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Isomerism in Formazans: Structure of the Yellow Isomer of 3-Methylthio-1,5-di(*o*-tolyl)formazan

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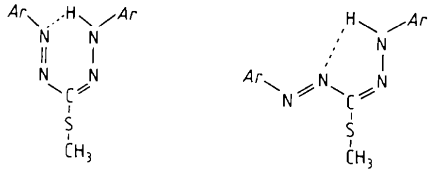
Abstract

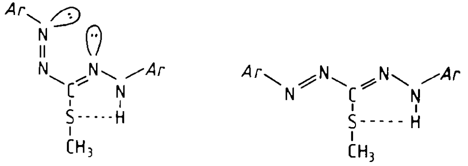
$C_{16}H_{18}N_4S$ is monoclinic, space group $P2_1/n$, with $a = 7{\cdot}993\ (4)$, $b = 20{\cdot}910\ (9)$, $c = 10{\cdot}154\ (5)$ Å, $\beta = 110{\cdot}43\ (5)^\circ$, $Z = 4$. The structure was determined by direct methods in which an average structure obtained from an E map was successfully refined to $R = 0{\cdot}064$ for 1319 observed reflections. Electron delocalization within the Ar—N—N—C—N—N—Ar chain results in essentially planar molecules. The imino proton participates in an intramolecular hydrogen bond to S which stabilizes the thiocarbazone chain in an *anti,s-trans* configuration relative to the formal double C=N and single C—N bonds. The nature of the pink ⇌ yellow isomerism in formazans is discussed.

Introduction

Fresh solutions of 3-methylthio-1,5-diphenylformazan [*S*-methyldithizone, (1)] in, for example, chloroform are permanganate pink, with well defined bands at 270 and 550 nm ($\varepsilon_{550} = 1225$ m^2 mol^{-1}). On standing in the dark at room temperature the solutions turn yellow and the spectrum then shows bands at 280, 420 and 540 nm ($\varepsilon_{420} = 1775$ m^2 mol^{-1}), the band originally at 550 nm becoming less intense as the new band appears at 420 nm. The process is kinetically first order, and is greatly accelerated by traces of acids and alkalis. The isomerism is reversed on illumination (Irving, 1977). Analogous effects appear with a number of formazans (Hausser, Jerchel & Kuhn, 1949; Kuhn & Weitz, 1953) and *S*-alkylated dithizones (Pel'kis & Dubenko, 1956, 1957).



(*a*) *syn,s-cis* (*b*) *syn,s-trans*



(*c*) *anti,s-cis* (*d*) *anti,s-trans*

(1): Ar = phenyl
(2): Ar = *p*-tolyl
(3): Ar = *o*-tolyl

On concentration of solutions of (1) (whether in the pink or yellow form) only the magenta-red solid (λ_{max} 550 nm) is deposited. X-ray crystallography (Preuss & Gieren, 1975) shows that the whole molecule is effectively planar and its *syn,s-trans* configuration† can be represented by structure (1*b*). NMR results (Hutton & Irving, 1980) show that on dissolution in chloroform, rotation about the C—N single bond occurs to form the equivalent tautomer of (1*b*) *via* the quasi-aromatic *syn,s-cis* structure (1*a*). We have synthesized the di(*p*-tolyl) (2) and di(*o*-tolyl) (3) analogues of (1) and find that (2) gives red needles which behave in exactly the same way as (1) upon dissolution and which very likely also contain molecules in configuration (2*b*). (3), on the other hand, crystallizes as yellow plates. Dissolving these crystals in chloroform gives an initially yellow solution (λ_{max} 420 nm, $\varepsilon = 2936$ m^2 mol^{-1}) which slowly turns red-brown to form an equilibrium between the yellow and pink isomers, giving peaks at 420 and 560 nm with a clearly defined isosbestic point. On dissolving (1) in CCl_4 the ν(N—H) band at 3342 cm^{-1} decreases in intensity with the appearance of a new ν(N—H) band at 3253 cm^{-1}, while the 3269 cm^{-1} band in a fresh yellow solution of (3) slowly diminishes with a concomitant appearance of a

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† Ignoring isomers which are unlikely to occur due to serious steric crowding (*i.e.* all the *cis* configurations relative to the N=N double bond), one is left with the four isomers (*a*)–(*d*) as a result of *syn–anti* isomerism about the C=N double bond and isomerization about the C—N single bond (designated *s-cis* and *s-trans*). Of these, (*c*) is unlikely to exist owing to the close proximity of the lone pairs of electrons on nitrogens 1 and 4.

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new band at 3361 cm^{-1}. In this paper we report the structure of the yellow isomer of (3), confirming for the first time the nature of the isomerism found to occur in many formazans.

Experimental

Preparation

An established route to 1,5-diphenyl-3-thioxoformazan (1,5-diphenylthiocarbazone, dithizone) (Bamberger, Padova & Ormerod, 1926) was used to obtain 3-thioxo-1,5-di(*o*-tolyl)formazan, which was then reacted with dimethyl sulphate to give the *S*-methylated product (3) (Irving & Bell, 1954). After purification by chromatography (alumina/benzene), (3) crystallized from ethanol as yellow-orange prismatic plates with m.p. 403–406 K, dec. (Composition: found: C 64·3, H 6·0, N 18·7%; calculated for $C_{16}H_{18}N_4S$: C 64·4, H 6·1, N 18·8%.)

Crystal and intensity data

$C_{16}H_{18}N_4S$, M_r = 298·40, monoclinic, a = 7·993 (4), b = 20·910 (9), c = 10·154 (5) Å, β = 110·43 (5)°, V = 1590·4 Å^3, D_m = 1·29 (by flotation in aqueous KI), Z = 4, D_c = 1·25 Mg m^{-3}, $F(000)$ = 632; Mo $K\alpha$ radiation, λ = 0·7107 Å; μ(Mo $K\alpha$) = 0·163 mm^{-1}. The systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group $P2_1/n$.

Preliminary cell dimensions and space-group symmetry were determined from photographs. A single crystal 0·5 × 0·4 × 0·05 mm was used for data collection. Accurate cell dimensions were obtained by least squares from the settings of 25 high-order reflections measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Intensities were collected by the ω–2θ scan technique [scan width 0·5° (θ), scan speed 0·01° (θ) s^{-1}] in the range $3 \le \theta \le 20°$. Background was established as a function of θ from counting at the systematic absences and then subtracted. The intensities of three reference reflections monitored after every 68 measured reflections remained constant to within ±1% of their mean values. 1542 reflections were collected; with the criterion $I_{\rm rel} > 2\sigma(I_{\rm rel})$ for an observed reflection and omitting systematic absences, 1319 unique reflections remained which were employed in the analysis. Lorentz–polarization corrections were applied but no correction was made for absorption.

Structure determination and refinement

The structure was solved by direct methods with *SHELX*76 (Sheldrick, 1978). Difficulty was experienced in interpretation of the E maps until it was realized that these had yielded two shifted molecules. Attempts at refining either of the individual molecules or using the Patterson map to seek prominent vectors which would dictate appropriate shifts of the molecule failed. The structure was solved by taking the average structure of two shifted molecules given by an E map, as shown in Fig. 1, the missing peaks being inferred from the geometry of the molecule (Caira, Giles, Nassimbeni, Sheldrick & Hazell, 1976). This correctly yielded all but three of the heavy-atom positions; these were found in subsequent difference maps. The vector between the two molecules equally displaced in opposite directions from the correct position turns out to be a prominent vector in the correct structure, where it comprises contributions from six C—C vectors and the S—C bond vector. This shift vector has additional importance because it is perpendicular to a 2_1 axis (Hazell & Hazell, 1975).

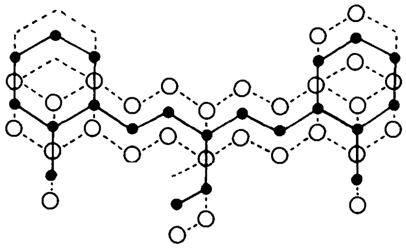

Fig. 1. Projection on the least-squares plane through peaks in the E map. The two shifted molecules are shown as open circles (not all atoms appear) and the average structure is shown as full circles.

The final full-matrix least-squares refinement was carried out with all the heavy atoms treated anisotropically, as was done for (1) (Preuss & Gieren, 1975). The aromatic and methyl H atoms were constrained to ride at 1·08 Å from their corresponding parent C atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were treated as two single parameters which refined to U = 0·103 (6) (aromatic H) and 0·142 (8) Å^2 (methyl H). The imino H(11), which had been revealed in a previous difference map, was fixed at 1·00 ± 0·01 Å from N(11) and its temperature factor was refined independently to U = 0·13 (2) Å^2 with fractional coordinates 0·099 (4), −0·010 (3), 0·235 (6). The refinement converged to R = 0·064 and $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$ = 0·059 with the weighting scheme $w = (\sigma^2 F_o)^{-1}$ chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o, as shown by an analysis of variance computed after the final cycle.* In the final cycle the

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* The analysis of variance, lists of structure factors, hydrogen-atom coordinates, anisotropic thermal parameters, least-squares-planes parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35274 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *of the non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	y	z
C(1)	6710 (8)	2076 (3)	6972 (6)
C(2)	8221 (11)	2454 (3)	7530 (6)
C(3)	9562 (10)	2451 (3)	6994 (8)
C(4)	9455 (8)	2055 (3)	5873 (7)
C(5)	7973 (8)	1672 (3)	5281 (5)
C(6)	6605 (7)	1683 (2)	5829 (5)
N(7)	5008 (5)	1322 (2)	5274 (4)
N(8)	4976 (5)	945 (2)	4283 (4)
C(9)	3408 (6)	596 (2)	3704 (5)
N(10)	3447 (5)	229 (2)	2687 (4)
N(11)	2063 (6)	−150 (2)	2077 (4)
C(12)	2055 (7)	−541 (2)	959 (5)
C(13)	3453 (6)	−526 (2)	446 (5)
C(14)	3400 (7)	−911 (3)	−675 (6)
C(15)	1971 (8)	−1311 (3)	−1283 (5)
C(16)	591 (7)	−1325 (3)	−761 (5)
C(17)	594 (6)	−942 (2)	362 (5)
S(18)	1535 (2)	674 (1)	4239 (1)
C(19)	2419 (7)	410 (3)	6048 (5)
C(20)	5247 (8)	2087 (3)	7588 (6)
C(21)	−937 (6)	−973 (3)	914 (5)

mean e.s.d. in the parameters of the non-hydrogen atoms was >100 times the average parameter shift. A final difference map showed no peaks >0·2 e Å^{-3}. Complex neutral-atom scattering factors were taken from Cromer & Mann (1968) for C, N and S, and from Stewart, Davidson & Simpson (1965) for H, with anomalous-dispersion corrections from Cromer & Liberman (1970). Table 1 lists the final positions of the non-hydrogen atoms.

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer with *SHELX*76 (data reduction, structure solution and refinement), *XANADU* (molecular geometry) and *PLUTO* (illustrations) (Sheldrick, 1978; Roberts & Sheldrick, 1975; Motherwell, 1975).

Results and discussion

Molecular structure

The molecular structure and atomic nomenclature are shown in Fig. 2; the numbering scheme is arbitrary but the same as that used by Preuss & Gieren (1975) in their analysis of (1). Molecules in crystals of (3) differ from those in (1) in that the configuration about C(9)=N(10) is *anti* (3*d*) rather than *syn* (1*b*), the imino H(11) forming a hydrogen bond to S(18) rather than to N(8). The thiocarbazone chain chromophore is thus altered and (3*d*) absorbs light of shorter wavelength (420 nm) than either (1*b*) or (2*b*) (both 550 nm). The difference between ν(N–H) in the two configurations is discussed below.

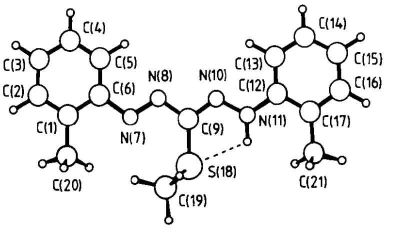


Fig. 2. The molecular structure and atomic nomenclature. H atoms are numbered according to the atom to which they are bonded. The dashed line indicates a hydrogen bond.

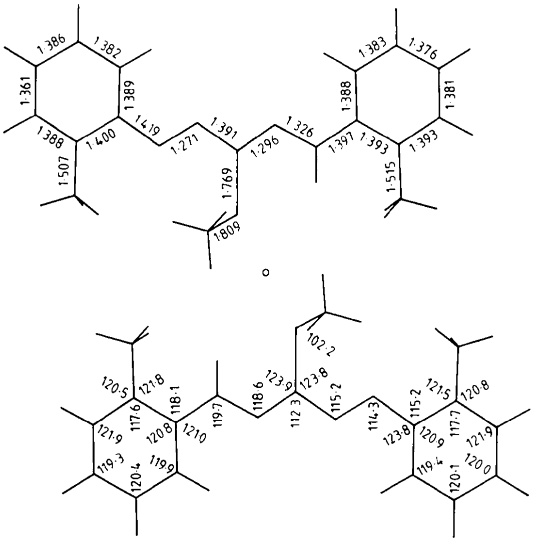


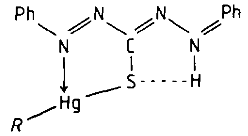
Fig. 3. The two molecules related by a centre of inversion. The upper molecule shows bond lengths (Å; e.s.d.'s are 0·006–0·008 for C–C and 0·004–0·006 Å for C–N, C–S and N–N), while the lower molecule gives the bond angles (°; e.s.d.'s are 0·2–0·6°).

Bond lengths and angles are given in Fig. 3 for two molecules which are related to each other by a centre of symmetry. The calculated bond lengths reveal a marked delocalization of π electrons within the N–N–C–N–N chain and with the *o*-tolyl rings. While the formal double bonds C(9)=N(10) (1·30 Å) and N(7)=N(8) (1·27 Å) are clearly extended in comparison with isolated double bonds (Burke-Laing & Laing, 1976), the formal single bonds C(9)–N(8) (1·39 Å) and N(10)–N(11) (1·33 Å) are noticeably shortened. This was also observed in (1) (Preuss & Gieren, 1975) and 3-carboxymethylthio-1,5-diphenylformazan (Hutton, Irving, Nassimbeni & Gafner, 1979). The S–C lengths are of the expected magnitude and show that the electron delocalization found in the Ar–N–N–C–N–N–Ar (Ar = *o*-tolyl) chain does not extend to the S atom: the C(9)–S(18) bond order is ~1·0 (Laing, 1977). The difference between C(9)–S(18) (1·77 Å) and S(18)–C(19) (1·81 Å) follows from the difference in hybridization of the two C atoms [C(9) sp^2, C(19) sp^3]. Bond distances and angles relating to the *o*-tolyl groups are generally satisfactory; the mean aromatic C–C distance in the two rings is 1·385 (10) Å.

The parameters for several least-squares planes and a list of torsion angles have been deposited (see deposition footnote). If the *S*-methyl group is ignored the remainder of the molecule is remarkably planar. The largest deviation from the C–N–N–C–N–N–C plane is 0·018 (4) Å, illustrating the expected planarity consequent on electron delocalization. The largest deviation from the least-squares plane calculated through all the non-hydrogen atoms of the molecule except the *S*-methyl atom, C(19), is only 0·214 (6) Å [for S(18)], with C(19) projecting 1·310 (8) Å above this plane. The N(8)–C(9)–S(18)–C(19) torsion angle (Klyne & Prelog, 1960) is −63·6 (5)° and N(10)–C(9)–S(18)–C(19) is 119·6 (5)°. The corresponding angles in (1) are −5·7 and 173·0° (Preuss & Gieren, 1975) and clearly the *S*-methyl group in (3) projects above the plane of the molecule in order to avoid steric interaction with N(7) or N(11), whereas interaction with N(11) in the *syn* configuration of (1*b*) is impossible and in (1) the atoms N(10)–C(9)–S(18)–C(19) form a synplanar arrangement. The torsion angles emphasize the remarkable planarity of the remainder of (3); there are no other torsion angles between non-hydrogen-atom sequences whose deviations from planarity (0 or 180°) are >5·6°. The difference in exterior angles at C(6) and C(12) [115·2 and 123·8° at C(6); 118·1 and 121·0° at C(12)] is the same as that in (1) (Preuss & Gieren, 1975) and is explained by the steric interaction of the *o*-tolyl rings with atoms in the N–N–C–N–N chain (Table 2). The angle between the normals to each *o*-tolyl ring plane is nevertheless only 1·0 (5)°. Similar reasoning explains the orientation of the *o*-tolyl methyl groups with respect to the thiocarbazone chain, steric interaction of C(20) with N(8) and of C(21) with N(10) being avoided in the configuration adopted.

Hydrogen bonding

The imino H(11) is internally hydrogen bonded to S(18), effectively locking the molecule in the *anti* configuration. The H(11)···S(18) distance of 2·42 (5) Å [for a fixed N(11)–H(11) length of 1·00 (1) Å] is significantly less than the sum of the van der Waals radii (Bondi, 1964), while the N(11)···S(18) separation is 2·94 (1) Å. The H(11)···S(18) distance is the same as that found in xanthane hydride (Stanford, 1963), where the H atoms were located approximately and the presence of an almost linear intermolecular N–H···S hydrogen bond was reported. Although the distances are favourable for a strong intramolecular hydrogen bond, the stereochemistry of the molecule does not allow linearity of the N(11)–H(11)···S(18) angle [97 (4)°] and thus the hydrogen bond formed is considerably weakened. Hydrogen bonding is nevertheless favoured here by the fact that in the configuration adopted one of the lone pairs of electrons on S(18) is oriented towards H(11). Consideration of the angles around N(11) [H(11)–N(11)–N(10) 118 (3); H(11)–N(11)–C(12) 122 (3)°] indicates a small attraction of H(11) towards S(18). Very similar distances have recently been found for the intramolecular N–H···S hydrogen bonds in methylmercury(II) dithizonate (4) and phenylmercury(II) dithizonate (5) (Hutton, Irving, Nassimbeni & Gafner, 1980). The H···S distances are 2·40 (9) (4) and 2·43 (8) Å (5) [for fixed N–H lengths of 1·00 (1) Å] while the N···S separations are 2·92 (3) (4) and 2·86 (2) Å (5).



(4): *R* = methyl
(5): *R* = phenyl

The stretching frequency ν(N–H) in (3) is at 3270 cm^{-1} (CsI pressed disk) and in (4) and (5) is at 3255 and 3253 cm^{-1} respectively, while the *syn*-configuration compounds (1), (2) and 3-carboxymethylthio-1,5-diphenylformazan (Hutton, Irving, Nassimbeni & Gafner, 1979), in which intramolecular N–H···N hydrogen bonds exist [as (1*b*)], show ν(N–H) at 3338, 3341 and 3332 cm^{-1} respectively. The substantial difference of 68 cm^{-1} between ν(N–H) in (1*b*) and (3*d*) leads to the conclusion that there is a special stability associated with the intramolecular N–H···S hydrogen bond in (3) [and, for that matter, (4) and (5)]. In terms of distances, we may regard the strength of hydrogen bonding as directly related to the difference $(W_H + W_B) - d(H\cdots B)$ where W_H and W_B are the van der Waals radii (Bondi, 1964) for the H atom and the acceptor atom *B*, respectively. This overlap is 0·55 Å in (3) and 0·56 Å for (1) [where H(11)···N(8) is 2·21 Å and N(11)···N(8) is 2·62 Å] and does not explain the apparently stronger hydrogen bond found in (3). Flett (1953) has pointed out an anomalously large shift of ν(N–H) to lower wavenumber found for intermolecular N–H···S hydrogen-bonding thioamides.

Table 2. *Selected intramolecular non-bonded distances* (Å)

C(20)···N(7)	2·79 (1)	S(18)···N(11)	2·94 (1)
C(19)···N(7)	3·11 (1)	C(5)···N(8)	2·72 (1)
S(18)···N(7)	2·93 (1)	C(13)···N(10)	2·77 (1)
C(21)···N(11)	2·85 (1)		

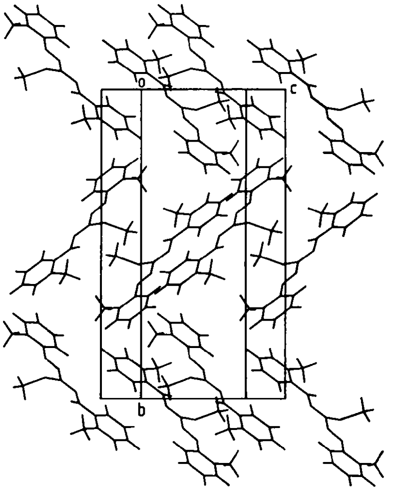


Fig. 4. The molecular packing viewed down **a***.

There is in the *anti* structure (3*d*) a noticeable shortening of the N(10)—N(11) formal single bond [1·326 (6) Å] over the lengths found in the *syn* structures (1*b*) [1·344 (4) Å] and 3-carboxymethylthio-1,5-diphenylformazan [1·352 (6) Å]. If the sum of the bond orders around N(11) is assumed to be 3·6* and with Burke-Laing & Laing's (1976) bond-length *versus* bond-order curves for C—N and N—N bonds in which both atoms are assumed to have sp^2 hybridization, bond orders of 1·02 and 1·06 may be derived for the N—H bonds in (1) and 3-carboxymethylthio-1,5-diphenylformazan respectively. The N—H bond orders in (3), (4) and (5) are found to lie in the range 0·92–0·95 and thus the lower ν(N—H) found in (3) and related structures (4) and (5) may, in part at least, be a result of increased electron delocalization over the thiocarbazone chain in *anti* configurations [in which N(10)—N(11) has more double-bond character than in *syn* configurations] rather than of a significantly stronger hydrogen bond to S.

Molecular packing

A projection of the packing in crystals of (3) is shown in Fig. 4. Pairs of molecules related by centres of inversion may be regarded as packing units and are stacked in alternate directions along **b**. Unlike the packing in (1), where many close contacts are reported (Preuss & Gieren, 1975), molecules of (3) exhibit no close intermolecular contacts. The distance between two neighbouring S atoms (*i.e.* between the reference molecule at *x*,*y*,*z* and the molecule at $-x$, $-y$, $1-z$) is 4·36 (2) Å, which exceeds significantly the sum of their van der Waals radii. This loose packing is reflected in the large average volume occupied by a non-hydrogen atom (18·9 Å^3, $D_c = 1{\cdot}25$ Mg m^{-3}) compared with (1) (17·9 Å^3, $D_c = 1{\cdot}33$ Mg m^{-3}) (Preuss & Gieren, 1975). The looser packing in (3) can be ascribed to the fact that the *S*-methyl group projects above the mean plane of the molecule in (3), whereas in (1) it lies virtually in the plane.

Conclusion

There are few X-ray determinations of the structures of *anti,s-trans* formazans. Why this configuration (3*d*) should be preferred to the *syn,s-trans* configuration [as in (1*b*)] is not obvious. Apparently molecular-packing considerations in the crystal are of prime importance and override stabilization through a possibly stronger hydrogen bond [as (1*b*)], while the extended thiocarbazone chain configuration (3*d*) provides a more highly conjugated and therefore more energetically favoured system. There seems to be no reason why the *o*-tolyl methyl groups should have any effect on the configuration adopted in the structure *per se*. The nature of the pink and yellow isomers of (1) and (3) respectively may be generally extended to the pink ⇌ yellow isomerism found in many formazans. These results support aspects of the speculative configurations proposed by Kuhn & Weitz (1953) but are contrary to those of Burns & Duncan (1966).

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* The *p* electrons on N in a conjugated C—N chain are delocalized if this atom is involved in three σ bonds (especially if one of these is to H). As a result the sum of the bond orders of that N is well above 3, *viz.* between 3·4 and 3·7 (Burke-Laing & Laing, 1976).

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Structure and Packing Arrangement of Molecular Compounds. IX.* 7,7,8,8-Tetracyanoquinodimethane–7,8-Benzoquinoline (1 : 1)†

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Abstract

Crystals of the title compound, $C_{12}H_4N_4.C_{13}H_9N$, are monoclinic, $P2_1$, with two units of the complex in a unit cell having a = 7·803 (1), b = 18·878 (2), c = 6·883 (1) Å and β = 100·55 (2)°. The structure was solved from three-dimensional precession diffractometer data by using Patterson search methods, and was refined to a conventional $R = 0·056$ and weighted $r = 0·044$. Almost parallel TCNQ and 7,8-benzoquinoline molecules are alternately stacked along the c axis. The layer-like arrangement of the complex is compared with that found in the (1:1) TCNQ:*o*-phenanthroline crystalline molecular compound [Goldberg & Shmueli (1977). *Acta Cryst.* B**33**, 2189–2197]. The differences between the packing modes of the two closely related compounds appear to be due mainly to a different relative contribution of the dipole–dipole interaction to the stabilization of the structures. A rigid-body anisotropic constrained refinement was carried out which converged to $R = 0·061$ and weighted $r = 0·051$. The results of the constrained refinement along with results of energy-profile calculations indicate that the (large) thermal parameters of 7,8-benzoquinoline describe genuine motion, unlike those of the related *o*-phenanthroline in the above-mentioned structure.

Introduction

Structural studies of crystalline molecular compounds are associated with problems concerning important stabilizing interactions, their effects on the molecular geometry, unequal dynamic behaviour of the constituent molecules and their degree of order in the crystalline state. These and related questions form the basis of the programme of studies, in which compounds involving 7,7,8,8-tetracyanoquinodimethane (TCNQ) have so far been investigated (Goldberg & Shmueli, 1973; Shaanan, Shmueli & Rabinovich, 1976), being carried out in this laboratory.

Our study of the TCNQ:1,10-phenanthroline (PHT) compound (Goldberg & Shmueli, 1977, hereafter GS) showed that the highly polar PHT molecule is disordered and, moreover, the rather frequently observed mixed-stack arrangement of donor and acceptor

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* Part VIII: Goldberg & Shmueli (1977).

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