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2-Thienylmethylenemalononitrile, $C_8H_4N_2S$

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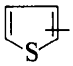
Abstract. $M_r = 160{\cdot}2$, monoclinic, $P2_1/c$, $a = 5{\cdot}701\ (2)$, $b = 18{\cdot}613\ (4)$, $c = 7{\cdot}473\ (3)$ Å, $\beta = 97{\cdot}57\ (3)°$, $V = 786{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}35$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 3{\cdot}31$ cm^{-1}, $F(000) = 328$, room temperature, $R = 0{\cdot}050$ for 929 reflections with $|F_o| > 4\sigma\ (|F_o|)$. The two planar parts in the molecule, the thiophene ring and the dicyanovinyl moiety, are inclined at 3·6 (5)° to one another and the vinylic H atom is *trans* with respect to the S atom. The electron-withdrawing properties of the cyanide groups affect two of the C—C bond lengths.

Introduction. Arylidene malononitriles, ArCH=C(CN)$_2$, one of the important physiologically active series of compounds, have been throughly investigated (Freeman, 1980). Surprisingly the thienylmethylene derivatives (Ar = ) failed to attract much attention even though the bio-isosteric relationship between benzene and thiophene is well known. In the course of an investigation on the latter (De, Bhattacharyya, Brunskill, Sidhu & Ewing, 1982), semi-empirical MO calculations at the CNDO/2 level were carried out on a number of compounds. In the absence of any experimental data on bond lengths or bond angles of the compounds under investigation, literature values of these for thiophene (Bak, Christensen, Hansen-Nygaard & Rastrup-Andersen, 1961) and the dicyanovinyl moiety (Auvray & Genet, 1971) were used. It was not possible to ascertain the orientation of the vinylic hydrogen, and the conformation of the molecule was assumed by analogy with that of 2-thiophenecarbaldehyde (Roques, Combrisson, Riche & Pascard-Billy, 1970). The present paper reports the crystal and molecular structure of 2-thienylmethylenemalononitrile.

Experimental. 0·275 × 0·15 × 0·125 mm crystal from ethanol, symmetry from oscillation and Weissenberg photographs, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, ω–2θ scans, accurate cell parameters from 25 random reflections $20{\cdot}6 < 2\theta < 27{\cdot}0°$, 1435 unique reflections with $h = -6$–6, $k = 0$–22, $l = 0$–8 and $2 \le \theta \le 25°$, 929 with $I \ge 2\sigma(I)$, corrected for Lp, absorption ignored, intensity variation of standards <3%; structure solved by Patterson–Fourier method, refined by anisotropic block-diagonal least squares (Vickery, Bright & Mallinson, 1971), H (from standard geometry) isotropic, $R = 0{\cdot}050$, $wR = 0{\cdot}067$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$: $|F_o| < 10{\cdot}3$, $\sigma(F) = 0{\cdot}13|F_o|$; $10{\cdot}3 < |F_o| \le 12{\cdot}3$, $\sigma(F) = 0{\cdot}12|F_o|$; $12{\cdot}3 < |F_o| \le 14{\cdot}3$, $\sigma(F) = 0{\cdot}09 \times |F_o|$; $14{\cdot}3 < |F_o| \le 16{\cdot}9$, $\sigma(F) = 0{\cdot}07|F_o|$; $16{\cdot}9 < |F_o| \le 19{\cdot}8$, $\sigma(F) = 0{\cdot}06|F_o|$; $19{\cdot}8 < |F_o| \le 24{\cdot}1$, $\sigma(F) = 0{\cdot}04|F_o|$; $|F_o| > 24{\cdot}1$, $\sigma(F) = 0{\cdot}03|F_o|$ (Seal & Ray, 1981); max. Δ/σ for non H 0·42 and av. Δ/σ for H 0·27 in final LS cycle, residual electron density in final ΔF synthesis within $\pm 0{\cdot}2$ e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974).

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Table 1. *Fractional atomic coordinates* ($\times 10^4$; $\times 10^3$ *for* H) *and isotropic thermal parameters* (*for non*-H *atoms expressed as* $\frac{1}{3}\sum_i B_{ii}$) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq}/B_{iso}(Å^2)
S	4053 (2)	3574 (1)	1623 (2)	5·3 (1)
N(1)	9379 (6)	943 (2)	3781 (6)	6·0 (2)
N(2)	2815 (6)	1852 (2)	1130 (5)	6·0 (2)
C(1)	4360 (8)	4472 (3)	1902 (7)	6·2 (2)
C(2)	6448 (10)	4661 (2)	2867 (8)	6·8 (3)
C(3)	7965 (8)	4098 (2)	3430 (6)	5·1 (2)
C(4)	6818 (6)	3428 (2)	2839 (5)	4·2 (2)
C(5)	7871 (6)	2745 (2)	3211 (5)	4·0 (2)
C(6)	6987 (6)	2081 (2)	2816 (5)	3·8 (2)
C(7)	8338 (6)	1447 (2)	3341 (5)	4·4 (2)
C(8)	4659 (7)	1955 (2)	1878 (5)	4·5 (2)
H(1)	312 (8)	481 (2)	138 (6)	5·0 (12)
H(2)	689 (9)	508 (3)	317 (7)	6·2 (13)
H(3)*	945	413	411	3·4
H(5)	950 (7)	277 (2)	389 (5)	2·8 (9)

* Not refined.

Table 2. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(1)—S—C(4)	91·0 (2)	S—C(1)—C(2)	113·0 (4)
C(1)—C(2)—C(3)	115·8 (5)	C(2)—C(3)—C(4)	108·6 (4)
C(3)—C(4)—S	111·6 (3)	C(3)—C(4)—C(5)	123·3 (3)
C(5)—C(4)—S	125·2 (3)	C(4)—C(5)—C(6)	129·8 (3)
C(5)—C(6)—C(7)	121·4 (3)	C(5)—C(6)—C(8)	123·4 (3)
C(7)—C(6)—C(8)	115·3 (3)	C(6)—C(7)—N(1)	178·7 (4)
C(6)—C(8)—N(2)	179·6 (4)		

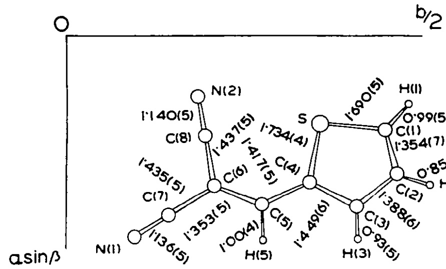

Fig. 1. *c*-axis view of the molecule with atom-numbering scheme and bond lengths (Å).

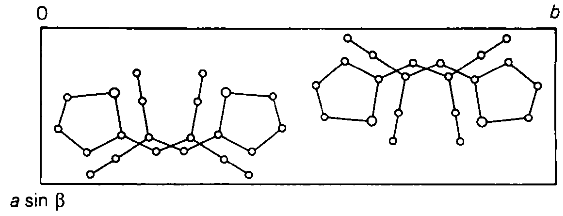

Fig. 2. The packing arrangement projected along **c**.

Discussion. Final atomic parameters and bond angles with e.s.d.'s are given in Tables 1* and 2, respectively; Fig. 1 shows a view of the molecule projected along **c** together with the atom-numbering scheme and bond lengths. All the bond lengths and angles except 1·449 (6) and 1·417 (5) Å for C(3)—C(4) and C(4)—C(5) are similar to those of thiophene (Gutiérrez-Puebla & Monge, 1981; Prout & Miao, 1982) and malononitrile derivatives (Adhikesavalu & Venkatesan, 1982). The partial single- and double-bond characters of C(3)—C(4) and C(4)—C(5), respectively, can be explained from consideration of the canonical forms of a thiophene ring carrying an electron-withdrawing substituent in the 2-position (Gronowitz, 1963). The dihedral angle between the two planar parts in the molecule, the thiophene ring and the dicyanovinyl moiety, is 3·6 (5)°. The torsion angles 177·0 (4) and 177·7 (10)° for C(3)—C(4)—C(5)—C(6) and S—C(4)—C(5)—H(5) reveal a *trans* junction about C(4)—C(5). The crystal structure consists of discrete molecules with no intermolecular distance shorter than the sum of the van der Waals radii (Pauling, 1960). A packing diagram is shown in Fig. 2.

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* Lists of structure factors, anisotropic thermal parameters and least-squares plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39143 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Adhikesavalu, D. & Venkatesan, K. (1982). *Acta Cryst.* B**38**, 855–859.

Auvray, P. & Genet, F. (1971). *Acta Cryst.* B**27**, 2424–2429.

Bak, B., Christensen, D., Hansen-Nygaard, L. & Rastrup-Andersen, J. (1961). *J. Mol. Spectrosc.* **7**, 58–63.

De, A., Bhattacharyya, S. P., Brunskill, J. S. A., Sidhu, K. K. & Ewing, D. F. (1982). *J. Chem. Res.* (*S*), pp. 312–313.

Freeman, F. (1980). *Chem. Rev.* **80**, 329–350.

Gronowitz, S. (1963). *Adv. Heterocycl. Chem.* **1**, 1–124.

Gutiérrez-Puebla, E. & Monge, A. (1981). *Acta Cryst.* B**37**, 277–279.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

Prout, C. K. & Miao, F. M. (1982). *Acta Cryst.* B**38**, 685–687.

Roques, B., Combrisson, S., Riche, C. & Pascard-Billy, C. (1970). *Tetrahedron*, **26**, 3557–3567.

Seal, A. & Ray, S. (1981). *Indian J. Phys.* **55**A, 414–416.

Vickery, B. L., Bright, D. & Mallinson, P. R. (1971). *XRAY ARC*. IBM 1130 program system for crystallography modified for the Burroughs computer.