

2,4-Dinitrobenzaldehyde (1*H*-Tetrazol-5-yl)hydrazone

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Abstract. C₈H₆N₈O₄, $M_r = 278.2$, monoclinic, $P2_1/n$, $Z = 4$, $T = 293$ K, $a = 10.991$ (2), $b = 9.056$ (2), $c = 11.706$ (2) Å, $\beta = 101.50$ (1)°, $V = 1141.8$ Å³, $D_m = 1.60$, $D_x = 1.62$ Mg m⁻³, $\mu = 0.118$ mm⁻¹, Cu $K\alpha$ radiation ($\lambda = 1.54051$ Å). Final $R = 0.049$ for 1228 independent reflections. The title compound, DBTYH, consists of a 2,4-dinitrobenzaldehyde moiety and a tetrazole moiety bridged by a hydrazone chain. Each molecule is hydrogen-bonded to three other molecules through four hydrogen-bond linkages (two acceptor and two donor) centered on the tetrazole ring. The entire molecule is approximately planar with the exception of one nitro group which is rotated 39° out of the plane of the benzene ring and has a short C—H...O distance that could indicate a weak intramolecular hydrogen bond.

Introduction. DBTYH, which was prepared by reacting (1*H*-tetrazol-5-yl)hydrazine with 2,4-dinitrobenzaldehyde (Thiele, 1898), has been used in the preparation of explosives (Jaffery, 1976) as have other tetrazole compounds (Duke, 1971; Bryden, 1958). Its thermal decomposition has been studied under dynamic and isothermal conditions using a differential scanning calorimeter (Om Reddy, Krishna Mohan, Mohan Murali & Chatterjee, 1981).

Oscillation and Weissenberg photographs of a yellow crystal of DBTYH (grown by slow evaporation from a 2:1 methanol-dioxane mixture) showed the crystal system to be monoclinic, with systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$, indicating space group $P2_1/n$, with general positions x, y, z and $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. The crystal density was measured by flotation using iodobenzene and kerosene.

Accurate unit-cell parameters were obtained by least-squares refinement of 15 carefully centered reflections and 1952 reflections ($2\theta_{\max} = 120^\circ$) were measured using the θ - 2θ scan mode on a Syntex $P2_1$ - F diffractometer (crystal size $0.06 \times 0.09 \times 0.11$ mm).

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The crystal was automatically recentered every 428 reflections, with four standard reflections checked after each 102 measurements. Of the resulting 1701 independent reflections, 1228 reflections with $F > 3\sigma(F)$ were used in the refinement. Lorentz-polarization corrections were applied; decay and absorption corrections were not necessary.

The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) using 141 reflections ($E_{\min} = 1.75$) and three general phase relationships. All but one of the non-H atoms were located in

Table 1. Fractional coordinates ($\times 10^4$, for H $\times 10^3$) and B_{eq} or B_{iso} (Å²) with *e.s.d.*'s in parentheses, and deviations ($\Delta \times 10^3$ Å) of non-hydrogen atoms from the least-squares plane (see text)

	$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			B_{eq} or B_{iso}	Δ
	<i>x</i>	<i>y</i>	<i>z</i>		
O(1)	-1246 (6)	4800 (7)	607 (5)	5.64 (20)	-526 (7)*
O(2)	34 (7)	6537 (7)	1264 (5)	5.73 (22)	813 (8)*
O(3)	850 (8)	39 (7)	1207 (6)	7.38 (26)	76 (8)
O(4)	1770 (7)	-528 (6)	2956 (6)	5.48 (22)	-137 (7)
N(1)	2158 (6)	7937 (7)	6850 (5)	3.16 (18)	132 (7)
N(2)	2490 (7)	8873 (7)	7769 (5)	3.74 (19)	173 (8)
N(3)	1856 (6)	10060 (7)	7482 (5)	3.59 (19)	-5 (7)
N(4)	1128 (6)	9973 (6)	6396 (5)	3.00 (17)	-139 (7)
N(5)	807 (6)	8066 (7)	4989 (5)	3.14 (17)	-132 (7)
N(6)	1127 (6)	6661 (6)	4715 (5)	2.99 (18)	-3 (7)
N(7)	-359 (6)	5283 (7)	1284 (5)	3.81 (20)	117 (7)
N(8)	1249 (7)	329 (8)	2222 (6)	4.52 (24)	-29 (8)
C(1)	818 (7)	4747 (8)	3296 (6)	2.92 (22)	20 (8)
C(2)	325 (7)	4262 (9)	2170 (6)	2.98 (22)	47 (8)
C(3)	450 (7)	2834 (9)	1800 (6)	3.20 (23)	29 (8)
C(4)	1113 (7)	1879 (8)	2593 (7)	3.15 (23)	7 (8)
C(5)	1649 (8)	2285 (9)	3717 (7)	3.36 (24)	6 (8)
C(6)	1484 (8)	3721 (9)	4065 (6)	3.37 (23)	-3 (9)
C(7)	614 (7)	6241 (8)	3700 (6)	3.25 (22)	45 (8)
C(8)	1341 (7)	8632 (8)	6030 (6)	2.61 (20)	-49 (8)
H(N1)	247 (8)	715 (10)	682 (7)	6 (2)	
H(N5)	36 (9)	860 (11)	452 (8)	8 (3)	
H(C3)	7 (6)	255 (8)	103 (6)	4 (2)	
H(C5)	214 (7)	152 (8)	424 (6)	4 (2)	
H(C6)	186 (6)	402 (7)	487 (5)	3 (2)	
H(C7)	0 (5)	673 (6)	319 (5)	2 (1)	

* Not included in the calculation of the least-squares plane.

the *E* map computed from the phase set having the highest figure of merit. The structure determination and refinement was completed by using difference Fourier and block-diagonal least-squares techniques. In the final least-squares cycle, 205 parameters were varied (nine per non-hydrogen atom, four per hydrogen atom, one scale factor), with convergence attained when the maximum shift/error was 0.25. The final unweighted and weighted residuals [$R = \sum |\Delta F| / \sum |F_o|$; $R_w = (\sum w|\Delta F|^2 / \sum |F_o|^2)^{1/2}$] were 0.049 and 0.052, respectively; $S = 0.86$; R for all 1701 independent reflections was 0.075.* The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$, where $\sigma(F_o)$ is based on counting statistics. The atomic scattering factors for the non-hydrogen atoms were taken from Cromer & Waber (1965) and those for the H atoms from Stewart, Davidson & Simpson (1965). The data-reduction and *MULTAN* programs were from the Syntex *XTL* crystallographic programs; all other programs used in this study were from the crystallographic library of the Indian Institute of Science. The final positional parameters and equivalent isotropic thermal parameters are listed in Table 1.

Discussion. The DBTYH molecule (Fig. 1) has bond lengths and angles commensurate with similar molecules (Table 2). The overall shape of the molecule is approximately planar since the tetrazole ring, hydrazone group, benzene ring and nitro groups are each planar* and, with the exception of one nitro group, all these planes lie within 9° of the plane of the benzene ring. Accordingly, all the non-hydrogen atoms [excluding O(1) and O(2)] fall within 0.17 Å of the least-squares plane ($10.01x + 2.47y + 5.68z - 0.10 = 0$) through these atoms (Table 1).

Although extensive electron delocalization has been reported in a C—N=N=C—N=N—C chain (McCallum,

* Lists of structure factors, anisotropic thermal parameters of the non-H atoms, bond lengths and angles involving H atoms, and equations for the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36829 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

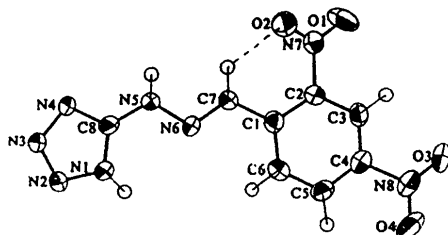


Fig. 1. An ORTEP drawing (Johnson, 1965) of the DBTYH molecule with the thermal ellipsoids scaled at the 50% probability level. The short intramolecular H...O distance is indicated by the dashed line (see text).

Table 2. Intramolecular bond lengths (Å) and angles (°) for non-hydrogen atoms in DBTYH

C(1)—C(2)	1.393 (10)	O(4)—N(8)	1.213 (9)
C(2)—C(3)	1.379 (11)	C(1)—C(7)	1.465 (11)
C(3)—C(4)	1.368 (10)	C(7)—N(6)	1.268 (9)
C(4)—C(5)	1.379 (10)	N(6)—N(5)	1.374 (9)
C(5)—C(6)	1.386 (11)	N(5)—C(8)	1.345 (9)
C(6)—C(1)	1.395 (10)	C(8)—N(1)	1.334 (9)
O(1)—N(7)	1.209 (8)	N(1)—N(2)	1.361 (8)
C(2)—N(7)	1.478 (9)	N(2)—N(3)	1.289 (9)
O(2)—N(7)	1.217 (9)	N(3)—N(4)	1.363 (8)
O(3)—N(8)	1.210 (10)	N(4)—C(8)	1.324 (9)
C(4)—N(8)	1.486 (10)		
C(2)—C(1)—C(6)	117.1 (7)	N(5)—C(8)—N(4)	124.7 (6)
C(2)—C(1)—C(7)	122.8 (6)	N(4)—C(8)—N(1)	109.7 (6)
C(6)—C(1)—C(7)	120.1 (6)	C(8)—N(1)—N(2)	108.1 (6)
C(1)—C(2)—C(3)	123.3 (7)	N(1)—N(2)—N(3)	105.5 (5)
C(1)—C(2)—N(7)	120.9 (7)	N(2)—N(3)—N(4)	112.4 (6)
C(3)—C(2)—N(7)	115.8 (6)	N(3)—N(4)—C(8)	104.2 (5)
C(2)—C(3)—C(4)	116.9 (7)	N(6)—N(5)—C(8)	118.6 (6)
C(3)—C(4)—C(5)	123.2 (7)	C(7)—N(6)—N(5)	114.2 (6)
C(3)—C(4)—N(8)	118.0 (7)	O(1)—N(7)—O(2)	124.6 (7)
C(5)—C(4)—N(8)	118.8 (7)	C(2)—N(7)—O(1)	117.7 (6)
C(4)—C(5)—C(6)	118.3 (7)	C(2)—N(7)—O(2)	117.7 (6)
C(5)—C(6)—C(1)	121.2 (7)	O(3)—N(8)—O(4)	125.8 (7)
C(1)—C(7)—N(6)	120.8 (6)	C(4)—N(8)—O(3)	117.0 (6)
N(5)—C(8)—N(1)	125.6 (6)	C(4)—N(8)—O(4)	117.2 (6)

Irving, Hutton & Nassimbeni, 1980), the C(1)—C(7) and C(7)—N(6) distances in the C—N=N=C—C chain of DBTYH reveal bond orders of 1.0 and 2.0, respectively (according to the criteria of Burke-Laing & Laing, 1976), thus indicating that, in DBTYH, (a) there is little or no conjugation in the hydrazone chain and (b) the tetrazole and 2,4-dinitrobenzaldehyde rings can be described independently.

A number of different tetrazole derivatives have been described in the literature, but only two of these have the same configuration as that found in DBTYH [*i.e.* H atom attached to N(1) and N bonded to C(8)]: tetrazene {1-amino-1-[(1*H*-tetrazol-5-yl)azo]guanidine monohydrate} (Duke, 1971) and 5-amino-1*H*-tetrazole monohydrate (Britts & Karle, 1967). The bond angles are not reported for the former compound, but the agreement between the latter compound and DBTYH is excellent. In both molecules the H(N1), N(3) and N(4) atoms are involved in the hydrogen-bonding scheme and the angles centered on N(3) and N(4) are the largest and smallest angles in the ring, respectively. The C(8)—N(1) and C(8)—N(4) interatomic distances in all three compounds fall within one e.s.d. of each other, while the N(1)—N(2), N(2)—N(3) and N(3)—N(4) distances are significantly different. However, the two sums of the latter three interatomic distances agree to within 0.007 Å. Using the criteria of Burke-Laing & Laing (1976) we find that the sum of the bond orders over these three bonds is nearly 4, as expected. Evidently, subtle differences between these molecules [*e.g.*, hydrogen-bonding schemes and sub-

Table 3. *Hydrogen bonding in DBTYH*

X—H...Y	X...Y (Å)	X—H (Å)	H...Y (Å)	$\angle X-H...Y$ (°)
N(5)—H(N5)...N(4) ⁱⁱ	2.989 (8)	0.82 (9)	2.19 (9)	165 (10)
N(1)—H(N1)...N(3) ⁱⁱ	2.870 (9)	0.80 (9)	2.13 (9)	154 (9)
C(7)—H(C7)...O(2) ⁱ	2.808 (9)	0.92 (5)	2.27 (5)	117 (5)

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

stituents on C(8)] result in different degrees of electron delocalizations in the sensitive tetrazole rings. Since the C(8)—N(1) and C(8)—N(4) distances fall within 2 e.s.d.'s of each other (in all three molecules), it is clear that electron delocalization occurs over these bonds and involves the N(5) atom as well. Thus, the tetrazole ring can be described in terms of the delocalization of electron density along the chain of four N atoms and the delocalization involving the C(8) atom. In the former set, we find the expected bond order of 4, while in the latter case, where the effects of the different types of substituent atoms are more pronounced, we cannot make any generalizations.

Substituted benzene rings are known to undergo deformation from regular hexagonal geometry (Cox, Cruickshank & Smith, 1958; Carter, McPhail & Sim, 1966; Domenicano & Vaciago, 1979), and in DBTYH the benzene ring is slightly deformed. The angles with apices at the C atoms bonded to the nitro groups are significantly larger than the other angles (Table 2).

The plane of the N(8) nitro group lies within 5° of the benzene ring, while there is a 39° angle between the plane of the N(7) nitro group and the benzene ring. It is interesting to note that the short O(2)...H(C7) distance and the out-of-plane twist by a nitro group adjacent to an aldehyde-type group found in DBTYH (Table 3 and Fig. 1) is similar to that found in 2-nitrobenzaldehyde (Coppens, 1964) for which the possibility of a C—H...O hydrogen bond is discussed. While Coppens attributes the short H...O distance and the out-of-plane twist to repulsive forces between adjacent nitro and aldehyde groups, Hamilton & Ibers (1968) are willing to accept the possibility that weak C—H...O bonds could exist. In DBTYH the closest intermolecular distances involving O(2) are 2.79 (7) Å to H(C3) and 3.034 Å to O(1). Since these two distances are equal to the sums of the van der Waals radii, it is obvious that the orientation of the N(7) nitro group is affected strongly by the repulsive steric forces of adjacent non-bonded atoms. However, it is also possible to conjecture that the crystal structure would be different if this conformation were not partially stabilized by the formation of a weak intramolecular C—H...O hydrogen bond. In the absence of any spectroscopic data, it is not possible to decide either way.

The crystal structure (Fig. 2) can be described as an infinite network of hydrogen-bonded tetrazole rings

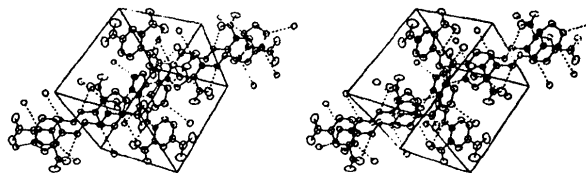


Fig. 2. Stereoview of the DBTYH unit cell, showing six complete molecules and the N atoms to which they are connected by hydrogen bonds (ORTEP, Johnson, 1965).

(Table 3) with the benzene moieties lying alternately above and below the tetrazole network: If the N(5) atom is considered as part of the tetrazole moiety (as discussed above), each tetrazole group is involved in two acceptor and two donor intermolecular hydrogen-bond linkages with three other molecules; H(N1) (donor) and N(3) (acceptor) are connected to different molecules, while the N(4) (acceptor) and H(N5) (donor) pair are involved in a centrosymmetric bonding arrangement with a third molecule in a manner comparable to the usual carboxylic acid dimer formation.

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3-(1-Pyrrolidinyl)propanoic Acid Hemihydrate

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Abstract. $C_7H_{13}NO_2 \cdot \frac{1}{2}H_2O$, monoclinic, $P2_1/a$, $a = 11.886$ (4), $b = 10.801$ (4), $c = 12.539$ (2) Å, $\beta = 103.60$ (2)°, $Z = 8$, $D_c(140\text{ K}) = 1.293$, $D_m(294\text{ K}) = 1.25\text{ Mg m}^{-3}$. Final $R = 0.0485$ for 2077 observed reflections. The two independent, zwitterionic amino acid molecules form chains, roughly parallel to \mathbf{b} , that are linked by alternating short [$N \cdots O = 2.649$ (3) Å] and unevenly bifurcated $NH \cdots O$ hydrogen bonds. Adjacent chains are connected in the \mathbf{a} direction by bridging water molecules. One pyrrolidine ring is unusual in that a C atom bonded to the N atom is the most puckered center.

Introduction. In a previous publication from this laboratory we noted that the $N \cdots O$ distance in $NH \cdots O$ hydrogen-bonded systems depends on both the number of hydrogen bonds from N and the formal charges on the donor and acceptor functional groups (Peterson, Hope & Nash, 1979). In particular, when an N atom having a formal positive charge and only a single functional H atom is hydrogen-bonded to a negatively charged O atom, very short $N \cdots O$ separations in the range 2.60 to 2.70 Å may occur. The crystal structure of the title compound was determined to obtain additional evidence bearing on the question of hydrogen-bond geometries in systems of the $NH^+ \cdots O^-$ type. Anhydrous 3-(1-pyrrolidinyl)propanoic acid, PPA, was prepared by the method of Horsma & Nash (1968). Several crystals of anhydrous PPA, grown in a convection tube (Hope, 1971) using benzene–ethylene chloride mixtures as solvents, were examined and all were found to be twinned. It was established, however, that the monoclinic unit cell had at least six molecules in the asymmetric unit.

Crystals of the title compound were grown in a convection tube from the anhydrous acid and purpor-

tedly anhydrous reagent-grade acetone. A crystal with dimensions $0.3 \times 0.25 \times 0.25$ mm was mounted on a Syntex $P2_1$ diffractometer and cooled to about 140 K with a stream of cold nitrogen gas. An Mo-target X-ray tube and a graphite monochromator were used. Axial photos showed that the cell is monoclinic.

The cell and orientation parameters were determined from 16 reflections in the range $25^\circ \leq 2\theta \leq 35^\circ$. The cell dimensions (140 K; $\lambda_{Mo\ K\alpha} = 0.71069$ Å) are given in the *Abstract*. The systematic absences $h0l$: h odd, and $0k0$: k odd, establish the space group $P2_1/a$.

The crystal density measured by flotation at room temperature is 1.25 Mg m^{-3} . From previous experience we would expect an increase to $1.29\text{--}1.30\text{ Mg m}^{-3}$ on lowering the temperature to 140 K. The calculated density is 1.216 Mg m^{-3} for eight molecules of PPA in the cell, and 1.293 Mg m^{-3} for eight PPA + four H_2O . The density data thus gave an early indication of the presence of water molecules in the crystal.

Intensities were measured by the ω -scan technique with scan speeds varying between 1 and 30° min^{-1} for $2\theta < 50^\circ$. Data were collected for 2759 unique reflections, of which 2077 had intensities greater than $3\sigma(I_{net})$ and were used in refinements. The intensities of two check reflections were measured after every 120 reflections to confirm that there was no systematic drift in the system. The data were corrected for Lorentz and polarization factors but no absorption corrections were applied ($\mu = 0.104\text{ mm}^{-1}$).

The structure was solved by direct methods using a program library developed in this laboratory. Sayre's (1952) equation, as programmed by Long (1965), was used to create 16 sets of signs for the 227 reflections with $E \geq 1.70$. The set with the highest consistency index (0.890) was used to produce an E map, from