

The Crystal Structure of Tetraphenylthieno[3,4-*c*]thiophene, a Nonclassical Thiophene*

BY MILTON D. GLICK AND RICHARD E. COOK

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.

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The structure of tetraphenylthieno[3,4-*c*]thiophene ($S_2C_{30}H_{20}$) has been determined by three-dimensional single-crystal X-ray diffraction. The crystals are monoclinic, space group $P2_1/a$, with $a = 17.431$ (8), $b = 5.953$ (3), $c = 13.842$ (6) Å, $\beta = 128.40$ (2)°, $Z = 2$. The conventional discrepancy index is 0.061 for 1446 diffractometer data. The molecule is located about a crystallographic inversion center, and the thieno[3,4-*c*]thiophene moiety is planar with approximate mmm (D_{2h}) symmetry. The phenyl groups are rotated out of plane by 39.6 and 58.4°. Averaged bond lengths within the rings are C-S, 1.706 Å; C_β - C_β , 1.452 Å; and C_α - C_β , 1.407 Å.

Introduction

The synthesis of a stable thieno[3,4-*c*]thiophene derivative, a 10 π -electron aromatic system for which the only uncharged resonance contributors are nonclassical structures containing tetravalent sulfur, has recently been reported by Cava & Husbands (1969). Molecular orbital calculations (Clark, 1968) on thiophene and the isomers of dithiophene have shown that the thieno[3,4-*c*]thiophene isomer is the least stable of those considered. A related compound, 1,3-dimethylthieno[3,4-*c*]thiophene, had previously been reported by Cava & Pollack (1967), but its existence was only transient. We now report the three-dimensional X-ray study of tetraphenylthieno[3,4-*c*]thiophene.

Structure determination

A violet, transparent crystal of tetraphenylthieno[3,4-*c*]thiophene, $S_2C_{30}H_{20}$, of size $0.08 \times 0.15 \times 0.30$ mm, generously supplied by Professor M. P. Cava, was mounted with Silastic medical adhesive on the end of a pulled glass fiber. Following preliminary film work, the crystal was transferred to a Picker four-angle card-controlled diffractometer where it was centered with X-rays. The monoclinic lattice constants of $a = 17.431$ (8), $b = 5.953$ (3), $c = 13.842$ (6) Å, and $\beta = 128.40$ (2)° were calculated from a least-squares analysis† of the diffractometer angles of 16 reflections

at 22°C ($\lambda = 1.5405$ Å). The systematic absences of h odd for $h0l$ and of k odd for $0k0$ were uniquely consistent with the space group $P2_1/a$.

The diffraction data were collected automatically using Cu $K\alpha$ radiation filtered through 0.0006 inch Ni foil with the pulse height analyzer set to accept 90% of the incoming radiation. The moving-counter moving-crystal (θ - 2θ) technique was used with a counter drive speed of 1° min^{-1} and a take-off angle of 2.0° . The intensity for each reflection was obtained from a minimum of 2.0° scan (0.9° before Cu $K\alpha_1$ and 1.10° after Cu $K\alpha_2$) and backgrounds of 10 sec at both ends of the scan. Reflection data were collected in the quadrant $\pm h, +k, +l$ out to a maximum 2θ of 125° .

1997 reflections were examined of which 1446 had net intensities above two standard deviations and were used throughout this study. The intensities of five standard reflections (603, 600, 412, 005, 020) were checked after every 100 data in order to follow the rate of decomposition or other systematic changes in intensity. The raw data were corrected for Lorentz and polarization factors, background, and loss of intensity due to decomposition. The rate of apparent decomposition was taken to be the average of the rates of decrease in intensity of the five standard reflections, each of which behaved similarly. They indicated no decrease in intensity for the first 600 data, but a linear decrease for the remaining data at the rate of 2% per 1000 reflections. Standard deviations for the intensities were calculated from $\sigma^2(I) = \sigma^2 \text{ count} + 0.0009I^2$. Absorption by the crystal was not taken into account. Since the reactivity of the crystal precluded a density measurement, we presupposed a density ($D_x = 1.315 \text{ g.cm}^{-3}$), corresponding to other organosulfur compounds which suggested two molecules per unit cell.

The presence of two molecules per unit cell in the space group $P2_1/a$ requires the molecule to have an inversion center coincident with a crystallographic inversion center; thus, the asymmetric unit comprises a half-molecule. The structure was determined using Patterson-Fourier techniques. The final full-matrix

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† Local versions of the following programs were used in the solution and refinement of this structure.

PICK 2 - J. A. Ibers' least-squares program for lattice constants and orientation angles based on W. C. Hamilton's MODE 1.

DACOR - D. L. Smith's program for the correction of diffractometer data and estimation of standard deviations. FORDAP - A. Zalkin's Fourier program.

ORFLS and ORFEE - W. Busing, K. Martin and H. Levy's full-matrix least-squares program and function and error program.

ORTEP - C. K. Johnson's program for drawing thermal ellipsoids of crystal structures.

least-squares refinement* [minimizing $\sum w(|F_o| - |F_c|)^2$] of the positional and anisotropic thermal parameters of the nonhydrogen atoms, and the positional param-

eters of the hydrogen atoms, yielded a conventional discrepancy index ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.061 and a weighted discrepancy factor $\{ = [\sum w(F_o - F_c)^2]^{1/2} / [\sum w F_o^2]^{1/2} \}$ of 0.075. The structure factors resulting from the refinement are presented in Table 1. The positional and thermal parameters for the atoms

* Atomic scattering factors were obtained from International Tables for X-ray Crystallography (1968).

Table 1. Comparison of observed and calculated structure factors ($\times 10$)

Table with multiple columns of numerical data representing structure factors for various reflections. The table is organized into several vertical sections, each corresponding to a different set of reflections (e.g., 0 0 1, 1 0 0, 1 1 0, etc.). Each section contains observed values (F_o), calculated values (F_c), and their differences (F_o - F_c). The data is presented in a dense, grid-like format with some cells containing asterisks or other symbols.

Table 2. Positional and thermal parameters for the atoms of tetraphenylthieno[3,4-*c*]thiophene

Final coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$) for nonhydrogen atoms. The anisotropic temperature factor expression is:

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$$

Standard deviations estimated by least-squares methods are given in parentheses for the least significant digit.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	3531 (1)	4545 (2)	4831 (1)	48 (1)	302 (5)	76 (1)	-20 (2)	42 (1)	-24 (2)
C(1)	3869 (4)	3437 (9)	4010 (4)	49 (3)	281 (18)	64 (4)	-13 (6)	35 (3)	-15 (7)
C(2)	440 (4)	1123 (9)	4199 (5)	55 (3)	296 (18)	80 (5)	7 (6)	49 (4)	10 (8)
C(3)	4799 (4)	4223 (8)	4490 (4)	54 (3)	243 (17)	61 (4)	-12 (6)	36 (3)	-7 (7)
C(4)	3178 (3)	1991 (9)	2937 (4)	44 (3)	283 (18)	75 (5)	-1 (6)	37 (3)	-15 (7)
C(5)	2878 (4)	2590 (11)	1781 (5)	59 (4)	357 (22)	75 (5)	-12 (8)	40 (4)	-10 (9)
C(6)	2250 (5)	1240 (13)	783 (5)	76 (5)	513 (30)	75 (6)	-2 (10)	40 (5)	-31 (11)
C(7)	1915 (5)	-728 (13)	898 (6)	62 (4)	516 (31)	107 (7)	-37 (10)	34 (5)	106 (13)
C(8)	2218 (5)	-1367 (11)	2041 (7)	65 (4)	331 (23)	155 (8)	-42 (8)	58 (5)	-47 (12)
C(9)	2839 (4)	-2 (10)	3062 (6)	61 (4)	319 (23)	102 (6)	-20 (7)	45 (4)	-6 (9)
C(10)	5367 (4)	2353 (9)	3317 (4)	48 (3)	294 (18)	68 (5)	7 (6)	34 (3)	-12 (8)
C(11)	5696 (4)	2993 (10)	2662 (5)	57 (4)	370 (22)	87 (5)	-2 (7)	53 (4)	-2 (9)
C(12)	5603 (5)	1548 (13)	1812 (5)	68 (4)	497 (28)	91 (6)	19 (9)	56 (5)	-18 (10)
C(13)	5181 (4)	-529 (12)	1595 (5)	66 (4)	443 (24)	103 (6)	28 (9)	54 (4)	-53 (11)
C(14)	4873 (4)	-1222 (10)	2252 (5)	55 (4)	317 (21)	108 (6)	14 (7)	43 (4)	-28 (9)
C(15)	4967 (4)	203 (9)	3121 (5)	51 (3)	294 (20)	93 (5)	14 (7)	44 (4)	-2 (9)

Table 2 (cont.)

Final coordinates ($\times 10^3$) and bond distances for hydrogen atoms. Standard deviations given in parentheses are for least significant figures.

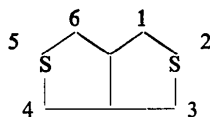
	<i>x</i>	<i>y</i>	<i>z</i>	<i>D</i>
H(C5)	317 (4)	390 (10)	173 (5)	0.96 (6) Å
H(C6)	205 (4)	170 (10)	1 (5)	0.93 (5)
H(C7)	146 (4)	-158 (10)	22 (5)	0.92 (6)
H(C8)	200 (4)	-280 (10)	217 (5)	0.99 (6)
H(C9)	304 (4)	-47 (10)	384 (5)	0.95 (5)
H(C11)	599 (4)	454 (9)	278 (5)	1.02 (5)
H(C12)	585 (4)	198 (9)	141 (5)	0.93 (5)
H(C13)	518 (4)	-157 (9)	101 (5)	1.02 (5)
H(C14)	458 (4)	-283 (9)	213 (5)	1.05 (5)
H(C15)	473 (4)	-36 (9)	364 (5)	1.09 (5)

of tetraphenylthieno[3,4-*c*]thiophene are listed in Table 2. All standard deviations are taken from the full variance-covariance matrix.

Description of structure

The molecular structure of tetraphenylthieno[3,4-*c*]thiophene, with bond lengths and angles,* is shown in Fig. 1. The only molecular symmetry possessed by the molecule is the crystallographically required inversion center. The fundamental thieno[3,4-*c*]thiophene framework is planar, with no deviations from planarity greater than 0.01 Å, and possesses idealized symmetry of *mmm*(D_{2h}), while the phenyl groups are rotated asymmetrically out of the plane.

* The ring index notation for this molecule is as shown:



Thus the correspondence between ring index notation and the notation used herein is 1 = C(1), 2 = S, 6 = C(2) for the independent atoms for which substitution is possible.

Bond lengths and angles in the thiophene framework are compared in Table 3 with those found in other thiophene derivatives. The carbon-carbon bonds adjacent to the sulfur atom in thieno[3,4-*c*]thiophene are 1.407 Å (average), 0.05 Å shorter than the fused $C_\beta-C_\beta$ bond of length 1.452 Å. These values correspond to bond orders of 1.37 and 1.18 respectively (Pauling, 1960). This difference in bond orders is consistent with the results of the related compounds and with simple valence bond considerations.

The adjacent and fused bond lengths are about 0.05 Å longer than those found in related compounds, while the S-C distances (1.706 Å, average) are slightly

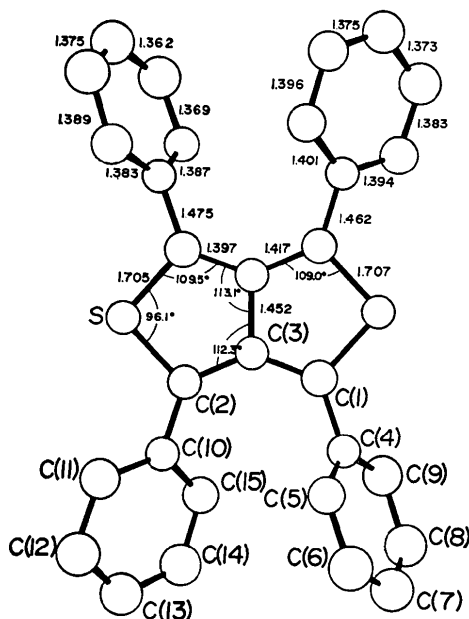


Fig. 1. The molecular structure of tetraphenylthieno[3,4-*c*]thiophene with bond lengths and angles. Standard deviations are 0.005-0.008 Å for distances and 0.2-0.6° for angles.

Table 3. *A comparison of interatomic distances and angles of thiophene and derivatives*
Distances, angles, and standard deviations for symmetry-related values are given as average values.
Symmetry assumed: C_{2v} .

	S-C $_{\alpha}$	C $_{\alpha}$ -C $_{\beta}$	C $_{\beta}$ -C $_{\beta}$	C $_{\alpha}$ -S-C $_{\beta}$	S-C $_{\alpha}$ -C $_{\beta}$	C $_{\alpha}$ -C $_{\beta}$ -C $_{\alpha}$
Thiophene ^a	1.714 (2) Å	1.370 (2) Å	1.423 (2) Å	92.2 (1)°	111.5 (2)°	112.5 (2)°
Tetracyanothiophene ^b	1.71 (2)	1.37 (2)	1.40 (2)	89.1 (8)	114.0 (10)	111.0 (10)
α -Thiophenecarboxylic acid ^c	1.70 (1)	1.36 (1)	1.41 (1)	92.0 (4)	111.8 (6)	112.2 (7)
Thieno[3,2- <i>b</i>]thiophene ^d	1.73 (1)	1.36 (2)	1.41 (2)			
Tetracyano-1,4-dithiin ^e	1.755 (3)	1.344 (5)				
Thieno[3,4- <i>c</i>]thiophene	1.706 (5)	1.407 (6)	1.452 (9)	96.1 (2)	109.3 (4)	112.7 (5)

- a. Bak, Christensen, Hansen-Nygaard & Rastrup-Anderson (1961).
b. Rychnovsky & Britton (1968).
c. Nardelli, Fava & Giraldi (1962).
d. Cox, Gillot & Jeffrey (1949).
e. Dollase (1965).

shorter. The thieno[3,4-*c*]thiophene differs from the other thiophene derivatives in that no simple valence bond structures may be written without invoking S-C double bonding. This explains the relatively smaller C-C bond order and the larger C-S bond order. Also consistent with this view are the results of self-consistent field molecular orbital calculations (Clark, 1968) of thiophene and the isomeric thienothiophenes, which predict much less π -bond stabilization in thieno[3,4-*c*]thiophene than in the other compounds considered.

Comparison of angles with the dithiophene derivatives shows that in thieno[3,4-*c*]thiophene, the carbon-sulfur-carbon bond angles have expanded about 4° and the sulfur-carbon-carbon bond angle has contracted correspondingly with no effect on the carbon-carbon-carbon bond angle. This distortion is a direct consequence of the lengthening of the carbon-carbon bonds.

The phenyls are rotated out of plane by 39.6 and 58.4°, destroying higher molecular symmetry. The lack of coplanarity of the phenyl groups with the dithiophene, and the approximate correspondence of the C-phenyl bond (1.48 Å) to an sp^2 - sp^2 single bond (1.46-1.49 Å, Sutton, 1965; 1.50 Å, Pauling, 1960), preclude any major delocalization of the π electrons between the dithiophene and the phenyl groups. Presumably, this rotation is a consequence of un-

favorable steric interactions between the two phenyl groups, if they should be coplanar. Of interest is the fact that the phenyl groups are not rotated 90° from the plane of the framework, which would have minimized hydrogen-hydrogen repulsive interactions and which is found in such compounds as tetraphenyl porphine derivatives (Hoard, Cohen & Glick, 1967). The difficulty of interpreting this phenomenon in the solid state is apparent from the fact that in biphenyl, the phenyl groups are skewed in the gas and liquid states (Almenningen & Bastiansen, 1958), yet are coplanar in the solid state (Hargreaves & Rivzi, 1962).

A packing diagram of tetraphenylthieno[3,4-*c*]thiophene, looking down the *b* axis, is given in Fig. 2. There are no unusual packing distances.

References

- ALMENNINGEN, A. & BASTIANSEN, O. (1958). *Det. Kogl. Norske Videnskabers Selskabs Skrifter*, No. 4.
BAK, B., CHRISTENSEN, D., HANSEN-NYGAARD, L. & RASTRUP-ANDERSON, J. (1961). *J. Mol. Spectrosc.* **7**, 58.
CAVA, M. P. & HUSBANDS, G. E. M., (1969). *J. Amer. Chem. Soc.* **91**, 3952.
CAVA, M. P. & POLLACK, N. M., (1967). *J. Amer. Chem. Soc.* **89**, 3639.
CLARK, D. T. (1968). *Tetrahedron*, **24**, 2567.
COX, E. G., GILLOT, R. J. J. H. & JEFFREY, G. A. (1949). *Acta Cryst.* **2**, 356.
DOLLASE, W. A. (1965). *J. Amer. Chem. Soc.* **87**, 979.
HARGREAVES, A. & RIVZI, S. H. (1962). *Acta Cryst.* **15**, 365.
HOARD, J. L., COHEN, G. H. & GLICK, M. D. (1967). *J. Amer. Chem. Soc.* **89**, 1992.
International Tables for X-ray Crystallography (1968). Vol. III, pp. 210-212. Birmingham: Kynoch Press.
NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 737.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
RYCHNOVSKY, V. & BRITTON, D. (1968). *Acta Cryst.* **B24**, 725.
SUTTON, L. E. (1965). *Interatomic Distances Supplement*, Special Publ. No. 18. London: The Chemical Society.

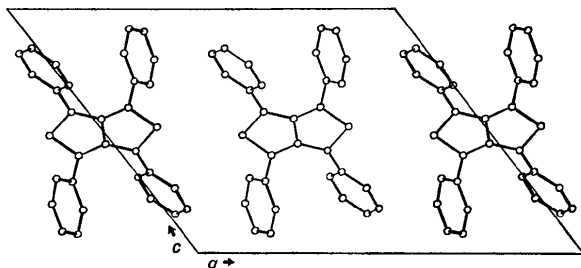


Fig. 2. The packing of tetraphenylthieno[3,4-*c*]thiophene as viewed down the *b* axis.