

Fig. 2. Stereoview perpendicular to the *bc* plane.

non-disordered carboxylic acid groups (Leiserowitz, 1976).

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References

CHANDRASEKHAR, K. & PATTABHI, V. (1977). *Acta Cryst.* B33, 1257–1259.
 KENNARD, C. H. L., SMITH, G. & WHITE, A. H. (1980). In preparation.
 LEISEROWITZ, L. (1976). *Acta Cryst.* B32, 775–802.
 SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1978). *Acta Cryst.* B34, 2885–2887.
 SMITH, G., KENNARD, C. H. L., WHITE, A. H. & HODGSON, P. G. (1977). *Acta Cryst.* B33, 2922–2924.
 SMITH, G., KENNARD, C. H. L., WHITE, A. H. & HODGSON, P. G. (1980). *Acta Cryst.* B36, 992–994.
 SYNERHOLM, M. E. & ZIMMERMAN, P. W. (1945). *Contrib. Boyce Thompson Inst.* 14, 91–103.
 WÄGNER, A. & MALMROS, G. (1979a). *Acta Cryst.* B35, 2220–2222.
 WÄGNER, A. & MALMROS, G. (1979b). *Acta Cryst.* B35, 2222–2225.

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Structure of (Z)-9,10-Dihydro-4H-benzocyclohepta[7,6-b]thiophen-4-ylideneacetic Acid

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Abstract. C₁₅H₁₂O₂S, *M_r* = 256, monoclinic, *P*2₁/*n*, *a* = 14.089 (4), *b* = 5.9123 (6), *c* = 16.9075 (6) Å, β = 112.65 (1)°, *U* = 1299.7 (6) Å³, *Z* = 4, *D_c* = 1.31 Mg m⁻³. Final *R* = 0.036 for 1751 observed reflexions. The COOH group is *cis* with respect to the thiophene ring.

Introduction. A clear, colourless, prismatic crystal prepared by Arribas & Vega (1980) was mounted on a four-circle CAD-4 diffractometer. The intensities of 2819 reflexions within 2 < θ < 27° were collected at 295 K with monochromatic Mo Kα radiation and an ω/2θ scan technique. Two reflexions were monitored periodically and showed no crystal decomposition. The intensities were corrected for Lorentz and polarization effects and 1751 of them were considered as observed,

I > 2σ(*I*). Absorption effects (μ = 0.228 mm⁻¹) were not corrected.

Scattering factors for neutral atoms and anomalous-dispersion corrections for S were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The best *E* map revealed all the non-hydrogen atoms. After

Table 1. Coefficients for the weighting scheme

	<i>a</i>	<i>b</i>
<i>F_o</i> < 6.9	1.40	-0.16
6.9 < <i>F_o</i> < 13.8	0.43	0.00
13.8 < <i>F_o</i>	0.14	0.02

Table 2. Atomic parameters

For the nonhydrogen atoms $U_{eq} = \frac{1}{3} \sum U_{ij} a_i^* a_j^* a_k^*$. For the H atoms $U_{iso} = \exp[-8\pi^2 U(\sin \theta/\lambda)^2]$.

	x	y	z	U_{eq} (Å ² × 10 ⁴)
S	0.22416 (4)	0.94568 (13)	0.60892 (4)	550 (3)
C(2)	0.25751 (19)	1.15554 (51)	0.68416 (16)	557 (10)
C(3)	0.35854 (17)	1.15161 (45)	0.73324 (15)	457 (9)
C(3a)	0.41265 (14)	0.97425 (39)	0.71034 (12)	366 (7)
C(4)	0.52614 (14)	0.95489 (37)	0.75143 (12)	348 (7)
C(4a)	0.58161 (14)	0.91725 (37)	0.69279 (12)	358 (7)
C(5)	0.65611 (17)	1.06874 (45)	0.69120 (15)	460 (9)
C(6)	0.70680 (19)	1.03203 (52)	0.63622 (17)	562 (10)
C(7)	0.68364 (19)	0.84564 (51)	0.58335 (15)	548 (10)
C(8)	0.61217 (18)	0.69134 (49)	0.58696 (15)	499 (9)
C(8a)	0.55932 (15)	0.72489 (39)	0.64049 (13)	391 (8)
C(9)	0.47972 (17)	0.55779 (42)	0.64251 (15)	451 (9)
C(10)	0.37068 (18)	0.64762 (48)	0.59848 (15)	488 (9)
C(10a)	0.34904 (15)	0.84854 (41)	0.64279 (13)	402 (8)
C(11)	0.58194 (15)	0.98144 (41)	0.83501 (13)	407 (8)
C(12)	0.54381 (15)	0.99080 (42)	0.90491 (13)	421 (8)
O(1)	0.61210 (13)	1.07128 (40)	0.97602 (10)	700 (8)
O(2)	0.46090 (12)	0.92246 (36)	0.90023 (10)	627 (7)
	x	y	z	U_{iso} (Å ² × 10 ³)
H(2)	0.209 (2)	1.255 (5)	0.686 (2)	42 (8)
H(3)	0.392 (2)	1.250 (4)	0.779 (2)	20 (6)
H(5)	0.673 (2)	1.193 (5)	0.727 (2)	21 (7)
H(6)	0.756 (2)	1.138 (5)	0.636 (2)	33 (7)
H(7)	0.716 (2)	0.815 (5)	0.545 (2)	34 (7)
H(8)	0.597 (2)	0.560 (5)	0.552 (2)	28 (7)
H(9,1)	0.482 (2)	0.423 (5)	0.610 (2)	28 (7)
H(9,2)	0.491 (2)	0.523 (4)	0.703 (2)	18 (6)
H(10,1)	0.322 (2)	0.525 (5)	0.597 (2)	36 (7)
H(10,2)	0.359 (2)	0.697 (4)	0.537 (2)	24 (6)
H(11)	0.656 (2)	0.990 (4)	0.853 (1)	14 (6)
H(O1)	0.585 (2)	1.078 (6)	1.018 (2)	66 (11)

anisotropic full-matrix least-squares refinement R for the observed reflexions was 0.069. A difference synthesis calculated with those reflexions with $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$ showed all H atoms as the highest peaks of the map.

To prevent bias on ΔF vs F_o or $\sin \theta/\lambda$ weights were assigned as $w = 1/(a + b|F_o|)^2$, with the coefficients shown in Table 1 and calculated by PESOS (Martínez-Ripoll & Cano, 1975).

After refinement with isotropic temperature factors for H atoms, the final $R = 0.036$ and $R_w = 0.040$, where $R_w = (\sum w \Delta^2 F / \sum w |F_o|^2)^{1/2}$.

A final difference synthesis had no electron density $> 0.21 \text{ e \AA}^{-3}$. Table 2 shows the final atomic parameters.*

Discussion. The title compound, which is an intermediate in the synthesis of isosteric thiophene deriva-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35618 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å) and angles (°) in C₁₅H₁₂O₂S

E.s.d.'s in distances and angles

	σ (Å)	σ (°)	
Involving S atom	0.003	0.12	
Involving H atoms	0.032	1.70	
Involving other atoms	0.003	0.20	
S—C(2)	1.708	C(7)—C(8)	1.377
—C(10a)	1.726	—H(7)	0.95
C(2)—C(3)	1.344	C(8)—C(8a)	1.390
C(2)—H(2)	0.91	—H(8)	0.95
C(3)—C(3a)	1.435	C(8a)—C(9)	1.505
—H(3)	0.93	C(9)—C(10)	1.522
C(3a)—C(4)	1.482	—H(91)	0.97
—C(10a)	1.368	—H(92)	1.00
C(4)—C(4a)	1.497	C(10)—C(10a)	1.497
—C(11)	1.336	—H(101)	0.99
C(4a)—C(5)	1.388	—H(102)	1.03
—C(8a)	1.400	C(11)—C(12)	1.476
C(5)—C(6)	1.390	—H(11)	0.96
—H(5)	0.92	C(12)—O(1)	1.306
C(6)—C(7)	1.377	—O(2)	1.210
C(6)—C(6)	0.93	O(1)—H(O1)	0.92
C(2)—S—C(10a)	92.4	C(4a)—C(8a)—C(8)	118.8
S—C(2)—C(3)	111.7	C(4a)—C(8a)—C(9)	120.5
S—C(2)—H(2)	119.6	C(8a)—C(9)—C(10)	112.4
C(3)—C(2)—H(2)	129	H(91)—C(9)—H(92)	112
C(2)—C(3)—C(3a)	113.1	C(8a)—C(9)—H(91)	110
C(2)—C(3)—H(3)	125	C(10)—C(9)—H(91)	105
C(3a)—C(3)—H(3)	122	C(8a)—C(9)—H(92)	110
C(3)—C(3a)—C(4)	121.3	C(10)—C(9)—H(92)	108
C(3)—C(3a)—C(10a)	112.2	C(10a)—C(10)—C(9)	113.2
C(4)—C(3a)—C(10a)	126.2	H(101)—C(10)—H(102)	110
C(3a)—C(4)—C(4a)	116.4	C(9)—C(10)—H(101)	109
C(3a)—C(4)—C(11)	125.2	C(10a)—C(10)—H(101)	109
C(4a)—C(4)—C(11)	118.3	C(9)—C(10)—H(102)	109
C(4)—C(4a)—C(5)	120.6	C(10a)—C(10)—H(102)	107
C(4)—C(4a)—C(8a)	119.5	S—C(10a)—C(3a)	110.7
C(5)—C(4a)—C(8a)	120.0	S—C(10a)—C(10)	118.4
C(4a)—C(5)—C(6)	120.0	C(3a)—C(10a)—C(10)	130.9
C(4a)—C(5)—H(5)	121	C(4)—C(11)—C(12)	127.2
C(6)—C(5)—H(5)	119	C(4)—C(11)—H(11)	118
C(5)—C(6)—C(7)	120.3	C(12)—C(11)—H(11)	115
C(5)—C(6)—H(6)	118	C(11)—C(12)—O(1)	112.6
C(7)—C(6)—H(6)	122	C(11)—C(12)—O(2)	125.1
C(6)—C(7)—C(8)	119.7	O(1)—C(12)—O(2)	122.2
C(6)—C(7)—H(7)	123		
C(8)—C(7)—H(7)	117	Hydrogen bond	
C(7)—C(8)—C(8a)	121.2	O(1)—O(2')	2.663
C(7)—C(8)—H(8)	121	H(O1)—O(2')	1.75
C(8a)—C(8)—H(8)	118	O(1)—H(O1)—O(2')	177
C(8)—C(8a)—C(9)	120.8		

tives, has been prepared and studied by spectroscopy by Arribas & Vega (1980). These derivatives have structures similar to those of benzocycloheptapyridoisoquinoline and are pharmacologically active in the central nervous system.

To establish the orientation of the carboxylic group with respect to the thiophene ring, the structure of the title compound has been determined.

Interatomic distances and angles are listed in Table 3. Fig. 1 shows the geometry of the molecule and the atom labelling.

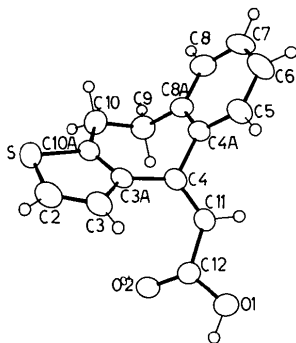


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule. The numbering corresponds to that in Table 3.

Table 4. Atomic deviations (Å) from least-squares planes

E.s.d.'s are in parentheses.

Plane I		Plane II	
C(11)	-0.005 (3)	C(10a)	0.031 (2)
C(12)	0.018 (3)	C(3a)	0.068 (2)
O(1)	-0.005 (3)	C(4)	-0.288 (2)
O(2)	-0.006 (2)	C(4a)	0.279 (2)
		C(8a)	-0.151 (2)
Plane III		Plane IV	
C(4a)	0.008 (3)	S	-0.001 (1)
C(5)	-0.009 (3)	C(2)	0.004 (3)
C(6)	-0.004 (4)	C(3)	0.000 (3)
C(7)	0.015 (3)	C(3a)	-0.004 (3)
C(8)	-0.012 (3)	C(10a)	-0.005 (3)
C(8a)	-0.001 (3)		

Angles between planes (°) (e.s.d.'s ~0.03°)

I and II	30.4	II and III	39.5
I and III	36.1	II and IV	21.8
I and IV	51.8	III and IV	55.5

All the groups of atoms forming planes deviate significantly from planarity at the 95% level.

The structure comprises molecules hydrogen bonded around centres of symmetry forming dimers in a manner typical of carboxylic acids. The carboxyl group is *cis* to the thiophene ring. The least-squares planes for various portions of the molecule, Table 4, have been computed by PARST5 (Nardelli, Musatti, Domiano & Andreotti, 1965). The molecule is not planar, the torsion angle C(8a)–C(9)–C(10)–C(10a) being $-64.8 (3)^\circ$.

Most of the calculations were carried out with XRAY 70 (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Computing Center of JEN (Madrid) for the facilities provided on the Univac 1100/80 computer.

References

- ARRIBAS, E. & VEGA, S. (1980). Private communication.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). PESOS program. Instituto Rocasolano, CSIC, Serrano 119, Madrid-6, Spain.
- NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREOTTI, G. D. (1965). *Ric. Sci.* **35**, 807–810.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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The Structure of 1,2,3,5-Tetrachlorobenzene

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Abstract. C₆H₂Cl₄, monoclinic, *P*2₁/*c*, *Z* = 8, *a* = 3.8530 (8), *b* = 24.010 (3), *c* = 17.226 (4) Å, β = 94.12 (2)°, *D*_c = 1.804 Mg m⁻³. The structure was solved by molecular-packing analysis and difference Fourier methods and refined to *R* = 0.047 for 2770 reflections.

Introduction. The crystal structure of the title compound was undertaken to provide a larger data base in connection with a study of Cl...Cl nonbonded interactions in crystals (Hsu & Williams, 1980). In the cited work, no evidence for nonbonded anisotropy above a threshold level was found in a study of five