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2,2-Dimethyl-1-(2,4,6-trinitrophenyl)hydrazine

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The title molecule (DMPH-H), $C_8H_9N_5O_6$, was investigated to provide comparison with 2,2-diphenyl-1-picrylhydrazine, which unlike DMPH-H is readily oxidizable to form a well known stable free radical (DPPH). The structure shows essential differences in the configuration of the hydrazine-N atoms, the *ortho*-nitro group orientations and the crystal packing. The bond angles of the dimethylamino N atom [107.90 (13), 108.96 (12) and 112.21 (13)°] are consistent with a tetrahedral N atom and sp^3 hybridization.

Comment

2,2-Dimethyl-1-picrylhydrazine (DMPH-H) reported herein is the latest member of a series of closely related picrylhydrazines being investigated in an ongoing study of their internal rotations (conformerizations), as well as the acidity and oxidizability of the hydrazinic moiety (*e.g.* Brown *et al.*, 1999; Tyson & Weil, 1990). Comparisons of the molecular structures, pseudo-thermodynamic conformerization activation parameters, chemical properties, and the results of molecular-orbital computations have been a vital component of this work (Brown *et al.*, 1999; Wang *et al.*, 1991).



DMPH-H was reported earlier as not being oxidizable to the corresponding hydrazyl radical (Poirier & Benington, 1954). We have confirmed this observation, of interest since 2,2-diphenyl-1-picrylhydrazine (DPPH-H) forms a very stable free radical (DPPH). The bond angles for N7 of DMPH-H [107.90 (13), 108.96 (12) and 112.21 (13)°] are consistent with a tetrahedral N atom and sp^3 hybridization, compared to the equivalent N atom in DPPH-H which is sp^2 hybridized (with some sp^3 character) (Wang *et al.*, 1991). Thus, the structural



Figure 1

A general *ORTEPII* (Johnson, 1976) view of the title compound with non-hydrogen displacement ellipsoids drawn at the 50% probability level. For clarity, the H atoms are drawn as small spheres of arbitrary size.

differences (e.g. of the π -electron systems) elucidate the chemical differences.

The structure of DMPH-H has an intramolecular hydrogen bond between the H atom on N1 and one of the O atoms on N2 (O21) [or N6 (O61)] to form a six-membered ring (Fig. 1), a structure found in all of the picryl hydrazines (Brown *et al.*, 1999; Wang *et al.*, 1991). The result is to put the plane of the N2 nitro group fairly close [22.62 (6)°] to the plane of the picryl ring {whereas the plane of the N6 nitro group adopts a conformation highly twisted [52.74 (6)°] relative to the plane of the picryl ring due to the proximity of atom N7} unlike the coplanar situation in DPPH-H (Wang *et al.*, 1991).

There are no solvent molecules trapped in the DMPH-H structure and no large cavities in the lattice, unlike DPPH-H which crystallizes with interstitial clathrate solvent molecules (Wang *et al.*, 1991).

Atom H1 forms a short intramolecular hydrogen bond with an *ortho* nitro group (as in DPPH-H) but also forms a long intermolecular hydrogen bond to atom O22 on an adjacent molecule $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ (unlike in DPPH-H).

Dynamic NMR and self-consistent-field molecular-orbital studies of DMPH-H are under way.

Experimental

A mixture of picryl chloride (2.48 g, 10 mmol) and K_2CO_3 (1.65 g, 12 mmol) was dissolved in 1:1 MeOH–H₂O (50 ml). To this solution, cooled to 273 K, was added dropwise a solution of 1,1-dimethylhydrazine (720 mg, 12 mmol) dissolved in MeOH (5 ml). After the addition was complete, the resulting deep-red-colored solution was stirred for 1 h. The reaction mixture was evaporated to the point of turbidity, warmed gently to afford a homogeneous solution and allowed to cool down slowly to afford a yellow solid. Filtration and recrystallization from absolute EtOH gave 2.2 g (82% yield) of the title compound [m.p. 411–413 K (literature 409–411 K; Latham *et al.*, 1976)]; IR (KBr) v_{max} : 3270 (*m*, N–H str), 3093 (*m*, C–H str), 1620 (*s*), 1590 (*m*), 1512 (*s*), 1456 (*m*), 1333 (*s*), 1301 (*m*), 1087 (*m*),

724 (*m*) cm⁻¹; ¹H NMR (300 MHz, CDCl₃, p.p.m.) δ : 2.59 (*s*, 6H), 8.30 (*bs*, 1H), 8.98 (*s*, exch, 1H), 9.16 (*bs*, 1H); ¹H NMR (300 MHz, DMSO-*d*₆, p.p.m.) δ : 2.57 (*s*, 6H), 8.81 (*s*, 2H), 9.73 (*s*, exch, 1H); ¹³C NMR [75 MHz, (CD₃)₂CO, p.p.m.] δ : 45.3 (*q*, CH₃), 123.9 (*s*, Ar–C), 124.8 (*s*, Ar–C), 133.8 (*d*, Ar–CH), 141.1 (*d*, Ar–CH); EI–MS *m/z* (relative intensity): calculated for C₈H₉N₅O₆ 271.0553; found 271.0550 (*M*⁺, 37), 254.0529 (100), 209 (15), 179 (11), 149 (17).

Note: In an alternative preparation, using a reported method (Nelsen & Weisman, 1973) based on reductive alkylation of hydrazines, a mixture of picryl hydrazine (2.43 g, 10 mmol), aqueous HCHO (37%, 8 ml), and NaBH₃CN (230 mg, 4 mmol) in 50 ml MeOH was stirred at ambient temperature for 2 h. Usual workup, *e.g.* extraction with EtOAc, washing with 10% NaHCO₃ and water, and evaporation of the organic extracts gave a yellow solid that was purified by crystallization (EtOH) to afford 1.6 g (58% yield) of the title compound with physical and spectroscopic characteristics essentially identical to the ones reported above.

Crystal data

 $\begin{array}{l} C_8 H_9 N_5 O_6 \\ M_r = 271.20 \\ \text{Orthorhombic, } P2_1 2_1 2_1 \\ a = 6.5156 \ (7) \ \text{\AA} \\ b = 8.2006 \ (11) \ \text{\AA} \\ c = 20.6704 \ (14) \ \text{\AA} \\ V = 1104.5 \ (2) \ \text{\AA}^3 \\ Z = 4 \\ D_x = 1.631 \ \text{Mg m}^{-3} \end{array}$

Data collection

Nonius CAD-4 diffractometer ω scans Absorption correction: ψ scan (North *et al.*, 1968) $T_{min} = 0.88$, $T_{max} = 0.96$ 2553 measured reflections 2479 independent reflections 2171 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.038$ $wR(F^2) = 0.100$ S = 1.0462479 reflections 175 parameters H atoms constrained Mo $K\alpha$ radiation Cell parameters from 25 reflections $\theta = 10.40-18.54^{\circ}$ $\mu = 0.141 \text{ mm}^{-1}$ T = 123 (2) KPrism, orange $0.42 \times 0.30 \times 0.25 \text{ mm}$

$n_{int} = 0.011$
$\theta_{\rm max} = 33.48^{\circ}$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 32$
3 standard reflections
every 200 reflections
intensity decay: none

 $R_{\rm H} = 0.044$

$w = 1/[\sigma^2(F_o^2) + (0.0563P)]$	$)^{2}$
+ 0.2264P]	
where $P = (F_o^2 + 2F_c^2)/2$	3
$(\Delta/\sigma)_{\rm max} < 0.001$	
$\Delta \rho_{\rm max} = 0.43 \ {\rm e} \ {\rm \AA}^{-3}$	
$\Delta \rho_{\rm min} = -0.35 \text{ e} \text{ \AA}^{-3}$	

The molecule is achiral but crystallizes in the non-centrosymmetric space group $P2_12_12_1$. The intermolecular hydrogen bonding described in Table 1 produces continuous spirals of molecules, resulting in the non-centrosymmetric space group. Using Mo radiation, and in the

Table 1

Hydrogen-bonding geometry (Å, $^{\circ}$).

$D - H \cdots A$	$D-\mathrm{H}$	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$\begin{array}{c} N1 - H1 \cdots O21 \\ N1 - H1 \cdots O22^{i} \end{array}$	0.88	2.11	2.6666 (18)	120.1
	0.88	2.60	3.358 (2)	144.6

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

absence of any atom with more electrons than oxygen, it is not possible to determine with certainty if the crystal used is all of one hand or is a racemic twin. During refinement, the structure was treated as a racemic twin.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *DIFDAT*, *SORTRF* and *ADDREF* in *Xtal* (Hall *et al.*, 1997); program(s) used to solve structure: *Xtal*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1101). Services for accessing these data are described at the back of the journal.

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