Pyramidal Bonding about Nitrogen in 1-Benzoyloxyindole determined by *X*-Ray Diffraction

R. Morrin Acheson
Department of Biochemistry, University of Oxford, South Parks Road, Oxford OX1 3QU
Michael H. Benn and John Jacyno
Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada
John D. Wallis *,†
Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD

The *X*-ray crystal structure of 1-benzoyloxyindole (6), refined to *R* 0.043, shows that the bonding at nitrogen is distinctly pyramidal, the bond angle sum at nitrogen being 355°.

The crystal structures[1] of five *ortho*-unsubstituted *NN*-dialkylanilines, not possessing *para*-conjugative substituents or being involved in donor–acceptor complexes, show that the three bonds to the nitrogen atom lie in one plane. However, the only *N*-alkylphenylhydroxylamine derivative (1) reported on[2] has pyramidal bonding at the exocyclic nitrogen atom, suggesting that the presence of an oxygen substituent on the nitrogen induces the pyramidality. In contrast the 1-methoxyindole (2) which could be regarded as a substituted phenylhydroxylamine derivative has planar nitrogen bonding.[3] This could be due to the extra stability conferred by the participation of the nitrogen lone pair in the 10 π electron ' aromatic ' system anticipated for an indole, but, alternatively, the compound is a vinylogous amide and the planarity at nitrogen may be induced solely by the conjugation of the nitrogen lone pair with the acetyl group through the intervening olefinic bond. Bond length comparisons[3] clearly indicate that this type of conjugation occurs. The crystal structure[4] of the 1-methoxyoxindole derivative gelsemine (3) also shows planar nitrogen bonding but the nitrogen is amidic and the accuracy of the structure is low (*R* 0.16). The *X*-ray crystal structure of 1-benzoyloxyindole has now been measured to see whether planar geometry at nitrogen, as observed for the 1-alkylindoles (4)[5] and (5),[6] is retained in the absence of conjugated electron-withdrawing substituents. The use of a 1-benzoyloxy substituent rather than a methoxy group was caused by the difficulty in obtaining suitable crystals from the available 1-hydroxyindole derivatives.[7] The indolic nitrogen atom is thus adjacent to one oxygen lone pair in an ' sp^2 ' orbital and one in a ' *p* ' type orbital rather than two in ' sp^3 ' type orbitals.

Discussion

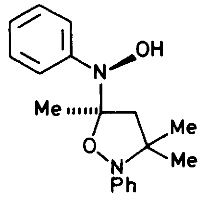
The crystal structure of (6) (Figures 1 and 2) shows that the geometry of the bonding to nitrogen is significantly pyramidal. The sum of the bond angles at nitrogen is 355° and the attached alkoxy-oxygen atom O(1) deviates by 0.345 Å from the best plane [see Supplementary Publication No. SUP 23516 (16 pp.)‡] through the indole ring system. The carbonyl group is orientated so that the sp^2 lone pair on O(1) is almost antiperiplanar to the sp^3 lone pair on the ring nitrogen atom. The torsion angle along N(1)–O(1) between the theoretically positioned lone pairs is 175.2° (Figure 3). The nitrogen atom deviates only very slightly (by 0.098 Å) from the plane of the carbonyloxy group. This structure appears to represent a compromise between, on the one hand, a classical 10 π electron aromatic system which would demand a planar nitrogen atom and, on the other hand, being a phenylhydroxylamine derivative which would be expected, by analogy with (1),[2] to have a bond angle sum at nitrogen of *ca.* 329° which is much smaller than that observed (355°). In contrast, *X*-ray diffraction has shown that the 1-nitrogen atom in 1-benzoyloxybenzotriazole (7)[8] has planar bonding geometry. This difference between (6) and (7) could be rationalised by the stronger stabilising effect of conjugation of a nitrogen lone pair (in a *p* orbital) with a nitrogen–nitrogen double bond rather than with a carbon–carbon double bond. Such interactions would lead to a build-up of a partial negative charge at the 3-position of the benzotriazole and indole rings, respectively, and this would be more readily tolerated by the nitrogen atom in (7) than by a carbon atom in the hypothetical form of (6) with planar nitrogen bonding. A more detailed comparison of (6) and (7) is not worthwhile since the structure of (7) is of limited accuracy (*R* 0.09, typical e.s.d. for a C–C bond length 0.013 Å). The fact that 1-alkylindoles such as (4)[5] and (5)[6] have planar bonding at the indolic nitrogen suggests that the pyramidality in (6) is induced by the presence of the 1-oxygen lone pair. The accurate crystal structures of 3-hydroxyxanthine (8)[9] and *N*-hydroxyurea (9),[9] the latter from neutron diffraction data, both show slight pyramidalisation of the nitrogen atoms of the hydroxylamino-residues, despite the fact that they are both part of amide systems. Thus in (8), the hydroxy oxygen deviates by 0.19 Å from the plane of the ring system while in (9) although all the non-hydrogen atoms are coplanar, the hydroxylamine moiety's N–H deviates by 0.23 Å from this plane. These results suggest that the observation of a planar nitrogen in the alkaloid gelsemine (3) should definitely be discounted because of the inaccurate measurement (*R* 0.16).[4] The authors of structures (8) and (9) suggest that the pyramidalisation of nitrogen is caused by the electrical dipole on oxygen, with the two lone pairs at the negative ' end ', polarising the *p*-orbital carrying the nitrogen lone pair. The structure of 1-benzoyloxyindole is in accord with this explanation, having the sp^2 lone pair on the oxygen and the developing sp^3 lone pair on nitrogen arranged in an antiperiplanar fashion.

The N–O bond length in 1-benzoyloxyindole is similar to that in the 1-methoxyindole (2) [1.397(5) *cf.* 1.394(7) Å] and very slightly shorter than those in the *NO*-dibenzoylhydroxylamines (10)—(13)[10] (1.402—1.412 Å). The C(1)–O(1) bond is also comparable to the equivalent bonds in (10)—(13) [1.375(6) and 1.358—1.380 Å]. The plane of the carbonyloxy group is almost perpendicular (89.1°) to the best plane through the indole ring and nearly coplanar with the benzene ring (interplanar angle 5°). In the indole ring the C(2)–C(3) bond

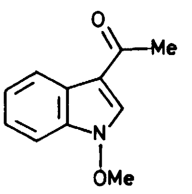
---

† *Present address:* Laboratorium für Organische Chemie, E.T.H. Zentrum, CH-8092 Zürich, Switzerland.

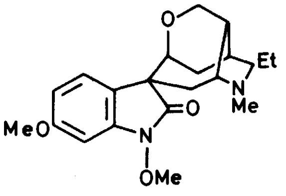
‡ For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.



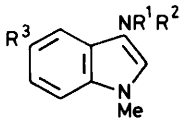
(1)



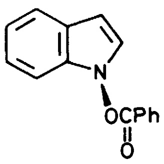
(2)



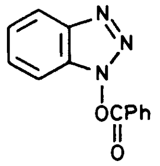
(3)



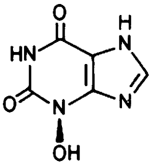
	R^1	R^2	R^3
(4)	4-ClC_6H_4	Me	Cl
(5)	4-$MeC_6H_4SO_2$	H	H



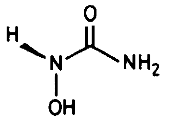
(6)



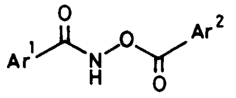
(7)



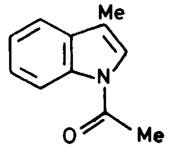
(8)



(9)



	Ar^1	Ar^2
(10)	C_6H_5	C_6H_5
(11)	o-ClC_6H_4	o-ClC_6H_4
(12)	C_6H_5	o-MeC_6H_4
(13)	C_6H_5	p-MeC_6H_4



(14)

is shorter than the N(1)–C(2) bond, in contrast to (2) where the 3-acetyl group is in strong resonance with the enamino system (Table 3). The difference between these bond lengths for (6) (0.037 Å) is larger than that (0.006 Å) for the averaged data from two reasonably accurate crystal structures of 1-unsubstituted 3-alkylindoles (Table 3), e.s.d. $\leqslant$ 0.005 Å, but not so large (0.067 Å) as for the *N*-acetyl derivative (14)[12] where the nitrogen lone pair is strongly inhibited from interacting with the indole ring. Thus the 1-oxy substituent in (6) appears to exert a small but significant electron-withdrawing effect on the nitrogen atom.

Experimental

Preparation of 1-*Benzoyloxyindole* (6).—A solution of crude *o*-nitrophenylacetaldehyde[7] (8.5 g, *ca.* 0.05 mol) in ether (280 ml) was added to a mixture of zinc dust (22.7 g, 0.35 g-atom) and ammonium chloride (4.0 g, 0.07 mol) in water (50 ml). The reaction was initiated by mechanical stirring and monitored by the disappearance of the carbonyl absorption at 1 725 cm^{-1} in the i.r. The mixture was filtered and the organic phase of the filtrate containing the 1-hydroxyindole separated and run into a stirred mixture of benzoyl chloride (8.5 g, 0.06 mol) and pyridine (60 ml). This mixture was stirred at room temperature for 4 h, poured into excess, saturated aqueous sodium hydrogencarbonate, stirred for 1 h, and then the layers separated. The aqueous portion was extracted three times with toluene (50 ml) and the combined organic fractions were washed three times with water. The organic layer was evaporated *in vacuo* and the residue repeatedly taken up in toluene and evaporated to remove residual pyridine. The resulting brown oil was chromatographed on silica gel, eluting with benzene, to give 1-*benzoyloxyindole* (6) (3.9 g), which was recrystallised from methanol at below 0 °C to give large rhombs, m.p. 49—50 °C (Found C, 75.8; H, 4.9; N, 5.9. $C_{15}H_{11}NO_2$ requires C, 75.9; H, 4.7; N, 5.9%); $\nu_{max.}$ (KBr) 1 775s, 1 240s, 1040 m, 1 000m, 760m, 740m, and 705m cm^{-1}, δ (60 MHz; $CDCl_3$) 8.3—7.9 (m, ArH), 7.8—6.8 (m, ArH), and 6.45 (d, 3-H), $J_{2,3}$ 4 Hz, *m*/*z* (probe 90 °C; source 230 °C) 237 (M^+, 13), 117 (43), and 105 ($C_6H_5C{\equiv}O^+$, 100).

Crystal Data for (6).—$C_{15}H_{11}NO_2$, M_r = 237.3, orthorhombic, space group $P2_12_12_1$, a = 7.864(3), b = 11.358(9), c 13.563(5) Å, Z = 4, D_c = 1.31 g cm^{-3}, μ (Mo-K_α) = 0.94

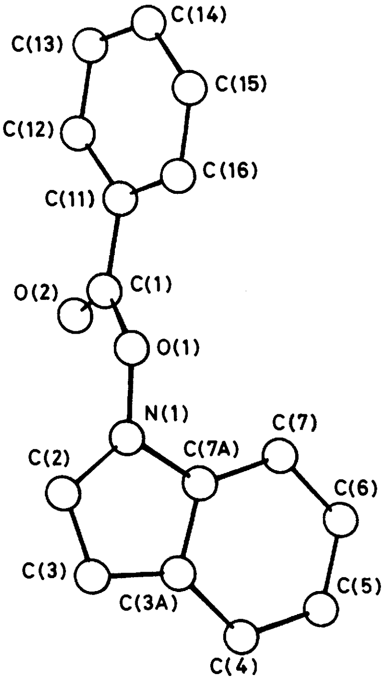


Figure 1. A ball and stick view of (6) showing the crystallographic numbering scheme

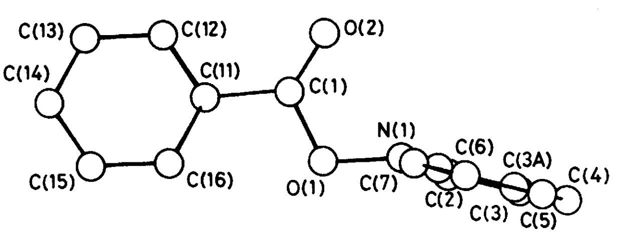


Figure 2. A view of (6) clearly showing the deviation of O(1) from the plane of the indole ring

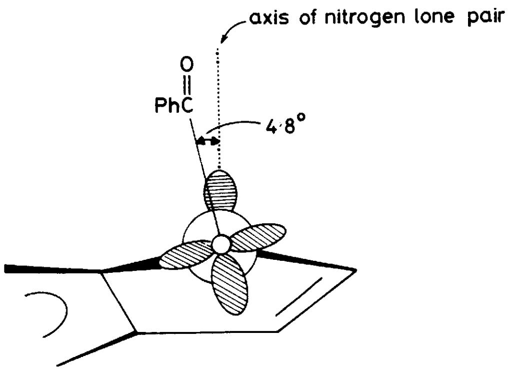


Figure 3. A Newman projection of (6) along the O(1)-N(1) bond, looking from O(1), showing the relative orientation of the lone pairs belonging to these two atoms

cm^{-1}, 790 unique reflections with $I \geqslant 3\sigma(I)$, final R value 0.043.

Table 1. Bond lengths (Å) for (6) with e.s.d.s in parentheses

O(1)-N(1)	1.397(5)	C(4)-C(5)	1.364(8)
O(1)-C(1)	1.375(6)	C(5)-C(6)	1.393(8)
O(2)-C(1)	1.200(6)	C(6)-C(7)	1.370(7)
N(1)-C(2)	1.387(6)	C(7)-C(7A)	1.378(6)
N(1)-C(7A)	1.366(6)	C(11)-C(12)	1.378(7)
C(1)-C(11)	1.468(7)	C(11)-C(16)	1.382(7)
C(2)-C(3)	1.350(7)	C(12)-C(13)	1.375(7)
C(3)-C(3A)	1.419(7)	C(13)-C(14)	1.378(8)
C(3A)-C(4)	1.480(7)	C(14)-C(15)	1.375(8)
C(3A)-C(7A)	1.403(6)	C(15)-C(16)	1.383(7)

Table 2. Bond angles (°) for (6) with e.s.d.s in parentheses

N(1)-O(1)-C(1)	113.4(4)	C(5)-C(6)-C(7)	121.6(5)
O(1)-N(1)-C(2)	122.3(5)	C(6)-C(7)-C(7A)	116.6(5)
O(1)-N(1)-C(7A)	122.0(4)	N(1)-C(7A)-C(3A)	105.9(5)
C(2)-N(1)-C(7A)	110.7(4)	N(1)-C(7A)-C(7)	130.5(5)
O(1)-C(1)-O(2)	122.6(5)	C(3A)-C(7A)-C(7)	123.6(5)
O(1)-C(1)-C(11)	110.7(5)	C(1)-C(11)-C(12)	118.0(5)
O(2)-C(1)-C(11)	126.7(5)	C(1)-C(11)-C(16)	122.0(5)
N(1)-C(2)-C(3)	107.4(5)	C(12)-C(11)-C(16)	119.9(5)
C(2)-C(3)-C(3A)	108.2(5)	C(11)-C(12)-C(13)	120.7(5)
C(3)-C(3A)-C(4)	134.4(5)	C(12)-C(13)-C(14)	119.4(5)
C(3)-C(3A)-C(7A)	107.5(5)	C(13)-C(14)-C(15)	120.1(5)
C(4)-C(3A)-C(7A)	118.1(5)	C(14)-C(15)-C(16)	120.6(6)
C(3A)-C(4)-C(5)	118.4(5)	C(11)-C(16)-C(15)	119.2(5)
C(4)-C(5)-C(6)	121.7(5)		

Table 3. Bond lengths (Å) in various indoles with e.s.d.s in parentheses

Bond [a]	(2)	(6)	(14)	Unsubstituted indoles [b]
N(1)-C(2)	1.362(8)	1.387(6)	1.406(5)	1.365(9)
C(2)-C(3)	1.379(9)	1.350(7)	1.339(5)	1.359(5)

[a] Numbering scheme for the indole ring as for (6) in Figure 1. [b] Averaged data for indol-3-ylacetic [11a] and indol-3-ylbutyric acids.[11b]

A crystal of (6) was lodged in a sealed glass capillary under a nitrogen atmosphere and the tube mounted on an Enraf–Nonius CAD-4-F computer-controlled four-circle diffractometer. Accurate cell parameters were determined from the setting angles of 25 strong reflections found initially by the SEARCH routine. Diffraction data (Mo-K_α radiation) were collected by ω-2θ scans using the ZIG-ZAG procedure out to θ 28° with periodic remeasurements on the positions and intensities of three standard reflections. Systematic absences showed the space group to be $P2_12_12_1$. Lorentz and polarisation corrections were applied, equivalent reflections merged and structure amplitudes derived for 1 770 unique reflections. The structure was solved with MULTAN 80 [13] which revealed all the non-hydrogen atoms. This structure was refined by full-matrix least-squares, including isotropic temperature factors, using the 790 reflections with $I \geqslant 3\sigma(I)$. All hydrogen atoms were placed by geometrical calculation, assigned an isotropic temperature factor of 0.06, and not included in the refinement. All other atoms were then assigned anisotropic temperature factors and refinement continued until convergence at an R value of 0.043. The final weighting scheme was provided by the Chebyshev series: $\omega = [59.3t_0(x) + 76.9t_1(x) + 26.1t_2(x)]^{-1}$ where $X = F_o/F_{\text{max.}}$.[14] Data reduction, structure refinement and all geometry calculations were performed using CRYSTALS [15] on a VAX 11/750 computer and the pictures were drawn with SNOOPI.[16] Final fractional atomic coordinates, anisotropic temperature factors and structure factor tables are available in SUP 23516.

Acknowledgement

We thank NATO for a research grant No. RG 090.80 (R. M. A.).

References

1 Cambridge Crystallographic Data Base.

2 R. Foster, J. Iball, and R. Nash, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1210.

3 R. M. Acheson, J. D. Wallis, and D. J. Watkin, *Acta Crystallogr.*, 1980, **B36**, 3125.

4 M. Przybylaska, *Acta Crystallogr.*, 1962, **15**, 301.

5 M. Zocchi, G. Tieghi, and A. Albinati, *Cryst. Struct. Commun.*, 1972, **1**, 139.

6 T. S. Cameron, C. K. Prout, R. Spagna, and E. White, *J. Chem. Soc., Perkin Trans. 2*, 1975, 176.

7 R. M. Acheson, P. G. Hunt, D. M. Littlewood, B. A. Murrer, and H. E. Rosenberg, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1978, 1117.

8 D. G. McCarthy, A. F. Hegarty, and B. J. Hathaway, *J. Chem. Soc., Perkin Trans. 2*, 1977, 224.

9 N. E. Thiessen, H. A. Levy, and B. D. Flaig, *Acta Crystallogr.*, 1978, **B34**, 2495.

10 S. Göttlicher and P. Ochsenreiter, *Chem. Ber.*, 1974, **107**, 398.

11 (*a*) K. Chandrasekhar, and S. Raghunathan, *Acta Crystallogr.*, 1982, **B38**, 2538; (*b*) K. Chandrasekhar and V. Pattabhi, *ibid.*, 1980, **B36**, 1165.

12 E. Surcouf, J.-P. Mornon, and C. Malgrange, *Acta Crystallogr.*, 1978, **B34**, 2169.

13 P. Main, ' MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data,' Department of Physics, University of York, York, 1980.

14 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr.*, 1979, **A35**, 698.

15 D. J. Watkin and J. R. Carruthers, ' CRYSTALS User Guide,' Chemical Crystallography Laboratory, University of Oxford, Oxford, 1981.

16 E. K. Davies, ' SNOOPI User Manual,' Chemical Crystallography Laboratory, University of Oxford, Oxford, 1981.

Received 9th August 1982; *Paper* 2/1384