

Table 3. *Hydrogen bonds and interatomic contacts (Å) less than 3.4 Å, and hydrogen bond angles (°)*

O(1)···O(2)	2.81 (2)	O(2)···O(1)	2.81 (2)
···N(31)	3.12 (2)	···O(3)	2.80 (4)
···N(32) ^{vi}	2.86 (2)	···O(1) ^{vi}	2.81 (2)
···N(12) ^v	3.19 (2)	···O(3) ^{vi}	2.80 (4)
N(12)—H(3)···O(1) 141.3 (6)			
O(3)···O(4)	2.84 (5)	O(4)···O(3)	2.84 (5)
···O(4) ^{iv}	2.74 (5)	···O(3) ^{iv}	2.74 (5)
···O(2)	2.80 (4)	···O(4) ^{iv}	2.77 (6)
···N(21) ⁱⁱⁱ	3.06 (3)	···N(31)	3.14 (4)
N(21)—H(5)···O(3) 157 (1)			

Symmetry code: (i) $x, 1.5 - y, 0.5 - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $0.5 - x, 1 - y, 1 + z$; (iv) $x, 0.5 - y, 1.5 - z$; (v) $x, 1.5 - y, 1.5 - z$.

molecule implies generally a rearrangement in the energy E_w of the water molecules set according to $E_w = (e_1 + H_{12}K_2)K_1 + [e_2 + H_{12}^{vi}K_1 + (H_{23} + H_{23}^{vi})K_3]K_2 + [e_3 + (H_{34} + H_{34}^{iv})K_4]K_3 + (e_4 + H_{43}^{iv}K_3 + H_{44}^{iv}K_4)K_4$ where: H_{ij} are the contributions to E_i arising from the HB's between i and j water molecules and e_i are the remaining parts of E_i . In this expression the K_i coefficients are coupled, affecting with their mutual influence both the single molecule energy and the global energy E_w . By making the approximation that $-E_w$ corresponds to the dehydration energy, employing the occupation coefficients of Table 1, and deriving from the E_i quantities the e_i and H_{ij} values, one obtains $-E_w = 284 \text{ J g}^{-1}$ which is in very good agreement with the experimental value of 279 J g^{-1} . This last computation supports the accuracy of the crystallographic work and the efficiency of the computational model (Ori, 1987).

On the basis of the known crystal structure of $\text{Ni(en)}_2\text{Ni(CN)}_4$ (Černák, Chomič, Baloghová & Dunaj-Jurčo, 1988) and the results obtained in this

work we may draw the conclusion that two different kinds of chains are formed in the synthesis under equivalent experimental conditions and the solvating water molecules are likely to play an important part in the stabilization of one type of chain.

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Azoles. 28. Structure of the Molecular Complex of 3,5-Dinitroindazole with Pyrrolidine (1/1)

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Abstract. 3,5-Dinitro-1*H*-indazole-pyrrolidine (1/1), $(\text{C}_7\text{H}_4\text{N}_4\text{O}_4 \cdot \text{C}_4\text{H}_9\text{N})_2$, $M_r = 558.51$, monoclinic,

$P2_1/n$, $a = 19.917 (3)$, $b = 9.751 (1)$, $c = 6.703 (1) \text{ \AA}$, $\beta = 90.90 (1)^\circ$, $V = 1301.6 (3) \text{ \AA}^3$, $Z = 2$, $D_m = 1.42 (1)$, $D_x = 1.425 \text{ Mg m}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54178 \text{ \AA}$, $\mu = 0.846 \text{ mm}^{-1}$, $F(000) = 584$, room

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2)

	$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$			U_{eq}
	x	y	z	
N(1)	-0.0532 (2)	0.2895 (3)	0.3530 (5)	0.073 (1)
N(2)	0.0135 (1)	0.2767 (3)	0.3310 (5)	0.068 (1)
C(3)	0.0268 (2)	0.1472 (4)	0.2828 (5)	0.057 (1)
C(4)	-0.0478 (2)	-0.0706 (4)	0.2344 (5)	0.059 (1)
C(5)	-0.1148 (2)	-0.1030 (4)	0.2423 (5)	0.063 (1)
C(6)	-0.1656 (2)	-0.0058 (6)	0.2829 (6)	0.071 (2)
C(7)	-0.1496 (2)	0.1259 (5)	0.3197 (6)	0.074 (2)
C(8)	-0.0812 (2)	0.1636 (4)	0.3160 (5)	0.063 (1)
C(9)	-0.0316 (2)	0.0660 (4)	0.2710 (5)	0.054 (1)
N(10)	0.0945 (1)	0.1049 (4)	0.2539 (5)	0.066 (1)
O(11)	0.1045 (1)	-0.0176 (3)	0.2205 (4)	0.077 (1)
O(12)	0.1395 (1)	0.1910 (3)	0.2657 (5)	0.088 (1)
N(13)	-0.1343 (2)	-0.2459 (4)	0.2104 (5)	0.085 (2)
O(14)	-0.0901 (2)	-0.3321 (3)	0.1926 (6)	0.106 (2)
O(15)	-0.1947 (2)	-0.2740 (3)	0.2038 (5)	0.111 (2)
N(16)	0.1016 (2)	0.5150 (4)	0.3731 (6)	0.069 (1)
C(17)	0.1757 (2)	0.4985 (5)	0.4056 (7)	0.082 (2)
C(18)	0.2045 (3)	0.5340 (9)	0.218 (1)	0.147 (4)
C(19)	0.1597 (4)	0.6215 (6)	0.1098 (9)	0.134 (3)
C(20)	0.0915 (2)	0.5864 (5)	0.1763 (7)	0.097 (2)

Table 2. Bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

N(1)—N(2)	1.345 (4)	C(8)—C(9)	1.408 (5)
N(1)—C(8)	1.370 (4)	N(10)—O(11)	1.232 (4)
N(2)—C(3)	1.331 (4)	N(10)—O(12)	1.229 (4)
C(3)—C(9)	1.409 (5)	N(13)—O(14)	1.224 (4)
C(3)—N(10)	1.426 (4)	N(13)—O(15)	1.234 (4)
C(4)—C(5)	1.373 (5)	N(16)—C(17)	1.496 (5)
C(4)—C(9)	1.392 (5)	N(16)—C(20)	1.501 (5)
C(5)—C(6)	1.416 (6)	C(17)—C(18)	1.433 (7)
C(5)—N(13)	1.460 (5)	C(18)—C(19)	1.424 (8)
C(6)—C(7)	1.345 (6)	C(19)—C(20)	1.476 (7)
C(7)—C(8)	1.412 (5)		
N(2)—N(1)—C(8)	107.2 (3)	C(3)—C(9)—C(8)	101.0 (3)
N(1)—N(2)—C(3)	108.4 (3)	C(4)—C(9)—C(8)	121.5 (3)
N(2)—C(3)—C(9)	112.3 (3)	C(3)—N(10)—O(11)	117.4 (3)
N(2)—C(3)—N(10)	120.0 (3)	C(3)—N(10)—O(12)	118.9 (4)
C(9)—C(3)—N(10)	127.7 (4)	O(11)—N(10)—O(12)	123.7 (3)
C(5)—C(4)—C(9)	115.9 (4)	C(5)—N(13)—O(14)	118.6 (4)
C(4)—C(5)—C(6)	123.5 (4)	C(5)—N(13)—O(15)	118.3 (4)
C(4)—C(5)—N(13)	118.0 (4)	O(14)—N(13)—O(15)	123.0 (4)
C(6)—C(5)—N(13)	118.6 (4)	C(17)—N(16)—C(20)	107.2 (3)
C(5)—C(6)—C(7)	120.4 (4)	N(16)—C(17)—C(18)	104.7 (4)
C(6)—C(7)—C(8)	118.1 (4)	C(17)—C(18)—C(19)	109.6 (5)
N(1)—C(8)—C(9)	111.1 (3)	C(18)—C(19)—C(20)	106.3 (4)
C(7)—C(8)—C(9)	120.7 (4)	N(16)—C(20)—C(19)	105.2 (4)

temperature, final $R = 0.055$ for 1348 reflections. The molecular complex consists of two molecules of 3,5-dinitroindazole and two molecules of pyrrolidine linked by hydrogen bonds, and lying on a centre of symmetry. The molecules in the complex are in ionized forms. The pyrrolidine molecule forms an ammonium cation as a result of the incorporation of one proton from the pyrrole N atom of the indazole molecule. The indazole system is approximately planar. The pyrrolidine ring makes a dihedral angle with it of about 74° .

Introduction. In a previous paper (Gzella, Wrzeczono & Borowiak, 1989) we reported the structure of the 2/1 molecular complex of 3,5-dinitroindazole with morpholine, obtained as a by-product in the reaction of 2,5-dinitroindazole with morpholine (Wrzeczono & Linkowska, 1980). The compound examined in this paper was prepared by treating 2,5-dinitroindazole with pyrrolidine according to the same method.

Experimental. Yellow prismatic crystals recrystallized from methanol, m.p. 491–492 K, D_m by flotation, crystal dimensions $0.5 \times 0.3 \times 0.2$ mm; Syntex $P2_1$ diffractometer, graphite-monochromated $\text{Cu K}\alpha$ radiation, lattice parameters from setting angles of 15 reflections with $18^\circ \leq 2\theta \leq 30^\circ$, $\theta-2\theta$ scan mode, $2\theta \leq 115^\circ$, two standard reflections monitored every 100 reflections, variation $< 2\%$, 2210 reflections measured, 1830 unique reflections, $R_{int} = 0.040$, range of hkl : $h - 20$ to 20 , $k 0$ to 10 , $l 0$ to 7 , profile analysis according to Lehmann & Larsen (1974), no absorption correction, 1348 reflections with $I \geq 1.96\sigma(I)$ considered observed and used in the refinement. Structure solved by direct methods using

SHELX76 (Sheldrick, 1976). Refinement on F by full-matrix least-squares method. 202 refined parameters, five H atoms – three of the indazole molecule and two at N(16) of pyrrolidine – found from ΔF map and refined with isotropic temperature parameters, the other ones generated from assumed geometries and included as a fixed isotropic contribution to F_c , $w^{-1} = \sigma^2(F)$, empirical isotropic extinction parameter x [$F_c' = F_c(1 - 0.0001x F_c^2/\sin\theta)$], x converged to 0.015 (1); final $R = 0.055$ and $wR = 0.057$, $(\Delta/\sigma) = 0.04$, $S = 5.0644$, max. and min. heights in the final ΔF map 0.35 and -0.30 e \AA^{-3} . Computer programs: *SHELX76* (Sheldrick, 1976), and local programs (Jaskólski, 1982); molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1976). Atomic scattering factors were taken from Sheldrick's programs.

Discussion. Atomic coordinates, and bond lengths and angles are given in Tables 1 and 2* respectively. The numbering system is given in Fig. 1. A stereoview of the molecular complex is shown in Fig. 2.

The complex consists of two molecules of 3,5-dinitroindazole and two molecules of pyrrolidine connected by hydrogen bonds, the geometries of which are as follows: N(1)···N(16ⁱ) 2.827 (5), N(1)---H(161ⁱ) 1.76 (4) \AA , N(1)---H(161ⁱ)—N(16ⁱ) 172(3) $^\circ$, N(2)···N(16) 2.923 (5), N(2)---H(162)

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52939 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1.98 (4) Å, N(2)---H(162)—N(16) 166 (3)° [symmetry code: (i) $-x, 1-y, 1-z$].

The complex lies in the centre of symmetry. The pyrrolidine molecule forms an ammonium cation, a proton from the pyrrole N atom, N(1), being

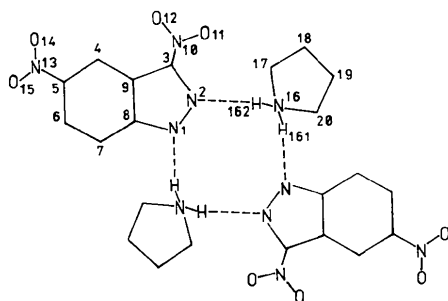


Fig. 1. Labelling scheme.

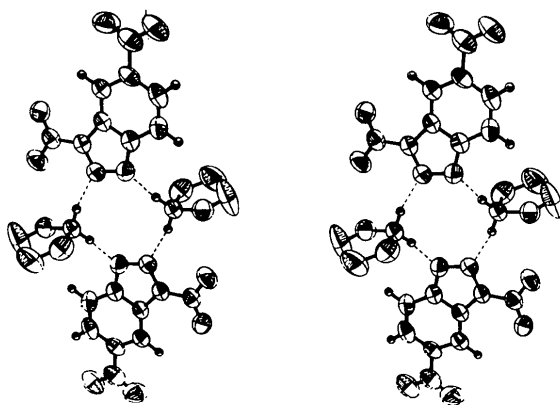


Fig. 2. Stereodrawing of the molecule.

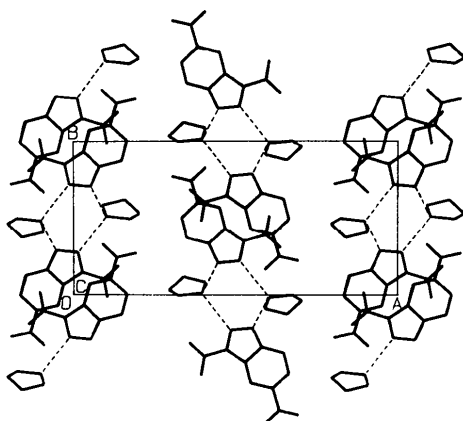


Fig. 3. Projection of the crystal structure along the *c* axis.

transferred to the N(16) atom. The N—H bonds are N(16)—H(16) 0.97 (4) and N(16)—H(162) 1.07 (4) Å. The indazole system is planar and forms a dihedral angle with the pyrrolidine molecule of about 74°.

The values of bond lengths and angles for the indazole system are similar to those observed for 3,5-dinitroindazole (molecule *A*) in its 2/1 molecular complex with morpholine (Gzella, Wrzeciono & Borowiak, 1989). The —NO₂ group at the C(5) atom forms a dihedral angle of 6.4 (2)° with the plane of the indazole system. The exocyclic bond C(3)—N(10) [1.426 (4) Å] is significantly shorter than the C(5)—N(13) bond, 1.460 (5) Å, which is consistent with those observed in other nitro compounds, *i.e.* *p*-dinitrobenzene [1.478 (2) Å (di Rienzo, Domenicano & Riva di Sanseverino, 1980)], *p*-nitrobenzamide [1.468 (2) Å (di Rienzo, Domenicano & Foresti-Serantoni, 1977)] and *p*-nitrobenzoic acid [1.476 (2) Å (Colapietro & Domenicano, 1977)]. The shortening is due to some resonance in the nitropyrazole part of 3,5-dinitroindazole.

The C atoms in the pyrrolidine ring have high anisotropic temperature coefficients, particularly C(18) and C(19) (see Table 1). This indicates disorder resulting from some ring motion. As a consequence, the C—C distances (Table 2) observed in the pyrrolidine ring are scarcely reliable, but appear shorter than standard values for C_{sp}³—C_{sp}³ single-bond distances.

The molecular packing in the unit cell is given in Fig. 3.

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