

The Synthesis and Molecular Structure of 2-Benzylsulfinyl-2-(1',3'-dithiolan-2'-ylidene)ethanonitrile

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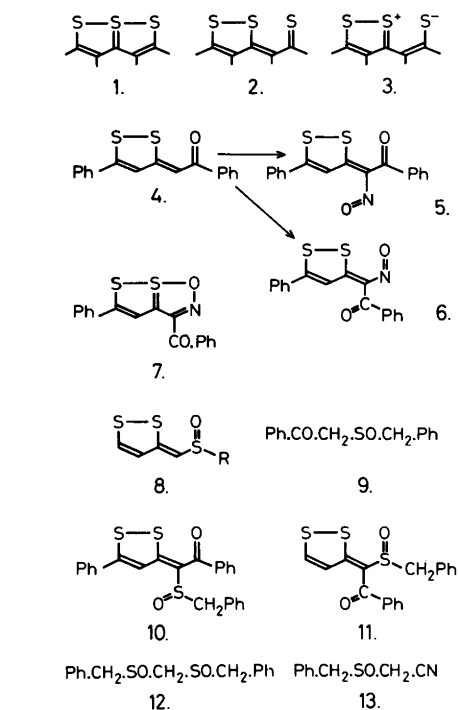
The title compound, one of a series in which a 1,2-dithiole or 1,3-dithiolan ring is conjugated with a sulfoxide group, crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$ and unit cell dimensions $a=8.5577(8)$ Å, $b=8.7232(9)$ Å, $c=10.1999(10)$ Å, $\alpha=96.17(1)^\circ$, $\beta=90.55(1)^\circ$, and $\gamma=118.90(1)^\circ$. The structure was solved by direct methods (MULTAN) and refined by least squares methods.

The 1,3-dithiolan-2-ylidene group has approximately 2-fold symmetry with bond lengths $C(sp^3)-S=1.798(7)$ and $1.798(9)$ Å, $C(sp^2)-S=1.721(5)$ and $1.720(4)$ Å, $C(sp^3)-C(sp^2)=1.456(9)$ Å, and $C(sp^2)-C(sp^2)=1.369(6)$ Å; the sp^3 carbons lie on opposite sides of a plane through the other atoms of the group at distances of 0.21 Å. The nitrile group lies close to this plane with $C-C=1.425(8)$ Å, $C-N=1.122(9)$ Å, and $C-C-N=174.4(6)^\circ$.

The environment of the sulfinyl sulfur is roughly tetrahedral. The oxygen atom points away from the nearest dithiolan sulfur, indicating that there is no energetically favourable interaction between the two atoms.

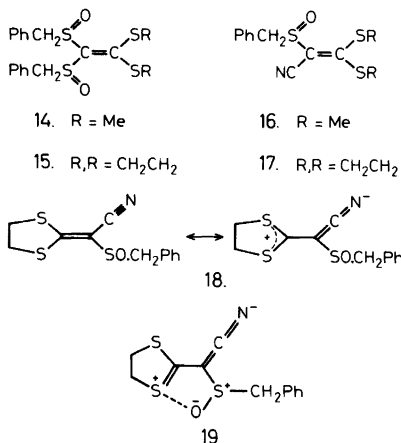
Infrared studies suggest that in 2-benzylsulfinyl-3,5-epidithio-1,5-diphenyl-2,4-pentadien-1-one the sulfoxide group does not compete with the carbonyl group for the *cis* position with respect to the S–S bridge.

Hypervalent sulfur compounds of the hetero-pentalene type have been much studied in recent years.¹ The best known and earliest reported representatives are the thiathiophthens (trithiapentalenes), usually represented as bicyclic systems 1.^{2–4} It is useful, however, from the point of view of synthesis, to regard these compounds as 1,2-dithiolyldiene thioketones 2, in which an electron-



rich dithiole system is conjugated with an electron-attracting thiocarbonyl group, producing polarized forms of type 3. The bicyclic system 1 can then be seen to result from the formation of a four-electron three-centre bond involving the three (linear) sulfur atoms.²

In some of the many structures of this type now known, there is the possibility of competition between two different electron attracting groups for



the energetically favourable position adjacent to the central sulfur atom. For example, nitrosation of the 1,2-dithiol-3-ylidene ketone **4** could give either structure **5** or **6**. In fact, the nitroso-group takes up the *cis* position; the product of the reaction has been shown to be **6** with partial bonding between the central sulfur atom and the oxygen atom, S—O = 2.034 Å.^{5,6} This product may therefore be formulated as a heteropentalene **7**.

Hoping to extend this area of sulfur chemistry, we set out to synthesize compounds in which an electron-rich sulfur-containing system is conjugated with a sulfoxide group. Our first objective was to prepare compounds of general type **8**, and attempts were made to condense either 5-phenyl-1,2-dithiole-3-thione or the related 3-methylthio-5-phenyl-1,2-dithiolium methosulfate with the ketosulfoxide **9**.

Difficulties were encountered in effecting these condensations, but using the dithiolium salt and triethylamine as base, it was possible to isolate a product with the expected composition. The infrared spectrum of this material showed strong absorption at 1550 cm⁻¹ but no bands in the normal carbonyl-stretching region, thus resembling the spectra of 1,2-dithiolylidene ketones⁷ and suggesting strongly that the product has structure **10** rather than **11**, which would be expected to have C=O absorption at a much higher wave number. The implication is that there is no marked stabilization associated with structures of type **8**.

Attempts to condense dithiole derivatives with bisbenzylsulfanyl methane **12** or with the cyanosulfoxide **13** have not been successful, but these two active methylene compounds are readily converted to products of interest in the present context by

base-catalyzed condensation with carbon disulfide and subsequent methylation of the dianion, or reaction with 1,2-dibromomethane.

All four products, **14**–**17**, have normal sulfoxide absorptions in the infrared (between 1030 and 1060 cm⁻¹). The C≡N stretching bands for compounds **16** (ν_{\max} 2218 cm⁻¹) and **17** (ν_{\max} 2195 cm⁻¹) show the effect of conjugation with the sulfur atoms, when compared with the corresponding band for compound **13** (ν_{\max} 2260 cm⁻¹). This conjugation, illustrated in diagram **18**, must imply some positive charge on the sulfur atoms, a situation which might be thought to be favourable for the development of an interaction or, at least, an attraction between the negatively charged oxygen of the sulfoxide group and a sulfur atom, as in diagram **19**.

For this reason, we have subjected compound **17** to detailed structural study.

STRUCTURE ANALYSIS

The crystals of compound **17** are colourless prisms elongated in the *bc*-diagonal direction.

Crystal data.

C₁₂H₁₁NOS₃ M.W. = 281.40

Space group $P\bar{1}$

$a = 8.5577(8)$ Å, $b = 8.7232(9)$ Å, $c = 10.1999(10)$ Å,

$\alpha = 96.17(1)^\circ$, $\beta = 90.55(1)^\circ$, $\gamma = 118.90(1)^\circ$

$V = 660.92$ Å³

$D_c = 1.414$ g/cm³, $D_m(\text{floatation}) = 1.43$ g/cm³

$Z = 2$

$\mu = 5.26$ cm⁻¹ (MoK α)

A crystal of approximate dimensions 0.15 × 0.30 × 0.35 mm was used for the X-ray analysis which was carried out on a computer-controlled Enraf-Nonius CAD4 diffractometer using graphite monochromatized MoK α radiation ($\lambda = 0.71069$ Å). The unit cell dimensions were determined from the 2θ values of 25 high order reflections, $t = 20$ °C. A least squares procedure gave the value quoted above.

The intensities of 3200 independent reflections within $\theta = 28^\circ$ were measured at $t = 20$ °C by the $\omega - 2\theta$ scan technique. Two standard reflections, $\bar{2}33$ and $\bar{1}22$, were measured at regular intervals, and their intensities decreased about 7 % during the data collection. This was accounted for during data reduction. Lp corrections were applied but absorption corrections were considered unnecessary. Reflections for which $I > 2\sigma(I)$, where $\sigma(I)$ is based on counting statistics, were accepted as observed.

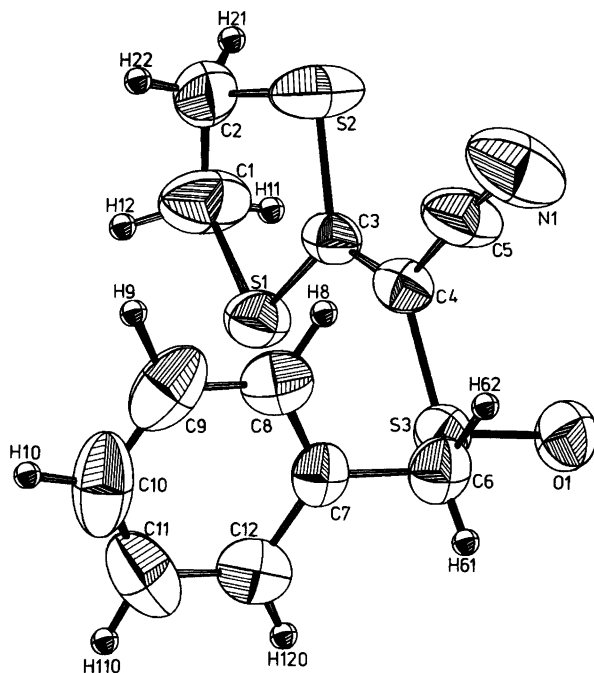


Fig. 1. ORTEP¹² drawing of the molecular structure of the title compound with numbering of atoms.

By this criterion 841 reflections were considered unobserved and excluded from the subsequent calculations.

The structure was solved by direct methods (MULTAN)⁸ and refined by means of CRYLSQ of X-ray-76⁹ to an *R* of 0.049. The hydrogen positions were found from difference maps. All the calculations were carried out on the UNIVAC 1110 of the University of Bergen.

Final atomic coordinates and temperature parameters are listed in Table 1. The final structure factor list is available on request.

Scattering factors given by Cromer and Mann were used for sulfur, oxygen, nitrogen and carbon.¹⁰ For hydrogen, the scattering factor curve given by Stewart *et al.*¹¹ was used.

DISCUSSION

The molecular structure of compound 17 as found in the present study is shown in Fig. 1. Bond lengths and angles are given in Table 2, and a stereoscopic view of the molecule is given in Fig. 2.

The standard deviations given in Table 2 are based on the standard deviations in positional parameters from the least squares refinement given in Table 1.

Least squares planes, **A** for the atoms of the phenyl group, **B** for S(1), S(2), C(3) and C(4), and **C** for S(3), C(3), C(4) and C(5), were calculated with equal weights. The equations for these planes are,

$$\mathbf{A} \quad -6.0699x + 0.8915y + 6.9941z = -1.2841$$

$$\mathbf{B} \quad -0.1962x + 7.7315y - 1.2773z = 1.7801$$

$$\mathbf{C} \quad -0.6799x + 7.8453y - 2.9241z = 1.1927$$

with *x*, *y* and *z* as fractional coordinates.

Deviations of atoms from the least squares planes are given in Table 2. One sees from the values for plane **A** that the phenyl group is planar within the error and that C(6) lies close to the plane. C(1) and C(2) of the dithiolane ring lie on opposite sides of plane **B** (through S(1), S(2), C(3) and C(4)) at distances of 0.212 and -0.208 Å, respectively, and the sulfanyl sulfur S(3) lies 0.386 Å out of this plane, *cf.* Figs. 1 and 2.

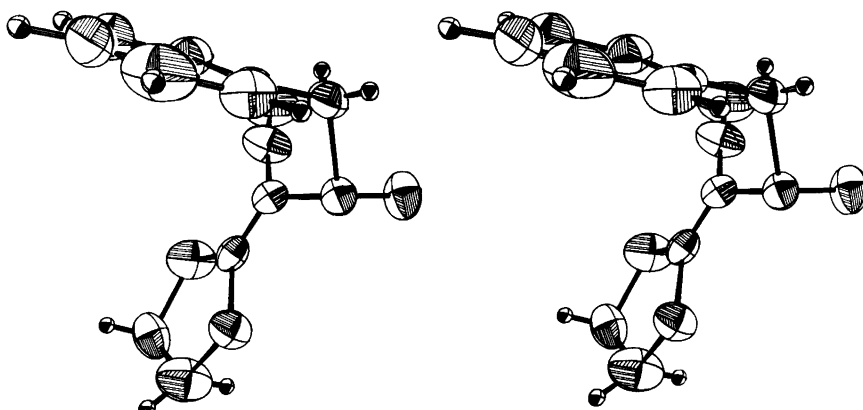


Fig. 2. A stereoscopic view of the molecule.

The twist about the C(3)–C(4) bond, taken as the angle between the normals of planes B and C, is 10.1° . C(4) lies about -0.07 \AA out of a plane through C(3), C(5) and S(3), and the configuration around C(4) is thus slightly pyramidal. Furthermore,

the oxygen atom O(1) points away from S(1), and there is no contact between these two atoms. Thus, in the solid state the structure of the present molecule is not of type 19.

A survey of bond lengths as found in 1,3-

Table 1. Fractional atomic coordinates, and temperature parameters U_{ij} (\AA^2) for sulfur, oxygen, nitrogen and carbon, and U (\AA^2) for hydrogen. The expressions used are $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ and $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$, respectively. Standard deviations in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	1.13799(16)	.27905(17)	.11624(12)	.0576(7)	.0761(9)	.0502(7)	.0386(7)	.0026(5)	.0089(6)
S(2)	.87816(19)	.23845(23)	-.08955(13)	.0736(9)	.1348(9)	.0451(8)	.0477(9)	-.0064(6)	.0084(8)
S(3)	.91618(14)	.35933(14)	.33841(11)	.0547(7)	.0448(6)	.0470(7)	.0242(5)	.0068(5)	.0102(5)
O(1)	.9367(5)	.5384(4)	.3665(3)	.100(3)	.048(2)	.067(2)	.037(2)	.010(2)	.013(2)
N(1)	.5276(6)	.2600(8)	.1145(5)	.069(3)	.157(5)	.117(5)	.065(4)	.001(3)	.044(4)
C(1)	1.2089(9)	.2803(13)	-.0492(6)	.088(5)	.141(8)	.050(4)	.061(5)	.018(3)	.021(4)
C(2)	1.0587(9)	.2057(9)	-.1482(6)	.104(5)	.074(4)	.053(3)	.055(4)	.016(3)	.013(3)
C(3)	.9348(5)	.2642(5)	.0767(4)	.046(2)	.036(2)	.045(2)	.013(2)	-.004(2)	.010(2)
C(4)	.8280(5)	.2803(5)	.1701(4)	.045(2)	.047(2)	.048(3)	.019(2)	.000(2)	.012(2)
C(5)	.6575(7)	.2619(8)	.1355(5)	.066(3)	.118(5)	.060(3)	.060(3)	.005(3)	.024(3)
C(6)	.7190(7)	.2172(7)	.4196(6)	.060(3)	.059(3)	.057(3)	.029(3)	.020(3)	.012(3)
C(7)	.6804(5)	.0285(6)	.4039(4)	.044(2)	.048(3)	.050(3)	.022(2)	.021(2)	.012(2)
C(8)	.5541(7)	-.0932(7)	.3087(5)	.057(3)	.065(4)	.056(3)	.022(3)	.012(2)	.015(3)
C(9)	.5149(8)	-.2675(8)	.2970(7)	.081(4)	.065(4)	.080(4)	.015(3)	.029(3)	-.004(3)
C(10)	.6007(10)	-.3204(9)	.3796(9)	.103(6)	.057(4)	.130(7)	.043(4)	.066(5)	.030(4)
C(11)	.7267(10)	-.2023(10)	.4720(8)	.084(5)	.103(6)	.109(5)	.064(4)	.034(4)	.053(5)
C(12)	.7685(7)	-.0245(8)	.4865(5)	.057(3)	.077(4)	.064(3)	.030(3)	.007(3)	.016(3)
Atom	x	y	z	U	Atom	x	y	z	U
H(11)	1.255(8)	.399(7)	-.033(6)	.16(3)	H(8)	.503(6)	-.048(6)	.247(5)	.08(2)
H(12)	1.258(8)	.197(8)	-.049(6)	.12(3)	H(9)	.421(7)	-.360(7)	.217(5)	.10(2)
H(21)	1.076(8)	.265(8)	-.210(7)	.12(3)	H(10)	.568(7)	-.442(8)	.353(5)	.10(2)
H(22)	1.004(6)	.081(6)	-.169(5)	.08(2)	H(110)	.789(7)	-.228(7)	.531(6)	.10(2)
H(61)	.754(6)	.260(6)	.505(5)	.06(2)	H(120)	.841(7)	.054(7)	.555(5)	.08(2)
H(62)	.608(6)	.219(6)	.375(5)	.08(2)					

Table 2. Bond lengths $l(ij)$, bond angles $\angle(ijk)$, and deviations Δ_j from least squares planes A, B, and C. Standard deviations in parentheses. The deviations for atoms which are included in the least squares plane calculations are printed in italics.

Atoms <i>i</i>	<i>j</i>	<i>k</i>	Bonds		Angles $\angle(ijk)^\circ$	Deviations of atoms <i>j</i> from planes		
			$l(ij)$ Å	$l(jk)$ Å		Δ_j (A) Å	Δ_j (B) Å	Δ_j (C) Å
C(1)	S(1)	C(3)	1.798(7)	1.721(5)	97.0(3)		.006	-.117
C(2)	S(2)	C(3)	1.798(9)	1.720(4)	97.2(3)		.006	.343
C(4)	S(3)	O(1)	1.789(4)	1.480(4)	106.7(2)		.386	.015
C(4)	S(3)	C(6)		1.817(5)	98.8(2)			
O(1)	S(3)	C(6)			105.3(3)			
S(1)	C(1)	C(2)		1.456(9)	112.1(5)		.212	.324
S(2)	C(2)	C(1)			111.3(5)		-.208	
S(2)	C(3)	S(1)			115.5(3)		-.019	.020
S(1)	C(3)	C(4)		1.369(6)	122.9(3)			
S(2)	C(3)	C(4)			121.6(4)			
S(3)	C(4)	C(3)			119.5(3)		.008	-.054
S(3)	C(4)	C(5)		1.425(8)	117.8(4)			
C(3)	C(4)	C(5)			122.0(4)			
C(4)	C(5)	N(1)		1.122(9)	174.4(6)		-.057	.019
S(3)	C(6)	C(7)		1.504(8)	112.6(4)	.048		
C(6)	C(7)	C(8)		1.373(6)	120.1(5)			
C(6)	C(7)	C(12)			120.3(4)			
C(8)	C(7)	C(12)		1.378(9)	119.6(5)	.004		
C(7)	C(8)	C(9)		1.381(9)	120.1(6)	-.003		
C(8)	C(9)	C(10)		1.365(13)	120.4(5)	-.002		
C(9)	C(10)	C(11)		1.345(10)	120.2(8)	.007		
C(10)	C(11)	C(12)		1.404(12)	120.5(9)	-.006		
C(7)	C(12)	C(11)			119.2(5)	-.001		

Table 3. A comparison of bond lengths (Å) and angles ($^\circ$). The value marked with an asterisk was not included in the mean value calculations. See text for further explanation.



Ref.	X	1	2	3	4	5	6	Ref.	7	8	\angle (CCN)
13	C	1.355(2)	1.760(2)	1.799(2)	1.479(2)	1.813(2)	1.756(2)	19	1.439(6)	1.123(7)	176.8(4)
14	C	1.368(5)	1.750(3)	1.775(6)	1.458(6)	1.803(4)	1.741(4)	19	1.440(5)	1.112(5)	176.7(4)
14	C	1.354(6)	1.754(3)	1.797(7)	1.392(8)*	1.783(4)	1.740(5)	20	1.443(3)	1.130(3)	175.7(3)
15	C	1.352(4)	1.739(2)	1.821(2)	1.479(4)	1.791(2)	1.740(2)	20	1.440(3)	1.133(3)	170.5(2)
16	C	1.369(10)	1.728(9)	1.787(15)	1.435(19)	1.787(15)	1.718(12)	21	1.462(6)	1.127(6)	178.4(5)
17	S		1.732(2)	1.812(3)	1.493(5)	1.808(3)	1.722(2)				
18	S=O		1.72(1)	1.80(2)	1.50(2)	1.81(2)	1.73(2)				
Mean values		1.356 ^a	1.742 ^a	1.803 ^a	1.477 ^a	1.803 ^a	1.742 ^a	1.441	1.126		
Present study		1.369(6)	1.721(5)	1.798(7)	1.456(9)	1.798(9)	1.720(4)	1.425(8)	1.122(9)	174.4(6)	

^a Assuming symmetric ring.

dithiolane-2-ylidene groups and in nitrile groups is given in Table 3. The mean values of the bond lengths given there have been calculated with weights equal to the inverse values of the respective standard deviations and, in case of the 1,3-dithiolane-2-ylidene group, under the assumption that the structure has a twofold axis running along X-C and the midpoint of the C-C bond. This assumption is strongly supported by the results of the present study, *cf.* Table 3 and Fig. 1.

It is realized that standard deviations in bond lengths may be overestimated when based on standard deviations in positional parameters from least squares refinement. According to Hamilton and Abrahams²² a more realistic estimate of the standard deviations would probably be obtained by multiplying those given by a factor of two.

With this in mind one may conclude that those bond lengths of the present molecule which are given in Table 3, agree with the average lengths for corresponding bonds as found in other molecules. Furthermore, one should note that the C-C-N sequence is not found to be exactly linear, and that the C-C-N angles lie within a rather wide range, 170.5(2)–178.4(5)°.

The C(1)–C(2) bond in the 1,3-dithiolan-2-ylidene group is a C(sp³)–C(sp³) bond for which the accepted bond length is 1.537 Å.²³ However, a smaller bond length is always found for this bond in 1,3-dithiolan-2-ylidene groups. The values given in Table 3 are in the range 1.44–1.50 Å with a mean of 1.477 Å. The value 1.456(6) of the present structure has not been included in the mean value calculations, and the same applies to the value 1.392 Å which the author reports may be incorrect due to disorder in the crystal structure.¹⁴ Difference maps of the present structure did not reveal any sign of disorder.

The temperature parameters of C(1) and C(2) are relatively large, *cf.* Table 1; consequently, one might expect to find a "short" C(1)–C(2) bond, but this is probably not the only reason.

The molecule has a rotation possibility about the C(4)–S(3) bond. By means of this rotation the S(3)–O(1) bond can be brought into the plane defined by S(1), S(2), C(3) and C(4). The S(1)–O(1) distance would then be *ca.* 2.50 Å, somewhat larger than the S–O contacts in dithiolylidene ketones but much less than the van der Waals separation of 3.10–3.25 Å. In fact, many compounds are known with S–O contacts in the range 2.50–2.70 Å.²⁴ Thus the failure of the molecule to adopt this

particular configuration suggests that there is no favourable interaction between S(1) and O(1). We note that in the actual configuration of the molecule S(3) has its sp³ lone pair direction close to the plane indicated above. The S(1)–S(3) distance is 3.20 Å, which should be compared with the van der Waals distance of 3.40–3.70 Å and with the Huggins "constant energy" distance of 2.92 Å.²⁴ It seems unlikely that the structure observed is dictated by an energetically favourable interaction between S(1) and S(3). There is some similarity between the S(1), C(3), C(4), S(3), O(1) system of the sulfoxide (17) and the S–S–N–S–S chain of the recently reported S₄N[−] anion²⁵ (in which an S–S contact of 3.140 Å appears to be important), but chemically the two structures are very different.

EXPERIMENTAL

2-Benzylsulfanyl-3,5-epidithio-1,5-diphenyl-2,4-pentadien-1-one (10). A solution of triethylamine (1 ml) in ethanol (25 ml) was added over 30 min to a stirred suspension of 3-methylthio-5-phenyl-1,2-dithiolium methosulfate (1 g) and benzyl phenacyl sulfoxide (0.8 g)²⁶ in ethanol (200 ml). The mixture was then heated under reflux for 5 h, cooled, filtered, and the resulting solution concentrated *in vacuo*. The material obtained after addition of water and extraction with chloroform (3 × 100 ml) was purified by chromatography on alumina. Elution with benzene–light petroleum and then with benzene gave bands containing 5-phenyl-1,2-dithiole-3-thione and 5-phenyl-1,2-dithiole-3-one. Further elution with benzene containing an increasing proportion of chloroform yielded the required product which formed yellow needles (0.1 g), m.p. 150–151 °C; ν_{\max} 1550 cm^{−1} (C=O) and 1043 cm^{−1} (S=O); δ (CDCl₃) 4.26(2H, dd) 6.96–7.93(16H, m); M⁺, *m/e* 434 (Found: C 66.1; H 4.25. C₂₄H₁₈O₂S₃ requires C 66.4; H 4.2).

Bisbenzylsulfynylmethane (12). Hydrogen peroxide (5.2 g of 30 % solution) was added dropwise to a stirred solution of bisbenzylthiomethane (5 g) in glacial acetic acid (200 ml) and stirring was continued for 24 h. The crystalline precipitate was collected and a further quantity of the product was obtained by concentration of the mother liquor (safety screen) *in vacuo*. The combined samples, after recrystallization from ethanol, gave bisbenzylsulfynylmethane as fine colourless needles (5.1 g), m.p. 208–210 °C (lit. m.p.,²⁷ 212–220 °C); ν_{\max} (nujol) 1030–1060 cm^{−1}; δ (CDCl₃) 3.43–4.56 (6H, overlapping A B systems), 7.22–7.42 (10H, m); M⁺, *m/e* 292.

2-(Bisbenzylsulfinyl)-methylene-1,3-dithiolan (15). Sodium hydride (0.4 g of 50% dispersion) was added in portions to a stirred suspension of bisbenzylsulfinylmethane (1 g) in tetrahydrofuran (200 ml) (N_2 atmosphere). When gas evolution had virtually ceased, carbon disulfide (5 ml) was added gradually, and stirring was continued for 1 h, and then for a further 12 h, after addition of 1,2-dibromoethane (5 ml). Precipitated sodium bromide was removed by filtration and the residue obtained by evaporation of solvent was treated with water and extracted into chloroform (3×100 ml). Crystallization of the extracted material from benzene-hexane gave the dithiolan as pale yellow needles (0.8 g) m.p. 183.5 °C; $\delta(CDCl_3)$ 3.12 (4H, s), 4.73–5.27 (4H, dd) 7.27–7.47 (10H, m); M^+ , m/e 394 (Found: C 54.7; H 4.6; S 32.4. $C_{18}H_{18}O_2S_4$ requires C 54.8; H 4.6; S 32.5).

2,2-Bisbenzylsulfinyl-1,1-bismethylthioethene (14). Prepared by the method used for the foregoing dithiolan, but replacing 1,2-dibromoethane by methyl iodide, this product was obtained in 68% yield as pale yellow needles, m.p. 182–183 °C; ν_{max} (nujol) 1035 cm^{-1} ; $\delta(CDCl_3)$ 2.14 (6H, s), 4.79–5.26 (4H, 2 equivalent A B systems), 7.32–7.50 (10H, m); M^+ , m/e 396 (Found: C 55.9; H 5.4. $C_{18}H_{20}O_2S_4$ requires C 54.55; H 5.05).

Benzylsulfinylacetone (13). Phenyl methanethiol (8.25 g) was added to a solution of sodium ethoxide [prepared from 1.55 g of sodium in dry ethanol (200 ml)]. After 15 min, chloroacetonitrile (5 g) was added gradually to the stirred solution, and the mixture was then heated under reflux for 30 min. Sodium chloride was removed by filtration, and the filtrate concentrated to small volume *in vacuo*. Addition of water and extraction with dichloromethane gave crude benzylthioacetone [ν_{max} (film) 2255 cm^{-1} ; $\delta(CDCl_3)$, 3.0(2H, s), 3.86 (2H, s); 7.3(5H, m)].

Without further purification, this product (5 g) was dissolved in methanol (200 ml) and oxidized by treatment with sodium metaperiodate (6.5 g) in water (100 ml). After 24 h the filtered mixture was concentrated, water added, and the product extracted with dichloromethane (3×100 ml). Crystallization from chloroform-hexane gave the sulfoxide as colourless needles (4.7 g), m.p. 109–110 °C; ν_{max} (nujol) 1043 cm^{-1} (S=O), 2260 cm^{-1} (C≡N); $\delta(CDCl_3)$ 3.33–3.64 (2H, dd) 4.21–4.35 (2H, dd) 7.35–7.44 (5H, m); M^+ , m/e 179 (Found: C 60.3; H 5.1; N 7.85. C_9H_9NOS requires C 60.3; H 5.0; N 7.8).

2-Benzylsulfinyl-2-(1',3'-dithiolan-2'-ylidene)-ethanonitrile (17). Prepared by the method described above for 2-(bisbenzylsulfinyl)-methylene-1,3-dithiolan (15), this compound formed colourless plates from dichloromethane-hexane m.p. 143–144 °C, ν_{max} (KBr disc) 2195 cm^{-1} (C≡N), 1040

cm^{-1} (S=O); ν_{max} ($CHCl_3$) 2200 cm^{-1} , 1040 cm^{-1} ; $\delta(CDCl_3)$ 3.46–3.60 (4H, m), 4.29–4.44 (2H, dd), 7.34 (5H, m); M^+ , m/e 281 (Found: C 51.0; H 3.9; N 5.0. $C_{12}H_{11}NOS_3$ requires C 51.25; H 3.9; N 5.0).

2-Benzylsulfinyl-3,3-bismethylthiopropenitrile (16). Similarly prepared this product crystallized from dichloromethane in colourless needles, m.p. 99–100 °C; ν_{max} (KBr) 1055 cm^{-1} (S=O), 2190 cm^{-1} (C≡N); $\delta(CDCl_3)$ 2.36 (3H, s), 3.62 (3H, s), 4.29–4.44 (2H, dd), 7.35 (5H, m); M^+ , m/e 283 (Found: C 51.0; H 4.7; N 5.0. $C_{12}H_{13}NOS_3$ requires C 50.9; H 4.6; N 4.95).

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