*Acta Cryst.* (1974). B30, 1119

# *o*-Iodobenzonitrile

By Sylvia Lam and Doyle Britton

*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota* 55455, *U.S.A.*

(*Received* 17 *August* 1973; *accepted* 10 *December* 1973)

**Abstract.** $C_6H_4(CN)I$ was prepared from *o*-iodoaniline *via* the Sandmeyer reaction and recrystallized by sublimation (m.p. 52°); orthorhombic, $Pna2_1$ (No. 33), $a = 11{\cdot}565$ (8), $b = 15{\cdot}056$ (21), $c = 4{\cdot}204$ (14) Å, $V = 731$ Å$^3$, $D_{calc} = 2{\cdot}08$, $D_{obs} = 2{\cdot}03$ g cm$^{-3}$. The molecular dimensions are normal except that the iodine atom is 0·14 Å out of the plane of the rest of the molecule. In contrast to *p*-iodobenzonitrile, there are no intermolecular CN···I contacts, but intermolecular I···I contacts of 3·83 Å are present.

**Introduction.** 787 independent reflections were collected for $0 < \theta < 24°$ on a Hilger and Watts 4-circle automated diffractometer using Zr-filtered Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation. Only the 422 reflections with $I > 2\sigma(I)$ were used in the subsequent calculations. A crystal $0{\cdot}28 \times 0{\cdot}14 \times 0{\cdot}10$ mm was used; no absorption corrections were made ($\mu = 42{\cdot}7$ cm$^{-1}$). Corrections were made for the slow decomposition of the crystal in the X-ray beam (the intensities of two check reflections decreased by 30% during the course of the data collection). Systematic extinctions ($0kl$, $k+l = 2n+1$; $h0l$, $h = 2n+1$) indicate the space group to be either *Pnam* or $Pna2_1$; the latter was confirmed by the eventual solution of the structure. A trial structure was found from Patterson and Fourier maps and refined by full-matrix least squares with all atoms with anisotropic thermal parameters. For details of the experimental arrangements, weights, calculations, and programs used, see Chow & Britton (1974). Corrections were made for the real and imaginary parts of the anomalous dispersion. The refinement converged with $R = 0{\cdot}053$. The final parameters are given in Table 1.*

**Discussion.** The bond distances and angles are shown on two of the molecules in Fig. 1. The e.s.d.'s are 0·02 Å for the I–C distance, 0·05 Å for the other distances,

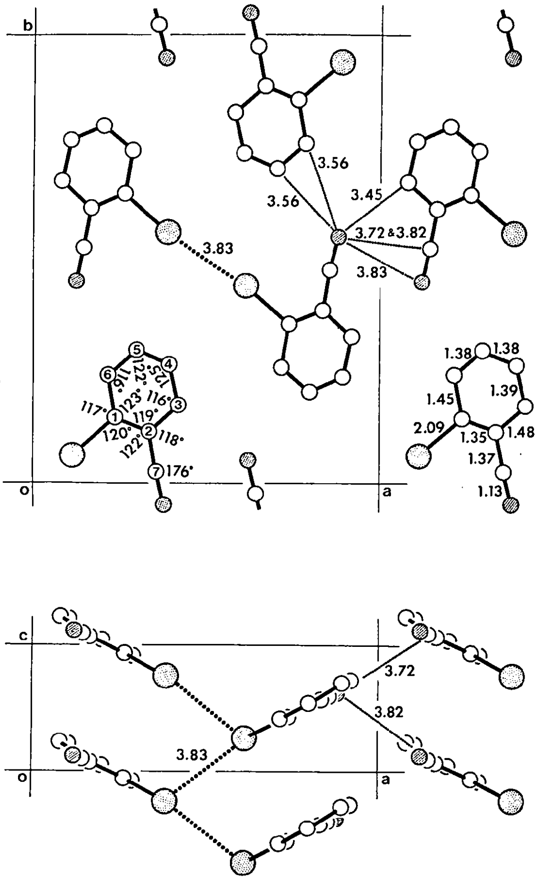

Fig. 1. The crystal structure of *o*-iodobenzonitrile. Top: view along **c**. Bottom: view along **b**. Bond lengths, in Å, and angles are shown in two of the molecules in the top figure. Intermolecular distances are shown in both figures. Hydrogen atoms are omitted for clarity.

Table 1. *Positional and thermal parameters* (× $10^4$)

Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \cdots + 2\beta_{12}hk + \cdots)]$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| I | 1130 (1) | 615 (1) | 2500 | 82 (1) | 51 (1) | 624 (11) | −16 (1) | −44 (12) | −59 (7) |
| N | 3772 (25) | −491 (20) | 6168 (75) | 128 (25) | 79 (16) | 1460 (330) | −46 (29) | −87 (74) | 110 (76) |
| C(1) | 2384 (19) | 1470 (18) | 4337 (62) | 41 (20) | 59 (17) | 371 (163) | −13 (15) | 17 (51) | −25 (47) |
| C(2) | 3350 (22) | 1136 (16) | 5688 (66) | 66 (23) | 29 (15) | 801 (215) | −12 (15) | 48 (65) | −111 (51) |
| C(3) | 4185 (20) | 1747 (18) | 7228 (189) | 106 (28) | 70 (16) | 920 (300) | −50 (17) | 158 (171) | 15 (133) |
| C(4) | 3920 (28) | 2643 (15) | 7035 (199) | 166 (32) | 17 (11) | 1133 (521) | −30 (19) | 216 (161) | −61 (80) |
| C(5) | 2971 (22) | 2969 (16) | 5426 (73) | 89 (27) | 30 (14) | 836 (239) | −17 (17) | −7 (73) | 62 (52) |
| C(6) | 2150 (23) | 2413 (16) | 4125 (81) | 105 (26) | 28 (14) | 741 (212) | −7 (17) | 123 (66) | 26 (47) |
| C(7) | 3542 (31) | 238 (27) | 5950 (82) | 154 (44) | 58 (17) | 660 (221) | −13 (26) | 147 (82) | −37 (66) |

---

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30316 (9 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England, or from the authors.

and 2–3° for the angles. Within these limits all of the distances and angles in the molecule are normal. The iodine atom is 0·14 Å out of the least-squares plane through the six ring atoms; the largest deviation of any of the eight light atoms from the plane is 0·03 Å.

The reason for studying this structure was to compare the packing with that of *p*-iodobenzonitrile. In *p*-iodobenzonitrile the molecules are aligned in linear chains held together by CN···I interactions between molecules (Schlemper & Britton, 1965). An interaction of this sort seemed a possibility for *o*-iodobenzonitrile. On the other hand, in 2,4,6-trichlorobenzonitrile and 2,4,6-tribromobenzonitrile (Carter & Britton, 1972) adjacent molecules are held together by pairs of nonlinear CN···X interactions, the cyanide group and an *ortho* halogen atom on one molecule interacting, respectively, with the *ortho* halogen atom and the cyanide group on the next molecule. Although this geometry seems less reasonable than the previous one, given the location of the lone pair of electrons on the cyanide group, nevertheless it does occur, and it also seemed a possibility for an interaction in *o*-iodobenzonitrile.

However, the packing of the molecules, shown in Fig. 1, does not involve any CN···I interaction. Rather, there are short I···I contacts of 3·83 Å similar in arrangement to those in $I_2$, where the I···I distance is 3·56 Å (Kitaigorodskii, Khocjanova & Stručkov, 1953), and in *p*-diiodobenzene, where it is 4·01 Å (Dun-Chaj & Stručkov, 1959). In addition the cyanide groups in adjacent molecules are approximately anti-parallel, which would favor dipole–dipole interactions, although the distance of 3·8 Å is not at all short. Indeed, in 4-cyanopyridine (Laing, Sparrow & Sommerville, 1971) where a similar arrangement occurs, except that the cyanide groups are exactly anti-parallel, the distance between groups is 3·6 Å. While the intermolecular interactions are different in the *ortho* and *para* compounds, both compounds have the same molecular volume, 183 Å$^3$; that is, the average efficiency of packing is the same in both compounds.

We thank the National Science Foundation for their support of this work.

### References

Carter, V. B. & Britton, D. (1972). *Acta Cryst.* **B28**, 945–950.

Chow, Y. M. & Britton, D. (1974). *Acta Cryst.* **B30**, 147–151.

Dun-Chaj, L. & Stručkov, Ju. T. (1959). *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, pp. 2095–2099. *Struct. Rep.* **23**, 649–650.

Kitaigorodskii, A. I., Khocjanova, T. L. & Stručkov, Ju. T. (1953). *Z. Fiz. Khim. SSSR*, **27**, 780–781. *Struct. Rep.* **17**, 315.

Laing, M., Sparrow, N. & Sommerville, P. (1971). *Acta Cryst.* **B27**, 1986–1990.

Schlemper, E. O. & Britton, D. (1965). *Acta Cryst.* **18**, 419–424.

---

*Acta Cryst.* (1974). B30, 1120

# $\mu_3$-Hydroxo(oxo)-tri-$\mu$-(2-propylamino-2-methyl-3-butanone oximato)-triaquo-tricopper(II) Perchlorate.$4H_2O$

By P. F. Ross, R. K. Murmann and E. O. Schlemper

*Department of Chemistry, University of Missouri, Columbia, Missouri* 65201, *U.S.A.*

(*Received* 7 *November* 1973; *accepted* 14 *December* 1973)

**Abstract.** $[Cu_3(C_8H_{17}N_2O)_3(H_2O)_3OH_{1/2}](ClO_4)_{3/2}(H_2O)_4$, trigonal, $R\bar{3}$, $a = 14·44\ (1)$, $c = 35·05\ (4)$ Å; $\varrho_o = 1·49\ (1)$, $\varrho_c = 1·502\ (3)$ g cm$^{-3}$ (six molecule ions per cell). In the trinuclear complex the copper atoms are arranged in an equilateral triangle (Cu–Cu = 3·246 Å) about a bridging oxygen on the threefold axis. Each copper atom is bonded to a square plane of ligand atoms including two nitrogen atoms (average Cu–N = 1·99 Å) and one oxygen atom of the bridging oxime groups and the central oxygen atom (average Cu–O = 1·95 Å). Above and below the square plane are a more weakly bonded perchlorate ion and a water molecule.

**Experimental.** The copper complex (CuPrAO) was prepared as described in the literature (Young & Murmann, 1963), and suitable crystals obtained by slow evaporation of an aqueous solution. The dark green hexagonal plates were mounted with a thin coating of epoxy resin to help prevent loss of water which occurred rapidly upon removal from the solvent.

Analysis: Calculated for $Cu_3C_{24}H_{65·5}N_6O_{17}Cl_{1·5}$ C = 30·04, H = 6·88, N = 8·76%. Found C = 30·83, H = 6·17, N = 9·03. This analysis reflects the partial dehydration which occurs spontaneously and may be compared with the dehydrated complex analysis (Young & Murmann, 1963). C = 33·53, H = 6·11, N = 9·97. Preliminary precession film studies using Cu $K\alpha$ radiation revealed trigonal symmetry with systematic absences on $hkl$ for $-h+k+l=3n$, indicative of rhombohedral space group $R3$ or $R\bar{3}$. The latter space group was indicated by the subsequent structure re-