

3,5-Bis[(*N,N*-dimethylamino)methyleneamino]-1-methyl-4-nitropyrazole from X-ray powder diffraction data

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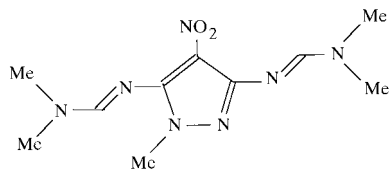
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The structure of the title compound, C₁₀H₁₇N₇O₂, was determined using a bond-restrained Rietveld refinement which gave bond lengths and angles within the expected ranges. Although the two nearly planar (*N,N*-dimethylamino)methyleneamino groups are inclined at approximately 46° to the pyrazole ring, the conformations of the two amino chains are different, owing to either a repulsion effect of the pyrazole-methyl group or a short interatomic contact with the nitro group in one of the chains.

Comment

The molecular structure of the title compound, (I), is shown in Fig. 1. All valence bond lengths and angles are within expected ranges. The whole molecule consists of three nearly planar fragments: a pyrazole ring with a nitro group attached to C1, and two (*N,N*-dimethylamino)methyleneamino groups



(I)

attached to C2 and C5. The planes of the latter groups are inclined to the plane of the pyrazole ring at 45.7 (4) and 47.9 (4)°, respectively. This arrangement may be considered as a consequence of either a repulsion effect caused by the methyl group attached to N3 or a short interatomic contact H23···O7. A possible intramolecular hydrogen bond C12—H23···O7 [H—A = 2.24 (4), D···A = 2.912 (9) Å, D—H···A = 121 (3)°] can explain this short interatomic contact. The interatomic contact H20···O8 might be expected in this molecule as well. However, this is not the case. There are two reasons causing the different conformational features of the

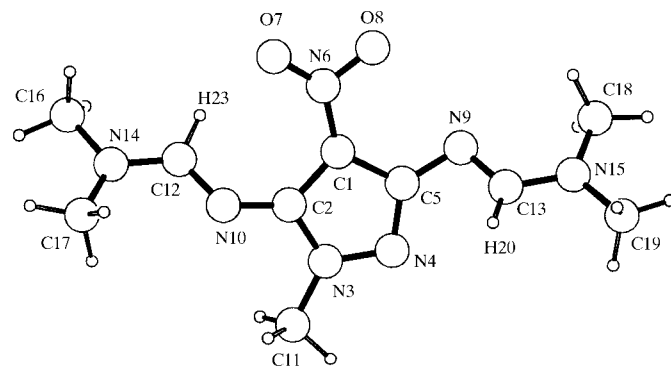


Figure 1
The molecular structure of (I) with the atomic numbering.

two (*N,N*-dimethylamino)methyleneamino groups attached to C5 and C2. Firstly, formation of a short H20···O8 contact would result in strong repulsion between lone pairs of N atoms N9 and N4. Secondly, the appearance of the short intramolecular contact C13—H20···N4 [H—A = 2.27 (4), D···A = 2.62 (1) Å, D—H···A = 98 (2)°] involving the substituent at C5 can play an important role in the different conformation of chemically identical groups.

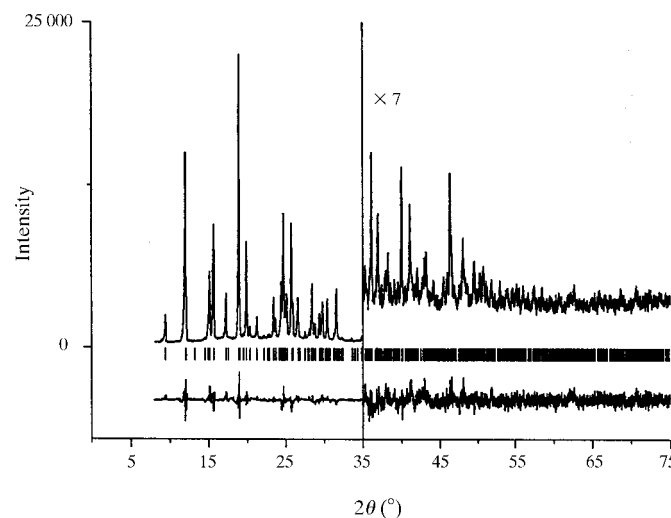


Figure 2
The Rietveld plot for (I), showing the observed and difference profiles. The reflection positions are shown above the difference profile.

Experimental

The title compound was prepared only in polycrystalline form according to Makarov *et al.* (2000).

Crystal data

C₁₀H₁₇N₇O₂
M_r = 267.31
Triclinic, P1̄
a = 9.577 (4) Å
b = 9.972 (4) Å
c = 7.602 (4) Å
α = 106.11 (3)°
β = 95.12 (3)°
γ = 78.22 (3)°
V = 682.4 (6) Å³

Z = 2
D_x = 1.301 Mg m⁻³
Cu Kα radiation
μ = 0.800 mm⁻¹
T = 295 (2) K
Specimen shape: flat sheet
7.0 × 7.0 × 1.5 mm
Particle morphology: needle
Yellow

Data collection

Guinier Johannson camera FR 552 (University of Amsterdam)	$T = 295 (2) \text{ K}$
Specimen mounting: pressed as a thin layer in the specimen holder of the camera	$h = 0 \rightarrow 7$ $k = -7 \rightarrow 7$ $l = -5 \rightarrow 5$ $2\theta_{\min} = 4.00, 2\theta_{\max} = 75.00^\circ$
Specimen mounted in transmission mode	Increment in $2\theta = 0.01^\circ$

Refinement

Refinement on I_{net}	H atoms treated by a mixture of independent and constrained refinement
$R_p = 0.068$	Weighting scheme based on measured s.u.'s
$R_{\text{wp}} = 0.087$	$(\Delta/\sigma)_{\max} = 0.05$
$R_{\text{exp}} = 0.033$	$\Delta\rho_{\max} = 0.5 \text{ e } \text{Å}^{-3}$
$S = 2.67$	$\Delta\rho_{\min} = -0.5 \text{ e } \text{Å}^{-3}$
$2\theta_{\min} = 8, 2\theta_{\max} = 75^\circ$	Preferred orientation correction: March–Dollase (Dollase, 1986)
Increment in $2\theta = 0.01^\circ$	
Excluded region(s): 4.00–7.99	
Profile function: split-type pseudo- Voigt	
149 parameters	

During the exposures, the specimen was spun in its plane to improve particle statistics. From the Guinier photographs, a triclinic unit cell was determined with the indexing program *ITO* (Visser, 1969) and refined with *LSPAID* (Visser, 1986) to $M_{20} = 44$ and $F_{30} = 88$ (0.007, 47) using the first 53 peak positions. The space group $P\bar{1}$ was assumed during the structure determination. Intensities for the structure determination and refinement were collected from the Guinier photographs in 0.01° steps using a Johannson LS18 line scanner. The structure was solved by the grid-search procedure (Chernyshev & Schenk, 1998). The diffraction profile and the difference between the measured and calculated profiles after the final bond-restrained Rietveld refinement are shown in Fig. 2. The strength of the restraints was a function of interatomic separation and for intramolecular bond lengths corresponds to an r.m.s. deviation of 0.03 Å . All non-H atoms were refined isotropically with two overall U_{iso} parameters: one parameter for C1–C11 and another one for C12–

C19. H atoms were placed in geometrically calculated positions and allowed to refine using bond restraints, with a common isotropic displacement parameter U_{iso} fixed at 0.05 Å^2 . The March–Dollase texture formalism (Dollase, 1986) was applied with 511 as a direction of preferred orientation. The texture parameter r refined to 1.19 (1).

Data collection: Johannson LS18 linescanner software; cell refinement: *LSPAID* (Visser *et al.*, 1986); data reduction: *Profit for Windows* (Philips, 1996); program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to refine structure: *MRIA*; molecular graphics: *PLUTON92* (Spek, 1992); software used to prepare material for publication: *MRIA*, *SHELXL93* (Sheldrick, 1993) and *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1291). Services for accessing these data are described at the back of the journal.

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