

temperature of melting. In these conditions the structural invariant element could be the zigzag conformation as found in the crystal. If we now suppose that, at the transition, the two-dimensional organization is conserved in the (011) plane, one can easily imagine not a columnar structure, but a lamellar structure in hexagonal network.

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Structure of Butanedione Bis(methylphenylhydrazine)

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Abstract. $C_{18}H_{22}N_4$, $M_r = 294.40$, monoclinic, $P2_1/c$, $a = 13.490$ (3), $b = 7.734$ (2), $c = 8.211$ (3) Å, $\beta = 97.60$ (4)°, $V = 849.6$ (4) Å³, $Z = 2$, $D_x = 1.15$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.66$ cm⁻¹, $F(000) = 316$, room temperature, $R = 0.052$, $wR = 0.053$ for 639 independent observed reflections. A π delocalization is observed between the aromatic ring and the aliphatic chain. Steric hindrance between the methyl groups and between methyl groups and the adjacent H atoms of the ring is avoided by rotation of the chain and by the enlargement of some angles.

Introduction. In the past ten years hydrazones have been considered as donors in complexes with a variety of π^* -organic acceptors (Bruni, Cardellini, Conti, Giorgini & Tosi, 1990, and references there-

in). Molecular complexes (MC) of different stability have been obtained in solution and the moderately weak interactions discussed in terms of ionization potentials, transition energies and thermodynamic properties.

Except with large-size acceptors (*e.g.* 9-dicyanomethylene-2,4,7-trinitrofluorene) (Bruni, Cardillo, Giorgini, Tosi, Bocelli & Rizzoli, 1990), we were unable to obtain crystalline complexes in order to verify the hypothesis (supported by spectroscopic results) that the hydrazono group $C=N-N$ can be considered the active donor centre (Bruni, Cardellini & Tosi, 1988).

All the experimental results were in agreement with the hypothesis that the factor which determines the spectroscopic and structural features (and conse-

Table 1. Atomic fractional coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^4$)

	x	y	z	U_{eq}
N1	2881 (2)	606 (5)	359 (4)	508 (11)
N2	3804 (2)	-296 (4)	496 (4)	493 (12)
C1	2296 (2)	56 (5)	1544 (5)	465 (12)
C2	1273 (3)	446 (6)	1384 (6)	631 (17)
C3	718 (4)	-3 (8)	2604 (7)	774 (21)
C4	1144 (4)	-797 (9)	3999 (9)	839 (27)
C5	2149 (4)	-1179 (6)	4195 (7)	683 (21)
C6	2721 (3)	-738 (6)	2990 (5)	527 (14)
C7	2375 (4)	899 (9)	-1293 (7)	712 (22)
C8	4531 (3)	507 (5)	-49 (5)	464 (14)
C9	4524 (4)	2327 (7)	-683 (8)	707 (19)

Table 2. Bond distances (\AA), angles ($^\circ$) and selected torsion angles ($^\circ$)

N1—N2	1.419 (4)	C2—C3	1.372 (8)
N1—C1	1.398 (5)	C3—C4	1.359 (9)
N1—C7	1.454 (6)	C4—C5	1.377 (8)
N2—C8	1.290 (5)	C5—C6	1.376 (7)
C1—C2	1.402 (5)	C8—C9	1.500 (7)
C1—C6	1.391 (6)	C8—C8'	1.482 (6)
C1—N1—C7	117.3 (3)	C2—C3—C4	121.3 (5)
N2—N1—C7	116.7 (3)	C3—C4—C5	119.8 (6)
N2—N1—C1	111.5 (3)	C4—C5—C6	120.0 (5)
N1—N2—C8	115.8 (3)	C1—C6—C5	121.1 (4)
N1—C1—C6	121.4 (3)	N2—C8—C8'	114.2 (3)
N1—C1—C2	120.6 (3)	N2—C8—C9	112.0 (4)
C2—C1—C6	117.7 (3)	C9—C8—C8'	118.8 (3)
C1—C2—C3	120.2 (4)		
C6—C1—N1—N2	22.5 (5)	C1—N1—N2—C8	-154.2 (3)
C6—C1—N1—C7	160.8 (4)	C7—N1—N2—C8	67.3 (5)
C2—C1—N1—N2	-164.0 (4)	N1—N2—C8—C9	5.1 (6)
C2—C1—N1—C7	-25.7 (6)	N1—N2—C8—C8'	-177.5 (3)

quently the possibility of MC interactions) is closely related to the steric interference of the substituents at the C and terminal N atoms of the hydrazono group (Tosi, Cardellini & Bocelli, 1988).

More recently we were able to confirm these suppositions by the X-ray analysis of the complex butanedione monophenylhydrazone-tetracyanoethylene (TCNE), in which TCNE clearly lies parallel to and above the imino group of the hydrazone. Attempts to obtain crystals from dihydrazones failed; in fact, a slow crystallization from the solution of the complex afforded starting compounds or tricyanovinyl adducts (Tosi, Giorgini & Bocelli, 1992), probably as a result of the presence of some steric hindrance in the dihydrazones. In order to prove these suppositions an X-ray analysis of the title compound was undertaken.

Experimental. Compound obtained by mixing 0.1 mol of 2,3-butanedione in 10 ml of benzene with 0.25 mol of phenylmethylhydrazine in 10 ml of benzene in the presence of a catalytic amount of sulfuric acid. The pale-yellow solid obtained after refluxing in a Marcussen condenser for 30 min and evaporation of the solvent under vacuum, was recrystallized in ethyl alcohol (m.p. 393–395 K; yield 45%). Prismatic

crystal of dimensions $0.09 \times 0.23 \times 0.35$ mm, Siemens AED single-crystal diffractometer controlled with an IBM PS2/30 personal computer (Belletti, Cantoni & Pasquinelli, 1988). Lattice parameters from least-squares refinement of 28 automatically centred reflections with $12.1 < \theta < 18.6^\circ$. Reflections measured at room temperature in the θ range $2\text{--}27^\circ$ with Mo $K\alpha$ radiation; 2139 reflections collected; hkl range $-15/15, 0/9, 0/9$. One standard reflection measured every 50 reflections displayed a decay of about 13% during the data-collection time. Reflection intensities were corrected for this decay, for Lorentz and polarization effects, but not for absorption. The low number of observed reflections results from the moderate crystal quality. The structure was solved with *SHELXS86* (Sheldrick, 1986) using the 639 unique ($R_{int} = 0.023$) observed reflections with $I > 2\sigma(I)$. H atoms were located in a difference Fourier map. Full-matrix least-squares refinement [function minimized $\sum w(\Delta F)^2$ with isotropic thermal parameters for H atoms, anisotropic parameters for other atoms] using *SHELX76* (Sheldrick, 1976), $R = 0.052$, $wR = 0.053$ with $w = 1.0/(\sigma^2 F + 0.02228 F^2)$, $S = 0.44$. Maximum Δ/σ in the final cycle refinement 0.82; $\Delta\rho_{min/max} = -0.26/0.16 \text{ e \AA}^{-3}$; 144 parameters refined. Atomic scattering factors were those incorporated in *SHELX76*. * All the calculations were performed on an IBM PS2/80 personal computer with the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreotti, 1987).

Discussion. Final atomic coordinates and equivalent isotropic displacement factors (Hamilton, 1959) are in Table 1. Table 2 contains the molecular structure parameters. A perspective view of the molecule is shown in Fig. 1.

Since there are two molecules per unit cell, the centre of the C—C bond of the aliphatic chain has to be on a crystallographic center of symmetry.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54787 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0236]

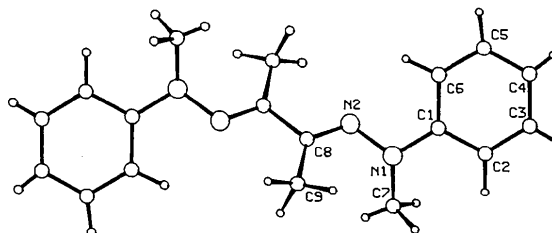


Fig. 1. Perspective view and atomic labelling of the molecule.

As previously observed in other phenylhydrazone derivatives (Tosi *et al.*, 1988; Chiba, Tani, Shuto, Haga & Tokonami, 1990), the bond distances in the chain show some shortening with respect to the expected theoretical values, probably depending on an extended π -electron conjugated system between the chain and the aromatic ring.

The phenyl ring is planar and forms a dihedral angle of 34.1° with the plane formed by N2, N1, C7. The rotation around the C1—N1 bond favours the release of steric hindrance between the H atoms of the phenyl and those of the C7 methyl group. The steric hindrance between the two methyls is probably also the cause of the opening of N2—C8—C9 with respect to the adjacent angles. Molecular packing is realized *via* van der Waals interactions.

The presence of some steric hindrance around the hydrazono skeleton may be responsible for the weak interactions, either in solution or in the solid state, with planar acceptors like tetracyanoethylene (Tosi *et al.*, 1988). As a matter of fact, as this acceptor is superimposed with the hydrazono skeleton rather than the phenyl rings (Tosi *et al.*, 1992), the molecular association is influenced by any steric interference on the donor. It is not surprising that the complex formed by the above compounds, but in the ratio $D/A = 1/2$, cannot be isolated due also to interference between the TCNE molecules. Stable crystalline

complexes can be isolated only in the case of mono-hydrazone of diketones where the packing between the donor and the acceptor is reinforced by intermolecular hydrogen bonding between the carbonyl O atom and the H atom of the amino N of the hydrazone (Tosi *et al.*, 1992).

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Structure of Ticlopidine Hydrochloride – a Platelet Antiaggregating Agent

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Abstract. 5-[(2-Chlorophenyl)methyl]-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine hydrochloride, $C_{14}H_{15}ClNS^+ \cdot Cl^-$, $M_r = 300.25$, triclinic, $P\bar{1}$, $a = 9.734$ (2), $b = 10.873$ (7), $c = 7.256$ (2) Å, $\alpha = 101.47$ (4), $\beta = 106.31$ (2), $\gamma = 81.60$ (4)°, $V = 719$ (1) Å³, $Z = 2$, $D_m = 1.37$ (2), $D_x = 1.389$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.57$ mm⁻¹, $F(000) = 312$, $T = 293$ K, $R = 0.044$ for 2520 observed reflections with $I > 3\sigma(I)$ and 163 parameters. The molecule consists

of two quasi-planar fragments with a dihedral angle of 61.2 (8)°. The hydrochloride part is associated with the N atom. There is an intramolecular hydrogen bond $H \cdots Cl = 2.035$ (1) Å with an $N-HN \cdots Cl$ angle of 172.3 (2)°. There are no intermolecular hydrogen bonds.

Introduction. In the last ten years much attention has been devoted to the potential interest of ticlo-