 3, and details of the molecular geometry are given in Table 2, which also contains corresponding data for the

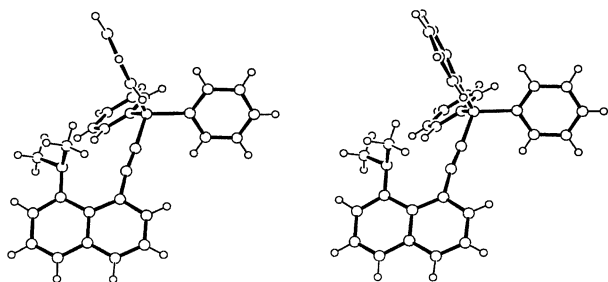


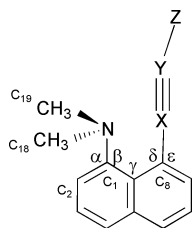
Fig. 3 Stereo-diagram of the molecular structure of **36**, indicating the asymmetric orientation of the dimethylamino group with respect to the naphthalene ring system, with anisotropic displacement parameters drawn at the 50% level.³⁵

nitrile **26** and diazonium salt **38**. The dimethylamino N atom lies 2.766(2) Å from the alkyne C atom attached to the naphthalene ring. The triple bond shows a *trans* distortion. The group deviates from linearity at each end of the triple bond by 8.3(2) and 3.5(2)° and the torsion angle about the triple bond is 167(2)°. Although both functional groups are displaced in the same direction in the plane of the naphthalene ring, the alkyne is displaced from its theoretical position by more (4.5°) than the dimethylamino group (1.7°). There are also displacements of the functional groups to opposite sides of the plane which increase their separation; the N atom lies 0.202(2) Å to one side of the plane and the two alkyne C atoms and the Si atom lie 0.182(2), 0.302(3) and 0.451(3) Å, respectively to the other side of the ring system. The 1,5 Me₂N...spC separation is similar in size to that between a dimethylamino group and a diisopropylamide group [2.764(3) Å in **37**]²³ and is slightly longer than that between a dimethylamino group and a 2-bromoethenyl group (averaged value: 2.742 Å).¹³ With this distance as a measure of the through-space electron attracting power for a functional group, the triphenylsilyl ethynyl group is among the least attracting of all groups considered to date. Compared to interactions with other triply bonded functional groups the separation is longer than that between a dimethylamino group and the more polar nitrile group in **2** [2.704(6) Å]⁶ or the diazonium cation **3** [2.54(1) Å].⁸ The dimethylamino group in **36** is oriented so that its lone pair axis makes an angle of 35° with the Me₂N...spC vector, further suggesting that this group is not attracted to the triple bond. The nitrile **2** and diisopropylamide **37** show similar orientations of their dimethylamino groups, while compound **9** with an electron deficient dicyanoethenyl group has the dimethylamino nitrogen atom's lone pair lying at only 13° to the Me₂N...sp²C vector.

In earlier work we proposed that the attractive nature of an interaction between a dimethylamino group and another *peri*-located functional group containing an alkene or carbonyl group could be judged by comparing the 1,5 N...sp²C distance with the 1,5 O...sp²C distance in the corresponding methoxy compound. Allowing for the greater size of the bonded N atom over the bonded O atom (*ca.* 0.15 Å),¹⁴ the increasing significance of an interaction is indicated by a larger value of the parameter [$d(\text{O} \cdots \text{C}) + 0.15 - d(\text{N} \cdots \text{C})$]. Thus, for interaction with a diisopropylamide group this function has the value 0.009 Å, but for interaction with a dicyanoethenyl group the value is 0.348 Å. Taking this approach to the 8-methoxy- and 8-dimethylamino-triphenylsilylalkynes **15** and **36**, and using an averaged value for the O...C interaction in the two independent molecules of **15**, the [$d(\text{O} \cdots \text{C}) + 0.15 - d(\text{N} \cdots \text{C})$] parameter has a value of only 0.018 Å, consistent with only a very weak attractive interaction. In other words the interaction is controlled primarily by steric factors when the alkyne is not activated to nucleophilic attack.

It was surprising that protonation of the anion **32** generated in the three-step ‘one-pot’ reaction did not furnish the corresponding terminal alkyne **33** or any other identifiable product. Kirby’s group was also unable to prepare this material, which in their particular studies was one candidate (subsequently rejected) for the intermediate in the intramolecular reaction of the (*Z*)-2-bromoalkenyl derivative **38** to the benzo[*de*]quinoline **39**.¹³ In contrast, the *peri*-methoxy ethynyl derivative **14** is stable under ambient conditions. It seems probable too that the instability of **33** is mirrored by its anion **32**, since, when the reaction mixture containing it was allowed to warm to room temperature before being quenched with chlorotrimethylsilane, the yield of product was small (11%). Quenching with iodomethane, chlorotriphenylsilane or tri(*n*-butyl)tin chloride at –78 °C all gave satisfactory yields of products. The groups must be reacting together since compounds in which the two groups are further apart, *e.g.* the 3- and 4-(dimethylamino)-phenylethyne, have been isolated. The highly electron-rich environment of the ethynyl group in neutral molecule **33** would

Table 2 Selected geometric data for molecules **36**, **2** and **3**, with distances in Å and angles in degrees. A_X , A_Y , A_Z , A_N : deviations of specified atoms from best plane of naphthalene ring



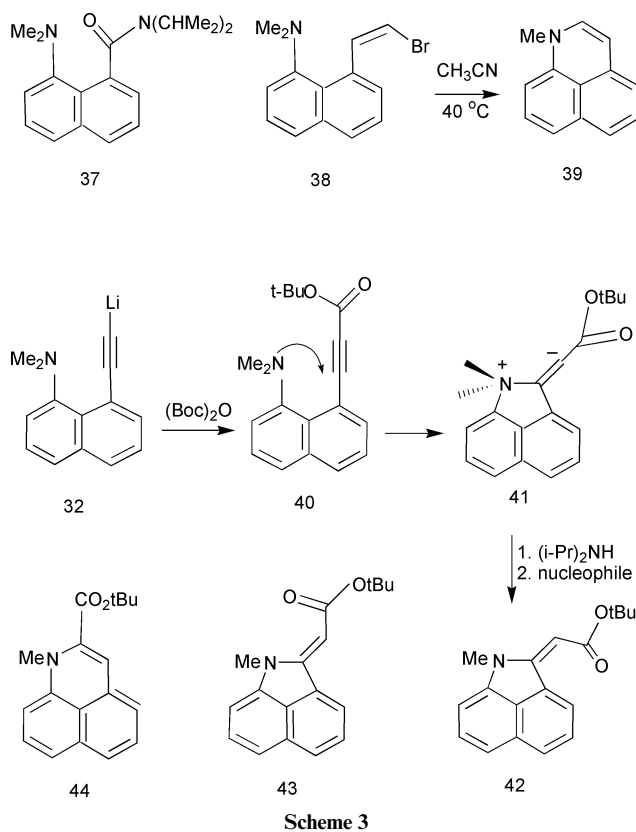
	X≡Y-Z	N...X	C ₈ -X≡Y	X≡Y-Z	C ₈ -X≡Y-Z	α	β	γ
36	-C≡SiPh ₃	2.766(2)	171.7(2)	176.5(2)	167(2)	121.9(2)	118.6(2)	125.0(2)
2	-C≡N	2.704(6)	171.2(4)	—	—	122.8(3)	117.9(4)	124.7(4)
3^a	- ⁺ N≡N	2.54(1)	167(1)	—	—	123(1)	117(1)	125(1)
	δ	ϵ	A_X	A_Y	A_Z	A_N	C1-C2-N1-C18	C1-C2-N1-C19
36	124.5(2)	115.4(2)	+0.182(2)	+0.303(3)	+0.451(3)	-0.202(2)	105.9(2)	-24.4(3)
2	123.4(3)	114.1(4)	+0.304(5)	+0.504(4)	—	-0.250(4)	109.2(5)	-22.2(6)
3^a	121(1)	113(1)	+0.07(1)	+0.08(1)	—	-0.03(1)	80(1)	-49(1)

^a BF₄⁻ counterion; there is a degree of disorder in packing of the cation, which may reduce the accuracy of this measurement.

be expected to favour oxidation of the terminal alkyne to a radical, which could then be involved in polymerization reactions. Indeed, even 1-dimethylaminonaphthalene undergoes slow oxidation in the atmosphere.

In an attempt to install an electron withdrawing ester group on the ethyne to promote an interaction between the dimethylamino group and the alkyne, the preparation of **40** was attempted by treating the anion **32** with di-*tert*-butyl dicarbonate [(Boc)₂O]. However, the only product isolated was the cyclised material **42** which has lost a methyl group. Alternative structures **43** and **44** were considered but only **42** accounts for the strong deshielding of an aromatic hydrogen atom (δ 9.24) by the carbonyl group, the size of the two-bond O=¹³C-C-H coupling constant (1.6 Hz)²⁴ and the chemical shifts of the enaminic C-H group (δ_H 5.38 and δ_C 91.66). The crystals of this material were highly twinned and structure determination was unsuccessful. The expected alkynyl product **40** probably underwent intramolecular addition of the dimethylamino group to the electron deficient triple bond (Scheme 3), and the resultant zwitterion **41** was protonated, possibly by diisopropylamine in the solution, and demethylated by attack of the diethyl phosphate anion or chloride. The *cis* isomer **42** is favoured over the *trans* isomer **43** by the lower steric hindrance experienced by the ester carbonyl with the *ortho* C-H group than with the methyl group. Although certain *peri* dimethylamino alkenes undergo the corresponding intramolecular nucleophilic addition to give isolable zwitterions such as **12** and **13**, in these cases the carbanionic centre is much less reactive than the vinyl carbanion in zwitterion **41**.

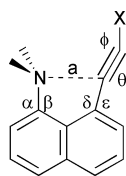
A preliminary investigation of the calculated structures of a series of naphthalenes with *peri* dimethylamino and alkyne groups has been made to determine whether it is possible to identify trends in the interaction between the groups as the terminal alkyne substituent is varied. The groups selected ranged from electron donating groups such as methoxy and amino to electron attracting groups such as nitro, trifluoromethyl and diazonium. Calculations were made using GAUSSIAN-94²⁵ at the RHF 3.21G level. The results are summarised in Table 3. The structures show 1,5 contacts between the *peri* nitrogen and sp carbon atom lying in the range 2.643–2.743 Å for the neutral species, with the shorter separations occurring when the alkyne substituent is electron withdrawing. When the substituent was a diazonium cation, the contact distance between *peri* atoms was noticeably reduced to 2.446 Å. In all structures calculated the alkyne group was always bent from linearity at the carbon



directly involved in the interaction by 4–11° and in the same sense as in the X-ray structure of **36**. There was no clear trend at the second sp C atom. Linear or near linear geometry was observed when the terminal functional group was electron donating or contained a triple bond. In other cases (e.g. -NO₂ or -CHO) the triple bond was bent at this position (by up to 11°) to form a *trans* distortion.

In summary, methoxy groups appear to make, at most, very weak through-space interactions with the carbon-carbon triple bonds. Although this appears a little surprising, it should be noted that the oxygen atom's p-type lone pair is conjugated with the aromatic ring, so the oxygen may bear a small net positive charge. Further insight into the nature of these interactions may be obtained by charge density studies using

Table 3 Selected molecular geometry of the calculated^a structures of 8-dimethylamino-1-naphthylethyne derivatives with distances in Å and angles in degrees



X	a	($\alpha - \beta$)/2	($\delta - \epsilon$)/2	θ	ϕ
OCH ₃	2.743	0.7	4.5	173.5	179.2
NH ₂	2.740	0.7	4.6	171.9	179.4
CH ₃	2.736	0.7	4.9	172.0	179.4
CH ₂ F	2.731	1.0	4.9	171.9	177.9
CHO	2.701	1.3	3.9	174.9	173.6
CHF ₂	2.686	1.7	3.0	175.5	173.1
CN ^b	2.673	1.6	3.8	169.4	178.6
NO ₂	2.668	1.8	3.7	176.7	176.4
CF ₃	2.643	2.0	3.3	174.7	169.4
N ₂ ⁺	2.446	4.8	2.7	170.0	178.9

^a Calculated using GAUSSIAN-94 at the RHF3-21G level. ^b In this case the calculations were made at the B3LYP 6-31G level.

the approach of Bader,²⁶ though the success of the method for identifying attractive interactions, as opposed to covalent bonds for which it works well, is under debate.²⁷ A charge density study of C=O...C≡C interactions has been completed recently.²⁸ The investigation of the corresponding interactions with dimethylamino groups is compromised by the reactivity of the system when the alkyne is electron deficient, and a less nucleophilic N-centred group will be investigated. The unactivated triphenylsilyl ethyne group showed little tendency to interact with a dimethylamino group, and as with the methoxy group, the interaction is primarily steric in nature.

Experimental

General

NMR spectra were measured on a JEOL GX 270 machine at 270 MHz for ¹H and at 67.8 MHz for ¹³C using CDCl₃ as the solvent and tetramethylsilane (TMS) as the standard, and measured in ppm downfield from TMS, unless otherwise stated. Coupling constants (*J*) are given in Hz. IR spectra were recorded on an ATI Mattson Genesis Series FTIR machine as liquid films or Nujol mulls. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre. Flash chromatography was performed on 40–63 silica gel (Merck).

1-Iodo-8-methoxynaphthalene

tert-BuLi in pentane (21 ml, 1.7 M, 33 mmol) was added to solution of 1-methoxynaphthalene (4.75 g, 30 mmol) in dry cyclohexane (60 ml) under a nitrogen atmosphere and the solution was stirred at room temperature for 24 h.²⁹ 8-Lithio-1-methoxynaphthalene precipitated and was filtered off under nitrogen using a sintered glass filter attached to the reaction vessel. The solid was washed with cyclohexane (40 ml), washed back into the reaction vessel with anhydrous ether (100 ml) and the suspension cooled to –78 °C in a solid CO₂–acetone bath. The suspension was quenched with a solution of iodine (10 g) in anhydrous ether (60 ml) and allowed to warm to room temperature over 4 h. The reaction mixture was washed with a saturated aqueous solution of sodium bisulfite (2 × 100 ml) followed by distilled water (2 × 100 ml). The organic layer was dried (MgSO₄) and evaporated, and purified by flash chromatography on silica eluting with hexane–methanol (95 : 5) to

yield 1-iodo-8-methoxynaphthalene as a white crystalline solid (4.60 g, 54%), mp 67 °C; δ_{H} 8.18 (1H, dd, *J* = 7.4, 1.1, 2-*H*), 7.75 (1H, dd, *J* = 8.1, 1.1, 4-*H*) 7.50–7.40 (2H, m, Ar-*H*₂) 7.02 (1H, dd, *J* = 8.1, 7.4, 3-*H*), 6.89 (1H, dd, *J* = 5.9, 2.9, 7-*H*), 3.93 (3H, s, O-CH₃); δ_{C} 154.17, 140.89, 136.05, 128.70, 126.94, 126.21, 125.53, 121.46, 103.68, 85.35 (Ar-C₁₀), 54.80 (O-CH₃); ν_{max} /cm⁻¹ 1262, 805, 760, 500; λ_{max} /nm 232, 307, 331; HRMS (EI): found 284.0963, C₁₁H₉IO requires: 284.0960.

1-Ethynyl-8-methoxynaphthalene (method 1) 14

Bis[triphenylphosphine]palladium(II) dichloride (140 mg, 0.2 mmol) and copper(I) iodide (10 mg, 0.1 mmol) were added to a mixture of 1-methoxy-8-iodonaphthalene (1.136 g, 4 mmol) and trimethylsilyl ethyne (0.85 ml, 0.59 g, 6 mmol) in triethylamine (40 ml) in dry apparatus under nitrogen. The reaction was stirred for 4 h. After *ca.* 0.5 h the yellow solution had turned grey/black. The reaction mixture was evaporated to dryness and the residue was extracted with chloroform (60 ml). The solution was filtered through Celite, washed with distilled water, dried (MgSO₄) and evaporated. The residue was chromatographed on silica eluting with ether–hexane (1 : 9) to yield 1-methoxy-8-trimethylsilyl ethynyl naphthalene (0.77 g, 70%) as a pale green oil; δ_{H} 7.74 (1H, dd, *J* = 6.7, 1.2, 4-*H*), 7.70 (1H, dd, *J* = 6.0, 1.2, 2-*H*), 7.50–7.30 (3H, m, Ar-*H*₃), 6.86 (1H, m, Ar-*H*₁), 4.00 (3H, s, OCH₃), 0.01 (9H, s, 3 × Si-CH₃); δ_{C} 156.32, 135.22, 134.10, 128.88, 127.61, 126.33, 125.34, 121.11, 117.82, 106.27 (Ar-C₁₀), 103.73 and 96.74 (C≡C), 55.37 (OCH₃), 0.35 [Si(CH₃)₃]; ν_{max} /cm⁻¹ 2953, 2142, 1574, 1272, 1249, 1075, 862, 838, 818, 753; λ_{max} /nm 251, 322; HRMS (EI): found 254.4032; C₁₆H₁₈OSi requires: 254.4031.

A solution of 1-methoxy-8-trimethylsilyl ethynyl naphthalene (3.05 g, 12 mmol) in methanol (20 ml) was treated with aqueous KOH (10 ml, 1 M) and stirred overnight at room temperature. The mixture was evaporated to dryness, after which the residue was extracted with chloroform (2 × 50 ml) and the solid filtered off. The filtrate was evaporated to yield **14** (1.96 g, 91%) as off-white crystals, mp 66–67 °C; δ_{H} 7.73 (2H, m, Ar-*H*₂), 7.34 (3H, m, Ar-*H*₃), 6.84 (1H, m, Ar-*H*₁), 3.93 (3H, s, O-CH₃), 3.38 (1H, s, C≡C-*H*); δ_{C} 156.16, 135.16, 134.32, 129.07, 126.38, 125.31, 125.27, 121.11, 116.87, 106.67 (Ar-C₁₀), 85.26 and 79.76 (C≡C), 55.5 (O-CH₃); ν_{max} /cm⁻¹ 3276, 1575, 1264, 1228, 1064, 818, 753; λ_{max} /nm 222, 246, 318; HRMS (EI): found 182.0731, C₁₃H₁₀O requires: 182.0732.

1-Ethynyl-8-methoxynaphthalene (method 2) 14

1-Iodo-8-methoxynaphthalene (0.85 g, 3 mmol) and 2-methylbut-3-yn-2-ol (0.34 g, 4 mmol) were dissolved in triethylamine (40 ml) under nitrogen and bis[triphenylphosphine]palladium(II) dichloride (140 mg, 2 mmol) and copper(I) iodide (10 mg, 1 mmol) added. The reaction was stirred for 12 h. The resulting black solution was evaporated to dryness and extracted with chloroform (2 × 50 ml). This organic extract was filtered through Celite, washed with distilled water (2 × 50 ml), dried (MgSO₄) and evaporated. The residue was subjected to flash chromatography on silica (ethyl acetate) to yield 4-(8'-methoxy-1'-naphthyl)-2-methylbut-3-yn-2-ol (0.51 g, 68%) as a tan oil; δ_{H} 7.70 (1H, dd, *J* = 8.2, 1.2, 4'-*H*), 7.61 (1H, dd, *J* = 7.2, 1.2, 2'-*H*), 7.40–7.30 (3H, m, Ar-*H*₃), 6.84 (1H, dd, *J* = 6.9, 1.9, 7'-*H*), 3.95 (3H, s, OCH₃), 2.52 (1H, br, OH), 1.68 [6H, s, C(CH₃)₂]; δ_{C} 156.22, 135.26, 133.15, 128.55, 126.23, 125.30, 124.96, 121.16, 117.26, 106.26 (Ar-C₁₀), 96.34 and 84.00 (C≡C), 65.85 (2-C), 55.57 (O-CH₃), 31.55 [C(CH₃)₂]; HRMS (EI): found 240.3016, C₁₆H₁₆O₂ requires: 240.3012. The alkyne (0.50 g, 2.08 mmol) was dissolved in toluene (50 ml), powdered sodium hydroxide (1.0 g) was added, and the reaction was refluxed for 6 h. The reaction solution was decanted, evaporated to dryness and purified by chromatography through a short plug of silica, eluting with toluene, to yield **14** (0.16 g, 41%).

Preparation of 8-methoxy-1-naphthylalkynes 15–20

General procedure. Ethynyl derivative **14** (1.10 g, 6 mmol) was dissolved in ether (20 ml, anhydrous) under nitrogen and cooled to $-55\text{ }^{\circ}\text{C}$. A mixture of methyllithium in ether (5 ml, 1.41 M, 7 mmol) in additional ether (10 ml), was added dropwise to the reaction over 20 min. The reaction was stirred for 1 h at $-50\text{ }^{\circ}\text{C}$, by which time a fine precipitate had formed. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ while the electrophile (see below) was added and then left to warm to room temperature overnight. The solution was diluted with wet ether (50 ml) and water was added dropwise (50 ml). The organic layer was separated, washed with water ($2 \times 50\text{ ml}$) and dried (MgSO_4), and the residue purified by flash chromatography.

1-(8'-Methoxy-1'-naphthyl)-2-triphenylsilylethyne 15. Reaction of **14** (2.7 mmol) with chlorotriphenylsilane (1.30 g, 4.5 mmol). Chromatography eluting with hexane–ether (20 : 1) yielded **15** as a white solid (0.86 g, 71%), mp $96\text{--}100\text{ }^{\circ}\text{C}$; δ_{H} 7.87–7.77 (8H, m, Ar- H_8), 7.47–7.35 (12H, m, Ar- H_{12}), 6.82 (1H, dd, $J = 6.2, 2.3\text{ Hz}$, 7'- H), 3.66 (3H, s, OCH_3); δ_{C} 156.4 (8'- C), 135.7 (*ortho* phenyl- C), 135.2, 134.6 (*ipso* phenyl- C), 134.3, 129.8 (*para* phenyl- C), 129.4, 127.9 (*meta* phenyl- C), 126.5, 125.4, 125.1, 121.0, 117.6 (1'- C), 111.7 (2- C), 106.1 (7'- C), 91.6 (1- C), 55.3 (OCH_3); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2139, 1571, 1428, 1380, 1268, 1114, 1077, 820, 700, 508; HRMS (ES): Found: 441.1682 ($\text{M} + \text{H}$)⁺, $\text{C}_{31}\text{H}_{24}\text{OSi}$ requires: 441.1674 ($\text{M} + \text{H}$)⁺.

4-(8'-Methoxy-1'-naphthyl)but-3-yn-2-one 16. Reaction of **14** (6 mmol) with acetic anhydride (5 ml). Chromatography eluting with ether–hexane (1 : 4) yielded **16** (0.73 g, 54%) as a white crystalline solid, mp $56\text{--}57\text{ }^{\circ}\text{C}$; δ_{H} 7.89 (1H, dd, $J = 8.2, 1.2$, 4'- H), 7.79 (1H, dd, $J = 7.1, 1.2$, 2'- H), 7.50–7.40 (3H, m, Ar- H_3), 6.93 (1H, m, Ar- H_1), 4.02 (3H, s, OCH_3), 2.51 (3H, s, CCH_3); δ_{C} 184.94 ($\text{C}=\text{O}$), 155.98, 135.31, 135.15, 131.17, 126.91, 125.4, 125.14, 121.29, 114.82, 106.83 (Ar- C_{10}), 93.50 and 91.20 ($\text{C}\equiv\text{C}$), 55.80 (OCH_3), 32.80 (1- C); $\nu_{\text{max}}/\text{cm}^{-1}$ 2183, 1650, 1248, 821, 757; $\lambda_{\text{max}}/\text{nm}$ 227, 366; HRMS (EI): found 224.0837, $\text{C}_{15}\text{H}_{12}\text{O}_2$ requires: 224.0837.

Methyl 3-(8'-Methoxy-1'-naphthyl)propynoate 17. Reaction of ethyne **14** (6 mmol) with methyl chloroformate (4 ml). Chromatography eluting with ether–hexane (1 : 9) yielded **17** (0.55 g, 38%) as a white crystalline solid, mp $77\text{ }^{\circ}\text{C}$; δ_{H} 7.89 (1H, dd, $J = 8.2, 1.2$, 4- H), 7.82 (1H, dd, $J = 7.3, 1.2$, 2- H), 7.50–7.40 (3H, m, Ar- H_3), 6.93 (1H, m, Ar- H_1), 4.02 (3H, s, OCH_3), 3.87 (3H, s, CO_2CH_3); δ_{C} 155.93 ($\text{C}=\text{O}$), 155.16, 135.21, 135.01, 131.07, 126.91, 125.35, 125.3, 121.13, 114.36, 106.71 (Ar- C_{10}), 88.98 and 82.93 ($\text{C}\equiv\text{C}$), 55.75 (OCH_3), 52.60 (CO_2CH_3); $\nu_{\text{max}}/\text{cm}^{-1}$ 2210, 1695, 1263, 1232, 822, 754; $\lambda_{\text{max}}/\text{nm}$ 231, 258, 355; HRMS (EI): found 240.0785, $\text{C}_{15}\text{H}_{12}\text{O}_3$ requires 240.0786.

3-(8'-Methoxy-1'-naphthyl)-*N*-phenylprop-2-ynamide 18. Reaction of ethyne **14** (4.8 mmol) with a solution of phenyl isocyanate (0.60 g, 0.55 ml, 5 mmol) in dry ether (10 ml). Chromatography eluting with ether–hexane (3 : 7) yielded **18** (0.85 g, 59%) as a white crystalline solid, mp $144\text{--}145\text{ }^{\circ}\text{C}$; δ_{H} 9.80 (1H, br s, N- H), 7.83 (1H, dd, $J = 8.2, 1.1$, 4'- H), 7.74 (1H, d, $J = 7.2, 2'$ - H), 7.60 (2H, d, $J = 7.4$, *ortho* phenyl H), 7.37–7.45 (5H, m, Ar- H_3 and *meta* phenyl H), 7.13 (1H, t, $J = 7.2$, *para* phenyl H), 6.90 (1H, m, Ar- H_1), 4.01 (3H, s, OCH_3); δ_{C} 155.88 (Ar- C_1), 151.75 ($\text{C}=\text{O}$), 137.63 (*ipso* phenyl C), 135.03, 134.49, 130.63 (Ar- C_3), 129.04 (*meta* phenyl C), 126.83, 125.32, 125.11 (Ar- C_5), 124.59 (*para* phenyl C), 121.23 (Ar- C_1), 119.72 (*ortho* phenyl C), 114.70, 106.70 (Ar- C_2), 88.27 and 86.19 ($\text{C}\equiv\text{C}$), 56.17 (OCH_3); $\nu_{\text{max}}/\text{cm}^{-1}$ 3254, 2206, 1630, 1277, 818, 759; $\lambda_{\text{max}}/\text{nm}$ 220, 227, 352; HRMS (EI): found 301.1101, $\text{C}_{20}\text{H}_{15}\text{NO}_2$ requires: 301.1103.

3-(8'-Methoxy-1'-naphthyl)prop-2-ynenitrile 19. Reaction of ethyne **14** (6 mmol) phenyl cyanate³⁰ (0.91 ml) at $-55\text{ }^{\circ}\text{C}$. Chromatography eluting with ether–hexane (1 : 9) yielded **19** (0.81 g, 65%) as white crystalline solid, mp $97\text{--}98\text{ }^{\circ}\text{C}$; δ_{H} 7.94 (1H, dd, $J = 8.2, 1.1$, 4'- H), 7.85 (1H, dd, $J = 7.3, 1.1$, 2'- H), 7.50–7.40 (3H, m, Ar- H_3), 6.92 (1H, m, Ar- H_1), 3.99 (3H, s, OCH_3); δ_{C} 155.31, 136.64, 134.79, 132.16, 127.33, 125.35, 125.22, 121.29, 112.29, 106.68 (Ar- C_{10}), 106.37 (CN), 84.83 (3- C), 65.16 (2- C), 55.55 (OCH_3); $\nu_{\text{max}}/\text{cm}^{-1}$ 2252, 2175, 1257, 816, 749; $\lambda_{\text{max}}/\text{nm}$ 230, 346; HRMS (EI): found 207.0685, $\text{C}_{14}\text{H}_9\text{NO}$ requires: 207.0684.

3-(8'-Methoxy-1'-naphthyl)prop-2-ynal 20. Reaction of ethyne **14** (6 mmol) with DMF (4 ml). Chromatography eluting with ether–hexane (1 : 9) yielded **20** (0.14 g, 11%) as a yellow oily solid; δ_{H} 9.54 (1H, s, $\text{H}-\text{C}=\text{O}$), 7.90 (1H, dd, $J = 8.2, 1.2$, 4'- H), 7.80 (1H, dd, $J = 7.3, 1.2$, 2'- H), 7.50–7.40 (3H, m, Ar- H_3), 6.91 (1H, m, Ar- H_1), 4.01 (3H, s, OCH_3); δ_{C} 177.21 ($\text{C}=\text{O}$), 155.80, 135.55, 135.01, 131.68, 127.06, 125.40, 125.01, 121.23, 114.26, 106.92 (Ar- C_{10}), 98.3 and 91.5 ($\text{C}\equiv\text{C}$), 55.63 (OCH_3); $\nu_{\text{max}}/\text{cm}^{-1}$ 2181, 1770, 1261, 823, 768; $\lambda_{\text{max}}/\text{nm}$ 220, 231, 323; HRMS (EI): found 210.0680, $\text{C}_{14}\text{H}_{10}\text{O}_2$ requires: 210.0681.

Preparation of (8-dimethylamino-1-naphthyl)ethyne derivatives 34–36

General procedure. LDA was prepared by stirring diisopropylamine (0.20 g, 1.96 mmol) and *n*-BuLi (1.27 ml, 1.55 M) in THF (5 ml) at $-40\text{ }^{\circ}\text{C}$ for 25 min under a nitrogen atmosphere. The reaction was cooled to $-78\text{ }^{\circ}\text{C}$ and the ketone **30**³¹ (0.40 g, 1.88 mmol) was added. Stirring was continued for 1 h at $-78\text{ }^{\circ}\text{C}$, after which diethyl chlorophosphate (0.36 g, 2.09 mmol) was added and the reaction was allowed to warm to room temperature over 1 h. The solution was carefully transferred (*via* a syringe) to a second dry flask held at $-78\text{ }^{\circ}\text{C}$ in which two equivalents of fresh LDA had been meanwhile produced from *n*-BuLi (2.60 ml, 1.55 M), diisopropylamine (0.41 g) and THF (10 ml). The reaction was stirred for 3 h at $-78\text{ }^{\circ}\text{C}$, the electrophile (see below) was added and the reaction allowed to warm to room temperature over 1 h. The solution was poured into a saturated aqueous NH_4Cl and extracted three times with diethyl ether. After separation, the organic layer was dried (MgSO_4) and purified by flash chromatography.

1-(8'-Dimethylamino-1'-naphthyl)prop-1-yne 34. Reaction of ketone **30** (0.40 g, 1.88 mmol) as above using iodomethane (1.20 g, 8.4 mmol) in THF (3 ml) as electrophile. Chromatography eluting with ether–hexane (1 : 80) yielded **34** (0.21 g, 53%) as an orange oil, δ_{H} 7.68 (1H, dd, $J = 8.1, 1.1$, 4'- H_1), 7.61 (1H, dd, $J = 7.1, 1.1$, 2'- H_1), 7.43 (1H, dd, $J = 8.1, 1.2$, 5'- H_1), 7.33 (2H, m, Ar- H_2), 7.06 (1H, dd, $J = 7.4, 1.2$, 7'- H_1), 2.81 [6H, s, $\text{N}(\text{CH}_3)_2$], 2.15 (3H, s, CCH_3); δ_{C} 151.1, 135.73, 133.38, 128.75, 128.52, 125.82, 124.78, 123.35, 119.71, 115.34 (Ar- C_{10}), 88.70 and 81.68 ($\text{C}\equiv\text{C}$), 45.91 [$\text{N}(\text{CH}_3)_2$], 4.93 (3- C); $\nu_{\text{max}}(\text{liquid film})/\text{cm}^{-1}$ 3052, 2938, 2913, 2853, 2826, 2776, 2246, 1575, 1476, 1450, 1425, 1379, 1334, 1050, 1032, 938, 909, 826, 760, 732; HRMS (EI): Found: 209.1209, $\text{C}_{15}\text{H}_{15}\text{N}$ requires 209.1204.

1-(8'-Dimethylamino-1'-naphthyl)-2-trimethylsilylethyne 35. Reaction of ketone **30** (0.40 g, 1.88 mmol) as above but reacting with electrophile chlorotrimethylsilane (1.20 g, 11 mmol) at room temperature for 30 min. Chromatography eluting with ether–hexane (1 : 80) yielded **35** (0.09 g, 18%) as a bright yellow oil, δ_{H} 7.79 (2H, br d, $J = 7.8$, Ar- H_2), 7.52 (1H, br d, $J = 8.1$, Ar- H_1), 7.39 (2H, m, Ar- H_2), 7.17 (1H, br d, $J = 7.4$, Ar- H_1), 2.84 [6H, s, $\text{N}(\text{CH}_3)_2$], 0.36 [9H, s, $\text{Si}(\text{CH}_3)_3$]; δ_{C} 151.09, 135.57, 134.66, 129.53, 129.08, 126.06, 124.79, 123.51, 118.78, 116.10 (Ar- C_{10}), 107.09 and 97.03 (1-, 2- C), 45.71 [$\text{N}(\text{CH}_3)_2$], 0.38 [$\text{Si}(\text{CH}_3)_3$]; $\nu_{\text{max}}(\text{liquid film})/\text{cm}^{-1}$ 3051, 2936, 2823, 2775, 2140,

1569, 1374, 1247, 1019, 910, 840, 767, 678; HRMS (EI): Found 267.1426, C₁₇H₂₁NSi requires 267.1443.

1-(8'-Dimethylamino-1'-naphthyl)-2-triphenylsilyl-1-ethyne

36. Reaction of ketone **30** (2.00 g, 9.4 mmol) as above with chlorotriphenylsilane (8.40 g, 28.5 mmol) in THF (15 ml) as electrophile, the reaction mixture was left to warm to room temperature over 48 h before work-up. Chromatography, eluting with ether–hexane (1 : 10) gave **36** (1.30 g, 31%) as a pale green solid, mp 120–121 °C; δ_{H} 7.89 (1H, dd, $J = 7.2, 1.2, 2'-H_1$), 7.79 (7H, m, 6 × *ortho* phenyl H and Ar- H_1), 7.49 (1H, dd, $J = 8.1, 1.0, 5'-H_1$), 7.21–7.46 (11H, m, *meta* and *para* phenyl H and Ar- H_2), 7.12 (1H, dd, $J = 7.4, 1.0, 7'-H_1$), 2.62 [6H, s, N(CH₃)₂]; δ_{C} 151.32 (Ar- C_1), 135.69 (6 × *ortho* phenyl C), 135.57 (Ar- C_1), 135.51 (3 × *ipso* phenyl C), 134.40, 130.14 (Ar- C_2), 129.75 (3 × *para* phenyl C), 129.00 (Ar- C_1), 127.90 (6 × *meta* phenyl C), 126.26, 124.86, 123.54, 118.44, 116.12 (Ar- C_3), 112.12 and 92.09 (C≡C), 45.73 [N(CH₃)₂]; $\nu_{\text{max}}/\text{cm}^{-1}$ 2144, 1378, 703, 509; Found C: 84.8, H: 6.1, N: 2.9%, C₃₂H₂₇NSi requires C: 84.7, H: 6.0, N: 3.1%.

(E)-tert-Butyl 1,2-dihydro-1-methylbenzo[*cd*]indol-2-ylideneacetate **42**

The ketone **30** (0.40 g, 1.88 mmol) was reacted with di-*tert*-butyl dicarbonate (0.879 g, 4 mmol) in THF (3 ml) at –78 °C. The solution was allowed to warm over 1 h to room temperature, after which it was poured into water and extracted three times with ether. The dried organic layer was evaporated to give orange blocks of **42** (0.21 g, 40%), mp 122 °C; δ_{H} 9.24 (1H, d, $J = 7.4, 3-H$), 7.82 (1H, d, $J = 8.1, 5-H$), 7.67 (1H, dd, $J = 8.1, 7.4, 4-H$), 7.38 (1H, dd, $J = 6.8, 8.3, 7-H$), 7.31 (1H, dd, $J = 8.3, 0.7, 6-H$), 6.66 (1H, dd, $J = 6.8, 0.7, 8-H$), 5.38 (1H, s, =CH), 3.36 (3H, s, NCH₃), 1.61 [9H, s, C(CH₃)₃]; δ_{C} 167.15 (C=O), 153.69 (2-C), 143.15 (9-C), 130.32 (2a-C), 129.83 (5a- or 8b-C), 128.89 (4-C), 127.97 (7-C), 127.88 (5-C), 127.86 (3-C), 126.39 (5a- or 8b-C), 117.48 (6-C), 101.45 (8-C), 91.66 (2=CH), 78.85 (OCMe₃), 29.55 (NCH₃), 28.58 [C(CH₃)₃]; $\nu_{\text{max}}/\text{cm}^{-1}$ 1685, 1680, 1576, 1301, 1249, 1225, 1208, 1147br, 1126, 1061, 1056, 1048, 1036, 1014, 995, 937, 817, 799, 770, 753, 743, 679, 620, 547; $\lambda_{\text{max}}/\text{nm}$ 219, 262, 269, 285sh, 338, 427; HRMS (EI): found 281.1410, C₁₈H₁₉NO₂ requires 281.1416.

X-Ray crystallography §

Diffraction data were collected at low temperatures using a Nonius-Kappa CCD area detector and a rotating anode source (Mo-K α radiation) by the EPSRC X-Ray Crystallography Service. Structures were solved at Nottingham Trent University using SHELXS-97³² and refined using SHELXL-97³³ with all hydrogen atoms found from difference Fourier maps and included in the refinement, unless otherwise stated. Molecular illustrations and geometry calculations were made with ORTEP3,³⁴ PLUTON-97³⁵ and PLATON-97.³⁵

Crystal data for 14. C₁₃H₁₀O, $M_r = 182.2$, orthorhombic, $a = 6.0319(1)$, $b = 10.3050(4)$, $c = 30.361(1)$ Å, $V = 1887.2$ Å³, $Z = 8$, $Pbca$, $D_c = 1.28$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.08$ mm⁻¹, $T = 150$ K, 1978 unique reflections, 1410 with $F > 4\sigma(F)$, $R = 0.053$, $wR = 0.142$.

Crystal data for 15. C₃₁H₂₄SiO, $M_r = 440.6$, triclinic, $a = 11.4096(3)$, $b = 13.7608(5)$, $c = 16.3519(7)$ Å, $\alpha = 93.9662(13)$, $\beta = 98.5825(14)$, $\gamma = 106.714(2)^\circ$, $V = 2414.2$ Å³, $Z = 4$, $P\bar{1}$, $D_c = 1.21$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.12$ mm⁻¹, $T = 120$ K, 8349 unique reflections, 4778 with $F > 4\sigma(F)$, $R = 0.057$, $wR = 0.111$. There is some disorder in the structure of one of the two

crystallographically unique molecules (molecule **B**) with one phenyl ring having two possible orientations, one of which allows space for a molecule of methanol to occupy space close to a centre of symmetry which is surrounded by the triphenylsilyl moieties of two **B** molecules.

Crystal data for 16. C₁₅H₁₂O₂, $M_r = 224.3$, orthorhombic, $a = 8.1848(2)$, $b = 13.7072(4)$, $c = 20.2962(6)$ Å, $V = 2266.8$ Å³, $Z = 8$, $Pbca$, $D_c = 1.31$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.09$ mm⁻¹, $T = 150$ K, 1899 unique reflections, 1622 with $F > 4\sigma(F)$, $R = 0.040$, $wR = 0.115$.

Crystal data for 17. C₁₅H₁₂O₃, $M_r = 240.3$, monoclinic, $a = 7.5576(5)$, $b = 7.5977(3)$, $c = 10.9690(7)$ Å, $\beta = 109.85(3)^\circ$, $V = 592.5$ Å³, $Z = 2$, $P2_1$, $D_c = 1.35$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.09$ mm⁻¹, $T = 150$ K, 2005 unique reflections, 1822 with $F > 4\sigma(F)$, $R = 0.046$, $wR = 0.127$.

Crystal data for 18. C₂₀H₁₅NO₂, $M_r = 301.3$, monoclinic, $a = 14.061(9)$, $b = 5.001(9)$, $c = 44.011(9)$ Å, $\beta = 91.99(4)^\circ$, $V = 3093.0$ Å³, $Z = 8$, $P2_1/c$, $D_c = 1.29$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.08$ mm⁻¹, $T = 180$ K, 4258 unique reflections, 2970 with $F > 4\sigma(F)$, $R = 0.054$, $wR = 0.140$. There are two orientations for the phenyl ring of one of the two crystallographically independent molecules. H atom positions were located, but were subsequently fixed geometrically.

Crystal data for 19. C₁₄H₉NO, $M_r = 207.2$, monoclinic, $a = 3.9353(2)$, $b = 11.2675(9)$, $c = 23.736(2)$ Å, $\beta = 93.518(4)^\circ$, $V = 1050.5$ Å³, $Z = 4$, $P2_1/c$, $D_c = 1.31$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.08$ mm⁻¹, $T = 150$ K, 2059 unique reflections, 1336 with $F > 4\sigma(F)$, $R = 0.056$, $wR = 0.148$.

Crystal data for 36. C₃₂H₂₇SiN, $M_r = 453.6$, triclinic, $a = 8.2787(2)$, $b = 9.0356(7)$, $c = 18.6385(10)$ Å, $\alpha = 80.022(1)$, $\beta = 80.964(1)$, $\gamma = 65.704(2)^\circ$, $V = 1245.8$ Å³, $Z = 2$, $P\bar{1}$, $D_c = 1.21$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.11$ mm⁻¹, $T = 150$ K, 5619 unique reflections, 3974 with $F > 4\sigma(F)$, $R = 0.062$, $wR = 0.170$.

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