International Tables for X-ray Crystallography (1962). Vol. III, p.202. Birmingham: Kynoch Press.
Longuet-Higgins, H. C. & Coulson, C. A. (1947). *Trans. Faraday Soc.* **43**, 87.
Orii, S., Nakamura, T., Takaki, Y., Sasada, Y. & Kakudo, M. (1963). *Bull. Chem. Soc. Japan*, **36**, 788.
Penfold, B. R. & White, J. C. B. (1959). *Acta Cryst.* **12**, 130.
Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
Robertson, J. M., Shearer, H. M. M., Sim, G. A. & Watson, D. G. (1962). *Acta Cryst.* **15**, 1.
Sasada, Y., Takano, T. & Kakudo, M. (1964). *Bull. Chem. Soc. Japan*, **37**, 940.
Sim, G. A., Robertson, J. M. & Goodwin, T. H. (1955). *Acta Cryst.* **8**, 157.
Takaki, Y., Sasada, Y. & Watanabé, T. (1960). *Acta Cryst.* **13**, 693.
Takaki, Y. & Sasada, Y. (1966). To be published.
Tamura, C., Kuwano, H. & Sasada, Y. (1961). *Acta Cryst.* **14**, 693.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151.
Wright, W. B. & King, G. S. (1954). *Acta Cryst.* **7**, 283.

Acta Cryst. (1966). **21**, 522

The Crystal and Molecular Structure of Lead Hexa-antipyrine Perchlorate

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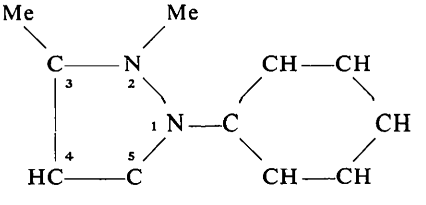
Lead hexa-antipyrine perchlorate is isomorphous with a series of metal hexa-antipyrine perchlorates, $M(C_{11}H_{12}ON_2)_6(ClO_4)_2$, where $M = Mg^{2+}$, Ca^{2+} or Zn^{2+}, and crystallizes in a hexagonal unit having dimensions $a = 14{\cdot}33\ (\pm 0{\cdot}03)$, $c = 9{\cdot}75\ (\pm 0{\cdot}03)$ Å and space group $P\bar{3}$ (C_{3i}^1). The solution of the structure in the c-axis projection was facilitated by the heavy-atom method using ($hki0$) reflexions. A knowledge of the z coordinates obtained previously from a study of the magnesium compound was utilized to work out the complete structure and the refinement was done by the three-dimensional least-squares method to an agreement index of 0·079 for 736 observed reflexions.

In the structure, each Pb^{2+} ion is surrounded by six antipyrine oxygen atoms in a slightly distorted octahedral form with Pb–O(6) = 2·446 (±0·016) Å. The five-membered pyrazolone ring is planar and is inclined at an angle of 68° to the phenyl ring. The tetrahedral ClO_4 ions occupy voids provided by the adjacent antipyrine groups. The two non-equivalent Cl–O bonds, corrected for effects of thermal oscillation, have lengths 1·453(1) and 1·457 Å(3) respectively.

Introduction

1-Phenyl-2,3-dimethyl-5-pyrazolone, $C_{11}H_{12}ON_2$, commonly known as antipyrine, is used as an antipyretic and is of high medicinal interest. Its chemical formula is schematized below:



Its high dipole moment (4·6 to 6·0 D) favours its acting as a coordinating ligand to a large number of metal ions through the oxygen atom in the keto group. Several metal–antipyrine complexes, including those of transition metals and rare-earths, have been synthesized (Schuyten, 1898, 1900; Kolb, 1913; Dörfurt & Schliephake, 1928, 1929). However, data concerning their crystal structure have not been reported in the literature, except in the case of $Tb(C_{11}H_{12}ON_2)_6I_3$, which crystallizes in the rhombohedral space group $R\bar{3}$ (C_{3i}^2) (Van Uitert & Soden, 1961). Additional structural details of this investigation are not available. Hence it was thought worth while to undertake detailed X-ray studies of these complexes and enquire into the nature of the metal–oxygen bonding in them, besides elucidating the geometry of the antipyrine ring system.

Lead hexa-antipyrine perchlorate is isomorphous with a series of metal hexa-antipyrine perchlorates, $M(C_{11}H_{12}ON_2)_6(ClO_4)_2$, where M = Mg, Ca or Zn (all divalent). As part of a programme of X-ray studies on antipyrine complexes, the first structure to be analysed in this laboratory was that of the magnesium compound, $Mg(C_{11}H_{12}ON_2)_6(ClO_4)_2$, which is at present in the final stages of three-dimensional least-squares refinement (Vijayan & Viswamitra, 1965). The isomorphism of the lead compound with the magnesium compound was rather surprising in view of the appreciable

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difference in the ionic radii of Mg^{2+} (0·65 Å) and Pb^{2+} (1·21 Å) (Wells, 1962) and a survey of the literature led us to believe that this was probably the only case where the replacement of Mg^{2+} by Pb^{2+} did not alter the isomorphism of the parent compounds. This isomorphism necessarily implies that the Pb^{2+} ion, like the Mg^{2+} ion in magnesium hexa-antipyrine perchlorate, exhibits an octahedral coordination of antipyrine oxygen atoms. An octahedral coordination of oxygen atoms around divalent lead is, again, rarely encountered. These special features of the lead–oxygen bonding in this compound prompted us, therefore, to take up the determination and refinement of its structure from three-dimensional X-ray data.

Experimental

Transparent, elongated and platy crystals of lead hexa-antipyrine perchlorate were grown from water as well as from methyl cyanide as solvents by slow evaporation at room temperature. The material used in this crystallization was obtained through the kind courtesy of Dr C.C. Patel, Department of Physical and Inorganic Chemistry, Indian Institute of Science, Bangalore 12.

Examination of the oscillation and Weissenberg photographs about the *c* axis taken with Cu $K\alpha$ radiation showed that the crystals are hexagonal with space group $P\bar{3}$ (C_{3i}^1) and have the unit-cell dimensions $a = 14{\cdot}33 \pm 0{\cdot}03$, $c = 9{\cdot}75 \pm 0{\cdot}03$ Å.

The cell dimensions of the isomorphous magnesium compound are $a = 14{\cdot}06 \pm 0{\cdot}03$, $c = 9{\cdot}76 \pm 0{\cdot}03$ Å.

Other crystal data

$M = 1534{\cdot}47$, $U = 1733{\cdot}91$ Å^3.
$D_m = 1{\cdot}488$ g.cm^{-3}, $Z = 1$, $D_x = 1{\cdot}472$ g.cm^{-3}.
Absorption coefficient for X-rays,
$\lambda = 1{\cdot}5418$ Å, $\mu = 61{\cdot}1$ cm^{-1}.

The crystalline forms $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ were found in most of the specimens and the thin prisms used were elongated in the direction of the *c* axis. As the crystals were very fragile, it was difficult to cut and grind them in the form of cylinders, and the crystal used for collecting intensity data was of dimensions $0{\cdot}015 \times 0{\cdot}037 \times 0{\cdot}075$ cm. Intensities were recorded on multiple-film Weissenberg photographs using Ni-filtered Cu $K\alpha$ radiation on Agfa Röntgen Texo-S films for six *hkil* levels with *l* from 0 to 5, and were visually estimated with calibrated intensity strips. Out of a possible 1668 reflexions distributed among these six levels, 736 were in the observable range, a large percentage of reflexions at high angles being too feeble to be measured. The intensity data were corrected for Lorentz and polarization factors. An absorption correction corresponding to a μr value of 0·8 (average value of *r* being 0·013 cm) was initially applied to the intensities. This was subsequently removed when the *R* index, $\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, was 0·12, as it was then considered that absorption errors could not be systematically corrected for, owing to the asymmetric shape of the crystal used.

Structure analysis

The multiplicity of the general position in the space group $P\bar{3}$ is sixfold, and as there is only one $Pb(C_{11}H_{12}ON_2)_6(ClO_4)_2$ unit in the cell the asymmetric part consists of a sixth of the formula unit, *viz*, one-sixth of a Pb^{2+} ion, one ($C_{11}H_{12}ON_2$) and one-third of the $(ClO_4)^-$ group. Considerations of space group symmetry require that the metal ion occupy a centre of inversion 1(*a*) at the origin of the cell (or 1(*b*) at 0, 0, $\frac{1}{2}$) and the chlorine and one of the perchlorate oxygen atoms at either of the two 2-fold special positions 2(*c*) at $\pm(0, 0, z)$ or 2(*d*) at $\pm(\frac{1}{3}, \frac{2}{3}, z)$. The rest of the atoms in the structure can be located at general positions.

The structure was worked out in the (0001) projection by the heavy atom method. Comparison of the F_{obs} values with the contributions of the lead atom at the origin yielded the phases of 50 out of 77 reflexions. A Fourier synthesis based on these signs indicated the chlorine position at $(\frac{2}{3}, \frac{1}{3})$ and the peak closest to Pb^{2+} was obviously the site of the coordinating oxygen atom. A knowledge of the already known structure of the magnesium compound aided in fixing the orientation of the antipyrine group in this projection. It might be mentioned here that although the general orientation of the antipyrine group was similar to that found in the structure of the magnesium compound, there were considerable shifts in the individual atom positions. The initial computation of *hki*0 structure factors was quite promising and the *R* index for all the observed reflexions in this zone was 0·36. This factor was reduced to 0·225 by three cycles of least-squares calculations with diagonal approximation.

The information about the heights of the atoms in terms of *c*-translation obtained from previous analysis of the isomorphous magnesium compound was used for subsequent refinement procedures by the least-squares method. All atoms were treated with individual isotropic temperature factors and unit weighting scheme was employed. The early cycles of refinement were carried out on Elliott 803-B computer at H.A.L., Bangalore, based on partial data to an *R* index of 0·19 for all the measured reflexions. The crystallographic least-squares refinement and the Fourier programs used with this computer were originally devised by Kannan (1965) and later modified for this work by one of us (M.V.). Six subsequent cycles done on the CDC-3600 computer system at Bombay with all the 736 reflexions brought the agreement index to 0·114. At this stage, calculation of the mean plane for the phenyl ring showed that it was distorted. Coordinate changes to correct this distortion resulted in an increase of the *R* value to 0·120. In the above calculations, the scattering factors for all the atoms were computed on the basis of the analytical expression involving five constants for each atom given by Forsyth & Wells (1959). As the analytical expression for the scattering factor of Pb^{2+} was not available at that time, the scattering factor of neutral lead was used.

The following modifications in the scattering factors and data were introduced at this stage of refinement. The nine-term analytical expressions for scattering factors of all the atoms including that of Pb^{2+} were just then available (Cromer & Waber, 1965) and hence were used in subsequent calculations. The absorption correction ($\mu r=0{\cdot}8$) applied earlier to the data was removed in view of its ambiguous nature referred to earlier. It was noted that the dispersion effect of lead was considerable ($\Delta f'=-4{\cdot}64$ and $\Delta f''=7{\cdot}83$ for Cu $K\alpha_1$ radiation; Cromer, 1965) and it was corrected for. In the application of the dispersion correction, the angle dependence of $\Delta f'$ and $\Delta f''$ (*International Tables for X-ray Crystallography*, 1962), being very small, was not taken into account. The real part $\Delta f'$ was added to the angle independent term in the analytical expression for the lead scattering factor. To allow for the imaginary component $\Delta f''$, the observed structure factors were modified, as indicated below, following Zachariasen & Plettinger (1959):

$$(F_o')^2=F_o^2-(\Delta f_{\rm Pb}'')^2\,[\cos 2\pi(hx+ky+lz)+\ldots]^2\exp\{-2B\sin^2\theta/\lambda^2\}$$

$$x=0,\ y=0,\ z=0,\ B=4{\cdot}04\ \text{Å}^2\ .$$

F_o' values instead of F_o values were used in further refinement. These modifications brought the R value to 0·109. Two more cycles of isotropic least-squares refinement, done on the Elliott 803-B computer, brought R to 0·091.

The isotropic temperature factors for all the atoms were found to be quite large. Though the temperature factor of lead was smaller than those of the other atoms in the structure, its numerical value ($B=4{\cdot}04$ Å^2) was considered to be a little too high in view of its mass and the fact that it is at the centre of an octahedron formed by the oxygen atoms. Systematic attempts to reduce the temperature factor of lead (and also of other atoms) resulted in large disagreements between observed and calculated structure factors. For example, the R value for certain groups of reflexions increased to as high a value as 0·15 from 0·08 when the temperature factor of lead ion was gradually reduced from $B=4{\cdot}04$ Å^2 to $B=1{\cdot}66$ Å^2. Also a fresh zero layer photograph on Ilford Ilfex film was taken with a different crystal, and the new intensities compared very well with the original intensities obtained on Agfa Röntgen Texo-S film. Hence it was construed that the temperature factors of the atoms including that of lead in the structure were all genuine.

The refinement of the structure was continued on the Elliott 803-B computer using individual anisotropic temperature factors of the form

$$\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{13}hl)\}$$

employing the weighting scheme

$$\sqrt{w}=1\Big/\left\{1+\left(\frac{kF_o-b}{a}\right)^2\right\}^{\frac{1}{2}}$$

suggested by Mills & Rollett (1960) with $a=40$, $b=25$ for $k=\frac{1}{2}$. Two cycles of anisotropic refinement brought R from 0·091 to 0·079 in stages of $R=0{\cdot}091$ (starting value), 0·082 and 0·079. As the next cycle did not show any significant improvement in the R value the refinement was terminated. In all the least-squares calculations diagonal approximation was used and the R values quoted are for observed reflexions alone.

The final positional parameters of the atoms in the asymmetric part and their standard deviations obtained from least-squares calculations (*International Tables for X-ray Crystallography*, 1959) using diagonal approximation are given in Table 1. Table 2 lists the components of the anisotropic temperature factor tensor together with the equivalent isotropic temperature factors calculated from Hamilton's formula (1959):

$$B=\tfrac{4}{3}\,\Sigma\,\Sigma\,B_{ij}\,\mathbf{a}_i\,.\,\mathbf{a}_j\ .$$

The anisotropic vibration parameters were transformed by the method of Rollett & Davies (1955) into magnitudes and direction cosines of principal axes of B-ellipsoids relative to the reciprocal crystallographic axes which are given in Table 3. The observed and

Table 1. *Fractional positional parameters and their standard deviations*

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Pb	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
Cl	0·6667	0·3333	0·4961	0·0000	0·0000	0·0012
O(1)	0·1540	0·0865	0·8440	0·0010	0·0010	0·0017
O(2)	0·5860	0·2315	0·4465	0·0013	0·0013	0·0021
O(3)	0·6667	0·3333	0·6410	0·0000	0·0000	0·0037
N(1)	0·3134	0·0832	0·8012	0·0010	0·0010	0·0018
N(2)	0·3537	0·0478	0·7000	0·0012	0·0012	0·0019
C(1)	0·2075	0·0545	0·7715	0·0013	0·0014	0·0023
C(2)	0·1825	−0·0032	0·6488	0·0015	0·0014	0·0025
C(3)	0·2743	−0·0045	0·6068	0·0016	0·0015	0·0025
C(4)(Me)	0·2890	−0·0623	0·4838	0·0017	0·0017	0·0027
C(5)(Me)	0·4568	0·0485	0·7160	0·0014	0·0014	0·0025
C(6)	0·3761	0·1501	0·9105	0·0012	0·0012	0·0021
C(7)	0·3536	0·1125	0·0474	0·0016	0·0016	0·0028
C(8)	0·4137	0·1805	0·1575	0·0016	0·0016	0·0027
C(9)	0·4935	0·2830	0·1294	0·0016	0·0016	0·0027
C(10)	0·5145	0·3188	0·9970	0·0015	0·0016	0·0025
C(11)	0·4592	0·2548	0·8830	0·0014	0·0015	0·0024

Table 2. *Anisotropic thermal parameters* ($\times 10^4$) *and the equivalent isotropic temperature factors* (Hamilton, 1959)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}	B
Pb	66	66	105	66	0	0	4·04 Å^2
Cl	102	102	151	102	0	0	6·11
O(1)	98	101	185	93	5	−17	6·51
O(2)	151	166	265	140	−20	−2	10·13
O(3)	175	175	250	175	0	0	10·36
N(1)	72	72	115	65	24	1	4·52
N(2)	95	102	130	99	−5	5	5·68
C(1)	74	81	140	73	23	−6	5·02
C(2)	96	82	136	90	4	−15	5·35
C(3)	99	106	149	92	30	−10	6·25
C(4)(Me)	127	109	162	126	25	−10	6·80
C(5)(Me)	88	90	141	65	37	−25	5·78
C(6)	75	69	90	61	28	22	4·25
C(7)	107	102	169	72	1	−35	6·87
C(8)	110	127	134	98	1	−7	6·85
C(9)	104	102	174	98	1	−18	6·49
C(10)	109	100	143	91	−20	1	6·30
C(11)	93	88	140	81	25	−3	5·63

Table 3. *Magnitudes and direction cosines, relative to the reciprocal crystallographic axes, of the principal vibration ellipsoids*

	Axis i	B_i	g_{i1}	g_{i2}	g_{i3}
Pb	1	4·07 Å^2	1	0·5000	0
	2	4·07	0	0·8660	0
	3	3·99	0	0	1
Cl	1	6·28	1	0·5000	0
	2	6·28	0	0·8660	0
	3	5·74	0	0	1
O(1)	1	7·38	0·3168	−0·2088	−0·8484
	2	6·30	−0·0603	−0·8110	0·4281
	3	5·89	0·9466	0·5464	0·3113
O(2)	1	11·29	0·1689	−0·6995	0·3900
	2	9·90	−0·2919	0·1416	0·8970
	3	9·18	0·9414	0·7005	0·2082
O(3)	1	10·77	1	0·5000	0
	2	10·77	0	0·8660	0
	3	9·51	0	0	1
N(1)	1	5·27	0·2194	−0·5742	−0·5730
	2	4·44	−0·9356	−0·4709	−0·3532
	3	3·82	0·2768	0·6697	−0·7396
N(2)	1	6·33	0·2557	0·9583	−0·1228
	2	5·84	−0·9555	−0·2774	−0·1828
	3	4·89	0·1469	−0·0687	−0·9755
C(1)	1	5·99	0·0917	−0·5292	−0·7421
	2	4·60	−0·7690	−0·8354	0·3709
	3	4·46	0·6325	−0·1485	0·5584
C(2)	1	6·15	0·8682	0·1937	−0·4114
	2	5·19	−0·4925	−0·7523	−0·6450
	3	4·76	0·0614	−0·6297	0·6440
C(3)	1	7·56	0·2229	−0·6287	−0·4690
	2	6·03	−0·9694	−0·6970	−0·0140
	3	5·13	0·1030	−0·3449	0·8831
C(4)(Me)	1	7·88	0·9694	0·3659	−0·2033
	2	7·07	−0·2362	−0·7645	−0·6222
	3	5·42	0·0664	−0·5308	0·7560
C(5)(Me)	1	7·87	0·3835	−0·4720	−0·5153
	2	5·00	−0·9200	−0·7771	−0·1400
	3	4·44	0·0814	−0·4163	0·8455
C(6)	1	5·16	0·6822	−0·2921	0·0091
	2	4·60	−0·6215	−0·8186	−0·5195
	3	2·99	0·3851	0·4945	−0·8545
C(7)	1	8·80	0·5590	−0·3667	−0·3617
	2	6·34	−0·2748	−0·6382	0·7682
	3	5·49	0·7824	0·6770	0·5282
C(8)	1	8·76	0·2132	−0·7387	−0·0433
	2	6·70	−0·9725	−0·6736	0·0859
	3	5·08	0·0932	0·0260	0·9954
C(9)	1	7·15	0·5442	−0·1359	−0·6943
	2	6·30	−0·3070	−0·9173	0·3578
	3	6·06	0·7807	0·3743	0·6246
C(10)	1	7·45	0·6458	−0·3112	0·2163
	2	6·23	−0·7477	−0·8496	0·3731
	3	5·19	0·1543	0·4259	0·9022
C(11)	1	6·56	0·4313	−0·4378	−0·4946
	2	5·58	−0·8784	−0·6350	−0·4211
	3	4·72	0·2060	0·6365	−0·7603

calculated structure factors are listed in Table 4. They do not include unobserved reflexions. Structure factors for the unobserved reflexions were also calculated with the final parameters. Most of them were very small, only 65 out of 932 unobserved reflexions being of the order of the minimum observed F_o. The final *hki*0 Fourier map, with the atomic positions marked, is shown in Fig. 1.

Discussion

Coordination around the Pb^{2+} *ion*

Purely from the radius ratio test (Pauling, 1960) one expects an eightfold or twelvefold coordination of oxygen atoms about the plumbous ion. However, the Pb^{2+} ion is known to exhibit a wide variety of coordination numbers ranging from 3 to 12 depending on the covalent nature of the bond involved and also on packing considerations. For example, in Pb_3O_4 the Pb^{2+} ion has three oxygen neighbours (Byström & Westgren, 1943) whereas in Pb_2O_3 the corresponding number is six (Byström, 1945). Many oxygen compounds of lead like $PbTiO_3$, $PbCeO_3$, $Pb_3MgNb_2O_9$, $Pb(Nb_{0·5}Sc_{0·5})O_3$ crystallize with a perovskite structure, the plumbous ion having a twelvefold coordination (Náray-Szabó, 1943, 1947; Ismailzade, 1959, 1960). In $PbSO_4$ and $Pb(NO_3)_2$ also a twelvefold coordination of oxygen atoms around the Pb^{2+} ion is observed (James & Wood, 1925; Hamilton, 1957). In orthorhombic $PbCrO_4$ the lead coordination may be considered to be tenfold (Collotti, Conti & Zocchi, 1959; Quareni & De Pieri, 1964; Náray-Szabó & Argay, 1964). $PbCO_3$ is isomorphous with aragonite and Pb^{2+} has a ninefold coordination (Colby & La Coste, 1933). In $PbUO_4$ a distorted eightfold coordination is found (Frondel & Barnes, 1958). Pb^{2+} exhibits a coordination of the type found in lead monoxide, *i.e.* four oxygen atoms at the apices of a distorted square on one side of the cation, in Ag_2PbO_2 (Byström & Evers, 1950). An octahedral coordination of plumbous ion is reported in $(NH_4)_2Pb(SO_4)_2$ and

$Pb_3Sb_2O_{8\cdot47}$ (Møller, 1954; Kuznetzov & Kożmin, 1958). The Pb(II)–O distances in these compounds are 2·51 and 2·435 Å respectively.

In lead hexa-antipyrine perchlorate the Pb^{2+} ion at the origin has an octahedral environment of six antipyrine oxygen atoms related by $\bar{3}$ symmetry. The Pb(II)–O distance is 2·446 ± 0·016 Å. The octahedral coordination is indicated in the perspective drawing of the structure (Fig. 2) and the relevant dimensions are listed in Table 5. As a consequence of the less dense packing of the molecules along the *c* axis, on either side of the octahedron, than in other directions, the

Table 4. *Observed and calculated structure factors*

Calculations were carried out for half the contents of the unit cell.

h	k	F_{obs}	F_{calc}
	l = 0		
2	0	13.74	-13.76
3	0	57.78	54.58
4	0	38.26	36.16
5	0	28.94	28.23
6	0	33.24	32.79
7	0	5.42	3.74
8	0	10.26	8.81
9	0	18.12	17.92
10	0	10.17	10.78
12	0	13.30	11.20
1	1	48.95	45.68
1	2	24.61	20.62
1	3	18.56	-15.10
1	4	12.14	20.47
1	5	36.18	34.17
1	6	33.68	32.23
1	7	16.33	17.96
1	8	12.58	12.05
1	9	9.56	11.96
1	10	18.66	21.56
1	11	7.84	8.30
1	13	8.31	9.26
2	1	50.87	48.04
2	2	34.81	34.07
2	3	12.30	12.01
2	4	35.53	32.38
2	5	39.60	36.58
2	6	9.99	10.67
2	7	24.08	24.31
2	8	16.54	18.72
2	9	12.89	11.99
2	10	7.82	6.98
3	1	43.73	41.34
3	3	40.54	39.90
3	4	15.36	11.22
3	5	23.16	24.32
3	6	27.32	25.43
3	7	14.07	14.06
3	8	8.82	8.59
3	9	8.58	9.84
4	1	35.78	37.24
4	2	20.29	21.10
4	3	44.41	43.13
4	4	23.16	23.29
4	5	21.76	22.30
4	6	21.83	24.64
4	7	20.51	23.00
4	8	8.22	10.54
5	1	7.80	9.75
5	2	56.60	55.53
5	3	14.67	12.40
5	4	20.96	21.20
5	5	21.59	23.22
5	6	17.25	17.33
5	7	11.66	13.08
6	1	21.37	20.80
6	2	13.21	12.66
6	3	23.00	23.77
6	4	17.26	19.35
6	5	8.89	9.96
6	6	13.65	12.24
7	1	27.01	31.94
7	3	11.20	10.73
7	4	17.79	19.96
7	5	8.13	9.65
8	1	12.58	13.91
8	2	13.31	14.14
8	3	14.72	15.36
8	4	10.32	11.87
8	5	11.93	12.73
9	2	10.72	10.50
9	3	17.59	18.02
9	4	7.84	6.09
10	1	11.66	12.56
10	2	12.65	12.90
11	1	13.39	12.89
11	2	10.19	11.12
	l = -1		
0	1	44.02	43.19
0	2	10.21	9.38
0	3	52.89	-45.93
0	4	12.97	10.65
0	5	8.68	9.66
0	6	5.17	6.20
0	7	15.86	18.13
0	8	15.94	19.62
0	9	13.67	17.42
0	10	13.56	14.77
0	11	8.69	12.46
0	13	9.75	9.51
1	10	53.89	52.54
1	1	25.83	-25.02
1	2	47.61	42.19
1	3	15.20	-8.09
1	4	11.64	13.75
1	5	37.59	38.59
1	6	33.39	32.19
1	7	11.96	13.29
1	8	14.93	16.78
1	9	18.49	20.04
2	0	55.75	55.72
2	1	71.51	65.98
2	2	28.87	28.69
2	3	54.70	51.93
2	4	27.26	25.47
2	5	28.13	23.63
2	6	23.08	23.01
2	7	[illegible]	20.[illegible]
2	8	13.17	12.[illegible]
3	0	5.20	3.62
3	1	48.09	44.15
3	2	32.22	28.94
3	3	16.93	16.74
3	4	31.57	31.60
3	5	34.76	36.12
3	6	19.89	22.39
3	7	16.73	16.15
3	8	10.17	9.86
3	9	12.34	14.28
4	0	68.28	62.49
4	1	16.80	15.06
4	2	21.58	23.99
4	3	37.04	36.11
4	4	26.43	24.97
4	5	22.59	20.92
4	6	21.10	21.04
4	8	9.23	12.02
5	0	42.38	43.03
5	1	22.16	23.49
5	2	40.06	37.82
5	3	33.19	32.20
5	4	11.20	13.17
5	5	7.44	8.83
5	6	12.96	16.39
5	7	14.96	16.00
6	0	20.15	20.53
6	1	16.65	16.31
6	2	25.77	23.83
6	4	16.97	18.17
6	5	14.27	14.37
6	6	8.44	9.94
7	0	9.01	12.06
7	1	11.96	11.58
7	2	12.74	12.33
7	3	17.70	18.48
7	5	14.96	16.15
7	6	13.88	16.25
7	7	8.56	9.80
8	0	24.49	25.42
8	1	19.64	18.90
8	3	18.40	18.65
8	4	15.02	13.97
8	5	10.71	10.68
9	1	11.61	11.10
9	2	14.80	14.03
9	3	8.60	10.45
9	4	12.66	12.26
10	0	12.57	14.27
10	1	7.61	5.74
10	2	15.20	14.95
10	3	13.81	13.01
11	1	8.73	7.51
12	2	8.06	8.42
14	1	6.40	5.18
2	-1	66.54	61.27
3	-1	96.27	91.83
3	-2	90.60	82.22
4	-1	6.75	3.16
4	-2	28.22	24.20
4	-3	75.44	68.15
5	-1	18.51	19.31
5	-2	44.65	44.87
5	-3	12.80	17.96
5	-4	3.73	6.20
6	-1	46.99	45.75
6	-2	27.26	23.55
6	-3	23.38	20.16
6	-4	27.47	30.24
6	-5	7.48	8.57
7	-1	5.66	7.26
7	-2	10.26	10.12
7	-3	28.65	30.64
7	-4	15.97	18.39
7	-5	31.52	31.56
7	-6	15.06	18.21
8	-2	27.76	31.92
8	-3	24.88	25.71
8	-4	6.82	7.12
8	-5	25.93	28.59
8	-6	29.99	30.47
8	-7	22.91	21.14
9	-1	20.53	21.57
9	-2	23.33	24.20
9	-3	17.10	19.68
9	-4	24.28	25.55
9	-5	21.57	24.06
9	-6	13.47	17.20
9	-7	17.87	18.59
9	-8	2[illegible].62	20.16
10	-1	11.61	10.01
10	-2	12.67	13.26
10	-3	19.43	22.58
10	-4	18.71	23.07
10	-6	20.52	28.51
10	-7	17.22	19.30
10	-9	14.27	14.93
11	-2	14.80	17.17
11	-3	13.23	14.59
11	-5	14.27	15.83
11	-6	14.27	15.69
11	-7	11.66	12.10
11	-8	14.53	17.35
11	-9	18.74	20.73
12	-2	13.23	12.71
12	-10	16.47	16.89
12	-11	[illegible]	[illegible]
13	-1	[illegible]	1[illegible].40
13	-4	12.86	11.97
13	-5	12.41	13.10
14	-4	8.42	8.13
14	-8	11.11	10.56
14	-9	12.14	12.50
	l = -2		
0	1	7.00	2.78
0	2	5.35	5.78
0	3	37.82	32.86
0	4	24.26	25.22
0	5	10.17	12.22
0	6	22.35	24.54
0	7	24.55	25.19
0	8	30.29	30.74
0	9	17.65	19.41
0	10	10.69	11.78
0	11	18.76	14.83
1	0	5.69	3.43
1	1	80.36	77.55
1	2	54.59	51.23
1	3	39.25	38.35
1	4	31.26	33.08
1	5	36.89	36.31
1	6	24.93	25.38
1	7	27.73	26.29
1	8	17.03	16.66
1	9	12.07	13.76
1	10	10.73	10.60
2	0	16.35	19.39
2	1	37.64	37.21
2	2	43.97	40.73
2	3	23.71	23.36
2	4	24.75	21.23
2	5	16.87	15.75
2	6	13.18	13.16
2	7	14.51	14.28
2	8	19.95	22.28
2	9	8.68	11.30
2	11	10.77	11.24
3	0	64.81	59.05
3	1	51.26	45.55
3	2	33.01	28.40
3	3	13.51	13.59
3	4	16.52	16.38
3	5	26.58	24.36
3	6	18.35	18.74
3	7	7.98	11.16
4	0	24.25	23.23
4	1	39.17	38.33
4	2	39.16	35.93
4	3	12.47	14.65
4	4	27.36	25.68
4	5	12.98	14.55
4	6	14.01	13.23
4	7	10.49	10.67
5	0	30.75	29.22
5	1	25.26	23.65
5	2	26.40	27.00
5	3	13.83	12.23
5	4	12.98	14.95
5	5	20.10	19.49
5	6	10.43	11.17
5	8	11.04	13.17
6	0	39.34	33.64
6	1	11.29	10.59
6	2	7.98	8.66
6	3	16.93	15.98
6	4	12.75	13.98
6	5	13.58	14.08
6	6	10.93	11.41
6	7	12.02	12.54
7	0	8.16	8.70
7	1	24.81	26.78
7	2	25.05	24.79
7	3	12.98	14.21
7	4	19.13	18.48
7	5	12.36	10.83
7	6	12.42	13.13
7	7	14.03	14.47
8	0	21.53	18.62
8	1	18.60	17.48
8	2	18.99	17.54
8	4	9.29	10.13
8	5	12.84	15.31
9	0	20.22	20.99
10	0	12.35	11.70
10	1	16.84	17.49
2	-1	38.87	40.67
3	-1	52.56	49.27
4	-1	48.80	45.17
4	-2	41.96	44.26
4	-3	8.00	6.82
5	-1	49.66	46.54
5	-2	17.95	18.91
5	-3	17.59	19.15
5	-4	4.28	6.68
6	-1	19.03	19.59
6	-2	25.57	23.97
6	-3	36.30	36.61
6	-4	19.45	20.55
7	-1	27.90	2[illegible].3[illegible]
7	-2	24.19	24.73
7	-3	11.62	11.70
7	-4	33.69	34.79
7	-5	28.49	32.37
8	-1	21.78	27.94
8	-3	22.44	23.64
8	-4	23.30	24.96
8	-5	16.08	16.52
8	-6	19.84	18.96
8	-7	32.48	33.39
9	-3	18.91	20.89
9	-4	11.66	12.66
9	-5	12.98	17.87
9	-6	16.83	19.83
9	-7	12.16	12.41
9	-8	14.97	15.91
10	-2	13.25	10.81
10	-3	14.19	15.13
10	-4	18.41	20.08
10	-5	15.10	15.88
10	-6	12.75	13.75
10	-7	15.41	17.63
10	-8	17.82	18.87
11	-1	10.97	9.91
11	-2	12.53	14.41
11	-3	10.67	11.42
11	-4	8.84	9.86
11	-7	21.03	22.71
11	-8	13.77	13.63
11	-10	15.57	16.69
12	-1	11.06	10.83
12	-2	14.29	13.87
12	-3	15.64	18.20
12	-6	14.14	15.10
12	-11	9.99	10.56
13	-4	11.01	11.64
13	-5	14.30	16.94
13	-6	10.99	12.46
13	-10	10.91	9.08
14	-3	8.44	7.96
14	-9	8.69	9.12
	l = -3		
0	1	36.96	38.79
0	2	46.06	43.82
0	3	51.26	45.74
0	4	38.56	36.41
0	5	39.29	37.85
0	6	36.75	35.12
0	7	20.15	23.51
0	8	22.13	24.06
0	9	11.80	13.22
0	10	12.56	13.58
0	11	10.95	12.05
1	0	17.85	17.28
1	1	28.06	26.02
1	2	16.64	19.42
1	3	36.78	32.01
1	4	25.04	21.99
1	5	17.19	15.87
1	7	17.96	18.39
1	8	18.82	16.20
2	0	45.20	43.40
2	1	20.71	21.23
2	2	14.67	17.94
2	3	37.03	37.05
2	4	25.24	25.85
2	5	10.79	11.66
2	6	13.18	15.02
2	7	20.37	20.03
2	9	13.22	13.30
2	10	13.45	14.33
3	0	20.42	18.68
3	1	46.37	43.96
3	2	29.95	32.90
3	3	22.40	20.79
3	4	17.62	16.60
3	5	8.96	10.36
3	6	18.75	17.89
3	8	9.14	11.23
4	0	28.64	29.83
4	1	27.77	26.39
4	2	20.06	19.81
4	3	22.55	20.89
4	4	11.69	10.82
4	5	7.83	7.76
4	6	13.76	14.89
4	8	11.56	13.30
5	0	22.11	23.63
5	1	31.54	30.24
5	2	11.90	12.21
5	3	19.82	21.07
5	4	18.39	17.67
5	5	8.51	8.57
5	6	14.48	13.52
5	7	9.29	11.44
6	0	25.78	26.61
6	1	20.78	22.30
6	2	12.94	12.65
6	3	18.70	19.32
6	4	18.73	19.66
6	5	17.16	19.21
6	6	9.29	9.07
7	0	30.39	29.65
7	2	18.47	18.21
7	3	15.28	14.60
7	4	12.95	13.67
7	5	13.30	10.8[illegible]
8	0	14.24	15.1[illegible]
8	1	10.45	10.1[illegible]
8	3	14.64	13.7[illegible]
8	4	16.44	14.5[illegible]
9	0	8.66	10.6[illegible]
9	1	17.16	18.9[illegible]
9	4	11.44	10.9[illegible]
10	0	14.75	14.3[illegible]
10	1	10.47	12.6[illegible]
10	2	11.57	11.5[illegible]
11	0	13.36	12.41
11	1	9.31	9.7[illegible]
2	-1	3.78	-0.50
3	-1	17.18	19.1[illegible]
3	-2	33.97	32.6[illegible]
4	-1	35.76	33.8[illegible]
4	-2	19.34	15.04
4	-3	34.94	33.77
5	-1	34.23	32.91
5	-2	57.96	51.91
5	-3	8.30	8.15
5	-4	18.28	20.39
6	-1	40.60	37.69
6	-2	30.96	29.13
6	-4	20.06	21.37
6	-5	38.04	38.39
7	-1	22.41	21.75
7	-2	12.87	13.20
7	-3	27.51	28.41
7	-4	15.38	16.76
7	-5	12.87	13.58
7	-6	27.84	31.25
8	-1	18.38	22.69
8	-2	14.32	12.48
8	-3	10.47	9.78
8	-5	14.04	15.68
8	-7	13.71	16.85
9	-1	20.94	19.54
9	-2	13.13	13.27
9	-4	17.94	18.96
9	-5	17.94	19.40
9	-7	10.06	12.80
9	-8	23.43	24.86
10	-1	9.02	9.04
10	-3	15.23	17.66
10	-4	15.08	15.78
10	-5	8.51	8.04
10	-6	12.40	13.43
10	-7	15.28	18.95
10	-8	19.82	19.59
10	-9	20.68	20.43
11	-1	13.39	11.48
11	-2	14.81	15.72
11	-3	14.64	14.97
11	-6	15.07	14.10
11	-8	14.64	14.01
12	-1	11.44	13.01
12	-2	13.38	12.56
12	-4	11.52	11.30
12	-5	13.30	12.38
12	-6	13.67	14.05
12	-7	14.97	15.26
12	-8	9.35	9.53
12	-11	9.31	10.93
13	-6	10.55	11.35
13	-7	10.55	12.17
13	-10	9.25	10.53
	l = -4		
0	1	3.12	1.50
0	2	40.49	40.90
0	3	56.59	53.73
0	4	13.25	14.60
0	5	17.98	19.94
0	6	22.86	20.94
0	9	15.46	15.92
1	0	28.41	31.33
1	1	21.68	22.06
1	2	28.06	25.13
1	3	29.[illegible]	27.22
1	4	10.89	14.29
1	5	30.96	26.28
1	6	10.01	9.96
1	7	12.87	14.97
1	8	17.94	21.40
1	9	13.43	14.91
2	0	19.39	20.29
2	1	20.55	18.41
2	2	32.76	30.05
2	3	18.34	17.34
2	4	20.66	20.21
2	5	33.17	23.68
2	6	10.73	10.90
2	7	16.67	15.36
2	8	13.14	12.91
2	10	8.69	9.84
3	0	30.08	29.64
3	1	22.20	18.93
3	2	31.36	29.36
3	3	17.39	17.32
3	4	17.94	18.23
3	5	6.76	6.03
3	6	15.39	14.08
3	7	12.91	12.03
3	9	13.53	1[illegible].98
4	0	9.10	9.67

Table 4 (*cont.*)

h	k	F_{obs}	F_{calc}
4	1	27.78	25.58
4	2	31.89	32.31
4	3	26.91	26.64
4	6	15.22	18.76
4	7	14.66	13.68
4	8	12.12	10.68
4	9	10.73	8.57
5	0	5.09	5.76
5	1	13.97	13.68
5	2	23.78	22.18
5	3	15.87	17.71
5	4	14.12	13.94
5	5	18.16	17.05
5	6	13.31	13.61
6	0	26.50	26.23
6	1	15.57	15.24
6	2	15.37	16.84
6	3	21.27	21.17
6	4	11.45	9.43
6	6	8.46	7.43
7	0	16.30	17.76
7	1	19.14	19.01
7	2	11.00	9.44
7	3	12.91	12.66
7	4	11.91	12.54
7	7	9.75	9.40
8	0	12.18	13.18
8	1	11.33	10.92
8	2	14.35	15.08
8	3	13.34	12.21
8	4	14.84	15.67
8	5	9.31	9.04
9	0	14.30	15.42
9	1	13.37	15.50
9	3	12.42	11.47
9	4	8.30	9.93
10	0	13.46	11.64
10	1	14.88	15.20
10	3	8.16	7.40
11	2	7.99	8.41
2	-1	32.31	33.07
3	-1	5.77	4.64
3	-2	10.78	12.93

h	k	F_{obs}	F_{calc}
4	-1	28.23	26.14
4	-2	31.05	32.38
4	-3	37.66	37.24
5	-1	28.13	25.93
5	-2	37.16	34.57
5	-3	30.07	29.07
5	-4	34.63	37.54
6	-1	8.42	9.25
6	-2	19.22	18.13
6	-3	16.17	19.02
6	-4	21.62	24.79
6	-5	32.81	34.81
7	-1	10.01	10.89
7	-2	28.18	26.83
7	-3	8.96	7.67
7	-5	17.53	21.61
7	-6	16.30	21.28
8	-1	24.26	24.84
8	-2	12.50	11.75
8	-3	15.77	15.94
8	-4	17.72	19.92
8	-5	8.73	10.42
8	-6	12.50	16.39
8	-7	17.07	19.01
9	-1	15.03	15.27
9	-2	12.33	12.55
9	-3	15.73	15.40
9	-4	11.96	12.78
9	-5	13.19	13.89
9	-6	17.65	16.89
9	-7	19.71	23.22
9	-8	9.37	10.40
10	-2	17.62	19.38
10	-3	9.94	9.94
10	-5	12.76	11.92
10	-8	17.66	20.15
11	-2	14.82	14.41
11	-3	14.73	16.47
11	-4	13.45	11.03
11	-5	8.28	8.21
11	-6	9.50	11.71
11	-7	8.30	8.65
11	-8	14.07	13.29

h	k	F_{obs}	F_{calc}
12	-3	8.66	8.38
12	-6	14.85	16.26
12	-7	14.86	12.58
12	-8	13.54	10.93
12	-9	14.83	13.10
13	-7	10.30	8.60
13	-8	8.28	9.47
13	-9	10.18	10.40

l = -5

h	k	F_{obs}	F_{calc}
0	1	29.74	38.20
0	2	12.17	13.80
0	3	18.15	18.40
0	4	30.57	29.66
0	5	19.87	20.27
0	6	11.65	14.48
0	7	13.86	12.62
0	10	12.79	14.51
1	0	22.00	30.31
1	1	25.34	26.02
1	2	26.61	27.24
1	3	18.94	18.93
1	4	22.88	24.08
1	5	20.46	18.66
1	6	14.38	14.63
1	7	12.20	14.37
1	8	14.21	16.83
1	9	12.00	14.27
2	0	28.51	29.89
2	1	12.05	12.58
2	2	13.71	13.58
2	3	15.47	14.91
2	4	17.63	18.09
2	5	23.07	22.68
2	6	21.02	19.67
2	7	9.79	9.04
2	9	12.00	11.70
3	0	7.56	7.06
3	1	36.18	32.61
3	2	23.68	23.68
3	3	9.27	9.59
3	4	22.54	21.96

h	k	F_{obs}	F_{calc}
3	5	20.68	19.34
3	7	14.43	15.75
3	8	10.36	11.78
4	0	24.10	22.25
4	1	14.95	14.57
4	2	21.18	19.46
4	3	15.73	12.89
4	6	18.23	19.83
4	7	12.01	12.58
5	0	14.95	14.55
5	1	10.03	9.77
5	2	10.81	10.59
5	3	18.79	20.16
5	4	11.11	11.17
5	5	10.02	9.13
5	6	12.00	13.02
6	0	9.44	10.91
6	1	16.00	15.25
6	2	23.25	24.70
6	3	9.59	12.12
6	5	8.39	7.67
7	0	22.25	22.39
7	1	12.20	15.55
7	2	15.12	14.55
7	3	8.17	9.65
7	6	8.10	7.17
8	0	18.02	18.57
8	1	8.04	8.07
8	2	10.26	11.15
8	3	17.20	17.80
9	0	11.74	12.04
9	1	14.71	14.54
9	2	8.34	9.84
10	0	13.43	12.67
2	-1	13.25	15.06
3	-1	7.05	9.36
3	-2	15.77	19.78
4	-1	30.37	28.15
4	-2	13.33	12.61
4	-3	29.21	33.80
5	-1	6.66	5.96
5	-2	21.79	20.82

h	k	F_{obs}	F_{calc}
5	-3	25.76	29.07
5	-4	14.50	18.52
6	-1	13.69	13.79
6	-2	14.46	15.23
6	-4	20.88	23.95
6	-5	19.18	22.78
7	-1	18.41	16.60
7	-2	9.65	8.29
7	-3	24.97	26.03
7	-4	20.49	22.25
7	-5	9.66	13.38
7	-6	13.91	16.97
8	-1	10.82	10.75
8	-2	11.89	13.09
8	-3	22.18	22.56
8	-4	15.32	16.33
8	-5	15.77	18.83
8	-6	14.07	17.21
9	-1	14.21	12.49
9	-2	7.91	7.43
9	-4	9.56	9.93
9	-5	13.63	14.83
9	-6	7.75	8.09
9	-7	11.38	12.09
10	-1	14.71	14.68
10	-2	8.33	9.06
10	-3	11.73	12.36
10	-4	15.64	16.72
10	-7	11.73	13.49
11	-2	8.34	8.97
11	-3	10.36	12.43
11	-4	12.01	10.83
11	-5	12.00	13.83
11	-6	14.71	14.45
11	-8	14.73	13.87
11	-9	12.00	10.83
12	-8	10.29	11.13
12	-9	10.17	9.87
13	-3	7.76	8.32
13	-4	9.76	8.49
13	-9	11.30	10.61
13	-10	10.97	9.13

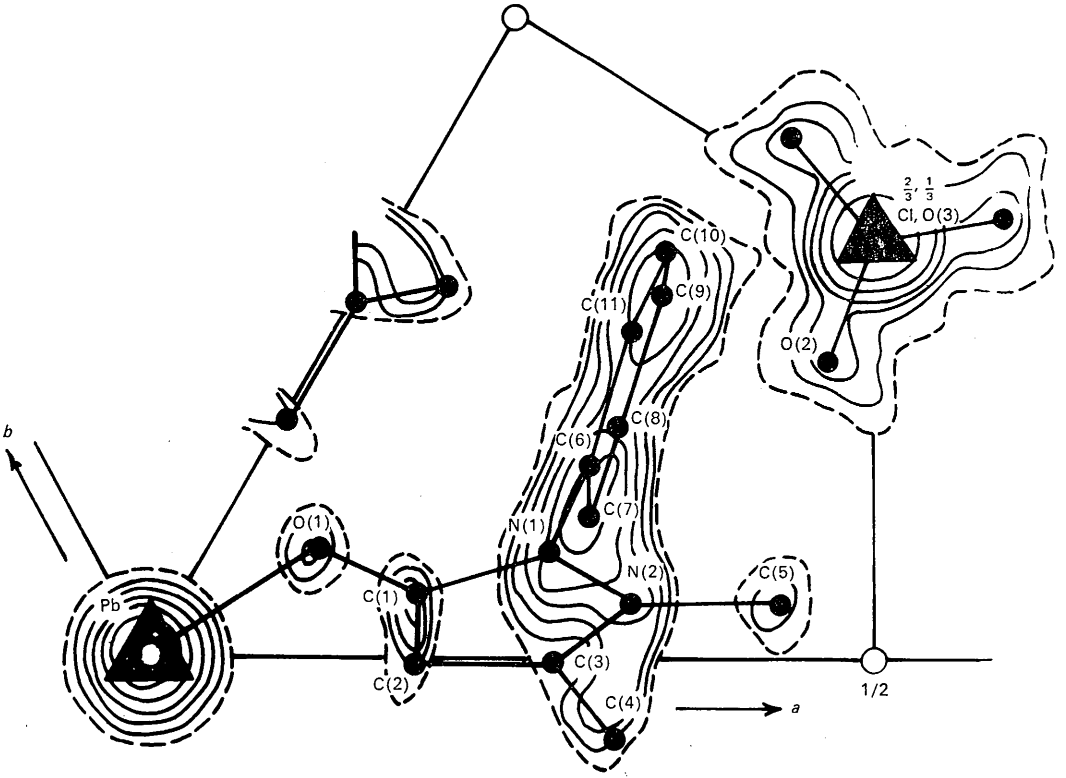

Fig. 1. Electron density projection on (0001). Contours are drawn at arbitrary intervals. Atomic positions are indicated.

octahedron is seen to be slightly elongated in this direction.

The antipyrine group

The bond lengths and bond angles in the antipyrine group together with their standard deviations are given in Table 6 and are shown schematically in Fig. 4. Both the phenyl ring and the five-membered pyrazolone ring are completely planar within experimental error. The equations of their mean planes referred to orthogonal axes $X' = x + y\cos\gamma$, $Y' = y\sin\gamma$ and $Z' = z$ (Blow, 1960) are given in Table 7. The displacements of the

Table 5. *Dimensions of the coordination polyhedron about* Pb^{2+}

Pb—O(1)	2·446 ± 0·016 Å	(×6)
O(1′)–O(1″)	3·319 ± 0·020	(×6)
O(1) –O(1′)	3·595 ± 0·024	(×6)
O(1′)–Pb–O(1″)	85·4 ± 0·5°	(×6)

ring atoms from, and their standard deviations normal to, the respective mean planes are also listed in Table 7. All the displacements are less than their estimated standard deviations normal to the planes of the rings.

The phenyl ring is found to be inclined by 68° with respect to the plane of the pyrazolone ring. If the N–C bond between the two rings were to be a pure single bond one would expect them to be perpendicular to each other, as this would correspond to a position of least steric hindrance between the phenyl ring and the methyl group attached to the nitrogen atom in the pyrazolone ring. The observed N–C distance is 1·414 ± 0·023 Å, which is significantly smaller than 1·47 Å, the value normally assigned to a pure N–C single bond. The angle of 68° between the two rings, therefore, is probably due to a small double bond character of the N–C bond as evidenced by the shortening of its length, in addition to probable intermolecular steric effects.

The average C–C distance in the phenyl ring is 1·394 ± 0·03 Å and the C–C–C angle varies from 116·6 to 123·8°. In the pyrazolone ring all the bond lengths lie between the corresponding single and double bond values and the internal angles range from 105·8 to 110°. The $N-CH_3$ and $C-CH_3$ bond lengths are 1·481 ± 0·027 and 1·531 ± 0·040 Å respectively, which compare well with the standard N–C and C–C single bond lengths. The C–O distance in the keto group is 1·284 ± 0·025 Å.

The perchlorate ion

The perchlorate ion in this structure, which is close to a regular tetrahedron, has two crystallographically non-equivalent oxygen atoms; one of them, O(3), occupies a special position on the threefold axis, while the other, O(2), is at a general position. The chlorine atom is also at a special position on the threefold axis. The bond lengths and angles in the perchlorate ion are listed in Table 8.

The two non-equivalent Cl–O distances in the structure are 1·418 ± 0·017 and 1·413 ± 0·038 Å, which are

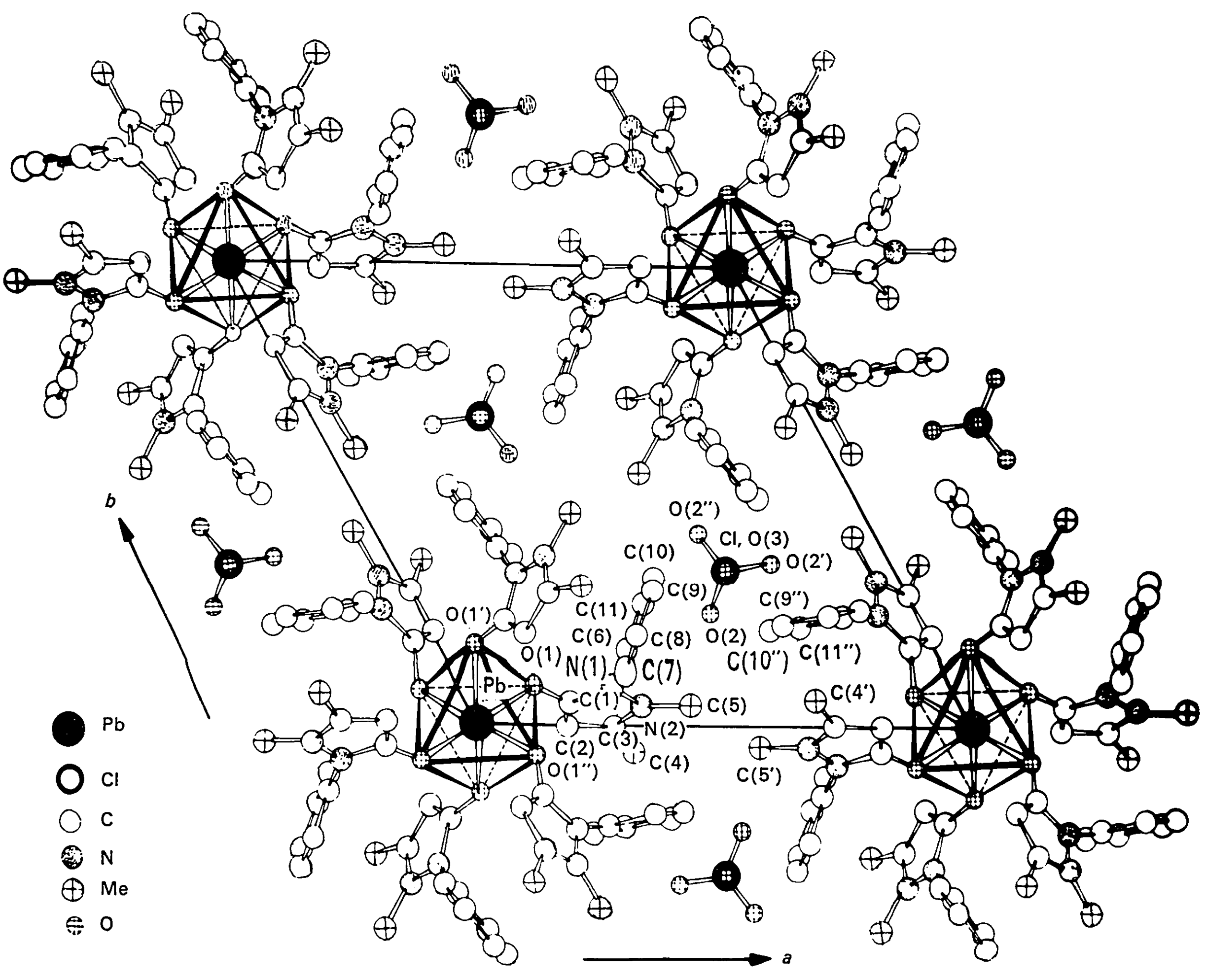

Fig. 2. Perspective view of the structure as seen along the *c* axis.

Table 6. *Interatomic distances and angles in the antipyrine group and their standard deviations*

	Length	σ
O(1) -C(1)	1·284 Å	0·025 Å
C(1)—C(2)	1·395	0·032
C(2)—C(3)	1·387	0·034
C(3)—C(4)	1·531	0·040
C(3)—N(2)	1·353	0·026
N(2) -C(5)	1·481	0·027
N(2) -N(1)	1·363	0·027
N(1) -C(1)	1·390	0·024
N(1) -C(6)	1·414	0·023
C(6)—C(7)	1·415	0·032
C(7)—C(8)	1·416	0·032
C(8)—C(9)	1·364	0·025
C(9)—C(10)	1·366	0·035
C(10)-C(11)	1·406	0·030
C(11)-C(6)	1·398	0·021

	Angle	σ
O(1) -C(1)—C(2)	131·4°	2·0°
O(1) -C(1)—N(1)	122·6	1·8
N(1) -C(1)—C(2)	105·8	1·8
C(1)—C(2)—C(3)	107·3	1·8
C(2)—C(3)—C(4)	128·8	2·2
C(4)—C(3)—N(2)	121·4	2·0
C(2)—C(3)—N(2)	109·6	2·0
C(3)—N(2) -C(5)	129·4	1·8
C(5)—N(2) -N(1)	121·9	1·7
C(3)—N(2) -N(1)	107·3	1·7
N(2) -N(1) -C(6)	123·6	1·6
C(6)—N(1) -C(1)	126·0	1·6
N(2) -N(1) -C(1)	110·0	1·6
N(1) -C(6)—C(11)	119·6	1·7
N(1) -C(6)—C(7)	120·4	1·7
C(11)-C(6)—C(7)	120·0	1·8
C(6)—C(7)—C(8)	120·6	2·1
C(7)—C(8)—C(9)	118·9	2·2
C(8)—C(9)—C(10)	120·2	2·2
C(9)—C(10)-C(11)	123·8	2·2
C(10)-C(11)-C(6)	116·6	2·0

Table 7. *Mean planes, displacements of atoms from the planes* (Å), *and their standard deviations* (Å) *normal to the planes* (Blow, 1960)

Phenyl ring: $0{\cdot}9442X' - 0{\cdot}3217Y' - 0{\cdot}0712Z' - 2{\cdot}8485 = 0$

	Δ	$\sigma_\perp$
C(6)	−0·006	0·017
C(7)	−0·001	0·022
C(8)	+0·004	0·022
C(9)	+0·001	0·022
C(10)	−0·008	0·021
C(11)	+0·011	0·020

$\chi^2 = 0{\cdot}63$; $n = 3$; $P > 0{\cdot}80$

Pyrazolone ring: $-0{\cdot}1341X' + 0{\cdot}8545Y' - 0{\cdot}5019Z' + 3{\cdot}5538 = 0$

	Δ	$\sigma_\perp$
C(1)	−0·010	0·019
C(2)	+0·009	0·019
C(3)	−0·005	0·020
N(1)	+0·007	0·014
N(2)	−0·001	0·016

$\chi^2 = 0{\cdot}76$; $n = 2$; $P > 0{\cdot}50$

Table 8. *Dimensions of the perchlorate ion*

Cl-O(2)	1·418 ± 0·017 Å	(×3)
Cl-O(3)	1·413 ± 0·038	(×1)
Weighted mean	1·417 ± 0·022	
O(2)-O(3)	2·319 ± 0·035	(×3)
O(2)-O(2′)	2·310 ± 0·021	(×3)
O(2)-Cl-O(3)	110·0 ± 1·3°	(×3)
O(2)-Cl-O(2′)	109·1 ± 1·1	(×3)

considerably smaller than the normal Cl–O distance varying from 1·440 to 1·450 Å. In view of the large thermal vibration amplitudes of the oxygen and the chlorine atoms, the Cl–O distances were corrected by Busing & Levy's scheme (1964). As the chlorine atom is considerably heavier than the oxygen atoms, and also in view of the fact that $[ClO_4]^-$ is a tightly bound ion, correction assuming 'in-phase' motion was applied (oxygen atoms 'riding' on chlorine). The corrected Cl–O(2) and Cl–O(3) distances are 1·457 and 1·453 Å respectively. For the sake of comparison, the uncorrected and corrected Cl–O distances in the perchlorate ions in some of the recently determined structures, together with the *B* values of the relevant atoms, calculated by Hamilton's formula from the reported anisotropic temperature parameters, are listed in Table 9.

Molecular packing

A perspective view of the structure as seen down the *c* axis is given in Fig. 2. In Fig. 3 are shown the contents of the unit cell projected on to the *ac* plane.

The structure can be described as consisting of two-dimensional arrays of hexagonal close-packed $[Pb(C_{11}H_{12}ON_2)_6]^{2+}$ complex cations in the (0001) plane, stacked perpendicular to the *c* axis, the interstices in this arrangement being filled by the perchlorate anions. Each complex cation is surrounded by twelve perchlorate ions disposed at the apices of a hexagonal prism of side *a*/3 and height *c*. The disposition of complex cations about each perchlorate ion is trigonal prismatic, the side of the basal triangle of the prism being *a* and the height *c*.

The perchlorate ions are situated in the holes formed by the phenyl rings and methyl groups of the surrounding antipyrine molecules. The packing of the nearest phenyl ring atoms around the perchlorate group as viewed along the *b** axis and that of the methyl groups as viewed down the *c* axis are shown in Fig. 5(*a*) and (*b*) respectively. The phenyl hydrogen atoms referred to were fixed by geometrical considerations, assuming a C–H distance of 1·08 Å. The perchlorate oxygen atom O(3) lying on the threefold axis is 'capped' by C(11) in the phenyl ring, the hydrogen attached to it and their threefold symmetry equivalents. On the other side of the perchlorate ion, the threefold related perchlorate oxygen atoms O(2), O(2′) and O(2″) are

Table 9. *Uncorrected and corrected* Cl–O *distances* (Å) *in some perchlorates and the B values* (Å^2) (*calculated from Hamilton's formula*) *of the chlorine and oxygen atoms*

Compound	Bond	Uncorrected distance	Corrected distance	B_{Cl}	B_O	Reference
NO_2ClO_4	Cl—O′	1·432	1·451	2·87	4·53	Truter, Cruickshank & Jeffrey, 1960
	Cl—O″	1·445	1·485		6·29	
H_3OClO_4	Cl—O(1)	1·427	1·453	3·92	5·98	Truter, 1961
	Cl—O(2)	1·412	1·439		6·48	
	Cl—O(3)	1·436	1·465		6·89	
$(CH_3SO)(ClO_4)_4$	Cl(1)–O(2)	1·410	1·450	3·27	8·91	Coulter, Gantzel, & McCullough, 1963
	Cl(2)–O(3)	1·414	1·450	3·32	7·47	
	Cl(2)–O(4)	1·413	1·450		10·37	
	Cl(2)–O(5)	1·488	1·530		9·81	
$Pb(C_{11}H_{12}ON_2)_6(ClO_4)_2$	Cl—O(2)	1·418	1·457	6·11	10·13	Present work
	Cl—O(3)	1·413	1·453		10·36	

'cushioned' by C(8), H(8), C(9), H(9) and their symmetry equivalents. The phenyl rings nearest to O(2), O(2′) and O(2″) are related to those nearest to O(3) by a cell translation along the *c* axis. The methyl groups C(5) and C(4′) fit into the spaces between O(2) and O(3) and between O(2) and O(2′) respectively. The various distances involved in these contacts are given in Table 10.

Table 10. *Interionic contacts involving atoms in the antipyrine groups with perchlorate oxygen atoms*

C(11)–O(3)	3·511 Å	(×3)
C(5)—O(3)	3·737	(×3)
C(8)—O(2)	3·572	(×3)
C(9)—O(2)	3·583	(×3)
C(9)—O(2″)	3·707	(×3)
C(5)—O(2)	3·515	(×3)
C(4′) -O(2)	3·727	(×3)
C(4′) -O(2′)	3·902	(×3)

Table 11. *Shortest intermolecular contacts*

C(9)—C(9″)	3·829 Å
C(9)—C(10″)	3·719
C(10)-C(10″)	3·610
C(11)-C(10″)	3·843
C(5)—C(10″)	3·939
C(5)—C(11″)	3·935
C(4)—C(5′)	4·048

The intermolecular contacts involving atoms in the antipyrine groups correspond to the expected van der Waals interactions. All contacts less than 4 Å are listed in Table 11. The only relevant contact more than 4 Å is that between the methyl carbon atoms C(4) and C(5′).

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References

Blow, D. M. (1960). *Acta Cryst.* **13**, 168.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.

Byström, A. (1945). *Ark. Kemi, Min. Geol.* A, **18**, no. 23, 1.

Byström, A. & Evers, L. (1950). *Acta Chem. Scand.* **4**, 613.

Byström, A. & Westgren, A. (1943). *Ark. Kemi, Min. Geol.* B, **16**, no. 14, 1.

Colby, M. Y. & La Coste, L. J. B. (1933). *Z. Kristallogr.* **84**, 299.

Collotti, G., Conti, L. & Zocchi, M. (1959). *Acta Cryst.* **12**, 416.

Coulter, C. L., Gantzel, P. K. & McCullough, J. D. (1963). *Acta Cryst.* **16**, 676.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.

Dörfurt, E. W. & Schliephake, O. (1928). *Z. anorg. allg. Chem.* **170**, 129.

Dörfurt, E. W. & Schliephake, O. (1929). *Z. anorg. allg. Chem.* **183**, 301.

Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.

Frondel, C. & Barnes, I. (1958). *Acta Cryst.* **11**, 562.

Hamilton, W. C. (1957). *Acta Cryst.* **10**, 103.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609.

International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Ismailzade, I. G. (1959). *Kristallografiya*, **4**, 417.

Ismailzade, I. G. (1960). *Kristallografiya*, **5**, 316.

James, R. W. & Wood, W. A. (1925). *Proc. Roy. Soc.* A, **109**, 598.

Kannan, K. K. (1965). Ph.D Thesis submitted to Indian Institute of Science, Bangalore.

Kolb, A. (1913). *Z. anorg. Chem.* **83**, 143.

Kuznetsov, V. G. & Kożmin, P. A. (1958). *Zh. neorg. Khim.* 3, 2361.

Møller, C. K. (1954). *Acta Chem. Scand.* **8**, 81.

Náray-Szabó, I. & Argay, G. (1964). *Acta Chim. Acad. Sci. Hung.* **40**(3), 283.

Náray-Szabó, S. von. (1943). *Naturwissenschaften*, **31**, 466.

Náray-Szabó, S. von. (1947). *Publi. Univ. Tech. Sci. Budapest*, **1**, 30.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

Quareni, S. & De Pieri, R. (1964). *Rend. Soc. Mineral. Ital.* **20**, 235.

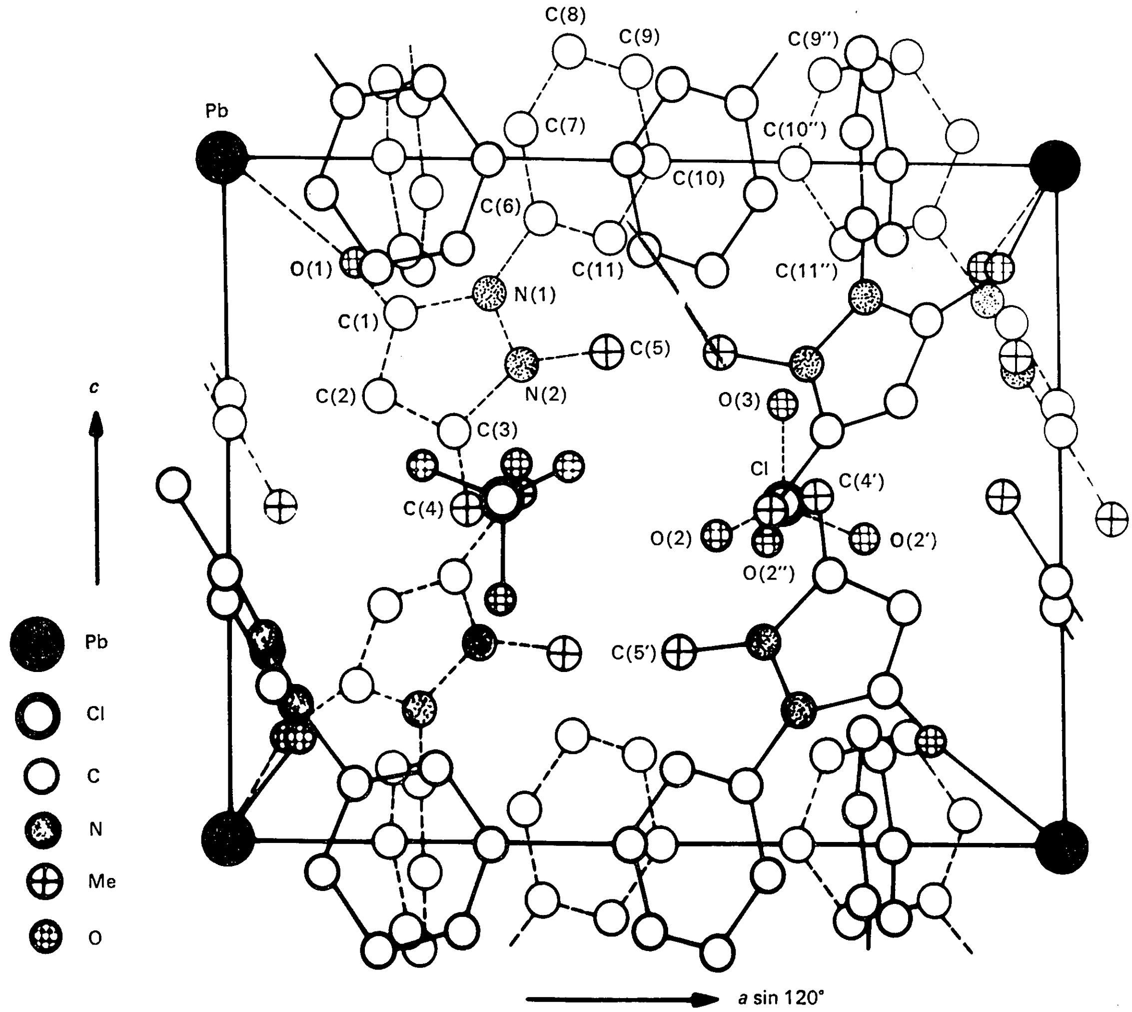

Fig. 3. The contents of the unit cell projected on the *ac* plane.

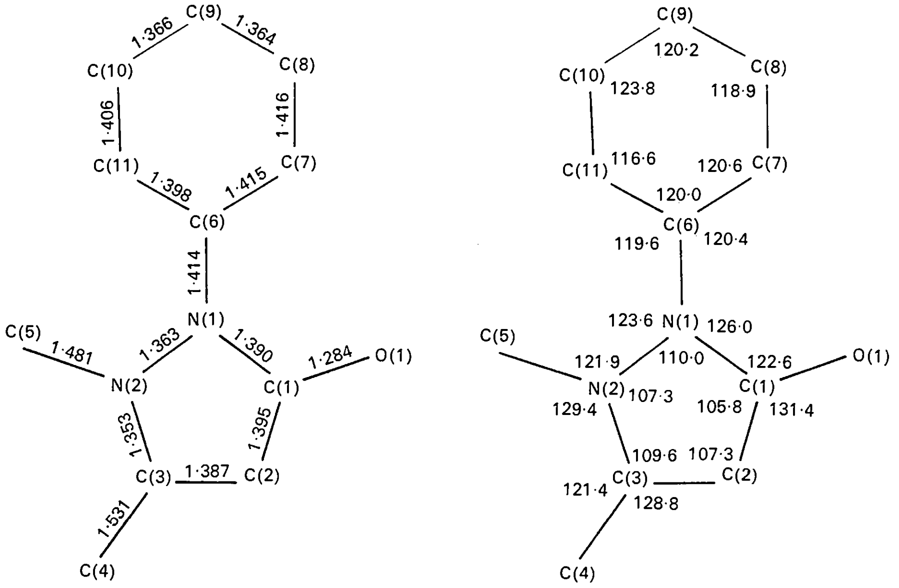

Fig. 4. Bond lengths (Å) and bond angles (°) in the antipyrine group.

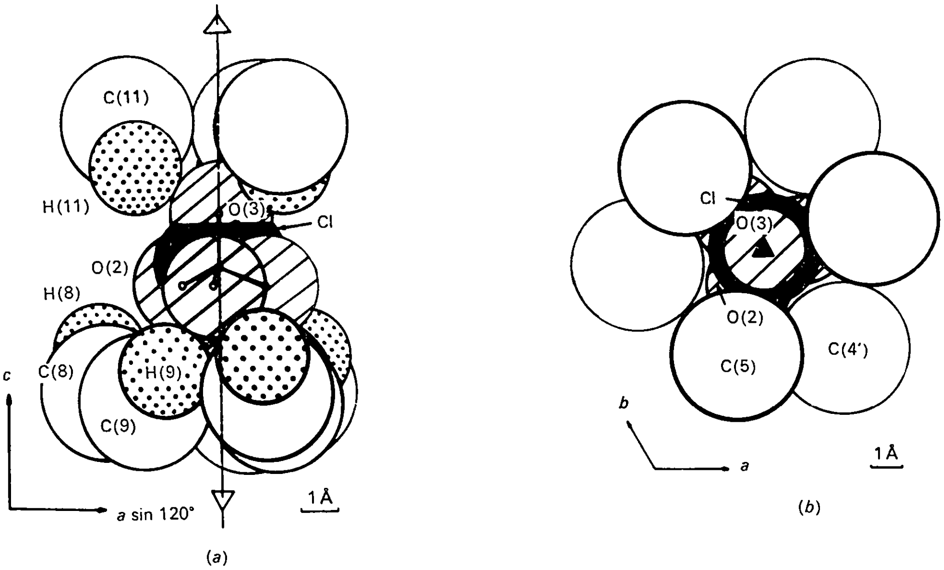

Fig. 5. (*a*) Packing of the phenyl ring atoms around the perchlorate ion, as viewed along the b^* axis. (*b*) Packing of the methyl groups around the perchlorate ion, as viewed along the c axis.

Rollett, J. S. & Davies, D. R. (1955). *Acta Cryst.* **8**, 125.

Schuyten, M. C. (1898). *J. Chem. Soc. Abstracts*, Part I, **74**, 452.

Schuyten, M. C. (1900). *J. Chem. Soc. Abstracts*, Part I, **78**, 57.

Truter, M. R. (1961). *Acta Cryst.* **14**, 318.

Truter, M. R., Cruickshank, D. W. J. & Jeffrey, G. A. (1960). *Acta Cryst.* **13**, 855.

Van Uitert, L. G. & Soden, R. R. (1961). *Advances in the Chemistry of Coordination Compounds.* p. 613. New York: MacMillan & Co.

Vijayan, M. & Viswamitra, M. A. (1965). *Indian J. Pure App. Physics*, **3**, 357.

Wells, A. F. (1962). *Structural Inorganic Chemistry.* Oxford: Clarendon Press.

Zachariasen, W. H. & Plettinger, H. A. (1959). *Acta Cryst.* **12**, 526.

Acta Cryst. (1966). **21**, 532

The Crystal and Molecular Structure of 4-(1,5-Diazabicyclo[3.2.1]oct-8-yl)pyridine, $C_{11}H_{15}N_3$

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4-(1,5-Diazabicyclo[3.2.1]oct-8-yl)pyridine crystallizes in the orthorhombic space group *Pnma* with four molecules in the unit cell. The lattice parameters are $a = 13{\cdot}58$, $b = 10{\cdot}99$, $c = 6{\cdot}93$ Å.

The structure was obtained by determining the phases directly from the structure factor magnitudes by means of the symbolic addition procedure. The structure was refined by means of three-dimensional least-squares to a final $R = 12{\cdot}4$ % for the observed data.

The molecule has a plane of symmetry. The cage portion consists of puckered five-, six- and seven-membered rings. The six-membered ring is in the chair configuration whereas the seven-membered ring has the boat configuration. The bond lengths in the pyridine ring resemble those in a quinoid type structure.

Introduction

One portion of 4-(1,5-diazabicyclo[3.2.1]oct-8-yl)pyridine consists of a cage formed by a five-, six,- and seven-membered ring. The investigation of the structure was undertaken to determine the stereoconfiguration of the cage, since several different models of the molecule appear *a priori* to be equally probable. The molecule lies on a plane of symmetry and for the pres-