Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (IV)*

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

	x	y	z	U_{eq}
S1	0.74755 (4)	1.37225 (5)	0.46078 (2)	0.0376 (3)
O1	0.9045 (1)	0.3331 (2)	0.70742 (7)	0.0476 (5)
O2	1.2742 (1)	0.6491 (2)	0.87107 (9)	0.0612 (6)
O3	0.6784 (1)	0.5690 (2)	0.63578 (8)	0.0553 (6)
O4	0.7438 (2)	0.8616 (2)	0.61533 (9)	0.0671 (8)
O5	0.7210 (1)	1.3437 (1)	0.36490 (6)	0.0399 (5)
N1	1.0838 (1)	0.4962 (2)	0.79035 (7)	0.0367 (5)
N2	1.0999 (1)	0.8284 (2)	0.79110 (7)	0.0359 (5)
N3	0.7666 (1)	0.7034 (2)	0.64869 (7)	0.0408 (6)
C1	0.9561 (1)	0.4872 (2)	0.73185 (8)	0.0334 (6)
C2	1.1617 (2)	0.6558 (2)	0.82096 (9)	0.0382 (6)
C3	0.9760 (2)	0.8389 (2)	0.73547 (8)	0.0344 (6)
C4	0.9014 (1)	0.6783 (2)	0.70557 (8)	0.0332 (6)
C5	0.6146 (2)	1.2221 (3)	0.5061 (1)	0.0529 (9)
C6	0.9134 (2)	1.2380 (4)	0.4937 (1)	0.0596 (10)

Table 5. *Selected geometric parameters (Å, °) for (IV)*

O1—C1	1.214 (2)	N2—C2	1.384 (2)
O2—C2	1.210 (2)	N2—C3	1.337 (2)
O3—N3	1.223 (2)	N3—C4	1.432 (2)
O4—N3	1.229 (2)	C1—C4	1.462 (2)
N1—C1	1.389 (2)	C3—C4	1.359 (2)
N1—C2	1.370 (2)		
C1—N1—C2	128.2 (1)	O2—C2—N1	123.5 (1)
C2—N2—C3	122.8 (1)	O2—C2—N2	121.9 (1)
O3—N3—O4	122.7 (1)	N1—C2—N2	114.6 (1)
O3—N3—C4	119.3 (1)	N2—C3—C4	121.5 (1)
O4—N3—C4	118.0 (1)	N3—C4—C1	121.4 (1)
O1—C1—N1	120.5 (1)	N3—C4—C3	117.6 (1)
O1—C1—C4	127.6 (1)	C1—C4—C3	121.0 (1)
N1—C1—C4	111.9 (1)		
O3—N3—C4—C3	−163.4 (1)	O4—N3—C4—C3	15.9 (2)

Table 6. *Hydrogen-bonding geometry (Å, °) for (IV)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5^{i}	0.88 (2)	1.98 (2)	2.859 (2)	171 (2)
N2—H2···O5^{ii}	0.83 (2)	1.90 (2)	2.733 (2)	175 (2)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}+x, \frac{5}{2}-y, \frac{1}{2}+z$.

Measurement of azimuthal scans showed insignificant absorption variations, so no corrections were applied.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program used to solve structure: *SIR* (Burla *et al.*, 1989). Program used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1206). Services for accessing these data are described at the back of the journal.

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3-Methylthio-1,2,4-triazine: a Comparison of Experimental and Theoretical Structures

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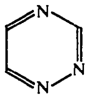
Abstract

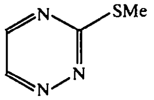
The theoretical equilibrium and X-ray crystallographic structures of 3-methyl-1,2,4-triazine, $C_4H_5N_3S$, show a high level of agreement. The calculated charge distributions are analysed for each of four conformers; that with lowest energy is present both in the solid and in mesitylene solution, as shown by dipole-moment measurements.

Comment

Although the Cambridge Structural Database (Allen & Kennard, 1993) contains about 70 crystal structures of molecules containing triazine moieties, there are no simple 1,2,4-triazine molecules. In recent work, we reported (Palmer *et al.*, 1995) an experimental and theoretical study of the parent compound (1). The synthesis of (1) proceeds *via* *S*-methylthiosemicarbazide and glyoxal, giving the 3-methylthio- derivative (2), and then through the 3-methoxy- and 3-hydrazino-compounds to (1) (Paudler & Chen, 1970; Paudler & Barton, 1966; Neunhoeffer & Hennig, 1968). Of these, only the 3-methylthio- compound, (2), provided crystals suitable for X-ray analysis and this is the subject of the present study.



(1)



(2)

Elementary considerations indicate the possibility of four conformers [numbered (3)–(6); see Fig. 2] depending on the orientation of the methyl group with respect to N2 or N4, each with rotational conformers within the CH$_3$ group.

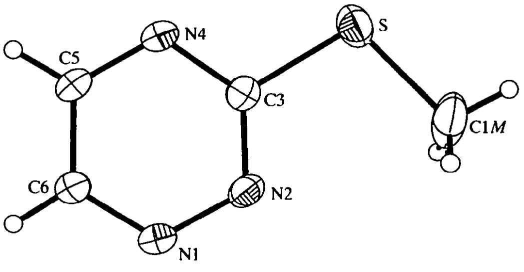
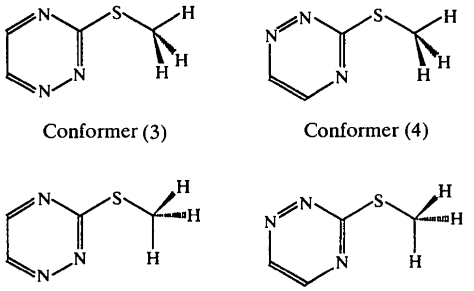


Fig. 1. A view of (2) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.



Conformer (3)

Conformer (4)

Conformer (5)

Conformer (6)

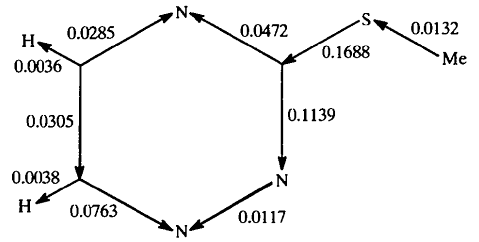
Fig. 2. Conformers of (2) corresponding to local energy minima. The energies (kJ mol^{-1}) relative to structure (3) are 0.00, 2.56, 6.19 and 8.44; the dipole moments (D; 1 D ≈ 3.33564 × 10^{-30} C m) are 1.2751, 3.9952, 1.2665 and 4.0399 for (3) to (6), respectively.

In order to consider the experimental structure in relation to potential gas-phase structures, we report a comparison with the *ab initio* equilibrium structures of each conformer, using a large basis set with a Møller–Plesset (MP2) treatment of electron correlation, which is correct to first order and generally yields structures in good agreement with experiment. We have also determined the dipole moments (in mesitylene and benzene as solvents), enabling a further comparison of the solution conformation with the other data.

The bond lengths (Table 1) within the heterocycle are consistent with the anticipated π-electron delocalization, and their ordering in terms of magnitude is very similar between the X-ray and calculated data. The sole exception to this is the reversal of the lengths of N2—C3 and N1—N2, and even here the absolute differences are only 0.01 Å. The two bonds to the S atom are correctly differentiated by the calculation, but here the absolute difference in the S—C(Me) bond is 0.025 Å. Similarly, the strict order of the values of the angles is indistinguishable, except for very fine differences in the two angles near 118°. For a molecule with three C—N bonds in an aromatic ring (for which correlation effects are generally substantial), this is excellent agreement. Structural elucidation of the gas-phase molecule by electron diffraction would be complicated by the similarity of the ring bond lengths, but with suitable ^{15}N enrichments it might be worthy of a microwave or infrared absorption study; indeed, we are currently analysing the vibrational bands at high resolution for the natural ^{14}N isotopomer.

The theoretical Mulliken atomic populations show the expected drift of total population from H to C and C to N, with the order for N being N4 > N1 > N2; the SMe group is overall a donor to the ring by about 0.14 e, with the bulk of this density shift arising from donation by S to the ring. Subdivision of the Mulliken atomic populations into σ and π components (Palmer & Kennedy, 1976) and analysis of the net atomic charges, as a set of bond dipoles, leads to the vector diagrams shown in Fig. 3. In more detail, the ring is a net electron

π-Bond moments



σ-Bond moments

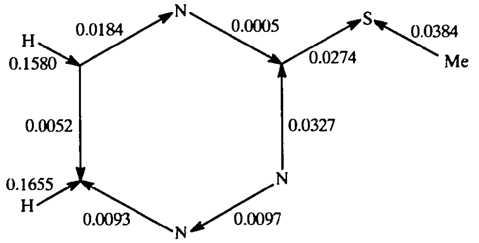


Fig. 3. Decomposition of the σ- and π-electron donation in (2). The methyl substituent is treated as a single group.

acceptor through the π system by 0.17 e, but the effect is highly site specific, with N1 and N2 being the principal π acceptors from the SMe group. In the σ system, the S atom is an acceptor from both the ring and methyl group, but these shifts of density are small relative to the $C^{\delta+}—H^{\delta-}$ polarization.

The molecular-orbital calculations described above predicted a sharp variation of dipole moment as a function of conformation (Fig. 2). With the aim of using this information to derive the conformation of (2) in solution, we determined its dipole moment in mesitylene [2.29 (3) D] and in benzene [2.41 (3) D]. Assuming that solvation has no effect on the dipole moments of the conformers (3)–(6), we calculate the weighted average dipole moment in solution to be 1.98 D. While the agreement here with the experimental values is only moderate, these data are consistent with the solution consisting of conformers of (2) in the order $3 > 4 \gg 5 > 6$.

The title compound packs to form chains *via* weak interactions through C5—H5 to N1$(-\frac{1}{2}+x, -\frac{1}{2}-y, -\frac{1}{2}+z)$, where the C···N distance is 3.362 (3) Å. The chains are disposed in classic herring-bone fashion. There appear to be no especially strong intermolecular interactions involving S atoms.

Experimental

Crystals grew from the distilled liquid on standing at room temperature.

Crystal data

$C_4H_5N_3S$
$M_r = 127.17$
Monoclinic
$P2_1/n$
$a = 7.808\ (2)$ Å
$b = 7.056\ (2)$ Å
$c = 11.090\ (3)$ Å
$\beta = 108.14\ (3)°$
$V = 580.6\ (3)$ Å^3
$Z = 4$
$D_x = 1.455$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 14–16°$
$\mu = 0.441$ mm^{-1}
$T = 150.0\ (2)$ K
Tablet
0.70 × 0.50 × 0.26 mm
Pale yellow

Data collection

Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.831$, $T_{max} = 0.892$
2493 measured reflections

1029 independent reflections
910 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.04°$
$h = -9 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 13$
3 standard reflections frequency: 60 min intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.083$
$S = 1.055$
1026 reflections
94 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.1168P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.047$

$\Delta\rho_{max} = 0.318$ e Å^{-3}
$\Delta\rho_{min} = -0.301$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1995)
Extinction coefficient: 0.013 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Comparison of observed and calculated*[a] *bond lengths (Å) and angles (°)*

Bond	X-ray	Calc.	Angle	X-ray	Calc.
N1—N2	1.350 (2)	1.340	C6—N1—N2	118.79 (14)	117.9
N2—C3	1.330 (2)	1.341	N1—N2—C3	117.30 (13)	118.2
C3—N4	1.350 (2)	1.350	N2—C3—N4	126.79 (14)	126.9
N4—C5	1.314 (2)	1.327	C3—N4—C5	114.53 (13)	114.0
C5—C6	1.395 (2)	1.396	N4—C5—C6	121.0 (2)	121.1
C6—N1	1.315 (2)	1.334	C5—C6—N1	121.5 (2)	121.9
C3—S	1.750 (2)	1.758	N2—C3—S	120.25 (12)	118.8
S—C(Me)	1.792 (2)	1.817	N4—C3—S	112.96 (11)	114.3
H5—C5	0.93 (2)	1.081	C3—S—C(Me)	102.60 (9)	100.4
H6—C6	0.94 (2)	1.079	N4—C5—H5	118.6 (12)	117.3
H—C(Me)	0.95 (5)[b]	1.087[c]	N1—C6—H6	115.7 (11)	122.3
		1.084[d]	S—C—H[c]	106 (2)	110.8
			S—C—H[d]	109 (2)	105.3

Notes: (*a*) the calculations are for conformer (3), the total energy is −716.66647 a.u.; (*b*) average value; (*c*) in-plane (H1*M*1); (*d*) out-of-plane (H1*M*2 and H1*M*3).

The *ab initio* calculations used a triple zeta valence + polarization (TZVP) of Dunning (1971), with Møller–Plesset second-order electron correlation (MP2) on an all-electron basis. Calculations were performed with the *GAMESS-UK* suite of computer programs (Guest *et al.*, 1995). These methods generally lead to a good correlation with experimental geometric parameters (Palmer & Parsons, 1996). The dipole moment of (2) was determined at 293 K from measurements of the capacitance of solutions in mesitylene and benzene, followed by solution of the Debye equation, using refractive-index and density measurements. The instrument was calibrated using chlorobenzene, cyclohexane, nitrobenzene, ethyl formate and trifluoromethyl benzene; these were chosen because they have dipole moments of relevant magnitudes.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

We thank the EPSRC for provision of a four-circle diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1207). Services for accessing these data are described at the back of the journal.

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3′,4″-Didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene

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Abstract

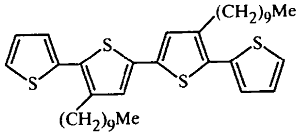
The title compound, $C_{36}H_{50}S_4$, lies about an inversion centre and the four thiophene rings are nearly coplanar. The outer rings are tilted by 3.6 (5)° from the inner rings. Each decyl chain is in the *trans* conformation and all C atoms are nearly coplanar. The dihedral angle between the aliphatic plane defined by atoms C41–C47 and the thiophene ring plane is 8.6 (1)°. There is slight disorder of the last three atoms of each decyl chain and all those of the outer thiophene rings, with occupancy factors of 65:35.

Comment

Recent progress in the synthesis of conjugated poly(3-alkylthiophenes) (P3AT) with flexible alkyl side chains of various lengths has stimulated interest because they are easily processed and maintain electrical and optical properties comparable to those of the unsubstituted polythiophenes (Genies *et al.*, 1990). It is assumed that the π-conjugated coplanar conformation of the backbone chain is retained after long-chain substitutions at suitable positions (Roux *et al.*, 1993).

In order to elucidate the structure–property relationship of novel conducting materials, oligothiophenes have been considered as model compounds for the parent polymer (Liao *et al.*, 1994). However, because of the difficulty of crystallization, X-ray data for oligothiophenes, especially those with long alkyl substituents, are scarce.

In a previous paper, the effects of alkyloxy substituents on the conformation of bithiophene were reported (Pelletier *et al.*, 1995). In order to elucidate the long-side-chain effect on P3AT, we have synthesized and structurally characterized the dialkyl-substituted title quaterthiophene, (I), a model for poly(3-decylthiophene) (P3DT).



(I)

An *ORTEP*II (Johson, 1976) drawing of the molecular structure of (I) with the atomic labelling is shown in Fig. 1. It is of interest that the molecule has a centre of symmetry at the midpoint of C2—C2($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$). The two inner thiophene rings are coplanar within 0.12°. The outer thiophene rings and the last three atoms of each side chain are disordered in the proportion 65.0 (4):35.0 (4). The S atoms in adjacent thiophene rings adopt the *anti* conformation in the major conformer, thus minimizing steric crowding. However, in the minor conformer, the S atoms are *syn* between the outer and the inner thiophenes. This result lends support to previous proposals that although the *anti* comformer dominates, the *syn* conformer exists in a small amount, thus generating structural defects in the backbone chain (Salaneck *et al.*, 1988). The molecular plane of each of the outer rings is only slightly tilted from that of the inner rings, with the dihedral angles between their mean planes being 3.6 (5)° in the major conformer and 5.0 (7)° in the minor conformer. Similar observations were noted for alkyl-substituted pentathiophene and hexathiophene (Liao *et al.*, 1994). The aliphatic chain (C41–C50) is in a zigzag conformation and nearly planar. The aliphatic plane defined by atoms C41–C47 is inclined with respect to the plane of the adjacent thiophene ring by 8.6 (1)°. The average C—C distance in the aromatic rings is 1.411 Å, and that in the decyl chains is 1.520 Å. It is observed that the C6—S7 bond [1.758 (7) Å] is longer than the other C—S bonds in the molecule. This feature has been noted previously, for example, in terthiophene and dimethylterthiophene