Stable 2-Thianaphthalenes: Synthesis and Reactions with Electrophiles

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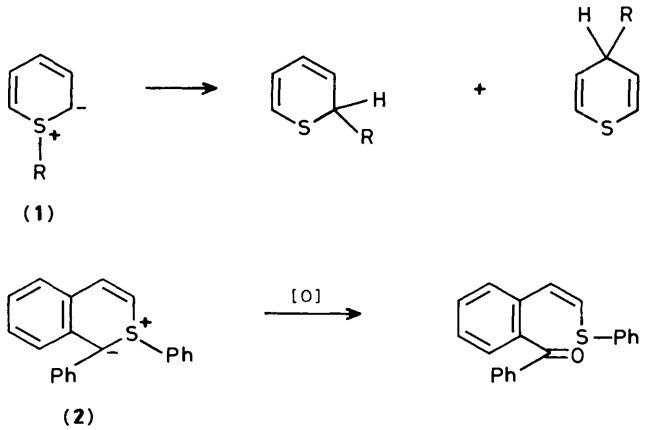
The stable and crystalline 2-thianaphthalene derivatives 2-methyl-2-thianaphthalene-1-carbonitrile (**8**) and 1-benzoyl-2-methyl-2-thianaphthalene (**9**) have been synthesized in high yields by proton abstraction from the corresponding benzothiopyrylium salts (**6**) and (**7**) with triethylamine in ethanol. The ylidic nature of the 2-thianaphthalenes was established on the basis of spectral and chemical evidence. The reaction of the 2-thianaphthalene (**8**) with dimethyl acetylenedicarboxylate (DMAD) in ethanol afforded the naphthalene derivative (**12**), while the same reaction using benzene as a solvent although giving no naphthalene derivative, afforded the dihydrocyclopropa[*a*]-naphthalene derivative (**15**) and the 5*H*-benzocycloheptene derivative (**16**). Moreover, the above reaction conducted in sulpholane solution gave, in addition to (**15**) and (**16**), a 2:1 adduct (**17**). The structure of the latter was confirmed by *X*-ray analysis. Treatment of compound (**8**) in benzene with methyl propiolate (MP) gave only a 2:1 adduct, (**20**). The reaction of the 2-thianaphthalene (**9**) with DMAD afforded only a dihydrocyclopropa[*a*]naphthalene derivative (**14**), whose structure was determined by *X*-ray crystallography. Parallel reactions with other electrophiles such as tetracyanoethylene, diphenylcyclopropenone, and diethyl azodicarboxylate gave a number of unexpected products for which reaction mechanisms are proposed.

We have been interested in the synthesis of cyclic sulphur ylides 'thiabenzenes' (**1**), in which the ylide bond forms part of a cyclic conjugated ring system containing six π-electrons. We and other groups have tried to synthesize such ylides from the corresponding cyclic sulphonium salts by deprotonation with base. However, the generated ylides having no stabilising substituents are too unstable to be isolated and, instead, 1,2- or 1,4-migration of substituents from sulphur to carbon occurs;[1-6] in the case of 1,2-diphenyl-2-thianaphthalene (**2**)[7] ring-opening occurred (see Scheme 1).

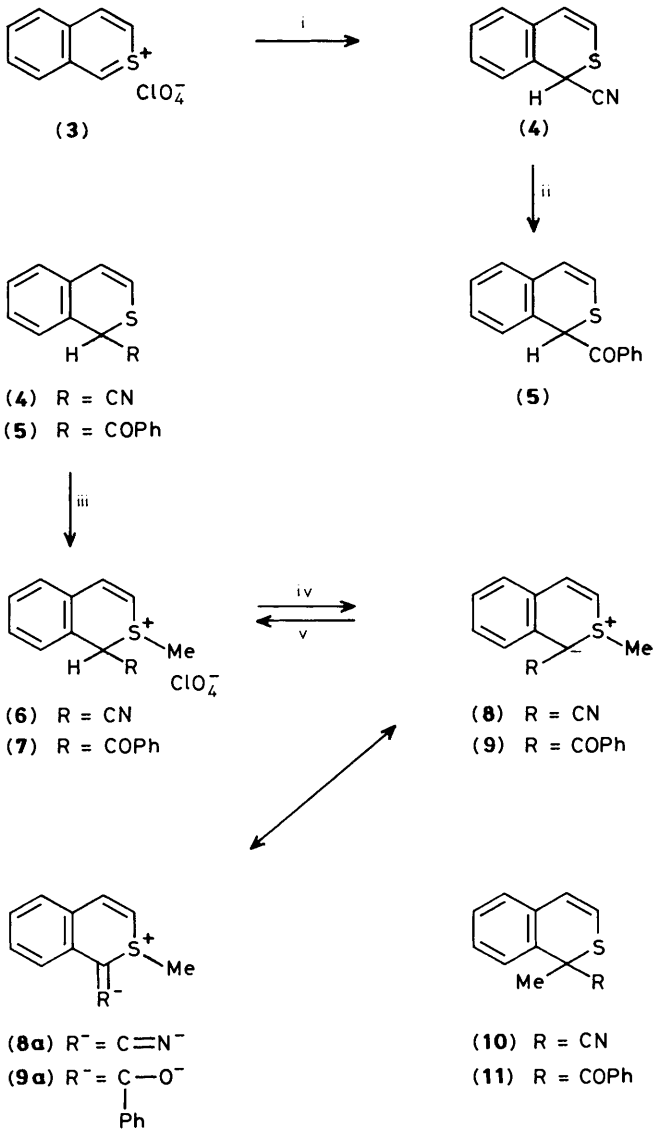


Scheme 1.

In a preliminary report we described the first isolation of the stable 2-thianaphthalenes (**8**) and (**9**) which have strongly electron-withdrawing substituents as a stabilising group at the 1-position.[8] Here we report the full details of this work together with the unexpected reactions of 2-thianaphthalenes with several electrophiles.

Results and Discussion

Synthesis of 2-Methyl-2-thianaphthalene-1-carbonitrile (**8**) *and 1-Benzoyl-2-methyl-2-thianaphthalene* (**9**).—Thianaphthalenes (**8**) and (**9**) were prepared in excellent yield by a route summarised in Scheme 2. 2-Thianaphthylium perchlorate (**3**), synthesized by the literature method,[9] was treated with potassium cyanide to give 1*H*-2-benzothiopyran-1-carbonitrile (**4**); this was allowed to react with phenylmagnesium bromide and the resulting product hydrolysed to afford 1-benzoyl-1*H*-2-benzothiopyran (**5**). The thiopyrans (**4**) and (**5**) were treated with methyl iodide in the presence of silver perchlorate to give 2-methyl-1*H*-2-benzothiopyrylium perchlorates (**6**) and (**7**) in moderate yields as a mixture of diastereoisomers [ratio of *cis* and *trans* 4:5 for (**6**), 1:2 for (**7**) in CF_3CO_2H by ^1H n.m.r.]. The methyl signal of the *cis* isomer of (**6**) appeared at lower field (δ 3.21) than that of the *trans* isomer (δ 3.13) due to anisotropy of the cyano group oriented in a *cis* configuration. The 1-H signal of the *trans* isomer of (**6**) appeared as a doublet (*J* 1.5 Hz), the multiplicity presumably arising from long-range through-space coupling to 3-H which lies almost in the same plane. In contrast, the 1-H signal of the *cis* isomer appeared as a singlet, indicating no through-space coupling to 3-H, probably because of deviation from the plane caused by steric hindrance between the *cis* substituents. The same arguments apply to the diastereoisomerism of (**7**). Interconversion between the two stereoisomers, observed during measurement of the ^1H n.m.r. spectra in CF_3CO_2H, is explained in terms of pyramidal inversion at the sulphur atom. Mislow *et al.* observed similar diastereoisomerism in the 2-methyl-1-pentafluorophenyl-1*H*-2-benzoselenothiopyrylium salt.[10] Deprotonation of compounds (**6**) and (**7**) with triethylamine in ethanol yielded 2-methyl-2-thianaphthalene-1-carbonitrile (**8**) and 1-benzoyl-2-methyl-2-thianaphthalene (**9**), respectively, as orange needles. These thianaphthalenes are stable at room temperature. When heated in benzene for 1 h, however, thianaphthalene (**8**) underwent a Stevens rearrangement to afford the corresponding benzothiopyran

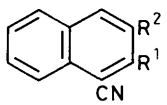


Scheme 2. *Reagents:* i, $KCN–H_2O–CH_2Cl_2$; ii, PhMgBr–ether; iii, $MeI–AgClO_4–ClCH_2CH_2Cl$; iv, Et_3N–EtOH; v, 70% $HClO_4$

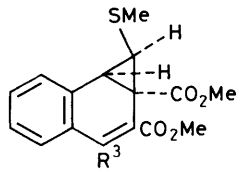
(**10**) in 86% yield. An e.s.r. signal for the above 1,2-rearrangement was observed which suggests that it proceeds *via* a radical intermediate as for the 1,2-rearrangement of benzylmethylsulphonium phenacylide.[11] The thianaphthalene (**9**), which is more stable than (**8**), gave a lower yield of the 1,2-rearranged product (**11**), even after a period of 46 h in refluxing benzene,[12] (45%) along with the demethylated compound (**5**) (12%) and recovered (**9**) (19%). The ^1H n.m.r. spectra of thianaphthalenes showed doublet signals for 3-H in the range expected for an olefinic proton [δ 5.83 (*J* 10 Hz) for (**8**); δ 6.05 (*J* 9.5 Hz) for (**9**)] and singlet signals for S–Me groups [δ 2.09 for (**8**) and 2.20 for (**9**)]; these were similar to those of vinylsulphonium ions such as (**6**) and (**7**). The i.r. spectra of these compounds showed strong CN absorption at 2 142 cm^{-1} (**8**) and also a strong band at 1 510 cm^{-1} due to the carbonyl stretching frequency of (**9**). This evidence indicates the delocalisation of the carbanion electron of (**8**) and (**9**) through the cyano and carbonyl groups, respectively, and suggests that the resonance forms (**8a**) and (**9a**) are important contributors to electronic distribution in (**8**) and (**9**). The 2-thianaphthalenes (**8**) and (**9**) were acidified with perchloric acid to give the corresponding 1*H*-2-benzothiopyrylium salts (**6**) and (**7**), respectively. Although the above spectral and chemical observations support the ylidic nature of the 2-thianaphthalenes, final confirmation was obtained by an *X*-ray crystal structure determination of the 1-benzoyl derivative (**9**), the details of which have already been published.[13]

Reactions of the 2-*Thianaphthalenes* (**8**) *and* (**9**) *with Electrophiles.*—Because of their ylidic nature the 2-thianaphthalenes were expected to give rise to interesting reactions and this proved to be so, since with electrophiles a variety of unexpected addition reactions occurred.

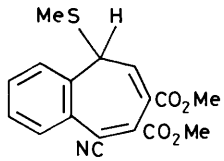
With acetylenic electrophiles. We first studied the reactions with activated acetylenic electrophiles such as dimethyl acetylenedicarboxylate (DMAD) and methyl propiolate (MP). A solution of compound (**8**) and DMAD in ethanol was stirred at room temperature to give a low yield (19%) of the non-sulphur containing naphthalene derivative (**12**) as the only product identified after preparative t.l.c. Similarly, desulphurisation occurred on reaction of compound (**8**) with MP to give (**13**) (27%), the structure of which was confirmed by comparison of its spectral data with those of an authentic sample prepared by a reported method.[14] Reaction of compound (**9**) with DMAD or MP under similar conditions to those described above was unsuccessful, only a complex product mixture being obtained. We next investigated the above reactions in other solvents (aprotic) and observed remarkable solvent effects for the



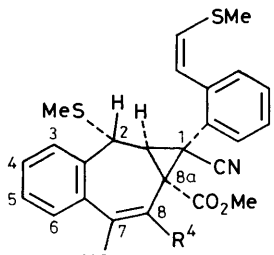
(**12**) $R^1 = R^2 = CO_2Me$
(**13**) $R^1 = H$, $R^2 = CO_2Me$



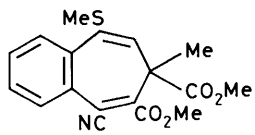
(**14**) $R^3 = COPh$
(**15**) $R^3 = CN$



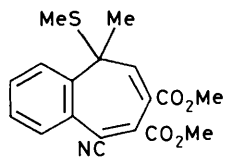
(**16**)



(**17**) $R^4 = CO_2Me$
(**20**) $R^4 = H$



(**18**)



(**19**)

reaction course. Treatment of compound (**9**) in benzene with DMAD at 60—70 °C afforded the dihydrocyclopropa[*a*]-naphthalene derivative (**14**) (63%) as a 1:1 adduct of (**9**) and DMAD. Using sulpholane as a solvent gave the same result to yield (**14**), but in lower yield (42%). The structure of (**14**) was

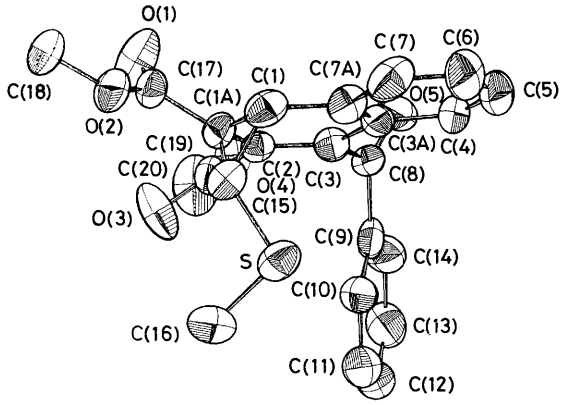


Figure 1. *X*-Ray structure of 1a,7b-dihydrocyclopropa[*a*]naphthalene derivative (**14**)

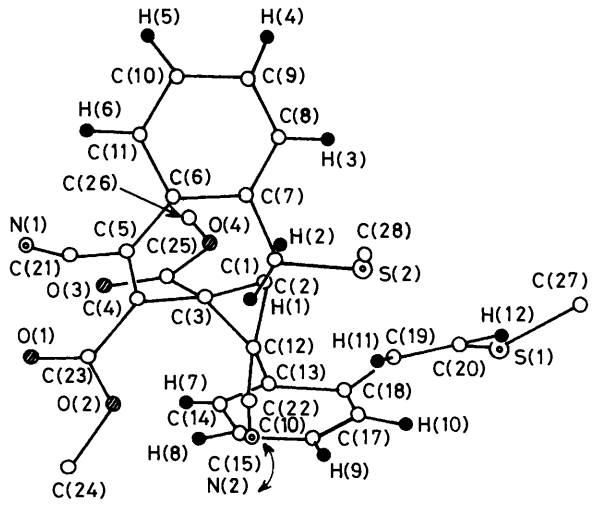


Figure 2. *X*-Ray structure of 1,1a,2,8a-tetrahydrobenzo[*a*]dihydrocyclopropa[*d*]cycloheptene derivative (**17**)

elucidated on the basis of spectral data (see Experimental section) and finally confirmed by an *X*-ray structure determination (see Figure 1). Next we examined the reaction of compound (**8**) with DMAD in benzene and obtained the dihydrocyclopropa[*a*]naphthalene derivative (**15**) (75%) and the 5*H*-benzocycloheptene derivative (**16**) (7.5%). The structure of (**15**) was elucidated by comparison of its spectral data with those of the analogous compound (**14**). The ^{1}H n.m.r. spectrum of (**16**) showed a broad singlet at δ 4.05 attributable to the methine proton of the seven-membered ring; the broadness of the methine proton arises as a result of coupling with an adjacent olefinic proton. This assumption was supported by the fact that the ^{1}H n.m.r. spectrum of the sulphone derivative of (**16**), prepared by oxidation with *m*-chloroperbenzoic acid, showed an apparent doublet signal (*J* 9.8 Hz) at δ 5.78 coupling with an olefinic proton appearing at δ 7.28. The ^{13}C n.m.r. spectrum of (**16**) showed a doublet signal for the methine carbon at δ 47.9. In order to gain more information about the structure of compound (**16**) it was treated with methyl iodide after deprotonation with sodium hydride in dimethyl sulphoxide to give two isomeric methylated compounds (**18**) (29%) and (**19**) (24%), the structures of which were determined mainly on the basis of their ^{1}H n.m.r. spectra. Thus the olefinic proton of (**19**) showed a large δ value (6.93) compared with that of (**18**) (δ 5.79); this indicated more deshielding of the olefinic proton of (**19**) by the adjacent ester carbonyl group situated in the same plane. On the other hand, the reaction of compound (**8**) with DMAD using sulpholane as an aprotic and polar solvent was performed and, interestingly, a 2:1 adduct (**17**) of (**8**) and DMAD appeared as a new product (14%) in addition to (**15**) (54%) and (**16**) (17%). The structure of this adduct (**17**) was determined by *X*-ray crystallography (see Figure 2).

In order to clarify the mechanism of formation for (**17**), its preparation from compound (**16**) and the ylide (**8**) in sulpholane (75%) was carried out; compound (**15**) failed to so react with (**8**). Interestingly, the reaction of compound (**8**) with 2 equiv. of DMAD no longer gave compound (**17**), compounds (**15**) (14%) and (**16**) (29%) being obtained instead. These results suggest that compound (**16**) is a precursor of (**17**).

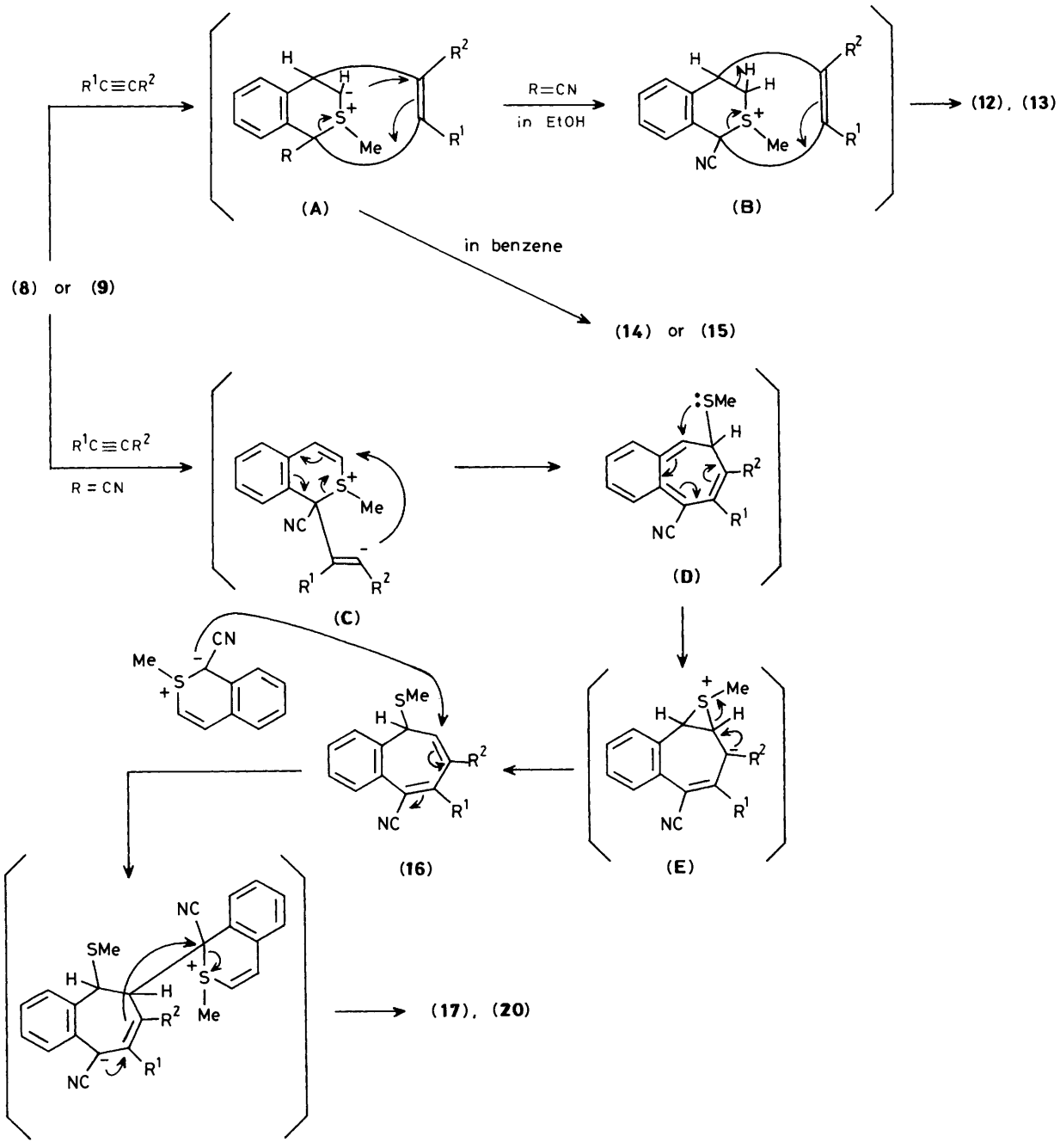
The reaction of compound (**8**) and MP in benzene or sulpholane, interestingly, gave, in high yields, only the 2:1 adduct (**20**) the structure of which was determined by a comparison of its spectral data with those of (**17**) which has a similar structure.

Plausible mechanisms for the reactions described above are presented in Scheme 3. 1,4-Addition of acetylenic compounds to the 2-thianaphthalenes (**8**) and (**9**) leads to the intermediate (**A**), the carbanion site of which is protonated with protic solvent to form the intermediate (**B**). The latter decomposes to give (**12**) and (**13**) presumably with the loss of methylthiomethylene moiety. In aprotic solvents, intramolecular Michael-type addition of the anion site of intermediate (**A**) to the double bond gives the product (**14**) or (**15**). On the other hand, a further possible intermediate (**C**), which is formed by Michael-type addition of the ylide (**8**) or (**9**) to acetylenic electrophiles, undergoes intramolecular cyclisation by attack of the anion site on C-3 to give the intermediate (**D**). The intermediate (**D**) undergoes a unique migration of the methylthio group *via* the episulphonium ion intermediate (**E**) to afford product (**16**). The driving force for the methylthio migration is assumed to be aromatisation of the six-membered ring of the intermediate (**D**). Furthermore, in a polar solvent, compound (**16**) is attacked easily by unchanged ylide to give a 2:1 adduct, (**17**) or (**20**), *via* a Michael-type addition.

Reactions of the 2-Thianaphthalenes (**8**) *and* (**9**) *with Olefinic Electrophiles.*—Treatment of compound (**8**) with tetracyanoethylene as an olefinic electrophile in tetrahydrofuran at room temperature gave the 1:1 adduct, the ring-opened cyclopropane derivative (**21**) (56%), the structure of which was determined mainly by ^{1}H and ^{13}C n.m.r. spectroscopy (see Experimental section). The formation of (**21**) can be interpreted as occurring *via* the 1,4-cycloaddition intermediate (**F**) as shown in Scheme 4. Next, the reaction of (**8**) with diphenylcyclopropenone in ethanol afforded a ring-opened ethyl ester (**22**) (81%) *via* the intermediates (**G**) and (**H**), the latter intermediate being attacked by ethanol: the geometry of the stilbene structure is uncertain at present. In contrast, the above reaction when performed in an aprotic solvent such as benzene or sulpholane gave, in moderate yield, the dihydro-5*H*-benzocycloheptene derivative (**23**) the structure of which was elucidated on the basis (i) that its i.r. spectrum showed absorption characteristic of a conjugated carbonyl group at 1 675 cm^{-1}; (ii) ^{13}C n.m.r. signals assignable to a conjugated carbonyl carbon appeared at δ 192, in addition to the two methine carbons (δ 63.8 and 70.2) and a quaternary carbon (δ 59.6); and (iii) from its molecular composition. The mechanism of formation for compound (**23**) is reasonably explained by postulating a 1,4-cycloaddition intermediate (**I**), which undergoes 1,2-rearrangement (Scheme 4).

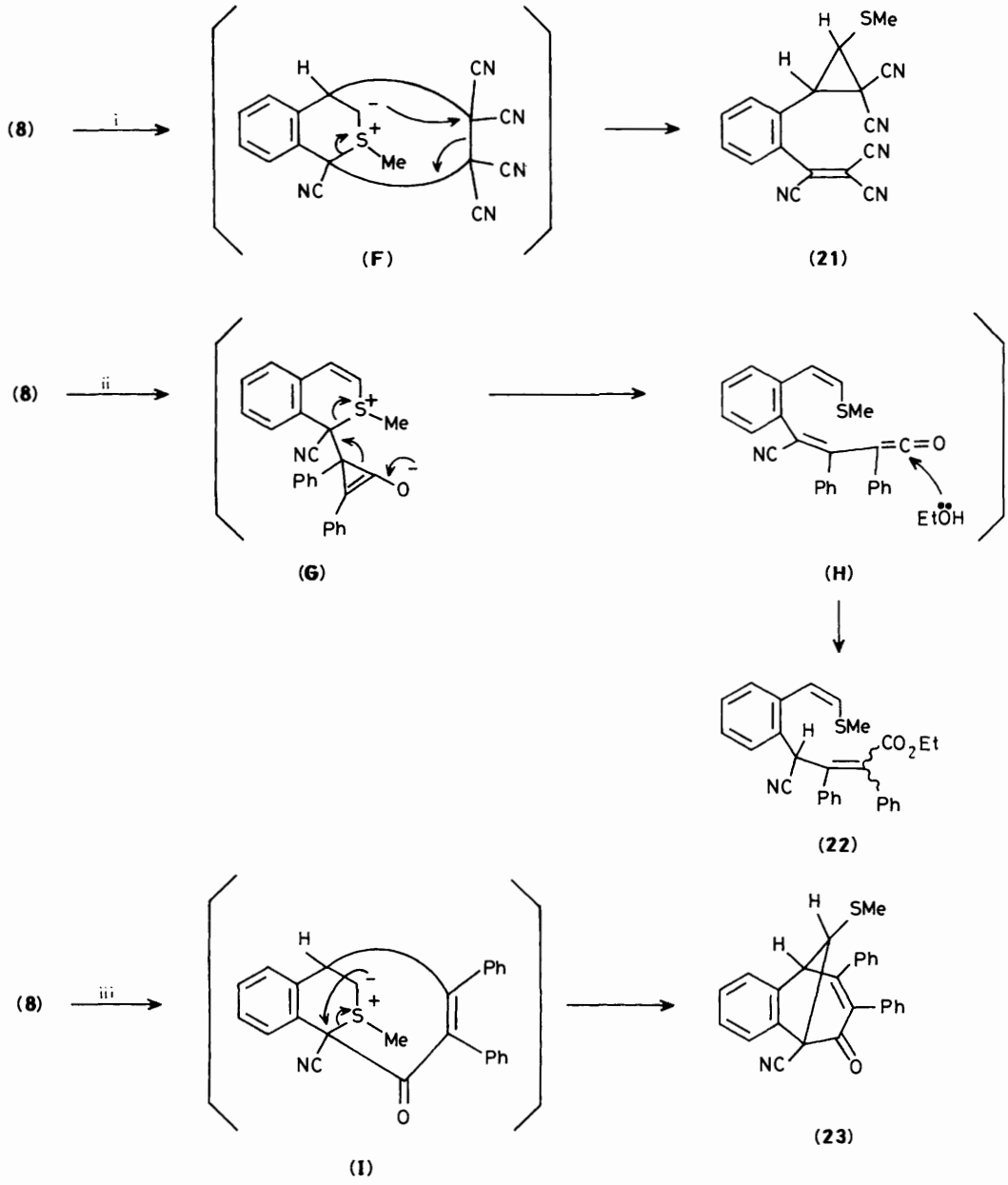
Finally, treatment of compound (**8**) with diethyl azodicarboxylate (DAD) in sulpholane gave two products, a 1:1 adduct (**24**) (58%) and compound (**25**) (7%) (see Scheme 5).

The structure of compound (**24**) was elucidated on the basis



Scheme 3.

of spectral results which showed i.r. absorption at 3 280 (NH), 2 240 (CN), and 1 745 and 1 695 cm^{-1} (ester); ^1H n.m.r. signals at δ 5.62 (NH, D_2O exchangeable) and 6.39 (olefinic H); ^{13}C n.m.r. signals at δ 67.2 (s, aliphatic quaternary carbon); and a mass spectral peak at *m/z* 361 (M^+). The structure of compound (**25**) was similarly elucidated: thus in its i.r. spectrum there was absorption for two ester groups at 1 807 cm^{-1}, but no NH and cyano absorption. The ester group's absorption at rather high wavenumber was similar to that observed in hydrazone diesters.[15] In addition, the ^1H n.m.r. spectrum showed a singlet at δ 7.52 attributable to an olefinic proton and a single pair of ethoxy group signals at δ 1.11 and 4.19; this suggested that the two ester groups are magnetically equivalent. From these results, evidence for the molecular composition based on the elemental analysis, and the mass spectrum which showed a molecular ion peak at *m/z* 334, the structure of (**25**) was deduced as one corresponding to that formed by subtraction of hydrogen cyanide from compound (**24**). When heated in refluxing toluene, compound (**24**) gave compound (**25**) in 92% yield by smooth loss of hydrogen cyanide; this indicated that compound (**24**) may be a precursor of the compound (**25**). Thus, formation of compounds (**24**) and (**25**) may be viewed as occurring *via* the 1,4-addition intermediate (**J**) which undergoes a 1,2-rearrangement to give the intermediate (**K**) (see Scheme 5). The reaction of thianaphthalene (**7**) with DAD under similar conditions to those described above gave no identifiable products.



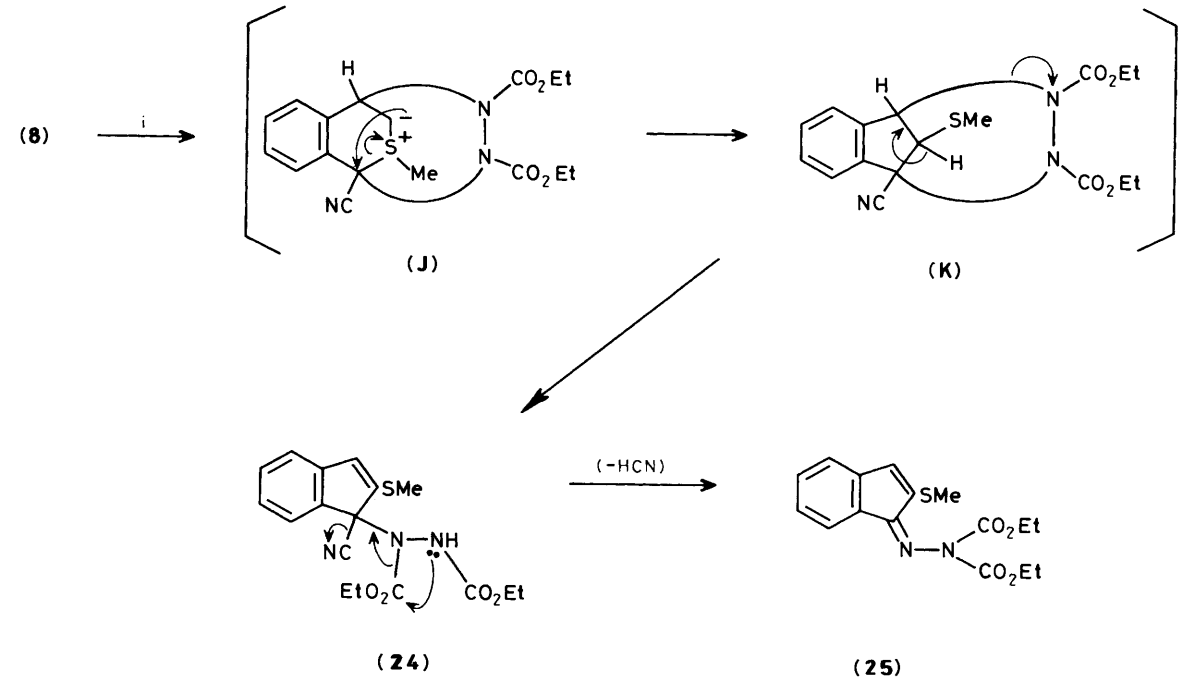
Scheme 4. *Reagents:* i, TCNE–THF; ii, diphenylcyclopropenone–EtOH; iii, diphenylcyclopropenone–benzene or sulpholane

Experimental

All m.p.s were measured on a Yanagimoto micro-melting point apparatus and are uncorrected. I.r. spectra were measured with a JASCO A-1 spectrophotometer. ^{1}H N.m.r. spectra were taken on Hitachi R-20B (60 MHz) or JEOL GX-270 (270 MHz) spectrometers with tetramethylsilane as an internal standard. ^{13}C N.m.r. spectra were obtained using a JEOL GX-270 spectrometer. Mass spectra were obtained by using a JEOL-D 300 spectrometer with a direct insertion probe at 70 eV. U.v. spectra were recorded on a Hitachi Model 200-100 spectrophotometer. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University.

1H-2-*Benzothiopyran*-1-*carbonitrile* (**4**).—Powdered 2-thianaphthylium perchlorate[9] (**3**) (10 g) was added in small portions to a stirred mixture of sodium cyanide (2.6 g), water (10 ml), and dichloromethane (200 ml) and the mixture was stirred for 6 h at room temperature. The dichloromethane layer was separated, washed with water several times, dried ($MgSO_4$), and evaporated under reduced pressure to give the *title compound* (6.5 g, 92.6%). Recrystallisation from propan-2-ol gave colourless needles, m.p. 84—85 °C; $\nu_{max.}$ 2 232 cm^{-1} (CN); $\delta_H(CDCl_3)$ 4.40 (1 H, d, *J* 1.5 Hz, 1-H), 6.48 (1 H, dd, *J* 10 and 1.5 Hz, 3-H), 6.96 (1 H, d, *J* 10 Hz, 4-H), and 7.05—7.55 (4 H, m, ArH) (Found: C, 69.2; H, 4.2; N, 8.1. $C_{10}H_7NS$ requires C, 69.4; H, 4.1; N, 8.1%).

1-*Benzoyl*-1H-2-*benzothiopyran* (**5**).—A solution of compound (**4**) (1.63 g) in dry ether (40 ml) was added dropwise to a stirred ethereal solution of phenylmagnesium bromide prepared



Scheme 5. *Reagents:* i, diethyl azodicarboxylate–sulpholane

from magnesium (0.27 g) bromobenzene (1.77 g) in dry ether (45 ml) and the mixture was stirred for 6 h at room temperature. A 10% HCl solution was added to the reaction mixture and refluxed for 3 h. The ether layer was separated and the water layer was extracted with benzene. The combined ether layer and extracts were washed with water, dried ($MgSO_4$), and evaporated. The residual solids were recrystallised from ethanol to give the *title compound* (1.1 g, 46%) as yellow needles, m.p. 145—146 °C; $\nu_{max.}$ 1 650 cm^{-1} (CO); $\delta_H(CDCl_3)$ 5.40 (1 H, d, *J* 1.5 Hz, 1-H), 6.18 (1 H, dd, *J* 10 and 1.5 Hz, 3-H), 6.81 (1 H, d, *J* 10 Hz, 4-H), 7.00—7.70 (7 H, m, ArH), and 7.95—8.15 (2 H, m, ArH) (Found: C, 76.1; H, 4.8. $C_{16}H_{12}OS$ requires C, 76.2; H, 4.8%).

1-*Cyano*-2-*methyl*-1H-2-*benzothiopyrylium Perchlorate* (**6**).—Silver perchlorate (0.97 g) was added portionwise with ice-cooling to a stirred solution of compound (**4**) (0.81 g) and methyl iodide (6.64 g) in 1,2-dichloroethane (30 ml) and the mixture was stirred for 17 h at room temperature. The precipitated material was filtered off and extracted thoroughly with hot acetone. The acetone extracts were diluted with ether to afford a white precipitate which after recrystallisation from acetone gave the *title compound* (0.9 g, 67.2%) as colourless needles which were an inseparable mixture of *cis* and *trans* stereoisomers, m.p. 178 °C (decomp.); $\nu_{max.}$ 2 216 (CN) and 1 100 cm^{-1} (ClO_4^-); $\delta_H(CF_3CO_2H)$ of *trans* isomer 3.13 (s, Me), 6.16 (d, *J* 1.5 Hz, 1-H), 6.76 (dd, *J* 10 and 1.5 Hz, 3-H), and 7.60—8.15 (m, 4-H and ArH); $\delta_H(CF_3CO_2H)$ of *cis* isomer 3.21 (s, Me), 6.39 (s, 1-H), 6.71 (d, *J* 10 Hz, 3-H). The ratio of the two isomers was determined as 5:4 based on the integration of S–Me (Found: C, 46.05; H, 3.7; N, 4.8. $C_{11}H_{10}ClNO_4S$ requires C, 45.9; H, 3.5; N, 4.9%).

1-*Benzoyl*-2-*methyl*-1H-2-*benzothiopyrylium Perchlorate* (**7**).—Silver perchlorate (498 mg) was added to a solution of compound (**5**) (606 mg) and methyl iodide (3.4 g) in 1,2-dichloroethane (20 ml) and the mixture was stirred overnight. Work-up as for compound (**6**) afforded the *title compound* (720 mg, 82%) as colourless prisms after recrystallisation from dichloromethane–ether, m.p. 158 °C; $\nu_{max.}$ 1 675 (CO) and 1 090 cm^{-1} (ClO_4^-); compound (**7**) was a mixture of inseparable configurational isomers; $\delta_H(CF_3CO_2H)$ of *trans* isomer 3.06 (s, Me), 6.64 (dd, *J* 9.5 and 1.5 Hz, 3-H), 6.80 (d, *J* 1.5 Hz, 1-H), and 7.40—8.20 (m, 4-H and ArH); $\delta_H(CF_3CO_2H)$ of *cis* isomer 2.96 (s, Me), 6.99 (d, *J* 9.5 Hz, 3-H), and 6.75 (s, 1-H) (Found: C, 55.5; H, 4.2. $C_{17}H_{15}ClO_5S$ requires C, 55.7; H, 4.1%).

2-*Methyl*-2-*thianaphthalene*-1-*carbonitrile* (**8**).—Triethylamine (620 mg) was added to a stirred suspension of compound (**6**) (900 mg) in ethanol (25 ml) with ice-cooling, and the mixture was stirred for 2 h. The reaction mixture was poured into water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and concentrated to dryness under reduced pressure. The residue was recrystallised from ether to afford the *title compound* (543 mg, 93%) as orange needles, m.p. 73—75 °C (decomp.); $\nu_{max.}$ 2 142 cm^{-1} (CN); $\delta_H(CDCl_3)$ 2.09 (3 H, s, Me), 5.79 (1 H, d, *J* 10 Hz, 3-H), 6.78—7.15 (1 H, m, ArH), and 7.18—7.60 (4 H, m, 4-H, and ArH); $\lambda_{max.}$(EtOH) 217 (log ε 3.08), 262 (3.47), and 382 nm (2.51) (Found: C, 70.8; H, 4.85; N, 7.4. $C_{11}H_9NS$ requires C, 70.55; H, 4.8; N, 7.5%).

1-*Benzoyl*-2-*methyl*-2-*thianaphthalene* (**9**).—Compound (**7**) (564 mg) was added portionwise to an ice-cooled, stirred mixture of triethylamine (312 mg) and ethanol (20 ml), and the mixture was stirred for 6 h at room temperature. Work-up as for compound (**8**) gave a crude solid, which was recrystallised from dichloromethane–ether to afford the *title compound* (400 mg, 93%) as orange needles, m.p. 185 °C (decomp.); $\nu_{max.}$ 1 510 cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.20 (3 H, s, Me), 6.05 (1 H, d, *J* 9.5 Hz, 3-H), and 6.70—7.70 (10 H, m, ArH and 4-H); $\lambda_{max.}$(EtOH) 234 (log ε 4.25), 266 (4.24), 301 (3.83), and 405 nm (3.79) (Found: C, 76.8; H, 5.3. $C_{17}H_{14}OS$ requires C, 76.6; H, 5.3%).

Thermal Rearrangement of 2-*Methyl*-2-*thianaphthalene*-1-*carbonitrile* (**8**).—A solution of compound (**8**) (100 mg) in benzene (5 ml) was refluxed for 1 h. The reaction mixture was concentrated to dryness and the residual oil was distilled to give 1-*methyl*-1H-2-*benzothiopyran*-1-*carbonitrile* (**10**) (94 mg, 94%) as a colourless oil, b.p. 130 °C (1 mmHg); $\nu_{max.}$ 2 240 cm^{-1} (CN);

$\delta_H(CDCl_3)$ 2.02 (3 H, s, Me), 6.44 (1 H, d, *J* 9.5 Hz, 3-H), 6.92 (1 H, d, *J* 9.5 Hz, 4-H), and 7.10—7.75 (4 H, m, ArH) (Found: C, 70.4; H, 4.8; N, 7.3. $C_{11}H_{19}NS$ requires C, 70.55; H, 4.8; N, 7.5%).

Reaction of the 2-Thianaphthalene (**8**) *with DMAD.*—(a) *In ethanol.* A solution of DMAD (212 mg) in ethanol (5 ml) was added to a stirred solution of compound (**8**) (300 mg) in absolute ethanol (20 ml), and the mixture was stirred for 5 days. The reaction mixture was concentrated to dryness under reduced pressure and the residual oil was submitted to preparative t.l.c. on silica gel using hexane–ethyl acetate (2:1) as solvent to give *dimethyl 1-cyanonaphthalene-2,3-dicarboxylate* (**12**) (81 mg, 18.8%), which recrystallised from ethanol as colourless needles, m.p. 133—134 °C; $\nu_{max.}$ 2 215 (CN) and 1 720 cm^{-1} (ester); $\delta_H(CDCl_3)$ 4.00 (3 H, s, OMe), 4.10 (3 H, s, OMe), 7.70—8.50 (4 H, m, ArH), and 8.76 (1 H, s, ArH); *m/z* 269 (M^+) (Found: C, 66.6; H, 4.1; N, 5.05. $C_{15}H_{11}NO_4$ requires C, 66.9; H, 4.1; N, 5.2%).

(b) *In benzene.* A mixture of compound (**8**) (1 g), DMAD (764 mg), and dry benzene (20 ml) was stirred for 2 days at room temperature after which it was concentrated to dryness under reduced pressure. The residue was separated with preparative t.l.c. on silica gel using hexane–ethyl acetate (2:1) as solvent into two fractions. The first fraction gave *dimethyl 3-cyano-1-methylthio-*1a,7b-*dihydrocyclopropa*[a]*naphthalene-*1a,2-*dicarboxylate* (**15**) (1.3 g, 75%) which recrystallised from hexane–dichloromethane as colourless columns, m.p. 93—95 °C; $\nu_{max.}$ 2 225 (CN), 1 735, and 1 725 cm^{-1} (ester); $\delta_H(CDCl_3)$ 2.06 (3 H, s, SMe), 3.29 (1 H, d, *J* 10 Hz, cyclopropane H), 3.65 (1 H, d, *J* 10 Hz, cyclopropane H), 3.73 (3 H, s, OMe), 3.93 (3 H, s, OMe), 7.32—7.51 (3 H, m, ArH), and 7.65—7.98 (1 H, m, ArH); $\delta_C(CDCl_3)$ 15.21 (q), 24.72 (d), 35.05 (s), 36.05 (d), 52.84 (q), 52.96 (q), 114.57 (s), 117.01 (s), 127.11 (s), 127.67 (d), 128.40 (d), 129.05 (d), 129.19 (d), 131.04 (d), 134.86 (s), 164.79 (s), and 169.23 (s); *m/z* 329 (M^+) (Found: C, 62.1; H, 4.6; N, 4.1. $C_{17}H_{15}NO_4S$ requires C, 62.0; H, 4.6; N, 4.25%). The second fraction afforded *dimethyl 9-cyano-5-methylthio-*5H-*benzocycloheptene-*7,8-*dicarboxylate* (**16**) (132 mg, 7.5%) as colourless needles after recrystallisation from hexane–ethanol, m.p. 151 °C; $\nu_{max.}$ 2 214 (CN), 1 740, and 1 720 cm^{-1} (ester); $\delta_H(CDCl_3)$ 2.09 (3 H, s, SMe), 3.76 (3 H, s, OMe), 3.98 (3 H, s, OMe), 4.05 (1 H, br s, CH), and 7.29—8.12 (5 H, m, ArH and olefinic H); $\delta_C(CDCl_3)$ 15.32 (q), 47.85 (d), 52.63 (q), 53.16 (q), 116.68 (s), 146.03 (s), and 165.03 (s); *m/z* 329 (M^+) (Found: C, 62.1; H, 4.6; N, 4.1. $C_{17}H_{15}NO_4S$ requires C, 62.0; H, 4.6; N, 4.25%).

(c) *In sulpholane.* A mixture of compound (**8**) (2.6 g) and DMAD (2.01 g) in sulpholane (30 ml) was stirred for 24 h to give a red-brown reaction mixture which was poured into water and extracted with ether. The ether layer was washed with water, dried ($MgSO_4$), and evaporated to provide an oil. This was subjected to preparative t.l.c. on silica gel using benzene–ethyl acetate (4:1) as solvent to afford three products: compounds (**15**) (610 mg, 53.7%) and (**16**) (778 mg, 16.8%), and *dimethyl* 1,7-*dicyano-*1-[o-(2-*methylthiovinyl*)*phenyl*]-2-*methylthio-*1,1a,2,-8a-*tetrahydrobenzo*[a]*cyclopropa*[d]*cycloheptene-*8,8a-*dicarboxylate* (**17**) (1.02 g, 14%) as pale yellow needles after recrystallisation from benzene–hexane, m.p. 198—199 °C; $\nu_{max.}$ 2 240 (CN), 1 738, and 1 723 cm^{-1} (ester); $\delta_H(CDCl_3)$ 2.20 (3 H, s, SMe), 2.39 (3 H, s, SMe), 3.01 (1 H, d, *J* 12 Hz, cyclopropane H), 3.30 (3 H, s, OMe), 4.11 (3 H, s, OMe), 4.14 (1 H, d, *J* 12 Hz, cyclopropane H), 6.79 (2 H, ABq, *J* 11 Hz, olefinic H), and 7.16—8.15 (8 H, m, ArH); $\delta_C(CDCl_3)$ 16.37 (q), 18.24 (q), 28.70 (s), 40.30 (s), 46.02 (d), 48.32 (d), 53.23 (q), 53.27 (q), 116.25 (s), 116.77 (s), 122.86 (d), 125.60 (s), 126.79 (d), 127.28 (d), 127.93 (s), 128.78 (d), 129.08 (d), 129.30 (d), 130.22 (s), 131.07 (d), 131.48 (d), 132.20 (d), 137.32 (d), 137.43 (d), 138.80 (s), 163.65 (s), and 165.80 (s); *m/z* 516 (M^+) (Found: C, 64.9; H, 4.7; N, 5.4. $C_{28}H_{24}N_2O_4S_2$ requires C, 65.1; H, 4.7; N, 5.4%).

Oxidation of Compound (**16**).—*m*-Chloroperbenzoic acid (260 mg) was added to a solution of compound (**16**) (212 mg) in dichloromethane (20 ml), and the mixture was stirred for 11 h at room temperature. After addition of saturated aqueous $NaHCO_3$, the organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated to give *dimethyl 9-cyano-5-methylsulphonyl-*5H-*benzocycloheptene-*7,8-*dicarboxylate* (194 mg, 87.3%) which recrystallised from hexane–dichloromethane as colourless prisms, m.p. 225—226 °C; $\nu_{max.}$ 2 225 (CN), 1 720 (ester), 1 290, and 1 140 cm^{-1} (SO_2); $\delta_H[(CD_3)_2SO]$ 3.38 (3 H, s, SO_2Me), 3.71 (3 H, s, OMe), 3.83 (3 H, s, OMe), 5.78 (1 H, d, *J* 9.8 Hz, CH), 7.28 (1 H, d, *J* 9.8 Hz, olefinic H), and 7.40—8.03 (4 H, m, ArH); *m/z* 361 (M^+) (Found: C, 56.2; H, 4.2; N, 3.8. $C_{17}H_{15}NO_6S$ requires C, 56.5; H, 4.2; N, 3.9%).

Methylation of Compound (**16**).—Sodium hydride (50% dispersion in mineral oil; 20 mg) was added to a stirred solution of compound (**16**) (150 mg) in dry DMSO (3 ml) under an N_2 atmosphere, and the mixture was stirred for 25 h at room temperature. Methyl iodide (65 mg) was added to this purple solution by syringe and the mixture stirred for 2.5 h. The pale brown reaction mixture was poured into water and extracted with dichloromethane. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated to give a brown oil which was subjected to preparative t.l.c. on silica gel using hexane–ethyl acetate (2:1); two fractions were obtained. The first fraction afforded *dimethyl 5-cyano-7-methyl-9-methylthio-*7H-*benzocycloheptene-*6,7-*dicarboxylate* (**18**) (39 mg, 24.4%) which recrystallised from hexane–ether as colourless prisms, m.p. 112—113 °C; $\nu_{max.}$ 2 218 (CN), 1 735, and 1 723 cm^{-1} (ester); *m/z* 343 (M^+); $\delta_H(CDCl_3)$ 1.53 (3 H, s, Me), 2.24 (3 H, s, SMe), 3.23 (3 H, s, OMe), 3.96 (3 H, s, OMe), 5.79 (1 H, s, olefinic H), 7.25—7.58 (2 H, m, ArH), and 7.65—8.05 (2 H, m, ArH); $\delta_C(CDCl_3)$ 16.47 (q), 22.63 (q), 48.15 (s), 52.64 (q), 53.09 (q), 112.67 (s), 116.80 (s), 128.26 (d), 128.76 (d), 128.85 (d), 128.98 (d), 129.61 (d), 130.78 (s), 136.12 (s), 137.49 (s), 151.69 (s), 165.21 (s), and 172.23 (s) (Found: C, 63.0; H, 4.9; N, 3.9. $C_{18}H_{17}NO_4S$ requires C, 63.0; H, 5.0; N, 4.1%). The second fraction gave *dimethyl 9-cyano-5-methyl-5-methylthio-*5H-*benzocycloheptene-*7,8-*dicarboxylate* (**19**) (47 mg, 29.4%). Recrystallisation of this from hexane–ether afforded colourless prisms, m.p. 104—106 °C; $\nu_{max.}$ 2 225 (CN), 1 735, and 1 720 cm^{-1} (ester); $\delta_H(CDCl_3)$ 2.13 (3 H, s, Me), 2.47 (3 H, s, SMe), 3.75 (3 H, s, OMe), 3.80 (3 H, s, OMe), 6.93 (1 H, s, olefinic H), and 7.23—8.02 (4 H, m, ArH), $\delta_C(CDCl_3)$ 16.11 (q), 21.22 (q), 38.84 (s), 52.65 (q), 52.81 (q), 118.52 (d), 119.33 (s), 122.37 (d), 127.94 (s), 128.59 (d), 128.96 (d), 131.44 (d), 133.86 (s), 136.09 (s), 136.46 (s), 148.10 (s), 165.19 (s), and 165.85 (s); *m/z* 343 (M^+) (Found: C, 63.15; H, 5.0; N, 3.8. $C_{18}H_{17}NO_4S$ requires C, 62.4; H, 5.0; N, 4.1%).

Reaction of Compound (**8**) *with Two Equivalents of DMAD.*—A mixture of compound (**8**) (1.5 g), DMAD (2.3 g), and sulpholane (20 ml) was stirred for 31 h at room temperature. The reaction mixture was poured into water and extracted with ether, and the extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was submitted to preparative t.l.c. on silica gel using benzene–ethyl acetate (4.5:1) to afford compounds (**16**) (831 mg, 28.7%), (**17**) (371 mg, 14.3%), and (**12**) (80 mg, 3.7%).

Reaction of Compound (**16**) *with the Ylide* (**8**).—A mixture of compounds (**16**) (35 mg) and (**8**) (21 mg) in sulpholane (4 ml) was stirred for 1 week at room temperature after which it was poured into water and extracted with ether. The ether layer was washed with water, dried ($MgSO_4$), and evaporated to leave

compound (**17**) (45 mg, 75%) which was identical with an authentic sample in all respects.

Reaction of the 2-*Thianaphthalene* (**9**) *with DMAD.*—A mixture of the ylide (**9**) (1.1 g) and DMAD (1 g) in benzene (50 ml) was stirred and heated at 70 °C for 30 h after which it was concentrated to dryness. The residual oil was triturated with ethanol to give crystals, which were recrystallised from ethanol to afford *dimethyl* 3-*benzoyl*-1-*methylthio*-1a,7b-*dihydrocyclopropa*[a]*naphthalene*-1a,2-*dicarboxylate* (**14**) (1.06 g, 62.8%) as colourless plates, m.p. 144—146 °C; $\nu_{max.}$ 1 731, 1 715 (ester), and 1 676 cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.17 (3 H, s, SMe), 3.24 (1 H, d, *J* 9.8 Hz, cyclopropane H), 3.59 (1 H, d, *J* 9.8 Hz, cyclopropane H), 3.52 (3 H, s, OMe), 3.74 (3 H, s, OMe), 7.05—7.80 (7 H, m, ArH), and 8.10—8.41 (2 H, m, ArH); *m/z* 408 (M^+) (Found: C, 67.8; H, 4.95. $C_{23}H_{20}O_5S$ requires C, 67.6; H, 4.9%). From the above reaction using sulpholane as solvent instead of benzene the same product (**14**) was obtained in 41.7% yield.

Reaction of Compound (**8**) *with Methyl Propiolate.*—(a) *In ethanol.* Methyl propiolate (MP) (449 mg) was added dropwise to a cooled and stirred solution of compound (**8**) (1 g) in absolute ethanol (100 ml), and the mixture was stirred further for 24 h. It was then concentrated to dryness to leave an oil, which was purified with preparative t.l.c. on silica gel using benzene to afford *methyl* 1-*cyanonaphthalene*-3-*carboxylate* (**13**) (300 mg, 27%) as colourless needles from ethanol, m.p. 105—106 °C; $\nu_{max.}$ 2 200 (CN) and 1 720 cm^{-1} (ester); $\delta_H(CDCl_3)$ 4.04 (3 H, s, OMe), 7.80—8.52 (5 H, m, ArH), and 8.83 (1 H, d, *J* 1 Hz, ArH); *m/z* 211 (M^+) (Found: C, 73.75; H, 4.3; N, 6.5. $C_{13}H_9NO_2$ requires C, 73.9; H, 4.3; N, 6.6%).

(b) *In benzene.* A mixture of compound (**8**) (300 mg) and MP (270 mg) in dry benzene (20 ml) was stirred for 2 weeks at room temperature under an N_2 atmosphere. The solvent was then evaporated to give crude crystals, which upon recrystallisation from ethanol–dichloromethane afforded *methyl* 1,7-*dicyano*-1-[o-(2-*methylthiovinyl*)*phenyl*]-2-*methylthio*-1,1a,2,8a-*tetrahydrobenzo*[a]*cyclopropa*[d]*cycloheptene*-8a-*carboxylate* (**20**) (207 mg, 47.6%) as white plates, m.p. 194 °C; $\nu_{max.}$ 2 240 (CN) and 1 740 cm^{-1} (ester); $\delta_H(CDCl_3)$ 2.29 (3 H, s, SMe), 2.40 (3 H, s, SMe), 3.14 (1 H, d, *J* 12 Hz, CH), 3.39 (3 H, s, OMe), 4.26 (1 H, d, *J* 12 Hz, CH), 6.62 (2 H, ABq, *J* 11 Hz, olefinic H), and 7.30—8.20 (9 H, m, ArH and olefinic H); $\delta_C(CDCl_3)$ 16.16 (q), 18.39 (q), 28.47 (s), 39.36 (s), 43.27 (d), 47.93 (d), 53.14 (q), 115.86 (s), 117.82 (s), 120.40 (s), 120.55 (d), 127.21 (d), 127.61 (d), 127.84 (s), 128.51 (d), 129.12 (d), 129.40 (d), 129.73 (d), 130.28 (d), 130.61 (d), 130.64 (s), 133.66 (d), 136.95 (s), 137.06 (s), 138.89 (d), and 165.23 (s); *m/z* 458 (M^+) (Found: C, 68.0; H, 4.8; N, 6.0. $C_{26}H_{22}N_2O_2S_2$ requires C, 68.1; H, 4.8; N, 6.1%).

The above reaction conducted in sulpholane as solvent gave a 48.3% yield of compound (**20**). Moreover, the reaction using 2 equiv. of MP also gave a 23.2% yield of compound (**20**).

Reaction of the 2-*Thianaphthalene* (**8**) *with Tetracyanoethylene.*—Tetracyanoethylene (205 mg) was added to a stirred, ice–salt-cooled solution of compound (**8**) (300 mg) in dry THF (15 ml) and the mixture was stirred for 3 h at the same temperature and then for 36 h at room temperature. The solvent was evaporated off to leave an oily residue which crystallised upon treatment with ether. Recrystallisation from hexane–dichloromethane gave o-(2,2-*dicyano*-3-*methylthiocyclopropyl*)-1,2,3-*tricyanovinylbenzene* (**21**) (283 mg, 56%) as yellow prisms, m.p. 139—141 °C; $\nu_{max.}$ 2 250 cm^{-1} (CN); $\delta_H(CDCl_3)$ 2.44 (3 H, s, SMe), 3.55 (1 H, d, *J* 9 Hz, cyclopropane H), 3.91 (1 H, d, *J* 9 Hz, cyclopropane H), and 7.50—7.90 (4 H, m, ArH); $\delta_C(CDCl_3)$ 15.32 (s), 16.18 (q), 37.43 (d), 37.52 (d), 99.83 (s), 110.02 (s), 110.27 (s), 110.68 (s), 112.95 (s), 113.74 (s), 128.76 (s), 128.90 (s), 130.72 (d), 131.13 (d), 132.53 (d), 134.83 (d), and 140.96 (s); *m/z* 315 (M^+) (Found: C, 64.5; H, 2.8; N, 22.0. $C_{17}H_9N_5S$ requires C, 64.75; H, 2.9; N, 22.2%).

Reaction of the 2-*Thianaphthalene* (**8**) *with Diphenylcyclopropenone.*—(a) *In ethanol.* A mixture of compound (**8**) (368 mg) and diphenylcyclopropenone (404 mg) in absolute ethanol (20 ml) was stirred for 14 h at room temperature after which the solvent was removed. The residual oil was submitted to preparative t.l.c. on silica gel using benzene as solvent to give *ethyl* α-*phenyl*-β-[α-*cyano*-2-(*methylthiovinyl*)*benzyl*]*cinnamate* (**22**) (697 mg, 81%) as an oil, b.p. 242 °C (0.8 mmHg); $\nu_{max.}$ 2 200 (CN) and 1 732 cm^{-1} (ester); $\delta_H(CDCl_3)$ 1.29 (3 H, t, *J* 7 Hz, CH_2CH_3), 2.34 (3 H, s, SMe), 4.30 (2 H, q, *J* 7 Hz, CH_2CH_3), 5.70 (1 H, s, CHCN), 6.35 (1 H, d, *J* 11 Hz, olefinic H), and 7.50—8.00 (15 H, m, ArH and olefinic H); *m/z* 440 (M^+) (Found: C, 76.4; H, 5.7; N, 3.0. $C_{28}H_{25}NO_2S$ requires C, 76.5; H, 5.7; N, 3.2%).

(b) *In benzene.* A mixture of compound (**8**) (550 mg) and diphenylcyclopropenone (606 mg) in dry benzene (40 ml) was stirred for 3 days at room temperature. The reaction mixture was concentrated to dryness to give a crude oil, which was purified by preparative t.l.c. on silica gel using benzene–light petroleum (7:3) as solvent to afford 9-*cyano*-10-*methylthio*-6,7-*diphenyl*-5,9-*methano*-5H-*benzocyclohepten*-8(9H)-*one* (**23**) (758 mg, 65.6%) as white needles after recrystallisation from ethanol–dichloromethane, m.p. 179 °C; $\nu_{max.}$ 2 280 (CN), and 1 675 cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.39 (3 H, s, SMe), 4.30 (1 H, s, CH), 4.51 (1 H, s, CH), and 6.60—7.90 (14 H, m, ArH); $\delta_C(CDCl_3)$ 16.25 (q), 59.61 (s), 63.80 (d), 70.21 (d), 117.21 (s), 123.49 (d), 126.78 (d), 127.52 (d), 128.13 (d), 128.25 (d), 128.79 (d), 128.94 (d), 129.13 (d), 130.34 (d), 132.08 (s), 132.82 (s), 135.64 (s), 137.45 (s), 143.15 (s), 156.84 (s), and 192.09 (s); *m/z* 393 (M^+) (Found: C, 79.4; H, 4.9; N, 3.3. $C_{26}H_{19}NOS$ requires C, 79.4; H, 4.9; N, 3.6%).

(c) *In sulpholane.* A mixture of compound (**8**) (300 mg) and diphenylcyclopropenone (331 mg) in sulpholane (20 ml) was stirred for 10 days at room temperature under an N_2 atmosphere. The reaction mixture was poured into water and extracted with ether. The ether extracts were washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by preparative t.l.c. on silica gel using ethyl acetate–hexane (1:2) to give compound (**23**) (200 mg, 32%) and an unidentified oil.

Reaction of the 2-*Thianaphthalene* (**8**) *with Diethyl Azodicarboxylate.*—Diethyl azodicarboxylate (470 mg) was added to a solution of the ylide (**8**) (500 mg) in sulpholane (25 ml) under an N_2 atmosphere, and the mixture was stirred for 4 days at room temperature. The reaction mixture was then poured into water and extracted with ether, and the extract washed with water and dried ($MgSO_4$). The solvent was evaporated off to give 1-(1-*cyano*-2-*methylthioinden*-1-*yl*)-1,2-*bis*(*ethoxycarbonyl*)*hydrazine* (**24**) (560 mg, 58%). Recrystallisation from hexane–dichloromethane afforded colourless prisms, m.p. 130 °C (decomp.); $\nu_{max.}$ 3 280 (NH), 2 240 (CN), 1 745, and 1 695 cm^{-1} (ester); $\delta_H(CDCl_3)$ 1.25 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 1.34 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 2.43 (3 H, s, SMe), 4.17 (2 H, q, *J* 7.5 Hz, CH_2CH_3), 4.29 (2 H, q, *J* 7.5 Hz, CH_2CH_3), 5.62 (1 H, s, NH, D_2O exchangeable), 6.39 (1 H, s, olefinic H), 7.07—7.47 (3 H, m, ArH), and 7.50—7.92 (1 H, m, ArH); $\delta_C(CDCl_3)$ 13.89 (q), 14.21 (q), 17.61 (q), 61.96 (t), 63.61 (t), 67.20 (s), 115.09 (s), 115.55 (d), 125.31 (d), 125.48 (d), 127.94 (d), 127.94 (s), 130.10 (s), 130.59 (d), 136.89 (s), 152.00 (s), and 153.29 (s); *m/z* 361 (M^+) (Found: C, 56.4; H, 5.1; N, 11.6. $C_{17}H_{19}N_3O_4S$ requires C, 56.5; H, 5.3; N, 11.6%). The filtrate separated from the product (**24**) was subjected to preparative t.l.c. on silica gel using hexane–ethyl acetate (2:1) to afford 2-*methylthioindenone bis*(*ethoxycarbonyl*)*hydrazone* (**25**) (63 mg, 7.05%) as colourless prisms after recrystallisation from hexane–dichloromethane, m.p. 102—

Table 1. Final fractional co-ordinates for non-hydrogen atoms ($\times 10^4$) in 1a,7b-dihydrocyclopropa[*a*]naphthalene derivative (**14**). Estimated standard deviations are given in parentheses

Atom	*x*	*y*	*z*
S	4 828(2)	6 179(0)	6 650(0)
O(1)	1 128(13)	4 892(2)	4 118(11)
O(2)	1 997(8)	4 786(2)	6 370(9)
O(3)	4 429(9)	5 299(2)	3 114(8)
O(4)	2 758(7)	5 694(1)	1 579(7)
O(5)	845(6)	6 685(2)	1 819(9)
C(1)	1 495(10)	5 824(3)	6 663(11)
C(1a)	2 255(9)	5 563(2)	5 383(9)
C(2)	2 395(8)	5 840(2)	4 039(8)
C(3)	1 907(9)	6 317(2)	3 930(10)
C(3a)	1 135(9)	6 573(2)	5 156(9)
C(4)	549(11)	7 056(2)	4 981(14)
C(5)	−187(13)	7 293(3)	6 123(12)
C(6)	−397(15)	7 056(3)	7 432(14)
C(7)	134(14)	6 585(3)	7 608(12)
C(7a)	928(10)	6 348(2)	6 447(9)
C(8)	2 068(9)	6 584(2)	2 517(9)
C(9)	3 793(10)	6 726(2)	2 026(9)
C(10)	5 118(10)	6 741(3)	2 976(12)
C(11)	6 722(13)	6 876(3)	2 473(14)
C(12)	6 942(13)	6 993(3)	1 097(13)
C(13)	5 659(13)	6 963(3)	116(13)
C(14)	4 071(11)	6 844(3)	601(12)
C(15)	3 325(10)	5 699(2)	6 665(10)
C(16)	6 651(17)	5 847(5)	6 005(25)
C(17)	1 722(10)	5 041(2)	5 215(10)
C(18)	1 543(19)	4 276(3)	6 371(23)
C(19)	3 319(10)	5 575(2)	2 878(9)
C(20)	3 626(25)	5 504(5)	363(14)

103 °C; $\nu_{max.}$ 1 807 cm^{-1} (ester); $\delta_H(CDCl_3)$ 1.11 (6 H, t, *J* 7.3 Hz, 2 × CH_2CH_3), 2.61 (3 H, s, SMe), 4.19 (4 H, q, *J* 7.3 Hz, 2 × CH_2CH_3), 7.52 (1 H, s, olefinic H), and 7.33—7.82 (4 H, m, ArH); $\delta_C(CDCl_3)$ 13.90 (q), 14.32 (q), 63.10 (t), 117.05 (d), 123.12 (s), 123.74 (d), 125.82 (d), 127.03 (s), 127.03 (d), 130.96 (d), 138.67 (s), 149.23 (s), 152.08 (s), and 152.17 (s); *m/z* 334 (M^+) (Found: C, 57.6; H, 5.5; N, 8.6. $C_{16}H_{18}N_2O_4S$ requires C, 57.5; H, 5.4; N, 8.4%).

Thermal Conversion of Compound (**24**) *into Compound* (**25**).—A solution of compound (**24**) (100 mg) in toluene (50 ml) was refluxed for 8 h, and the solvent was removed under reduced pressure to afford compound (**25**) (85 mg, 92%), which was identical with an authentic sample in all respects.

*X-Ray Study of Dimethyl 3-Benzoyl-1-methylthio-*1a,7b-*dihydrocyclopropa*[a]*naphthalene-*1a,2-*dicarboxylate* (**14**).—*Crystal data.* $C_{23}H_{20}O_5S$, *M* = 408.4. Orthorhombic, *a* = 7.979(2), *b* = 27.458(7), *c* = 9.330(3) Å, *U* = 2 044 Å^3, D_m = 1.32 g cm^{-3} (flotation), *Z* = 4, D_c = 1.327 g cm^{-3}, space group $Pna2_1$ from systematic absences, *F*(000) = 856, Mo-K_α radiation, λ = 0.7107 Å (Mo-K_α) = 1.917 cm^{-1}.

Crystals of the title compound were prepared and recrystallized from methanol to afford colourless prisms, elongated along the *a* axis. Preliminary space-group data were determined from Weissenberg and precession photographs by use of Cu-K_α (λ = 1.5418 Å) radiation, and accurate unit-cell dimensions were obtained by least-squares refinement of the setting angles of 20 reflections measured on the automatic diffractometer.

Three-dimensional intensity data were collected on a Hilger and Watts automatic four-circle Y 290 diffractometer controlled by a PDP 8 computer. Intensities were measured for θ < 27.5° by the ω—2θ scan technique with Mo-K_α radiation. Each reflection was integrated in 80 steps of 0.01°. A standard reflection was monitored every 10 reflections to check crystal stability. A total of 2 423 independent reflections were recorded, of which 1 855 having intensities $I > 3\sigma$ (*I*) were considered observed. All intensities were collected for Lorentz and polarization factors, but no absorption corrections were applied. Structure determination and refinement. The structure was solved by the SEARCHER program for automatic heavy-atom analysis, written[16] for the CDC 3600 computer (later modified for CDC 6600 computer). Initial co-ordinates for the sulphur atom were easily derived from a three-dimensional Patterson synthesis. The atomic co-ordinates of 28 light atoms, which were treated as carbon atoms, were found from the first cycle of the program. The co-ordinates of the 29 atoms from the first SEARCHER cycle were refined[17] by full-matrix least-squares calculations. After three cycles, with isotropic temperature factors, *R* was 0.107. At this stage, a three-dimensional difference-Fourier synthesis was calculated and the positions of the 20 hydrogen atoms were found and their positions were refined subsequently (*B* values were fixed at 2.0 Å^2). The final five cycles of full-matrix least-squares refinement decreased *R* to 0.081 for the 1 855 observed reflections. In this

Table 2. Bond distances (Å) and angles (°) in the 1a,7b-dihydrocyclopropa[*a*]naphthalene derivative (**14**). Standard deviations are given in parentheses

Bond distances (Å)			
S–C(15)	1.781(8)	C(2)–C(19)	1.498(10)
S–C(16)	1.818(16)	C(3)–C(3a)	1.477(12)
O(1)–C(17)	1.199(13)	C(3)–C(8)	1.514(12)
O(2)–C(17)	1.303(11)	C(3a)–C(4)	1.415(10)
O(2)–C(18)	1.444(12)	C(3a)–C(7a)	1.364(12)
O(3)–C(19)	1.186(10)	C(4)–C(5)	1.379(16)
O(4)–C(19)	1.333(10)	C(5)–C(6)	1.393(17)
O(4)–C(20)	1.427(16)	C(6)–C(7)	1.372(15)
O(5)–C(8)	1.205(10)	C(7)–C(7a)	1.414(14)
C(1)–C(1a)	1.518(13)	C(8)–C(9)	1.502(10)
C(1)–C(7a)	1.521(11)	C(9)–C(10)	1.379(12)
C(1)–C(15)	1.499(12)	C(9)–C(14)	1.385(14)
C(1a)–C(2)	1.472(11)	C(10)–C(11)	1.413(14)
C(1a)–C(15)	1.516(12)	C(11)–C(12)	1.334(18)
C(1a)–C(17)	1.502(10)	C(12)–C(13)	1.375(16)
C(2)–C(3)	1.369(10)	C(13)–C(14)	1.384(14)
Bond angles (°)			
C(15)–S–C(16)	99.8(5)	C(6)–C(7)–C(7a)	118.7(10)
C(17)–O(2)–C(18)	118.6(10)	C(1)–C(7a)–C(3a)	120.6(7)
C(19)–O(4)–C(20)	118.0(8)	C(1)–C(7a)–C(7)	117.8(8)
C(1a)–C(1)–C(7a)	117.4(8)	C(3a)–C(7a)–C(7)	121.4(8)
C(1a)–C(1)–C(15)	60.3(5)	O(5)–C(8)–C(3)	120.8(7)
C(7a)–C(1)–C(15)	120.3(7)	O(5)–C(8)–C(9)	121.1(7)
C(1)–C(1a)–C(2)	117.0(6)	C(3)–C(8)–C(9)	118.0(6)
C(1)–C(1a)–C(15)	59.2(5)	C(8)–C(9)–C(10)	120.8(7)
C(1)–C(1a)–C(17)	114.7(6)	C(8)–C(9)–C(14)	119.9(7)
C(2)–C(1a)–C(15)	120.0(6)	C(10)–C(9)–C(14)	119.1(8)
C(2)–C(1a)–C(17)	115.2(7)	C(9)–C(10)–C(11)	119.1(10)
C(15)–C(1a)–C(17)	118.5(6)	C(10)–C(11)–C(12)	120.1(10)
C(1a)–C(2)–C(3)	122.4(7)	C(11)–C(12)–C(13)	121.8(10)
C(1a)–C(2)–C(19)	113.6(5)	C(12)–C(13)–C(14)	118.5(11)
C(3)–C(2)–C(19)	123.4(7)	C(9)–C(14)–C(13)	121.0(9)
C(2)–C(3)–C(3a)	121.0(7)	S–C(15)–C(1)	119.1(5)
C(2)–C(3)–C(8)	120.2(7)	S–C(15)–C(1a)	123.7(6)
C(3a)–C(3)–C(8)	118.5(6)	C(1)–C(15)–C(1a)	60.4(6)
C(3)–C(3a)–C(4)	119.6(8)	O(1)–C(17)–O(2)	126.0(7)
C(3)–C(3a)–C(7a)	121.1(6)	O(1)–C(17)–C(1a)	121.6(8)
C(4)–C(3a)–C(7a)	119.1(8)	O(2)–C(17)–C(1a)	112.2(7)
C(3a)–C(4)–C(5)	119.5(10)	O(3)–C(19)–O(4)	125.1(8)
C(4)–C(5)–C(6)	120.5(9)	O(3)–C(19)–C(2)	122.9(8)
C(5)–C(6)–C(7)	120.5(11)	O(4)–C(19)–C(2)	111.9(6)

Table 3. Final fractional co-ordinates for non-hydrogen atoms ($\times 10^4$) in 1,1a,2,8a-tetrahydrobenzo[*a*]cyclopropa[*d*]cycloheptene derivative (**17**). Estimated standard deviations are given in parentheses

Atom	*x*	*y*	*z*
S(1)	6 015(5)	3 150(1)	−891(4)
S(2)	4 390(3)	2 245(1)	4 493(3)
C(1)	4 221(9)	1 605(3)	4 075(9)
C(2)	4 548(8)	1 520(3)	2 451(10)
C(3)	4 821(8)	1 012(3)	2 024(11)
C(4)	4 835(9)	616(3)	3 160(10)
C(5)	3 891(10)	569(3)	4 169(10)
C(6)	2 806(9)	895(3)	4 392(11)
C(7)	2 916(8)	1 390(3)	4 391(10)
C(8)	1 849(9)	1 676(3)	4 638(11)
C(9)	675(11)	1 462(4)	4 929(12)
C(10)	544(11)	977(4)	4 973(14)
C(11)	1 591(11)	697(4)	4 721(12)
C(12)	5 880(11)	1 393(3)	1 953(11)
C(13)	6 469(9)	1 541(3)	441(11)
C(14)	6 879(11)	1 198(4)	−545(13)
C(15)	7 417(12)	1 308(5)	−1 942(13)
C(16)	7 598(12)	1 783(5)	−2 291(13)
C(17)	7 254(14)	2 135(4)	−1 280(14)
C(18)	6 678(9)	2 032(4)	110(12)
C(19)	6 271(10)	2 414(4)	1 123(12)
C(20)	5 981(12)	2 862(4)	846(14)
C(21)	3 860(10)	159(4)	5 205(12)
C(22)	6 825(10)	1 376(4)	3 184(12)
C(23)	5 885(11)	248(4)	3 034(13)
C(24)	7 995(13)	89(5)	2 171(20)
C(25)	4 377(10)	822(3)	499(12)
C(26)	3 376(15)	1 003(5)	−1 835(15)
C(27)	5 262(14)	3 722(5)	−474(19)
C(28)	4 231(13)	2 235(5)	6 578(12)
N(1)	3 725(11)	−130(4)	6 082(12)
N(2)	7 566(9)	1 364(4)	4 102(12)
O(1)	5 809(9)	−139(3)	3 588(12)
O(2)	6 870(7)	399(3)	2 270(10)
O(3)	4 480(8)	407(2)	172(8)
O(4)	3 810(8)	1 154(3)	−335(8)

refinement the function minimized was $\Sigma w(F_o - F_c)^2$ with unit weights. Scattering factors for non-hydrogen atoms were taken from ref. 18, that for hydrogen from ref. 19. Final atomic parameters are given in Table 1, bond distances and angles in Table 2. Tables of the hydrogen atomic co-ordinates and the anisotropic thermal parameters are available on request from the Cambridge Crystallographic Data Centre.*

X-*Ray Study of Dimethyl* 1,7-*Dicyano*-1-[o-(2-*methylthiovinyl*)*phenyl*]-2-*methylthio*-1,1a,2,8a-*tetrahydrobenzo*[a]*cyclopropa*[d]*cycloheptene*-8,8a-*dicarboxylate* (**17**).—*Crystal data.* $C_{28}H_{24}N_2O_4S_2$, M = 516.6. Orthorhombic, a = 10.465(2), b = 27.882(3), c = 8.838(2) Å, V = 2 578.8(9) Å^3, D_m = 1.32 g m^{-3}, Z = 4, D_c = 1.330 g cm^{-3}, space group $P2_12_12_1$. Crystals of suitable quality for *X*-ray analysis were obtained from benzene–hexane in the form of pale yellow plates elongated along the *b* axis. The three-dimensional intensity data were collected on a Rigaku automatic four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71 073 Å). The density was measured by the flotation method in carbon tetrachloride–light petroleum using the 2θ values of 25 strong reflections in the range $24 < 2\theta < 35°$. The three-dimensional intensity data were collected with a ω/2θ scan technique at a constant scanning rate of 2°/min. Three standard reflections were monitored every 50 reflections, and their intensities showed a good stability. Reflections having an intensity exceeding the corresponding standard deviations by three times were treated as observed. 1 777 Reflections with $2\theta < 65°$ were retained and corrected for Lorentz and polarization factors but not for absorption and extinction factors. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with w = 1.0 for all the reflections used.

Structure determination and refinement. The structure was solved by the heavy-atom method. The positions of the sulphur atoms were obtained from a three-dimensional Patterson synthesis which revealed all atoms except hydrogen atoms attaching to methyl carbons. The final *R*-value for 1 777 reflections was 0.080. The scattering factors for C, O, N, and S

Table 4. Bond distances (Å) and angles (°) in 1,1a,2,8a-tetrahydrobenzo[*a*]cyclopropa[*d*]cycloheptene derivative (**17**). Standard deviations are given in parentheses

Bond distances (Å)

C(1)–C(2)	1.495(13)	C(17)–C(18)	1.399(16)
C(2)–C(3)	1.494(13)	C(18)–C(13)	1.415(14)
C(3)–C(4)	1.491(13)	C(18)–C(19)	1.457(14)
C(4)–C(5)	1.337(14)	C(19)–C(20)	1.307(15)
C(5)–C(6)	1.467(14)	C(20)–S(1)	1.732(13)
C(6)–C(7)	1.385(13)	S(1)–C(27)	1.819(14)
C(7)–C(1)	1.518(13)	S(2)–C(1)	1.831(9)
C(7)–C(8)	1.389(13)	S(2)–C(28)	1.850(11)
C(8)–C(9)	1.390(15)	C(21)–C(5)	1.466(15)
C(9)–C(10)	1.357(16)	C(21)–N(1)	1.127(15)
C(10)–C(11)	1.366(16)	C(22)–N(2)	1.122(15)
C(11)–C(6)	1.416(15)	C(23)–C(4)	1.508(15)
C(12)–C(2)	1.504(14)	C(23)–O(1)	1.187(14)
C(12)–C(3)	1.537(14)	C(23)–O(2)	1.302(16)
C(12)–C(13)	1.529(14)	C(24)–O(2)	1.462(14)
C(12)–C(22)	1.471(15)	C(25)–C(3)	1.520(11)
C(13)–C(14)	1.363(15)	C(25)–O(3)	1.198(12)
C(14)–C(15)	1.392(17)	C(25)–O(4)	1.324(15)
C(15)–C(16)	1.371(17)	C(26)–O(4)	1.463(15)
C(16)–C(17)	1.376(17)		

Bond angles (°)

C(7)–C(1)–C(2)	108.7(7)	C(3)–C(12)–C(22)	115.6(8)
C(7)–C(1)–S(2)	115.7(6)	C(2)–C(12)–C(22)	114.5(8)
S(2)–C(1)–C(2)	109.1(6)	C(13)–C(12)–C(22)	112.6(9)
C(1)–C(2)–C(3)	115.9(8)	C(12)–C(13)–C(18)	120.3(8)
C(1)–C(2)–C(12)	122.0(8)	C(12)–C(13)–C(14)	119.7(9)
C(3)–C(12)–C(2)	558.8(6)	C(12)–C(22)–N(2)	178.6(12)
C(2)–C(3)–C(12)	59.5(6)	C(18)–C(13)–C(14)	119.9(9)
C(3)–C(2)–C(12)	61.7(6)	C(14)–C(15)–C(16)	118.0(11)
C(3)–C(4)–C(5)	120.9(9)	C(15)–C(16)–C(17)	120.4(10)
C(2)–C(3)–C(25)	119.7(8)	C(16)–C(17)–C(18)	122.3(11)
C(4)–C(3)–C(12)	122.1(8)	C(17)–C(18)–C(13)	116.6(9)
C(4)–C(3)–C(25)	110.0(8)	C(17)–C(18)–C(19)	121.0(9)
C(3)–C(4)–C(23)	117.4(8)	C(13)–C(18)–C(19)	122'4(9)
C(5)–C(4)–C(23)	121.4(9)	C(18)–C(19)–C(20)	130.7(10)
C(4)–C(5)–C(6)	127.0(9)	C(19)–C(20)–S(1)	127.1(9)
C(4)–C(5)–C(21)	120.6(9)	C(20)–S(1)–C(27)	102.3(6)
C(6)–C(5)–C(21)	112.5(9)	C(5)–C(21)–N(1)	172.1(11)
C(5)–C(6)–C(7)	123.5(8)	C(4)–C(23)–O(1)	122.6(11)
C(5)–C(6)–C(11)	118.7(8)	C(4)–C(23)–O(2)	113.3(9)
C(7)–C(6)–C(11)	117.7(9)	O(1)–C(23)–O(2)	124.0(11)
C(1)–C(7)–C(6)	117.9(8)	C(23)–O(2)–C(24)	118.6(10)
C(1)–C(7)–C(8)	121.8(8)	C(3)–C(25)–O(3)	121.5(9)
C(6)–C(7)–C(8)	120.3(8)	C(3)–C(25)–O(4)	112.8(9)
C(8)–C(9)–C(10)	121.4(10)	O(3)–C(25)–O(4)	125.5(10)
C(9)–C(10)–C(11)	119.0(11)	C(25)–O(4)–C(26)	116.2(9)
C(10)–C(11)–C(6)	122.0(10)	C(1)–S(2)–C(28)	100.3(5)
C(2)–C(12)–C(13)	124.5(8)		

* See Instructions for Authors (1988), para. 5.6.3., *J. Chem. Soc., Perkin Trans. 1*, 1988, Issue 1.

were given by Cromer and Mann,[20] and that for H by Stewart *et al.*[19] For these calculations, computer programs made by Stewart *et al.*[21] were used. Final atomic parameters are given in Table 3, bond distances and angles in Table 4. Tables of the hydrogen atomic co-ordinates and the anisotropic thermal parameters are available on request from the Cambridge Crystallographic Data Centre.

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