pound, however, the N^4 atoms are involved in the coordination of copper and, while all the N^1—H groups contribute to the bridge system, only half of the potential hydrogen-bond acceptor N^2 atoms are involved in hydrogen bridges.

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Structure of 3,4-Bis(phenylthio)cyclobutene-1,2-dione

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Abstract. $C_{16}H_{10}O_2S_2$, $M_r = 298{\cdot}4$, monoclinic, $C2/c$, $a = 19{\cdot}555\,(2)$, $b = 9{\cdot}082\,(1)$, $c = 16{\cdot}719\,(2)$ Å, $\beta = 109{\cdot}0\,(3)°$, $V = 2808\,(5)$ Å^3, $Z = 8$, $D_m = 1{\cdot}400$ g cm^{-3}, $D_x = 1{\cdot}411$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}23$ cm^{-1}, $F(000) = 1232$, $T = 293$ K, final $R = 0{\cdot}050$ for 1925 observed reflexions $[I > 2{\cdot}5\sigma(I)]$, 3387 unique reflexions. The lack of reactivity of the title compound in Diels–Alder cycloadditions is related to the steric hindrance at the C—C double bond. The molecule has a non-symmetric conformation, the two phenyl rings being almost orthogonal to the cyclobutenedione ring.

Introduction. Vinyl sulfides geminally substituted with electron-withdrawing groups are usually very reactive dienophiles in Diels–Alder cycloadditions (De Lucchi & Pasquato, 1988). Their reactivity is higher not only with respect to vinyl sulfide but also with respect to electron-deficient olefins (De Lucchi & Pasquato, 1988; Knapp, Lis & Michna, 1981; Boucher & Stella, 1986). Following our interest in the reactivity of sulfur-substituted olefins in Diels–Alder reactions, we have synthesized the hitherto unknown bis(phenylthio)cyclobutenedione [(1), R = SPh] and tested its reactivity in [4 + 2] cycloaddition reactions. Surprisingly, compound (1) proved to be unreactive in Diels–Alder cycloaddition, also with very reactive dienes such as cyclopentadiene or butadiene (generated *in situ* from 3-sulfolene), and even in the presence of Lewis acids ($AlCl_3$), in contrast to the corresponding electron-deficient olefin, *i.e.* cyclobutene-1,2-dione [(2), R = H], which is a very reactive dienophile, because of

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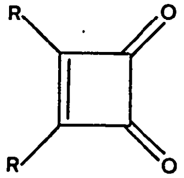
both inductive and mesomeric effects and ring strain (Albert, Heller, Iden, Martin, Martin, Mayer & Oftring, 1985).

It was of interest to determine the crystal structure of (1) in order to relate its molecular geometry to its lack of reactivity.



(1) R = SPh

(2) R = H

(3) R = Cl

Experimental. (1) was prepared by reaction of 3,4-dichlorocyclobutene-1,2-dione [(3), R = Cl] (De Selms, Fox & Riordan, 1970) with thiophenol in the presence of triethylamine; after standard work up, the desired product was obtained as pale-yellow needles by crystallization from dichloromethane/n-pentane in 52% yield, m.p. 422–424 K, elemental analysis for $C_{16}H_{10}O_2S_2$: calculated: C = 64·41, H = 3·38; found: C = 64·51, H = 3·36%; IR (KBr): (ν, cm^{-1}) 1804, 1755, 1739, 1439, 1138, ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 7·33–7·59 (m). D_m measured at 293 K by flotation. Pale-yellow crystal, approximate dimensions 0·12 × 0·12 × 0·3 mm recrystallized from dichloromethane/n-pentane, mounted on a Philips PW 1100 four-circle diffractometer. Lattice parameters were measured with 25 reflections in the range $8 < \theta < 12°$. No absorption corrections were applied. Maximum value of 2θ was 50°. Range of $\pm h, k, l$ to 24, 12 and 19. Three standard reflections, 241, $\bar{4}22$ and $\bar{2}23$, and their intensity variations were checked with no variation over 10%. 3493 reflexions measured, with 3387 unique reflexions, $R_{\rm int} = 0·02$, 1462 unobserved reflexions, $I < 2·5\sigma(I)$.

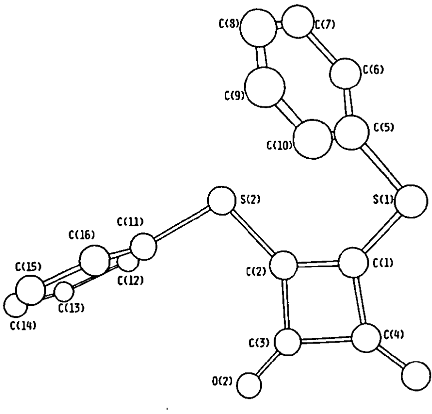


Fig. 1. The molecular conformation of (1), showing the atomic numbering.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$U_{\rm eq}$
S(1)	8003 (1)	2968 (1)	3303 (1)	5·45
S(2)	6385 (1)	562 (1)	3065 (1)	5·83
O(1)	8778 (2)	1394 (4)	5272 (2)	7·03
O(2)	7368 (2)	−642 (4)	5196 (2)	7·75
C(1)	7765 (2)	1706 (4)	3923 (2)	4·23
C(2)	7177 (2)	826 (4)	3871 (2)	4·21
C(3)	7526 (2)	208 (5)	4742 (3)	5·22
C(4)	8188 (2)	1170 (5)	4785 (3)	5·06
C(5)	7155 (2)	3256 (5)	2499 (2)	4·49
C(6)	7018 (2)	2610 (5)	1716 (3)	5·12
C(7)	6351 (3)	2808 (6)	1105 (3)	6·18
C(8)	5836 (3)	3664 (6)	1275 (3)	6·66
C(9)	5975 (3)	4316 (6)	2058 (3)	6·55
C(10)	6645 (2)	4136 (5)	2667 (3)	5·50
C(11)	5871 (2)	−603 (5)	3516 (2)	4·42
C(12)	5966 (2)	−2097 (5)	3542 (3)	5·51
C(13)	5519 (3)	−2984 (6)	3826 (3)	6·25
C(14)	4973 (3)	−2373 (7)	4057 (3)	6·15
C(15)	4871 (3)	−882 (7)	4023 (3)	6·85
C(16)	5321 (3)	23 (6)	3753 (3)	6·06

Structure solved by direct methods using the *MULTAN*80 program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Refinement based on F, full-matrix least squares, anisotropic for non-H atoms, $w = 1$. H atoms were located on a ΔF map, and isotropically refined. 221 parameters were refined and maximum least-squares shift to e.s.d. = 0·5. Usual R value = 0·0504, S = 1·6. In final ΔF synthesis, maximum height = 0·34 and minimum = −0·32 e Å^{-3}. Computer program used: *SHELX*76 (Sheldrick, 1976), and atomic scattering factors reported therein.*

Discussion. Fig. 1 shows the molecular conformation of (1). Final atomic coordinates for non-H atoms are in Table 1. The bond lengths and the valence angles are listed in Table 2. Torsion angles that describe the planarity of the cyclobutenedione ring, and the relative orientations of the aromatic rings, can also be found in Table 2. The hybridization of C(1) and C(2) appears from their bond lengths to be sp^2. It is interesting to observe that (1) adopts a non-symmetric conformation, with the two aromatic rings almost orthogonal to the cyclobutenedione ring. In particular, there is a short distance between S(2) and the aromatic ring not bonded to it; indeed, the distances between S(2) and the atoms C(5) to C(10) vary between 3·174 (5) and 3·994 (7) Å. It is also interesting to note the interatomic distances between C(1) and C(5), 2·687 (7) Å, and between C(2) and C(5), 3·173 (5) Å. These conformational characteristics account for steric hindrance at the C(1)—C(2)

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* 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 51442 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

S(1)—C(1)	1·708 (4)	S(1)—C(5)	1·781 (7)
S(2)—C(2)	1·706 (7)	S(2)—C(11)	1·876 (5)
O(1)—C(4)	1·193 (6)	O(2)—C(3)	1·191 (6)
C(1)—C(2)	1·379 (6)	C(1)—C(4)	1·490 (7)
C(2)—C(3)	1·501 (6)	C(3)—C(4)	1·543 (6)
C(5)—C(6)	1·378 (6)	C(5)—C(10)	1·376 (6)
C(6)—C(7)	1·381 (7)	C(7)—C(8)	1·373 (8)
C(8)—C(9)	1·380 (7)	C(9)—C(10)	1·382 (7)
C(11)—C(12)	1·368 (6)	C(11)—C(16)	1·383 (8)
C(12)—C(13)	1·381 (8)	C(13)—C(14)	1·365 (9)
C(14)—C(15)	1·367 (9)	C(15)—C(16)	1·382 (8)
C(1)—S(1)—C(5)	100·7 (3)	C(2)—S(2)—C(11)	103·9 (2)
S(1)—C(1)—C(4)	129·1 (4)	S(1)—C(1)—C(2)	137·4 (3)
C(2)—C(1)—C(4)	93·4 (4)	S(2)—C(2)—C(1)	130·8 (3)
C(1)—C(2)—C(3)	92·8 (4)	S(2)—C(2)—C(3)	136·2 (4)
O(2)—C(3)—C(2)	136·8 (6)	C(2)—C(3)—C(4)	86·7 (4)
O(2)—C(3)—C(4)	136·4 (5)	O(1)—C(4)—C(3)	137·5 (5)
O(1)—C(4)—C(1)	135·4 (6)	S(1)—C(5)—C(10)	119·3 (3)
S(1)—C(5)—C(6)	119·9 (5)	C(6)—C(5)—C(10)	120·7 (5)
C(5)—C(6)—C(7)	119·4 (5)	C(6)—C(7)—C(8)	120·0 (5)
C(7)—C(8)—C(9)	120·5 (7)	C(8)—C(9)—C(10)	119·6 (6)
C(5)—C(10)—C(9)	119·6 (5)	S(2)—C(11)—C(16)	118·3 (4)
S(2)—C(11)—C(12)	120·7 (5)	C(12)—C(11)—C(16)	120·5 (6)
C(11)—C(12)—C(13)	119·6 (5)	C(12)—C(13)—C(14)	120·0 (5)
C(13)—C(14)—C(15)	120·5 (7)	C(14)—C(15)—C(16)	120·1 (7)
C(11)—C(16)—C(15)	119·0 (6)		
S(1)—C(1)—C(2)—S(2)	3·5 (12)	S(1)—C(1)—C(4)—O(1)	−1·8 (13)
S(2)—C(2)—C(3)—O(2)	−3·5 (14)	O(2)—C(3)—C(4)—O(1)	1·6 (16)
C(5)—S(1)—C(1)—C(2)	11·5 (9)	C(11)—S(2)—C(2)—C(3)	8·4 (9)
C(1)—S(1)—C(5)—C(10)	77·6 (6)	C(2)—S(2)—C(11)—C(16)	103·0 (6)

double bond which can explain the observed lack of reactivity.

The molecules are held in the crystal by van der Waals forces. The packing of the molecules in the unit cell is illustrated in Fig. 2.

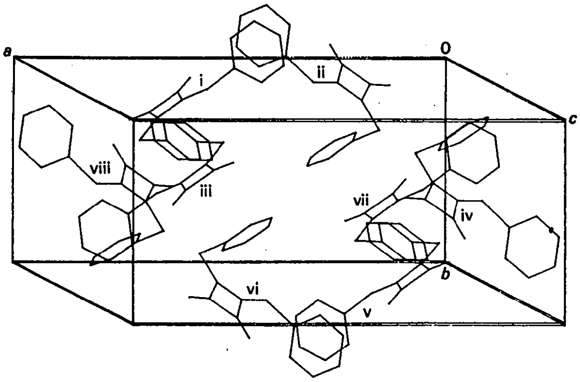

Fig. 2. Packing diagram of the contents of the unit cell. (i) x, y, z; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $1-x, 1-y, 1-z$; (vi) $x, 1-y, \frac{1}{2}+z$; (vii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (viii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

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Structure of *N*-Phosphonomethyl-L-proline

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Abstract. $C_6H_{12}NO_5P$, $M_r = 209{\cdot}15$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}623$ (2), $b = 7{\cdot}857$ (2), $c = 19{\cdot}635$ (5) Å, $V = 867{\cdot}5$ (4) Å^3, $Z = 4$, $D_m = 1{\cdot}60$ (1), $D_x = 1{\cdot}60$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}32$ mm^{-1}, $F(000) = 440$, $T = 293$ K, $R = 0{\cdot}038$ for 1009 reflexions with $I > 1{\cdot}96\sigma(I)$. The title compound was prepared by reaction of the sodium salt of L-proline, formaldehyde and diethylphosphite. The molecule exists as a zwitterion; the amino group is protonated and the carboxyl group is un-ionized, the phosphonic acid group being ionized. The pyrrolidine ring adopts a half-chair [$\Delta C_2 = 2{\cdot}8$ (7)°] conformation.

Introduction. *N*-Phosphonomethyl-L-proline (2) was prepared in the course of our work on the synthesis and

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