Crystal Structure and Conformation of 3-[Bis(methylthio)methylene]-pentane-2,4-dione

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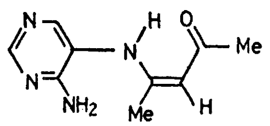
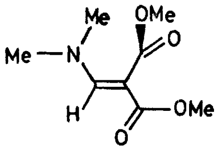
3-[Bis(methylthio)methylene]pentane-2,4-dione (3) crystallises in space group $P2_12_12$, Z = 2, with a = 8.05(1), b = 7.97(1), c = 8.10(1) Å. The molecule is slightly twisted about the axis of the carbon double bond, while its two acyl groups take up a highly twisted *E,E*-conformation. This latter feature is shown to explain certain unusual features in its i.r. spectrum, which is contrasted with those characteristic of other conformations. It is concluded on spectroscopic evidence that the *E,E*-conformation is also found for this molecule in solution. The structure was determined from diffractometer data and refined to R 0.045 for 731 observed intensities.

CONJUGATION between a carbonyl group and a carbon double-bond is maximal if the two groups are coplanar. In the absence of steric constraints one might therefore expect coplanarity for compounds such as (1), where indeed the pyrimidine ring and the ethylenic unit subtend intersecting planes.[1] Furthermore, our i.r. studies on compounds of this and related types have revealed certain regularities, *e.g.* additive rules for double-bond frequency,[2] which are difficult to explain unless a close approach to planarity represents the norm.

Such coplanarity, while equally favourable on energetic grounds, is much more problematical for 1,1-diacylethylenes, where steric interactions may force one or both carbonyl groups out of plane. Few relevant crystal structures are known: an exception is the amino-derivative (2), in which the carbon double-bond and the *trans*-carbonyl group are planar as shown, the *cis*-ester group being inclined at an angle of 68° to the molecular plane.[3] We are interested in the conformations of such compounds and the extent to which these can be assigned by examination of their i.r. spectra.[4] A consistent picture has emerged from these studies,[5] marred chiefly by anomalies connected with the dithio-derivative (3).[6] Its solution i.r. spectrum fits no pattern seen elsewhere, while its solid-state spectrum is different again and still more unexpected. Accordingly, the crystal structure of (3) has been determined.



(1)



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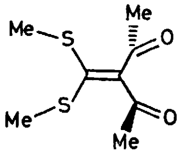


(3)

EXPERIMENTAL

Crystallographic.—*Crystal data.* $C_8H_{12}O_2S_2$, M = 204.3, Orthorhombic, a = 8.05(1), b = 7.97(1), c = 8.10(1) Å, U = 519(1) Å^3, D_c = 1.31 g cm^{-3}, Z = 2. Mo-K_α radiation, λ = 0.710 7 Å; μ(Mo-K_α) = 4.18 cm^{-1}. Space group $P2_12_12_1$.

After preliminary X-ray photographs to determine space group and crystal quality, accurate cell-dimensions and intensity data were measured on a Picker card-controlled four-circle diffractometer ($2\theta \leqslant 50°$) with niobium-filtered Mo-K_α radiation for a crystal *ca.* 0.25 × 0.25 × 0.75 mm. A total of 746 independent reflections was observed. The trial structure determined by direct methods was refined isotropically by full-matrix least squares, the 731 observed intensities having $I \geqslant 3\sigma(I)$, to R 0.122. The ethylenic carbon atoms lie on the two-fold axis parallel to c, and the other atoms in general positions. Refinement of non-hydrogen atoms with anisotropic thermal parameters for atoms except C(1), C(2) (Figure 1) reduced R to 0.068. Inclusion of hydrogen atoms as rigid rotatable methyl groups assuming C–H 1.08 Å resulted in R 0.045. One least-squares variable was allotted to each methyl group, as a common U value for the hydrogen atoms of that group; the final weighting factor was $w = 3.76/[\sigma^2(F) + 0.006F^2]$. A final difference synthesis had no features >0.17e. All calculations after the initial intensity processing were done by use of SHELX.[7]

The molecule, with bond-lengths and -angles, is shown in Figure 1, and a projection down the axis of the ethylenic double-bond in Figure 2. Figure 3 gives an impression of the intermolecular packing. Positional parameters are given in Table 1 and torsion angles in Table 2. Observed

TABLE 1

Final positional (× 10^4) parameters, with estimated standard deviations in parentheses

	x/a	y/b	z/c
C(1)	0	0	557(7)
C(2)	0	0	2 225(7)
C(3)	8 858(5)	1 053(5)	3 251(7)
C(4)	7 044(5)	612(7)	3 270(6)
H(1)	6 964	−126	2 154
H(2)	6 132	1 605	3 230
H(3)	6 809	−180	4 325
C(5)	7 763(9)	476(7)	−2 055(7)
H(4)	7 388	1 410	−2 946
H(5)	6 681	8	−1 415
H(6)	8 374	−547	−2 683
S	8 944(1)	1 604(1)	−505(1)
O	9 422(5)	2 152(5)	4 120(5)

TABLE 2

Torsion angles (°)

O–C(3)–C(2)–C(3′)	65
C(3)–C(2)–C(1)–S	14
S′–C(1)–S–C(5)	47

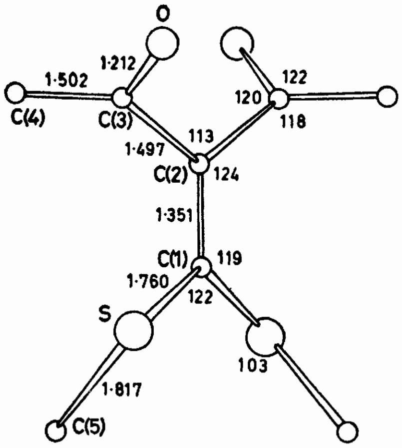


FIGURE 1 The crystal structure of (3) showing bond-lengths (Å) and angles (°); estimated standard deviations are *ca.* 0.005 Å and 0.4°

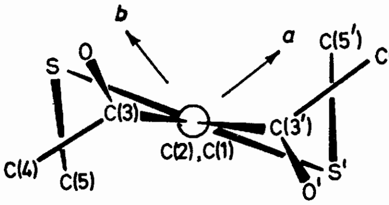


FIGURE 2 View down the two-fold axis (crystallographic *c* axis)

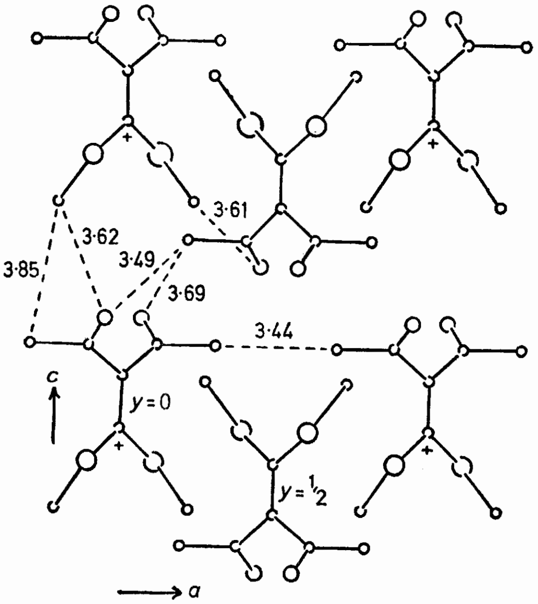


FIGURE 3 Details of the intermolecular packing

and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22425 (7 pp.).*

Spectroscopic.—I.r. spectra were obtained as described previously.[2] Figure 4 contrasts the solid-state and solution spectra of (3) with the spectrum of the diester (4) [8] in solution.

The 100 MHz ^{1}H n.m.r. spectrum of (3) in CDCl$_3$ consists of two sharp singlets of equal intensity at δ 2.38 and 2.42 p.p.m., neither of which resolves at low temperatures.

DISCUSSION

The i.r. spectrum of (3) in Nujol (Figure 4) shows strong overlapping ν(CO) bands as a doublet at 1 688 and 1 673 cm^{-1} with a medium-strength carbon double-bond vibration at 1 544 cm^{-1}. In other symmetrical compounds we find a separation between ν(CO) for nominally equivalent carbonyl groups of 30 cm^{-1} or more, the lower band always being the stronger,[5] as in (4), with bands at 1 720m and 1 674s cm^{-1} (for Nujol). This pattern results sometimes from coupling, sometimes from differences in conjugation or conformation; [5] either way, the low separation found for (3) is anomalous. It can be understood in terms of the crystal structure: while the two carbonyl groups occupy identical environments, the angle between the lines C(3)=O and C(3′)=O′ (109°) is such as to minimise coupling, which should pass through zero at an angle of 90°.

Increased conjugation in solution is demonstrated by the drop in carbon double-bond frequency to near 1 480 cm^{-1}. At *ca.* 1 690 and 1 660 cm^{-1} the separation of the carbonyl frequencies is now normal, but the upper band is the stronger, which feature is also unique. It is found however for the imide (5), whose solid-state conformation is as shown,[9] with carbonyl bands at 1 740s and 1 681m cm^{-1} in the solid state.[10] We speculate therefore that the twisted *E*,*E*-conformation found for (3) in the solid state becomes much more nearly planar in solution. On the imide analogy, either of the alternative conformations should result in

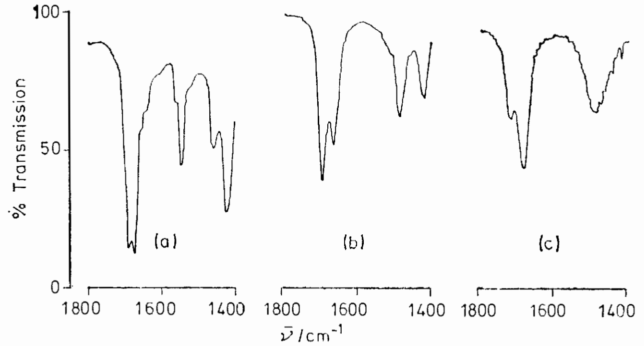
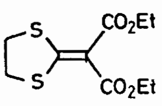
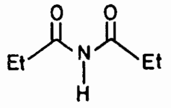


FIGURE 4 I.r. spectra of: (a), (3) in Nujol; (b), (3) in CCl$_4$; (c), (4) in CCl$_4$



(4)



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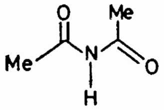

(6)

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1978, Index issue.

the reversed intensity order shown by (4); *cf.* succinimide[11] with bands at 1 772m and 1 700vs cm^{-1}, and the imide (6),[12] which possesses the *Z*,*E*-conformation and bands at 1 736m and 1 701vs cm^{-1} (both spectra for the solid state).

Dipolar repulsion is at a maximum in the *E*,*E*-conformation, which may account for its rarity among 1,1-diacylethylenes.[5] Nevertheless it is well established for carboxylic anhydrides[13] and diacyl sulphides,[14] so cannot be ruled out *a priori* on those grounds. The approach to this conformation exhibited by (3) in the solid state is not an artefact of the crystal packing, since there are no specially short contacts (see Figure 3) and nothing to suggest intermolecular charge-transfer complex formation. Since the methyl group occupies more space than does the carbonyl, it is possible that coplanarity would be even more difficult to attain in the *Z*,*Z*- or *Z*,*E*-conformations than in the *E*,*E*-conformation to which, on the foregoing evidence, (3) approximates. However, ethoxy-groups pack more readily than methyl, so this problem is less acute for diesters such as (4) which form the main class of compounds we have examined,[5] and either of the alternative conformations becomes more probable.

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