

(*MULTAN82*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). All H atoms from difference Fourier map. Full-matrix least-squares anisotropic (β_y) refinement (H atoms isotropic, not refined), $R = 0.062$, $wR = 0.082$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/[\sigma(|F_o|^2) + (0.07 F_o)^2]$, $S = 1.94$, $(\Delta/\sigma)_{\max} = 0.01$, $\Delta\rho_{\max} = 0.65 \text{ e } \text{\AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows a perspective view of the crystal structure. Final atomic parameters are in Table 1,* bond distances and angles on Fig. 2.

We are concerned here with the relative positions of the methylthio substituents. They are *trans* to each other on a planar TTF unit located at a center of symmetry in the crystal. The sulfur atom S(5) of the methylthio substituent is in the TTF plane while the methyl carbon C(7) is 1.29 Å out of this plane.

All the bond lengths are longer than in TTF itself (Cooper, Kenny, Edmonds, Nagel, Wudl & Coppens,

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and least-squares-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39985 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1971). The dissymmetry imposed by the non-coplanar methylthio substituents is reflected strongly in the disparity of the C—S bond lengths. Of particular interest is the pronounced departure from the usual *m* molecular symmetry due to alternating long–short bonds in the –C–S– sequence. This indicates that the difference in coordination (and possibly in charge) of carbon atoms C(2) and C(3) bearing different substituents is reflected over to the inner S(1) and S(2) atoms. Then the *trans* configuration of the two TTF halves across the center of symmetry ($\bar{1}$) may indeed minimize repulsions between equivalently charged sulfur atoms.

References

- COOPER, W. F., KENNY, N. C., EDMONDS, J. W., NAGEL, A., WUDL, F. & COPPENS, P. (1971). *J. Chem. Soc. Chem. Commun.* p. 889.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- SOUZI, A. & ROBERT, A. (1984). *Tetrahedron*, **40**(10), 1817–1822.

Acta Cryst. (1985). **C41**, 929–931

2-Methyl-1-benzothiophene, C₉H₈S

BY H. H. SUTHERLAND AND A. RAWAS

Physics Department, The University of Hull, Hull HU6 7RX, England

(Received 3 December 1984; accepted 11 February 1985)

Abstract. $M_r = 148.2$, orthorhombic, $Pna2_1$, $a = 11.71$ (2), $b = 11.03$ (2), $c = 5.96$ (1) Å, $V = 769.8$ Å³, $Z = 4$, $D_m = 1.27$, $D_x = 1.28$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 2.876$ mm⁻¹, $F(000) = 312$, $T = 283$ K, $R = 0.079$ for 553 observed densitometer and visually measured equi-inclination Weissenberg data. The five- and six-membered rings are planar and inclined to one another at 0.6 (4)°. The average C—C bond length in the phenyl ring is 1.398 (20) Å. In the five-membered ring the average C—S bond length is 1.756 (16) Å, the C—S—C angle is 92.4 (6)°; the C—C bond lengths are 1.485 (17) and 1.382 (16) Å. The C—Me bond makes an angle of 1.5 (4)° with the five-membered ring.

Introduction. This paper forms part of an investigation into 1-benzothiophene derivatives. These frequently discolour on exposure to the atmosphere and sublime quite rapidly under X-ray irradiation.

Experimental. D_m measured by flotation using aqueous cadmium *n*-dodecatungstoborate. White transparent crystals used in data collection about c and b had dimensions 0.08 × 0.1 × 0.3 mm and 0.09 × 0.15 × 0.12 mm respectively. Since 2-methyl-1-benzothiophene sublimes rapidly, these crystals together with some additional material were sealed in Lindemann-glass capillaries. Data for 400 reflexions measured with Joyce–Loebl flying-spot densitometer and 500 by

visual estimation from multiple-film Weissenberg photographs, Cu $K\alpha$ radiation. Data merged to give 553 unique observed reflections. hkl : $0 \leq h \leq 14$; $0 \leq k \leq 13$; $0 \leq l \leq 6$, $R_{\text{int}} = 0.05$. Structure solved by Patterson synthesis and refined (on F) by block-diagonal least squares with anisotropic thermal parameters for non-hydrogen atoms. H-atom positions, initially obtained from difference synthesis and placed at geometrically reasonable positions, refined with isotropic thermal parameters. Final $R = 0.079$, $wR = 0.085$, $w^{-1} = \sigma^2(F_o) + 0.002 F_o^2$. $(\Delta/\sigma)_{\text{max}}$ in final refinement cycle 0.06 for positional and 0.12 for thermal parameters. Max. and min. heights in final $\Delta\rho$ map $+0.29$ and $-0.49 \text{ e } \text{\AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs used: *SHELX76* (Sheldrick, 1976) and local programs supplied by HHS and Drs C. Morgan and M. J. Mottram.

Discussion. Table 1* gives atomic parameters and Table 2 bond lengths and angles. The atomic numbering is shown in Fig. 1.

The individual five- and six-membered rings are planar but the molecule as a whole shows a small deviation from planarity, the rings being inclined at $0.6 (4)^\circ$ to one another. A similar angle of 0.6° was determined in 5-bromo-2,3-dimethyl-1-benzothiophene (Hogg & Sutherland, 1974). C(9) of the methyl group is displaced by $0.039 (11) \text{ \AA}$ from the five-membered ring with the C(9)–C(8) bond inclined at $1.5 (4)^\circ$ to the five-membered ring. The C(8)–C(9) bond length of $1.451 (16) \text{ \AA}$ is smaller than the values of $1.499 (15)$ and $1.493 (15) \text{ \AA}$ found in 5-bromo-2,3-dimethyl-1-benzothiophene.

The C(1)–S bond of $1.741 (10) \text{ \AA}$ is in good agreement with the value of $1.740 (8) \text{ \AA}$ found in dibenzothiophene (Schaffrin & Trotter, 1970). The C(8)–S bond of $1.772 (16) \text{ \AA}$ is similar to the value of $1.767 (10) \text{ \AA}$ in 2,3-dichloro-1-benzothiophene (Sutherland & Ali-Adib, 1985). The C(6)–C(7) bond of $1.485 (17) \text{ \AA}$ is larger than the corresponding values of $1.441 (1)$ and $1.445 (6) \text{ \AA}$ in dibenzothiophene and 1:1 trinitrobenzene-1-benzothiophene-3-carbaldehyde (Pascard & Pascard-Billy, 1972) respectively. The C(7)–C(8) bond of $1.382 (16) \text{ \AA}$ is in good agreement with the corresponding bond of 1.369 \AA in thiophene (Harshbarger & Bauer, 1970). The C–S–C bond angle of $92.4 (6)^\circ$ is similar to those in related molecules.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, intermolecular distances and mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42055 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The authors wish to thank Mr G. Collier for providing the crystals. One of us (AR) is indebted to the University of Aleppo, Syria, for the award of a research studentship.

Table 1. *Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses*

$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}$$

| | x | y | z | U_{eq} |
|------|-----------|-----------|------------|-----------------|
| S | 584 (2) | 2169 (2) | 0 | 63 (2) |
| C(1) | 1730 (8) | 1166 (9) | 146 (32) | 55 (6) |
| C(2) | 2584 (10) | 1005 (12) | -1533 (22) | 61 (8) |
| C(3) | 3401 (11) | 150 (14) | -1083 (31) | 74 (9) |
| C(4) | 3421 (10) | -509 (11) | 977 (30) | 63 (8) |
| C(5) | 2584 (10) | -349 (10) | 2545 (22) | 54 (6) |
| C(6) | 1712 (9) | 508 (10) | 2127 (26) | 54 (7) |
| C(7) | 754 (9) | 847 (9) | 3634 (22) | 52 (6) |
| C(8) | 76 (9) | 1734 (10) | 2683 (28) | 56 (7) |
| C(9) | -961 (10) | 2270 (9) | 3574 (22) | 70 (8) |

Table 2. *Bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses*

| | | | |
|----------------|------------|----------------|------------|
| C(1)–C(2) | 1.426 (19) | C(5)–C(6) | 1.414 (16) |
| C(1)–C(6) | 1.386 (22) | C(6)–C(7) | 1.485 (17) |
| C(1)–S | 1.741 (10) | C(7)–C(8) | 1.382 (16) |
| C(2)–C(3) | 1.370 (19) | C(8)–C(9) | 1.451 (16) |
| C(3)–C(4) | 1.427 (24) | C(8)–S | 1.772 (16) |
| C(4)–C(5) | 1.366 (19) | | |
| C(1)–C(2)–C(3) | 116.0 (12) | C(7)–C(8)–C(9) | 128.3 (12) |
| C(2)–C(3)–C(4) | 122.1 (14) | C(7)–C(8)–S | 111.7 (9) |
| C(3)–C(4)–C(5) | 120.7 (13) | C(9)–C(8)–S | 120.1 (9) |
| C(4)–C(5)–C(6) | 119.0 (12) | C(8)–S–C(1) | 92.4 (6) |
| C(5)–C(6)–C(1) | 119.3 (12) | S–C(1)–C(6) | 111.3 (10) |
| C(5)–C(6)–C(7) | 127.4 (11) | S–C(1)–C(2) | 125.8 (10) |
| C(7)–C(6)–C(1) | 113.3 (11) | C(6)–C(1)–C(2) | 122.9 (12) |
| C(6)–C(7)–C(8) | 111.4 (10) | | |

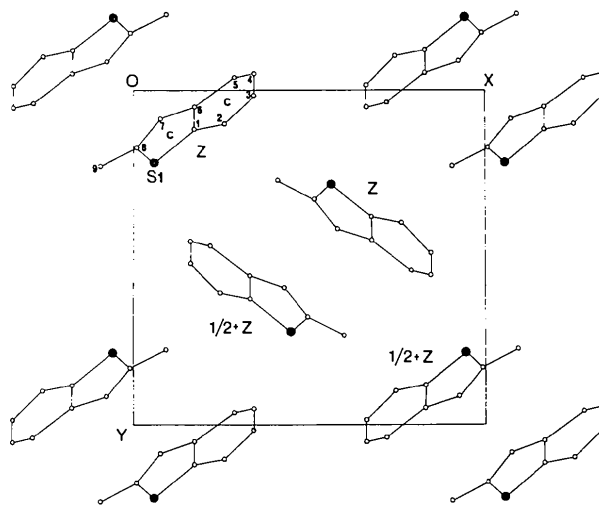


Fig. 1. The arrangement of the molecules in the unit cell viewed along c .

References

- HARSHBARGER, W. R. & BAUER, S. H. (1970). *Acta Cryst.* B26, 1010–1020.
- HOGG, J. H. C. & SUTHERLAND, H. H. (1974). *Acta Cryst.* B30, 2058–2059.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- PASCARD, R. & PASCARD-BILLY, C. (1972). *Acta Cryst.* B28, 1926–1935.
- SCHAFFRIN, R. M. & TROTTER, J. (1970). *J. Chem. Soc.* pp. 1561–1565.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SUTHERLAND, H. H. & ALI-ADIB, Z. (1985). In preparation.

Acta Cryst. (1985). C41, 931–933

Structure from a Twinned Crystal of the Triclinic Form of the 1:1 Complex between *N,N*-Dimethylaniline and Hexafluorobenzene [$C_8H_{11}N.C_6F_6$] at 120 K

BY TOR DAHL

Institute of Mathematical and Physical Sciences, University of Tromsø, PO Box 953, N-9001 Tromsø, Norway

(Received 15 October 1984; accepted 13 February 1985)

Abstract. $M_r = 307.24$, triclinic, $P\bar{1}$, $a = 6.780$ (3), $b = 8.256$ (3), $c = 12.327$ (3) Å, $\alpha = 99.47$ (2), $\beta = 92.01$ (3), $\gamma = 106.04$ (3)°, $V = 651.7$ (4) Å³, $Z = 2$, $D_x = 1.566$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.167$ mm⁻¹, $F(000) = 312$, $T = 120$ K, $R = 0.060$ for 1581 observed non-overlapping reflections. The molecules are stacked alternately in infinite columns. Although the N atom has a partially tetrahedral geometry, the overlap between adjacent molecules is approximately equal on both sides of the dimethylaniline molecule, indicating that it is a π donor. The corresponding mean interplanar distances are 3.382 (2) and 3.392 (2) Å.

Introduction. In the monoclinic room-temperature form of the title compound, *N,N*-dimethylaniline (DMA) is situated on a twofold axis and it has therefore been concluded that the geometry of the N atom is planar, and that DMA is a π donor in this complex (Dahl, 1977). As, however, the observed thermal vibrations are large, this twofold symmetry may also be a result of orientational disorder. In the complex with tetrafluoro-*p*-benzoquinone the tetrahedral geometry of the N atom and the large differences in intermolecular distances on different sides of the molecule indicate that DMA is an n donor (Dahl, 1981). The present low-temperature study was initiated in order to elucidate the nature of DMA as an electron donor in the complex with hexafluorobenzene (HFB).

Experimental. Crystals formed by mixing equimolar amounts of the components. Unstable on exposure to atmosphere at room temperature. After sealing in capillaries at low temperature, large crystals grown by sublimation at room temperature. Crystal used for data collection $0.5 \times 0.5 \times 0.5$ mm.

With transformation matrix $(111/13\bar{1}/\bar{1}00)$, the triclinic cell may be transformed to a pseudo-monoclinic cell similar to that of the room-temperature form, but with the a and b axes doubled. There is thus a pseudo-mirror plane $(01\bar{1})$ in the cell, and twins of the pseudo-merohedral type (Cahn, 1954) with an obliquity of only 0.7° were formed when the crystals were cooled below the transition point. Overlap may occur for reflections from different individuals with indices related by the matrix $A = (100/\bar{1}\bar{1}\bar{1}/\bar{1}\bar{1}\bar{1})$ and consequently only for reflections with $h + k + l = 2n$.

Enraf–Nonius CAD-4 diffractometer and cooling device, unit-cell parameters and orientation matrix from setting angles of 25 reflections ($6 < \theta < 20^\circ$) with $h + k + l = 2n + 1$. Intensity collection by $\omega/2\theta$ scan, $\theta_{\max} = 28^\circ$, $0 \leq h \leq 8$, $-9 \leq k \leq 9$, $-14 \leq l \leq 14$. 3 standard reflections, no systematic decay, but two sharp falls down to 75%, probably due to ice formation. No absorption correction. 2294 unique reflections measured, 378 unobserved [$I < 2\sigma(I)$]. From all observed reflections non-H atoms located from a Patterson map, but least-squares refinement could not bring R below 0.15. 323 reflections with F_o considerably greater than F_c , and $F_c(hkl) \leq F_c(h'k'l')$, $h'k'l'$ related to hkl by A , were assumed to be affected by overlap and left out in subsequent refinement. 12 reflections, apparently influenced by ice formation indicated by standard reflections, were also left out. In last stage of refinement all H atoms located from difference map. Positional parameters for all atoms and thermal parameters, anisotropic for non-H atoms, isotropic for H atoms, refined. Final $R = 0.060$, $wR = 0.087$, goodness of fit $S = 1.16$, $w - 1$ for $|F_{\text{obs}}| \leq 8$ else $w = (8/|F_{\text{obs}}|)^2$. Max. $\Delta/\sigma = 0.09$. Max. and min. electron densities in final difference map 0.39 and -0.29 e Å⁻³. Table 1 gives atomic coordinates and Fig.