$V = 1495.6$ (2) Å^3
$Z = 4$
$D_x = 1.365$ Mg m^{-3}

0.80 × 0.55 × 0.45 mm
Colourless
Crystal source: grown from ethyl acetate/hexane solution

Data collection

Siemens Stoe AED-2 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.481$, $T_{\max} = 0.622$
2130 measured reflections
1913 independent reflections

1766 observed reflections $[|F_o| > 4\sigma(F_o)]$
$\theta_{\max} = 22.5°$
$h = -11 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 16$
4 standard reflections
frequency: 120 min
intensity variation: 0.36%

Refinement

Refinement on F
$R = 0.0350$
$wR = 0.0498$
$S = 1.303$
1766 reflections
181 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.000060F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.257$ e Å^{-3}
$\Delta\rho_{\min} = -0.279$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
N(1)	0.10402 (15)	−0.06385 (24)	0.28621 (12)	0.0340 (11)
C(2)	−0.00601 (19)	−0.0593 (3)	0.31189 (17)	0.0440 (15)
C(3)	−0.00961 (22)	−0.1888 (4)	0.38304 (18)	0.0516 (17)
C(4)	0.08798 (22)	−0.1679 (4)	0.45593 (17)	0.0505 (17)
O(5)	0.19167 (14)	−0.17680 (20)	0.42223 (10)	0.0398 (10)
C(6)	0.20147 (18)	−0.0593 (3)	0.35495 (14)	0.0329 (13)
C(7)	0.29152 (19)	−0.1184 (3)	0.30553 (15)	0.0353 (14)
C(8)	0.24594 (20)	−0.1561 (3)	0.21934 (16)	0.0384 (15)
C(9)	0.12484 (20)	−0.1238 (3)	0.20782 (16)	0.0365 (14)
O(10)	0.05559 (15)	−0.14692 (24)	0.14251 (11)	0.0524 (12)
C(11)	0.30853 (24)	−0.2214 (3)	0.16014 (18)	0.0519 (17)
C(12)	0.4204 (3)	−0.2447 (4)	0.18893 (21)	0.0632 (21)
C(13)	0.46653 (24)	−0.2046 (4)	0.27443 (22)	0.0613 (20)
C(14)	0.40296 (20)	−0.1416 (3)	0.33475 (18)	0.0476 (17)
S(1′)	0.26498 (6)	0.24926 (8)	0.30941 (4)	0.0431 (4)
C(2′)	0.21661 (20)	0.1200 (3)	0.39186 (15)	0.0352 (14)
S(3′)	0.30770 (7)	0.12121 (9)	0.49747 (5)	0.0596 (5)
C(4′)	0.3015 (3)	0.3420 (4)	0.52080 (20)	0.0675 (21)
C(5′)	0.3399 (3)	0.4539 (4)	0.45272 (21)	0.0647 (20)
C(6′)	0.26530 (24)	0.4483 (3)	0.36402 (19)	0.0551 (18)

Table 2. *Selected geometric parameters* (Å, °)

N(1)—C(6)	1.464 (3)	C(8)—C(7)	1.387 (3)
N(1)—C(9)	1.358 (3)	C(9)—C(8)	1.488 (3)
C(2)—N(1)	1.462 (3)	C(9)—O(10)	1.222 (3)
C(4)—O(5)	1.446 (3)	C(2′)—S(1′)	1.809 (2)
C(6)—O(5)	1.420 (3)	C(2′)—S(3′)	1.819 (3)
C(6)—C(2′)	1.552 (3)	S(3′)—C(4′)	1.819 (3)
C(7)—C(6)	1.510 (3)	C(6′)—S(1′)	1.809 (3)
C(2)—N(1)—C(9)	123.83 (20)	C(14)—C(7)—C(6)	129.90 (21)
C(2)—N(1)—C(6)	119.08 (18)	C(9)—C(8)—C(11)	129.28 (23)
C(9)—N(1)—C(6)	113.78 (18)	C(2′)—S(1′)—C(6′)	99.39 (12)
C(4)—O(5)—C(6)	113.96 (18)	S(3′)—C(2′)—S(1′)	113.50 (13)
N(1)—C(6)—O(5)	110.82 (17)	C(2′)—S(3′)—C(4′)	98.18 (13)
C(2)—N(1)—C(6)—C(2′)	−74.78 (24)		
C(9)—N(1)—C(6)—O(5)	−111.48 (21)		
C(9)—N(1)—C(6)—C(7)	3.06 (24)		
C(9)—N(1)—C(6)—C(2′)	124.96 (20)		
N(1)—C(6)—C(2′)—S(3′)	162.71 (15)		
O(5)—C(6)—C(2′)—S(3′)	39.81 (22)		
O(5)—C(6)—C(2′)—S(1′)	164.77 (15)		

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). Refinement was carried out with *SHELX*76 (Sheldrick, 1976). Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985). The atomic numbering scheme is shown in Fig. 1 which was produced by *XP* (Sheldrick, 1989).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: HA1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,5-Bis(methylthio)-7,7′,8,8′-tetracyanoquinodimethane

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Abstract

The title compound 2,2′-[2,5-bis(methylthio)-2,5-cyclohexadiene-1,4-diylidene]bis(propanedinitrile),

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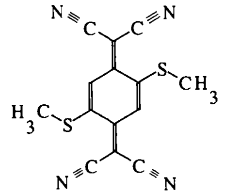
$C_{14}H_8N_4S_2$, a thiomethyl derivative of tetracyanoquinodimethane, belongs to point group C_i and is nearly planar except for two H atoms of each methyl group. Within the molecular plane, however, there is considerable distortion in the vicinity of the cyano groups due to steric repulsion between the —SCH_3 and —C≡N groups. The molecules are stacked in a herringbone fashion with an interplanar distance of 3.40 (1) Å along the b axis. In the direction of the a axis, the molecules are arranged in parallel and there are relatively close intermolecular S···N contacts of 3.200 (3) Å between the S atom of the —SCH_3 group of one molecule and the N atom of the —C≡N group of the neighbouring molecule.

Comment

2,5-Bis(methylthio)-7,7′,8,8′-tetracyanoquinodimethane [BMT-TCNQ (I); Fig. 1] is a newly synthesized thiomethyl derivative of TCNQ. TCNQ is known to be a strong π-electron acceptor. A number of charge-transfer complexes have been synthesized by combining TCNQ with a variety of electron donors (*i.e.* forming a two-component system), leading to semiconductors and even to metals (Coleman, Cohen, Sandman, Yamagishi, Garito & Heeger, 1973; Conwell, 1988). Our goal is, on the contrary, to achieve high electrical conductivity by an organic single-component system. An attempt was made to introduce two —SCH_3 groups at the 2 and 5 positions of unsubstituted TCNQ in order to bridge closely two TCNQ molecules through intermolecular S···N contacts and to enhance electron delocalization in the solid state. In fact, we have attained extremely high electrical conductivity of $\sigma = 2 \times 10^{-5}$ S cm^{-1} at room temperature with evaporated BMT-TCNQ (Zambounis, Mizuguchi, Rihs, Chauvet & Zuppiroli, 1994). The present structure determination has been undertaken in order to gain more insight into the correlation between the crystal structure and electrical conductivity.



(I)

BMT-TCNQ was prepared by a method analogous to the DuPont procedure in four steps starting from 1,4-bis(methylthio)benzene (Wheland & Martin, 1975). The dark brown powder was purified twice by vacuum sublimation using apparatus described previously (Mizuguchi, 1981). The single crystals were then grown from a tetrahydrofuran solution by slow solvent evaporation over several days.

The molecule is nearly planar with the exception of two H atoms (H12 and H13) of each methyl group. The largest deviation from the least-squares plane calculated through all non-H atoms was for H11, with a deviation of 0.120 (3) Å. It should be noted that the —SCH_3 and —C≡N groups repel each other, causing considerable deformation in the vicinity of the cyano groups, as described below. The C4′—C6—C7 and C5—C6—C7 angles are not 120°, but 125.4 (2) and 117.0 (1)°, respectively. Likewise, the C6—C7—C8 and C6—C7—C9 angles are 128.2 (1) and 119.6 (2)°, respectively. Furthermore, the atoms C7, C8 and N2 are not exactly aligned

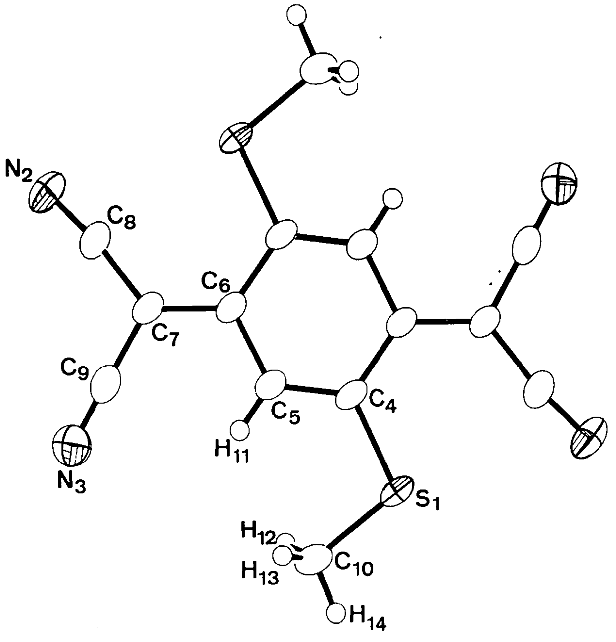


Fig. 1. *ORTEP* (Johnson, 1976) plot of BMT-TCNQ showing the numbering of the non-H atoms. Displacement ellipsiods are scaled to the 40% probability level.

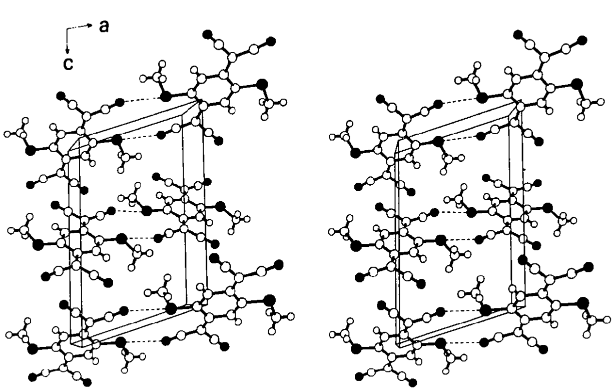


Fig. 2. Stereoview of the crystal structure of BMT-TCNQ. Intermolecular S···N contacts are represented by dashed lines.

[C7—C8—N2 172.3 (3)°], whereas the C7—C9—N3 moiety is almost linear [179.5 (3)°]. Despite this steric hindrance, the intramolecular distances between S1′ and C8, and between S1′ and N2, are relatively short [2.870 (3) and 3.287 (3) Å, respectively].

Fig. 2 shows a stereodiagram of the crystal structure of BMT-TCNQ. The molecules are stacked in a herringbone fashion along the *b* axis. In the direction of the *a* axis, the molecules are arranged in parallel and there are relatively close intermolecular S···N contacts of 3.200 (3) Å between the S atom of the —SCH_3 group of one molecule and the N atom of the —C≡N group of the neighbouring molecule. These S···N contacts are shorter than the sum of the van der Waals radii (3.35 Å), indicating considerable overlap of π electrons between the molecules. Along the *c* axis, the molecules have a zigzag arrangement.

The molecular absorption of BMT-TCNQ in dioxane appears at 474 nm and is considerably red-shifted relative to that of unsubstituted TCNQ (404 nm). This is brought about by enhanced electron delocalization due to the S atom of the —SCH_3 group as well as close intramolecular S1···C8 and S1···N2 contacts. In the solid state, the corresponding absorption band occurs at 590 nm, showing a large bathochromic shift in going from solution to solid. The present spectral shift of BMT-TCNQ has been interpreted as resulting from close intermolecular S···N contacts. The conduction mechanism is now under investigation on the basis of the present structure analysis (Zambounis, Mizuguchi, Rihs, Chauvet & Zuppiroli, 1994).

Experimental

Crystal data

$C_{14}H_8N_4S_2$
$M_r = 296.364$
Monoclinic
$P2_1/c$
$a = 9.208$ (1) Å
$b = 5.391$ (1) Å
$c = 14.343$ (2) Å
$\beta = 106.80$ (1)°
$V = 681.6$ (4) Å^3
$Z = 2$
$D_x = 1.444$ Mg m^{-3}
$D_m = 1.415$ Mg m^{-3}
D_m measured by flotation in $CHCl_3$–CH_2Cl_2

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 11$–18°
$\mu = 0.368$ mm^{-1}
$T = 293$ K
Plate
0.76 × 0.26 × 0.08 mm
Black

Data collection

Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2261 measured reflections
1831 independent reflections
1008 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 7$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity variation: 2%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.033$
$S = 1.12$
1008 reflections
107 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\rm max} = 0.012$
$\Delta\rho_{\rm max} = 0.183$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.164$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.65343 (6)	0.1555 (1)	0.44851 (5)	0.0491 (4)
N2	1.32222 (2)	−0.6020 (5)	0.3917 (2)	0.0669 (5)
N3	0.8534 (3)	−0.6064 (5)	0.2691 (2)	0.0707 (5)
C4	0.8421 (2)	0.0648 (4)	0.4763 (2)	0.0356 (4)
C5	0.8887 (2)	−0.1266 (5)	0.4311 (2)	0.0383 (4)
C6	1.0445 (2)	−0.2007 (4)	0.4497 (2)	0.0341 (4)
C7	1.0737 (2)	−0.3975 (4)	0.3959 (2)	0.0370 (4)
C8	1.2174 (3)	−0.5024 (5)	0.3982 (2)	0.0445 (4)
C9	0.9514 (3)	−0.5139 (5)	0.3251 (2)	0.0451 (4)
C10	0.5593 (3)	−0.0544 (6)	0.3538 (2)	0.0584 (4)

Table 2. *Selected geometric parameters* (Å, °)

S1—C4	1.737 (2)	C4—C6$^{\rm i}$	1.453 (3)
S1—C10	1.788 (3)	C5—C6	1.438 (3)
N2—C8	1.131 (3)	C6—C7	1.384 (3)
N3—C9	1.135 (3)	C7—C8	1.430 (3)
C4—C5	1.353 (3)	C7—C9	1.426 (3)
C4—S1—C10	103.3 (1)	C5—C6—C7	117.0 (1)
S1—C4—C5	122.7 (1)	C6—C7—C8	128.2 (1)
S1—C4—C6$^{\rm i}$	119.1 (2)	C6—C7—C9	119.6 (2)
C5—C4—C6$^{\rm i}$	118.3 (2)	C8—C7—C9	112.1 (2)
C4—C5—C6	124.1 (2)	N2—C8—C7	172.3 (3)
C4$^{\rm i}$—C6—C5	117.6 (2)	N3—C9—C7	179.5 (3)
C4$^{\rm i}$—C6—C7	125.4 (2)		

Symmetry code: (i) $2 - x, -y, 1 - z$.

Program used to solve structure: *MULTAN*11/82 (Main *et al.* 1982). Refinement was carried out by full-matrix least-squares methods. Molecular graphics: *ORTEP*II (Johnson, 1976).

The authors would like to express their sincere thanks to Messrs G. Giller and H. R. Walter for experimental assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the IUCr (Reference: SH1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-*tert*-Butyl-2,6-bis[(4-methyl-1-piperazinyl)methyl]phenol

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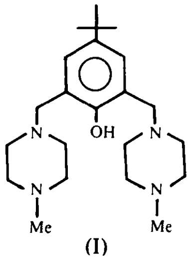
Abstract

In the title compound, $C_{22}H_{38}N_4O$, both the piperazine rings are in perfect chair conformations and the substituents attached to the N atoms of the piperazine rings are in equatorial positions. The tertiary butyl group is oriented in such a way that the plane of the phenyl group nearly bisects the angle between two of the methyl C atoms of the butyl group, while the third methyl C atom lies in the plane of the phenyl ring.

Comment

The X-ray structure analysis of the title compound, (I), a binucleating ligand, has been undertaken to study the conformational features of the piperazine rings. The compound was synthesized by a modification of a procedure reported in the literature (Hodgkin, 1984). The molecular geometry is in agreement with that reported for similar molecules (Allen *et al.*, 1987; Domenicano, Vaciago & Coulson, 1975; Schwarzenbach, 1968).



(I)

Each piperazine ring adopts a perfect chair conformation (Bassi & Scordamagila, 1977; Sbit, Dupont, Diderberg, Liegeois & Delarge, 1992) similar to that found in morpholine (Shanmuga Sundara Raj, Ponnuswamy, Shanmugam & Kandaswamy, 1993) and piperidine (Shanmuga Sundara Raj, Velmurugan, Ponnuswamy, Shanmugam & Kandaswamy, 1994). The substituents at the N atoms of the piperazine rings are in equatorial positions (Allinger, Carpenter & Karkowski, 1965). The molecular packing is based on van der Waals interactions.

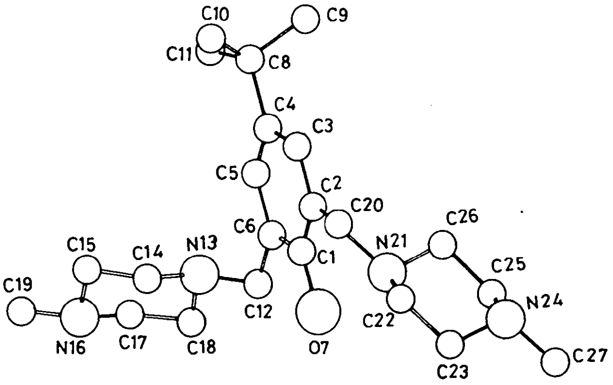


Fig. 1. Perspective view of the molecule with atomic numbering scheme.

Experimental

Crystal data

$C_{22}H_{38}N_4O$
$M_r = 374.6$
Triclinic
$P\bar{1}$
$a = 9.720$ (1) Å
$b = 9.945$ (1) Å
$c = 12.172$ (3) Å
$\alpha = 84.53$ (1)°
$\beta = 84.97$ (2)°
$\gamma = 83.49$ (1)°
$V = 1160.2$ (3) Å^3
$Z = 2$
$D_x = 1.07$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 15$–25°
$\mu = 0.45$ mm^{-1}
$T = 298$ K
Transparent needle
0.3 × 0.25 × 0.2 mm
White

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† DCB Contribution No. 836.