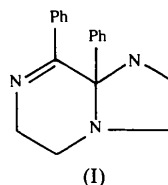


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sedatives. However, crystal structure analyses of only a few derivatives have been carried out (Lumma & Springer, 1981).

The title compound, (I), was synthesized for the first time in good yield by the reaction of 3-aza-1,5-diaminopentane with benzil in the presence of HgCl₂ under refluxing conditions in methanol (Parihar, 1993).



An *ORTEP* (Johnson, 1965) diagram of the molecule is shown in Fig. 1. The molecule consists of a nine-membered fused bicyclic ring system containing five- and six-membered heterocycles which are joined at C(6) and N(2). C(6) is a chiral centre with typical tetrahedral bond angles. The geometry about N(2) is distorted tetrahedral. The values of the N(2)—C(4)—C(5), C(4)—C(5)—N(3), C(5)—N(3)—C(6), N(3)—C(6)—N(2) and C(6)—N(2)—C(4) bond angles are typical of a strained saturated five-membered ring system.

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An Imidazo[1,2-*a*]pyrazine Derivative, C₁₈H₁₉N₃

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Abstract

Interaction of benzil in methanol with 3-aza-1,5-diaminopentane in the presence of HgCl₂ yields the title compound, 1,2,3,5,6,8a-hexahydro-8,8a-diphenylimidazo[1,2-*a*]pyrazine. The molecule consists of a bicyclic system containing five- and six-membered heterocycles which are joined at C(6) and N(2). C(6) is a chiral centre and N(2) has distorted tetrahedral geometry around it. The molecule is puckered at the C(6)—N(2) bond.

Comment

The first derivative of imidazo[1,2-*a*]pyrazine, a bicyclic system, was reported in 1957 as a perchlorate salt in low yields (Martin & Tarasiejska, 1957). More recently, several derivatives of imidazo[1,2-*a*]pyrazine have been reported (Bradac *et al.*, 1977; Abignente *et al.*, 1981; Bonnet, Sablayrallis & Chapat, 1984; Katsunori, Minoru, Tetsuya & Toshio, 1992). These derivatives have been attracting increasing attention (Lumma, 1980; Lumma *et al.*, 1983; Sablayrallis, Bonnet, Cros, Chapat & Bouchard, 1988; Zaitsev, Glushkov, Mashkovskii & Andreova, 1989) because of their interesting structural features, as well as a wide range of applications, *e.g.* as antispasmodics, uterine relaxants, bronchodilators and

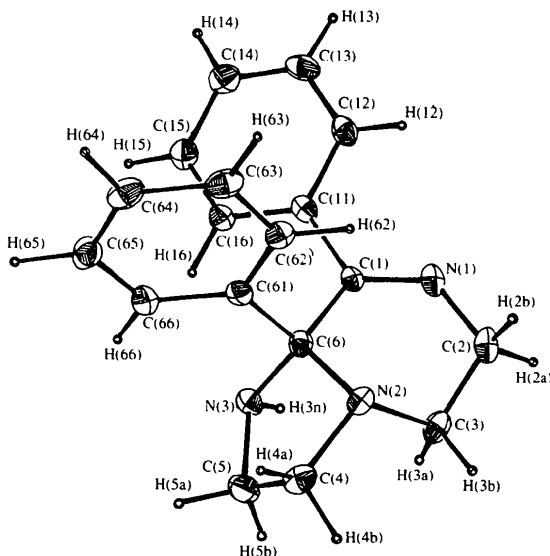


Fig. 1. View of the molecule with displacement ellipsoids drawn at the 50% probability level and H atoms as small spheres of arbitrary size.

The C(1)—N(1) bond distance of 1.274 (4) Å is comparable to the reported value of C=N (1.307 Å) in 3-(1-hydroxyethyl)imidazo[1,2-*a*]pyrazine (Lumma & Springer, 1981). The average bond distance of C(2)—N(1), C(3)—N(2), C(4)—N(2), C(6)—N(2), C(6)—N(3) and C(5)—N(3) is 1.474 (4) Å, which is very

close to that reported for C—N single bonds in 2,2',2''-tris(salicyclideneimine)triethylamine (Gündüz *et al.*, 1985).

The dihedral angle between the C(1)—N(1)—C(2)—C(3)—N(2)—C(6) and N(2)—C(4)—C(5)—N(3)—C(6) planes is 56.23(17)°, indicating that the molecule is puckered at the line joining C(6) and N(2). The puckering may be due to the attachment of the bulky groups at C(6) and C(1).

Experimental

Benzil (0.02 mol) in 10 ml of methanol was added to a methanolic solution of HgCl₂ (0.01 mol) in 15 ml of methanol. A solution of 3-aza-1,5-diaminopentane (0.02 mol in 10 ml of methanol) was added with stirring. The mixture was refluxed for 4 h. Excess solvent was removed by distillation and when the volume of the yellow solution was reduced to one third, 20 ml of CH₃CN was added to this solution. On keeping this solution for a few days, a crystalline product separated out, which was further purified by recrystallization from DMSO to yield colourless fine crystals of 1,2,3,5,6,8a-hexahydro-8,8a-diphenylimidazo[1,2-*a*]pyrazine, which were characterized by elemental and spectroscopic analyses. Yield 60%; m.p. 434 K.

Crystal data

C₁₈H₁₉N₃
 $M_r = 277.37$
 Monoclinic
 $P2_1/n$
 $a = 9.452(6) \text{ \AA}$
 $b = 14.330(16) \text{ \AA}$
 $c = 11.826(4) \text{ \AA}$
 $\beta = 112.98(4)^\circ$
 $V = 1474.7 \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.249 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 2-25^\circ$
 $\mu = 0.070 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Plate
 $0.2 \times 0.1 \times 0.1 \text{ mm}$
 Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2853 measured reflections
 2696 independent reflections
 1269 observed reflections
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.093$
 $\theta_{\text{max}} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 17$
 $l = -14 \rightarrow 14$
 2 standard reflections
 frequency: 30 min
 intensity decay: none

Refinement

Refinement on F
 $R = 0.048$
 $wR = 0.050$
 $S = 0.51$
 1269 reflections
 266 parameters
 All H-atom parameters refined

$w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\text{max}} = 0.33$
 $\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *SDP-Plus* (Enraf-Nonius, 1983)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
N(1)	0.1077 (3)	0.0422 (2)	0.6721 (2)	3.68 (7)
N(2)	-0.0594 (3)	-0.0984 (2)	0.7374 (2)	3.26 (6)
N(3)	-0.2540 (3)	-0.0507 (2)	0.5473 (2)	3.20 (6)
C(1)	-0.0342 (3)	0.0557 (2)	0.6484 (2)	2.92 (7)
C(2)	0.1760 (3)	-0.0483 (3)	0.7229 (3)	4.38 (9)
C(3)	0.0617 (4)	-0.1266 (3)	0.6964 (3)	3.97 (8)
C(4)	-0.1827 (4)	-0.1682 (3)	0.7038 (3)	4.18 (8)
C(5)	-0.2883 (4)	-0.1482 (3)	0.5697 (3)	4.35 (9)
C(6)	-0.1431 (3)	-0.0160 (2)	0.6673 (2)	2.72 (7)
C(11)	-0.0951 (3)	0.1509 (2)	0.6042 (2)	2.97 (7)
C(12)	0.0020 (3)	0.2276 (3)	0.6421 (3)	3.82 (8)
C(13)	-0.0509 (4)	0.3157 (3)	0.6022 (3)	4.59 (9)
C(14)	-0.2004 (4)	0.3304 (3)	0.5227 (3)	4.60 (9)
C(15)	-0.2981 (4)	0.2558 (2)	0.4840 (3)	4.14 (8)
C(16)	-0.2477 (3)	0.1669 (2)	0.5250 (3)	3.31 (8)
C(61)	-0.2262 (3)	0.0268 (2)	0.7429 (2)	2.64 (7)
C(62)	-0.1377 (3)	0.0560 (2)	0.8619 (3)	3.19 (7)
C(63)	-0.2066 (4)	0.0932 (2)	0.9362 (3)	3.96 (8)
C(64)	-0.3648 (4)	0.1006 (3)	0.8920 (3)	4.29 (8)
C(65)	-0.4536 (3)	0.0733 (2)	0.7738 (3)	4.03 (8)
C(66)	-0.3845 (3)	0.0358 (2)	0.6993 (3)	3.43 (8)

Table 2. Selected geometric parameters ($\text{\AA}$, °)

N(1)—C(1)	1.274 (4)	N(3)—C(6)	1.482 (3)
N(1)—C(2)	1.468 (5)	C(1)—C(6)	1.531 (5)
N(2)—C(3)	1.463 (5)	C(1)—C(11)	1.493 (4)
N(2)—C(4)	1.468 (4)	C(2)—C(3)	1.504 (5)
N(2)—C(6)	1.481 (4)	C(4)—C(5)	1.535 (4)
N(3)—C(5)	1.481 (4)	C(6)—C(61)	1.531 (5)
C(1)—N(1)—C(2)	118.8 (3)	N(3)—C(5)—C(4)	105.1 (2)
C(3)—N(2)—C(4)	111.3 (3)	N(2)—C(6)—N(3)	107.0 (2)
C(3)—N(2)—C(6)	110.5 (3)	N(2)—C(6)—C(1)	112.0 (2)
C(4)—N(2)—C(6)	101.4 (3)	N(2)—C(6)—C(61)	106.1 (2)
C(5)—N(3)—C(6)	105.6 (2)	N(3)—C(6)—C(1)	110.5 (2)
N(1)—C(1)—C(6)	125.1 (3)	N(3)—C(6)—C(61)	111.1 (2)
N(1)—C(1)—C(11)	116.4 (3)	C(1)—C(6)—C(61)	110.1 (3)
C(6)—C(1)—C(11)	118.4 (2)	C(1)—C(11)—C(12)	119.6 (2)
N(1)—C(2)—C(3)	114.2 (2)	C(1)—C(11)—C(16)	122.7 (3)
N(2)—C(3)—C(2)	108.4 (3)	C(6)—C(61)—C(62)	118.0 (2)
N(2)—C(4)—C(5)	106.2 (3)	C(6)—C(61)—C(66)	123.2 (2)

The structure was solved by routine direct methods and refined by full-matrix least squares with non-H atoms anisotropic. H atoms were located on a difference map and refined with isotropic temperature factors. Programs from the Enraf-Nonius *SDP-Plus* package (Enraf-Nonius, 1983) were run on a PDP 11/73 computer.

One of us (DSP) is thankful to CSIR, New Delhi, for financial assistance. We thank UGG, New Delhi, for providing the X-ray diffractometer facility for our department.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Kommentar

Die Einwirkung von cyclischen Aminen auf 3,5-Dinitroindazol (1) führt zu Molekularverbindungen, von denen diese von (1) und Morpholin (Gzella, Wrzeciono & Borowiak, 1989), Pyrrolidin (Gzella & Wrzeciono, 1990), Piperazin (Gzella & Wrzeciono, 1991a), Thiomorpholin (Gzella & Wrzeciono, 1991b) bzw. N-Methylpiperazin (Gzella, Wrzeciono & Łukaszewski, 1994) von uns bereits röntgenographisch untersucht worden sind. In dieser Mitteilung soll über die Struktur der Molekularverbindung von (1) und Piperidin berichtet werden [Verbindung (2)]. Diese Verbindung ist neben anderen, vorangehend beschriebenen Molekularverbindungen von (1) in Bezug auf potentielle radiosensibilisierende Eigenschaften interessant (Gzella, Wrzeciono & Łukaszewski, 1994).

Mehrere breite Banden im IR Spektrum von (2) im Bereich von 3000–2180 cm⁻¹ weisen auf die Ammoniumstruktur hin. Bei einem Vergleich der ¹H NMR Spektren von Piperidin und (2) läßt sich eine bemerkenswerte Tieffeldverschiebung des N-Protonensignals im Piperidin beobachten [Piperidin: $\delta = 1,62$; (2): $\delta = 6,41$ p.p.m.], was die Lokalisierung der positiven Ladung auf dem Piperidin-Stickstoff-Atom in (2) ermöglicht. Näheres über die Struktur von (2) läßt sich aufgrund röntgenographischer Untersuchungen aussagen.

Im asymmetrischen Teil der Elementarzelle befinden sich je zwei Moleküle von (1) und Piperidin. Ähnlich wie es bei den oben zitierten und bereits von uns beschriebenen Molekularverbindungen von (1) der Fall war, liegt auch in (2) (1) als Anion und Piperidin als Kation vor. Die Komponenten der Molekularverbindung sind durch Wasserstoffbrücken in ein Dimer gebunden (Fig. 1, Tabelle 3), das auf keinem Symmetrie-Element im Kristallgitter liegt.

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Struktur der Molekularverbindung von 3,5-Dinitroindazol und Piperidin. 39. Azole†

A. GZELLA UND U. WRZECIONO

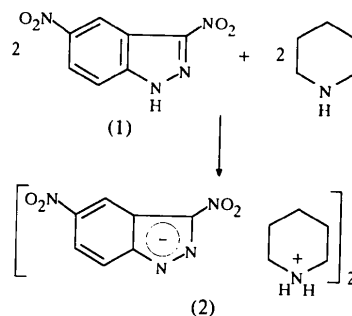
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(Eingegangen am 23. Dezember 1993; angenommen am 1. August 1994)

Abstract

The title molecular complex, piperidinium indazolid, 2C₅H₁₂N⁺·2C₇H₃N₄O₄⁻, was obtained by treatment of 3,5-dinitroindazole with piperidine. It consists of two ionized molecules of each component, connected by hydrogen bonds. The piperidine molecules form H₂N⁺ < ammonium cations as a result of the incorporation of the pyrrolic H atoms of (1). The complex occupies a general position in the crystal lattice. The structure of the complex is determined on the basis of IR and ¹H-NMR spectra as well as X-ray analysis.

† 38. Mitteilung: Gzella & Wrzeciono (1995).



An den Wasserstoffbrücken N(16A)··N(1B) und N(16B)··N(1A) sind die axialen H-Atome der Piperidinkationen und die Pyrrol-artigen N-Atome der 3,5-Dinitroindazol-Anionen beteiligt. An den zwei übrigen Wasserstoffbrücken N(16A)··N(2A) und N(16B)··N(2B) nehmen die äquatorialen H-Atome und Piperidin-artigen N-Atome der entsprechenden Moleküle teil. Die durch die erwähnten Wasserstoffbrücken miteinander