

A Reinvestigation of the Structure of (3-Indolyl)acetic Acid

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Abstract. $C_{10}H_9NO_2$, $M_r = 175.2$, monoclinic, $P2_1/c$, $a = 17.938$ (7), $b = 5.254$ (2), $c = 9.591$ (4) Å, $\beta = 106.34$ (2)°, $V = 867.4$ Å³, $Z = 4$, $D_c = 1.361$, $D_m = 1.37$ Mg m⁻³. Starting with the atomic coordinates reported by Karle, Britts & Gum [*Acta Cryst.* (1964), **17**, 496–499] the structure has been refined to $R = 0.045$ for 921 counter reflections. The angle between the indole ring and carboxyl-group planes is 89.9 (4)°.

Introduction. The biochemical basis of plant-growth hormonal activity is yet to be elucidated thoroughly and in this context (3-indolyl)acetic acid (IAA), perhaps the best established and one of the most potent natural auxins, is of particular interest.

The crystal structure of IAA (Fig. 1) was reported by Karle *et al.* (1964) with visually estimated data ($R = 0.182$). While in all other auxins studied to date the ring system is either coplanar with ('recognition' conformation) or perpendicular to ('modulation' conformation) the carboxyl-group plane (Raghunathan & Pattabhi, 1981), Karle *et al.* (1964) reported an inclination of 62.9° in IAA. In view of this as well as to locate the H atoms, a refinement of the structure with diffractometer data was undertaken.

IAA was crystallized from chloroform and accurate cell parameters were obtained by least-squares refinement (Main & Woolfson, 1963) from 23 Bragg angles measured at $\pm 2\theta$ (22–70°) on a Picker four-circle diffractometer. Intensities were collected with Fe-filtered Co $K\alpha$ radiation ($\lambda = 1.7903$ Å) in the ω - 2θ mode with a scan rate of 2° min⁻¹ and scan width of 2°. Backgrounds were counted at either extreme of

the scan width for 10 s. 921 independent, non-zero intensities were measured and were not corrected for absorption.

Three cycles of block-diagonal least-squares refinement (Shiono, 1968) of the atomic positions and isotropic temperature factors ($B_{eq} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij}$) of Karle *et al.* (1964) reduced R to 0.115. A difference Fourier map then revealed all the H atoms close to their stereochemically expected positions. The H atoms were included for further calculations with isotropic temperature factors of the atoms to which they are bonded. Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1961) with anisotropic thermal parameters for the non-H atoms, isotropic for the H atoms and unit weights for all reflections led to convergence at $R = 0.045$.† Scattering factors were taken from *International Tables for X-ray Crystallography* (1968).

Discussion. Final atomic parameters are listed in Table 1 and interatomic distances and angles in Tables 2 and 3. Bond lengths and angles compare well with those reported for 4-(3-indolyl)butyric acid (Chandrasekhar & Pattabhi, 1980). The indole-ring dimensions agree within 2σ with values tabulated by Falkenberg & Carlström (1971) as well as with other later crystallographic studies, for example those of the (3-indolyl)acetic acid–nicotinamide complex (Inoue, Sakaki, Fujiwara & Tomita, 1978).

The torsion angle C(4)–C(3)–C(10)–C(11) is -86.3 (4)° yielding the synclinal conformation that is most commonly observed in compounds possessing auxin activity or herbicidal property (Smith & Kenard, 1979). Two least-squares planes, one through the indole ring and the other through the acid group, characterize the molecule and the dihedral angle between these two planes is 89.9 (4)°, significantly at variance with the value of 62.9° quoted by Karle *et al.* (1964).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36621 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Contribution No. 574.

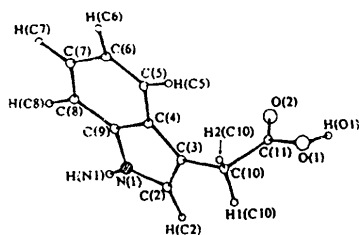


Fig. 1. Perspective view with atom-numbering scheme.

Table 1. Fractional positional ($\times 10^4$, $\times 10^3$ for H) and isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij} \text{ with } \sigma(B_{eq}) = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j \sigma(\beta_{ij}).$$

	x	y	z	B_{eq}/B (\AA^2)
N(1)	2847 (2)	7341 (6)	3104 (3)	4.99 (13)
C(2)	2111 (2)	8251 (7)	2564 (4)	4.93 (15)
C(3)	1999 (2)	10265 (6)	3380 (3)	4.00 (10)
C(4)	2715 (2)	10589 (5)	4488 (3)	3.30 (9)
C(5)	2971 (2)	12340 (6)	5627 (4)	4.04 (14)
C(6)	3721 (2)	12164 (7)	6511 (4)	5.24 (16)
C(7)	4226 (2)	10300 (8)	6300 (4)	5.58 (17)
C(8)	3995 (2)	8561 (7)	5193 (4)	4.73 (17)
C(9)	3239 (2)	8745 (6)	4308 (3)	3.78 (9)
C(10)	1285 (2)	11817 (9)	3127 (5)	5.20 (13)
C(11)	739 (2)	11013 (7)	3990 (3)	4.43 (10)
O(1)	167 (2)	12616 (5)	3896 (3)	5.56 (9)
O(2)	813 (1)	9074 (5)	4696 (2)	5.09 (9)
H(N1)	309 (3)	619 (9)	293 (5)	3.6*
H(C2)	171 (2)	759 (7)	166 (4)	4.4
H(C5)	259 (2)	1355 (6)	569 (3)	2.7
H(C6)	398 (2)	1337 (8)	736 (4)	7.2
H(C7)	482 (2)	1030 (7)	696 (3)	4.4
H(C8)	434 (2)	726 (6)	505 (3)	3.1
H1(C10)	98 (2)	1160 (7)	212 (4)	5.9
H2(C10)	141 (2)	1348 (8)	338 (4)	4.2
H(O1)	-21 (3)	1214 (12)	414 (6)	10.5

* The e.s.d.'s in B range from 0.7 to 2.2 \AA^2 with an average value of 1.2 \AA^2 .

Table 2. Bond lengths (\AA) with e.s.d.'s in parentheses

N(1)—C(2)	1.361 (5)	C(11)—O(1)	1.310 (4)
C(2)—C(3)	1.363 (5)	C(11)—O(2)	1.210 (4)
C(3)—C(4)	1.428 (4)		
C(4)—C(5)	1.404 (4)	N(1)—H(N1)	0.79 (5)
C(5)—C(6)	1.376 (5)	C(2)—H(C2)	1.02 (3)
C(6)—C(7)	1.387 (6)	C(5)—H(C5)	0.95 (3)
C(7)—C(8)	1.373 (5)	C(6)—H(C6)	1.04 (4)
C(8)—C(9)	1.386 (4)	C(7)—H(C7)	1.07 (3)
C(9)—C(4)	1.393 (4)	C(8)—H(C8)	0.96 (3)
C(9)—N(1)	1.384 (4)	C(10)—H1(C10)	0.98 (3)
C(3)—C(10)	1.480 (5)	C(10)—H2(C10)	0.92 (4)
C(10)—C(11)	1.511 (6)	O(1)—H(O1)	0.82 (6)

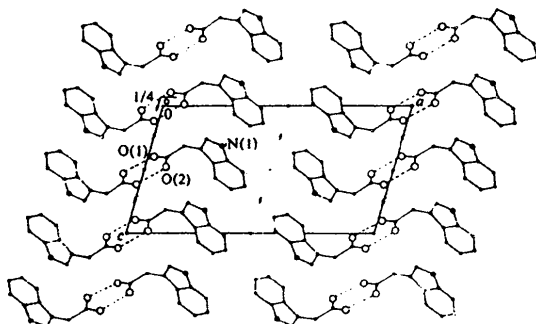


Fig. 2. Crystal structure projected down b . Hydrogen bonds are shown by broken lines.

Table 3. Bond angles ($^\circ$) with e.s.d.'s in parentheses

N(1)—C(2)—C(3)	109.7 (3)	H(N1)—N(1)—C(2)	136 (2)
C(2)—C(3)—C(4)	105.8 (3)	N(1)—C(2)—H(C2)	125 (1)
C(3)—C(4)—C(9)	108.7 (3)	H(C2)—C(2)—C(3)	125 (1)
C(3)—C(4)—C(5)	133.3 (3)	C(4)—C(5)—H(C5)	114 (1)
C(4)—C(9)—N(1)	105.8 (3)	H(C5)—C(5)—C(6)	127 (1)
C(4)—C(5)—C(6)	119.0 (3)	C(5)—C(6)—H(C6)	126 (2)
C(5)—C(6)—C(7)	121.5 (3)	H(C6)—C(6)—C(7)	112 (2)
C(6)—C(7)—C(8)	121.0 (3)	C(6)—C(7)—H(C7)	120 (1)
C(7)—C(8)—C(9)	117.2 (3)	H(C7)—C(7)—C(8)	119 (1)
C(8)—C(9)—C(4)	123.4 (3)	C(7)—C(8)—H(C8)	121 (1)
C(8)—C(9)—N(1)	130.8 (3)	H(C8)—C(8)—C(9)	122 (1)
C(9)—C(4)—C(5)	117.9 (3)	C(9)—N(1)—H(N1)	114 (2)
C(9)—N(1)—C(2)	109.9 (3)	C(3)—C(10)—H1(C10)	109 (2)
C(2)—C(3)—C(10)	126.4 (3)	C(3)—C(10)—H2(C10)	110 (2)
C(4)—C(3)—C(10)	127.7 (3)	H1(C10)—C(10)—C(11)	104 (2)
C(3)—C(10)—C(11)	114.9 (3)	H2(C10)—C(10)—C(11)	106 (2)
C(10)—C(11)—O(1)	113.5 (3)	H1(C10)—C(10)—H2(C10)	114 (2)
C(10)—C(11)—O(2)	123.8 (3)	C(11)—O(1)—H(O1)	119 (2)
O(1)—C(11)—O(2)	122.7 (3)		

The packing of the molecule is shown in Fig. 2. The carboxyl group adopts the synplanar motif and the molecules dimerize with O—H...O hydrogen bonds across centres of symmetry. The O...O distance of 2.653 (4) \AA is similar to distances in many other acid dimers and the O—H...O angle is 160 (4) $^\circ$.

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References

- CHANDRASEKHAR, K. & PATTABHI, V. (1980). *Acta Cryst.* **B36**, 1165–1169.
- FALKENBERG, G. & CARLSTRÖM, D. (1971). *Acta Cryst.* **B27**, 411–418.
- GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Program *UCLALS 1*, Univ. of California.
- INOUE, M., SAKAKI, T., FUJIWARA, T. & TOMITA, K. (1978). *Bull. Chem. Soc. Jpn*, **51**, 1118–1122.
- International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.
- KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* **17**, 496–499.
- MAIN, P. & WOOLFSON, M. M. (1963). *Acta Cryst.* **16**, 731–733.
- RAGHUNATHAN, S. & PATTABHI, V. (1981). *Int. J. Quantum Chem.* **20**, 151–158.
- SHIONO, R. (1968). Block-diagonal least-squares program for the IBM-1130 computer. Department of Crystallography, Univ. of Pittsburgh.
- SMITH, G. & KENNARD, C. H. L. (1979). *J. Agric. Food Chem.* **27**, 779–786.