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Weak Attractive Interactions between Methylthio Groups and Electron-Deficient Alkenes in *peri*-Naphthalenes: A Competition with Conjugative Effects

Jane O'Leary and John D. Wallis*[a]

Abstract: The solid-state conformations of five *peri*-disubstituted naphthalenes bearing a methylthio group and an electron-deficient alkene indicate a weak attractive interaction between the functional groups in four cases in which out-of-plane displacements lead to a common orientation of the MeS···sp^2-C vector to the alkene bond. In some cases the interaction is not strong enough to outweigh the tendency of the alkene to conjugate with the aromatic ring, and in one case this optimisation of conjugation alone controls the molecular conformation. The methylthio group lies close to the aromatic plane in all but one example for which the plane of the sulfide group is presented to the alkene.

Keywords: conjugation · sulfur · through-space interactions · X-ray diffraction

Introduction

Bürgi, Dunitz and Schefter interpreted the short intramolecular interactions between amino groups and carbonyl groups in the solid-state structures of a group of alkaloids as representing partially completed chemical reactions,[1] which was consistent with the unexpected chemical properties observed for these compounds.[2] Kirby and co-workers have recently shown that in some of these cases the interaction observed in the crystalline state may be promoted by intermolecular hydrogen bonding to the carbonyl oxygen atom.[3] Subsequently the *peri*-naphthalene molecular skeleton (**1**) has provided a very useful system for investigating such electrophile/nucleophile interactions, since the *peri*-carbon atoms of the naphthalene framework are just 2.5 Å apart, well within the sum of van der Waals radii for most pairs of atoms. Dunitz and co-workers first used this system for investigating the interactions of dimethylamino or methoxy groups with various carbonyl functionalities[4] for example, in **2** and **6**, and with nitriles[5] for example, in **7**, and others have extended this to interactions with an aldehyde[6] as in **3** and with various carboxamides as in **4** and **5**.[7,8]

We have broadened these studies to the interactions of dimethylamino or methoxy groups with C=C double bonds.[8–11] For the 1,5 interaction with an electron-deficient alkene there is substantial variation in the inter-group separation when the nucleophilic group is dimethylamino depending on the particular alkene, varying from 2.749(5) Å in **8** for a -CH=CHBr group,[6] to 2.6417(16) Å in **9** for a -CH=CHNO$_2$ group,[8] to 2.531(2) Å in **10** for a -CH=C(CN)CO$_2$Et group[11] to 2.413(2) Å in **11** for a -CH=C(CN)$_2$ group[9] and culminating in the near complete formation of a single bond in zwitterions **12**[9] (C–N 1.651(3) Å) and **13** (C–N 1.6397(17) Å).[8] In contrast, for interactions where the methoxy group is the electron-rich centre there is very little variation in the separation between groups (2.53–2.67 Å) and even for interaction with a carbocation in **14** the MeO···C$^+$ separations are 2.43(1) and 2.45(1) Å long.[12] It is noteworthy that in most cases in the dimethylamino and methoxy series, the "attacked" sp^2-C atom does show a small pyramidality with the carbon atom displaced towards the other *peri*-located group. Charge density studies provide more insight into these interactions. For both **4** and **11**, containing the interactions of dimethylamino groups with a carboxamide[13] or an alkene dinitrile,[14] a (3,−1) critical point has been observed between the groups with electron densities at this point of 0.11(1) and 0.19(2) e Å^{-3}, respectively. No such studies on the methoxy series have yet been made. Recently we prepared a series of six biphenyls containing 1,6 interactions between a dimethylamino group and an aldehyde or an electron-deficient alkene.[15] These all show short contacts between groups, but either at about 2.9–3.0 Å, as in **15**–**17**, or by bond formation to give a zwitterion such as **18**. In the uncyclised materials

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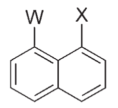
[a] Dr. J. O'Leary, Prof. J. D. Wallis
School of Biomedical and Natural Sciences
Nottingham Trent University
Clifton Lane, Nottingham NG11 8NS (UK)
Fax: (+44) 115-848-6636
E-mail: john.wallis@ntu.ac.uk



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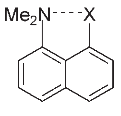
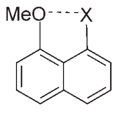
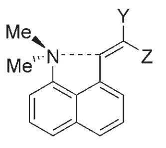


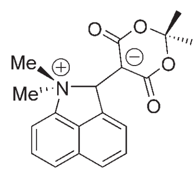
2 X = COMe
3 X = CHO
4 X = CONMe$_2$
5 X = CONHPh



6 X = CO$_2$H
7 X = CN



8 Y = Br; Z = H
9 Y = NO$_2$; Z = H
10 Y = CO$_2$Et; Z = CN
11 Y = Z = CN



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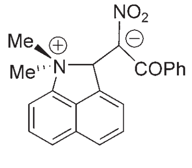

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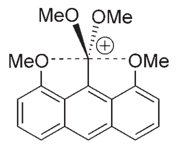

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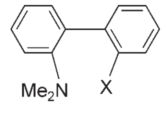
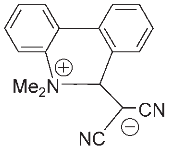


15 X = CHO
16 X = CH=C(CN)CO$_2$Me
17 X = CH=CHNO$_2$



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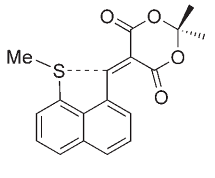
there is no pattern of pyramidalisation of the sp^2-C atoms, suggesting that these represent intermolecular interactions, while the *peri*-naphthalene series is indeed probing covalent bond formation. *Peri*-naphthalenes have also been utilised in studying interactions of dimethylamino groups with selenium or silicon centred groups,[16,17] probing the effect on reactivity of hydrogen bonding to the nitrogen atom of an amide,[18] and charge density analyses of the salts of proton sponges to understand these particularly interesting hydrogen-bonded systems.[19]

We decided to extend these studies by using the methylthio group as the nucleophilic group. The sulfur atom is more nucleophilic than the oxygen atom, but it is a larger atom. Furthermore, there is the issue of which lone pair on sulfur is involved in the interaction and the asymmetric effective shape of the bonded sulfur atom.[20] Here we report the structures of the five molecules **19**–**23** in which a methylthio group lies *peri* to an electron-deficient alkene. Molecule **22**, with just a *trans*-disubstituted alkene, differs from the others since the alkene substituent *cis* to the naphthalene ring is just a hydrogen atom, whereas the other molecules have the larger carbon atom at that position (as carbonyl, nitrile or methyl) which may have a role to play in controlling the orientation of the alkene by repulsion with the *ortho*-hydrogen atom of the naphthalene system.

Discussion

The preparative route for the desired *peri* methylthio-naphthyl-alkenes (Scheme 1) depends on the *peri*-methylthioaldehyde **27**, which was prepared in six steps from naphthalic anhydride. Conversion of the latter to thiolactone **24** by known procedures,[21,22] followed by ring opening and esterification gave the methyl ester **25**. Reduction with diisobutylaluminium hydride (DIBAL) at low temperature gave only the alcohol **26** which was converted to aldehyde **27** by Swern oxidation. The target alkenes **19**–**23** were made from the aldehyde by Knoevenagel condensations. Crystals were grown by slow evaporation of solutions and most structures were measured at 120 K (150 K for **20**) using Mo$_{K\alpha}$ radiation. The structures of **19**–**23** show MeS···sp^2-C separations in the range 2.787(2)–2.9226(14) Å, a range of orientations for the alkene group lying at 36.4(3)–57.2(3)° to the neighbouring aromatic bond C7−C8, and displacements of the *peri* substituents to opposite sides of the naphthalene ring which vary from small (<0.1 Å) to quite substantial (>0.4 Å). The methylthio group lies close to the aromatic plane in all cases apart from **21** where it lies nearer to perpendicular to the aromatic plane. The molecular structures are illustrated in Figures 1–3 showing views perpendicular and edge-on to the aromatic planes. Selected molecular geometry for **19**–**23** is given in Table 1 along with data for the



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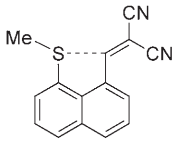

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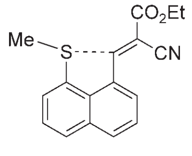

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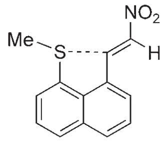

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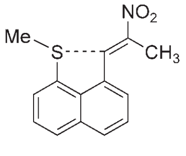

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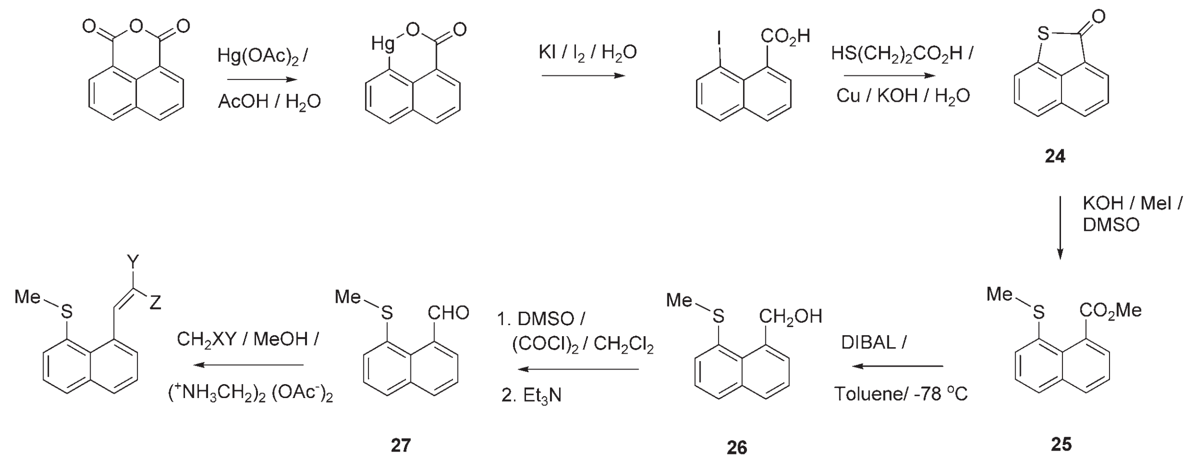


Scheme 1.

naphthalene-1-diazonium cation with a *peri*-methylthio group (**34**) and the atomic-labelling scheme.

Structures of compounds 19–23: Compound **19** has the alkene group lying at 57.2(3)° to the aromatic C7–C8 bond so that it presents a face to the methylthio group, and the MeS···sp^2-C separation is 2.787(2) Å, the shortest in the

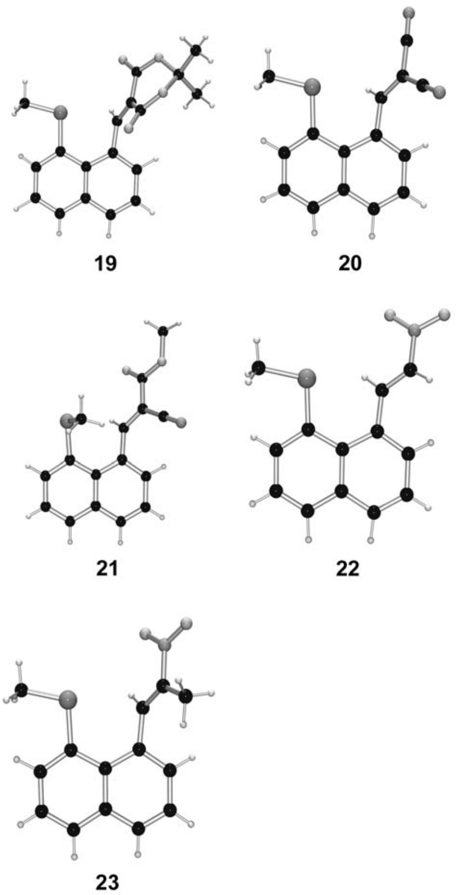


Figure 1. Views of molecules **19**–**23** perpendicular to the aromatic ring.

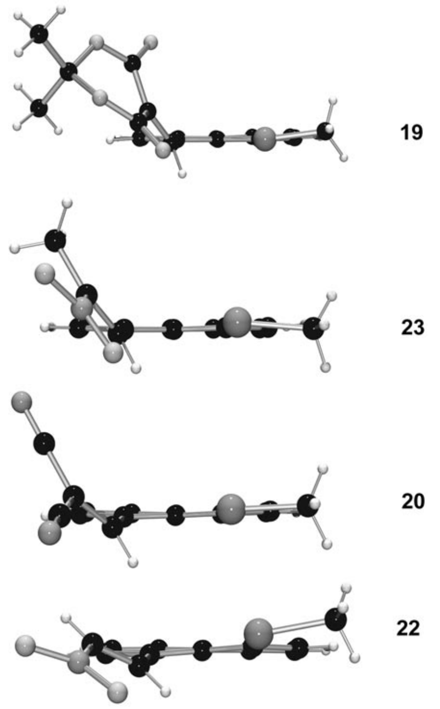


Figure 2. Views of molecules **19**–**20** and **22**–**23** edge-on to the aromatic ring in order of *decreasing angular rotation* of the alkene out of the naphthalene plane and increasing displacements of the functional groups from this plane.

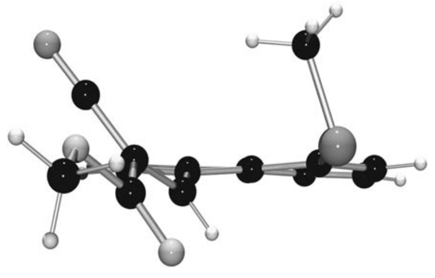
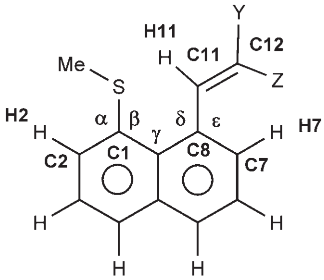


Figure 3. View of molecule **21** edge-on to the aromatic ring.

Table 1. Selected molecular geometry for compounds **19**–**23** and **34**.[a]



	S···C11 [Å][b]	α[°]	β [°]	γ [°]	δ [°]	ε [°]	ΔC′ [Å]
19	2.787(2)	121.37(19)	119.36(16)	124.8(2)	123.87(19)	115.93(19)	0.049(9)
20	2.850(3)	120.9(2)	119.73(19)	125.8(2)	123.5(2)	115.9(2)	0.037(11)
21	2.9226(14)	117.04(11)	122.88(10)	124.78(12)	121.71(11)	117.94(12)	0.036(6)
22	2.8948(19)	119.55(15)	120.51(13)	125.83(16)	122.98(16)	116.70(16)	0.014(8)
23	2.8296(19)	120.10(15)	120.19(14)	125.29(17)	123.38(16)	117.24(18)	0.030(8)
34[32]	2.938(6)	118.9(3)	122.5(3)	127.7(3)	121.7(3)	112.4(3)	–

	C11–C12 [Å]	ΔS [Å]	ΔC [Å][c]	T1 [°]	T2 [°]	θ [°]	S···H11 [Å]
19	1.339(3)	0.018(2)	−0.069(3)	5.6(2)	57.2(3)	114.61(14)	2.63(2)
20	1.338(4)	0.120(3)	−0.257(4)	1.7(3)	48.5(4)	118.2(2)	2.58(2)
21	1.3489(18)	0.3397(14)	−0.4532(18)	109.15(12)	46.70(19)	115.85(8)	2.715(14)
22	1.326(3)	0.361(2)	−0.297(3)	5.26(19)	36.4(3)	125.94(13)	2.49(2)
23	1.332(3)	0.1308(18)	−0.1172(3)	7.94(18)	53.55(26)	115.59(13)	2.61(2)
34[32]	–	0.232(6)	−0.196(6)	65.4(3)	–	99.8(3)	–

[a] ΔC′: deviation of C11 from plane [C8, C12, H11]; ΔS and ΔC: deviation of S and C11 from the plane defined by the ten ring carbon atoms; T1: torsion C2-C1-S-C(H$_3$); T2: torsion C7-C8-C11-C12; θ: angle S···C11−C12. [b] S···N for **32**. [c] ΔN for **32**.

series. The methylthio group lies very close to the aromatic plane, and is displaced slightly towards the alkene (by 1.0°) due to the steric interaction between the S-methyl group and the *ortho*-hydrogen atom H2 of the naphthalene group (H2···C(H$_3$): 2.48(3) Å; H2···H(CH$_2$S-): 2.22(4) and 2.30(4) Å). The alkene group is displaced significantly away from the methylthio group (by 4.0°). The out of plane displacements of the sulfur and carbon atoms attached to the *peri* positions are the smallest in the series (ΔS: 0.018(3), ΔC: −0.069(3) Å). The sp^2-C atom is pyramidalised towards the sulfur atom and shows the largest value in the series (0.049(9) Å). The angle of approach of the sulfur atom to the alkene bond is 114.61(14)°.

Compared to **19**, in molecule **20** the dicyanoethenyl group is oriented at just 48.5(4)° to the aromatic C7−C8 bond, that is, about 9° less than for the substituted alkene in **19**, and the *peri*-sulfur and -carbon atoms are displaced further out of the aromatic plane in opposite directions (ΔS: 0.120(3), ΔC: −0.257(4) Å). The in-plane displacements of the *peri* substituents are very similar to those in **19**, but the exocyclic angle between the two rings of the naphthalene system (γ) is widened by 1.0°. The increase in the MeS···sp^2-C distance by 0.064 Å to 2.850(3) Å is mainly due to the larger out of plane displacements. These act to produce an angle of approach of the sulfur atom to the alkene of 118.2(2)°. The decrease in the tilt of the alkenyl group relative to the aromatic plane increases the conjugation with the aromatic system, but there is a 1,6 contact between a cyano-carbon atom and the *ortho*-hydrogen atom H7 (2.71(2) Å), which prevents the alkene lying at an even lower angle to the aromatic system. In contrast, in **19** which contains the bislactone ring, the orientation of the alkene is not controlled by the corresponding contact between a carbonyl carbon atom and the *ortho*-hydrogen atom, which lie 3.07(3) Å apart—well outside of van der Waals contact.

The structure of compound **21** is distinctly different from the other four structures. The methylthio group lies completely out of the aromatic plane; the torsion angle of the CH$_3$−S bond with the aromatic C1−C2 bond is 109.15(12)°. The alkenyl group lies at 46.70(19)° to the aromatic C7−C8 bond (similar to **20**), and the MeS···sp^2-C separation is the largest in the series at 2.9226(14) Å. Without a steric interaction with *ortho*-hydrogen atom H2, the methylthio group is now displaced *away* from the alkene group by 2.9°, and the alkene is only displaced away from the methylthio group by 1.9° compared to double that amount in **19** and **20**. The displacements of the *peri*-sulfur and -carbon atoms from the aromatic plane have increased to 0.3397(14) and −0.453(2) Å. This produces an angle of approach of the sulfur atom to the alkene of 115.85(8)°, similar to that in **19** and **20**. Thus, the increase in the MeS···sp^2-C separation is a consequence of increases in both the in-plane and out-of-plane displacements of *peri* substituents. Nevertheless, the S−CH$_3$ bond lies alongside the alkene and is not directed to the other side of the naphthalene plane, but there is only one near van der Waals contact between them: C11···H-

(CH_2S) 2.875(18) Å. There is little change in the length of the S–C bond to the aromatic ring with the change in torsion about this bond.

The bonded sulfur atom is known to be asymmetric in shape. For thiocarbonyl sulfur atoms Nyberg's estimation from intermolecular S···S contacts suggest values of 1.6 and 2.0 Å for the minimum and maximum radii[23] corresponding to the effective sizes in the thiocarbonyl plane and perpendicular to it. From the CSD[24] the shortest S···S contacts between sulfur atoms in sp^3-C–S–sp^3-C sulfide groups are about 3.25 Å[25] for in-plane/in-plane contacts (Figure 4a), while for face-to-face contacts (Figure 4b) the shortest contacts are about 3.75 Å[26] corresponding to effective radii of about 1.62 and 1.87 Å. For our intramolecular case we can refer to the *peri*-dithionaphthalene derivatives **28**–**30**. Compound **28**, with face-to-face disulfide contacts, shows a S–S separation of 3.182(1) Å.[27] The two molecules of compound **30**, in which the sulfide groups are not too far from both being in the aromatic plane and thus edge on to each other, show S–S separations of 2.918(2) and 2.934(2) Å,[28] and other intramolecular contacts between the shorter radii for sulfide and thiocarbonyl sulfur atoms have been observed at about 2.9 Å.[20] *peri*-Naphthalene **29** with an edge-to-face contact between the sulfide groups has an intermediate S···S separation (3.005(1) Å).[27] This suggests that in the strained situation of the *peri*-naphthalenes the effective radius of the bonded sulfide sulfur atom is about 0.13 Å larger perpendicular to the sulfide plane than in this plane, though our estimates are based, of course, only on a small amount of data. This factor will contribute to the larger separation of the *peri*-S and -C11 atoms in **21**. However, the observed separation is only about 0.07 Å larger than that in **20** for which the alkene adopts a similar orientation. This may be due to the greater susceptibility of the lone pair perpendicular to the sulfide plane to attack by electrophiles,[29] but ideally further structures with out-of-plane methylthio groups are needed for comparison. The adoption of this structure, rather than one with the methylthio group lying in the aromatic plane, may be a result of preferable packing effects. A search for polymorphs, or structural measurements on different esters would be instructive.

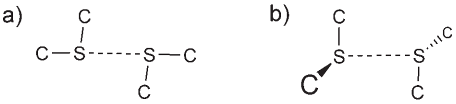
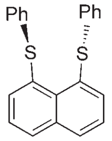


Figure 4. Orientations of sulfide groups for a) minimum S···S van der Waals contact, b) maximum S···S van der Waals contact.

Compound **22** is different from the other four molecules in that it has a terminal hydrogen atom on the alkene *cis* to the naphthalene ring. Thus, whereas in compounds **20** and **21** the minimum angular orientation between the aromatic system and the alkene is controlled by a sp-C···H steric interaction, in the nitroethenyl compound **22** it is controlled by a H···H interaction. In the structures of **20** and **21** the alkenyl group lies at 48.5(4) and 46.70(19)° to the aromatic plane, and the corresponding H7···C(≡ N) distances are 2.71(2) and 2.648(15) Å, which are close to the van der Waals separations for a hydrogen atom and a carbon atom, thus strongly suggesting that these structures are exhibiting the minimum possible angular orientation of the alkene to the aromatic ring. In contrast, in the nitroethenyl derivative **22** the alkenyl group lies at the lowest angle to the aromatic plane in this series, 36.4(3)°, (Figure 2) with a H7···H12 separation between the alkene and the aromatic ring of just 2.34(3) Å. In this structure the methylthio group lies close to the aromatic plane, and the *peri* groups are strongly displaced to opposite sides of the naphthalene ring to increase the separation between the sulfur atom and the alkenyl hydrogen atom H11 to 2.49(2) Å—the shortest such separation observed in this series. Indeed, both this S···H11 contact and the H7···H12 contact are controlling the angular position of the alkenyl group. The out-of-plane displacements of the *peri* substituents (ΔS: 0.361(2), ΔC11: −0.297(3) Å) are only exceeded by those of the cyano ester **21** in this series. The MeS···sp^2-C separation of 2.8948(19) Å is also one of the



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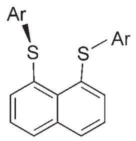
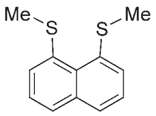


29 **Ar = 2-(MeO$_2$C)C$_6$H$_4$**



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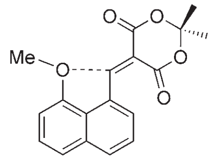

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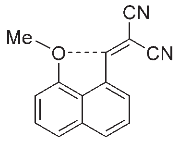

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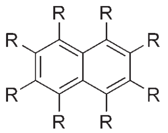
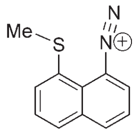


33 **R = (*E*)-CH=CH-*t*Bu**



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longest in the series. The in-plane displacements of the *peri* groups are similar to those in **19** and **20**, but the methylthio group is displaced slightly away from the alkene (by 0.5°, cf. 0.6–1.0° towards the alkene in **19** and **20**), and the alkene is displaced slightly less away from the methylthio group (by 3.2°, cf. 3.6–4.0° in **19** and **20**). Thus, the molecule has preferred to optimise the conjugation of the alkene with the aromatic ring at the expense of an interaction between the *peri* groups. It is also notable that the barely significant pyramidalisation of C11 (0.014(8) Å) and the angle of approach of the sulfur to the alkene bond (125.94(13)°) are totally out of step with the values for the other four compounds (0.030(8)–0.049(9) Å, 114.61(14)–118.2(2)°). The orientation of the alkene mitigates strongly against an interaction between the *peri* groups.

Compound **23** differs from compound **22** in that geminal to the nitro group it carries a methyl group whose steric interaction with *ortho*-hydrogen atom H7 forces the alkene group to lie much further out of the aromatic plane making an angle of 53.55(26)° with the C7−C8 bond. The contact between the methyl group and hydrogen atom (C14···H7 2.855(18), H14C···H7 2.44(3) Å) is close to van der Waals separation, but longer than in **20** and **21** where the corresponding contact is with a cyano-carbon atom rather than a methyl group. The molecular conformation adopted is intermediate between those of structures **19** and **20**. Thus, there is an in-plane methylthio group, the MeS···C11 distance is 2.8296(19) Å and the sum of the out-of-plane displacements of the *peri*-substituent atoms (0.248 Å) is intermediate between those for **19** (0.087 Å) and **20** (0.377 Å). The degree of pyramidalisation of carbon C11 is similar to that of **19** and **20** as is the angle of approach of sulfur to the alkene (115.59(13)°). The methylthio group is displaced one degree less towards the alkene which is itself displaced by one degree less away from the methylthio group compared to **19** and **20**.

The three compounds **20**–**22** adopt conformations in which the alkene substituent has optimized its conjugation with the naphthalene ring, the limiting factor being a steric interaction with the *ortho*-hydrogen atom H7 (for **20** and **21**) and also with the *peri*-sulfur atom for **22**. However, in compounds **19** and **23** the alkene lies at larger angles (54–57°) to the aromatic C7−C8 bond. The bislactone **19**, which shows the shortest MeS···sp^2-C separation (2.787(2) Å) in the series, whose conformation is not determined by a steric interaction, and which shows the largest pyramidality at the carbon, provides the strongest evidence for an attractive interaction between the methylthio group and the electron-deficient alkene group. Compound **23**, in which the alkene is forced by a steric interaction to adopt a similar conformation to that of **19**, shows a slightly longer MeS···sp^2-C interaction (by 0.043 Å). Most notable, however, are the out-of-plane distortions which maintain a common angle of approach of the sulfur atom to the alkene in all compounds but **22**, indicative of an interaction. All molecules but **22** show a significant pyramidalisation of the sp^2-C atom towards the sulfur atom. In the corresponding series of interactions involving dimethylamino groups, the bislactone group is the most reactive, leading to bond formation between the groups in zwitterion **12**. Furthermore, the alkene holds an orientation of 50—60° to the aromatic C7−C8 bond for the shorter interactions involving dimethylamino groups (2.413–2.642 Å in **9**–**11**) and only defers to optimisation of conjugation with the aromatic ring for Me$_2$N···sp^2-C separations greater than about. 2.7 Å for example, in the (*E*)-2-bromoethenyl derivative **8**. For comparison, in the dimethylamino derivative **9**, the nitroethenyl group lies at 51.38(6)° to the aromatic system, whereas in the methylthio analogue **22** it lies at 30.33(8)°. Thus, the interactions of electron-deficient alkenes with methylthio groups are clearly weaker than those with dimethylamino groups, and only for the bislactone **19** does the interaction appear to control the conformation of the molecule. For the methoxynaphthalenes **31** and **32**, the analogues of **19** and **20** containing the bis(lactone) or dicyanoethenyl groups, only the former retains an alkene orientation comparable to its dimethylamino and methylthio analogues (55.9° to the C7−C8 bond), whereas the latter adopts a smaller torsional rotation of the alkene (46.2°), which is limited by a (N≡)C···H11 steric interaction with the *ortho*-hydrogen atom (2.625(16) Å). The out-of-plane displacements in dinitrile **32**: (O −0.024(1), C11 0.154(1) Å) are also distinctly larger than for bis(lactone) **31** (O −0.018(2), C11 0.078(2) Å). Thus, these two structures mirror the results from the methylthio series.

The effective radii of the sulfur and carbon atoms in a *peri*-naphthalene containing an in-plane methylthio group may be estimated from the separation between like groups in the symmetrical *peri*-naphthalenes **30** (2.918(2) Å) and **33** (2.799(2) Å).[30] Thus, a purely steric MeS···sp^2-C interaction could be estimated to be about 2.86 Å. Only the separation in compound **19** is significantly shorter than this. When the face of the sulfide group is presented to the alkene, the MeS···sp^2-C steric interaction would be estimated at 2.99 Å from symmetrical structures **28** and **33**. Only compound **21** shows such an orientation and the MeS···sp^2-C separation is notably shorter at 2.9226(14) Å. In *ortho*-unsubstituted methylthiobenzenes the methylthio group usually lies close to the benzene plane,[24] but there are a few examples with torsional displacements of up to 42°.[31] The only other *peri*-naphthalene containing a methylthio group is the diazonium salt **34**[32] (Table 1), in which the methylthio group is rotated 65.4° out of the naphthalene plane and the sulfur atom lies at 2.938(5 Å from the α-nitrogen atom, just slightly longer than the MeS···sp^2-C separation in compound **21** for which the methylthio group lies well out of the aromatic plane. Glaser and co-workers have demonstrated that the electron density in an aryldiazonium group is concentrated at the α-nitrogen atom which may account for the long MeS···α-N separation.[33]

The optimisation of crystal packing can also influence the precise conformation adopted by a particular molecule, and can affect the separation between adjacent groups. Hence, we should not read too much into the precise separations between the functional groups, since in the cases studied here the interaction between them is not generally strong enough to dominate the effects of crystal packing, unlike in the corresponding dimethylamino series. However, it is the patterns in the conformations which provide the lead to our conclusions, most notably the constant orientation of sulfur relative to the alkene bond, and comparisons with the corresponding dimethylamino series. In addition, the consistent observation of small pyramidalisations of the sp^2-C atom suggests a weak interaction between methylthio and alkene groups. Nevertheless, one should not forget that the calculation of these pyramidalities needs some caution since they depend on the refined position of a hydrogen atom, which are not as securely located as the heavier atoms. However, the observation of significant pyramidalities in those compounds with a constant orientation of the sulfur atom to the alkene is consistent with a weak interaction at work between the methylthio and alkene groups.

Conclusions

A MeS···sp^2-C attractive interaction controls the solid-state structure of compound **19**, whereas in compounds **20**, **21** and **23** the conformation is determined both by this interaction, and optimisation of conjugation between the alkene and the aromatic system subject to steric interactions. In all four cases the orientation of the MeS···C vector lies at 114—118° to the alkene and the attacked carbon atom is slightly pyramidalised. The conformation of compound **22** is determined solely by optimisation of conjugation in direct contrast to the dimethylamino analogue, indicating the weaker nature of the MeS···sp^2-C interaction. These molecules, in which conjugation, steric effects and attractive interactions between functional groups are competing, will be of particular interest for charge density studies which are now being used to characterise weaker bonding interactions. Since sulfides prefer to attack electrophiles perpendicular to the plane of the sulfide group, it will be interesting to study compounds where the face of the sulfide is forced to be disposed to the alkene as in **21**.

Experimental Section

General comments: NMR spectra were measured at 25 °C 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 PerkinElmer Spectrum RX 1 FT-IR spectrometer and are reported in cm^{-1}. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 25 instrument and are reported in nm. 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. Flash chromatography was performed on 40–63 silica gel (Merck).

Methyl 8-methylthionaphth-1-oate (25): Powdered KOH (0.5 g, 9 mmol) was stirred in DMSO (2 mL) and after 5 min the thiolactone **24**[20,21] (0.14 g. 0.75 mmol) was added followed by MeI (0.2 mL, 3 mmol). The resulting dark green mixture gradually lightened to a yellow colour and the reaction was complete after 40 min. The mixture was poured on to water (20 mL) and extracted with CH_2Cl_2. The organic extracts were washed with water and brine, dried ($MgSO_4$) and evaporated to yield a yellow oil, which was purified by flash chromatography on silica gel (cyclohexane/diethyl ether, 3:1) to yield the product **25** as a colourless oil (0.13 g, 74 %); ^{1}H NMR ($CDCl_3$)**:** $\delta = 7.88$ (dd, $J = 8.2$, 1.2 Hz, 1 H; Ar-H_1), 7.77–7.73 (m, 2 H; Ar-H_2), 7.60 (d, $J = 6.9$ Hz, 1 H; Ar-H_1), 7.48–7.41 (m, 2 H; Ar-H_2), 3.96 (s, 3 H; OCH_3), 2.41 ppm (s, 3 H; SCH_3); ^{13}C NMR ($CDCl_3$)**:** $\delta = 171.8$ (C=O), 134.6, 134.6, 132.7, 131.6, 131.3, 130.5, 128.3, 127.7, 126.3, 124.9 (Ar-C_{10}), 52.7 (OCH_3), 21.5 ppm (SCH_3); FTIR (liquid film): $\tilde{\nu} = 2922$, 2848, 1724, 1498, 1431, 1276, 1200, 1147, 1064, 1019, 963, 826, 769 cm^{-1}; HRMS (ES): *m/z*: calcd for $C_{13}H_{12}O_2S + NH_4$; found: 250.0909 $[M+NH_4]^+$.

1-Hydroxymethyl-8-methylthionaphthalene (26): Diisobutylaluminium hydride (1.5 M solution in toluene, 62 mL, 92 mmol) was added at −78 °C to a stirred solution of methyl 8-methylthionaphthoate (**25**; 9.75 g, 42 mmol) in dry toluene (100 mL), under nitrogen. The mixture was stirred at this temperature for 1 h, allowed to warm to room temperature and stirred for 30 min. The mixture was quenched at −78 °C with 1 M HCl (62 mL) and warmed to room temperature. The mixture was transferred to a separating funnel and washed with 1 M HCl. The organic solution was dried ($MgSO_4$) and evaporated. The crude oil was purified by flash chromatography on silica gel (cyclohexane/diethyl ether, 3:1) to yield a yellow solid, which was recrystallised from hexane to yield the product **26** as a white solid (6.6 g, 77 %), m.p. 52–55 °C; ^{1}H NMR ($CDCl_3$)**:** $\delta = 7.73$ (d, $J = 7.9$ Hz, 1 H; Ar-H_1), 7.65 (dd, $J = 7.9$, 1.5 Hz, 1 H; Ar-H_1), 7.50 (dd, $J = 6.9$, 1.5 Hz, 1 H; Ar-H_1), 7.44 (dd, $J = 7.5$, 1.5 Hz, 1 H; Ar-H_1), 7.38–7.31 (m, 2 H; Ar-H_2), 5.21 (br. s, 2 H; CH_2OH), 3.45 (br. s, 1 H; OH), 2.51 ppm (s, 3 H; SCH_3); ^{13}C NMR ($CDCl_3$)**:** $\delta = 137.2$, 135.7, 133.9, 131.1, 130.3, 130.1, 128.1, 127.7, 125.7, 125.1 (Ar-C_{10}), 65.9 (CH_2OH), 19.4 ppm (SCH_3); FTIR (KBr): $\tilde{\nu} = 3330$, 2918, 1654, 1566, 1498, 1425, 1358, 1318, 1206, 1169, 1092, 1056, 995, 803, 760 cm^{-1}; HRMS (ES): calcd for $C_{12}H_{12}OS + NH_4$: 222.0953; found: 222.0945 $[M+NH_4]^+$.

Preparation of 8-methylthio-1-naphthaldehyde (27): A solution of dry DMSO (2.75 g, 35.5 mmol) in CH_2Cl_2 (10 mL) was added at −78 °C to a stirred solution of oxalyl chloride (1.55 mL, 17.8 mmol) in CH_2Cl_2 (100 mL) under nitrogen. After 2 min a solution of the alcohol **26** (3.3 g, 16 mmol) in CH_2Cl_2 (15 mL) was added. After 20 min Et_3N (11.5 mL) was added and the mixture stirred for a further 5 min. The mixture was transferred to a separating funnel and the aqueous phase extracted with CH_2Cl_2. The combined organic extracts were sequentially washed with 2 M HCl, saturated $NaHCO_3$ and brine, dried ($MgSO_4$) and evaporated to yield the product **27** as a brown oil (2.94 g, 90 %), which solidified on standing, m.p. 40–43 °C (lit. [21] 43–44 °C); ^{1}H NMR ($CDCl_3$)**:** $\delta = 11.10$ (s, 1 H; CHO), 7.86 (dd, $J = 8.2$, 1.2 Hz, 1 H; Ar-H_1), 7.72–7.64 (m, 3 H; Ar-H_3), 7.45–7.33 (m, 2 H; Ar-H_2), 2.34 ppm (s, 3 H; SCH_3); ^{13}C NMR ($CDCl_3$)**:** $\delta = 191.9$ (C=O), 136.8, 134.2, 133.3, 132.8, 131.6, 131.1, 128.1, 128.0, 126.0, 125.1 (Ar-C_{10}), 20.3 ppm (SCH_3); FTIR (KBr): $\tilde{\nu} = 1677$, 1498, 829, 798, 761 cm^{-1}.

2,2-Dimethyl-5-(8′-methylthionaphthyl-1′-methylidene)-1,3-dioxane-4,6-dione (19): Meldrum's acid (0.54 g, 3.75 mmol) and ethylenediammonium diacetate (0.05 g, 0.3 mmol) were added to a stirred solution of the aldehyde **27** (0.5 g, 2.5 mmol) in dry methanol (7 mL) under nitrogen. After stirring for 1 h at room temperature a precipitate was obtained, which was collected by vacuum filtration and washed with methanol to yield the product **19** as a yellow solid (0.34 g). The filtrate was evaporated and the residue purified by flash chromatography on silica gel (cyclohexane/diethyl ether, 1:1) to yield further product **19** as a yellow solid (0.16 g), total yield (0.50 g, 61 %), m.p. 136–138 °C; ^{1}H NMR ($CDCl_3$)**:** $\delta = 9.58$ (s, 1 H; =CH), 7.90 (d, $J = 8.2$ Hz, 1 H; Ar-H_1), 7.87–7.81 (m, 2 H; Ar-H_2), 7.49–7.37 (m, 3 H; Ar-H_3), 2.36 (s, 3 H; SCH_3), 1.85 ppm (s, 6 H; C-$(CH_3)_2$); ^{13}C NMR ($CDCl_3$)**:** $\delta = 163.0$ (C=O), 161.9 (=CH), 160.6 (C=O), 135.0, 133.8, 133.4, 133.2, 132.3, 131.7, 129.6, 128.5, 126.4, 125.5 (Ar-C_{10}) 109.6 (=$\mathit{C}(CO)_2$), 105.5 ($\mathit{C}(CH_3)_2$), 27.8 (SCH_3), 22.1 ppm ($C(\mathit{C}H_3)_2$); FTIR(KBr): $\tilde{\nu} = 1734$, 1605, 1559, 1396, 1352, 1280, 1193, 1020, 926, 823, 762 cm^{-1}; UV/Vis (methanol): $\lambda_{max} = 225$, 306, 324 nm; HRMS (EI): calcd for $C_{18}H_{16}O_4S$: 328.0769; found: 328.0777 $[M]^+$.

1,1-Dicyano-2-(8′-methylthionaphth-1′-yl)ethene (20): Malononitrile (0.25 g, 3.75 mmol) and ethylenediammonium diacetate (0.05 g, 0.3 mmol) were added to a stirred solution of the aldehyde **27** (0.50 g, 2.5 mmol) in dry methanol (7 mL) under nitrogen. The mixture was stirred at room temperature overnight. The resulting precipitate was collected by vacuum filtration and washed with methanol to yield the product as a yellow solid (0.06 g). The filtrate was evaporated and the residue purified by flash chromatography on silica gel (cyclohexane/diethyl ether, 5:1) to yield the product **20** as a yellow solid (0.40 g), total yield (0.46 g, 75 %), m.p. 114–116 °C; ^{1}H NMR (CDCl$_3$): $\delta=9.27$ (s, 1 H; 2-H), 8.02 (d, $J=7.9$ Hz, 1 H; Ar-H$_1$), 7.88–7.80 (m, 2 H; Ar-H$_2$), 7.67–7.49 (m, 3 H; Ar-H$_3$), 2.43 ppm (s, 3 H; SCH$_3$); ^{13}C NMR (CDCl$_3$): $\delta=164.9$ (2-C), 135.2, 133.9, 133.7, 133.6, 132.2, 130.2, 129.8, 129.5, 127.1, 125.8 (Ar-C$_{10}$), 113.8 (CN), 112.5 (CN), 80.9 (1-C), 21.5 ppm (SCH$_3$); FTIR (KBr): $\tilde{\nu}=3027$, 2228, 1578, 1493, 1431, 1348, 1206, 914, 833, 798, 764 cm^{-1}; UV/Vis (methanol): $\lambda_{\max}=2212$, 298; HRMS (EI): calcd for C$_{15}$H$_{10}$N$_2$S: 250.0565; found: 250.0564 $[M]^+$.

Methyl (*E*)-2-cyano-3-(8′-methylthionaphth-1′-yl)-1-propenoate (21): Methyl cyanoacetate (0.15 g, 1.5 mmol) and ethylenediammonium diacetate (0.018 g, 0.09 mmol) were added to a stirred solution of the aldehyde **27** (0.2 g, 1.0 mmol) in dry methanol (3 mL) under nitrogen. After stirring for 1 h. at room temperature a precipitate was obtained, which was collected by vacuum filtration and washed with methanol to yield the product **21** as a yellow solid (0.14 g, 51 %), m.p. 106–108 °C; ^{1}H NMR (CDCl$_3$): $\delta=9.55$ (s, 1 H; 3-H), 7.96 (d, $J=8.2$ Hz, 1 H; Ar-H$_1$), 7.81 (dd, $J=8.2$, 1.0 Hz, H; Ar-H$_1$), 7.75–7.69 (m, 2 H; Ar-H$_2$), 7.56–7.45 (m, 2 H; Ar-H$_2$), 3.97 (s, 3 H; OCH$_3$), 2.41 ppm (s, 3 H; SCH$_3$); ^{13}C NMR (CDCl$_3$): $\delta=163.1$ (C=O), 160.5 (3-C), 135.1, 134.3, 132.8, 132.4, 132.2, 130.8, 129.7, 128.9, 126.5, 125.6 (Ar-C$_{10}$), 115.4 (CN), 101.2 (2-C), 53.2 (OCH$_3$), 21.2 ppm (SCH$_3$); FTIR (KBr): $\tilde{\nu}=2944$, 2222, 1728, 1590, 1429, 1274, 1239, 1088, 830, 757 cm^{-1}; UV/Vis (methanol): $\lambda_{\max}=223$, 295; HRMS (ES): calcd for C$_{16}$H$_{12}$NO$_2$S + H: 284.0745; found: 284.0743 $[M+\mathrm{H}]^+$.

(*E*)-1-(8′-Methylthionaphth-1′-yl)-2-nitroethene (22): Nitromethane (0.08 mL, 1.5 mmol) and ethylenediammonium diacetate (0.018 g, 0.09 mmol) were added to a stirred solution of the aldehyde **27** (0.18 g, 1.0 mmol) in dry methanol (3 mL) under nitrogen. After the mixture had been stirred for several hours at room temperature, TLC (cyclohexane/diethyl ether, 5:1) showed just starting materials were present so piperidine (2 drops) was added and the mixture stirred overnight. The methanol was evaporated and the residue purified by flash chromatography on silica gel (cyclohexane/diethyl ether, 5:1) to yield the product **22** as an orange solid (0.032 g, 13 %), m.p. 73–78 °C; ^{1}H NMR (CDCl$_3$): $\delta=9.38$ (d, $J=13.1$ Hz, 1 H; 1-H), 7.92 (dd, $J=7.4$, 2.2 Hz, 1 H; Ar-H$_1$), 7.76 (dd, $J=8.2$, 1.2 Hz, 1 H; Ar-H$_1$), 7.64 (dd, $J=7.4$, 1.2 Hz, 1 H; Ar-H$_1$), 7.50–7.42 (m, 3 H; Ar-H$_3$), 7.30 (d, $J=13.1$ Hz, 1 H; 2-H), 2.46 ppm (s, 3 H; SCH$_3$); ^{13}C NMR (CDCl$_3$): $\delta=143.1$ (1-C), 135.2, 135.1 (Ar-C$_2$), 132.3 (2-C), 131.7, 130.2, 129.3, 129.0, 128.1, 126.5, 125.5 (Ar-C$_8$'one peak is doubly degenerate), 20.3 ppm (SCH$_3$); FTIR (KBr): $\tilde{\nu}=1627$, 1489, 1345, 962, 823, 763, 737 cm^{-1}; UV/Vis (methanol): $\lambda_{\max}=223$, 296; HRMS (ES): calcd for C$_{13}$H$_{11}$NO$_2$S + H: 246.0589; found: 246.0591 $[M+\mathrm{H}]^+$.

(*E*)-1-(8′-Methylthionaphth-1′-yl)-2-nitroprop-1-ene (23): Nitroethane (0.15 mL, 2.0 mmol), ethylenediammonium diacetate (0.018 g, 0.09 mmol) and piperidine (3 drops) were added to a stirred solution of the aldehyde **27** (0.20 g, 1.09 mmol) in dry methanol (3 mL) under nitrogen. After the mixture had been stirred for two days, the methanol was evaporated and the residue purified by flash chromatography on silica gel (cyclohexane/diethyl ether, 5:1) to yield the product **23** as an orange solid (0.094 g, 36 %), m.p. 76–77 °C; ^{1}H NMR (CDCl$_3$): $\delta=8.93$ (s, 1 H; 1-H), 7.80 (dd, $J=8.9$, 0.8 Hz, 1 H; Ar-H$_1$), 7.64 (dd, $J=7.5$, 1.8 Hz, 1 H; Ar-H$_1$), 7.40 (m, 3 H; Ar-H$_3$), 7.17 (dd, $J=7.3$, 1.6 Hz, 1 H; Ar-H$_1$), 2.39 (s, 3 H; SCH$_3$), 2.19 ppm (s, 3 H; 3-H$_3$); ^{13}C NMR (CDCl$_3$): $\delta=145.3$ (2-C), 138.0 (1-C), 135.9, 135.1, 131.1, 130.8, 130.7, 128.4, 127.8, 127.3, 126.2, 125.3 (Ar-C$_{10}$), 19.4 (SCH$_3$); 13.7 ppm (3-C); FTIR (KBr): $\tilde{\nu}=1646$, 1509, 1424, 1385, 1325, 1308, 977, 824, 796, 762 cm^{-1}; UV/Vis (methanol): $\lambda_{\max}=220$, 297; HRMS (CI): calcd for C$_{14}$H$_{13}$NO$_2$S + H: 260.07453; found: 260.07336 $[M+\mathrm{H}]^+$.

X-ray analyses: Diffraction data (Mo$_{K\alpha}$ radiation) was collected at low temperature (120–150 K) on a Bruker-Nonius KappaCCD diffractometer using phi and omega scans to fill Ewald sphere at low temperature Table 2. Data reduction included a correction for Lorentzian polarisation and an absorption correction was applied from multiple scan measurements. Structures were solved with SHELXS[34] and refined against F^2 with SHELXL[35]. Hydrogen atoms were located in difference maps and refined in almost all cases. CCDC-295225—CCDC-295229 contain the supplementary crystallographic data for this paper. These data can be ob-

Table 2. Details of crystallographic measurements and refinements.

	19	**20**	**21**	**22**	**23**
crystallisation solvent	ethyl acetate	acetone	ethyl acetate	diethyl ether	diethyl ether
formula	C$_{18}$H$_{16}$O$_4$S	C$_{15}$H$_{10}$N$_2$S	C$_{16}$H$_{13}$NO$_2$S	C$_{13}$H$_{11}$NO$_2$S	C$_{14}$H$_{13}$NO$_2$S
M_r	328.38	250.3	283.35	245.30	259.31
T [K]	120	150	120	120	120
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*Cc*	$P2_1/c$	$C2/c$	$P2_12_12_1$	$P2_1/c$
a [Å]	10.6181(5)	7.5941(4)	16.2151(2)	4.7575(2),	7.8992(3)
b [Å]	11.5922(5)	13.6436(9)	7.9116(1)	14.4311(7),	19.0699(6)
c [Å]	13.0123(6)	12.2968(8)	22.0688(4)	16.5082(10)	8.0840(4)
β[°]	105.599(2)°	107.972(3)°	105.0853(7)°	-	93.216(2)
V[Å^3]	1542.65	1211.92	2733.58	1133.39	1215.83
Z	4	4	8	4	4
ρ_{calcd} [g cm^{-3}]	1.41	1.37	1.38	1.44	1.42
μ[mm^{-1}]	0.23	0.25	0.24	0.27	0.26
F(000)	688	520	1184	512	544
crystal size [mm]	0.20 × 0.20 × 0.10	0.15 × 0.15 × 0.02	0.15 × 0.15 × 0.15	0.20 × 0.15 × 0.02	0.35 × 0.20 × 0.10
Θ range [°]	2.66-27.46	0.21-30.51	2.93-27.45	2.91-27.48	3.35-27.50
no. reflections collected	4997	8654	19361	8789	15149
no. independent reflections	2679	2916	3040	2540	2794
no reflections with $[F^2>4\sigma(F^2)]$	2468	1583	2456	2201	1880
R_{int}	0.042	0.099	0.055	0.050	0.066
parameters	261	203	233	198	215
GOF on F^2	1.16	0.92	1.06	1.04	0.99
$R1\ [F^2>4\sigma(F^2)]/wR2$	0.039/0.082	0.061/0.151	0.037/0.102	0.038/0.087	0.045/0.112
residual electron density, max./min. [e Å^3]	0.420/−0.268	0.564/−0.643	0.241/−0.389	0.221/−0.314	0.258/−0.322

tained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) H. B. Bürgi, J. D. Dunitz, E. Schefter, *J. Am. Chem. Soc.* **1973**, *95*, 5065–5067; b) A. S. Cieplak in *Structure Correlation* (Eds.: H. B. Burgi, J. D. Dunitz), VCH, Weinheim, **1994**, p. 205–302.

[2] W. H. Perkin, Jr., *J. Chem. Soc.* **1916**, *109*, 815–1028.

[3] J. E. Davies, A. J. Kirby, I. V. Komarov, *Helv. Chim. Acta* **2003**, *86*, 1222–1233.

[4] W. B. Schweizer, G. Procter, M. Kaftory, J. D. Dunitz, *Helv. Chim. Acta* **1978**, *61*, 2783–2808.

[5] a) M. Parvez, I. I. Schuster, *Acta Crystallogr. Sect. C* **1990**, *46*, 947–948; b) G. Procter, D. Britton, J. D. Dunitz, *Helv. Chim. Acta* **1981**, *64*, 471–477.

[6] D. R. W. Hodgson, A. J. Kirby, N. Feeder, *J. Chem. Soc. Perkin Trans. 1* **1999**, 949–954.

[7] J. Clayden, C. McCarthy, M. Helliwell, *Chem. Commun.* **1999**, 2059–2060.

[8] J. O'Leary, W. Skranc, X. Formosa, J. D. Wallis, *Org. Biomol. Chem.* **2005**, *3*, 3273–3283.

[9] P. C. Bell, J. D. Wallis, *Chem. Commun.* **1999**, 257–258.

[10] J. O'Leary, P. C. Bell, J. D. Wallis, W. B. Schweizer, *J. Chem. Soc. Perkin Trans. 2* **2001**, 133–139.

[11] P. C. Bell, M. Drameh, N. Hanly, J. D. Wallis, *Acta Crystallogr. Sect. C* **2000**, *56*, 670–671.

[12] K. Akiba, H. Yamashita, Y. Yamamoto, S. Nagase, *J. Am. Chem. Soc.* **1999**, *121*, 10644–10645.

[13] K. A. Lyssenko, S. M. Aldoshin, M. Y. Antipin, *Mendeleev Commun.* **2004**, 98–100.

[14] C. S. Frampton, L. H. Straver, J. D. Wallis, S. C. Coles, *Gordon Conference*, Mount Holyoke College, USA, **2004**.

[15] a) J. O'Leary, J. D. Wallis, M. L. Wood, *Acta Crystallogr. Sect. C* **2001**, *57*, 851–853; b) J. O'Leary, J. D. Wallis, manuscript in preparation.

[16] A. Panda, G. Mugesh, H. B. Singh, R. J. Butcher, *Organometallics* **1999**, *18*, 1986–1993.

[17] a) C. Breliere, F. Carre, R. J. P. Corriu, M. Poirier, G. Royo, *Organometallics* **1986**, *5*, 388–390; b) F. Carre, G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye, *New J. Chem.* **1992**, *16*, 63–69; c) C. Breliere, F. Carre, R. J. P. Corriu, W. E. Douglas, M. Poirier, G. Royo, M. W. C. Man, *Organometallics* **1992**, *11*, 1586–1593; d) F. Carre, R. J. P. Corriu, A. Kpoton, M. Poirier, G. Royo, J. C. Young, C. Belin, *J. Organomet. Chem.* **1994**, *470*, 43–57.

[18] C. Cox, H. Wack, T. Lectka, *Angew. Chem.* **1999**, *111*, 864–867; *Angew. Chem. Int. Ed.* **1999**, *38*, 798–800.

[19] a) P. R. Mallison, G. T. Smith, C. C. Wilson, E. Grech, K. Wozniak, *J. Am. Chem. Soc.* **2003**, *125*, 4259–4270; b) K. Wozniak, P. R. Mallinson, G. T. Smith, C. C. Wilson, E. Grech, *J. Phys. Org. Chem.* **2003**, *16*, 764–771.

[20] R. F. Hudson, J. D. Wallis, D. P. Hansell, *Heterocycles* **1994**, *37*, 1933–1950.

[21] R. J. Bailey, P. J. Card, H. Shechter, *J. Am. Chem. Soc.* **1983**, *105*, 6096–6103.

[22] J. Rabai, *Synthesis* **1989**, 523–525.

[23] S. C. Nyberg, C. H. Faerman, *Acta Crystallogr. Sect. B* **1985**, *41*, 274–279.

[24] Cambridge Structural Database, F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380–388.

[25] a) J. Schultz, M. Nieger, F. Vogtle, *Chem. Ber.* **1991**, *124*, 2797–2810; b) A. De, M. Kusunoki, *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 57–60; c) B. Gordillo, Z. J. Dominguez, N. Sanchez, R. Gonzalez, M. Salas, E. Barragan, *Tetrahedron Lett.* **2003**, *44*, 5293–5297.

[26] a) A. G. Griesbeck, M. Oelgemoller, J. Lex, A. Haeuseler, M. Schmittel, *Eur. J. Org. Chem.* **2001**, 1831–1843; b) A. Taylor, A. J. Blake, A. J. Holder, T. I. Hyde, M. Schroder, *New. J. Chem.* **1991**, *15*, 511–514; c) T. Moriguchi, S. Kitamura, K. Sakata, A. Tsuge, *Polyhedron* **2001**, *20*, 2315–2320.

[27] P. Nagy, D. Szabo, I. Kapovits, A. Kucsman, G. Argay, A. Kalman, *J. Mol. Struct.* **2002**, *606*, 61–76.

[28] R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen, G. S. Wilson, *J. Am. Chem. Soc.* **1989**, *111*, 4036–4045.

[29] R. E. Rosenfield, R. Parthasarathy, J. D. Dunitz, *J. Am. Chem. Soc.* **1977**, *99*, 4860–4862.

[30] B. Stulgies, P. Prinz, J. Magull, K. Rauch, K. Meindl, S. Ruhl, A. De Meijere, *Chem. Eur. J.* **2005**, *11*, 308–320.

[31] a) R. H. Laitinen, H. Riihimaki, M. Haukka, S. Jaaskelainen, T. A. Pakkanen, J. Pursiainen, *Eur. J. Inorg. Chem.* **1999**, 1253–1258; b) I. Wharf, M. J. Simard, *Acta Crystallogr. Sect. C* **1991**, *47*, 1605–1609; c) D. Christendat, I. Wharf, A.-M. Lebuis, I. S. Butler, D. F. R. Gilson, *Inorg. Chim. Acta* **2002**, *329*, 36–44.

[32] J. D. Wallis, R. J. C. Easton, J. D. Dunitz, *Helv. Chim. Acta* **1993**, *76*, 1411–1424.

[33] a) R. Glaser, C. Horan, *Can. J. Chem.* **1996**, *74*, 1200–1214; C. J. Horan, C. L. Barnes, R. Glaser, *Chem. Ber.* **1993**, *126*, 243–249; b) C. J. Horan, C. L. Barnes, R. Glaser, *Acta Crystallogr. Sect. C* **1993**, *49*, 507–509; c) C. J. Horan, P. E. Haney, C. L. Barnes, R. Glaser, *Acta Crystallogr. Sect. C* **1993**, *49*, 1525–1528; d) R. Glaser, C. J. Horan, E. D. Nelson, M. K. Hall, *J. Org. Chem.* **1992**, *57*, 215–228.

[34] G. M. Sheldrick, SHELXS, Computer program for solution of crystal structures, University of Göttingen, Germany, **1997**.

[35] G. M. Sheldrick, SHELXL, Computer program for refinement of crystal structures, University of Göttingen, Germany, **1997**.

[36] The United Kingdom Chemical Database Service, D. A. Fletcher, R. F. McMeeking, D. J. Parkin, *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746–749.

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