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Structure of a 1,3-Dicyanoazimine

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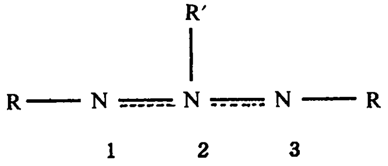
Abstract. (E,Z)-1,3-Dicyano-2-phenylazimine, $C_8H_5N_5$, M_r = 171·1, monoclinic, $P2_1/a$, a = 17·450 (3), b = 6·151 (2), c = 7·871 (1) Å, β = 91·61 (1)°, V = 844·5 (4) Å^3, Z = 4, D_x = 1·346 Mg m^{-3}, λ(Cu $K\alpha_1$) = 1·54050 Å, μ = 0·764 mm^{-1}, F(000) = 352, T = 293 K, final R = 0·048 for 1170 reflexions. The (E,Z)-conformation and a true dipolar system were observed. In the crystal structure, the molecules within a column are held together by the perpendicular stacking and no intermolecular hydrogen bonds or short non-bonded contacts are observed.

Introduction. The 1,3-dipolar azimines, acyclic isomers of triaziridines, have attracted considerable interest in the theoretical characterization of polyaza compounds (Nguyen, Kaneti, Hoesch & Dreiding, 1984).

1,3-Dicyano-2-phenylazimine (I) is the first example which contains an identical substituent (—C≡N) in the 1 and 3 positions. The present paper describes details of the structure analysis of (I) which makes a contribution to the theoretical studies of E–Z isomerization in this class of compound.



(I) R′ = Ph, R = CN

Experimental. Compound (I) was prepared by oxidation of 4,5-diamino-2-phenyl-1,2,3-triazole (Thiele & Schleussner, 1897) using Pb(OAc)$_4$ in CH_2Cl_2. Recrystallization from $C_2H_5OC_2H_5/C_6H_{14}$ gave colorless prisms having m.p. 364–364·5 K. The combustion analysis of this compound was consistent with the structure. Intensity data collected from a crystal of dimensions 0·35 × 0·08 × 0·55 mm.

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}(Å^2)
N(1)	0·9646 (1)	0·2213 (2)	0·7505 (1)	3·94 (4)
N(2)	0·9080 (1)	0·2272 (2)	0·8535 (1)	3·25 (3)
N(3)	0·9197 (1)	0·2425 (2)	1·0168 (1)	3·60 (4)
C(4)	0·9446 (1)	0·2238 (3)	0·5844 (2)	4·79 (5)
N(5)	0·9371 (1)	0·2267 (4)	0·4395 (2)	7·27 (7)
C(6)	0·9942 (1)	0·2612 (2)	1·0629 (2)	3·65 (5)
N(7)	1·0556 (1)	0·2771 (2)	1·1175 (2)	4·84 (5)
C(8)	0·8273 (1)	0·2141 (2)	0·7993 (2)	3·39 (4)
C(9)	0·8026 (1)	0·0330 (3)	0·7115 (2)	4·44 (5)
C(10)	0·7259 (1)	0·0208 (4)	0·6643 (2)	5·34 (6)
C(11)	0·6769 (1)	0·1872 (4)	0·7040 (2)	5·57 (6)
C(12)	0·7035 (1)	0·3662 (4)	0·7911 (2)	5·52 (6)
C(13)	0·7798 (1)	0·3822 (3)	0·8420 (2)	4·45 (5)

Table 2. *Bond lengths* (Å) *and angles* (°)

N(1)—N(2)	1·296 (2)	C(8)—C(9)	1·373 (3)
N(2)—N(3)	1·299 (2)	C(9)—C(10)	1·381 (3)
N(1)—C(4)	1·344 (3)	C(10)—C(11)	1·375 (3)
C(4)—N(5)	1·145 (3)	C(11)—C(12)	1·371 (4)
N(3)—C(6)	1·346 (2)	C(12)—C(13)	1·383 (3)
C(6)—N(7)	1·148 (3)	C(13)—C(8)	1·373 (3)
N(2)—C(8)	1·462 (2)		
N(1)—N(2)—N(3)	121·2 (1)	C(8)—C(9)—C(10)	117·8 (1)
N(2)—N(3)—C(6)	113·4 (1)	C(9)—C(10)—C(11)	120·1 (2)
N(3)—C(6)—N(7)	173·6 (1)	C(10)—C(11)—C(12)	120·5 (2)
N(2)—N(1)—C(4)	115·2 (1)	C(11)—C(12)—C(13)	120·7 (2)
N(1)—C(4)—N(5)	171·4 (2)	C(12)—C(13)—C(8)	117·2 (2)
N(1)—N(2)—C(8)	124·1 (1)	C(13)—C(8)—C(9)	123·4 (1)
N(3)—N(2)—C(8)	114·5 (1)		

D_m not measured. Rigaku AFC5 four-circle diffractometer used with θ–2θ scan method, scan width $(1·3 + 0·41\tan\theta)°$ and scan speed 16° min^{-1}. Lattice parameters obtained from least-squares analysis of 20 reflexions with 2θ values ranging from 54 to 60°. 1550 reflexions scanned within index range h: −19–19, k: 0–6, l: 0–8 up to $(\sin\theta)/\lambda \leq 0·56$ Å^{-1} including 110 equivalent reflexions ($R_{int} = 0·015$), 1253 unique reflexions classified as observed. Three standard reflexions measured every 120 reflexions. Intensities corrected for Lorentz and polarization factors, absorption correction not applied. Structure solved using *SAPI85* (Yao, Zheng, Qian, Han, Gu & Fan, 1985), a version of *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors for non-H atoms. The function minimized was $\sum w[|(|F_o|)^2 - (|F_c|)^2|]^2$ with $w = 1/[\sigma^2(F_o) + 0·02(F_o)^2]$, $\sigma(F_o)$ determined from counting statistics. All H atoms were located from the difference map. Initial thermal parameters were set at the equivalent isotropic thermal parameters of the bonded atoms. Final discrepancy indices, $R = 0·048$, $wR = 0·055$, $S = 1·404$ for 1170 reflexions with $F > \sigma(F)$. Maximum $\Delta/\sigma = 0·07$ in final least-squares cycle. Final difference Fourier map showed no residuals greater than 0·39 e Å^{-3}. All calculations performed using a PANAFACOM computer with the *RCRYSTAN* (Rigaku Corp., Tokyo, Japan) X-ray analysis program. The atomic scattering factors were those from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters for this molecule are listed in Table 1.* The bond lengths and angles are listed in Table 2. Fig. 1 shows the

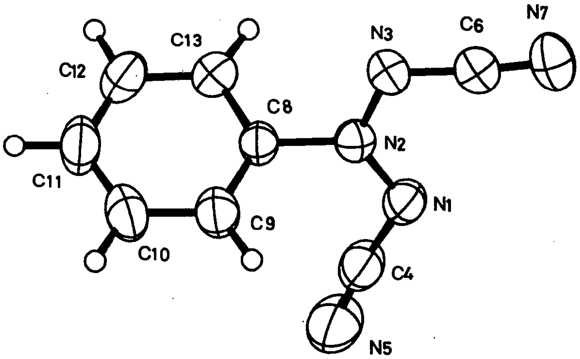

Fig. 1. *ORTEP* (Johnson 1965) drawing. Thermal ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

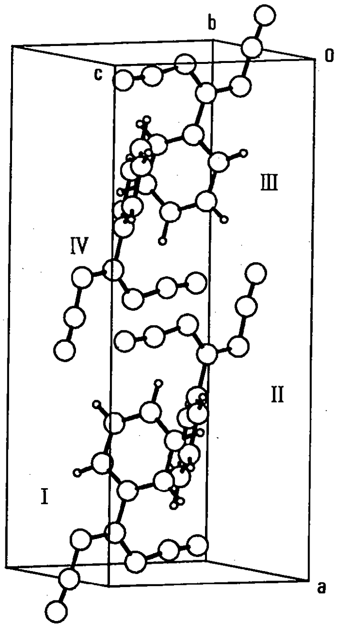

Fig. 2. The crystal structure.

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52495 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ORTEP (Johnson, 1965) drawing of the molecule with atomic labelling. Fig. 2 shows the crystal structure. Fig. 1 clearly indicates the (*E*,*Z*)-conformation. The internal rotation angles of N(1)—N(2)—N(3)—C(6) and N(3)—N(2)—N(1)—C(4) are 2·8 (2) and −174·6 (2)°, respectively.

The N(1)—N(2), N(2)—N(3) distances, 1·296 (2), 1·299 (2) Å respectively, indicate remarkable electron delocalization. A more detailed experiment carried out for (1*E*,2*Z*)- and (1*Z*,2*E*)-2,3-dimethyl-1-phthalimidoazimine (Moor, Grieb, Niggli, Hoesch & Dreiding, 1979) indicates 1·301 (10), 1·332 (6) Å for N(1)—N(2) and 1·268 (9), 1·263 (5) Å for N(2)—N(3) distances, respectively. The differences of 0·03 and 0·06 Å between the N(1)—N(2) and N(2)—N(3) distances, respectively, are caused by the steric and electronic effects of the phthalimido moiety connected to N(1). In the case of (I) the azimine moiety, having identical substituents connected to N(1) and N(2) whose bond lengths suggest the N=N character, exhibits a higher 1,3-dipolar contribution (Moor *et al.*, 1979). The phenyl ring is twisted about the N(2)—C(8) bond to reduce the steric hindrance between C(4) and H(9); the non-bonded separation is 2·7 (2) Å. The dihedral angle between the phenyl ring and the azimine plane is 58·1 (2)°.

In the crystal structure the molecules within a column are held together by the perpendicular stacking. Intermolecular hydrogen bonds and unusual short non-bonded contacts are not observed.

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Structure of 1-Hydroxy-10-isopropyl-7-methyl-*cis*-bicyclo[4.4.0]decan-3-one*

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Abstract. $C_{14}H_{24}O_2$, $M_r = 224·3$, monoclinic, $P2_1$, $a = 7·400$ (1), $b = 15·967$ (2), $c = 11·755$ (2) Å, $\beta = 105·79$ (1)°, $V = 1336·5$ (2) Å^3, $Z = 4$, D_m (flotation in KBr solution) = 1·12, $D_x = 1·11$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·79$ cm^{-1}, $F(000) = 496$, $T = 293$ K, $R = 0·049$ for 1749 observed reflections. The structure has a non-steroid *cis* conformation with its decalin ring in double-chair form. The structure is stabilized by two intermolecular O—H···O hydrogen bonds [2·956 (4) and 2·933 (4) Å].

Introduction. The sesquiterpene lactone 'qinghaosu' or artimisinin is an antimalarial drug. In an attempt to synthesize totally this key product the title compound was synthesized (Salunke, Phadke & Kulkarni, 1988). X-ray structure determination was essential to establish uniquely the stereochemistry of this key intermediate.

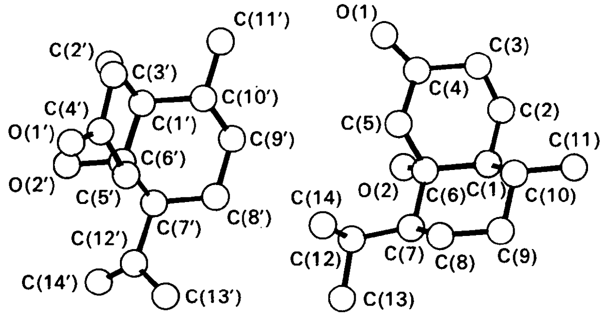

Fig. 1. *PLUTO* diagram (Motherwell & Clegg, 1978) of the molecule showing the atomic numbering scheme.

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