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Structures of Bis(3-phenylsydnone) Sulfide (1), Bis[3-(*p*-methoxyphenyl)sydnone] Sulfide (2), and Bis[3-(*p*-ethoxyphenyl)sydnone] Sulfide (3)

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Abstract. (1) $C_{16}H_{10}N_4O_4S$, $M_r = 354$, monoclinic, $P2_1/n$, $a = 10.347$ (2), $b = 7.777$ (1), $c = 19.796$ (4) Å, $\beta = 100.33$ (2)°, $V = 1567.13$ Å^3, $Z = 4$, $D_m = 1.52$ (3), $D_x = 1.50$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7093 Å, μ(Mo $K\alpha$) = 2.26 cm^{-1}, $F(000) = 728$, $T = 298$ K, final $R = 0.033$ for 2922 observed reflections. (2) $C_{18}H_{14}N_4O_6S$, $M_r = 414$, monoclinic, $P2_1/c$, $a = 14.255$ (2), $b = 9.344$ (1), $c = 15.250$ (2) Å, $\beta = 116.61$ (1)°, $V = 1816.12$ Å^3, $Z = 4$, $D_m = 1.50$ (3), $D_x = 1.52$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7093 Å, μ(Mo $K\alpha$) = 2.14 cm^{-1}, $F(000) = 856$, $T = 298$ K, final $R = 0.039$ for 2066 observed reflections. (3) $C_{20}H_{18}N_4O_6S$, $M_r = 442$, monoclinic, $C2/c$, $a = 20.724$ (5), $b = 12.157$ (3), $c = 8.201$ (3) Å, $\beta = 95.10$ (2)°, $V = 2057.88$ Å^3, $Z = 4$, $D_m = 1.45$ (3), $D_x = 1.43$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7093 Å, μ(Mo $K\alpha$) = 1.94 cm^{-1}, $F(000) = 920$, $T = 298$ K, final $R = 0.039$ for 1088 observed reflections. The bond lengths of the sydnone ring are similar in all three compounds and comparable to those of other 3,4-disubstituted sydnone derivatives. The N(1)—C(7) bonds of the title compounds are apparently longer than those of 3-substituted sydnone derivatives which may be attributed to steric effects. A survey of S—C bond lengths and angles between planes of different substituted diaryl sulfides does not show any correlation with the type of substituents. The shortening of the S—C bond lengths of the title compounds *versus* the average bond lengths in the cyclic 1,3,5-trithiane may be attributable to orbital electronegativity effects. In contrast to the 'morino' conformation found in most other diaryl sulfides, all three title compounds appear in the butterfly conformation.

Introduction. The crystal structures of a few 3,4-disubstituted sydnone derivatives have recently been studied (Ueng, Wang & Yeh, 1987*a*,*b*) and the bond lengths of the sydnone rings were compared with those of 3-substituted sydnone derivatives. As part of a series of studies on 3,4-disubstituted sydnone compounds, the three bis-sydnone sulfide structures were investigated in order to confirm further the steric effect between the phenyl ring and the sydnone ring. In addition, the lone-pair electrons on the S atom may have some effect

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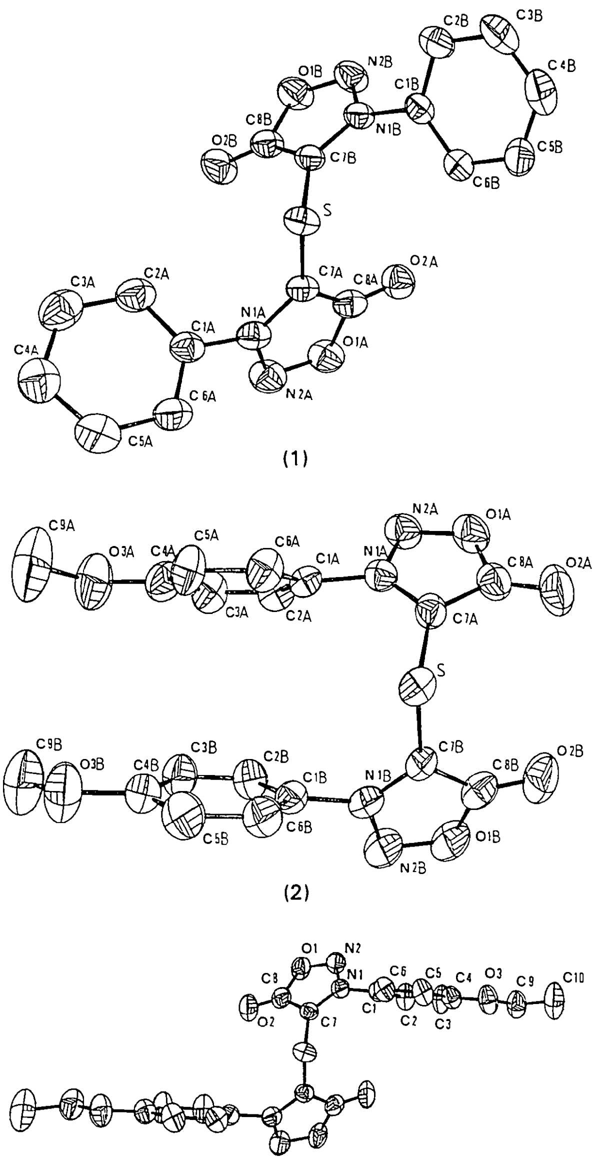
on the S—C bond for these compounds. The conformation of such compounds around the S atom is also of interest.

Table 1. *Atomic positional parameters and equivalent isotropic temperature factors for* (1), (2) *and* (3)

$$B_{eq} = (8/3)\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Compound (1)				
S	0·9319 (1)	0·2026 (1)	0·37728 (2)	3·1 (1)
C1*A*	0·6655 (1)	0·3777 (2)	0·2852 (1)	3·1 (1)
C2*A*	0·6579 (2)	0·4576 (2)	0·3461 (1)	3·7 (1)
C3*A*	0·5355 (2)	0·4717 (3)	0·3645 (1)	4·6 (1)
C4*A*	0·4260 (2)	0·4090 (3)	0·3226 (1)	4·9 (1)
C5*A*	0·4362 (2)	0·3302 (3)	0·2618 (1)	4·8 (1)
C6*A*	0·5569 (2)	0·3135 (3)	0·2417 (1)	3·9 (1)
C7*A*	0·9058 (1)	0·2990 (2)	0·2969 (1)	2·9 (1)
C8*A*	0·9986 (2)	0·3242 (2)	0·2535 (1)	3·5 (1)
N1*A*	0·7920 (1)	0·3656 (2)	0·2635 (1)	3·0 (1)
N2*A*	0·7964 (1)	0·4264 (2)	0·2023 (1)	4·0 (1)
O1*A*	0·9252 (1)	0·4027 (2)	0·1948 (1)	4·3 (1)
O2*A*	1·1142 (1)	0·2957 (2)	0·2580 (1)	4·9 (1)
C1*B*	1·2362 (1)	0·1406 (2)	0·4572 (1)	3·1 (1)
C2*B*	1·2750 (2)	0·0805 (2)	0·5231 (1)	3·6 (1)
C3*B*	1·3435 (2)	−0·0721 (3)	0·5322 (1)	4·1 (1)
C4*B*	1·3722 (2)	−0·1593 (2)	0·4767 (1)	4·1 (1)
C5*B*	1·3307 (2)	−0·0977 (3)	0·4109 (1)	4·4 (1)
C6*B*	1·2619 (2)	0·0545 (2)	0·4003 (1)	3·8 (1)
C7*B*	1·0483 (1)	0·3466 (2)	0·4181 (1)	2·9 (1)
C8*B*	1·0342 (2)	0·5246 (2)	0·4276 (1)	3·5 (1)
N1*B*	1·1719 (1)	0·3061 (2)	0·4490 (1)	3·1 (1)
N2*B*	1·2402 (1)	0·4359 (2)	0·4785 (1)	4·2 (1)
O1*B*	1·1564 (1)	0·5751 (2)	0·4649 (1)	4·3 (1)
O2*B*	0·9470 (1)	0·6275 (2)	0·4117 (1)	4·4 (1)
Compound (2)				
S	0·0283 (1)	0·3751 (1)	0·0874 (1)	3·1 (1)
C7*A*	0·0003 (2)	0·2709 (3)	0·1663 (2)	2·9 (1)
N1*A*	0·0708 (2)	0·2017 (2)	0·2466 (2)	3·1 (1)
N2*A*	0·0310 (2)	0·1239 (3)	0·2926 (2)	4·3 (1)
O1*A*	−0·0757 (2)	0·1430 (2)	0·2395 (2)	4·8 (1)
O2*A*	−0·1883 (2)	0·2678 (3)	0·1059 (2)	5·5 (2)
C8*A*	−0·0996 (2)	0·2362 (3)	0·1591 (2)	3·9 (2)
C1*A*	0·1843 (2)	0·2014 (3)	0·2902 (2)	2·9 (1)
C2*A*	0·2366 (2)	0·0731 (3)	0·3148 (2)	3·7 (2)
C3*A*	0·3439 (2)	0·0725 (3)	0·3634 (2)	4·0 (2)
C4*A*	0·3980 (2)	0·2004 (4)	0·3866 (2)	3·8 (2)
C5*A*	0·3449 (2)	0·3286 (3)	0·3606 (2)	3·7 (2)
C6*A*	0·2361 (2)	0·3294 (3)	0·3117 (2)	3·5 (1)
O3*A*	0·5044 (2)	0·1891 (3)	0·4350 (2)	5·0 (1)
C9*A*	0·5642 (3)	0·3162 (5)	0·4667 (3)	6·9 (3)
C7*B*	0·0222 (2)	0·2490 (3)	0·0019 (2)	2·8 (1)
N1*B*	0·1053 (2)	0·1903 (2)	−0·0049 (2)	3·1 (1)
N2*B*	0·0817 (2)	0·0916 (3)	−0·0728 (2)	4·2 (1)
O1*B*	−0·0258 (2)	0·0812 (2)	−0·1135 (1)	4·4 (1)
O2*B*	−0·1611 (2)	0·1900 (3)	−0·0987 (2)	5·0 (1)
C8*B*	−0·0679 (2)	0·1820 (3)	−0·0705 (2)	3·7 (2)
C1*B*	0·2149 (2)	0·2256 (3)	0·0508 (2)	3·0 (1)
C2*B*	0·2836 (2)	0·1205 (3)	0·1027 (2)	3·9 (2)
C3*B*	0·3885 (2)	0·1532 (4)	0·1544 (2)	4·1 (2)
C4*B*	0·4224 (2)	0·2899 (4)	0·1504 (2)	4·1 (2)
C5*B*	0·3518 (3)	0·3946 (3)	0·0963 (2)	4·5 (2)
C6*B*	0·2470 (2)	0·3639 (3)	0·0466 (2)	3·7 (1)
O3*B*	0·5243 (2)	0·3337 (3)	0·1985 (2)	5·6 (2)
C9*B*	0·6034 (3)	0·2288 (5)	0·2450 (3)	6·9 (3)
Compound (3)				
S	0·5000	0·0334 (1)	0·2500	3·5 (1)
C1	0·3520 (1)	0·1074 (2)	0·1155 (3)	3·4 (1)
C2	0·3091 (1)	0·1824 (2)	0·1700 (4)	4·6 (2)
C3	0·2533 (2)	0·1448 (2)	0·2302 (4)	4·8 (2)
C4	0·2414 (1)	0·0335 (2)	0·2376 (4)	4·0 (2)
C5	0·2858 (1)	−0·0404 (2)	0·1819 (4)	4·5 (2)
C6	0·3414 (1)	−0·0040 (2)	0·1207 (4)	4·1 (2)
C8	0·5104 (1)	0·1933 (2)	0·0040 (4)	3·8 (2)
C7	0·4727 (1)	0·1247 (2)	0·0970 (3)	3·1 (1)
C9	0·1403 (2)	0·0605 (3)	0·3534 (4)	5·6 (2)
C10	0·0840 (2)	−0·0080 (3)	0·3893 (5)	8·1 (3)
N1	0·4098 (1)	0·1491 (2)	0·0508 (3)	3·4 (1)
N2	0·4018 (1)	0·2231 (2)	−0·0652 (3)	4·6 (2)
O1	0·4635 (1)	0·2534 (2)	−0·0944 (2)	4·8 (1)
O2	0·5671 (1)	0·2096 (2)	−0·0009 (3)	5·3 (1)
O3	0·1879 (1)	−0·0123 (2)	0·2945 (3)	5·2 (2)

Experimental. (1) $C_{16}H_{10}N_4O_4S$, crystal 0·4 × 0·4 × 0·6 mm. CAD-4 diffractometer. Unit-cell dimensions: 25 reflections, 2θ range 17 to 31°. D_m by flotation ($CCl_4/CHCl_3$). Absorption corrections were made according to experimental ψ rotation; normalized transmission coefficients 0·97–1·00. $2\theta_{max} = 60°$. Ranges of h, k, l; −14 to 14, 0 to 10, 0 to 27, respectively. Three standard reflections monitored every 2 h: variation < 3%. 4538 unique reflections, 2922 observed with $I > 3\sigma(I)$. $R = 0·033$, $wR = 0·028$, $S = 2·30$. Weighting scheme from counting statistics. Structure solved by heay-atom method. H atoms found in difference Fourier map after isotropic refinement and then refined. $(\Delta/\sigma)_{max} = 0·37$. Peaks in final $\Delta\rho$ map



(3)

Fig. 1. The crystal structures of (1), (2) and (3).

0·24 to −0·21 e $Å^{-3}$. Extinction coefficient 1·96 (length in μm). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computing programs: NRCC *SDP PDP*-11 package (Gabe & Lee, 1981), *MULTAN* and *ORTEP* from Enraf–Nonius (1979) *Structure Determination Package.* (2) $C_{18}H_{14}N_4O_6S$, crystal 0·2 × 0·4 × 0·4 mm. Unit cell: 25 reflections, 2θ range 15 to 23°. Normalized transmission coefficients 0·97–1·00. Ranges of *h, k, l*: −20 to 20, 0 to 13, 0 to 21, respectively. 5267 unique reflections, 2066 observed with $I > 2\sigma(I)$. $R = 0·039$, $wR = 0·037$, $S = 1·63$. Structure solved by direct method using the *MULTAN* program. $(\Delta/\sigma)_{max} = 0·37$. Peaks in final $\Delta\rho$ map 0·17 to −0·18 e $Å^{-3}$. Extinction coefficient 0·302 (length in μm). Other details as for (1). (3) $C_{20}H_{18}N_4O_6S$, crystal 0·2 × 0·2 × 0·3 mm. Unit cell: 25 reflections, 2θ range 10 to 24°. D_m by flotation (CCl_4/CH_2Cl_2). Normalized transmission coefficients 0·94–1·00. Ranges of *h, k, l*: −29 to 29, 0 to 17, 0 to 11, respectively. 3004 unique reflections, 1088 observed with $I > 2\sigma(I)$. $R = 0·039$, $wR = 0·033$, $S = 1·67$. Structure solved by direct method using the *MULTAN* program, $(\Delta/\sigma)_{max} = 0·31$. Peaks in final $\Delta\rho$ map 0·15 to −0·16 e $Å^{-3}$. Extinction coefficient 0·078 (length in μm). Other details as for (1).

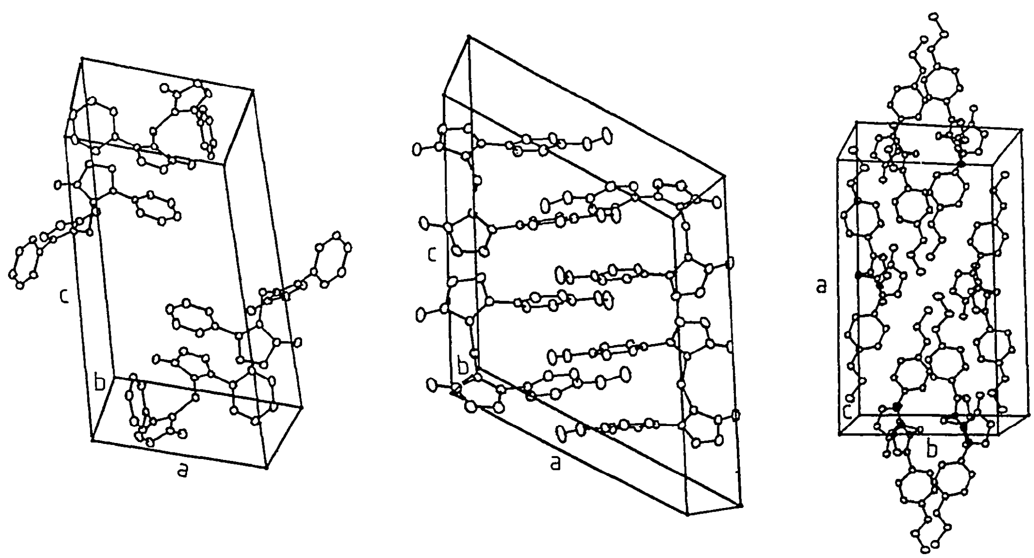
Discussion. Atomic positional parameters and equivalent isotropic temperature factors are listed in Table 1.* The molecular structures and the crystal packing diagrams are shown in Figs. 1 and 2. The bond lengths and angles are shown in Tables 2 and 3.

The bond lengths of the sydnone ring are listed in Table 4 and compared with those from other 3,4-disubstituted sydnone derivatives. The bond lengths of the sydnone ring are similar in these three title structures and comparable to those of other 3,4-disubstituted sydnone derivatives. The N(1)—C(7) bond lengths of the title compounds are 1·350 (1), 1·352 (3) and 1·358 (3) Å, respectively. As found before, the lengthening of the N(1)—C(7) bond compared with the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51476 (95 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *for* (1), (2) *and* (3)

Compound (1)								
S	C7*A*	1·736 (2)	S	C7*B*	1·735 (2)	C1*A*	C2*A*	1·373 (2)
C1*A*	C6*A*	1·381 (2)	C1*A*	N1*A*	1·452 (2)	C2*A*	C3*A*	1·382 (2)
C3*A*	C4*A*	1·369 (3)	C4*A*	C5*A*	1·370 (3)	C5*A*	C6*A*	1·383 (3)
C7*A*	C8*A*	1·412 (2)	C7*A*	N1*A*	1·347 (2)	C8*A*	O1*A*	1·409 (2)
C8*A*	O2*A*	1·204 (2)	N1*A*	N2*A*	1·308 (2)	N2*A*	O1*A*	1·380 (2)
C1*B*	C2*B*	1·376 (2)	C1*B*	C6*B*	1·377 (2)	C1*B*	N1*B*	1·445 (2)
C2*B*	C3*B*	1·377 (3)	C3*B*	C4*B*	1·369 (3)	C4*B*	C5*B*	1·383 (3)
C5*B*	C6*B*	1·378 (3)	C7*B*	C8*B*	1·408 (2)	C7*B*	N1*B*	1·352 (2)
C8*B*	O1*B*	1·402 (2)	C8*B*	O2*B*	1·205 (2)	N1*B*	N2*B*	1·307 (2)
N2*B*	O1*B*	1·383 (2)						
Compound (2)								
S	C7*A*	1·729 (3)	S	C7*B*	1·730 (3)	C7*A*	N1*A*	1·351 (4)
C7*A*	C8*A*	1·415 (4)	N1*A*	N2*A*	1·303 (3)	N1*A*	C1*A*	1·448 (3)
N2*A*	O1*A*	1·377 (3)	O1*A*	C8*A*	1·416 (3)	O2*A*	C8*A*	1·194 (3)
C1*A*	C2*A*	1·373 (4)	C1*A*	C6*A*	1·366 (4)	C2*A*	C3*A*	1·369 (4)
C3*A*	C4*A*	1·380 (5)	C4*A*	C5*A*	1·378 (4)	C4*A*	O3*A*	1·361 (4)
C5*A*	C6*A*	1·388 (4)	O3*A*	C9*A*	1·414 (5)	C7*B*	N1*B*	1·352 (4)
C7*B*	C8*B*	1·411 (4)	N1*B*	N2*B*	1·312 (3)	N1*B*	C1*B*	1·443 (3)
N2*B*	O1*B*	1·375 (3)	O1*B*	C8*B*	1·425 (4)	O2*B*	C8*B*	1·201 (4)
C1*B*	C2*B*	1·362 (4)	C1*B*	C6*B*	1·382 (4)	C2*B*	C3*B*	1·376 (4)
C3*B*	C4*B*	1·377 (5)	C4*B*	C5*B*	1·381 (5)	C4*B*	O3*B*	1·364 (4)
C5*B*	C6*B*	1·369 (4)	O3*B*	C9*B*	1·421 (5)			
Compound (3)								
S	C7	1·732 (3)				C1	C2	1·376 (4)
C1	C6	1·373 (4)	C1	N1	1·445 (4)	C2	C3	1·375 (4)
C3	C4	1·378 (4)	C4	C5	1·392 (4)	C4	O3	1·359 (4)
C5	C6	1·370 (4)	C8	C7	1·411 (4)	C8	O1	1·410 (4)
C8	O2	1·196 (4)	C7	N1	1·358 (3)	C9	C10	1·483 (5)
C9	O3	1·442 (4)	N1	N2	1·309 (3)	N2	O1	1·373 (3)



(1) (2) (3)

Fig. 2. Packing diagrams for (1), (2) and (3).

Table 3. *Bond angles* (°) *for* (1), (2) *and* (3)

Compound (1)							
C7*A*	S	C7*B*	97·38 (7)	C2*A*	C1*A*	C6*A*	122·9 (2)
C2*A*	C1*A*	N1*A*	119·1 (1)	C6*A*	C1*A*	N1*A*	117·9 (1)
C1*A*	C2*A*	C3*A*	117·9 (2)	C2*A*	C3*A*	C4*A*	120·6 (2)
C3*A*	C4*A*	C5*A*	120·4 (2)	C4*A*	C5*A*	C6*A*	120·7 (2)
C1*A*	C6*A*	C5*A*	117·5 (2)	S	C7*A*	C8*A*	127·4 (1)
S	C7*A*	N1*A*	126·5 (1)	C8*A*	C7*A*	N1*A*	106·1 (2)
C7*A*	C8*A*	O1*A*	103·7 (1)	C7*A*	C8*A*	O2*A*	134·8 (2)
O1*A*	C8*A*	O2*A*	121·5 (1)	C1*A*	N1*A*	C7*A*	129·4 (1)
C1*A*	N1*A*	N2*A*	115·7 (1)	C7*A*	N1*A*	N2*A*	115·0 (1)
N1*A*	N2*A*	O1*A*	104·2 (1)	C8*A*	O1*A*	N2*A*	110·9 (1)
C2*B*	C1*B*	C6*B*	123·0 (2)	C2*B*	C1*B*	N1*B*	117·4 (1)
C6*B*	C1*B*	N1*B*	119·5 (1)	C1*B*	C2*B*	C3*B*	118·2 (2)
C2*B*	C3*B*	C4*B*	120·2 (2)	C3*B*	C4*B*	C5*B*	120·7 (2)
C4*B*	C5*B*	C6*B*	120·3 (2)	C1*B*	C6*B*	C5*B*	117·6 (2)
S	C7*B*	C8*B*	128·1 (1)	S	C7*B*	N1*B*	125·6 (1)
C8*B*	C7*B*	N1*B*	106·3 (1)	C7*B*	C8*B*	O1*B*	103·9 (1)
C7*B*	C8*B*	O2*B*	135·2 (2)	O1*B*	C8*B*	O2*B*	120·9 (2)
C1*B*	N1*B*	C7*B*	129·6 (1)	C1*B*	N1*B*	N2*B*	115·9 (1)
C7*B*	N1*B*	N2*B*	114·4 (1)	N1*B*	N2*B*	O1*B*	104·4 (1)
Compound (2)							
C7*A*	S	C7*B*	101·0 (1)	S	C7*A*	N1*A*	126·2 (2)
S	C7*A*	C8*A*	127·8 (2)	N1*A*	C7*A*	C8*A*	106·0 (2)
C7*A*	N1*A*	N2*A*	115·4 (2)	C7*A*	N1*A*	C1*A*	129·9 (2)
N2*A*	N1*A*	C1*A*	114·7 (2)	N1*A*	N2*A*	O1*A*	104·1 (2)
N2*A*	O1*A*	C8*A*	111·3 (2)	C7*A*	C8*A*	O1*A*	103·3 (2)
C7*A*	C8*A*	O2*A*	136·0 (3)	O1*A*	C8*A*	O2*A*	120·7 (3)
N1*A*	C1*A*	C2*A*	119·1 (3)	N1*A*	C1*A*	C6*A*	118·7 (3)

Table 3 (*cont.*)

C2*A*	C1*A*	C6*A*	122·0 (3)	C1*A*	C2*A*	C3*A*	119·4 (3)
C2*A*	C3*A*	C4*A*	119·8 (3)	C3*A*	C4*A*	C5*A*	120·5 (3)
C3*A*	C4*A*	O3*A*	115·5 (3)	C5*A*	C4*A*	O3*A*	124·0 (3)
C4*A*	C5*A*	C6*A*	119·8 (3)	C1*A*	C6*A*	C5*A*	118·6 (3)
C4*A*	O3*A*	C9*A*	118·4 (3)	S	C7*B*	N1*B*	125·7 (2)
S	C7*B*	C8*B*	127·8 (2)	N1*B*	C7*B*	C8*B*	106·4 (2)
C7*B*	N1*B*	N2*B*	115·0 (2)	C7*B*	N1*B*	C1*B*	128·1 (2)
N2*B*	N1*B*	C1*B*	116·9 (2)	N1*B*	N2*B*	O1*B*	104·3 (2)
N2*B*	O1*B*	C8*B*	111·1 (2)	C7*B*	C8*B*	O1*B*	103·3 (2)
C7*B*	C8*B*	O2*B*	136·5 (3)	O1*B*	C8*B*	O2*B*	120·2 (3)
N1*B*	C1*B*	C2*B*	119·0 (3)	N1*B*	C1*B*	C6*B*	118·7 (3)
C2*B*	C1*B*	C6*B*	122·3 (3)	C1*B*	C2*B*	C3*B*	119·1 (3)
C2*B*	C3*B*	C4*B*	119·6 (3)	C3*B*	C4*B*	C5*B*	120·5 (3)
C3*B*	C4*B*	O3*B*	124·4 (3)	C5*B*	C4*B*	O3*B*	115·1 (3)
C4*B*	C5*B*	C6*B*	120·3 (3)	C1*B*	C6*B*	C5*B*	118·2 (3)
C4*B*	O3*B*	C9*B*	118·5 (3)				
Compound (3)							
C7	S	C7	100·3 (1)	C2	C1	C6	122·3 (3)
C2	C1	N1	117·8 (3)	C6	C1	N1	119·9 (3)
C1	C2	C3	118·9 (3)	C2	C3	C4	120·2 (3)
C3	C4	C5	119·5 (3)	C3	C4	O3	124·9 (3)
C5	C4	O3	115·5 (3)	C4	C5	C6	120·9 (3)
C1	C6	C5	118·2 (3)	C7	C8	O1	103·3 (2)
C7	C8	O2	135·0 (3)	O1	C8	O2	121·6 (3)
S	C7	C8	127·6 (2)	S	C7	N1	125·8 (2)
C8	C7	N1	106·4 (2)	C10	C9	O3	107·2 (3)
C1	N1	C7	128·9 (2)	C1	N1	N2	116·9 (2)
C7	N1	N2	114·2 (2)	N1	N2	O1	104·5 (2)
C8	O1	N2	111·5 (2)	C4	O3	C9	117·9 (2)

Table 4. *Comparison of selected bond lengths* (Å) *and some conformational parameters of the sydnone ring in 3,4-disubstituted compounds*

	(1)[a]	(2)[a]	(3)[a]	(4)[b]	(5)[b]	(6)[c]	(7)[d]	(8)[e]§
O(1)—C(8)	1·409 (2) 1·402 (2)	1·416 (3) 1·425 (4)	1·410 (4)	1·419 (4)	1·399 (2)	1·406 (3)	1·400 (4)	1·416 (6)
O(1)—N(2)	1·380 (2) 1·383 (2)	1·377 (3) 1·375 (3)	1·373 (3)	1·379 (3)	1·382 (2)	1·379 (2)	1·380 (4)	1·368 (5)
N(2)—N(1)	1·308 (2) 1·307 (2)	1·303 (3) 1·312 (3)	1·309 (3)	1·295 (3)	1·309 (2)	1·318 (2)	1·325 (4)	1·318 (5)
N(1)—C(7)	1·347 (2) 1·352 (2)	1·351 (4) 1·352 (4)	1·358 (3)	1·350 (3)	1·352 (2)	1·351 (2)	1·350 (4)	1·358 (6)
C(7)—C(8)	1·412 (2) 1·408 (2)	1·415 (4) 1·411 (4)	1·411 (4)	1·413 (4)	1·420 (3)	1·416 (2)	1·418 (4)	1·417 (7)
C(8)—O(2)	1·204 (2) 1·205 (2)	1·194 (3) 1·201 (4)	1·196 (4)	1·196 (3)	1·212 (2)	1·217 (2)	1·205 (4)	1·196 (6)
C(7)—C(9)				1·444 (2)	1·453 (4)	1·465 (3)	1·464 (4)	1·429 (6)
S—C(7)	1·736 (2) 1·735 (2)	1·729 (3) 1·730 (3)	1·732 (3)					
Δ[O(2)]*	0·047 (3) 0·015 (3)	0·037 (5) 0·029 (5)	0·044 (4)	0·011 (6)	0·001 (3)	0·041 (2)	0·013 (2)	0·019 (4)
Δ[S]†	0·053 (3) 0·045 (3)	0·078 (5) 0·100 (5)	0·055 (4)					
ω(°)	53·7 (1) 62·8 (1)	51·0 (1) 59·2 (1)	53·5 (1)	68·4 (2)	78·6 (1)	54·9	63·8	63·0 (2)
χ^2‡	84·5 43·4	7·1 41·4	37·0	5·4	16·4	195·6	21·1	0·7
Color	Light brown	Transparent	Transparent	Brown	Light brown	Transparent	Bright yellow	Light brown

References: (*a*) this work; (*b*) Ueng, Wang & Yeh (1987*a*); (*c*) Hašek, Obrda, Kuml, Nešpůrek, Chojnacki & Šorm (1978); (*d*) Hašek, Obrda, Kuml, Nešpůrek & Šorm (1979); (*e*) Ueng, Wang & Yeh (1987*b*).

* Deviation (Å) of O(2) the mean plane of the sydnone ring.

† Deviation (Å) of S from the mean plane of the sydnone ring.

‡ χ^2 is defined as $\sum_{i=1}^{n} \Delta d_i^2/(\sigma_x^2 + \sigma_y^2 + \sigma_z^2)$ as in (*b*).

§ (4) 4-acetyl-3-(*p*-tolyl)sydnone; (5) 4-acetyl-3-phenylsydnone oxime; (6) 4-(3-methyl-1-buten-2-yl)-3-phenylsydnone; (7) 4-(cyclohexen-1-yl)-3-phenylsydnone; (8) 3-phenyl-4-(*N*-carbamoyl-1,4,2-oxathiazolimin-3-yl)sydnone.

corresponding bond in 3,4-disubstituted sydnone derivatives may also be attributed to the steric effect (Ueng, Wang & Yeh, 1987*a,b*).

The bond lengths (S—C), bond angles (CSC′) and the angles between the CSC′ plane and the sydnone ring of the title compounds and other diaryl sulfides are comparable (Von Deuten & Klar, 1981). There is no apparent trend in such bond lengths. A π interaction between the S atom and the sydnone ring would be expected if the CSC plane and the aryl ring were coplanar. However, this is not obvious; as an example 4-(dimethylamino)phenyl 4-nitrophenyl sulfide (Von Deuten & Klar, 1981) does have one of the aryl rings which is coplanar with the CSC plane, but both S—C lengths are about the same. The shortening of the S—C bonds of the title compounds relative to those of other diaryl sulfides and the average bond lengths of 1,3,5-trithiane [1·818 (5) Å (Fleming & Lynton, 1967)] may be attributable to orbital eletronegativity effects.

The C(7)—S(1)—C(7′) bond angles of the title compounds [97·4 (1), 101·0 (1) and 100·3 (1)°] are comparable with corresponding angles in the cyclic 1,3,5-trithane [99·2 (6) and 100·7 (5)°]. The dihedral angles (ω) between the sydnone ring and the phenyl ring are listed in Table 4 for 3,4-disubstituted compounds. It is certainly clear that all such compounds have angles greater than 50°.

Compound (3) has exact C_2 molecular symmetry bisecting the C—S—C′ angle which coincides with the crystallographic twofold axis along the *b* axis. Compound (1) has a pseudo twofold axis; the two sydnone-aryl parts of the compound are essentially the same. However, compound (2) adopts a quite different conformation from those of the other two compounds. The difference can be seen clearly in Fig. 1. The packing in the crystal is also quite different (Fig. 2).

Instead of the 'morino' conformation (Von Deuten & Klar, 1981) with one ring in the C—S—C′ plane and the other perpendicular, as found in most other diaryl sulfides, the three title compounds have the butterfly conformation [61·7 (1), 59·3 (1); 88·1 (1), 73·6 (1); 72·9 (1), 72·9 (1)°, respectively].

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Structures of two Psychoactive 1,4-Benzodiazepines

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Abstract. (I) 8-Chloro-6-(2-chlorophenyl)-2-methyl-4*H*-imidazo[1,2-*a*][1,4]benzodiazepine, $C_{18}H_{13}Cl_2N_3$, $M_r = 342{\cdot}2$, monoclinic, $P2_1/c$, $a = 13{\cdot}168$ (3), $b = 14{\cdot}852$ (3), $c = 8{\cdot}286$ (2) Å, $\beta = 94{\cdot}45$ (2)°, $V = 1615{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}407$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}95$ cm^{-1}, $F(000) = 704$, $T = 293$ K, $R = 0{\cdot}042$ for 796 observed reflections. (II) 8-Chloro-6-(2-chlorophenyl)-1-(4-pyridyl)-1,2,4-triazolo[4,3-*a*][1,4]benzodiazepine, $C_{21}H_{13}Cl_2N_5$, $M_r = 406{\cdot}3$, orthorhombic, *Pbca*, $a = 21{\cdot}560$ (3), $b = 8{\cdot}790$ (1), $c = 19{\cdot}866$ (5) Å, $V = 3764{\cdot}9$ Å^3, $Z = 8$, $D_x = 1{\cdot}434$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}5$ cm^{-1}, $F(000) = 1664$, $T = 293$ K, $R = 0{\cdot}042$ for 2196 observed reflections. The angle between the mean planes of the chlorophenyl ring and the fused benzo moiety is 77 (1)° in (I) and 78 (1)° in (II). The seven-membered heterocyclic ring adopts a cycloheptatriene-like boat conformation with bow and stern angles of 55 (1) and 33 (1)° in (I), and 53·4 (7) and 34·3 (7)° in (II). In both compounds the five-membered heterocyclic ring and the two aromatic rings are each planar to within ±0·02 Å. Bond lengths and angles are normal.

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