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

J. Wilson Quail,* John A. Weil and Malvinder P. Singh

Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan, Canada S7N 5C9
Correspondence e-mail: wilson.quail@usask.ca

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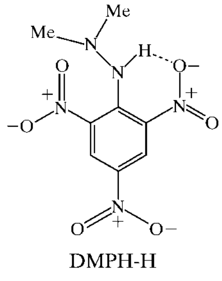
The title molecule (DMPH-H), $C_8H_9N_5O_6$, was investigated to provide comparison with 2,2-diphenyl-1-picrylhydrazine, which unlike DMPH-H is readily oxidizable to form a well known stable free radical (DPPH). The structure shows essential differences in the configuration of the hydrazine-N atoms, 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

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

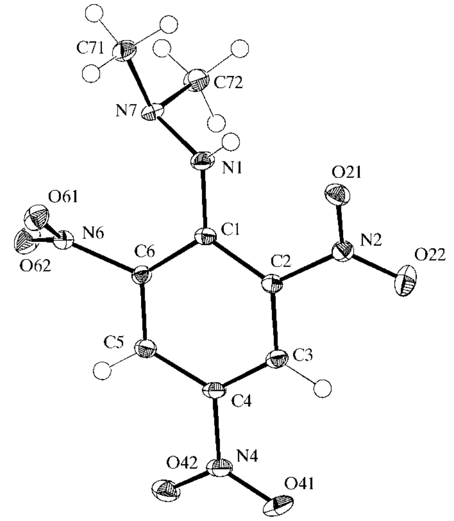


Figure 1
A general *ORTEP*II (Johnson, 1976) view of the title compound with non-hydrogen displacement ellipsoids drawn at the 50% probability level. For clarity, the H atoms are drawn as small spheres of arbitrary size.

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–H_2O (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) ν_{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}; ^{1}H NMR (300 MHz, CDCl$_3$, p.p.m.) δ: 2.59 (s, 6H), 8.30 (bs, 1H), 8.98 (s, exch, 1H), 9.16 (bs, 1H); ^{1}H NMR (300 MHz, DMSO-d_6, p.p.m.) δ: 2.57 (s, 6H), 8.81 (s, 2H), 9.73 (s, exch, 1H); ^{13}C NMR [75 MHz, (CD$_3$)$_2$CO, p.p.m.] δ: 45.3 (q, CH$_3$), 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 $C_8H_9N_5O_6$ 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 NaBH$_3$CN (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% NaHCO$_3$ 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

$C_8H_9N_5O_6$
$M_r = 271.20$
Orthorhombic, $P2_12_12_1$
$a = 6.5156\ (7)$ Å
$b = 8.2006\ (11)$ Å
$c = 20.6704\ (14)$ Å
$V = 1104.5\ (2)$ Å^3
$Z = 4$
$D_x = 1.631$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.40$–$18.54°$
$\mu = 0.141$ mm^{-1}
$T = 123\ (2)$ K
Prism, orange
0.42 × 0.30 × 0.25 mm

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 $I > 2\sigma(I)$

$R_{\rm int} = 0.044$
$\theta_{\max} = 33.48°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 32$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.100$
$S = 1.046$
2479 reflections
175 parameters
H atoms constrained

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

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O21	0.88	2.11	2.6666 (18)	120.1
N1—H1$\cdots$O22$^{\rm i}$	0.88	2.60	3.358 (2)	144.6

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

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: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Xtal*; software used to prepare material for publication: *SHELXL*97.

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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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