

The crystal packing is illustrated in Fig. 3. In the *b* direction there is a zigzag succession of molecules linked by a hydrogen bond involving the 17 β -ol function: O(97)—H \cdots O(83) [$d = 2.80(1) \text{ \AA}$]. In the other directions crystal cohesion is achieved by attractive van der Waals forces. We observe only one repulsive contact between the C(92) methyl group and the C(10) atom [$d = 3.52(1) \text{ \AA}$].

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3-Acetyl-1-methoxyindole

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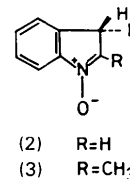
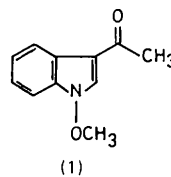
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Abstract. C₁₁H₁₁NO₂, triclinic, $P\bar{1}$, $a = 8.35(1)$, $b = 10.39(1)$, $c = 11.58(1) \text{ \AA}$, $\alpha = 98.50(8)$, $\beta = 97.68(6)$, $\gamma = 91.69(10)^\circ$, $Z = 4$, $\mu = 0.094 \text{ mm}^{-1}$ (Mo $K\alpha$ radiation), $R = 0.054$. The bonds about the N atom lie in one plane and the acetyl group is almost coplanar with the indole ring. Bond lengths suggest π -electron delocalization between the N atom and the carbonyl group.

Introduction. Five derivatives of 1-methoxyindole have been isolated from plant sources (Acheson, 1979), and further members have been synthesized (Acheson, Hunt, Littlewood, Murrer & Rosenberg, 1978). The investigation of the crystal structure of one of these synthetic analogues (1) was undertaken to determine the geometry of the bonds about N and to investigate the conformation about the N—O bond. The ¹³C NMR spectrum of 1-methoxyindole is very similar to that of indole, suggesting a planar N atom, but the ready tautomerism of 1-hydroxyindole and 1-hydroxy-2-methylindole to the nitrene tautomers (2) and (3) suggests that there is not a large energy factor in favour of retaining aromaticity in the five-membered ring.



Crystals of (1) were grown by diffusion of petrol vapour into an ethyl acetate solution. Oscillation and Weissenberg photographs and the crystal density showed the crystal system to be triclinic with $Z = 4$. Cell dimensions were determined on an Enraf-Nonius CAD-4 four-circle diffractometer. Intensities were collected with Mo $K\alpha$ radiation to $2\theta \leq 44^\circ$ by an $\omega/2\theta$ scan with standard reflections checked hourly. Lorentz and polarization corrections were applied to the 2429 observed reflections, equivalent reflections merged and structure amplitudes derived for 948 with $I > 3\sigma(I)$. Application of *MULTAN 77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) gave two solutions, each containing a promising fragment, but neither would serve as a sufficiently good phasing model for the determination of the rest of the structure. The solution (Fig. 1) was finally obtained from *MULTAN 77* by making two changes. The scaling of

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Table 1. Atomic coordinates with *e.s.d.*'s in parentheses

| | <i>x</i> | <i>y</i> | <i>z</i> |
|---------|------------|------------|------------|
| O(1) | 0.8727 (6) | 0.8658 (5) | 0.6206 (5) |
| O(2) | 1.2542 (7) | 0.4098 (5) | 0.6933 (6) |
| N(1) | 0.9780 (8) | 0.7628 (6) | 0.6172 (6) |
| C(2) | 0.9809 (9) | 0.6730 (8) | 0.6912 (7) |
| C(3) | 1.0987 (9) | 0.5881 (7) | 0.6638 (7) |
| C(3a) | 1.1692 (9) | 0.6341 (7) | 0.5695 (7) |
| C(4) | 1.295 (1) | 0.5930 (8) | 0.5054 (7) |
| C(5) | 1.336 (1) | 0.6649 (9) | 0.4218 (7) |
| C(6) | 1.255 (1) | 0.7757 (9) | 0.3998 (8) |
| C(7) | 1.132 (1) | 0.8191 (8) | 0.4588 (8) |
| C(7a) | 1.092 (1) | 0.7435 (8) | 0.5412 (7) |
| C(8) | 0.7198 (9) | 0.8285 (8) | 0.5420 (8) |
| C(9) | 1.146 (1) | 0.4785 (8) | 0.7235 (8) |
| C(10) | 1.055 (1) | 0.4517 (8) | 0.8231 (9) |
| H(21) | 0.9122 | 0.6721 | 0.7549 |
| H(41) | 1.3541 | 0.5143 | 0.5205 |
| H(51) | 1.4292 | 0.6379 | 0.3761 |
| H(61) | 1.2833 | 0.8223 | 0.3365 |
| H(71) | 1.0740 | 0.8973 | 0.4438 |
| H(81) | 0.6740 | 0.7614 | 0.5687 |
| H(82) | 0.6470 | 0.9033 | 0.5445 |
| H(83) | 0.7415 | 0.8014 | 0.4593 |
| H(101) | 1.1210 | 0.4040 | 0.8691 |
| H(102) | 1.0325 | 0.5354 | 0.8687 |
| H(103) | 0.9534 | 0.4004 | 0.7883 |
| O(1') | 0.2390 (7) | 1.0559 (5) | 0.7226 (5) |
| O(2') | 0.7817 (8) | 0.7680 (5) | 0.9144 (5) |
| N(1') | 0.3790 (8) | 1.0148 (7) | 0.7810 (5) |
| C(2') | 0.410 (1) | 0.8865 (8) | 0.7826 (7) |
| C(3') | 0.5640 (9) | 0.8822 (8) | 0.8420 (6) |
| C(3a') | 0.6269 (9) | 1.0142 (8) | 0.8773 (7) |
| C(4') | 0.773 (1) | 1.0738 (9) | 0.9389 (7) |
| C(5') | 0.794 (1) | 1.2086 (9) | 0.9582 (8) |
| C(6') | 0.669 (1) | 1.2842 (8) | 0.9191 (8) |
| C(7') | 0.523 (1) | 1.2316 (9) | 0.8565 (7) |
| C(7a') | 0.506 (1) | 1.0949 (9) | 0.8381 (7) |
| C(8') | 0.119 (1) | 1.0769 (9) | 0.8028 (8) |
| C(9') | 0.643 (1) | 0.7647 (9) | 0.8636 (7) |
| C(10') | 0.555 (1) | 0.6350 (8) | 0.8200 (8) |
| H(21') | 0.3364 | 0.8118 | 0.7452 |
| H(41') | 0.8617 | 1.0203 | 0.9686 |
| H(51') | 0.8991 | 1.2506 | 0.9994 |
| H(61') | 0.6877 | 1.3820 | 0.9386 |
| H(71') | 0.4381 | 1.2875 | 0.8254 |
| H(81') | 0.0615 | 0.9831 | 0.8119 |
| H(82') | 0.1730 | 1.1183 | 0.8832 |
| H(83') | 0.0344 | 1.1334 | 0.7730 |
| H(101') | 0.6287 | 0.5612 | 0.8346 |
| H(102') | 0.4528 | 0.6239 | 0.8431 |
| H(103') | 0.5375 | 0.6240 | 0.7238 |

the normalized structure factors was modified by replacing the calculated value of B (1.35 \AA^2) with a higher value (2.50 \AA^2) and the set of reflections automatically chosen by the program for initiating phase determination was replaced by a hand-picked set. The structure was refined to $R = 0.105$ with anisotropic temperature factors and then the positions of all the H atoms were calculated. The parameters for each independent molecule were blocked separately and the structure refined to convergence at $R = 0.054$ by blocked-matrix least squares including an isotropic

Table 2. Interatomic distances (\AA) and their *e.s.d.*'s

| | | | |
|-------------|------------|---------------|------------|
| O(1)—N(1) | 1.405 (7) | O(1')—N(1') | 1.382 (7) |
| O(1)—C(8) | 1.470 (9) | O(1')—C(8') | 1.457 (9) |
| O(2)—C(9) | 1.224 (9) | O(2')—C(9') | 1.224 (8) |
| N(1)—C(2) | 1.356 (8) | N(1')—C(2') | 1.368 (8) |
| N(1)—C(7a) | 1.380 (8) | N(1')—C(7a') | 1.362 (9) |
| C(2)—C(3) | 1.378 (9) | C(2')—C(3') | 1.381 (10) |
| C(3)—C(3a) | 1.440 (10) | C(3')—C(3a') | 1.436 (10) |
| C(3)—C(9) | 1.445 (10) | C(3')—C(9') | 1.442 (10) |
| C(3a)—C(4) | 1.404 (10) | C(3a')—C(4') | 1.405 (10) |
| C(3a)—C(7a) | 1.382 (9) | C(3a')—C(7a') | 1.403 (9) |
| C(4)—C(5) | 1.379 (10) | C(4')—C(5') | 1.388 (10) |
| C(5)—C(6) | 1.390 (11) | C(5')—C(6') | 1.390 (11) |
| C(6)—C(7) | 1.364 (11) | C(6')—C(7') | 1.387 (11) |
| C(7)—C(7a) | 1.388 (10) | C(7')—C(7a') | 1.405 (10) |
| C(9)—C(10) | 1.515 (11) | C(9')—C(10') | 1.502 (11) |

Table 3. Interbond angles ($^\circ$) (*e.s.d.*'s $0.5\text{--}0.8^\circ$)

| | | | |
|------------------|-------|---------------------|-------|
| N(1)—O(1)—C(8) | 111.2 | N(1')—O(1')—C(8') | 109.6 |
| O(1)—N(1)—C(2) | 123.1 | O(1')—N(1')—C(2') | 123.4 |
| O(1)—N(1)—C(7a) | 124.3 | O(1')—N(1')—C(7a') | 124.8 |
| C(2)—N(1)—C(7a) | 112.6 | C(2')—N(1')—C(7a') | 111.7 |
| N(1)—C(2)—C(3) | 107.4 | N(1')—C(2')—C(3') | 107.4 |
| C(2)—C(3)—C(3a) | 106.2 | C(2')—C(3')—C(3a') | 107.3 |
| C(2)—C(3)—C(9) | 126.0 | C(2')—C(3')—C(9') | 125.1 |
| C(3a)—C(3)—C(9) | 127.7 | C(3a')—C(3')—C(9') | 127.7 |
| C(3)—C(3a)—C(4) | 134.2 | C(3')—C(3a')—C(4') | 134.9 |
| C(3)—C(3a)—C(7a) | 109.1 | C(3')—C(3a')—C(7a') | 107.1 |
| C(4)—C(3a)—C(7a) | 116.7 | C(4')—C(3a')—C(7a') | 117.9 |
| C(3a)—C(4)—C(5) | 118.8 | C(3a')—C(4')—C(5') | 119.7 |
| C(4)—C(5)—C(6) | 121.3 | C(4')—C(5')—C(6') | 120.1 |
| C(5)—C(6)—C(7) | 122.3 | C(5')—C(6')—C(7') | 123.2 |
| C(6)—C(7)—C(7a) | 114.9 | C(6')—C(7')—C(7a') | 115.3 |
| N(1)—C(7a)—C(3a) | 104.7 | N(1')—C(7a')—C(3a') | 106.6 |
| N(1)—C(7a)—C(7) | 129.1 | N(1')—C(7a')—C(7) | 129.5 |
| C(3a)—C(7a)—C(7) | 126.0 | C(3a')—C(7a')—C(7) | 123.9 |
| O(2)—C(9)—C(3) | 120.9 | O(2')—C(9')—C(3') | 121.5 |
| O(2)—C(9)—C(10) | 121.4 | O(2')—C(9')—C(10') | 119.2 |
| C(3)—C(9)—C(10) | 117.7 | C(3')—C(9')—C(10') | 119.3 |

extinction parameter.* Weights were computed from the Chebyshev series $w = [158.79t_0(x) + 221.10t_1(x) + 76.38t_2(x)]^{-1}$, where $(x) = F_o/F_{\max}$ (Carruthers & Watkin, 1979). Data reduction and structure refinement were performed with *CRYSTALS* (Carruthers, 1975) and all calculations were made on the Oxford University ICL 1906A computer. Positional parameters are in Table 1, interatomic distances in Table 2 and interbond angles in Table 3.

Discussion. The two independent molecules (Fig. 2) have very similar dimensions. The bonds about N deviate only slightly from one plane and the 3-acetyl

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35361 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

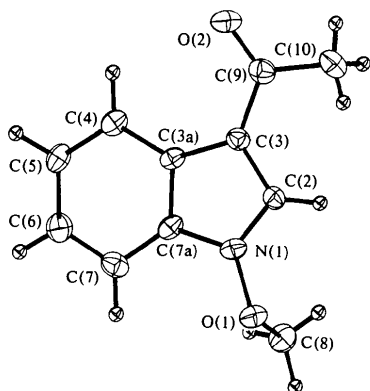


Fig. 1. 3-Acetyl-1-methoxyindole.

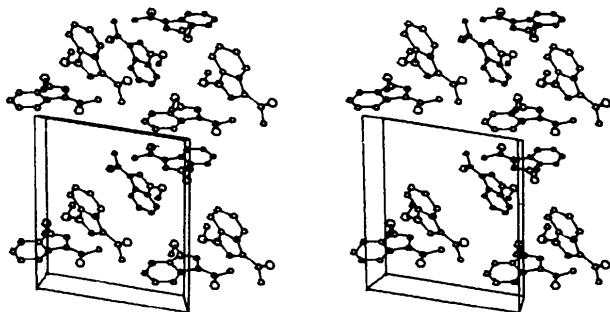
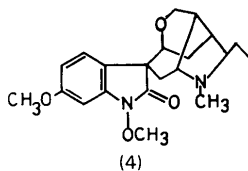


Fig. 2. Packing diagram.

group is almost coplanar with the heterocyclic ring (dihedral angle 2°). The N—O bond makes an angle of only 2° with the plane of the indole ring and the two dihedral angles between the O—CH₃ bond and this plane are very nearly equal (91°). The N—O length (1.39 Å) is similar to that in *N,O*-dibenzoylhydroxylamine (1.406 Å) (Göttlicher & Ochsenreiter, 1974). It is unwise to trust the much shorter N—O length (1.343 Å) measured for the *N*-alkoxy-2,3-dihydroindol-2-one (4) (Przybylska, 1962), since *R* was rather high (0.16).

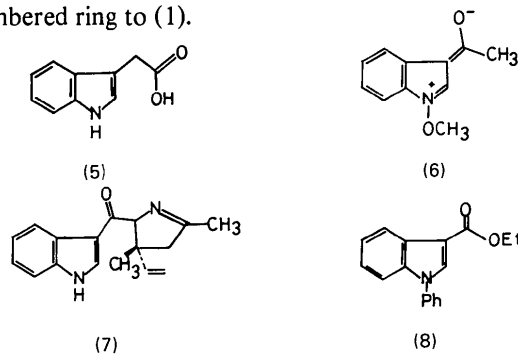


Compared with the data for indole-3-acetic acid (5) (Karle, Britts & Gum, 1964) (Table 4), the N(1)—C(2) bond in (1) is shorter (by 0.04 Å) and the C(2)—C(3) bond is longer (by 0.04 Å) which is consistent with electron delocalization from the N atom into the acetyl group as represented by the canonical (6). The indole (7) (Damak & Riche, 1977), which also possesses a 3-carbonyl group but which is unsubstituted on the ring N atom, shows an almost identical shortening of N(1)—C(2) and lengthening of C(2)—C(3) compared to indole-3-acetic acid. This leads to the unlikely conclusion that substitution of an electronegative O

Table 4. Comparison of some bond lengths (Å) for compounds (1), (5), (7) and (8)

| Compound | N(1)—C(2) | C(2)—C(3) |
|----------|-----------|-----------|
| (1) | 1.36 | 1.38 |
| (5) | 1.37 | 1.38 |
| (7) | 1.40 | 1.34 |
| (8) | 1.36 | 1.38 |
| (8) | 1.37 | 1.40 |

atom on the ring N made little difference to the π -donor ability of N. However, the electron-withdrawing power of the O atom may be offset by the strong α effect between the two hetero-atoms (Fleming, 1976). The indole (8) (Hecht & Luger, 1974) which has a 3-ester substituent shows similar bond lengths in the five-membered ring to (1).



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