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The Crystal and Molecular Structure of *o*-Phenanthroline

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The crystal structure of *o*-phenanthroline, $C_{12}H_8N_2$, has been determined from three-dimensional X-ray data collected by the counter method. Hygroscopic single crystals obtained by sublimation in vacuum belong to the monoclinic space group *C*2, with unit-cell dimensions: $a = 19{\cdot}914\ (3)$, $b = 7{\cdot}405\ (1)$, $c = 9{\cdot}451\ (1)$ Å, $\beta = 99{\cdot}60\ (1)°$. The unit cell contains six molecules, four of which (type I) are located at general positions, while the other two (type II) are assigned to special positions with crystallographic symmetry 2 (C_2). The structure was solved by the *R*-map method and refined by least-squares procedures to a conventional *R* of 0·059 for 747 observed $[|F_o| > 3\sigma(F_o)]$ reflexions. Molecules (I) and (II) with approximate symmetry *mm* (C_{2v}) have similar bond lengths and angles, but somewhat different planarities. All bond lengths and angles are in the expected range. The crystal structure consists of herringbone-like two-dimensional layers of (I) interleaved with layers of (II); the dipole-moment vectors of the molecules are favourably arranged for an attractive interaction in the crystals.

Introduction

o-Phenanthroline (*o*-phen, or 1,10-phen) is well known as a bidentate ligand in coordination chemistry. Many metal complexes involving *o*-phen as a ligand have been studied by X-ray crystallographic analysis. However, no successful structure determination of *o*-phen itself has been reported.† Thus the crystal structure analysis of *o*-phen has been undertaken to obtain an accurate molecular structure and to provide a structural basis for the transition-metal–*o*-phen chelating system. Moreover, it is of interest to compare the crystal and molecular structure of *o*-phen with that of phenanthrene (Trotter, 1963; Kay, Okaya & Cox, 1971). *o*-Phen is a polar molecule having a finite dipole moment of 4·11 D (1 D = $3{\cdot}335\ 640 \times 10^{-30}$ C m), whereas phenanthrene is non-polar with zero moment (McClellan, 1963). The present study is part of the structural studies of molecules used as bidentate ligands in coordination chemistry, and a short report has already appeared (Nakatsu, Yoshioka, Matsui, Koda & Ooi, 1972).

Experimental

o-Phenanthroline hydrate of guaranteed reagent grade from Wako Pure Chemical Industries Ltd, Japan, was sublimed slowly in vacuum at about 100°C to produce anhydrous single crystals. The crystals were thin colourless platelets elongated along **b**. Very hygroscopic crystals were sealed in a nitrogen-filled glass capillary tube for X-ray work. Preliminary oscillation and Weissenberg photographs indicated that the space group was either *C*2, *Cm*, or *C*2/*m*; *C*2 was later proved to be correct on the basis of the successful structure analysis (see below). Accurate cell parameters were obtained by a least-squares procedure applied to 12 reflexions measured on a diffractometer with Mo *Kα* radiation.

Crystal data of o-phenanthroline

$C_{12}H_8N_2$, $M_r = 180{\cdot}209$, monoclinic, $a = 19{\cdot}914\ (3)$,† $b = 7{\cdot}405\ (1)$, $c = 9{\cdot}451\ (1)$ Å, $\beta = 99{\cdot}60\ (1)°$, $U = 1374\ (2)$ Å^3, $D_x = 1{\cdot}307$ g cm^{-3}, $Z = 6$, $F(000) = 564$, μ(Mo $K\alpha$) = 0·86 cm^{-1}. Systematic absences: *hkl* when $h + k$ is odd. Space group *C*2.

A specimen approximately $0{\cdot}61 \times 0{\cdot}35 \times 0{\cdot}09$ mm was used for X-ray data collection on a manual four-circle goniometer. Three-dimensional integrated intensity data were collected at 25 °C with graphite-monochromatized Mo *Kα* radiation ($\lambda = 0{\cdot}7107$ Å). The θ–2θ scan technique was used at a scan rate of 1·0° min^{-1} (in 2θ), with stationary background counts of 20 s duration on either side of the peak. As a check on the deterioration of the specimen and the stability of the electronic circuit, the intensities of three reflexions were measured periodically during the nine days of data collection; the intensities of these reflexions remained satisfactorily constant throughout the run. The intensities were corrected for Lorentz and polarization

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† Donnay, Donnay & Harding (1965) reported and discussed the crystal data of *o*-phen.H_2O and Nishigaki, Yoshioka & Nakatsu (1975) established its space group. (The structure of *o*-phen.H_2O has also been determined but will be reported separately.)

† Throughout this paper the estimated standard deviation (e.s.d.) in the least significant digit of the preceding value is given in parentheses.

effects and converted to structure amplitudes in the usual way. No corrections were applied for absorption or extinction. 1309 unique intensities with $2\theta < 50°$ were measured and of these only 747 reflexions with $|F_o| > 3\sigma(F_o)$ were used for the structure determination.

Structure determination and refinement

On the basis of the shape and size of the molecule, the Patterson map, and the cell dimensions, the space group $C2$ was considered, and of the six molecules in a cell four (I) were assigned to general positions [4(*c*)] and the other two (II) to the special positions 2(*a*) having twofold symmetry. The *R*-map method, or a systematic trial method to obtain minimum *R*, was employed to locate the molecules. The rigid molecular model used was constructed by the use of appropriate bond lengths and angles. After several trials, one model with the lowest *R* index of 0·31 for the 38 lowest-angle reflexions was subjected to rigid-body structure-factor least-squares refinement, using a modified version of the program written by M. Shiro (private communication). In this procedure both molecules are treated separately to refine six parameters (orientation and translation) and one parameter (rotation about the twofold axis) for (I) and (II) respectively. Only a limited data set was used (319 reflexions) and the *R* index was reduced from 0·43 to 0·17.

Table 1. *Final fractional coordinates* ($\times 10^4$ *for* N *and* C; $\times 10^3$ *for* H) *with their e.s.d.'s*

The hydrogen atoms are numbered according to the heavier atoms to which they are bonded.

	x	*y*	*z*
Molecule I			
N(1)	1121 (2)	4567 (8)	5310 (5)
C(2)	830 (3)	4377 (11)	3967 (7)
C(3)	1181 (4)	3892 (12)	2856 (7)
C(4)	1861 (4)	3620 (11)	3164 (7)
C(5)	2908 (4)	3581 (12)	5050 (10)
C(6)	3206 (3)	3799 (11)	6407 (10)
C(7)	3097 (4)	4613 (15)	8941 (9)
C(8)	2711 (5)	5147 (16)	9909 (9)
C(9)	2014 (4)	5336 (13)	9419 (7)
N(10)	1711 (3)	5052 (10)	8096 (5)
C(11)	2108 (3)	4544 (9)	7112 (6)
C(12)	1802 (3)	4288 (10)	5634 (6)
C(13)	2194 (3)	3814 (10)	4595 (7)
C(14)	2817 (3)	4278 (11)	7489 (8)
H(2)	30 (3)	433 (10)	363 (6)
H(3)	95 (3)	378 (11)	180 (6)
H(4)	210 (3)	349 (12)	237 (6)
H(5)	313 (3)	309 (11)	434 (6)
H(6)	371 (3)	343 (11)	665 (7)
H(7)	357 (4)	458 (15)	927 (7)
H(8)	283 (3)	553 (12)	1092 (7)
H(9)	176 (3)	592 (9)	1002 (6)
Molecule II			
N(1′)	285 (3)	1623 (8)	−1215 (5)
C(2′)	535 (3)	1616 (12)	−2409 (7)
C(3′)	656 (3)	70 (15)	−3165 (7)
C(4′)	531 (4)	−1596 (14)	−2624 (7)
C(5′)	123 (3)	−3289 (11)	−614 (7)
C(12′)	145 (2)	0*	−671 (6)
C(13′)	268 (3)	−1659 (11)	−1308 (7)
H(2′)	58 (3)	280 (9)	−294 (6)
H(3′)	86 (3)	3 (13)	−408 (6)
H(4′)	70 (3)	−280 (10)	−295 (6)
H(5′)	22 (3)	−433 (9)	−96 (6)

* Held invariant to fix the origin in space group $C2$.

The structure was then refined by the usual least-squares procedure, in which the function $\Sigma\, w(\Delta F)^2$ was minimized, where $\Delta F = |F_o| - |F_c|$ and w is the weight. The weighting scheme employed in the final stage of the refinement was $w = 1/[\sigma^2(F_o) + 0{\cdot}0014|F_o|^2]$. Isotropic followed by anisotropic block-diagonal least-squares refinement gave $R = 0{\cdot}094$. The y coordinate of C(12′) (Fig. 1) was held invariant to fix the origin in the space group $C2$. A difference Fourier map calculated at this stage revealed all the H atoms, which were refined isotropically. The final cycle of the least-squares calculations gave $R = 0{\cdot}059$ and $R_w = [\Sigma\, w(\Delta F)^2/\Sigma\, w|F_o|^2]^{1/2} = 0{\cdot}065$. In the final difference Fourier map all the residual peaks were less than 0·14 e Å^{-3}, equivalent to less than 4% of a C atom and 31% of an H atom. In the calculations of F_c the atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

All computations were carried out on a FACOM 270/20 computer of this university with programs developed by the authors. *DEAM* was used for drawing thermal ellipsoids (A. Takenaka, private communication), and *RBLS* for *R*-map and rigid-body least-squares calculations (M. Shiro, private communication).

The final positional parameters are presented in Table 1.*

Description of the structure and discussion

Fig. 1 shows the molecular structures with thermal ellipsoids at the 20% probability level and the atomic labelling scheme. Both molecules have approximate *mm* (C_{2v}) symmetry. Table 2 lists the bond lengths and angles. The e.s.d.'s are rather large (means for the non-hydrogen atoms: 0·01 Å and 0·6°) because of the limited number of reflexions available for the present complex structure (the number of parameters determined is 237). Table 3 gives equations of relevant least-

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33101 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

squares planes and the deviations of atoms from these planes. Molecule (I) assumes a shallow-boat shape: significant deviations of the atoms from the central plane (*B*) are observed, though each of the six-membered rings is exactly planar. On the other hand, molecule (II) is slightly twisted around its twofold axis (this is apparent from Fig. 2). Thus molecules (I) and (II) exhibit somewhat different distortions from complete planarity; this is probably because of their different environments.

As shown in Table 2, the lengths of chemically equivalent bonds [over (I) and (II)] are in fairly good agreement with each other within their error limits, except for those of C(11)–C(12) in (I) and C(12)–C(12′) in (II); the former is almost significantly shorter than the latter. Among the chemically equivalent angles, *cd*, *ei* and *fi* differ. The mean bond angle at the N atoms (117·7°) agrees well with those so far observed for ring N atoms without any extra-annular attachment (Singh, 1965), and also with those found in *o*-phen complexes; this suggests that the electronic state of the N atom is not influenced appreciably on coordination to metal atoms.

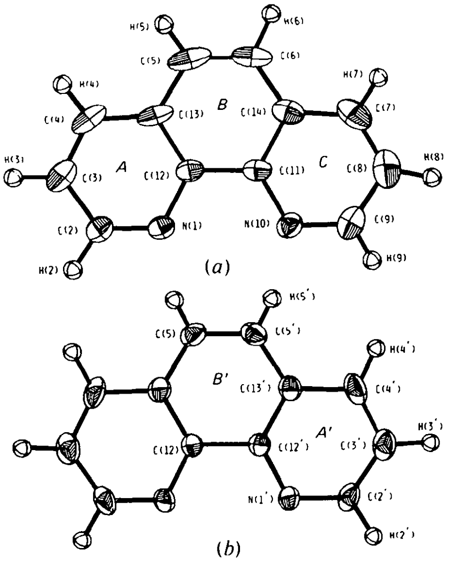
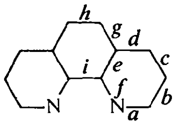


Fig. 1. Molecular structure of *o*-phenanthroline. Thermal ellipsoids are drawn to include the 20% probability level, except those for H atoms, which are represented by spheres of an arbitrary fixed radius. (*a*) Molecule (I), (*b*) molecule (II).

Table 2. *Bond distances* (Å) *and angles* (°)



Bond	Molecule (I) Left half		Molecule (I) Right half		Molecule (II)		Weighted mean*	Calculated length
a	1–2	1·317 (7)	9–10	1·312 (8)	1′–2′	1·307 (9)	1·313 (5)	1·330
b	2–3	1·402 (11)	8–9	1·394 (12)	2′–3′	1·391 (13)	1·396 (7)	1·409
c	3–4	1·352 (11)	7–8	1·348 (13)	3′–4′	1·374 (15)	1·356 (7)	1·387
d	4–13	1·410 (9)	7–14	1·414 (11)	4′–13′	1·429 (10)	1·417 (6)	1·414
e	12–13	1·397 (10)	11–14	1·412 (8)	12′–13′	1·407 (11)	1·406 (5)	1·411
f	1–12	1·354 (7)	10–11	1·369 (8)	1′–12′	1·354 (10)	1·359 (5)	1·347
g	5–13	1·427 (10)	6–14	1·426 (12)	5′–13′	1·425 (11)	1·426 (6)	1·437
h		5–6	1·330 (12)		5′–5	1·333 (13)	1·331 (9)	1·368
i		11–12	1·441 (8)		12′–12	1·478 (11)	1·454 (6)	1·445

Angle	Molecule (I) Left half		Molecule (I) Right half		Molecule (II)		Mean
ab	1–2–3	123·8 (6)	8–9–10	125·1 (8)	1′–2′–3′	124·7 (8)	124·4 (4)
bc	2–3–4	118·9 (6)	7–8–9	116·9 (7)	2′–3′–4′	119·3 (7)	118·4 (4)
cd	3–4–13	119·0 (7)	8–7–14	122·2 (7)	3′–4′–13′	118·0 (8)	119·9 (4)
de	4–13–12	118·2 (6)	7–14–11	115·8 (7)	4′–13′–12′	117·3 (7)	117·2 (4)
ef	1–12–13	122·3 (5)	10–11–14	122·2 (5)	1′–12′–13′	123·4 (5)	122·6 (3)
af	2–1–12	117·9 (5)	9–10–11	117·8 (6)	2′–1′–12′	117·2 (6)	117·7 (3)
dg	4–13–5	124·2 (7)	7–14–6	124·5 (6)	4′–13′–5′	124·0 (7)	124·3 (4)
gh	6–5–13	122·5 (8)	5–6–14	120·9 (6)	5–5′–13′	122·2 (7)	121·7 (4)
eg	5–13–12	117·7 (6)	6–14–11	119·6 (6)	5′–13′–12′	118·7 (6)	118·7 (3)
ei	11–12–13	121·3 (5)	12–11–14	118·1 (6)	12–12′–13′	119·2 (7)	119·8 (3)
fi	1–12–11	116·5 (5)	10–11–12	119·7 (5)	1′–12′–12	117·4 (6)	117·9 (3)

* Weighted mean for the chemically equivalent bonds. The mean value (p_a) and its e.s.d. (σ_a) were estimated according to $p_a = \Sigma_i(p_i/\sigma_i^2)$ and $\sigma_a = [1/\Sigma_i(1/\sigma_i^2)]^{1/2}$, where p_i and σ_l were individual values.

In the last two columns of Table 2 the mean bond lengths are compared with the theoretical values calculated by an SCF–MO method (K. Nishimoto, private communication). The agreement is fairly good, except for bonds *a* and *h*, whose MO lengths are somewhat larger than the X-ray values. This implies that, as expected from the MO theory, the formula for obtaining bond length from bond order is inadequate for those bonds in which a high π-bond order is involved. Bond *h* is as short as the olefinic double bond, and bond *i* is the longest in the molecule. Thus *o*-phen may be regarded, from the viewpoint of MO theory, as containing a C=C bond fused at the 6 and 6′ positions of 2,2′-bipyridyl.

A comparison of the mean bond distances and angles of *o*-phen with the corresponding X-ray values of phenanthrene (Kay, Okaya & Cox, 1971), except for those including the N atoms, indicates that the bond angles *de*, *eg*, *dg*, and *bc* (see Table 2) differ significantly, while the other angles and distances are in close agreement. The cause of these discrepancies is not obvious.

Fig. 2 shows the molecular packing viewed down **b**. The crystal structure consists of alternate layers of molecules (I) and (II) along **a**, each layer being parallel to the *bc* plane. Both molecular planes are nearly perpendicular to each other (88°). The packing of molecule (I) in its layer (shown in Fig. 3) is interpenetrating and herringbone-like. The normal of molecule (I) makes an angle of 15·5° with **b**. The dipole-moment vectors of molecules (I) related by the 2_1 axes are favourably oriented to attain an attractive

Table 3. *Equations of the least-squares planes and deviations* (Å) *of atoms from them*

Equations of planes (X, Y and Z are orthogonal coordinates in Å along **a**, **b** and **c*** respectively)

(A) $0{\cdot}1907X + 0{\cdot}9672Y - 0{\cdot}1676Z = 2{\cdot}7080$
(B) $0{\cdot}1802X + 0{\cdot}9676Y - 0{\cdot}1771Z = 2{\cdot}6319$
(C) $0{\cdot}1857X + 0{\cdot}9578Y - 0{\cdot}2193Z = 2{\cdot}3310$
(A') $0{\cdot}8549X - 0{\cdot}0300Y + 0{\cdot}5179Z = 0{\cdot}0259$
(B') $-0{\cdot}8539X - 0{\cdot}5204Z = 0{\cdot}0$

	Molecule (I)			Molecule (II)	
	(*A*)	(*B*)	(*C*)	(*A*′)	(*B*′)
N(1)	0·000*	0·016	0·082	0·000*	−0·059
C(2)	0·003*	0·035	0·154	0·012*	−0·066
C(3)	−0·004*	0·028	0·199	−0·011*	−0·007
C(4)	0·002*	0·018	0·186	0·000*	0·017
C(5)	0·021	0·001*	0·105	0·043	0·006*
C(6)	0·037	0·001*	0·052		
C(7)	0·106	0·055	−0·003*		
C(8)	0·162	0·112	0·007*		
C(9)	0·124	0·093	−0·002*		
N(10)	0·052	0·036	−0·007*		
C(11)	0·022	0·005*	0·010*		
C(12)	−0·002*	−0·003*	0·060	−0·012*	−0·012*
C(13)	0·001*	0·000*	0·112	0·011*	0·003*
C(14)	0·031	−0·004*	−0·005*		
Δ†	0·002	0·003	0·006	0·009	0·008

* Atoms included in the calculation of the best plane.
† R.m.s. deviation for the atoms marked with an asterisk.

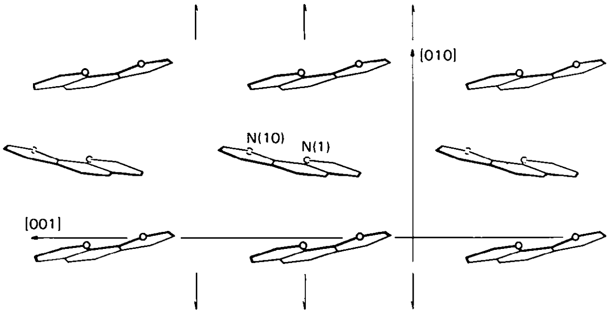


Fig. 3. Intralayer stacking of molecule (I) projected along **a***.

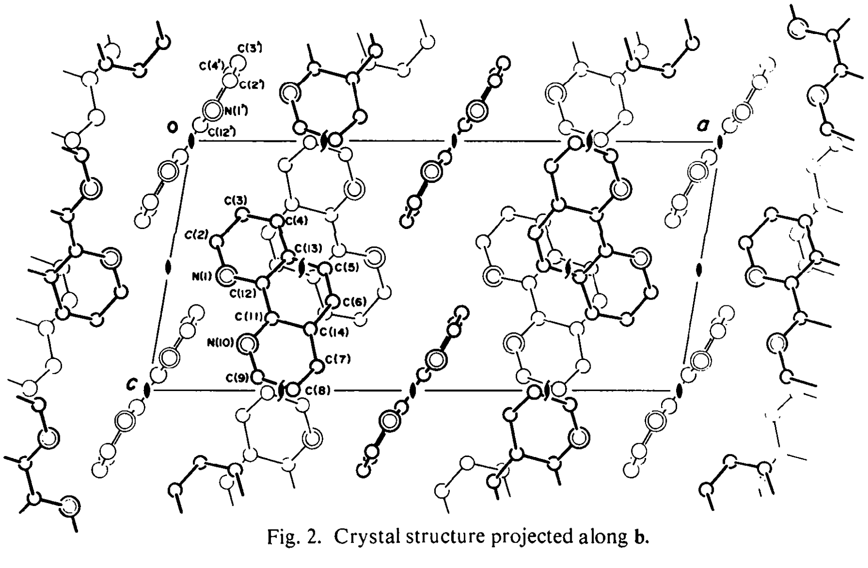


Fig. 2. Crystal structure projected along **b**.

Table 4. *Selected intermolecular distances* (Å)

Tabulated distances are: C$\cdots$C and N$\cdots$C < 3·45 Å, C$\cdots$H and N$\cdots$H < 2·90 Å, and H$\cdots$H < 2·30 Å.

(*a*) Molecule (I)–molecule (I)

C(4)$\cdots$C(14^{iv})	3·36 (1)
C(5)$\cdots$C(12^{iv})	3·31 (1)
C(12)$\cdots$H(5^{v})	2·82 (8)

(*b*) Molecule (I)–molecule (II)

N(1)$\cdots$C($2'^{\mathrm{i}}$)	3·41 (1)
N(10)$\cdots$C($2'^{\mathrm{i}}$)	3·44 (1)
N(10)$\cdots$C($4'^{\mathrm{ii}}$)	3·41 (1)
N(10)$\cdots$H($4'^{\mathrm{ii}}$)	2·62 (6)
N(1)$\cdots$H($4'^{\mathrm{ii}}$)	2·77 (7)
N(1)$\cdots$H($2'^{\mathrm{i}}$)	2·49 (7)
H(2)$\cdots$C($2'^{\mathrm{iii}}$)	2·74 (6)
H(7)$\cdots$C($12'^{\mathrm{v}}$)	2·55 (7)
H(2)$\cdots$H($2'^{\mathrm{iii}}$)	2·10 (9)

Symmetry code

None	x,y,z	(iii)	$-x,y,-z$
(i)	$x, y, 1+z$	(iv)	$\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$
(ii)	$x, 1+y, 1+z$	(v)	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$

dipole–dipole interaction. On the other hand, molecule (II) lies almost on (401) and aligns along **b** in an identical orientation, as required by symmetry. This implies that the dipole moments are aligned in a head-to-tail manner to give the best dipole–dipole attraction. Thus, the large dipole moment of the *o*-phen molecule apparently plays an important role in the packing of the molecules.

In contrast to the mode of packing of *o*-phen, crystals of 9,10-diazaphenanthrene (van der Meer, 1972), another polar diaza substituent, consist of centrosymmetric dimeric pairs; this should be another effect of dipole–dipole interaction. In the case of the non-polar phenanthrene (Trotter, 1963; Kay, Okaya & Cox, 1971), the molecules are arranged around the 2_1 axes in space group $P2_1$, but the mode of packing is different from that of *o*-phen.

Table 4 gives selected intermolecular distances. C(5)$\cdots$C(12^{iv}) and C(4)$\cdots$C(14^{iv}) are slightly shorter than the interlayer separation of about 3·4 Å in graphite. Some C$\cdots$H and N$\cdots$H distances are less than the sum of the van der Waals radii. On the whole, the intermolecular distances in *o*-phen are shorter than those in phenanthrene; this reflects the smaller molecular volume of *o*-phen (U/Z: 229 Å^3) than that of phenanthrene (245 Å^3), implying a denser packing in *o*-phen, and supports the idea that an effective dipole–dipole interaction is present in crystals of *o*-phen.

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