

- CARREIRA, L. A., JIANG, G. J., PERSON, W. B. & WILLIS, J. N. (1972). *J. Chem. Phys.* **56**, 1440–1443.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DUNITZ, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, pp. 425–431. Ithaca: Cornell Univ. Press.
- MARGULIS, T. N., DALTON, L. R. & KWIRAM, A. L. (1973). *Nature (London) Phys. Sci.* **242**, 82–83.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. A program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1986). **C42**, 1169–1172

Structures of Radical Anion TCNQ⁻ Salts with 1,2-Dithiole Derivatives. II. 3-*p*-Methoxyphenyl-1,2-dithiolium—7,7,8,8-Tetracyano-*p*-quinodimethanide (1/1.5)

BY FRANÇOIS MATHIEU*

Institut des Sciences de la Matière et du Rayonnement, Université de Caen, 14032 Caen CEDEX, France

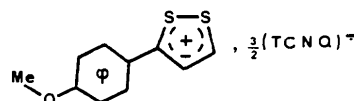
(Received 10 October 1985; accepted 21 February 1986)

Abstract. C₁₀H₉OS₂⁺.₂³C₁₂H₄N₄⁻, *M_r* = 515.6, triclinic, *P* $\bar{1}$, *a* = 7.836 (1), *b* = 16.316 (2), *c* = 10.050 (1) Å, α = 90.3 (1), β = 71.0 (1), γ = 87.6 (1)°, *V* = 1213.6 (5) Å³, *Z* = 2, *D_m* = 1.40, *D_x* = 1.411 Mg m⁻³, Mo *K*α, λ = 0.71093 Å, μ = 0.253 mm⁻¹, *F*(000) = 530, *T* = 293 K, *R* = 0.042 and *wR* = 0.045 for 2878 reflections. The TCNQ and 3-*p*-methoxyphenyl-1,2-dithiolium ions form segregated stacks along the crystallographic *c* and *a* axes respectively. The stacking of the TCNQ ions is triadic with a spacing of 3.175 Å between the TCNQ⁻ of a triad and 3.43 Å between triads. The material is expected to be an insulator along the stacking direction of the TCNQ⁻.

Introduction. For more than ten years, many investigations have been undertaken in the field of organic conductors, particularly since the studies on the charge-transfer complex TTF–TCNQ (Ferraris, Cowan, Walatka & Perlstein, 1973; Phillips, Kistenmacher, Ferraris & Cowan, 1973; Kistenmacher, Phillips & Cowan, 1974), which exhibits a metallic state (Coleman, Cohen, Sandman, Yamagishi, Garito & Heeger, 1973). Besides the theoretical investigations carried out on this material and the models proposed to explain the behavior of organic conductors (Bardeen, 1973; Soos, 1974; Perlstein, 1977; Torrance & Silverman, 1977; Soos, 1978; Benoit, Galtier & Montaner, 1979), numerous charge-transfer complexes have been synthesized and investigated from derivatives of TTF–TCNQ (Delhaes, Keryer, Gaultier, Fabre & Giral, 1982).

In order to contribute to this new field of solid-state chemistry, Amzil, Le Coustumer & Mollier (1981)

prepared a series of TCNQ salts with 1,2-dithiole derivatives as electron donors. In these derivatives, the dithiole ring is planar and carries a sextet of π electrons which gives it aromatic character. We have already studied the structure of a complex salt of 1:2 stoichiometry (Mathieu, 1984) which shows semiconductor behavior with respect to temperature. In the present work we study the structure of a salt of the same series but with a 2:3 stoichiometry, 3-*p*-methoxyphenyl-1,2-dithiolium sesqui(7,7,8,8-tetracyano-*p*-quinodimethanide), of formula



Experimental. Very absorbent grey-blue crystals (in acetonitrile by evaporation and cooling); *D_m* by immersion in toluene–carbon tetrachloride (5:13.4); 0.20 × 0.30 × 0.30 mm; automatic diffractometer CAD-4 Enraf–Nonius; Mo *K*α with graphite-plate monochromator, Bragg angle max. $\theta_m = 32^\circ$, ω – 2θ scan, amplitude $\Delta = (0.95 + 0.35 \tan \theta)^\circ$, counter aperture (3.00 + 0.80 tan) mm, scan speed $\sigma(I)/I = 0.018$ for max. counting time 60 s; 25 reflections for redetermination of cell parameters; 2878 independent reflections with $I \geq 3\sigma(I)$; Lorentz–polarization corrections; $-9 \leq h \leq 11$, $-24 \leq k \leq 24$, $0 \leq l \leq 11$; 3 standard reflections, intensity fluctuations <3%; heavy-atom method; atomic scattering factors from Cromer & Waber (1965) with anomalous-scattering correction for sulfur (Cromer, 1965); H atoms localized by difference Fourier synthesis; refined parameters: scale factor, coordinates *x*, *y*, *z*, anisotropic thermal factors of all non-hydrogen atoms; least-squares refinement based on

* Present address: Laboratoire de Chimie des Matériaux Inorganiques, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse CEDEX, France.

F , weighting from $\langle \omega AF \rangle$ curve as a function of $\langle \sin \theta \rangle$ (program *NANOVA* of Hamilton); final $R = 0.042$, $wR = 0.045$; $(\Delta/\sigma)_{\max} < 0.2$; heights of final difference Fourier synthesis peaks $< 0.3 \text{ e } \text{Å}^{-3}$.*

Discussion. The atomic coordinates are given in Table 1 and a projection of the structure along [010] is shown in Fig. 1.

Stacking. The structure of this complex consists of segregated stacks of radical anions TCNQ^- and of cations 3-*p*-methoxyphenyl-1,2-dithioliylum along the crystallographic directions [001] and [100] respectively, the long axis of the crystal being [100]. Fig. 2 which is the projection of the structure along the [100] axis shows these stacks; the TCNQ^- ion stacks are triadic, whereas the cations form diads. The averaged radical-ion planes make angles of the order of $14 (1)^\circ$ with the stacking direction [001], but they are not strictly parallel: they form an angle of $1.1 (5)^\circ$. The distance of $3.175 (10) \text{ Å}$ between anions in a triad is the distance from the barycentre of the central TCNQ^- ion to the averaged planes of the others: the equations of these planes have been calculated from the quinonic cores. These distances reveal a relatively important overlapping between TCNQ^- of a triad, of the order of the one encountered in the charge-transfer complex TTF-TCNQ (Kistenmacher, Phillips & Cowan, 1974), whereas in radical-ion salts we generally observe distances greater than 3.20 Å , e.g. 3.25 Å in $2(\text{morpholinium}^+).3(\text{TCNQ})^{2-}$ (Sundaresan & Wallwork, 1972*a*) and 3.26 Å in $2(\text{trimethylammonium}^+).3(\text{TCNQ})^{2-}$ (Kobayashi, Danno & Saito, 1973), although it is only, in this last salt, a question of diadic stacking of TCNQ^- . The overlap for the TCNQ^- ions is of 'REB' type (Herbstein, 1971), that is with the exocyclic $\text{C}=\text{C}$ double bond over the quinonoid ring of the adjacent molecule, with gliding parameters, according to the scheme of André, Bieber & Gautier (1976), $\delta_y = 2.029 (5)$ and $\delta_x = 0.026 (5) \text{ Å}$. We do not observe interactions between radical-ion columns along the [100] direction, the intermolecular distances being greater than the van der Waals distances. Neither are there interactions between radical ions of neighboring triads in a column along the [001] direction, the distance between two adjacent triads being $3.430 (5) \text{ Å}$. Although there is no overlap on this side, nevertheless we can characterize the reciprocal position of two neighboring TCNQ^- ions of two adjacent triads by the parameters $\delta_y = 1.685 (5)$ and $\delta_x = 0.509 (5) \text{ Å}$; it is neither superposition of 'REB' type nor of diagonal gliding as in the structure of $[N-(n\text{-propyl})-$

quinolinium] $^+ \cdot 2(\text{TCNQ})^-$ (Sundaresan & Wallwork, 1972*b*). There is a rather strong interaction between columns of cations and of radical anions which is characterized by a distance of $2.966 (3) \text{ Å}$ between $\text{S}(41)^*$ and $\text{N}(33)$, the sum of van der Waals radii being

* Symmetry code: (i) $-x, -1-y, 1-z$.

Table 1. Fractional coordinates ($\times 10^4$) of atoms and isotropic thermal parameters $B_{\text{eq}} (\text{Å}^2)$

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
C(1)	-1029 (4)	721 (1)	-65 (2)	2.1
C(2)	-1849 (4)	-53 (1)	238 (3)	2.3
C(3)	-843 (4)	-748 (1)	301 (3)	2.3
C(7)	2072 (4)	-1430 (1)	159 (3)	2.4
C(8)	1334 (4)	-2218 (1)	449 (3)	2.8
C(9)	3965 (5)	-1411 (1)	-99 (3)	3.0
N(13)	801 (5)	-2861 (2)	689 (3)	4.0
N(14)	5491 (4)	-1413 (2)	-295 (4)	4.5
C(21)	-293 (4)	509 (1)	3274 (3)	2.3
C(22)	-1150 (4)	-714 (1)	3570 (3)	2.6
C(23)	-167 (4)	-1420 (1)	3605 (3)	2.7
C(24)	1718 (4)	-1420 (1)	3360 (3)	2.5
C(25)	2578 (4)	-653 (1)	3067 (3)	2.6
C(26)	1609 (4)	54 (1)	3027 (3)	2.4
C(27)	2707 (4)	-2147 (1)	3446 (3)	2.9
C(28)	1856 (5)	-2906 (2)	3794 (3)	3.6
C(29)	4587 (5)	-2175 (2)	3220 (3)	3.5
C(30)	-1297 (4)	772 (1)	3232 (3)	2.5
C(31)	-545 (4)	1555 (2)	2987 (3)	3.0
C(32)	-3196 (5)	786 (2)	3486 (3)	3.3
N(33)	1194 (6)	-3518 (2)	4096 (4)	5.0
N(34)	6117 (6)	-2218 (2)	3045 (4)	5.2
N(35)	-24 (5)	2006 (2)	2812 (4)	4.8
N(36)	-4715 (5)	827 (2)	3687 (4)	5.4
S(41)	-1815 (2)	-5096 (1)	4197 (1)	4.2
S(42)	-2446 (2)	-4236 (1)	2964 (1)	4.9
C(43)	-2258 (4)	-4872 (1)	1572 (3)	2.8
C(44)	-1757 (4)	-5686 (2)	1772 (3)	3.1
C(45)	-1497 (5)	-586 (2)	3012 (3)	3.4
C(46)	-2603 (4)	-4559 (2)	336 (3)	2.8
C(47)	-2938 (5)	-3717 (2)	188 (3)	3.2
C(48)	-3291 (5)	-3425 (2)	-987 (3)	3.4
C(49)	-3339 (5)	-3972 (2)	-2044 (3)	3.3
C(50)	-2992 (5)	-4809 (2)	-1916 (3)	3.3
C(51)	-2631 (5)	-5098 (2)	-752 (3)	3.1
O(52)	-3673 (4)	-3751 (1)	-3230 (3)	4.2
C(53)	-4079 (8)	-2898 (3)	-3392 (5)	5.7

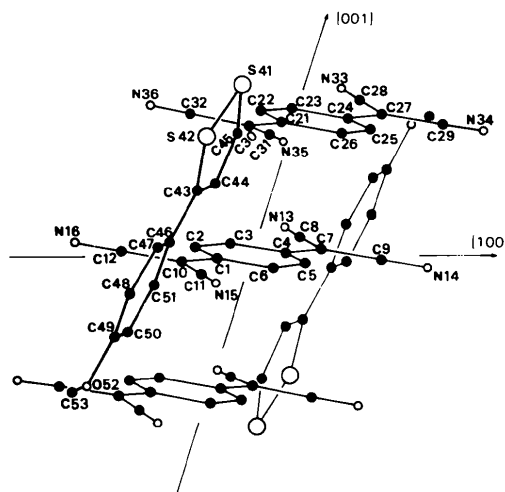


Fig. 1. Projection of the structure along [010] and numbering of atoms.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a projection of the structure along [001] have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42929 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3.35 Å. As is seen in Fig. 2, the cations form diadic stacks arranged head to tail but without superposition, which excludes overlapping.

As for all radical-ion salts, it is interesting to know the amount of charge transfer. According to the assumption of Flandrois & Chasseau (1977), by investigation of the bond lengths in the radical anions TCNQ⁻ we find that there is a charge of about +0.80 (13) on TCNQ(1) and a charge of about +0.70 (15) on TCNQ(2): if the standard deviations on the bond lengths are taken into account, the charges possessed by each of the three TCNQ of the triad can be seen as equivalent.

Ions. Intramolecular distances and angles observed in the radical ions and the cation are collected in Table 2. The radical ions TCNQ⁻ are planar with small deformations which are revealed by angular deviations from 0 to 3.2 (5)° between the nitrile groups and the average plane of the quinonic core to which they are linked. The cation consists of two planar rings, phenyl and dithiole, which form an angle of 6.6 (5)°.

Because of the size of the available crystals, it was not possible to measure the DC conductivity. Nevertheless, given the distance of 3.43 Å between triads of radical ions, the compound can be expected to behave as an insulator along the stacking direction of TCNQ⁻.

The synthesis of this complex was done by Professor Mollier's team of the Laboratoire des Composés Thioorganiques (Université de Caen). The study was done in the Laboratoire de Cristallographie et Chimie

Table 2. *Interatomic distances (Å) and angles (°)*

TCNQ (1)			
C(1)–C(2)	1.430 (3)	C(7)–C(8)	1.424 (3)
C(2)–C(3)	1.367 (3)	C(7)–C(9)	1.422 (5)
C(3)–C(4)	1.410 (4)	C(8)–N(13)	1.144 (4)
C(4)–C(7)	1.409 (3)	C(9)–N(14)	1.147 (5)
TCNQ (2)			
C(21)–C(22)	1.429 (4)	C(27)–C(29)	1.414 (5)
C(22)–C(23)	1.365 (4)	C(28)–N(33)	1.142 (4)
C(23)–C(24)	1.416 (5)	C(29)–N(34)	1.153 (6)
C(24)–C(25)	1.432 (4)	C(21)–C(30)	1.397 (4)
C(25)–C(26)	1.362 (4)	C(30)–C(31)	1.418 (4)
C(26)–C(21)	1.429 (4)	C(30)–C(32)	1.425 (5)
C(24)–C(27)	1.409 (4)	C(31)–N(35)	1.147 (4)
C(27)–C(28)	1.421 (4)	C(32)–N(36)	1.140 (6)
Dithiolium ion			
S(41)–S(42)	2.026 (1)	C(47)–C(48)	1.380 (5)
S(42)–C(43)	1.701 (3)	C(48)–C(49)	1.396 (5)
C(43)–C(44)	1.403 (4)	C(49)–C(50)	1.397 (4)
C(44)–C(45)	1.365 (5)	C(50)–C(51)	1.371 (5)
C(45)–S(41)	1.675 (3)	C(51)–C(46)	1.405 (4)
C(43)–C(46)	1.447 (4)	C(49)–O(52)	1.349 (5)
C(46)–C(47)	1.407 (4)	O(52)–C(43)	1.436 (5)
C(1)–C(2)–C(3)	120.8 (2)	C(26)–C(21)–C(30)	121.4 (2)
C(2)–C(3)–C(4)	121.0 (2)	C(21)–C(30)–C(31)	123.6 (3)
C(3)–C(4)–C(5)	118.2 (2)	C(21)–C(30)–C(32)	122.4 (3)
C(3)–C(4)–C(7)	121.5 (2)	C(31)–C(30)–C(32)	114.0 (3)
C(5)–C(4)–C(7)	120.3 (3)	C(30)–C(31)–N(35)	176.6 (3)
C(4)–C(7)–C(8)	122.8 (2)	C(30)–C(32)–N(36)	177.5 (4)
C(4)–C(7)–C(9)	121.8 (2)	C(45)–S(41)–S(42)	94.5 (1)
C(8)–C(7)–C(9)	115.3 (2)	S(41)–S(42)–C(33)	96.7 (1)
C(7)–C(8)–N(13)	177.4 (3)	S(42)–C(43)–C(44)	113.5 (2)
C(7)–C(9)–N(14)	178.5 (3)	C(43)–C(44)–C(45)	117.3 (3)
C(21)–C(22)–C(23)	120.6 (2)	C(44)–C(45)–S(41)	117.9 (3)
C(22)–C(23)–C(24)	121.5 (3)	S(42)–C(43)–C(46)	120.4 (2)
C(23)–C(24)–C(25)	118.0 (2)	C(44)–C(43)–C(46)	126.1 (3)
C(24)–C(25)–C(26)	120.9 (2)	C(43)–C(46)–C(47)	121.6 (3)
C(25)–C(26)–C(21)	121.0 (2)	C(43)–C(46)–C(51)	120.4 (3)
C(26)–C(21)–C(22)	118.1 (2)	C(46)–C(47)–C(48)	121.2 (3)
C(23)–C(24)–C(27)	121.0 (2)	C(47)–C(48)–C(49)	119.8 (3)
C(25)–C(24)–C(27)	121.0 (2)	C(48)–C(49)–C(50)	119.6 (3)
C(24)–C(27)–C(28)	121.5 (3)	C(49)–C(50)–C(51)	120.6 (3)
C(24)–C(27)–C(29)	123.0 (3)	C(50)–C(51)–C(46)	120.8 (3)
C(28)–C(27)–C(29)	115.4 (3)	C(51)–C(46)–C(47)	118.1 (3)
C(27)–C(28)–N(33)	178.5 (4)	C(48)–C(49)–O(52)	124.5 (3)
C(27)–C(29)–N(34)	178.4 (4)	C(50)–C(49)–O(52)	116.0 (3)
C(22)–C(21)–C(30)	120.6 (2)	C(49)–O(52)–C(53)	117.9 (3)

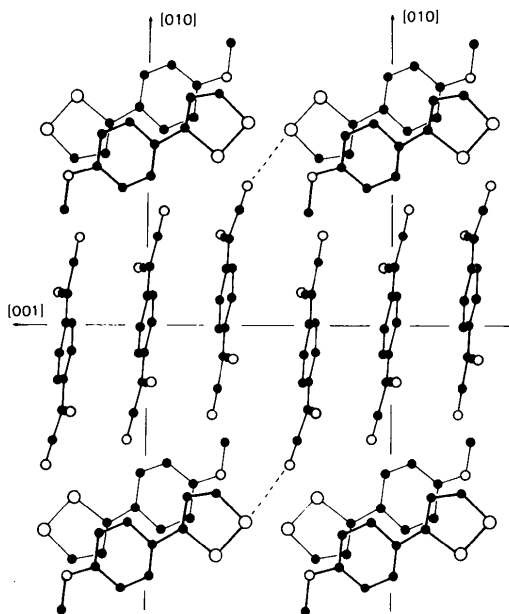


Fig. 2. Projection of the structure along [100]. The dotted line indicates the S...N interaction.

du Solide, LA 251 (Université de Caen), where the X-ray recording was performed.

References

- AMZIL, J., LE COUSTOMER, G. & MOLLIER, Y. (1981). *Chem. Scr.* **17**, 65–66.
- ANDRÉ, J.-J., BIEBER, A. & GAUTIER, F. (1976). *Ann. Phys. (Paris)*, **1**, 145–256.
- BARDEEN, J. (1973). *Solid State Commun.* **13**, 357–359.
- BENOIT, C., GALTIER, M. & MONTANER, A. (1979). *Phys. Status Solidi B*, **91**, 269–274.
- COLEMAN, L. B., COHEN, M. J., SANDMAN, D. J., YAMAGISHI, F. G., GARITO, A. F. & HEEGER, A. J. (1973). *Solid State Commun.* **12**, 1125–1132.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- DELHAES, P., KERYER, G., GAULTIER, J., FABRE, J. M. & GIRAL, L. (1982). *J. Chim. Phys.* **79**, 299–324.
- FERRARIS, J. P., COWAN, D. O., WALATKA, V. JR & PERLSTEIN, J. H. (1973). *J. Am. Chem. Soc.* **95**, 948–949.
- FLANDROIS, S. & CHASSEAU, D. (1977). *Acta Cryst.* **B33**, 2744–2750.
- HERBSTSTEIN, F. H. (1971). *Perspectives in Structural Chemistry*, Vol. IV, edited by J. D. DUNITZ & J. A. IBERS. New York: John Wiley.

- KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* B30, 763–768.
- KOBAYASHI, H., DANNO, T. & SAITO, Y. (1973). *Acta Cryst.* B29, 2693–2699.
- MATHIEU, F. (1984). *Acta Cryst.* C40, 1026–1029.
- PERLSTEIN, J. H. (1977). *Angew. Chem. Int. Ed. Engl.* 16, 519–534.
- PHILLIPS, T. E., KISTENMACHER, T. J., FERRARIS, J. P. & COWAN, D. O. (1973). *J. Chem. Soc. Chem. Commun.* pp. 471–472.
- SOOS, Z. G. (1974). *Annu. Rev. Phys. Chem.* 25, 121–153.
- SOOS, Z. G. (1978). *J. Chem. Educ.* 55, 546–552.
- SUNDARESAN, T. & WALLWORK, S. C. (1972a). *Acta Cryst.* B28, 491–497.
- SUNDARESAN, T. & WALLWORK, S. C. (1972b). *Acta Cryst.* B28, 1163–1169.
- TORRANCE, J. B. & SILVERMAN, B. D. (1977). *Phys. Rev. B*, 15, 788–801.

Acta Cryst. (1986). C42, 1172–1175

Crystal and Energy-Refined Structures of 2,2',4,4',5,5'-Hexachlorobiphenyl*

BY P. SINGH

Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, PO Box 12233, Research Triangle Park, NC 27709, USA

L. G. PEDERSEN

Department of Chemistry, University of North Carolina, Chapel Hill, NC 27514, USA

AND J. D. MCKINNEY†

Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, PO Box 12233, Research Triangle Park, NC 27709, USA

(Received 5 August 1985; accepted 5 February 1986)

Abstract. $C_{12}H_4Cl_6$, $M_r = 360.82$, monoclinic, $P2_1/n$, $a = 12.395$ (2), $b = 8.044$ (1), $c = 13.388$ (2) Å, $\beta = 94.45$ (1)°, $V = 1330.83$ Å³, $Z = 4$, $D_x = 1.80$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 12.7$ cm⁻¹, $F(000) = 712$, $T = 293$ K, $R = 0.024$ for 1075 observed reflections. The bond distances and bond angles in the title compound are similar to those found in other halogenated biphenyls. The two benzene rings are planar; however, the two rings are not coplanar. Taking the *trans*-coplanar arrangement of Cl(2) and Cl(2') as 0°, the dihedral angle between the rings is 58.3°. The crystal structure is compared with the energy-minimized molecular structures using the *ab initio* quantum-mechanical and molecular-mechanics methods, giving results in substantial agreement. The results are discussed for their possible use and importance in assessing the polychlorinated biphenyl *ortho* effect which appears to be important in determining receptor binding potency and toxicity of these compounds in biological systems.

Introduction. Polychlorinated biphenyls (PCB's) are a well known class of chemicals which have been industrially produced in several countries for many

years. The complexity of PCB mixtures introduced into the environment results in the presence of many individual PCB congeners in human tissues. Jensen & Sundstrom (1974) determined 40 PCB congeners in human tissue. One compound, 2,2',4,4',5,5'-hexachlorobiphenyl, accounted for 22% of the PCB's in tissue. Thus, this PCB may be the single most important (from a concentration point of view) congener found in human tissue and is representative of the many *ortho*-substituted PCB's which constitute the PCB residue in humans. Identification and characterization of specific PCB structures in human tissues may be important not only for assessment of long-term persistence but also for evaluation of potential health effects (McKinney, Chae, McConnell & Birnbaum, 1985).

X-ray crystallographic determinations can provide a highly accurate picture of molecular geometry in a specific solid-state environment. For most uncharged molecules like the title compound, a structure observed in the solid state is at or very near a local minimum-energy conformation. Because the active forms of toxic compounds may not necessarily be low-energy forms, it is important to have reliable information on the various conformations and their relative energies of a given molecule that may not be readily crystallizable. In this work, we compare the crystal and energy-refined structures of 2,2',4,4',5,5'-hexachlorobiphenyl.

* The following paper reports an independent structure determination of this compound.

† Author to whom reprint requests should be addressed.