Crystal and Molecular Structure of the Enol Form of 1,1′-Diphenyl-2,2′-dithiobis(butane-1,3-dione)

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The crystal structure of the title compound has been determined by *X*-ray diffraction methods. Crystals are orthorhombic, space group *Pcab*, with $Z = 8$ in a unit cell of dimensions: $a = 26.708(1)$, $b = 18.917(7)$, $c = 7.591(1)$ Å. The structure was solved by the heavy-atom method and refined by full-matrix least squares to a final R of 0.072 for 2 218 observed reflections. The butane-1,3-dione groups are planar and the phenyl groups lie at 47.8 and 50.3° to these planes. The distances between the oxygen atoms within the butanedione groups are 2.374 and 2.436 Å, indicating strong, intramolecular hydrogen bonds. The compound is in fact better named 3,3′-dihydroxy-3,3′-diphenyl-2,2′-dithiobisbut-2-en-1-one. S(1)–S(2) is 2.078 ± 0.005 Å and the dihedral angle, C(5)–S(2)–S(1)–C(17), is 66.4°.

SEVERAL structural investigations of the enol forms of various β-diketones have been reported. These compounds are of interest because they have short, intramolecular hydrogen bonds of the form O · · · H · · · O and there is strong evidence that some of them contain a non-statistical, asymmetric hydrogen bond and exist predominantly in one of the two possible enol forms. For dibenzoylmethane, Williams [1] found that the hydrogen bond is asymmetric whereas a recent *X*-ray analysis [2] indicates a symmetric hydrogen bond. A neutron analysis currently being undertaken [3] confirms the asymmetry of the hydrogen bond. For tetra-acetylethane, the original *X*-ray analysis [4] did not provide an answer to the type of hydrogen bonding, but a later neutron-diffraction study [5] established the asymmetric form and a more accurate *X*-ray analysis [6] agrees with this. *X*-Ray [7] and

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[1] D. E. Williams, *Acta Cryst.*, 1966, **21**, 340.

[2] F. J. Hollander, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1973, **B29**, 1552.

[3] R. D. G. Jones, personal communication, 1974.

[4] J. P. Schaefer and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1966, 588.

[5] L. F. Power, K. E. Turner, and F. H. Moore, *J. Cryst. Mol. Struct.*, 1975, **5**, 59; *Inorg. Nuclear Chem. Letters*, 1972, **8**, 313.

[6] L. Reid and J. P. Schaefer, personal communication, 1972.

[7] L. F. Power and R. D. G. Jones, *Acta Cryst.*, 1971, **B27**, 181.

neutron-diffraction[8] analyses have shown that 3,3′-trithiobis(pentane-2,4-dione) also has an asymmetric hydrogen bond. Semmingsen,[9] who recently determined the molecular structure of benzoylacetone by *X*-rays showed the hydrogen bond to be asymmetric and this has been confirmed by a neutron-diffraction analysis by Jones,[3] who has also shown by *X*-ray that in thenoyltrifluoroacetone the hydrogen bond is also asymmetric and that the hydrogen atom lies nearest the carbonyl oxygen atom adjacent to the trifluoromethyl group.

Even though bis-(*m*-bromobenzoyl)methane[10] and bis-(*m*-chlorobenzoyl)methane[11] have short intramolecular hydrogen bonds, the bond is symmetrical and the compounds exist as the resonance hybrid of the two possible enolic forms. Studies are currently under way[3] to establish the nature of the hydrogen bonding in *p*-nitro- and *p*-bromo-benzoylacetone.

Reaction of sulphur chlorides (SCl_2, S_2Cl_2) with benzoylacetone[12] results in the formation of sulphur-bridged bis-(β-diketones), which are useful in the formation of co-ordination polymers.[13] On the basis of i.r. and ^1H n.m.r. spectra, the title compound has been shown to be enolised with the formation of strong intramolecular hydrogen bonds.[14] This crystal structure analysis was carried out to determine the nature of the hydrogen bonding and the stereochemistry of the sulphide linkage, and it has shown the presence of a short, asymmetric hydrogen bond and one enol form. The compound should be more correctly named 3,3′-dihydroxy-3,3′-diphenyl-2,2′-dithiobis(but-2-en-1-one).

EXPERIMENTAL

Crystal Data.—$C_{20}H_{18}O_4S_2$, $M = 386.3$. Orthorhombic $a = 26.708(1)$, $b = 18.917(7)$, $c = 7.591(1)$ Å, $U = 3\,853$ Å^3, $D_m = 1.36$ (by flotation), $Z = 8$, $D_c = 1.34$, $F(000) = 1\,616$. Cu-K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 26.2$ cm^{-1}. Space group *Pcab*.

The compound was prepared by the method of ref. 12 and, after several recrystallizations from ethanol, needle-shaped yellow crystals were grown by sublimation at 30 °C and 0.01 mmHg pressure. Weissenberg photographs taken with Cu-K_α radiation established the orthorhombic space group *Pcab* by systematic absences.

A crystal measuring 0.40 × 0.21 × 0.09 mm was mounted with the *b*-axis coincident with the ϕ axis of a card-controlled Picker diffractometer. Cell dimensions were determined from high-angle reflections by use of Cu-K_α radiation. Intensity data were collected with nickel-filtered Cu-K_α radiation by the θ—2θ scan method, each reflection being scanned 2° in 2θ at 2° min^{-1}. At each end of the scan range, the background scattering was recorded for 15 s. Two standard reflections monitored regularly showed no significant variation in intensity throughout data collection. In this manner, data for 3 255 distinct reflections in the copper sphere were recorded.

Each intensity was corrected for background and the Lorentz-polarization factor. No absorption correction was applied. If the net count for a reflection was $< 3\sigma$ [$\sigma = \{C_T + 4(B_1 + B_2)\}^{\frac{1}{2}}$, C_T = total count, B_1 and B_2 are the background counts], the reflection was considered unobserved. The number of observed reflections was 2 218. A Wilson plot[15] was determined to obtain an approximate absolute scale factor and overall temperature factor.

Structure Determination.—No sulphur–sulphur vector could be unambiguously located in an unsharpened Patterson map. However sulphur positions could be determined from a sharpened, origin-removed vector map using $E^2 - 1$ as Patterson coefficients. Successive interactions of structure-factor calculations and electron-density syntheses allowed location of all non-hydrogen atoms; *R* was 0.38. Refinement of atomic parameters by block-diagonal least-squares methods, allowing each atom an isotropic temperature factor and each reflection unit weight, reduced *R* to 0.16. Further refinement with anisotropic thermal parameters for all non-hydrogen atoms and with reflections weighted according to $w = (0.082|F_o| + 0.0114|F_o|^2)^{-1}$ caused convergence to *R* 0.072 and *R*′ 0.123. In the final cycles, full-matrix least-squares methods were used.

A final electron-density difference map allowed location of all 18 hydrogen atoms. In the final refinement the hydrogen positions were not refined and were assigned the isotropic temperature factors of the atoms to which they are bonded.

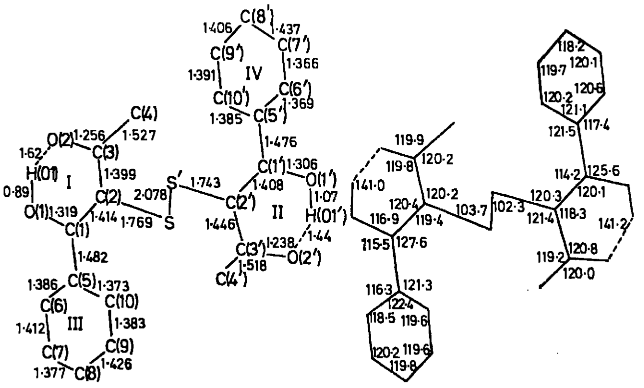

FIGURE 1 Bond lengths (Å) and angles (°)

Scattering factors for sulphur, oxygen, and carbon were taken from ref. 16, and for hydrogen from ref. 17. Final observed and calculated structure factors, and thermal parameters are listed in Supplementary Publication No. SUP 21491 (7 pp.).*

DISCUSSION

Final positional parameters are shown in Table 1, and bond lengths and angles in Figure 1; estimated standard

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[8] L. F. Power, K. E. Turner, R. D. G. Jones, and F. H. Moore, *J. Cryst. Mol. Struct.*, 1975, **5**, 125

[9] D. Semmingsen, *Acta Chem. Scand.*, 1972, **26**, 143.

[10] D. E. Williams, W. L. Dumke, and R. E. Rundle, *Acta Cryst.*, 1962, **15**, 627.

[11] G. R. Engebretson and R. E. Rundle, *J. Amer. Chem. Soc.*, 1964, **86**, 574.

* See Notice to Authors No. 7, in *J.C.S. Perkin* II, 1974, Index issue.

[12] V. Vaillant, *Bull. Chem. Soc. Paris*, 1898, **19** (*III*), 833.

[13] L. F. Power and R. D. G. Jones, *Austral. J. Chem.*, 1971, **24**, 735.

[14] R. D. G. Jones, Ph.D. Thesis, University of Queensland, 1969.

[15] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[16] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[17] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

deviations for bond lengths and angles are *ca.* 0.008 Å and 0.5°. Molecular geometry is shown in Figure 2, and crystal packing in Figure 3.

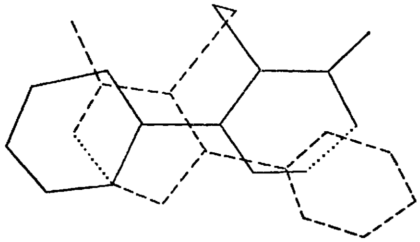

FIGURE 2 A projection of the molecule on the *bc* plane, with one half of the molecule (full lines) above the other half (dashed lines). The hydrogen bonds are shown as dotted lines

The molecule consists of the enol forms of two benzoylacetone moieties joined together at the medial carbon of each enol ring by a disulphide bridge. With respect to the disulphide linkage, the organic groups are arranged *cis* whereas the phenyl groups are arranged *trans* with respect to C(2)–S–S′–C(2′).

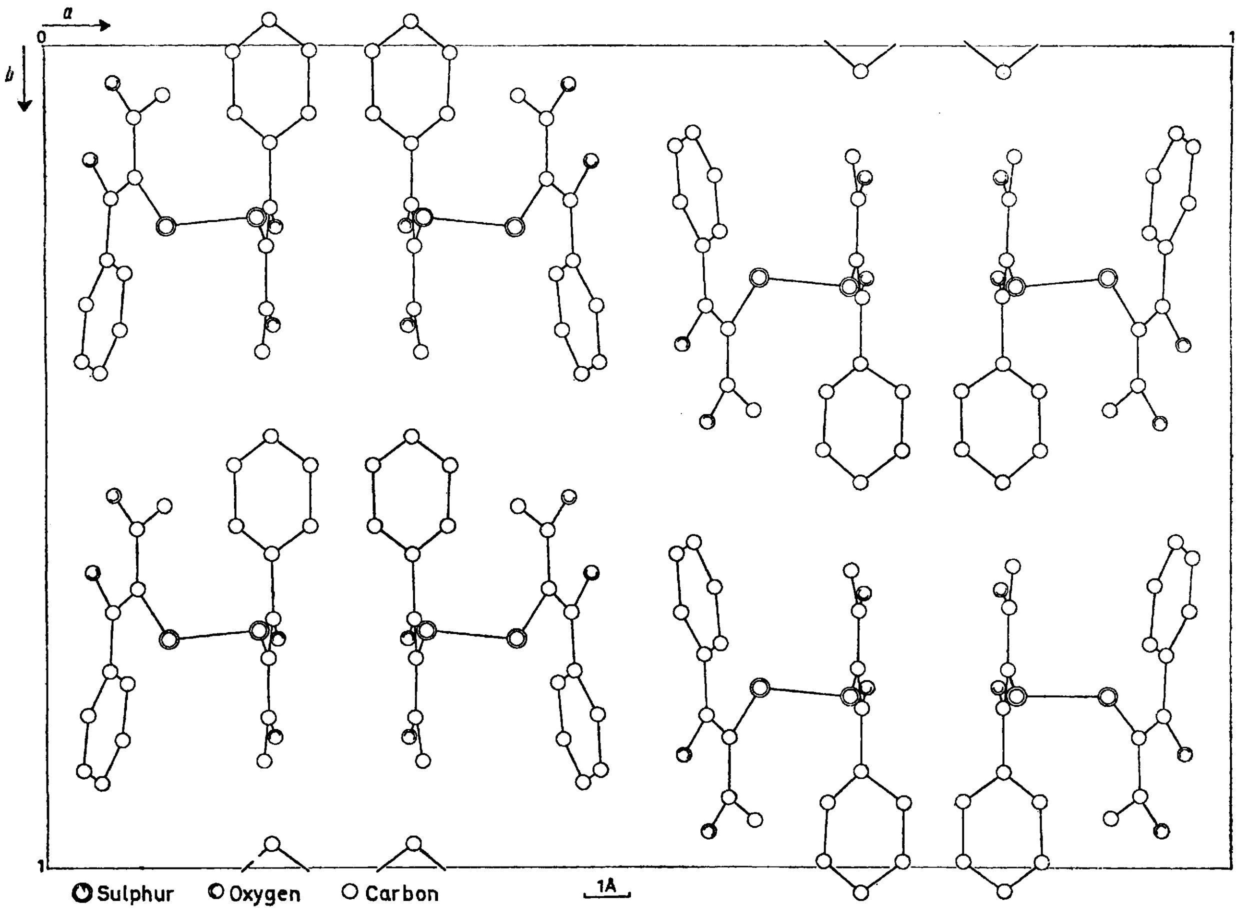

FIGURE 3 The contents of the unit cell as seen down the *c* axis

S(1)–S(2) is 2.078 Å, the value expected for a single bond.[18] It is slightly longer than that expected [19] from the dihedral angle C(2)–S–S′/S–S′–C(2)′ (66.4°). Both S′–C(2′) and S–C(2) (1.743 and 1.769 Å) are shorter than the normal single-bond value [18] and using parameters derived by Trinajstic,[20] the π-bond order for these bonds is substantial. However, the result does not reflect conjugation between the benzoylacetone residues *via* the sulphide linkage.

The dicarbonyl groups are planar (Table 2), and evidence indicates double-bond localization. Bond distances C(2)–C(3) and C(1)–C(2) are not significantly different and are intermediate in length between bond lengths for carbon–carbon single and double bonds. Bonds C(3)–O(2) (1.256 Å) and C(1)–O(1) (1.319 Å) are significantly different. The position found for the enol hydrogen in the difference Fourier map lies 1.62 from O(2) and 0.89 Å from O(1), the angle O(2)–H–O(1) being 141°. Such evidence indicates that the hydrogen probably prefers the environment of O(1). Similar relationships occur in ring II except that C(2′)–C(3′) and C(1′)–C(2′) appear to be significantly different. For this second dicarbonyl group, a hydrogen atom was located 1.44 from O(2′) and 1.07 Å from O(1)′. It is our inten-

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[18] S. C. Abrahams, *Quart. Rev.*, 1956, **10**, 407.

[19] A. Hordvik, *Acta Chem. Scand.*, 1966, **20**, 1885.

tion to obtain unambiguous evidence of the position of the enol hydrogen atoms by neutron diffraction.

For each dicarbonyl group, the longer carbon–oxygen bond is adjacent to the attached phenyl group. Since the dihedral angle between the phenyl group and the dicarbonyl group is large (I–III 47.8 II–IV 50.3°), it is doubtful if this bond lengthening is due entirely to conjugation.[21] Fischer-Hjalmars [22] has calculated the energy of non-bonded interactions and the conjugation energy for biphenyl. If the total energy is plotted against the dihedral angle between the phenyl groups, the minimum in the curve lies near 40°. She concludes that the final conformation is a compromise between non-bonded interactions and the conjugation energy and that the conformation cannot be explained by either factor alone.

TABLE 1

Fractional co-ordinates ($\times 10^4$; H atoms $\times 10^3$), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
S	1 801(1)	2 092(2)	2 409(3)
S′	1 035(1)	2 194(2)	2 001(3)
C(1)	570(2)	1 853(3)	5 112(6)
C(2)	769(2)	1 590(3)	3 516(6)
C(3)	769(2)	864(3)	3 170(7)
C(4)	1 009(3)	579(4)	1 486(10)
C(5)	538(2)	2 600(2)	5 691(6)
C(6)	678(2)	2 737(3)	7 416(7)
C(7)	643(2)	3 438(3)	8 044(9)
C(8)	466(2)	3 967(3)	6 963(9)
C(9)	317(2)	3 805(4)	5 204(9)
C(10)	354(2)	3 117(3)	4 599(6)
C(1′)	1 907(2)	1 951(3)	5 980(6)
C(2′)	1 873(2)	2 419(2)	4 541(7)
C(3′)	1 880(2)	3 171(3)	4 891(10)
C(4′)	1 823(3)	3 684(3)	3 367(13)
C(5′)	1 910(2)	1 172(3)	5 868(6)
C(6′)	1 605(2)	810(4)	7 003(7)
C(7′)	1 589(3)	88(4)	6 975(9)
C(8′)	1 905(3)	−300(4)	5 786(10)
C(9′)	2 237(3)	82(4)	4 705(8)
C(10′)	2 233(2)	817(3)	4 747(6)
O(1)	390(2)	1 383(3)	6 230(6)
O(2)	580(2)	444(3)	4 265(6)
O(1′)	1 940(2)	2 198(3)	7 583(6)
O(2′)	1 926(2)	3 397(3)	6 412(6)
H(01)	36	95	580
H(01′)	197	276	745
H(6)	80	236	818
H(7)	75	355	925
H(8)	44	445	740
H(9)	19	418	443
H(10)	25	300	340
H(6′)	140	107	784
H(7′)	136	−17	777
H(8′)	189	−82	573
H(9′)	247	−17	393
H(10′)	246	108	398
H(41)	97	3	149
H(42)	139	63	157
H(43)	86	73	46
H(41′)	205	359	245
H(42′)	150	370	280
H(43′)	186	418	380

In the present compound, the phenyl group is involved in two nonbonded interactions. The contact distances S ··· C(10) (3.2 Å) and O(1) ··· C(6) (2.82 Å) are both less than the van der Waals contacts. This means that if C(10) were to move closer to S, so as to make the phenyl group coplanar with the dicarbonyl group, the O(1) ··· C(6) contact would be too close. Therefore the orientation of the phenyl group with respect to the dicarbonyl group is a compromise between resonance and non-bonded interaction. Similar relationships occur in rings II and IV.

TABLE 2

Equations of best least-squares planes in the form $AX + BY + CZ = D$, where X, Y, and Z are orthogonal (Å) co-ordinates and $X = ax$, $Y = by$, and $Z = cz$. Deviations (Å $\times 10^4$) of relevant atoms from the planes are given in square brackets

Plane (I): C(1)—(5), O(1), O(2)

$$-0.8933X + 0.0878Y - 0.4408Z = -2.7603$$

[C(4) −48(8), C(3) 8(5), C(2) 13(5), C(1) −2(5), C(5) 4(5), O(2) 23(5), O(1) −25(5), S −1995(3)]

Plane (II): C(1′)—(5′), O(1′), O(2′)

$$0.9959X + 0.0023Y - 0.0902Z = 4.6744$$

[C(4′) −40(8), C(3′) 5(5), C(2′) 7(5), C(1′) −3(5), C(5′) 9(5), O(2′) 24(5), O(1′) −24(5), S′ −2049(3)]

The hydrogen bonding is intramolecular, the length of these bonds being quite short: O(1) ··· O(2) 2.374, and O(1′) ··· O(2′) 2.436 Å. These values are comparable with those found previously for β-diketones: trithiobis(acetylacetone) 2.461,[7] tetra-acetylethane 2.448,[6] benzoylacetone 2.498,[9] dibenzoylmethane 2.468,[1] bis-(*m*-chlorobenzoyl)methane 2.475,[11] and bis-(*m*-bromobenzoyl)methane 2.464 Å.[10]

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[20] N. Trinajstic, *Tetrahedron Letters*, 1968, 1529.

[21] G. Allen and R. A. Dwek, *J. Chem. Soc.*, 1966, 161.

[22] I. Fischer-Hjalmars, *Tetrahedron*, 1963, **19**, 1805.