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### 3-Diazoindazole

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**Abstract.** C<sub>7</sub>H<sub>4</sub>N<sub>4</sub>, FW 144.1, monoclinic, space group *P2<sub>1</sub>/n*, *a* = 6.070 (1), *b* = 13.140 (1), *c* = 8.173 (1) Å,  $\beta = 97.10(2)^\circ$ , *V* = 646.9 Å<sup>3</sup>, *D<sub>m</sub>* = 1.50 (2) (floatation), *D<sub>x</sub>* = 1.480 g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 8.316 \text{ cm}^{-1}$ , *Z* = 4, at 20 (1)°C. The distances in the group >C–N–N were found to be 1.338 (3) Å for >C–N and 1.110 (3) Å for N–N, thus suggesting the carbanionic character >C<sup>⊖</sup>–N<sup>⊕</sup>≡N:. Essentially planar molecules are packed nearly parallel to the *ac* plane.

**Introduction.** 3-Diazoindazole (hereinafter DIN) was prepared according to the procedure described by Bamberger (1899). Transparent pale-yellow needles elongated along *a* were crystallized from *n*-heptane. The systematically absent reflexions (*Ok0*: *k* = 2*n* + 1 and *h0l*: *h* + *l* = 2*n* + 1) on Weissenberg photographs and the centric distribution of  $|E|$  values ( $\langle E^2 \rangle = 1.000$ ;  $\langle |E^2 - 1| \rangle = 0.996$ ;  $\langle |E| \rangle = 0.795$ ) indicate space group *P2<sub>1</sub>/n* (No. 14). Unit-cell dimensions were obtained from a least-squares fit of the  $2\theta$  values of 30 reflexions measured on a CAD-4 diffractometer [Cu *K*<sub>α</sub> radiation,  $\lambda = 1.54051$  Å, *t* = 20 (1)°C]. A single crystal with approximate dimensions 0.2 × 0.2 × 0.5 mm was used for data collection on an automatic computer-controlled Enraf–Nonius CAD-4 four-circle diffractometer with Ni-filtered Cu *K*<sub>α</sub> radiation. Reflexions were scanned in the  $\omega$ – $2\theta$  mode (moving crystal–moving counter) with a variable scan rate. Details of data collection and reduction are shown in Table 1. The compound is sensitive to light and the crystal decayed

in the X-ray beam during the data collection. The data were corrected for variation in reference reflexions and Lorentz–polarization effects. No absorption corrections were made.

The structure was solved by direct methods with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). An *E* map with the highest combined figure of merit CFOM (3.000) obtained with the unit weighting of ABSFOM (1.137),  $\psi_0(322)$  and RESID (16.78), computed with 200 phases ( $|E| > 1.40$ ), revealed the positions of all the heavy atoms. The

Table 1. *Data collection summary for DIN*

Temperature (°C)	20 (1)
Diffractometer	CAD-4, automatic, four-circle
Radiation	Cu <i>K</i> <sub>α</sub> (Ni-filtered) ( $\lambda = 1.5418$ Å)
Scan method	$\omega$ – $2\theta$
$2\theta$ scan width (°)	0.6 + 0.2 tan $\theta$
Scan rate (° min <sup>-1</sup> )	Minimum: 1.3; maximum: 20.1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{\text{max}}$ (°)	150
Maximum scan time (s)	45
Aperture (mm)	2.5 + 0.9 tan $\theta$
Reference reflexions	121, 131, 141
Intensity decrease (%)	24.2
Measured reflexions	3560
Averaged reflexions	1328
Mean discrepancy on <i>I</i> (%)	3.1 for 3380 reflexions
Observed reflexions	783
Unobserved reflexions	545 [ $I < 3\sigma(I)$ ]
$\sigma(I)$ base	Counting statistics
Linear absorption coefficient (cm <sup>-1</sup> )	8.316 for Cu <i>K</i> <sub>α</sub>

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Table 2. *Refinement summary*

Final refinement cycle	
Scale factor ( $k$ )	0.735
$R = \sum  \Delta F  / \sum  F_o $	0.040
$R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$	0.049
Average shift/error	0.031
Maximum shift/error	0.176
Data( $m$ )-to-variable( $n$ ) ratio	9.40
$[\sum w(\Delta F)^2 / (m - n)]^{1/2}$	0.439
Final difference map	
Maximum $\Delta\rho$ (e Å <sup>-3</sup> )	0.20

Table 3. *Final fractional coordinates* ( $\times 10^4$ ; for H  $\times 10^3$ ) *with standard deviations in parentheses*

	$x$	$y$	$z$
N(1)	2114 (3)	4267 (2)	7239 (2)
N(2)	3544 (3)	4234 (2)	8578 (2)
N(3)	7323 (3)	3858 (2)	9252 (2)
N(4)	8810 (4)	3833 (1)	10190 (3)
C(3)	5528 (3)	3895 (2)	8125 (2)
C(3a)	5378 (3)	3698 (2)	6410 (2)
C(4)	6779 (4)	3371 (2)	5285 (3)
C(5)	5895 (4)	3323 (2)	3656 (3)
C(6)	3703 (4)	3613 (2)	3132 (3)
C(7)	2307 (4)	3932 (2)	4230 (3)
C(7a)	3167 (3)	3963 (2)	5903 (2)
H(4)	824 (5)	319 (2)	566 (3)
H(5)	684 (5)	308 (2)	284 (4)
H(6)	316 (5)	360 (2)	199 (3)
H(7)	76 (5)	417 (2)	385 (3)

structure refinement was by full-matrix least squares, minimizing the function  $\sum w(F_o - kF_c)^2$ , where the weighting function was determined empirically:  $w = w_F w_S$ , where  $w_F (|F_o| < 2.5) = (|F_o|/2.5)^2$ ,  $w_F (|F_o| > 14.0) = (14.0/|F_o|)^3$ ,  $w_F (2.5 < |F_o| < 14.0) = 1.0$ ; and  $w_S (\sin \theta < 0.5) = (\sin \theta/0.5)^{2.5}$ ,  $w_S (\sin \theta > 0.9) = (0.9/\sin \theta)$ ,  $w_S (0.5 < \sin \theta < 0.9) = 1.0$ . All the H atoms were located in a difference Fourier map. They were included in the refinement with isotropic temperature factors. A final difference electron density map was featureless. Final refinement parameters are given in Table 2. Atomic scattering factors for H were those of Stewart, Davidson & Simpson (1965) and for other atoms those of Cromer & Mann (1968). All calculations were carried out on the CDC Cyber 72 computer at RRC Ljubljana. The XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used.

The final atomic coordinates are in Table 3.\*

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32969 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

**Discussion.** The X-ray structure determination of DIN was undertaken because there is little information on bond distances in heterocyclic diazo compounds. Recently, the crystal structures of two diazocarbonyl compounds (5-diazo-6-methoxy-6-hydroxuracil and 2'-deoxy-5-diazo-6-hydro-*O*<sup>6</sup>,5'-cyclouridine hemihydrate) have been determined (Abraham, Cochran & Rosenstein, 1971). The C—N bond distances in the  $>C-N-N$  group (1.332 and 1.308 Å) were found to be intermediate between a double and a single bond and significantly shorter than the corresponding average C—N bond length [1.40 (2) Å] found in aromatic diazonium compounds (Abraham, Cochran & Rosenstein, 1971, and references therein). However, these distances are close to the values of aliphatic diazo compounds: 1.32 Å in diazomethane (Cox, Thomas & Sheriden, 1958) and 1.313 (2) Å in 1,4-bis(diazo)-2,3-butanedione (Hope & Black, 1972). The N—N distances of the diazo groups in the two compounds were found to be 1.113 and 1.120 Å respectively. These results suggested a 'carbanionic' dipolar character,  $>C^{\ominus}-N^{\oplus}\equiv N:$ , rather than  $\text{>C}-N^{\oplus}\equiv N:$  or  $\text{>C}-N^{\oplus}=\text{N}^{\ominus}:$ .

Fig. 1 shows a molecule of DIN together with the values of the interatomic bond lengths. Bond distances and angles with estimated standard deviations are given in Table 4. The distances C(3)—N(3) [1.338 (3) Å] and N(3)—N(4) [1.110 (3) Å] observed in DIN also demonstrate the substantial 'carbanionic' character of the group  $>C(3)-N(3)-N(4)$ . All the other bond lengths are intermediate between double and single bonds, thus indicating the presence of considerable conjugation in this heterocyclic compound.

The indazole part of DIN is planar, and is described by the equation:  $0.3022X + 0.9441Y - 0.1678Z = 4.7096$  Å, where  $X = ax \sin \beta$ ,  $Y = by$  and  $Z = ax \cos \beta + cz$ . The largest deviations from the least-squares plane are  $-0.021$ ,  $0.023$ ,  $0.022$  and  $-0.022$  Å for N(1), C(3), C(6) and C(7a) respectively, whereas the displacements for N(3) and N(4) are 0.151 and 0.264 Å. The separate six- and five-membered rings are

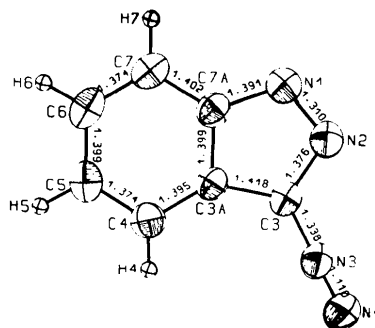


Fig. 1. A molecule of DIN viewed along the normal to the mean plane. The atoms are represented by thermal ellipsoids drawn at the 50% probability level (Johnson, 1965).

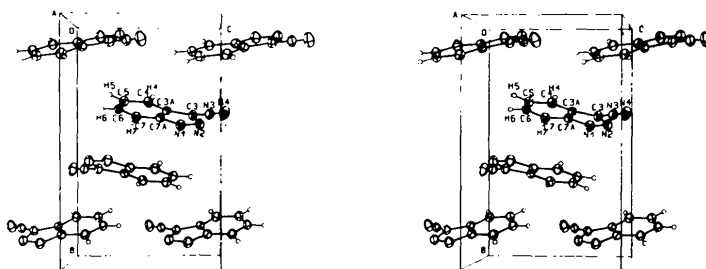


Fig. 2. A stereoscopic view of the unit cell along [100].

Table 4. Bond distances (Å) and bond angles (°)

N(1)—N(2)	1.310 (3)	C(3a)—C(4)	1.395 (3)
N(1)—C(7a)	1.391 (3)	C(3a)—C(7a)	1.399 (3)
N(2)—C(3)	1.376 (3)	C(4)—C(5)	1.374 (3)
N(3)—N(4)	1.110 (3)	C(5)—C(6)	1.399 (3)
C(3)—N(3)	1.338 (3)	C(6)—C(7)	1.374 (3)
C(3)—C(3a)	1.418 (3)	C(7)—C(7a)	1.402 (3)
C(4)—H(4)	0.93 (3)	C(6)—H(6)	0.95 (3)
C(5)—H(5)	0.98 (3)	C(7)—H(7)	1.00 (3)
N(2)—N(1)—C(7a)	108.9 (2)	C(4)—C(3a)—C(7a)	121.5 (2)
N(1)—N(2)—C(3)	107.3 (2)	C(3a)—C(4)—C(5)	117.1 (2)
N(4)—N(3)—C(3)	179.6 (2)	C(4)—C(5)—C(6)	121.8 (2)
N(2)—C(3)—N(3)	119.5 (2)	C(5)—C(6)—C(7)	121.6 (2)
N(2)—C(3)—C(3a)	111.9 (2)	C(6)—C(7)—C(7a)	117.4 (2)
N(3)—C(3)—C(3a)	128.4 (2)	N(1)—C(7a)—C(3a)	110.9 (2)
C(3)—C(3a)—C(4)	137.6 (2)	N(1)—C(7a)—C(7)	128.5 (2)
C(3)—C(3a)—C(7a)	100.9 (2)	C(3a)—C(7a)—C(7)	120.6 (2)

planar to within 0.011 Å and the dihedral angle between the two rings is 2.0°. These effects are presumably due to molecular packing.

A stereoview of the molecular packing is given in Fig. 2. The molecules are arranged in layers nearly parallel to the *ac* plane, the interlayer separation being approximately 3.4 Å; the molecules are held together by van der Waals forces.

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## 1-*p*-Tolyl-4-(β-D-erythrofuransyl)imidazoline-2-thione

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**Abstract.**  $\text{SN}_2\text{O}_3\text{C}_{14}\text{H}_{16}$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 26.215$  (14),  $b = 7.608$  (5),  $c = 7.142$  (4) Å;  $Z = 4$ ;  $D_c = 1.36$ ,  $D_m = 1.37$  g cm<sup>-3</sup>. The structure was solved by direct methods and refined by full-matrix

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least-squares procedures to a final  $R$  of 0.040. The sugar-ring puckering has the twist conformation  ${}_3T$ . The molecules are linked by hydrogen bonds and van der Waals forces.