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4,6-Diphenyl-2-methylthieno[3,4-*d*]-1,2,3-triazole

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Abstract. $C_{17}H_{13}N_3S$, $M_r = 291{\cdot}38$, monoclinic, $P2_1/c$, $Z = 4$. At 238 K, $a = 12{\cdot}043$ (2), $b = 5{\cdot}725$ (1), $c = 21{\cdot}409$ (3) Å, $\beta = 104{\cdot}95$ (2)°, $V = 1426{\cdot}2$ Å^3, $D_c = 1{\cdot}358$ Mg m^{-3}. Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}222$ mm^{-1}. Syntex diffractometer, 2510 reflections, 242 variables refined by full-matrix least squares, $R = 0{\cdot}040$. The two chemically-equivalent halves of the molecule are related by a virtual mirror plane with the two phenyl substituents nearly in the plane of the heterocyclic fused-ring system. The average C—S distance, 1·732 Å, is similar to that found in classical thiophenes; the C—S—C angle, 96·4°, however is typical of 'non-classical' thiophenes.

Introduction. Orange crystals of the title compound were grown by slow evaporation from an acetonitrile solution. The crystal used in this investigation was a cleaved fragment with approximate dimensions of 0·14 × 0·21 × 0·66 mm. The crystal was mounted on a Syntex diffractometer (Mo $K\alpha$ radiation monochromated with a graphite crystal) equipped with a low-temperature apparatus which kept the crystal cooled to 238 K. The unit-cell dimensions at this temperature were refined by the least-squares method using the Bragg angles of 30 reflections.

Intensity data for 3026 unique reflections ($4 < 2\theta < 50$°) were collected with the ω-scan technique. Scans of 1·0° were employed with scan rates which ranged from 1·5 to 5·0° min^{-1} depending on the number of counts accumulated in a rapid preliminary scan. Background measurements were taken at both ends of the scan with ω displaced by 1·0° from the $K\alpha$ peak; each measurement was made for one-half of the scan time. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted. The intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu = 0{\cdot}222$ mm^{-1}).

The structure was solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971), the H atoms were located in a difference map. Refinement of the structure by a full-matrix least-squares procedure was carried out using only those 2510 reflections for which $I > 2\sigma(I)$. The refinement of all positional and thermal (anisotropic for the non-hydrogen atoms; isotropic for the H atoms) parameters converged at a conventional R of 0·040. The largest peak in the final difference map had a magnitude of 0·24 e Å^{-3} and was located near N(1). The final positional and thermal parameters are given in Table 1.* The computational details are noted elsewhere (Harlow & Simonsen, 1976).

Table 1. *Final positional coordinates, and isotropic thermal parameters for hydrogen atoms with estimated standard deviations*

	x	y	z	$U_{\rm iso}$ (Å^2)
S	0·04377 (6)	−0·27063 (12)	0·69639 (3)	
N(1)	0·02941 (16)	0·2500 (4)	0·57781 (9)	
N(2)	0·13427 (17)	0·3412 (4)	0·59648 (9)	
N(3)	0·21047 (16)	0·2499 (4)	0·64673 (9)	
C(1)	−0·03465 (21)	−0·1090 (4)	0·63146 (11)	
C(2)	0·03672 (20)	0·0718 (4)	0·62131 (11)	
C(3)	0·14805 (20)	0·0717 (4)	0·66370 (11)	
C(4)	0·16890 (20)	−0·1091 (4)	0·70899 (11)	
C(5)	0·16524 (28)	0·5418 (6)	0·56280 (16)	
C(61)	−0·15009 (20)	−0·1699 (4)	0·59499 (11)	
C(62)	−0·20440 (22)	−0·3753 (5)	0·60629 (13)	
C(63)	−0·31485 (23)	−0·4272 (5)	0·56992 (13)	
C(64)	−0·37185 (23)	−0·2777 (5)	0·52185 (13)	
C(65)	−0·31867 (24)	−0·0743 (5)	0·51009 (14)	
C(66)	−0·20961 (23)	−0·0212 (5)	0·54604 (13)	
C(71)	0·27533 (20)	−0·1718 (4)	0·75613 (11)	
C(72)	0·28749 (24)	−0·3804 (5)	0·79124 (12)	
C(73)	0·39284 (25)	−0·4361 (5)	0·83371 (13)	
C(74)	0·48528 (24)	−0·2894 (5)	0·84117 (12)	
C(75)	0·47368 (23)	−0·0821 (5)	0·80728 (13)	
C(76)	0·37019 (22)	−0·0231 (5)	0·76546 (12)	
H(5*a*)	0·204 (3)	0·498 (7)	0·536 (2)	0·099 (14)
H(5*b*)	0·208 (3)	0·654 (7)	0·589 (2)	0·107 (15)
H(5*c*)	0·098 (3)	0·623 (7)	0·539 (2)	0·118 (15)
H(62)	−0·164 (2)	−0·474 (4)	0·639 (1)	0·033 (7)
H(63)	−0·352 (2)	−0·564 (4)	0·579 (1)	0·033 (7)
H(64)	−0·450 (2)	−0·314 (4)	0·493 (1)	0·041 (7)
H(65)	−0·357 (2)	0·035 (5)	0·477 (1)	0·048 (8)
H(66)	−0·180 (2)	0·115 (5)	0·538 (1)	0·059 (9)
H(72)	0·226 (2)	−0·488 (4)	0·785 (1)	0·038 (7)
H(73)	0·402 (2)	−0·585 (4)	0·856 (1)	0·038 (7)
H(74)	0·562 (2)	−0·328 (4)	0·872 (1)	0·040 (7)
H(75)	0·536 (2)	0·017 (4)	0·811 (1)	0·035 (7)
H(76)	0·361 (2)	0·113 (4)	0·742 (1)	0·035 (7)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33803 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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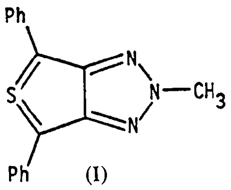
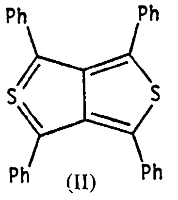
Discussion. 4,6-Diphenyl-2-methylthieno[3,4-*d*]-1,2,3-triazole (I) is an example of a ten π-electron heteropentalene; it is also termed a 'non-classical' thiophene because of the tetravalent nature of the S atom. Although such condensed thiophenes are generally noted for their reactivity with O and with a variety of dipolarophiles, the title compound is relatively inert. It was thus of interest to compare its structure with that of tetraphenylthieno[3,4-*c*]thiophene (II), the first non-classical thiophene to be studied by X-ray diffraction methods (Glick & Cook, 1972). The thiophene framework of this compound was found to be planar with an idealized *mmm* (D_{2h}) symmetry. The sample for this investigation was supplied by Professor K. T. Potts who has recently published a review of the chemical and physical properties of heteropentalenes (Potts, 1977).

The most obvious difference in the structures of (I) and (II) is the conformation of the phenyl substituents. In compound (II), the mutual steric interactions of the phenyl groups force them to rotate out of the dithiophene plane by 39·6 and 58·4°, while in compound (I) the phenyl groups are more nearly coplanar with the thienotriazole moiety. Fig. 1 pictures the conformation of (I); the numerical details are listed in Table 2. The dihedral angles between the phenyl substituents and the thienotriazole ring average 9·5° and are the result of both a twist and a bend about the exocyclic bonds. The thienotriazole moiety itself is slightly folded such that the two five-membered rings make a dihedral angle of 2·4°. Bond lengths and angles are shown in Fig. 2.



(I)



(II)

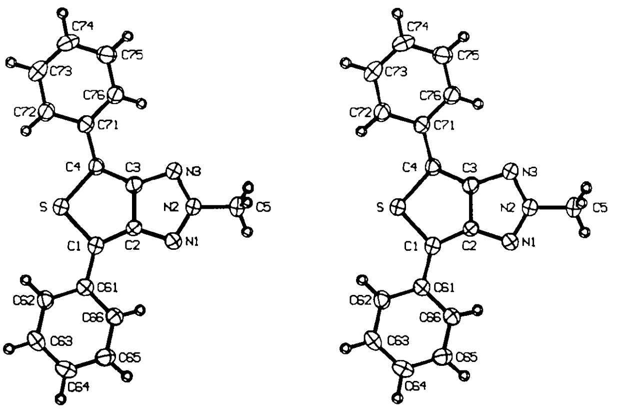


Fig. 1. Conformation and atom-numbering scheme. Each hydrogen atom is numbered in accord with the carbon atom to which it is bonded.

Although the conformation of the phenyl groups could affect the reactivity of the thiophene ring, the chemical differences of (I) and (II) probably exist for electronic, rather than steric, reasons (Potts, 1977) and one might therefore expect to find significant differences in the geometries of their respective thiophene rings. A comparison of the bond distances and angles shows that the average C—S distance in (I), 1·732 Å, is somewhat longer than in (II), 1·706 Å, and in fact more closely resembles the C—S distance of 1·74 Å

Table 2. *Details of the molecular conformation*

(*a*) Deviations (Å) from calculated mean planes

Plane *A*: The methylthienotriazole moiety containing atoms S, N(1–3), and C(1–5)

S	0·022 (1)	C(1)	0·011 (3)	C(5)	0·026 (3)
N(1)	−0·009 (2)	C(2)	−0·030 (2)	C(61)	0·015 (2)
N(2)	0·008 (2)	C(3)	−0·030 (2)	C(71)	0·124 (2)
N(3)	−0·009 (2)	C(4)	0·011 (2)		

Plane *B*: The phenyl group containing atoms C(61–66) is planar to within 0·003 Å. Atom C(1) deviates from this plane by 0·011 (3) Å.

Plane *C*: The phenyl group containing atoms C(71–76) is planar to within 0·007 Å. Atom C(4) deviates from this plane by 0·071 (2) Å.

(*b*) Dihedral angles

Planes *A*–*B*, 8·5° Planes *A*–*C*, 10·5°

(*c*) Selected torsion angles (°)

S–C(1)–C(61)–C(62)	−5·1
S–C(1)–C(61)–C(66)	175·9
C(2)–C(1)–C(61)–C(62)	171·2
C(2)–C(1)–C(61)–C(66)	−7·9
S–C(4)–C(71)–C(72)	5·7
S–C(4)–C(71)–C(76)	−176·4
C(3)–C(4)–C(71)–C(72)	−169·4
C(3)–C(4)–C(71)–C(76)	8·5

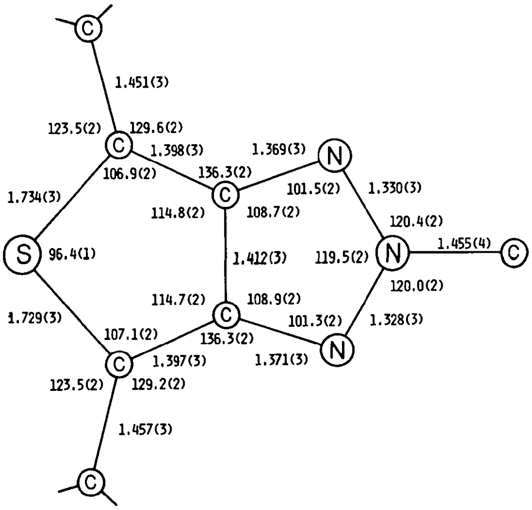


Fig. 2. Bond distances (Å) and angles (°) for the heterocyclic, fused-ring moiety.

found in classical fused-ring thiophenes (McKenzie, 1975; Hogg & Sutherland, 1974). On the other hand, the C—S—C angles, 96·4 and 96·1° for (I) and (II) respectively, are virtually identical but consistently different from the classical value of 92°. The geometry about the S atom in (I) thus appears to be something intermediate between a classical and non-classical thiophene. Other differences include the much shorter fused bond length in (I) (undoubtedly because of the stricter steric requirements of the triazole ring) and the correspondingly smaller S—C—C angles. The average lengths of the C—C bonds adjacent to the S atom are however very similar: 1·398 Å in (I) and 1·407 Å in (II).

Does the presence of a non-classical thiophene ring alter the geometry of the fused triazole? Crystal structures of nine compounds containing a (2*H*)-1,2,3-triazole moiety have been reported (Manotti-Lanfredi, Tiripicchio & Tiripicchio-Camellini, 1977; Harlow, Brown, Dewar & Simonsen, 1977; Kálmán, Párkányi & Schawartz, 1977; Kálmán, Párkányi, Schawartz & Simon, 1976; Lopez de Lerma, Cano, García-Blanco & Martínez-Ripoll, 1976; Singh & Hodgson, 1975; Foces-Foces, Cano & García-Blanco, 1975*a*,*b*; Kozlowski, Singh & Hodgson, 1974). Although the substituents vary widely and six of the compounds involve a six-membered ring fused to the five-membered ring, the mean geometries of the triazole rings are quite similar; the overall average distances and angles for the nine structures are: N—N = 1·332, C—N = 1·338, C—C = 1·394 Å; N—N—N = 116·6, C—N—N = 102·7, C—C—N = 109·0°. A comparison of these average values with those found for the title compound reveals two major differences. Firstly, the C—N bond distances in (I) are considerably longer (on average 0·032 Å, the longest C—N distance of the nine structures is 1·358 Å) although the N—N distances are quite ordinary. Secondly, the N—N—N angle in (I) is larger by 2·9° (the largest N—N—N angle of the nine structures is 117·4°); the C—N—N angles are correspondingly somewhat smaller. Thus, the fusion to a non-classical thiophene 'appears' to have altered the geometry of the triazole ring.

As first pointed out by Glick & Cook (1972) and supported by the present study, non-classical thiophene rings have a larger C—S—C angle and longer C—C bonds (adjacent to the S atom) than non-classical rings. How curious it is to find the same type of differences (larger N—N—N angle and longer C—N bonds) when comparing the geometry of the triazole ring in (I) with that of nine 'classical' triazoles. The association with the non-classical thiophene ring has either induced the changes in the triazole ring, or the triazole ring itself is 'non-classical'.

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