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Structure of the Complex Formed Between Ammonium Picrate and 1,10-Phenanthroline

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Abstract

$NH_4(C_6H_2N_3O_7).C_{12}H_8N_2$, $M_r = 426{\cdot}31$, crystallizes as yellow plates, space group $P2_1/c$, with $a = 12{\cdot}540\,(3)$, $b = 7{\cdot}710\,(2)$, $c = 18{\cdot}871\,(3)$ Å, $\beta = 90{\cdot}42\,(2)°$, $U = 1824{\cdot}4$ Å^3, $D_c = 1{\cdot}552$, $D_m = 1{\cdot}54$ Mg m^{-3}, $Z = 4$, $F(000) = 880$, μ(Mo $K\alpha$) = 0·133 mm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å. Final $R = 0{\cdot}043$ for 2178 observed reflections. The molecule is essentially a dimer of centrosymmetrically related units. Each ammonium ion forms seven hydrogen bonds: three chelating, bifurcated pairs (one to the phenanthroline molecule and two to picrate ions), and a seventh which lies approximately parallel to **c** and creates a network of dimers linked through the NH_4^+ ions and the *o*-nitro groups.

Introduction

Complexes of Na$^+$, K$^+$ and Rb$^+$ have been described with combinations of various chelating anionic and neutral ligands such as salicylate, picrate, *o*-nitrophenolate, polyethers, and 1,10-phenanthroline (Layton, Nyholm, Banerjee, Fenton, Lestas & Truter, 1970; Truter, 1971; Poonia & Truter, 1973; Poonia, 1975*a*,*b*). Studies of these complexes have been made to investigate the environments and coordination requirements of the alkali-metal ions (Bush, Lüth & Truter, 1971; Bush & Truter, 1971; Hughes, 1973, 1975; Hughes, Mortimer & Truter, 1978). Other monovalent ions with a similar radius to K$^+$ are NH_4^+ and Tl$^+$ and these may mimic K$^+$ in certain biological systems (Williams, 1970). Complexes of these ions were prepared to investigate their formation and structure (Poonia & Truter, 1972; Poonia, 1975*a*,*b*). Ammonium picrate–1,10-phenanthroline was one such complex which crystallized readily from ammoniacal solution.

Experimental

Preliminary photographic studies indicated the space group and approximate cell parameters. The latter were redetermined more accurately on a diffractometer.

3761 reflections with $2\theta < 50°$ were measured by an ω–2θ scan on an Enraf–Nonius CAD-4 automatic diffractometer (Mo $K\alpha$ radiation, Zr filter). Reflections were measured such that $\sigma(I)/I$ was ≤3%, but a maximum limit of 5 min per reflection was applied. Lorentz and polarization corrections were applied but no absorption corrections were needed as the transmission curve as a function of φ for the reflection 040 was essentially flat (North, Phillips & Mathews, 1968). 2178 significant ($I > 3\sigma_I$) structure amplitudes resulted.

Structure analysis

The structure was determined by direct methods with two different approaches. In the former, use was made of *MULTAN* 76 (Main, Lessinger, Woolfson, Germain & Declercq, 1976) which allowed molecular scattering factors to be calculated for the phenanthroline and picrate moieties. The structure factors were normalized by the analytical *K*-curve method which gave a hypercentric distribution for the calculated *E* values (Lipson & Cochran, 1966). The picrate and the phenanthroline fragments can be regarded as related by a pseudo centre of symmetry and hence give rise to the hypercentric distribution.

One phase set showed considerably more consistency than the others with a CFOM of 2·59 and a residual FOM of 28·68. The *E* map of this set (250 reflections with $E > 1{\cdot}48$) showed 13 of the 14 non-H phenanthroline atoms and 11 of the 16 non-H picrate atoms together with the N of the NH_4^+ ion between the two fragments.

The second approach used *SHELX* (Sheldrick, 1976), without molecular scattering factors, and yielded

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the same phenanthroline fragment and a slightly different picrate fragment but the NH_4^+ ion was not apparent. On the other hand, *MULTAN*, without molecular scattering information, gave ambiguous solutions with peaks at the centres of the rings.

All the H atoms except two were found from difference syntheses; the positions for the remaining H atoms were calculated. Block refinement of the structure with *SHELX* led to $R = 0{\cdot}068$. With XRAY 74 (Stewart, 1974) full-matrix refinement (all non-hydrogen atoms with anisotropic thermal parameters and H atoms isotropic) gave $R = 0{\cdot}06$, with all reflections equally weighted. A weighting scheme was then introduced: $w = 1$ except for reflections with (*a*) $\sin\theta < 0{\cdot}05$ and $F_o > 80$, where $w = (\sin\theta/0{\cdot}05)\,(80/F_o)$, or (*b*) $0{\cdot}8F_o > |F_c|$, where $w = 0$. Refinement was concluded with $R = 0{\cdot}043$ for the 2178 reflections.*

The largest features in the final difference map are peaks of $0{\cdot}1\ \text{e}\,\text{Å}^{-3}$ in the regions of the C—C, C—N, N—O bonds in the picrate and phenanthroline molecules.

Description of the structure and discussion

Table 1 lists the coordinates of the atoms of the crystal chemical unit (c.c.u.). A second c.c.u. is related to the first by the centre of symmetry at ($\frac{1}{2}$,0,0) and produces a dimer pair which is the main structural feature. The atom numbering is shown in Fig. 1. Fig. 2 shows the dimensions of the picrate and phenanthroline ligands.

The NH_4^+ ion is hydrogen bonded to seven acceptor atoms (Table 2 and Fig. 3). The four H atoms of this ion are well defined and refined satisfactorily in the analysis. Table 3, which lists the short intermolecular distances, also identifies the symmetry-related atomic positions in the space group, *e.g.* (I) represents coordinates at $(1-x, -y, -z)$.

Three of the H atoms of the NH_4^+ ion form bifurcated, chelating hydrogen bonds with: (i) the pair of N atoms of the phenanthroline ligand; (ii) O(1) and O(21) of the picrate ion; and (iii) O(1) and O(62) of the symmetry-related picrate ion (I). The fourth H atom is bonded singly to O(61) of another symmetry-related picrate ion (II) in a neighbouring dimer. These hydrogen bonds link the dimer pairs throughout the structure parallel to **c**.

Table 1. *Atomic coordinates (fractional* $\times 10^4$) *and isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

E.s.d.'s are in parentheses. An asterisk denotes U_{eq}, the equivalent value of the anisotropic temperature factor coefficients, calculated from the expression $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{iso}
Ammonium ion				
*A*N	5421 (2)	−1059 (4)	922 (1)	47 (1)*
*A*H(1)	6224 (35)	−935 (48)	823 (18)	107 (12)
*A*H(2)	5150 (26)	−18 (49)	912 (16)	62 (11)
*A*H(3)	5095 (26)	−1763 (44)	596 (17)	74 (10)
*A*H(4)	5376 (35)	−1493 (58)	1347 (25)	97 (15)
Picrate ion				
C(1)	4158 (2)	−3563 (3)	−693 (1)	36 (1)*
C(2)	3317 (2)	−4518 (3)	−342 (1)	35 (1)*
C(3)	2558 (2)	−5471 (3)	−695 (1)	38 (1)*
C(4)	2590 (2)	−5624 (3)	−1422 (1)	37 (1)*
C(5)	3397 (2)	−4843 (3)	−1803 (1)	38 (1)*
C(6)	4151 (2)	−3866 (3)	−1457 (1)	36 (1)*
O(1)	4802 (1)	−2575 (2)	−386 (1)	50 (1)*
N(2)	3205 (2)	−4464 (3)	429 (1)	43 (1)*
O(21)	3888 (2)	−3773 (3)	793 (1)	67 (1)*
O(22)	2420 (2)	−5149 (3)	689 (1)	67 (1)*
N(4)	1741 (2)	−6519 (3)	−1791 (1)	46 (1)*
O(41)	1014 (2)	−7127 (3)	−1439 (1)	62 (1)*
O(42)	1780 (2)	−6634 (3)	−2438 (1)	63 (1)*
N(6)	4952 (2)	−3079 (3)	−1905 (1)	45 (1)*
O(61)	4948 (2)	−3427 (4)	−2529 (1)	100 (1)*
O(62)	5598 (2)	−2083 (3)	−1664 (1)	72 (1)*
H(3)	2056 (22)	−6028 (36)	−452 (13)	55 (8)
H(5)	3443 (19)	−4957 (31)	−2296 (12)	47 (7)
Phenanthroline molecule				
N(11)	7370 (2)	−296 (3)	231 (1)	44 (1)*
C(12)	7349 (2)	−582 (4)	−460 (1)	48 (1)*
C(13)	8073 (3)	118 (4)	−930 (1)	60 (1)*
C(14)	8859 (2)	1177 (4)	−671 (1)	60 (1)*
C(15)	9716 (2)	2632 (4)	375 (2)	58 (1)*
C(16)	9763 (2)	2880 (4)	1071 (2)	59 (1)*
C(17)	9047 (3)	2291 (4)	2280 (2)	60 (1)*
C(18)	8288 (3)	1514 (4)	2679 (1)	67 (1)*
C(19)	7489 (2)	550 (4)	2352 (1)	57 (1)*
N(20)	7421 (2)	308 (3)	1656 (1)	47 (1)*
C(21)	8185 (2)	1058 (3)	1253 (1)	37 (1)*
C(22)	8148 (2)	759 (3)	493 (1)	37 (1)*
C(23)	8913 (2)	1540 (3)	61 (1)	45 (1)*
C(24)	9005 (2)	2089 (3)	1537 (1)	46 (1)*
H(12)	6796 (22)	−1384 (36)	−658 (13)	53 (7)
H(13)	7985 (24)	−182 (42)	−1474 (15)	80 (9)
H(14)	9412 (24)	1751 (38)	−957 (14)	71 (8)
H(15)	10270 (32)	3081 (47)	37 (19)	95 (11)
H(16)	10285 (25)	3526 (40)	1270 (15)	57 (8)
H(17)	9622 (28)	3072 (48)	2514 (18)	97 (12)
H(18)	8250 (29)	1580 (47)	3187 (18)	87 (11)
H(19)	6970 (22)	56 (38)	2647 (14)	65 (8)

The structures of a number of ammonium salts and complexes have been determined, and the H atoms located satisfactorily in several. A list of inorganic salts in Khan & Baur (1972) shows that the NH_4^+ ion has coordination numbers in the range 4–9 and the authors imply the existence of multiple hydrogen bonding by one H atom. Bifurcated bonds have been identified in several ammonium structures; for example: (i) in ammonium fluoroacetate (Wei & Ward, 1976), one H atom is almost equidistant from two O atoms and the N—H···O angles are 131 and 118°, showing the bonds to be approximately equivalent; (ii) in guanine picrate monohydrate and the isostructural 6-thioguanine

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35785 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

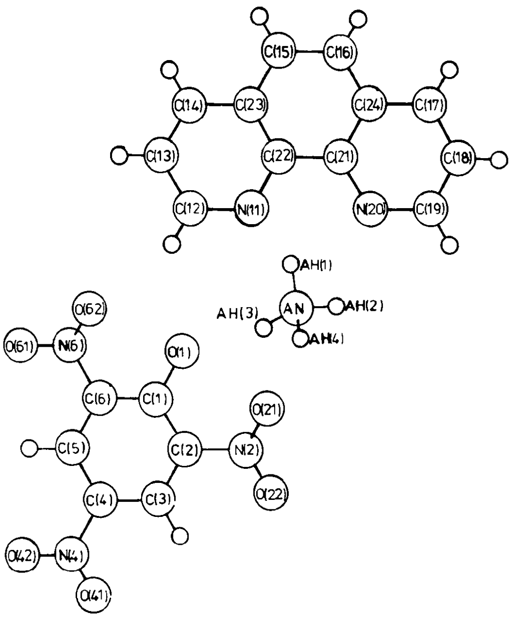

Fig. 1. The chemical crystal unit of the complex, showing the atomic numbering: unlabelled H atoms have the same numbers as their bonded C atoms.

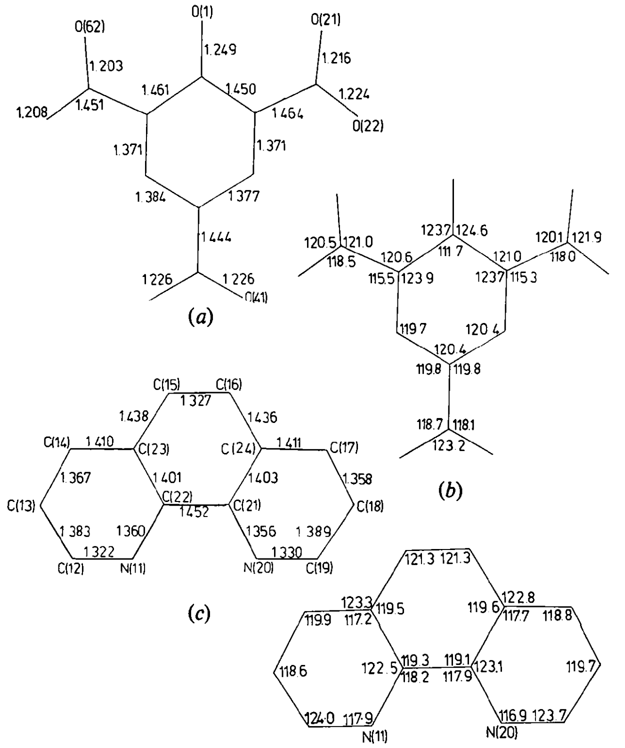

Fig. 2. Molecular dimensions in the ligands. (*a*) Picrate ion, bond lengths (Å); mean e.s.d. 0·003 Å. (*b*) Picrate ion, valence angles (°); mean e.s.d. 0·2°. (*c*) Phenanthroline ligand, bond lengths (Å); mean e.s.d. 0·004 Å. (*d*) Phenanthroline ligand, valence angles (°); mean e.s.d. 0·3°.

crystal (Bugg & Thewalt, 1975), one bond of a bifurcated pair appears slightly stronger than the second; and (iii) in ammonium picrate (Maartmann-Moe, 1969), the two independent H atoms each form markedly lop-sided bifurcated bonds: one H atom forms bonds with H···O and N–H···O dimensions of 2·02/2·45 Å and 153/116°; for the other the dimensions are 2·20/2·49 and 159/110°. In our complex, the bonds of *A*H(1) and *A*H(3) are decidely lop-sided, whereas those of *A*H(2) are almost equivalent; *A*H(4) forms a normal, single hydrogen bond. In ammonium hydrogen croconate (Baenziger & Williams, 1966), there are seven N···O distances in the range 2·86–3·02 Å, and, although the H atoms are not clearly defined, it seems probable that, as in our complex, the cation is involved in one single plus three bifurcated hydrogen bonds.

The dimensions of the picrate ion are normal. In the ring, the angle at C(1) is typically low at 111·7° and

Table 2. *Dimensions of the ammonium ions and the hydrogen-bonding schemes about these ions: distances in Å, angles in degrees*

E.s.d.'s for N–H and H···*A* lengths are 0·03–0·05 Å, for N···*A* lengths 0·003–0·004 Å, for N–H···*A* angles 3–4° and for *A*···H···*A*′ angles 1°.

Donor (*D*)	N–H	Acceptor (*A*)	H···*A*	N···*A*	N–H···*A*	*A*···H···*A*′
*A*N–*A*H(1)	1·03	N(11) N(20)	1·89 2·37	2·841 3·044	152 122	79
*A*N–*A*H(2)	0·87	O(1$^{\mathrm{I}}$) O(62$^{\mathrm{I}}$)	2·23 2·35	2·992 3·080	145 141	70
*A*N–*A*H(3)	0·92	O(1) O(21)	1·99 2·20	2·834 2·851	153 127	79
*A*N–*A*H(4)	0·87	O(61$^{\mathrm{II}}$)	2·19	3·013	157	

Roman superscripts denote symmetry-related coordinates of those (x,y,z) of Table 1: (I) is at $1-x, -y, -z$, and (II) at $x, -\frac{1}{2}-y, \frac{1}{2}+z$.

Angles about *A*N (e.s.d.'s 3–4°)

*A*H(1)–*A*N–*A*H(2)	107	*A*H(2)–*A*N–*A*H(3)	111
*A*H(1)–*A*N–*A*H(3)	111	*A*H(2)–*A*N–*A*H(4)	110
*A*H(1)–*A*N–*A*H(4)	106	*A*H(3)–*A*N–*A*H(4)	111

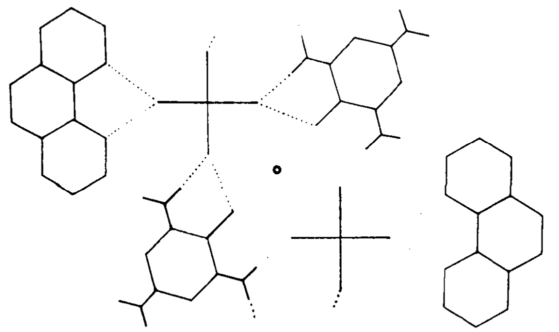

Fig. 3. Diagram showing the coordination of two NH_4^+ ions related by a centre of symmetry, thus forming the dimer referred to in the text. The heavier lines show parts of the structure nearer the viewer. The centre of symmetry is marked and hydrogen bonds are shown dotted. The bonds to the neighbouring dimers are shown from the NH_4^+ ions and *o*-nitro groups.

Table 3. *Selected short intermolecular distances* (Å)

Atoms *a* and *b* have coordinates (*x*,*y*,*z*) of Table 1; subscripts *i* and *j* indicate symmetry-related positions. E.s.d.'s for distances not involving H atoms are 0·003–0·004 Å, for O···H and C···H distances 0·03–0·04 Å, and for H···H distances 0·05 Å.

a or a_j	b or b_i	$a \cdots b_i$ or $a_j \cdots b$	i	j
C(1)	O(21)	3·204	III	III
C(2)	C(22)	3·442	I	I
C(3)	N(11)	3·380	III	III
C(3)	C(16)	3·597	I	I
C(4)	C(24)	3·386	I	I
C(6)	O(21)	3·299	III	III
C(6)	N(20)	3·397	I	I
O(22)	C(12)	3·333	III	III
N(4)	C(19)	3·424	III	III
O(41)	C(14)	3·343	IV	V
O(41)	C(21)	3·211	III	III
O(42)	C(13)	3·370	VI	VII
O(42)	C(19)	3·159	III	III
O(62)	C(12)	3·555		
C(13)	C(16)	3·576	VIII	VIII
C(14)	C(15)	3·480	VIII	VIII
O(22)	H(18)	2·65	IX	X
O(41)	H(14)	2·37	IV	V
O(42)	H(13)	2·36	VI	VII
O(62)	H(12)	2·47		
C(13)	H(18)	3·05	XI	XII
C(14)	H(18)	2·86	XI	XII
H(3)	H(15)	2·52	IV	V
H(14)	H(18)	2·52	XI	XII

Symmetry relationships *i* and *j*

(I)	$1-x$,	$-y$,	$-z$
(III)	$1-x$,	$-1-y$,	$-z$
(IV)	$-1+x$,	$-1+y$,	z
(V)	$1+x$,	$1+y$,	z
(VI)	$1-x$,	$-\frac{1}{2}+y$,	$-\frac{1}{2}-z$
(VII)	$1-x$,	$\frac{1}{2}+y$,	$-\frac{1}{2}-z$
(VIII)	$2-x$,	$-y$,	$-z$
(IX)	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
(X)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
(XI)	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
(XII)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$

Other relationships

(II)	x,	$-\frac{1}{2}-y$,	$\frac{1}{2}+z$
(XIII)	x,	$-\frac{1}{2}-y$,	$-\frac{1}{2}+z$
(XIV)	x,	$1+y$,	z

the C—C bonds show characteristic variations in length. The ring is not planar (Table 4, planes *A* and *B*) with C(1) displaced 0·06 Å from the plane through the other five atoms. O(1) is 0·17 Å from this plane, but forms a good mean plane with C(1) and its two adjoining C atoms (plane *C*). The three nitro groups are tilted only slightly from the mean plane of the benzene ring by 6·7, 1·8 and 4·9° for the groups of N(2), N(4) and N(6); the rotations appear to be toward neighbouring NH_4^+ ions but are limited by stacking constraints (see below). The participation of several of the O atoms as acceptor atoms in hydrogen-bonding schemes is typical of picrate ions. In ammonium picrate and our complex, pairs of cations are linked by hydrogen bonds to the phenolato O atoms, as pairs of K^+ and Tl^+ ions are bridged in their picrate salts (Maartmann-Moe, 1969; Palenik, 1972; Herbstein, Kapon & Wielinski, 1977).

The formation of chelating, bifurcated H bonds, involving the phenolato and *o*-nitro-group O atoms, is also found in, for example, ammonium picrate, guanine picrate monohydrate (and the isostructural 6-thioguanine complex) and a polyether dicarboxylic acid complex of potassium picrate (Hughes, Mortimer & Truter, 1978).

The dimensions of the phenanthroline ligand also conform with previously found values, both of the free molecule (Nishigaki, Yoshioka & Nakatsu, 1978) and of molecules coordinated with various metal atoms (Poonia, 1975*a*,*b*; Frenz & Ibers, 1972; Hughes & Truter, 1972). Similarly, the non-planarity of our ligand (plane *J*) is not unusual; in our structure, only the six-membered ring containing N(11) may be considered planar, the other rings (and the whole molecule) showing marked twisting and folding. There seems little consistency in the pattern or degree of distortion from planarity in phenanthroline molecules, but in our case, it appears to result from the effects of closely stacked molecules.

The ammonium *A*N and *A*H(1), to which both N(11) and N(20) of the phenanthroline molecule are bonded, are 0·83 and 0·33 Å from the plane of the phenanthroline molecule; Na^+, Rb^+ and Tl^+ are displaced by similar amounts from the ligand plane in their complexes. However, whereas the metal cations are normally almost equidistant from the two N atoms of the phenanthroline molecule, in our complex the hydrogen bond of *A*H(1) to N(11) is much stronger and more direct than that to N(20).

Fig. 4 gives an indication of the parallel arrangements of the picrate and phenanthroline ligands within the dimers.

The normals to the mean planes of these ligands are almost parallel (0·9° apart) and the ring systems are stacked at normal van der Waals distances. Within the dimer, the picrate ring is 3·4 Å from the phenanthroline ring of molecule I, and the overlap of these ligands is shown in Fig. 5.

Between the dimers the overlap is not so complete, but there are picrate rings 3·2 Å apart, and phenanthroline ligands 3·5 Å apart, across centres of symmetry at ($\frac{1}{2}$,$\frac{1}{2}$,0) and (0,0,0).

A second structural feature involves the stacking of the dimers which results in the existence of two planar systems with normals 73° apart. These two systems can be seen in Fig. 4. All the planes about $z = 0$ are inclined by *ca* 36·5° to **b**, while all those about $z = \frac{1}{2}$ are inclined by a similar amount in the opposite direction.

Some of the shorter intermolecular contacts are in Table 3. These are principally van der Waals contacts between stacked planar systems, but there are also three distinctly short C—H···O contacts which we describe as weak hydrogen bonds: (i) between C(12)

Table 4. *Mean planes*

(i) Deviations (Å) from mean planes

E.s.d.'s for deviations of all atoms used in determining the mean planes are 0·002–0·003 Å; for all additional atoms, e.s.d.'s are shown in parentheses.

Picrate ion

Plane *A*: carbon ring

C(1) 0·028, C(2) –0·22, C(3) 0·001, C(4) 0·018, C(5) –0·010, C(6) –0·013, O(1) 0·120 (3), N(2) –0·051 (4), N(4) 0·145 (3), N(6) –0·020 (3), $A\mathrm{N}$ 0·372 (5), $A\mathrm{H(3)}$ 0·23 (3), $A\mathrm{N^{I}}$ 2·648 (4), $A\mathrm{H(2^{I})}$ 1·80 (4), $A\mathrm{N^{II}}$ –0·494 (7), $A\mathrm{H(4^{II})}$ –0·27 (4)

Plane *B*: C(2)—C(6)

C(1) 0·060 (3), C(2) –0·003, C(3) 0·000, C(4) 0·007, C(5) –0·011, C(6) 0·007, O(1) 0·169 (3), N(2) –0·023 (4), N(4) 0·113 (3), N(6) 0·009 (4)

Planc *C*: about C(1)

C(1) –0·007, C(2) 0·002, C(6) 0·002, O(1) 0·002, $A\mathrm{N}$ 0·103 (5), $A\mathrm{H(3)}$ 0·02 (3), $A\mathrm{N^{I}}$ 2·461 (4), $A\mathrm{H(2^{I})}$ 1·63 (4)

Plane *D*: about C(2)

C(1) 0·004, C(2) –0·012, C(3) 0·005, N(2) 0·003, O(21) –0·121 (4), O(22) 0·126 (4), $A\mathrm{N}$ 0·411 (6), $A\mathrm{H(3)}$ 0·26 (3)

Plane *E*: about C(4)

C(3) 0·007, C(4) –0·019, C(5) 0·007, N(4) 0·006, O(41) 0·044 (3), O(42) –0·011 (4)

Plane *F*: about C(6)

C(5) 0·004, C(6) –0·010, C(1) 0·003, N(6) 0·003, O(61) –0·073 (4), O(62) 0·103 (3), $A\mathrm{N^{I}}$ 2·631 (5), $A\mathrm{H(2^{I})}$ 1·78 (4), $A\mathrm{N^{II}}$ –0·389 (7), $A\mathrm{H(4^{II})}$ –0·18 (4)

Plane *G*: nitro group of N(2)

C(2) –0·001, N(2) 0·005, O(21) –0·002, O(22) –0·002, $A\mathrm{N}$ 0·849 (5), $A\mathrm{H(3)}$ 0·62 (3)

Plane *H*: nitro group of N(4)

C(4) 0·000, N(4) 0·000, O(41) 0·000, O(42) 0·000

Plane *I*: nitro group of N(6)

C(6) 0·001, N(6) –0·004, O(61) 0·002, O(62) 0·002, $A\mathrm{N^{I}}$ 2·394 (5), $A\mathrm{H(2^{I})}$ 1·57 (4), $A\mathrm{N^{II}}$ –0·146 (8), $A\mathrm{H(4^{II})}$ 0·00 (4)

Phenanthroline molecule

Plane *J*: whole molecule

N(11) –0·006, C(12) –0·028, C(13) –0·037, C(14) –0·017, C(15) 0·037, C(16) 0·015, C(17) –0·062, C(18) –0·061, C(19) 0·001, N(20) 0·042, C(21) 0·021, C(22) 0·017, C(23) 0·020, C(24) –0·006, $A\mathrm{N}$ 0·825 (4), $A\mathrm{H(1)}$ 0·33 (4)

Plane *K*: ring of N(11)

N(11) –0·001, C(12) 0·004, C(13) –0·001, C(14) –0·004, C(22) –0·002, C(23) 0·004

Plane *L*: ring of N(20)

C(17) –0·002, C(18) –0·009, C(19) 0·004, N(20) 0·004, C(21) –0·010, C(24) 0·011

Plane *M*: ring of C(15)

C(15) 0·014, C(16) 0·001, C(21) 0·011, C(22) –0·003, C(23) –0·007, C(24) –0·013

(ii) Angles (°) between normals to the planes (e.s.d.'s are in parentheses)

Plane *B*–*C* 4·7 (8), *E*–*H* 1·8 (22), *A*–*J* 0·9 (27), *D*–*G* 6·7 (6), *F*–*I* 4·9 (9)

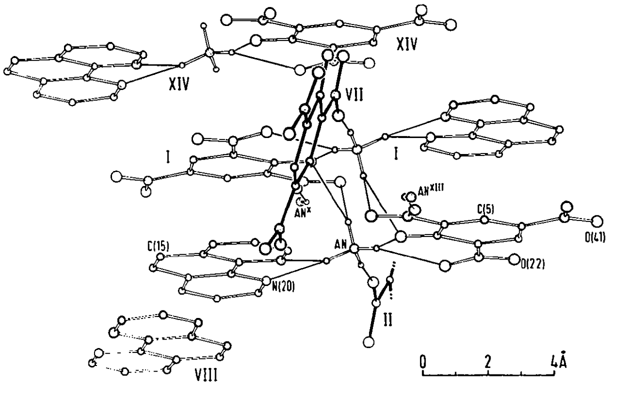

Fig. 4. View of a dimer unit (the molecule with some atoms labelled, plus molecule I) and some neighbouring units. Symmetry operations, denoted by Roman numerals, are given in Table 3.

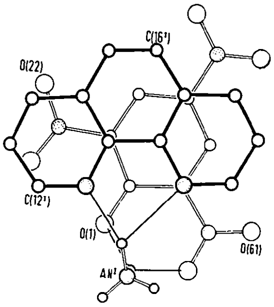

Fig. 5. Projection of the phenanthroline ligand of molecule I on to the plane of the picrate ring, showing the stacking of ring systems within the dimer unit.

and O(62) with a C—H···O angle of 147°, a bond within the ligands of the c.c.u.; (ii) between C(13) and $\mathrm{O(42^{VII})}$ with an angle at H(13) of 159°, an interlayer contact; and (iii) between C(14) and $\mathrm{O(41^{V})}$, where the angle is 167° and the contact connects dimers within the layers.

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References

Baenziger, N. C. & Williams, D. G. (1966). *J. Am. Chem. Soc.* **88**, 689–692.

Bugg, C. E. & Thewalt, U. (1975). *Acta Cryst.* B**31**, 121–127.

Bush, M. A., Lüth, H. & Truter, M. R. (1971). *J. Chem. Soc. A*, pp. 740–745.

Bush, M. A. & Truter, M. R. (1971). *J. Chem. Soc. A*, pp. 745–750.

Frenz, B. A. & Ibers, J. A. (1972). *Inorg. Chem.* **11**, 1109–1116.

HERBSTEIN, F. H., KAPON, M. & WIELINSKI, S. (1977). *Acta Cryst.* B**33**, 649–654.
HUGHES, D. L. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2347–2354.
HUGHES, D. L. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2374–2378.
HUGHES, D. L., MORTIMER, C. L. & TRUTER, M. R. (1978). *Inorg. Chim. Acta*, **28**, 83–89.
HUGHES, D. L. & TRUTER, M. R. (1972). *J. Chem. Soc. Dalton Trans.* pp. 2214–2219.
KHAN, A. A. & BAUR, W. H. (1972). *Acta Cryst.* B**28**, 683–693.
LAYTON, A. J., NYHOLM, R. S., BANERJEE, A. K., FENTON, D. E., LESTAS, C. N. & TRUTER, M. R. (1970). *J. Chem. Soc. A*, pp. 1894–1896.
LIPSON, H. & COCHRAN, W. (1966). *The Determination of Crystal Structures*, 3rd ed. London: Bell.
MAARTMANN-MOE, K. (1969). *Acta Cryst.* B**25**, 1452–1460.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1976). *MULTAN 76. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
NISHIGAKI, S., YOSHIOKA, H. & NAKATSU, K. (1978). *Acta Cryst.* B**34**, 875–879.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
PALENIK, G. J. (1972). *Acta Cryst.* B**28**, 1633–1635.
POONIA, N. S. (1975*a*). *J. Inorg. Nucl. Chem.* **37**, 1855–1858.
POONIA, N. S. (1975*b*). *J. Inorg. Nucl. Chem.* **37**, 1859–1861.
POONIA, N. S. & TRUTER, M. R. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1791–1795.
POONIA, N. S. & TRUTER, M. R. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2062–2065.
SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
STEWART, J. M. (1974). The XRAY 74 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
TRUTER, M. R. (1971). *Chem. Br.* **7**, 203–207.
WEI, K.-T. & WARD, D. L. (1976). *Acta Cryst.* B**32**, 2768–2773.
WILLIAMS, R. J. P. (1970). *Q. Rev. Chem. Soc.* **24**, 331–365.

Acta Cryst. (1981). B**37**, 1553–1557

A Study of the Temperature Variation of Molecular Rotations in Chloranil below T_c

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Abstract

The variation with temperature of the molecular rotations in chloranil (tetrachloro-*p*-benzoquinone) has been followed below $T_c \simeq 94$ K, within the temperature range 10 to 89 K. The amplitudes of molecular rotations vary continuously with temperature, in agreement with a displacive process. In contrast to early work on the chloranil low-temperature structure, it is shown here that the molecule not only rotates around an axis perpendicular to its plane with a notably larger amplitude than that previously estimated but also performs not negligible rotations around an axis within its plane.

Introduction

At room temperature the chloranil structure is monoclinic, space group $P2_1/a$ (Chu, Jeffrey & Sakurai, 1962). Nuclear quadrupole resonance first revealed the existence of the phase transition at $T_c \simeq 92$ K (Richardson, 1963; Chihara, Nakamura & Tachiki, 1971; Chihara & Nakamura, 1973). As a result of the transition the monoclinic unit cell doubles along the c axis and the molecular displacements were considered as corresponding to a staggered rotation about axes perpendicular to the molecular planes (Terauchi, Sakai & Chihara, 1975) (Fig. 1). The low-temperature phase is described as $P2_1/n$ for convenience. A soft mode has been observed in Raman spectroscopy below T_c (Hanson, 1975). Ellenson & Kjems (1977) have used elastic and inelastic neutron scattering to study this transition, particularly the temperature dependence of the order parameter from superlattice Bragg intensities (the critical exponent $\beta = 0{\cdot}33$) and the pronounced softening of the zone-boundary phonon whose eigenvector corresponds to the distortion below T_c. Below 140 K the spectrum also contains a central component diverging at T_c.

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