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Structure of 3,3′-Dimethoxy-2,2′-bithiophene and Comparison with Quantum-Mechanical Calculations

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Abstract

3,3′-Dimethoxy-2,2′-bithiophene (3,3′-dimethoxy-2,2′-bithienyl), $C_{10}H_{10}O_2S_2$, $M_r = 226{\cdot}32$, monoclinic, $P2_1/c$, $a = 7{\cdot}524$ (2), $b = 10{\cdot}702$ (2), $c = 6{\cdot}789$ (1) Å, $\beta = 106{\cdot}53$ (1)°, $V = 524{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}434$, D_m(flotation in aqueous K_2HgI_4 solution) $= 1{\cdot}43$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}458$ mm^{-1}, $F(000) = 236$, $T = 295$ K, $R = 0{\cdot}098$, $wR = 0{\cdot}041$ for 915 observed $[F^2 > \sigma(F^2)]$ of 1041 unique reflections. The molecule lies on a crystallographic centre of symmetry, and the two rings are coplanar. The two S atoms are *trans* relative to the C1—C1′ bond. All intermolecular distances in the crystal are significantly longer than the generally accepted van der Waals distances. In addition to the crystallographic study of the title compound, *ab initio* geometry refinements were performed for the homologous 3,3′-dihydroxy-2,2′-bithiophene at a level (4-21G) at which differences between comparable parameters usually agree to within a few thousandths of an ångström and a few tenths of a degree with experimental results of systems in a non-perturbed state. Characteristic trends in the calculated equilibrium structure and the observed crystal structure are in good, but not exact, agreement. Deviations in parameter differences in the two sets, involving C and S atoms, are found at about 0·03–0·04 Å and 1–2°, respectively, and bond-distance differences are typically larger in the crystal than in the calculated geometry.

Introduction

An interesting conflict has arisen in structural studies of bithiophene derivatives which we are currently pursuing. For 3,3′-dimethoxy-2,2′-bithiophene (DMTDT, Fig. 1), MNDO calculations yield a lower conformational energy (about 17 kJ mol^{-1}) for the form in which the planes of both rings are perpendicular to each other than for the coplanar arrangement. This is in some contrast to the crystal structure, discussed below, in which the coplanar form is found. On the basis of general considerations (*e.g.*, electron delocalization) one should expect the coplanar form to be more stable than the non-coplanar one. This hypothesis appears to be confirmed by the crystallographic results, but the possible effects of crystal-packing forces must also be kept in mind.

In order to obtain further information on the conformational properties of the DMTDT bithiophene system, we have performed *ab initio* geometry optimizations for several forms of the homologous 3,3′-dihydroxy-2,2′-bithiophene (DHDDT). The resulting geometries also allow a comparison of some of the calculated and experimental structural trends found for the bithiophene system.

Experimental and structure solution

DMTDT was prepared in 50% yield by reacting equimolar amounts of 3-methoxythiophene with butyl lithium in *tert*-butyl methyl ether at 273 K and oxidatively coupling the resulting 2-lithio derivative with half an equivalent of anhydrous copper(II) chloride.

Crystals of the air-sensitive compound were made by recrystallization from *n*-hexane in a glove box filled with argon. A crystal of dimensions 0·02 × 0·08 × 0·5 mm was sealed into a Mark tube to protect it from the atmosphere. 25 reflections with $\theta > 5°$ were used for the cell refinement. Nicolet *R*3 computer-controlled diffractometer, $2\theta/\theta$ scan, $\theta_{\max} = 26°$, 3° min^{-1}, no correction for absorption or extinction, one standard reflection ($12\bar{1}$) showed no significant intensity variation, h −8→8, k 0→13, l −8→9, $R_{\rm int} = 0{\cdot}039$, solution of the phase problem by direct methods (Germain, Main & Woolfson, 1970) with the program *SHELXTL* (Sheldrick, 1983). H atoms of the methyl group could not be located in a difference Fourier synthesis of the electron density and were given calculated atomic coordinates with assumed C—H distances of 0·96 Å and temperature factors fixed at 1·2 times the equivalent isotropic value for the methyl C atom. The non-H atoms were refined anisotropically [least-squares refinement on F with 915 data, 75 parameters, $w = 1/\sigma^2(F)$,

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Table 1. *Atomic coordinates and isotropic temperature coefficients of* 3,3′-*dimethoxy*-2,2′-*bithiophene*

x, y, z are in units of the cell constants, with standard deviations in units of the last digit in parentheses. U_{eq} values are mean-square deviations from equilibrium in Å^2. $U_{eq} = (\mathrm{trace}\ \tilde{U})/3$.

	x	y	z	U_{eq}
C1	0·5435 (5)	0·4676 (4)	0·4346 (5)	0·040 (2)
C2	0·4633 (6)	0·4093 (4)	0·2506 (6)	0·050 (2)
C3	0·5907 (8)	0·3523 (5)	0·1632 (7)	0·067 (3)
C4	0·7644 (8)	0·3672 (5)	0·2779 (8)	0·073 (3)
C5	0·1979 (7)	0·3467 (5)	−0·0131 (7)	0·078 (3)
H3	0·548 (5)	0·322 (4)	0·048 (6)	0·07 (2)
H4	0·851 (4)	0·355 (3)	0·256 (5)	0·03 (1)
H51	0·068 (7)	0·3605 (5)	−0·0360 (7)	0·103
H52	0·2243 (7)	0·2591 (5)	0·0067 (7)	0·103
H53	0·2340 (7)	0·3755 (5)	−0·1301 (7)	0·103
O1	0·2739 (4)	0·4104 (3)	0·1744 (4)	0·064 (2)
S1	0·7819 (2)	0·4498 (2)	0·4953 (2)	0·060 (1)

$R_1 = 0{\cdot}098$, $R_2(=wR) = 0{\cdot}041$, $S = 1{\cdot}37$, max. $\Delta/\sigma < 0{\cdot}1$, ten largest peaks in final difference electron density between 0·32 and 0·43 e Å^{-3}, calculations performed with a Nova 3/12 computer and *SHELXTL* (Sheldrick, 1983)];* the scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Atomic coordinates are given in Table 1. The molecular structure and atom numbering are shown in Fig. 1. The crystal structure is shown in Fig. 2.

Computational procedures

Semi-empirical calculations were performed with the MNDO procedure (Dewar & Thiel, 1977) using the *MOPAC* program package (Stewart, 1982). Geometry optimizations were carried out using the Fletcher–Powell–Davidson algorithm (Fletcher & Powell, 1963; Davidson, 1968) implemented in the package.

Ab initio calculations were performed by gradient optimization using standard procedures (Pulay, 1969, 1979) with the 4-21G basis set for first-row elements (Pulay, Fogarasi, Pang & Boggs, 1979) and the 3-321G basis set (Gordon, Binkley, Pople, Pietro & Hehre, 1982) for S [*d* functions constructed according to Pulay (1979)]. Detailed analyses (Schäfer, 1983; Schäfer, Van Alsenoy & Scarsdale, 1982) have shown that differences between similar bond distances and angles in organic molecules obtained by such calculations are accurate at a level of a few thousandths of an ångström and a few tenths of a degree. Therefore, experimental and calculated parameter *differences* can be compared meaningfully for unperturbed systems, even though absolute values of calculated and experimental structures are different by definition. When crystal structures are compared with calculations for isolated molecules, differences may arise from intermolecular interactions which are interesting to study. Distinct trends are often still found to be the same in the *ab initio* geometries and the crystal structures (*e.g.*, Schäfer, Klimkowski, Momany, Chuman & Van Alsenoy, 1984).

MNDO calculations were performed for the planar and perpendicular forms of DMTDT, as well as eight intermediates. Because of the size of the system, *ab initio* calculations were performed for the smaller homolog, DHDDT. It is reasonable to expect that replacing O—CH$_3$ by O—H will not significantly affect the structures of the rings. During the geometry refinements of DHDDT, the conformational energy turned out to depend on internal hydrogen bonding (between O—H and S) in an unexpected way. Therefore, energies for four DHDDT structures were calculated, consisting of the coplanar and non-coplanar forms, with and without hydrogen bonding, respectively. Geometries for the three most stable forms of this series were fully refined and the final parameters are listed in Table 2. The largest residual forces in the *ab initio* structures are 10^{-11} N, or less.

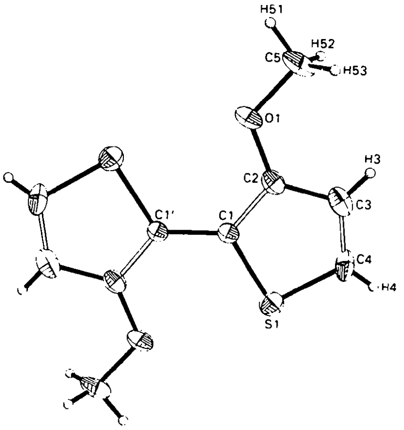

Fig. 1. Molecular structure and atom numbering for 3,3′-dimethoxy-2,2′-bithiophene.

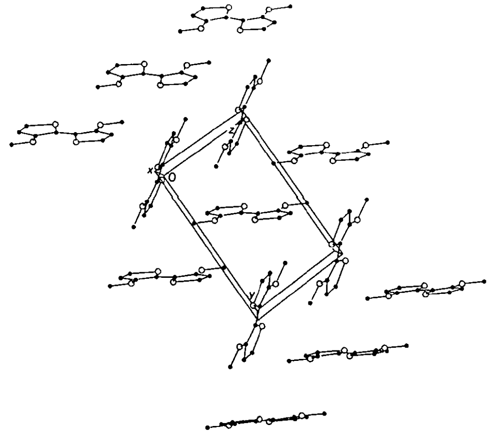

Fig. 2. Projection of the unit cell of 3,3′-dimethoxy-2,2′-bithiophene along the *a* axis.

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44813 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results and discussion

It is seen from Table 1 and Figs. 1 and 2 that the planar form of DMTDT is found in the solid state. Deviations from coplanarity in torsional angles involving C, O, or S, at most range from a few tenths to about one degree. Thus, the system is similar to other centrosymmetric bithiophene derivatives whose molecules are situated on crystallographic centres of symmetry (Korte, Lipka & Mootz, 1985; Visser, Heeres, Wolters & Vos, 1968; Lipka & von Schnering, 1977; Panfilova, Antipin, Struchkov, Churkin & Lipkin, 1980).

In contrast to this, the non-planar form of DMTDT, in which the two rings are perpendicular to each other, turned out in the MNDO calculations to be about 17 kJ mol^{-1} more stable than the optimized equivalent of the crystal structure. This contrast could be an artifact of the calculations or it may reflect a difference between the molecular stability in isolation and in the solid state.

For further clarification of this question, *ab initio* calculations were performed for several DHDDT structures. When this bithiophene derivative is compared with DMTDT, the possible effects of internal hydrogen bonding, which can exist in the former but not in the latter, must be considered. In the hydrogen-bonded form (O—H points to S1′ and C1—C2—O1—H = 0·0°), somewhat to our surprise the 4-21G energy of the 90° form was 32·2 kJ mol^{-1} below the planar conformation. However, in the non-hydrogen-bonded configuration, in which C1—C2—O1—H is the same as C1—C2—O1—C5 in the crystal structure of DMTDT, the planar arrangement is 23·4 kJ mol^{-1} more stable than the perpendicular one. Therefore, because of the similarity of DMTDT and DHDDT, we believe that the crystal structure reflects the true conformational stability of isolated DMTDT and that the MNDO calculations in this case are not accurate. In MNDO calculations of DHDDT the non-planar forms, both in the hydrogen-bonded and in the non-hydrogen-bonded configurations, also turned out to be more stable than the planar forms.

In the crystal structure (Table 2) the C—S bonds, C1—S1 and C4—S1, differ by 0·040 (6) Å. The differences (C1—C1′) − (C2—C3), (C1—C2) − (C3—C4), (C3—H3) − (C4—H4) are 0·024 (10), 0·046 (9) and 0·11 (6) Å, respectively. In the 4-21G geometry of the planar non-hydrogen-bonded form of DHDDT (Table 2), the corresponding differences are smaller, but have the same sign, and are 0·029, 0·017, 0·008 and 0·003 Å, respectively. In contrast to this, the opposite trend is obtained for (C1—C1′) − (C2—C3) in the MNDO calculations.

Table 2. *Bond distances* (Å) *and angles* (°) *for* 3,3′-*dimethoxy*-2,2′-*bithiophene and* 3,3′-*dihydroxy*-2,2′-*bithiophene*

The X-ray column gives the results of the X-ray diffraction crystal structure of 3,3′-dimethoxy-2,2′-bithiophene (DMTDT) (see Table 1); the MNDO column gives parameters of DMTDT obtained by geometry optimization with the MNDO procedure; the DHDDT (4-21G) columns give the parameters of the 4-21G *ab initio* geometry optimization of the planar form of 3,3′-dihydroxy-2,2′-bithiophene (DHDDT) with hydrogen bonding [PL(HB)], planar DHDDT without hydrogen bonding [PL(no HB)], and of the 90° non-planar conformation with hydrogen bonding [90(HB)].

			DHDDT (4-21G)		
	X-ray	MNDO	PL(HB)	PL(no HB)	90 (HB)
C1–S1	1·733 (3)	1·70	1·7511	1·7450	1·7443
C1–C1′	1·425 (7)	1·45	1·4611	1·4493	1·4612
C1–C2	1·373 (5)	1·40	1·3575	1·3519	1·3504
C2–O1	1·371 (5)	1·35	1·3778	1·3851	1·3715
C2–C3	1·401 (7)	1·47	1·4392	1·4319	1·4367
C3–H3	0·83 (4)		1·0667	1·0693	1·0666
C4–C3	1·327 (7)	1·37	1·3359	1·3435	1·3418
C4–S1	1·693 (5)	1·68	1·7208	1·7159	1·7213
C4–H4	0·72 (4)		1·0659	1·0668	1·0669
C5–O1	1·414 (5)	1·40	0·9571*	0·9600*	0·9638*
C1′–C1–C2	128·9 (4)	130·9	130·19	126·50	126·06
C1′–C1–S1	122·2 (3)	119·4	120·64	123·51	123·41
C2–C1–S1	108·9 (3)	109·7	109·18	109·99	110·53
C1–C2–C3	114·0 (4)	112·1	113·87	114·21	113·71
C1–C2–O1	118·6 (4)	122·1	130·54	120·72	126·57
C3–C2–O1	127·4 (3)	125·8	115·59	125·07	119·72
C2–C3–C4	112·2 (4)	110·7	112·85	111·48	111·74
C2–C3–H3	116· (3)	122·8	121·46	123·81	122·64
C4–C3–H3	131· (3)	126·5	125·69	124·71	125·62
C3–C4–H4	131· (3)	128·6	127·53	126·41	126·39
C3–C4–S1	113·2 (5)	112·9	111·63	112·86	112·79
H4–C4–S1	115· (2)	118·5	120·84	120·74	120·82
C2–O1–C5	116·5 (3)	123·3	116·47*	113·36*	112·09*
C1–S1–C4	91·8 (2)	94·6	92·47	91·47	91·23
S1–C1–C1′–S1′	180·0		180·0	180·0	−90·3
S1–C1–C1′–C2′	0·0		0·0	0·0	90·0
C2–C1–C1′–S1′	0·0		0·0	0·0	90·0
C2–C1–C1′–C2′	180·0		180·0	180·0	−89·7
C1′–C1–C2–C3	−179·0 (5)		180·0	180·0	179·5
C1′–C1–C2–O1	−0·1 (7)		0·0	0·0	−0·5
S1–C1–C2–C3	0·2 (4)		0·0	0·0	−0·3
S1–C1–C2–O1	179·1 (3)		180·0	180·0	179·8
C1′–C1–S1–C4	179·2 (4)		180·0	180·0	−179·5
C2–C1–S1–C4	−0·1 (3)		0·0	0·0	0·3
C1–C2–C3–C4	−0·2 (6)		0·0	0·0	0·1
C1–C2–C3–H3	−175· (3)		180·0	180·0	−179·9
O1–C2–C3–C4	−179·1 (4)		180·0	180·0	−179·9
O1–C2–C3–H3	6· (3)		0·0	0·0	0·0
C1–C2–O1–C5	−178·6 (3)		0·0*	180·0*	−2·2*
C3–C2–O1–C5	0·2 (6)		180·0*	0·0*	177·8*
C2–C3–C4–H4	−169· (4)		180·0	180·0	−179·9
C2–C3–C4–S1	0·2 (6)		0·0	0·0	0·1
H3–C3–C4–H4	5· (5)		0·0	0·0	0·1
H3–C3–C4–S1	174· (3)		180·0	180·0	−179·9
C3–C4–S1–C1	0·0 (4)		0·0	0·0	−0·2
H4–C4–S1–C1	171· (3)		180·0	180·0	179·8

* O—H, C—O—H and C—C—O—H parameters for DHDDT. The total *ab initio* energy of 90(HB) is −3274806·9 kJ mol^{-1}. PL(HB), PL(no HB), and 90(no HB) are 32·2, 14·7 and 38·1 kJ mol^{-1}, respectively, less stable than 90(HB). The number of significant digits used for the *ab initio* parameters was chosen to make accurate reproduction of the calculations possible.

Various reasons can be discussed for the quantitative differences in magnitude observed here for the relative parameter extensions in crystal DMTDT and isolated DHDDT. The R value of the crystal structure is relatively large and the data were not measured at low temperature. Thus the crystal structure may not be accurate enough for comparisons at this level of accuracy. At the same time, at least for parameters involving heavy atoms, the differences may also be indicative of electronic effects which exist in the solid state but not in the single molecule. (Only one intermolecular contact is smaller than 3 Å: H53···C4 = 2·932 Å; van der Waals distance 2·8 Å).

Table 3. *Coefficients of the anisotropic temperature factors* (Å^2, *standard deviations in parentheses in units of the last digits*) *for* 3,3′-*dimethoxy*-2,2′-*bithiophene*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0·044 (2)	0·035 (2)	0·041 (2)	−0·001 (2)	0·009 (1)	0·002 (2)
C2	0·066 (3)	0·040 (2)	0·044 (2)	−0·001 (2)	0·012 (2)	0·000 (2)
C3	0·093 (4)	0·052 (3)	0·056 (3)	0·004 (3)	0·019 (3)	−0·007 (3)
C4	0·072 (4)	0·078 (3)	0·068 (3)	0·026 (3)	0·035 (3)	−0·004 (3)
C5	0·094 (3)	0·088 (3)	0·051 (3)	−0·023 (3)	−0·008 (2)	−0·016 (3)
O1	0·064 (2)	0·080 (2)	0·048 (2)	−0·013 (2)	−0·003 (1)	−0·018 (1)
S1	0·050 (1)	0·064 (1)	0·065 (1)	0·006 (1)	0·011 (–)	0·000 (1)

Relative extensions of comparable bond angles determined for the crystal structure are also fairly well reproduced by the calculated parameters. The C—S—C angle is 91·8 (2)° in the crystal structure of DMTDT, and 91·5° in the 4-21G geometry of DHDDT. The differences, (C3—C2—C1) − (C2—C3—C4), and (C2—C1—S1) − (C3—C4—S1) are 1·8 (6) and −4·3 (6)° for crystal DMTDT; and 2·7 and −2·9°, for 4-21G DHDDT, respectively.

It is noteworthy that the bond lengths and angles as predicted by *ab initio* calculations compare well with those in the crystal structure. The origin of the quantitative differences discussed above cannot be determined from the present study. It is nevertheless interesting to find that the order of magnitude of these differences in relative bond distances and angles does not exceed a few hundredths of an ångström and a few degrees.

References

Davidson, W. C. (1968). *Comput. J.* **10**, 406–413.
Dewar, M. J. S. & Thiel, W. (1977). *J. Am. Chem. Soc.* **99**, 4899–4907, 4907–4917.
Fletcher, R. & Powell, M. J. D. (1963). *Comput. J.* **6**, 163–175.
Germain, G., Main, P. & Woolfson, M. M. (1970). *Acta Cryst.* B**26**, 274–285.
Gordon, M. S., Binkley, J. S., Pople, J. A., Pietro, W. J. & Hehre, W. J. (1982). *J. Am. Chem. Soc.* **104**, 2797–2803.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Korte, L., Lipka, A. & Mootz, D. (1985). *Z. Anorg. Allg. Chem.* **524**, 157–167.
Lipka, A. & von Schnering, H. G. (1977). *Chem. Ber.* **110**, 1377–1381.
Panfilova, L. V., Antipin, M. Yu, Struchkov, Yu, T., Churkin, Yu. D. & Lipkin, A. E. (1980). *Zh. Strukt. Khim.* **21**, 190–192.
Pulay, P. (1969). *Mol. Phys.* **17**, 197–204.
Pulay, P. (1979). *Theor. Chim. Acta*, **50**, 299–312.
Pulay, P., Fogarasi, G., Pang, F. & Boggs, J. E. (1979). *J. Am. Chem. Soc.* **101**, 2550–2560.
Schäfer, L. (1983). *J. Mol. Struct.* **100**, 51–73.
Schäfer, L., Klimkowski, V. J., Momany, F. A., Chuman, H. & Van Alsenoy, C. (1984). *Biopolymers*, **23**, 2335–2347.
Schäfer, L., Van Alsenoy, C. & Scarsdale, J. N. (1982). *J. Mol. Struct.* **86**, 349–364.
Sheldrick, G. M. (1983). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.
Stewart, J. P. (1982). *QCPE Bull.* (2), 31.
Visser, G. J., Heeres, G. J., Wolters, J. & Vos, A. (1968). *Acta Cryst.* B**24**, 467–473.

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Preliminary Study of a Phase Transformation in Insulin Crystals using Synchrotron-Radiation Laue Diffraction

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Abstract

Synchrotron-radiation Laue diffraction photographs have been recorded showing the transformation of single 4Zn insulin crystals [$a = 80{\cdot}7\,(1)$, $c = 37{\cdot}6\,(1)$ Å, space group $R3$] to 2Zn insulin [$a = 82{\cdot}5\,(1)$, $c = 34{\cdot}0\,(1)$ Å, space group $R3$]. The transformation was brought about by changing the mother liquor in the capillary in which the crystal was mounted. Photographs were taken at 10 min intervals (exposure time 3 s) from 0·5 h after mounting. They showed initially a well ordered 4Zn insulin crystal ($d_{\min}$ *ca*

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