Reactivity of Phenyliodonium Bis(arylsulphonyl)methylides towards Alkenes and Alkynes: Crystal Structure of 9-Phenylsulphonyl-1,2,3,4,4a,9a-hexahydro-1,4-methanofluorene

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Thermal or photochemical reactions of phenyliodonium bis(arylsulphonyl)methylides with alkenes lead normally to gem-(arylsulphonyl)cyclopropanes. Norbornene and *trans*-stilbene, however, afford 1-(phenylsulphonyl)indane derivatives. The crystal structure of the title compound $\{R = 0.038$ for 3 468 unique observed reflections $[I/\sigma(I) \geqslant 3.0]\}$ confirmed the identity of the product with norbornene. Diarylacetylenes give 1-(arylsulphonyl)indenes. Thermal decomposition of the ylides involves a new rearrangement, with formation of aryl arenethiosulphonates.

Carbenes or carbenoids undergo cycloaddition to alkenes and to a lesser degree to alkynes to form cyclo-propanes and -propenes, respectively. Phenyliodonium ylides constitute one of the less well known classes of carbene precursors, the reactions of which are little known and not widely applicable.[1,2] Recently we have shown[3] that phenyliodonium bis(phenyl-sulphonyl)methylide, (3), easily obtainable from the disulphone (2) with diacetoxyiodobenzene, (1), gives, with cyclohexene under photolytic conditions, the cycloaddition product (4). This

PhI(OAc)$_2$ + CH$_2$(SO$_2$Ph)$_2$ $\xrightarrow[-10^{\circ}C]{\text{KOH}}$ PhI$^+$C$^-$(SO$_2$Ph)$_2$

(1)   (2)   (3)

(4)
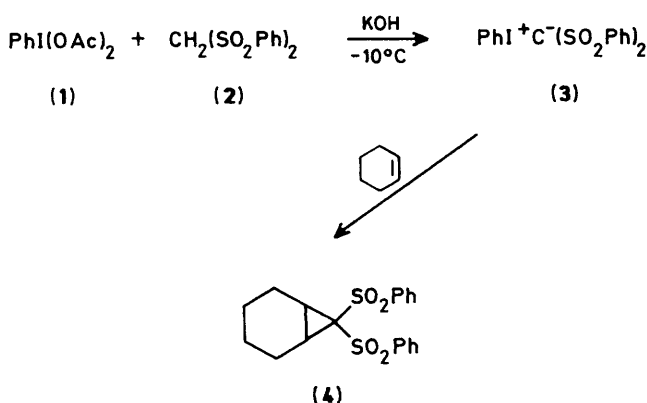
finding, together with the inability of bis(phenylsulphonyl)-diazomethane to react as an efficient carbene precursor[4] and the current interest in gem-cyclopropyl disulphones[5,6] has led us to study the reactivity of (3).

Results and Discussion

Reaction with Alkenes.—Simple olefins react with the methylide (3) under a variety of conditions to give the expected cycloaddition products in moderate yield (Table 1). The most satisfactory conditions are either photolytic (in acetonitrile) or thermal (in chloroform or methylene dichloride), with catalysis by cupric acetylacetonate, Cu(acac)$_2$. There are no general trends and any individual olefin may give better yields photochemically or thermally. Norbornene and phenylalkenes react photochemically or thermally without any catalysis affording either oxidation products or various types of indanes or both. Other products not shown in Table 1 include the disulphone (2) and phenyl benzenethiosulphonate, PhSO$_2$SPh. Product identification
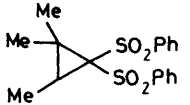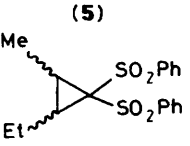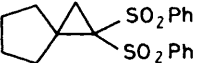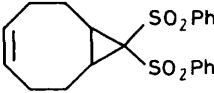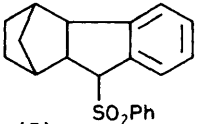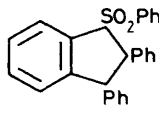
was based on elemental analysis and spectroscopic data, including mass spectra, where a molecular ion of small intensity was always present. The ^{1}H n.m.r. spectra were unhelpful in assigning the cyclopropyl protons, which generally appeared as multiplets mixed with methyl or methylene protons, *e.g.* the aliphatic protons of (4) resonate in the range δ 0.88—2.72 (10 H, m). This prevented attempts to use separated geometric isomers of alkenes, to determine the stereochemistry of the products.

Cyclopropyl gem-disulphones have been known for some time and recently their utility as synthons for propene 1,3-dipoles has been demonstrated.[6] They have been prepared by a number of methods, without any noticeable lability. We find that the gem-disulphones [(4)—(8); Table 1] are somewhat labile, since extensive decomposition occurred upon storage for 2 months at room temperature. A dramatic manifestation of this instability was provided by the reaction of (3) with norbornene, where the only isolable product after the reaction had been stirred at room temperature for 6 days was the indane monosulphone (9) in high yield, whose structure has been confirmed by an X-ray analysis. The mildness of the reaction conditions makes it unlikely that (3) is decomposed into phenyl iodide and bis(phenylsulphonyl)carbene, as may be assumed in the cases of photolysis or Cu(acac)$_2$-catalysed decomposition. The initial product, possibly through a π-complex or even a four-membered hypervalent iodine intermediate (which should be favoured because of the T-shaped geometry around hypervalent iodine), must be the disulphone (13) (not necessarily the *exo*-isomer shown); subsequently (13) loses SO$_2$ homolytically to afford the phenylated sulphone (14), also unstable. We suggest that (14) is converted into the isoindane (15) and this by a prototropic shift gives the final product (9) (Scheme 1).

The easy loss of SO$_2$ from gem-cyclopropyl disulphones is apparently a characteristic but unprecedented reaction of this class of compound. Other gem-disulphones have to be pyrolysed at 650—700 °C in order to expel SO$_2$.[7] The trans-formation (14) to (15) in analogous systems could also not be effected either thermally[8] or photochemically,[9] although 1-phenyl 2-methylenecyclopropane rearranges thermally to an indene.[10] The presence of the phenylsulphonyl group is likely to facilitate this transformation, even at room temperature.

The reactions of phenylated alkenes with (3) give mainly oxidation products, but *trans*-stilbene also gives an indane, (11), along with oxidation products and the phenyl disulphone (10). The indane sulphone (11) may be formed by a similar pathway

Table 1. Reaction products of alkenes and compound (3)

Alkene	Conditions*	Products (% yield)
Cyclohexene	(a); (b)	(4) (a, 31; b, 14)
Me$_2$C=CHMe	(a)	(5) (30)
MeCH=CHEt (*cis* + *trans*)	(a)	(6) (25)
Methylenecyclopentane	(a)	(7) (69)
Cyclo-octa-1,5-diene	(a); (b)	(8) (a, 27; b, 37)
Norbornene	(c)	(9) (74)
PhCH=CH$_2$	(a)	PhCHO (68) + PhCH(SO$_2$Ph)$_2$ (11) (10)
Ph$_2$C=CH$_2$	(a)	Ph$_2$CO (81)
PhCH=CHPh (*trans*)	(c)	(11) Ph (44) + PhCHO (12) + Ph$_2$CHCHO (4) + (10)(8)

* (a), Photolysis; (b), thermolysis catalysed by Cu(acac)$_2$; (c), thermolysis without catalysis.

Scheme 1.

Table 2. Reaction products of tolans with phenyliodonium bis(sulphonyl)methylides

| Ylide	Alkyne	Product (% yield)
[PhI][C(SO₂Ph)₂] (3)	PhC≡CPh	(17) (61)
[PhI][C(SO₂Tol)₂] (18)	PhC≡CPh	(19) (47)
[PhI][C(SO₂Tol)(SO₂Me)] (20)	PhC≡CPh	(21) (32)
[PhI][C(SO₂Ph)₂] (3)	AnC≡CAn	(22) (53)

Tol is *p*-MeC₆H₄ and An is *p*-MeOC₆H₄.
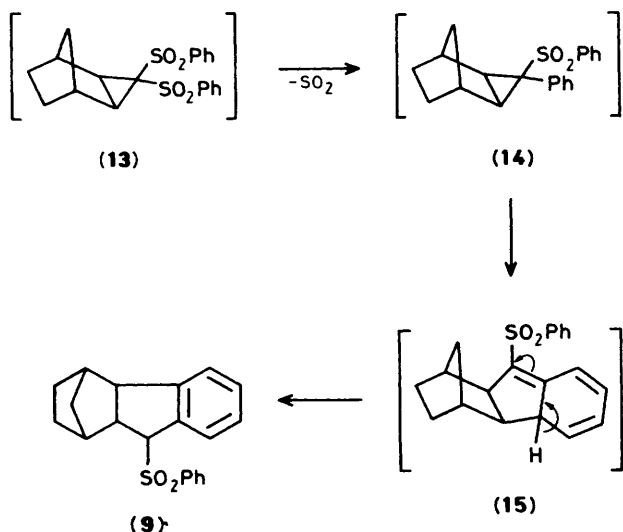
to that of Scheme 1, although there is also a possibility that the fused benzene ring of the indane comes not from the Ph of a PhSO₂ group (as above) but from a Ph group of the stilbene, as occurs with tolans (*vide infra*).

The structure of (11) is supported by its ¹H n.m.r. spectrum, where two doublets appear at δ 4.31 and 5.11, assigned to 3-H and 1-H, respectively, and one apparent triplet at δ 3.63, due to 2-H. The sharp melting point of (11) and its $J_{1,2}$ and $J_{2,3}$ values of 7 Hz suggest that it is a pure isomer of *cis-cis* configuration. This is supported by a study of isomeric 1-benzyl-2,3-diphenyl-indanes,[11] where it was found that the *cis-cis* isomer had both *J* values of 7.8 Hz, whereas the *trans-trans* isomer had *J* values of 9.5 Hz.

The phenyl disulphone (10) is a by-product not only of *trans*-stilbene but also of styrene. We tentatively suggest that it may arise from the initial cyclopropyl gem-disulphones (12) through phenyl migration; the alkenes, *e.g.* (16) from stilbene, may fragment to phenylacetylene (or acetylene from styrene) and (10) (Scheme 2).

PhC≡CH + PhCH(SO₂Ph)₂

(10)
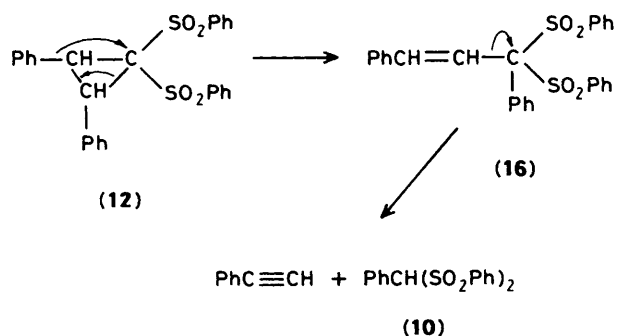
Scheme 2.

However, no evidence has been found for any alkyne formation, in the cases when (10) was formed. As previously reported, the main product is (10) (65% yield) from the photochemical reaction of (3) in benzene.[3] That reaction is probably a carbene insertion, although an alternative mechanism involving a phenyl rearrangement similar to that observed in phenyliodonium ylides of β-diketones[12] cannot be completely ruled out.

The oxidation products of phenylalkenes are either benzaldehyde or benzophenone, *i.e.* products of oxidative cleavage of the double bond. Benzophenone was the only product isolated from the photochemical reaction of 1,1-diphenylethylene with (3), besides phenyl iodide. It is unlikely that participation of the sulphonyl group is involved, because it was not possible to detect any reduction product of it, *e.g.* PhSO₂C(PhSO)=CHPh or PhSO₂CH₂SOPh. We think that more probably some iodosylbenzene is formed from hydrolysis of (3) due to residual moisture and this can cleave the double bond, presumably *via* an oxirane. We have also found that *trans*-1,2-diphenyloxirane reacts thermally with (3) to give a mixture of benzaldehyde (41%) and diphenylacetaldehyde (55%); the latter product was also formed from the reaction of stilbene with (3). Another possibility is photo-oxidation by dissolved oxygen, as suggested in a related oxidative cleavage.[13]

A further by-product of several reactions is phenyl benzenesulphonate, which becomes the major product of the reaction of (3) in t-butyl alcohol; its formation is discussed separately below.

Reaction with Alkynes.—Phenylacetylene reacts with (3) to give a complex mixture of products, from which no pure compounds could be isolated. Diphenylacetylene (tolan) gave, with (3), an indene monosulphone and similar products were obtained from *p,p'*-dimethoxytolan and also from two other phenyliodonium bis-sulphonyl methylides (Table 2), by stirring in a nitrogen atmosphere in CH₂Cl₂, without any catalyst; benzil was also formed as a by-product. The structure of the

Table 3. Thermal decomposition of phenyliodonium bis(sulphonyl)methylides

Ylide	Conditions	Products (% yield)
(3)	(a)	PhSO$_2$SPh (85)
		(28)
[PhI][C(SO$_2$Ar)$_2$]	(a)	ArSO$_2$SAr (55)
(27)		(29)
	(b)	(ArSO$_2$)$_2$CHSAr (47)
		(30)
[PhI][C(SO$_2$Tol)$_2$]	(a)	TolSO$_2$STol (55) + TolSO$_2$CH=CHSO$_2$Tol (22)
(18)		(31) (32)
[PhI][C(SO$_2$Tol)(SO$_2$Me)]	(a)	TolSO$_2$SO$_2$Tol (5)
(20)		(33)

(a), Heating in Bu^{t}OH with Cu(acac)$_2$ in N$_2$; (b), as in (a) in atmospheric air; Ar is p-ClC$_6$H$_4$ and Tol is p-MeC$_6$H$_4$.

indenes of Table 2 was established by their reduction with Na-amalgam which gave, unexpectedly, indenones, *e.g.* (24) from (17) (Scheme 3). The expected product from (17) was the indene (23), which was apparently oxidised by atmospheric oxygen to the known[14] indenone (24). Such autoxidations of 2,3-diarylindenes in basic solution are effected easily.[14]
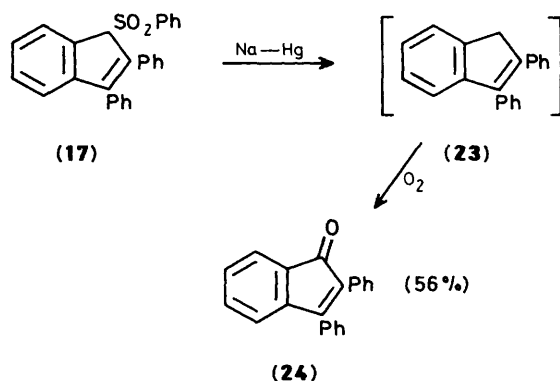
Scheme 3.

An analogous reduction–autoxidation took place with (19) and (22) which gave the indenones (25) and (26), respectively.

(An = p - MeOC$_6$H$_4$)
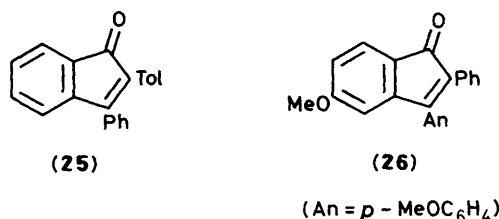
In the reaction of (3) with stilbene we mentioned the possibility that the benzene ring of the indane might come not from a phenylsulphonyl group but from a phenyl of stilbene. We have proved from the reactions with the substituted compounds that this is the case in the reaction of tolans.

Thus, the bistolylsulphonyl ylide (18) gave (19) which was further transformed into the known indenone (25). Therefore, the aryl group of C-2 comes from the arylsulphonyl group. Further confirmation comes from the reaction of (3) with p,p'-dimethoxytolan, in which the indene (22) is transformed into the known indenone (26), *i.e.* the aryl group of C-3 comes from tolan. In the case of methylsulphonyl p-tolylsulphonyl ylide (20), which was not converted into its indenone, it is the

methylsulphonyl group that loses SO$_2$, rather than the phenylsulphonyl group, to give the 2-methylindene sulphone (21).
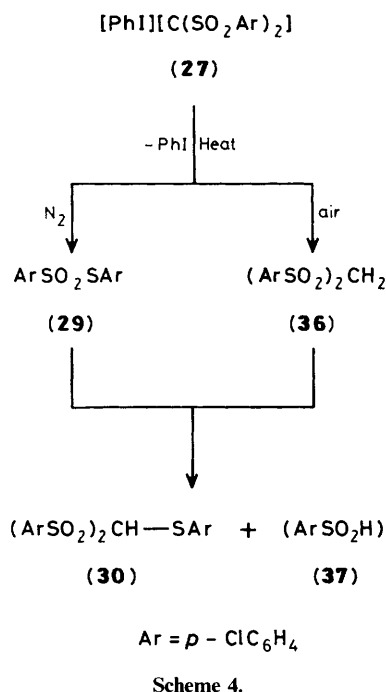
In connection with the mechanism of these reactions, it is pointed out that in contrast to phenylcyclopropanes which are not known to isomerise into indanes, arylcyclopropenes isomerise to indenes with incorporation of the 3-aryl group into the indene ring.[15] In the present work however, we have shown that, if a cyclopropene is initially formed, the 1-phenyl group, *i.e.* from tolan, is incorporated into the indene ring. The data available do not permit the choice of a pathway, from several possibilities. It is of interest to note that the photochemical reaction of tolan with (3) takes a completely different course and the sole isolated product is benzil.

Catalysed Thermal Decomposition of Phenyliodonium Bis-(arylsulphonyl)methylides.—All attempts to recrystallise the ylide (3) were unsuccessful, extensive decomposition occurring with formation of the disulphone (PhSO$_2$)$_2$CH$_2$; a further by-product, also found in most thermal reactions, *i.e.* phenyl benzenethiosulphonate, PhSO$_2$SPh, (28), was identified. This unexpected product was produced in high yield when (3) was refluxed in t-butyl alcohol and these conditions were applied in the thermolysis of other related ylides. The results are shown in Table 3. Although formation of aryl arenethiosulphonates appears to be general, there are also unusual features to the reaction and other products can be formed upon thermolysis of this type of ylide. No such esters could be isolated from photolysis experiments, no doubt because of their photolability.[16] Indeed, when (3) was photolysed in methanol the only products formed were the disulphone (PhSO$_2$)$_2$CH$_2$ and the known[4] ether (PhSO$_2$)$_2$CHOMe, in 45 and 54% yield, respectively, as shown from the ^{1}H n.m.r. spectrum of the reaction mixture.

Production of the ester (28) is accompanied by evolution of CO$_2$, as confirmed by a thermolysis experiment of (3) without any solvent in a stream of nitrogen; CO$_2$ identification was effected by bubbling the gas into a Ca(OH)$_2$ solution and observing formation of turbidity, which cleared upon acidification. A mechanistic scheme has been proposed for this new rearrangement involving carbene formation.[3] Both atoms of oxygen come from the same sulphone group, because the unstable ylide (34), prepared *in situ* from the sulphone PhSO$_2$CH$_2$SPh and PhI(OAc)$_2$ at -10 °C in methanol, when allowed to come to room temperature decomposed to CO$_2$ and diphenyl disulphide (35).

[PhI][C(SPh)SO$_2$Ph] ⟶ (PhS)$_2$ + CO$_2$ + PhI

(34)   (35)
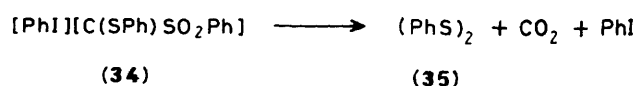
Phenyliodonium bis(p,p'-dichlorophenylsulphonyl)-methylide (27) gave the thiosulphonate (29), but in air rather than a nitrogen atmosphere no (29) was produced, the only product isolated, apart from phenyl iodide, being the p-chlorophenylthiodisulphone (30). This change in reactivity may be attributed to enhanced production of the disulphone (36), which interacts with the ester (29) to produce (30) and the non-isolated sulphinic acid (37) (Scheme 4).

[PhI][C(SO$_2$Ar)$_2$]

(27)

- PhI | Heat

N$_2$ / air

ArSO$_2$SAr   (ArSO$_2$)$_2$CH$_2$

(29)   (36)

(ArSO$_2$)$_2$CH—SAr   +   (ArSO$_2$H)

(30)   (37)

Ar = p - ClC$_6$H$_4$

Scheme 4.

Reactions of β-disulphones with thiosulphonates are known to give arylthio derivatives[17] such as (30).

Phenyliodonium bis(p-tolylsulphonyl)methylide (18) in addition to the thiosulphonate (31) also gave the ethylene *cis*-disulphone (32), a known compound.[18]

A plausible route leading to (32) may involve formation of the unstable ylide (39), if one assumes that the enhanced basic character of (18) results in the formation of the iodonium salt (38), which is converted into the ester (37) (not isolated) and (39); the latter may further dissociate to carbene (40), which with (39) gives (32) (Scheme 5).

Phenyliodonium (methylsulphonyl)(p-tolylsulphonyl)-methylide (20) was used in order to test which ester would be

[PhI][C(SO$_2$Ar)$_2$]   +   ROH   ⇌   PhÏ—CH(SO$_2$Ar)$_2$RO$^-$

(18)   (38)

(Ar = p - MeC$_6$H$_4$ [PhÏ—C̄H(SO$_2$Ar)]   +   ArSO$_2$OR

R = Bu)   (39)   (37)

(39) $\xrightarrow{-PhI}$ [ArSO$_2$C̈H] $\xrightarrow[-PhI]{(39)}$ ArSO$_2$CH=CHSO$_2$Ar

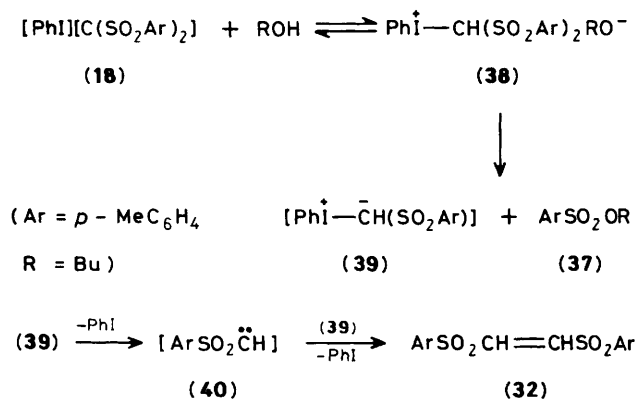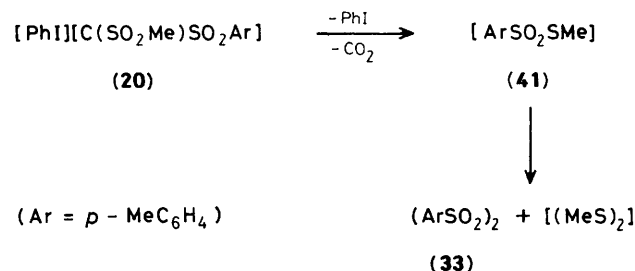(40)   (32)

Scheme 5.

Table 4. Bond lengths (Å) in (9). The crystallographic numbering for molecule (2) corresponds to that for molecule (1), with S(2), O(21), O(22), for S(1), O(11), O(12), and C(21)–C(40) replacing C(1)–C(20)

S(1)–O(11)	1.439(2)	S(1)–O(12)	1.440(2)
S(1)–C(6)	1.763(3)	S(1)–C(7)	1.806(3)
S(2)–O(21)	1.439(2)	S(2)–O(22)	1.434(2)
S(2)–C(26)	1.769(3)	S(2)–C(27)	1.796(3)
C(1)–C(2)	1.394(5)	C(1)–C(6)	1.375(4)
C(2)–C(3)	1.369(5)	C(3)–C(4)	1.366(6)
C(4)–C(5)	1.377(5)	C(5)–C(6)	1.385(4)
C(7)–C(8)	1.543(4)	C(7)–C(16)	1.505(4)
C(8)–C(9)	1.547(4)	C(8)–C(14)	1.552(4)
C(9)–C(10)	1.524(5)	C(9)–C(13)	1.525(5)
C(10)–C(11)	1.540(5)	C(11)–C(12)	1.535(5)
C(12)–C(13)	1.515(5)	C(12)–C(14)	1.539(5)
C(14)–C(15)	1.492(4)	C(15)–C(16)	1.382(4)
C(15)–C(20)	1.397(4)	C(16)–C(17)	1.382(5)
C(17)–C(18)	1.383(6)	C(18)–C(19)	1.374(6)
C(19)–C(20)	1.362(6)	C(21)–C(22)	1.376(5)
C(21)–C(26)	1.375(4)	C(22)–C(23)	1.360(5)
C(23)–C(24)	1.363(6)	C(24)–C(25)	1.375(5)
C(25)–C(26)	1.371(4)	C(27)–C(28)	1.547(4)
C(27)–C(36)	1.506(4)	C(28)–C(29)	1.532(4)
C(28)–C(34)	1.552(4)	C(29)–C(30)	1.530(5)
C(29)–C(33)	1.524(5)	C(30)–C(31)	1.543(5)
C(31)–C(32)	1.528(5)	C(32)–C(33)	1.522(5)
C(32)–C(34)	1.554(5)	C(34)–C(35)	1.498(4)
C(35)–C(36)	1.383(4)	C(35)–C(40)	1.387(5)
C(36)–C(37)	1.392(5)	C(37)–C(38)	1.381(5)
C(38)–C(39)	1.374(6)	C(39)–C(40)	1.382(6)

produced. Its decomposition gave no thiosulphonate but a complex mixture of products, from which only the α-disulphone (33) was isolated in 5% yield. It may be assumed that initially the relatively labile ester (41) was produced, *i.e.* the CO_2 evolved contained the O atoms from the more electronegative methylsulphonyl group;[19] under the reaction conditions (41) disproportionated[16] into (33) and the volatile dimethyl disulphide, which was not isolated (Scheme 6).

[PhI][C(SO$_2$Me)SO$_2$Ar] $\xrightarrow[-CO_2]{-PhI}$ [ArSO$_2$SMe]

(20)   (41)

(Ar = p - MeC$_6$H$_4$)

(ArSO$_2$)$_2$ + [(MeS)$_2$]

(33)

Scheme 6.

It is likely that active methylene compounds of the general formula Ar(R)SO$_2$CH$_2$X, where X is an electron-withdrawing group, may also rearrange to R(Ar)SX, through their iodonium ylides.

Crystal Structure Analysis.—Structure determination of the product from the reaction of (3) with norbornene allowed us to identify the unexpected indane monosulphone (9). The crystal contains two independent molecules, which are virtually identical in dimensions. Figure (a) shows one molecule with the crystallographic numbering and Figure (b) shows the boat-conformation of the bridged cyclohexane unit; the C–C–C bridgehead angles are 94.8(3) and 94.3(3)°. Bond distances (Table 4) are normal, with mean S=O of 1.438(2) Å, S–C (aromatic) 1.766(2) Å, S–C (aliphatic) 1.802(2) Å.
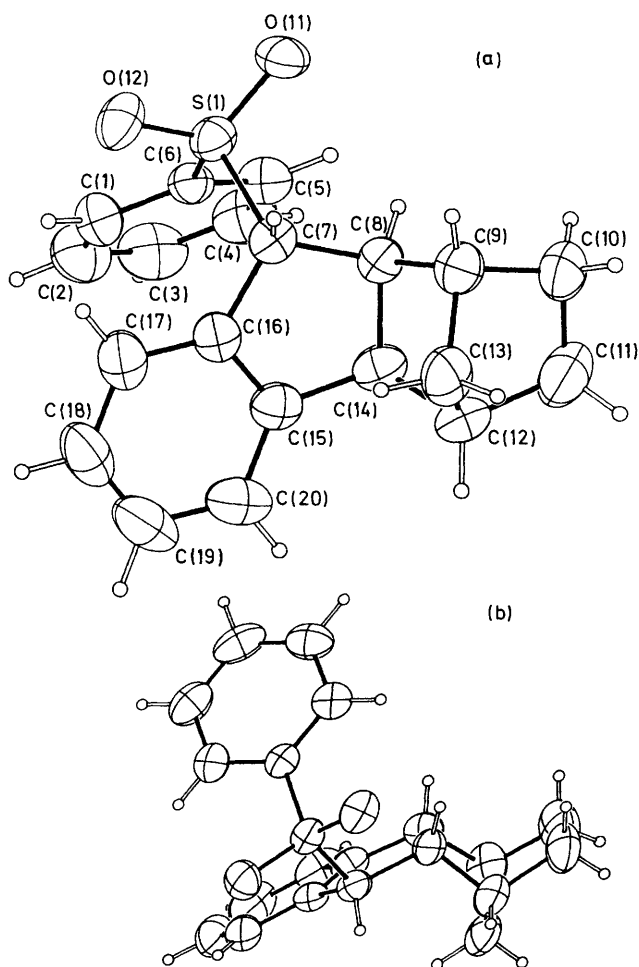
Figure. (a) View of one molecule of (**9**) showing the crystallographic numbering. The second molecule has prefix (2) for S and O atoms, and C atoms numbered C(21)–C(40), corresponding to C(1)–C(20). (b) Side view of one molecule of (**9**) showing the cyclohexane ring conformation

Experimental

U.v. spectra were recorded with a Shimatzu 210A spectrophotometer, i.r. spectra (all in Nujol) with a Perkin-Elmer 257 spectrometer, and ^{1}H n.m.r. spectra on a Varian A-60A spectrometer. Mass spectra were obtained from a Hitachi–Perkin-Elmer RMU-6L single focussing spectrometer at 70 eV. All starting materials were known compounds and were prepared by standard methods or purchased. With the exception of ylides, all reaction products were obtained by column chromatography on silica gel, using mixtures of methylene dichloride–hexane as the eluant. Phenyl iodide, produced in all reactions of the ylides, was the first to be eluted.

Preparation of Phenyliodonium Bis(arylsulphonyl)methylides: General Procedure.—A cold solution of KOH (40 mmol) in MeOH (10 ml) was added to a stirred suspension of the disulphone (10 mmol) in MeOH (10 ml) at −10 °C and the mixture stirred for 15 min [60 min for bis(*p*-chlorophenyl-sulphonyl)methane]. Diacetoxyiodobenzene (10 mmol) in MeOH (10 ml) was then added gradually, the temperature being kept at −5 °C. After being stirred for 30 min (60 min for the dichloro derivative), the reaction mixture was set aside at −10 °C for 12 h, to complete precipitation. The ylide was filtered off, washed with cold MeOH, and dried *in vacuo*. The

ylides can be stored for at least 2 weeks at −10 °C without any decomposition. Although no recrystallisation could be effected, satisfactory elemental analyses have been obtained.

Phenyliodonium bis(phenylsulphonyl)methylide (**3**) was obtained in 92% yield, m.p. 129—131 °C; $\lambda_{max.}$(EtOH) 225 (ϵ 38 300), 268 (ϵ 3 100), and 275 nm (ϵ 2 300); $\nu_{max.}$ 1 295 and 1 125 cm^{-1}; δ(CD$_3$)$_2$SO 7.17—7.38 (m, 9 H) and 7.60—7.82 (m, 6 H) (Found: C, 45.9; H, 2.9. C$_{19}$H$_{15}$IO$_4$S$_2$ requires C, 45.79; H, 3.03%).

Phenyliodonium bis(p-tolylsulphonyl)methylide (**18**) was obtained in 89% yield m.p. 151—153 °C; $\nu_{max.}$ 1 285 and 1 130 cm^{-1}; δ[(CD$_3$)$_2$SO] 2.35 (s, 6 H), 7.10—7.40 (m, 7 H), and 7.65—7.83 (m, 6 H) (Found: C, 47.8; H, 3.6. C$_{21}$H$_{19}$IO$_4$S$_2$ requires C, 47.92; H, 3.64%).

Phenyliodonium bis(p-chlorophenyl)methylide (**27**) was obtained in 85% yield, m.p. 153—155 °C; $\nu_{max.}$ 1 300, 1 280, and 1 140 cm^{-1}; δ[(CD$_3$)$_2$SO] 7.32—7.57 (m, 7 H) and 7.73—8.02 (m, 6 H) (Found: C, 40.2; H, 2.2. C$_{19}$H$_{13}$Cl$_2$IO$_4$S$_2$ requires C, 40.23; H, 2.31%).

Phenyliodonium (methylsulphonyl)(p-tolylsulphonyl)methyl-ide (**20**) was obtained in 95% yield, m.p. 91—92 °C; $\nu_{max.}$ 1 280—1 135 cm^{-1}; δ[(CD$_3$)$_2$SO] 2.28 (s, 3 H), 3.08 (s, 3 H), 7.20 (d, 2 H, J 8 Hz), 7.37—7.65 (m, 5 H), and 7.68—8.00 (m, 2 H) (Found: C, 39.8; H, 3.5. C$_{15}$H$_{15}$IO$_4$S$_2$ requires C, 40.01; H, 3.36%).

Reactions of Alkenes with the Ylide (**3**).—(a) The photochemical conditions involved irradiation with a Philips 400 W low-pressure mercury lamp in Pyrex tubes of the ylide (**3**) (1 mmol, 500 mg) in MeCN (10 ml) and the alkene. The reaction mixture was concentrated to dryness and chromatographed. The disulphones were obtained after phenyl iodide. In this way the following compounds have been obtained (in brackets: amount of alkene and irradiation time).

7,7-Bis(phenylsulphonyl)bicyclo[4.1.0]*heptane* (**4**) (10 ml, 4 h) was obtained in 31% yield, m.p. 145—147 °C (from chloroform–hexane); $\nu_{max.}$ 1 310 and 1 150 cm^{-1}; δ(CDCl$_3$) 0.88—2.72 (m, 10 H) and 7.38—8.05 (m, 10 H); *m/z* 376 (*M*$^+$, 4), 235 (7), and 125 (29) (Found: C, 60.4; H, 5.4. C$_{19}$H$_{20}$O$_4$S$_2$ requires C, 60.61; H, 5.35%).

2,2,3-Trimethyl-1,1-bis(phenylsulphonyl)cyclopropane (**5**) (10 ml, 6.5 h) was obtained in 30% yield, m.p. 131—133 °C (from chloroform–hexane); $\nu_{max.}$ 1 305 and 1 150 cm^{-1}; δ(CDCl$_3$) 0.83—2.65 (m, 10 H), 7.33—7.70 (m, 6 H), and 7.77—8.12 (m, 4 H); *m/z* 364 (*M*$^+$, 3) (Found: C, 59.2; H, 5.3. C$_{18}$H$_{20}$O$_4$S$_2$ requires C, 59.32; H, 5.53%).

2-Ethyl-3-methyl-1,1-bis(phenylsulphonyl)cyclopropane (**6**) (10 ml, 1 h) was obtained as a mixture of diastereoisomers in 25% yield, m.p. 124—126 °C (from chloroform–hexane); $\nu_{max.}$ 1 325 and 1 150 cm^{-1}; δ(CDCl$_3$) 0.70—2.67 (m, 10 H), 7.33—7.70 (m, 6 H), and 7.80—8.07 (m, 4 H); *m/z* 364 (*M*$^+$, 18) (Found: C, 59.0; H, 5.1. C$_{18}$H$_{20}$O$_4$S$_2$ requires C, 59.32; H, 5.53%).

1,1-Bis(phenylsulphonyl)spiro[2.4]*heptane* (**7**) (1.02 g, 1.2 h) was obtained in 69% yield, m.p. 150—152 °C (from chloroform–hexane); $\nu_{max.}$ 1 340 and 1 140 cm^{-1}; δ(CDCl$_3$) 1.27—2.50 (m, 10 H), 7.42—7.75 (m, 6 H), and 7.90—8.17 (m, 4 H) (Found: C, 60.85; H, 5.0. C$_{19}$H$_{20}$O$_4$S$_2$ requires C, 60.62; H, 5.35%).

α,α-*Bisphenylsulphonyltoluene* (**10**) was obtained from styrene (5 ml, 1.25 h) in 11% yield. It was eluted from the column after phenyl iodide, benzaldehyde, and the disulphone (**2**), m.p. 198—200 °C (from chloroform–hexane); $\nu_{max.}$ 1 345 and 1 175 cm^{-1}; δ(CDCl$_3$) 5.38 (s, 1 H), 7.31—7.43 (m, 11 H), and 7.55—7.97 (m, 4 H); *m/z* 372 (*M*$^+$, 2) (Found: C, 61.4; H, 4.2. C$_{19}$H$_{16}$O$_4$S$_2$ requires C, 61.3; H, 4.3%). The same compound was obtained as the sole product (65% yield) when (**3**) was irradiated in benzene for 11 h.

(b), (c). The thermal reactions were also performed with 1 mmol of (**3**) as follows. 9,9-*Bis(phenylsulphonyl)bicyclo-*

[6.1.0]*non*-4-*ene* (**8**). Compound (**3**) was refluxed in chloroform (10 ml) containing *cis,cis*-cyclo-octa-1,5-diene (3 ml) with Cu(acac)$_2$ (1 mg) in N$_2$ for 75 min. The residue after removal of volatiles was chromatographed to give some hydrocarbon and phenyl benzenethiosulphonate and then compound (**8**) in 37% yield, m.p. 193—195 °C (from chloroform–hexane); $\nu_{max.}$ 1 360 and 1 150 cm^{-1}; δ(CDCl$_3$) 1.18—3.20 (m, 10 H), 5.67 (m, 2 H), and 7.23—8.17 (m, 10 H); m/z 402 (M^+, 31) (Found: C, 62.7; H, 5.5. C$_{21}$H$_{22}$O$_4$S$_2$ requires C, 62.66; H, 5.51%).

9-*Phenylsulphonyl*-1,2,3,4,4a,9a-*hexahydro*-1,4-*methanofluorene* (**9**).—Compound (**3**) was stirred in methylene dichloride (10 ml) and norbornene (0.7 g) under N$_2$ for 6 days. The residue after removal of volatiles was chromatographed and gave (**9**) in 74% yield, m.p. 140—141 °C (from chloroform–hexane); $\nu_{max.}$ 1 285 and 1 125 cm^{-1}; δ(CDCl$_3$) 0.87 (m, 2 H), 1.15—1.63 (m, 4 H), 2.08 (m, 2 H), 2.50—2.92 (m, 2 H), 4.32 (m, 1 H), and 7.03—8.00 (m, 9 H); m/z 324 (M^+, trace) (Found: C, 73.8; H, 6.2. C$_{20}$H$_{20}$O$_2$S requires C, 74.04; H, 6.21%).

2,3-*Diphenyl*-1-*phenylsulphonylindane* (**11**).—Compound (**3**) and *trans*-stilbene (1.0 g) were stirred in methylene dichloride (10 ml) under N$_2$ for 36 h. Removal of solvent and column chromatography afforded *trans*-stilbene, a mixture of benzaldehyde and diphenylacetaldehyde and compound (**11**) in 44% yield, m.p. 139—141 °C (from chloroform–hexane); $\nu_{max.}$ 1 305 and 1 130 cm^{-1}; δ(CDCl$_3$) 3.63 (t, 1 H, J 7 Hz), 4.31 (d, 1 H, J 7 Hz), 5.11 (d, 1 H, J 7 Hz), and 6.63—8.00 (m, 19 H); m/z 410 (M^+, 2) (Found: C, 78.7; H, 5.6. C$_{27}$H$_{22}$O$_2$S requires C, 78.99; H, 5.40%). After (**11**) compounds (**10**) and (**2**) were also obtained in small quantities.

Reactions of Tolans with the Ylides (**3**), (**18**), *and* (**20**).—All reactions were performed with 1 mmol of ylide and 5.6 mmol of tolan in methylene dichloride. The mixture was stirred for 12 h, the solvent evaporated, and the residue chromatographed. Phenyl iodide was eluted first and unchanged tolan (or *p,p'*-dimethoxytolan) subsequently.

1-*Phenylsulphonyl*-2,3-*diphenylindene* (**17**) was obtained from the reaction between (**3**) and tolan in 61% yield, m.p. 148—150 °C (from chloroform–hexane); $\lambda_{max.}$(MeOH) 306 (ε 10 600) and 316 nm (ε 10 400); $\nu_{max.}$ 1 315 and 1 175 cm^{-1}; δ(CDCl$_3$) 5.65 (s, 1 H) and 6.72—8.23 (m, 19 H); m/z 408 (M^+, 28) (Found: C, 80.0; H, 4.9. C$_{27}$H$_{20}$O$_2$S requires C, 79.41; H, 4.90%).

3-*Phenyl*-1-(p-*tolylsulphonyl*)-2-(p-*tolyl*]*indene* (**19**) was obtained from (**18**) and tolan in 47% yield, m.p. 179—181 °C (from chloroform–hexane); $\nu_{max.}$ 1 600, 1 305, and 1 170 cm^{-1}; δ(CDCl$_3$) 2.33 (s, 3 H), 2.48 (s, 3 H), and 6.73—7.92 (m, 17 H); m/z 436 (M^+, 13) (Found: C, 79.2; H, 5.6. C$_{29}$H$_{24}$O$_2$S requires C, 79.82; H, 5.50%).

2-*Methyl*-3-*phenyl*-1-(p-*tolylsulphonyl*)*indene* (**21**). This was obtained from (**20**) and tolan in 32% yield, m.p. 176—178 °C (from chloroform–hexane); $\nu_{max.}$ 1 600, 1 310, and 1 175 cm^{-1}; δ(CDCl$_3$) 2.35 (s, 3 H), 2.48 (s, 3 H), 5.38 (s, 1 H), and 7.17—8.00 (m, 13 H); m/z 360 (M^+, 21) (Found: C, 76.25; H, 5.0. C$_{23}$H$_{20}$O$_2$S requires C, 76.67; H, 5.55%).

6-*Methoxy*-3-(p-*methoxyphenyl*)-1-*phenylsulphonyl*-2-*phenylindene* (**22**). This was obtained from (**3**) and *p,p'*-dimethoxytolan in 53% yield, m.p. 209—210 °C (from chloroform–hexane); $\nu_{max.}$ 1 605, 1 310, and 1 170 cm^{-1}; δ(CDCl$_3$) 3.78 (s, 3 H), 3.92 (s, 3 H), 5.52 (s, 1 H), and 6.63—7.80 (m, 17 H); m/z 460 (M^+, 1) (Found: C, 74.1; H, 5.05. C$_{29}$H$_{24}$O$_2$S requires C, 74.33; H, 5.16%).

Conversion of 1-*Arylsulphonylindenes into Indenones.*—The indene, *e.g.* (**17**) (0.109 g, 267 mmol) was stirred with Na$_2$HPO$_4$ (96 mg) and Na-amalgam (5%; 260 mg) in methanol (10 ml) for 24 h. Water was added (150 ml) and then diethyl ether. The

ethereal extracts were washed with water, dried (Na$_2$SO$_4$), and the residue was chromatographed to give the indenone.

2,3-*Diphenylindenone* (**24**). This was obtained from (**17**) in 56% yield, m.p. 151—152 °C (lit.,[14] m.p. 155—156 °C).

2-p-*Tolyl*-3-*phenylindenone* (**25**). This was obtained from (**18**) in 88% yield, m.p. 177—179 °C (lit.,[20] m.p. 168—169 °C).

6-*Methoxy*-3-(p-*methoxyphenyl*)-2-*phenylindenone* (**26**). This was obtained from (**22**) in 69% yield, m.p. 157—158 °C (lit.,[21] m.p. 153—154 °C).

Thermal Decomposition of Ylides.—(a) The ylide (**3**) (0.5 g, 1 mmol) was refluxed in t-butyl alcohol (30 ml) under N$_2$ with Cu(acac)$_2$ (1 mg) for 5 h. Removal of solvent and column chromatography afforded phenyl iodide and phenyl benzenethiosulphonate (**28**) in 80% yield, m.p. 44—45 °C (lit.,[22] m.p. 40—41 °C).

(b) Under conditions similar to those described above the ylide (**27**) gave *p*-chlorophenyl *p*-chlorobenzenethiosulphonate (**29**) in 55% yield, m.p. 134—136 °C (lit.,[22] m.p. 134—136 °C). When the reaction was performed with exposure to air, no (**29**) was produced but p-*chlorophenylthio*-α,α-*bis*-p-*chlorophenylsulphonyltoluene* (**30**) was isolated in 47% yield, m.p. 205—207 °C (from chloroform–hexane); $\nu_{max.}$ 1 345 and 1 160 cm^{-1}; δ(CDCl$_3$) 5.10 (s, 1 H), 7.30 (s, 4 H), 7.60 (d, 4 H, J 8 Hz), and 8.03 (d, 4 H, J 8 Hz); m/z 328 (0.3), 269 (0.2) (Found: C, 44.4; H, 2.5. C$_{19}$H$_{13}$Cl$_3$O$_4$S$_3$ requires C, 44.94; H, 2.60%).

(c) Under conditions similar to those described in (a) the ylide (**18**) afforded *p*-tolyl toluene-*p*-thiosulphonate (**31**) in 55% yield, m.p. 75—76 °C (lit.,[22] m.p. 73—75 °C) and *cis*-1,2-(*p*-tolylsulphonyl)ethylene (**32**) in 22% yield, m.p. 145—148 °C (lit.,[23] m.p. 152—153 °C).

(d) Under conditions similar to those described in (a) the ylide (**20**) gave bis-*p*-tolyl α-disulphone (**33**) in 5% yield, m.p. 220—223 °C (lit.,[24] m.p. 221 °C).

In situ Formation of Phenyliodonium Phenylsulphonyl(phenylthio)methylide (**34**) *and Decomposition.*—A suspension of phenyl phenylthiomethyl sulphone (0.5 g) in MeOH (10 ml) at −10 °C was treated with a solution of KOH (0.4 g) in MeOH (10 ml). After the mixture had been stirred for 15 min PhI(OAc)$_2$ (0.61 g) in MeOH (10 ml) was added when the temperature gradually rose to ambient. Removal of MeOH and chromatography gave diphenyl disulphide (95 mg), m.p. 58—59 °C (lit.,[25] m.p. 59—61 °C).

Crystal Structure Analysis.—*Crystal data.* Compound (**9**) C$_{20}$H$_{20}$O$_2$S, $M = 324.4$, Monoclinic, $P2_1/n$, $a = 9.246(2)$, $b = 25.678(5)$, $c = 13.968(2)$ Å, $\beta = 95.65(1)°$, $U = 3\,300(1)$ Å^3, $Z = 8$, $D_c = 1.29$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 0.97 cm^{-1}, $T = 293$ K.

White block-shaped crystals were obtained from chloroform–hexane. Data were collected with a Syntex $P2_1$ four circle diffractometer; maximum 2θ was 50° with scan range $\pm 1.1°$ (2θ) around the $K_{\alpha_1} - K_{\alpha_2}$ angles, scan speed 2.5—29° min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. *hkl* Ranges were: 0,0, $-16 \longrightarrow 12$, 30, 16. Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection: the data were rescaled to correct for this. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($20 < 2\theta < 22$). Reflections were processed using profile analysis to give 5 547 unique reflections ($R_{int} = 0.0241$); 3 468 were considered observed [$I/\sigma(I) \geqslant 3.0$] and used in refinement; they were corrected for Lorentz, polarisation, and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0.97 and 0.98. Crystal dimensions were 0.34 × 0.32 × 0.28 mm. Systematic absences:

Table 5. Atom co-ordinates ($\times 10^4$)

Atom	x	y	z
S(1)	4 167.8(8)	2 382.1(3)	2 171.8(5)
S(2)	4 951.9(9)	163.2(3)	2 531.6(6)
O(11)	4 590.9(23)	2 913.0(8)	2 022.1(16)
O(12)	5 287.4(21)	2 013.8(9)	2 492.6(15)
O(21)	3 785.9(21)	515.8(9)	2 227.4(16)
O(22)	4 606.3(23)	−371.2(9)	2 701.4(16)
C(1)	3 055.2(33)	1 624.2(13)	943.8(23)
C(2)	2 324(4)	1 454(2)	80(3)
C(3)	1 816(4)	1 808(2)	−606(3)
C(4)	2 002(4)	2 329(2)	−448(2)
C(5)	2 712.8(33)	2 507.2(13)	400.9(22)
C(6)	3 236.2(29)	2 150.3(12)	1 094.6(20)
C(7)	2 845.4(31)	2 389.7(11)	3 041.2(20)
C(8)	2 396.4(32)	1 838.4(12)	3 337.5(21)
C(9)	2 450.2(36)	1 763.0(13)	4 439.5(22)
C(10)	2 216.6(38)	1 185.4(13)	4 623.4(27)
C(11)	605(4)	1 102(2)	4 261(3)
C(12)	96.0(37)	1 650.2(14)	3 943.8(26)
C(13)	995.5(37)	1 989.5(14)	4 661.6(24)
C(14)	751.0(32)	1 786.3(12)	3 003.9(23)
C(15)	312.6(32)	2 308.9(12)	2 607.7(21)
C(16)	1 460.3(32)	2 655.3(12)	2 649.5(20)
C(17)	1 258.6(40)	3 166.8(14)	2 356.6(23)
C(18)	−125(5)	3 329(2)	2 020(3)
C(19)	−1 270(5)	2 986(2)	1 987(3)
C(20)	−1 079(4)	2 482(2)	2 275(2)
C(21)	5 809.7(34)	936.0(13)	3 794.4(24)
C(22)	6 434.5(38)	1 122.3(14)	4 661.9(26)
C(23)	7 129(4)	791(2)	5 316(3)
C(24)	7 232(4)	274(2)	5 114(3)
C(25)	6 586.9(39)	79.6(13)	4 260.0(23)
C(26)	5 879.5(30)	411.8(12)	3 601.9(20)
C(27)	6 201.1(30)	173.4(11)	1 625.3(20)
C(28)	6 584.9(31)	727.6(12)	1 298.0(21)
C(29)	6 118.3(34)	834.5(13)	233.3(21)
C(30)	6 487.4(38)	1 400.9(14)	18.9(26)
C(31)	8 154(4)	1 395(2)	5(3)
C(32)	8 539(4)	832(2)	276(2)
C(33)	7 273(4)	539(2)	−254(2)
C(34)	8 268.3(32)	750.2(13)	1 346.3(23)
C(35)	8 778.9(32)	237.0(13)	1 764.4(21)
C(36)	7 634.0(34)	−90.1(13)	1 910.7(21)
C(37)	7 890.0(39)	−594.6(14)	2 252.1(24)
C(38)	9 309(4)	−756(2)	2 472(3)
C(39)	10 447(4)	−428(2)	2 341(3)
C(40)	10 199(4)	68(2)	1 975(3)

hko: $k \neq 2n$; *001*; $1 \neq 2n$ indicate space group $P2_1/n$. The structure was solved by direct methods using SHELXTL to reveal two independent molecules in the asymmetric unit. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.07$ Å^2, and were inserted at calculated positions and not refined; final refinement was on F by cascaded least-squares methods refining 415 parameters. Largest positive and negative

peaks on a final difference Fourier synthesis were of height 0.16 and 0.27 el. Å^{-3}.

A weighting scheme of the form $w = 1/[{}^2(F) + gF^2]$ with $g = 0.000\,95$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.038$, $R_w = 0.041$. Maximum shift/error in final cycle 1.028. Computing was with SHELXTL,[26] on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors were as in SHELXTL. Final atomic co-ordinates are given in Table 5. Hydrogen co-ordinates and thermal parameters are available on request from the Cambridge Crystallographic Data Centre.*

* For details see 'Instruction for Authors (1988),' *J. Chem. Soc., Perkin Trans. 1*, 1988, Issue 1.

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