

values than were any of the other atomic parameters.

The present structure and that of von Stackelberg and Paulus are related geometrically to the structure of fluorite; this is illustrated in Fig. 2. Consider one fluorite-type unit cell with As^{3-} replacing Ca^{2+} and Cd^{2+} replacing F^- , but with two cube-diagonally opposite fluorite sites vacant. The unit cell of Goodyear and Steigmann contains 16 such units in the orientation shown in Fig. 2(a), the tail and head of the arrow being situated at the upper and lower vacant sites, respectively, in one unit. Fig. 2(b) shows the orientation of such units in the structure of Stackelberg and Paulus, there being 4 units in one unit cell of structure.

Cd-As and As-As bond lengths in each type of As tetrahedron are given in Table 4. The variation in some of the As-As distances shows that there is appreciable distortion from cubic close-packing of As ions.

We wish to thank Dr D. W. G. Ballentyne and Mr G. L. Bucknell for providing us with specimens and Dr P. J. Wheatley, of Monsanto Research S.A., for permitting us to use some of his computer programs.

References

- BOND, W. L. (1959). *Acta Cryst.* **12**, 375.
 CLARK, G. L. (1955). *Applied X-rays*, 4th edition. New York: McGraw-Hill.
 COLE, H., CHAMBERS, F. W. & DUNN, H. M. *Acta Cryst.* **9**, 685.
 GOODYEAR, J. & DUFFIN, W. J. (1957). *Acta Cryst.* **10**, 597.
Handbook of Chemistry and Physics (1961). 43rd edition. Cleveland: Chemical Rubber Publishing Co.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham, Kynoch Press.
 PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746.
 STACKELBERG, M. VON & PAULUS, R. (1935). *Z. physik. Chem.* **28B**, 427.

Acta Cryst. (1968). B24, 1067

A Refinement of the Structure of Calcium Hexa-antipyrine Perchlorate and a Comparative Study of Some Metal Hexa-antipyrine Perchlorates

BY M. VIJAYAN* and M. A. VISWAMITRA

Department of Physics, Indian Institute of Science, Bangalore 12, India

(Received 26 June 1967 and in revised form 23 October 1967)

Calcium hexa-antipyrine perchlorate, $\text{Ca}(\text{C}_{11}\text{H}_{12}\text{ON}_2)_6(\text{ClO}_4)_2$, is isomorphous with the corresponding magnesium and lead compounds and crystallizes in the trigonal space group $P\bar{3}$ with one formula unit in an elementary cell of dimensions $a = 14.33$ and $c = 9.78$ Å. The structure was refined by structure-factor least-squares method to an R value of 0.118 for 1131 observed reflexions. The structural features of magnesium, calcium and lead hexa-antipyrine perchlorates are compared. The coordination of antipyrine oxygen atoms around the metal ion is octahedral in all three cases; this octahedron becomes elongated along the $\bar{3}$ axis as the size of the metal ion increases. The nature of the metal-oxygen bonds is discussed on the basis of the known electronegativity coefficients of the relevant atoms and the observed metal-oxygen distances. In the antipyrine molecule, both the phenyl and the pyrazolone rings are planar and are inclined with respect to each other by angles varying from 62 to 68°. An attempt has been made to explain the observed bond lengths in the pyrazolone ring in terms of the major canonical structures proposed.

Introduction

The present study forms part of a program of systematic X-ray investigation of some metal antipyrine compounds undertaken in this laboratory to study the nature of the metal-oxygen bonding in these and also to elucidate the geometry of the antipyrine ring system.

Independent analyses of the isostructural lead and magnesium hexa-antipyrine perchlorates have already been reported (Vijayan & Viswamitra, 1966, 1967). Divalent calcium has an ionic radius ($r = 0.99$ Å) mid-way between those of Mg^{2+} ($r = 0.65$ Å) and Pb^{2+} ($r = 1.21$ Å) (Wells, 1962) and hence it was thought worth while to analyse the structure of the calcium compound to facilitate a study of the changes introduced in the molecular geometry and packing as a result of the change in the size of the central metal ion. In addition, it would

* Present address: Chemical Crystallography Laboratory South Parks Road, Oxford, England.

enhance the knowledge about the molecular geometry of antipyrine already derived from the analysis of the magnesium compound.

Experimental

Morphological and X-ray examination showed that calcium hexa-antipyrine perchlorate,



crystallizes in the trigonal space group $P\bar{3}$ with one formula unit in an elementary cell of dimensions $a=14.33$, $c=9.78$ Å. The measured and calculated densities were 1.330 and 1.310 g.cm⁻³ respectively (Vijayan & Viswamitra, 1965).

Intensity data were recorded with use of an approximately cylindrical specimen of mean radius 0.25 mm with Cu $K\alpha$ radiation on multiple film equi-inclination Weissenberg photographs about the c axis for reciprocal levels hkl , $l=0$ through 7. $h0\bar{h}l$ zonal data were also collected likewise with a crystal cut along the a_2 axis and ground approximately to the same radius. The intensities were visually estimated by comparison with calibrated strips. Out of a total number of 2648 independent reflexions in the copper sphere 2181 were recorded of which 1131 were in the measurable range.

The data were corrected for Lorentz and polarization factors and the variation in spot shape in upper level Weissenberg photographs with the use of Nambudiri's program (Nambudiri, Kannan & Vijayan, 1966) on the Elliott 803-B computer at the Hindustan Aeronautics Ltd, Bangalore. Absorption corrections corresponding to $\mu r=0.5$ ($\mu=20.1$ cm⁻¹ for $\lambda=1.5418$ Å; $r=0.25$ mm) were also applied to the intensities (*International Tables for X-ray Crystallography*, 1959). The intensities were put on the same scale by comparison with the data from the isomorphous magnesium compound.

Refinement

As the ionic radius of Ca²⁺ is mid-way between those of Mg²⁺ and Pb²⁺, the average values of the positional coordinates and the equivalent isotropic temperature factors found in the magnesium and the lead compounds were used as the initial parameters in refinement procedures. Structure-factor calculations with these parameters gave a residual index of 0.230 for $hki0$ and $h0\bar{h}l$ reflexions. The structure was refined with the use of zonal data to an R index of 0.139 by three cycles of isotropic structure-factor least-squares calculations.

The first three-dimensional SFLS cycle computed on the Elliott 803-B machine at Bangalore with the parameters refined from zonal data gave an R value of 0.169 for 1131 measured reflexions. The indicated shifts in the individual isotropic temperature factors were of the order of the corresponding standard deviations and hence individual anisotropic temperature factors of the form

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

were used in further refinement cycles carried out on the CDC-3600 computer system installed in the Tata Institute of Fundamental Research, Bombay. The first anisotropic structure-factor calculations yielded a discrepancy index of 0.144. In six diagonal SFLS cycles this index was reduced to 0.118. In the final cycle all the indicated shifts except one were less than the corresponding standard deviations, the average and the maximum shifts being 0.29 σ and 1.10 σ respectively.

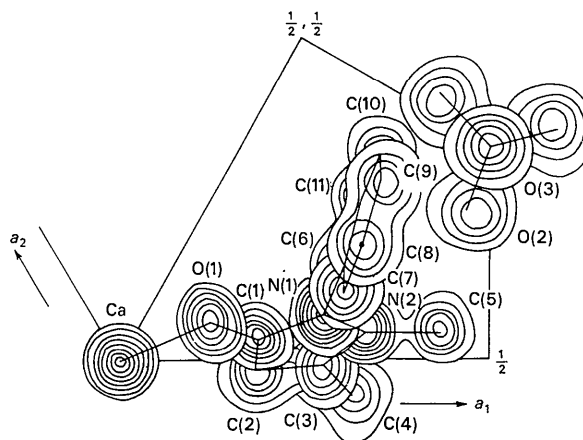


Fig. 1. Final three-dimensional electron density projection along the c axis. Contours are at intervals 1, 2, 3, ... e.Å⁻³ for C, N and O and 1, 5, 10, ... e.Å⁻³ for Ca. The position of Cl is below O(3).

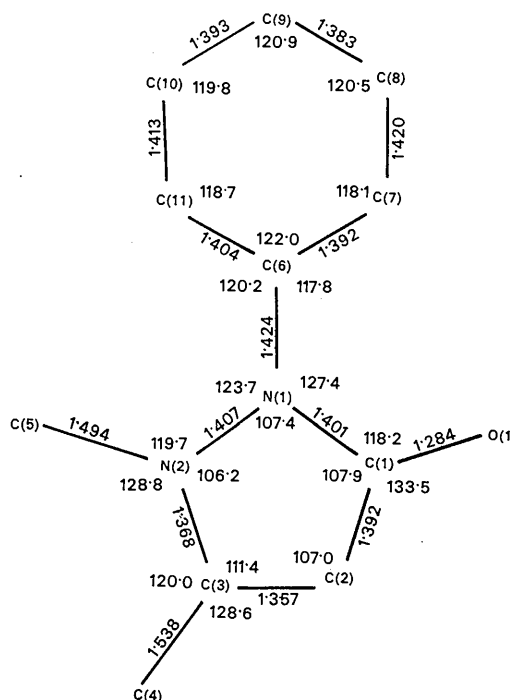


Fig. 2. Dimensions of the antipyrine molecule.

In the above calculations, reflexions with kF_o greater than 6 and less than 35 were given unit weights whereas those with kF_o less than 6 and greater than 35 were given half weights. Five low angle reflexions with kF_o greater than 50 were assigned zero weights as they were believed to be affected by extinction. The F_o 's were scaled to correspond to half the contents of the unit cell. Scattering factors for all the atoms were computed by means of the nine-term analytical expressions given by Cromer & Waber (1965).

The computer programs used in this analysis were those developed in this laboratory (Nambudiri *et al.*, 1966; Kannan, 1965; Vijayan, 1966).

Results

In Table 1 are listed the final positional parameters and their standard deviations calculated from least-squares residues. The components of the anisotropic temperature factor tensors and the equivalent isotropic temperature factors (Hamilton, 1959) are given in Table 2. Table 3 lists the magnitudes and direction cosines with respect to a^* , b^* and c^* axes of the principal axes of thermal vibration ellipsoids. The bond lengths and valency angles in the structure together with their standard deviations are listed in Table 4. The observed and calculated structure factors (unobservables excluded) are given in Table 5.

A final Fourier synthesis was computed and superposed sections of the corresponding electron density distribution are given in Fig. 1. Atomic positions are also indicated in the Figure. A difference Fourier synthesis was also computed in an attempt to locate hydrogen atoms, but their positions could not be determined unambiguously from the difference diagram.

Description of the structure

Coordination around Ca^{2+}

The Ca^{2+} ion in the structure occupies a position of $\bar{3}$ symmetry at the origin of the unit cell. The octa-

Table 1. *Fractional positional parameters*

Standard deviations are given in parentheses

	x	y	z
Ca	0	0	0
Cl	0.66667 (0)	0.33333 (0)	-0.51063 (50)
O(1)	0.14833 (49)	0.06146 (50)	-0.14038 (69)
O(2)	0.58767 (81)	0.23044 (79)	-0.56196 (99)
O(3)	0.66667 (0)	0.33333 (0)	-0.36506 (130)
N(1)	0.30982 (54)	0.07315 (54)	-0.19791 (74)
N(2)	0.35251 (58)	0.04850 (57)	-0.31288 (80)
C(1)	0.20066 (66)	0.03567 (66)	-0.22424 (96)
C(2)	0.17568 (69)	-0.01611 (68)	-0.35049 (99)
C(3)	0.26776 (73)	-0.00843 (71)	-0.39980 (95)
C(4)	0.28439 (93)	-0.05587 (93)	-0.53256 (114)
C(5)	0.45477 (79)	0.04538 (77)	-0.29987 (114)
C(6)	0.37424 (66)	0.14462 (65)	-0.09207 (92)
C(7)	0.35236 (81)	0.10698 (78)	0.04197 (107)
C(8)	0.41435 (89)	0.17872 (90)	0.14835 (114)
C(9)	0.49437 (82)	0.28278 (83)	0.11851 (116)
C(10)	0.51461 (81)	0.32012 (80)	-0.01584 (122)
C(11)	0.45479 (74)	0.25015 (74)	-0.12379 (106)

hedral coordination of antipyrine oxygen atoms around Ca^{2+} is, thus, determined by the symmetry of the space group. The six $\bar{3}$ equivalent Ca^{II} -O distances have a value of 2.304 ± 0.006 Å, which compares well with those found in other compounds (*International Tables for X-ray Crystallography*, 1962).

The antipyrine group

The dimensions of the antipyrine molecule in the structure are shown in Fig. 2.

The equations of the mean planes of the phenyl and the pyrazolone rings with respect to orthogonal axes $X' = x + y \cos \gamma$, $Y' = y \sin \gamma$ and $Z' = z$ and the displacements of the ring atoms from and their standard deviations normal to the mean planes are given in Table 6. The r.m.s. displacements of the atoms in the phenyl ring and of those in the pyrazolone ring from their respective mean planes are 0.005 Å and 0.015 Å respectively. The mean plane of the phenyl ring makes an angle of $62^\circ 31'$ with that of the pyrazolone ring.

Table 2. *Anisotropic thermal parameters ($\times 10^5$) and the equivalent isotropic temperature factors*

	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}	B
Ca	311	311	498	311	0	0	1.91 Å ²
Cl	970	970	1062	970	0	0	5.34
O(1)	898	885	1408	873	-188	-88	5.48
O(2)	1881	1796	2347	1635	-27	112	10.82
O(3)	1851	1851	774	1851	0	0	8.59
N(1)	700	737	920	628	-125	26	4.25
N(2)	784	775	1079	636	-39	-113	4.77
C(1)	674	585	1094	453	-60	77	4.22
C(2)	749	657	1090	529	-35	0	4.51
C(3)	723	873	828	687	52	228	4.49
C(4)	1449	1172	1223	1134	-109	321	7.18
C(5)	843	876	1740	891	-82	99	7.04
C(6)	630	576	870	474	45	210	3.76
C(7)	978	872	1058	815	125	285	5.30
C(8)	1054	1158	1189	975	72	188	6.25
C(9)	1071	952	1528	1023	-64	-158	6.09
C(10)	922	873	1737	960	12	-246	5.81
C(11)	683	796	1474	745	51	-161	4.88

Table 3. *Magnitudes and direction cosines of the principal axis of the vibration ellipsoids*

Atom	Axis <i>i</i>	<i>B_i</i> 1.92 Å ²	<i>g_{i1}</i>	<i>g_{i2}</i>	<i>g_{i3}</i>
Ca	1	1.92	1	0.5000	0
	2	1.92	0	0.8660	0
	3	1.91	0	0	1
Cl	1	5.98	1	0.5000	0
	2	5.98	0	0.8660	0
	3	4.06	0	0	1
O(1)	1	5.88	0.2299	0.7251	-0.6714
	2	5.60	-0.9028	-0.0946	0.1235
	3	4.96	0.3636	0.6822	0.7308
O(2)	1	12.67	0.6415	-0.3385	0.0953
	2	10.86	-0.7625	-0.9410	-0.0303
	3	8.94	0.0847	-0.0038	-0.9950
O(3)	1	11.41	1	0.5000	0
	2	11.41	0	0.8660	0
	3	2.96	0	0	1
N(1)	1	5.10	0.3173	-0.6365	0.2374
	2	4.22	-0.9483	-0.7394	0.0832
	3	3.42	0.0036	0.2196	0.9679
N(2)	1	5.71	0.5370	-0.4547	-0.1191
	2	4.59	-0.7501	-0.8404	0.3854
	3	4.02	0.3859	0.2948	0.9150
C(1)	1	5.15	0.6237	-0.3035	0.3259
	2	4.07	-0.2673	0.0378	0.9431
	3	3.45	0.7346	0.9521	0.0665
C(2)	1	5.48	0.6702	-0.3058	0.0575
	2	4.18	-0.2061	-0.1992	0.9722
	3	3.89	0.7130	0.9310	0.2269
C(3)	1	5.87	0.1246	-0.7935	0.0892
	2	4.63	-0.9309	-0.5932	-0.3343
	3	2.96	0.3435	0.1359	-0.9383
C(4)	1	9.88	0.8113	-0.0697	0.2014
	2	7.23	-0.5706	-0.9941	0.0681
	3	4.45	0.1274	-0.0837	-0.9772
C(5)	1	6.77	0.1231	-0.1314	0.9671
	2	5.39	-0.6962	-0.9663	-0.0759
	3	4.95	0.7072	-0.2214	-0.2430
C(6)	1	4.70	0.6603	-0.2550	0.3278
	2	3.58	-0.4871	-0.8649	-0.4979
	3	3.00	0.5717	0.4323	-0.8029
C(7)	1	6.64	0.7889	-0.1021	0.2214
	2	5.43	-0.5277	-0.9710	-0.2343
	3	3.82	0.3151	0.2164	-0.9466
C(8)	1	7.74	0.2371	-0.7215	0.0526
	2	6.52	-0.9468	-0.6837	-0.2113
	3	4.45	0.2178	0.1091	-0.9760
C(9)	1	6.79	0.9093	0.3023	-0.3773
	2	5.79	-0.0650	-0.8598	0.2886
	3	5.68	0.4112	0.4120	0.8799
C(10)	1	6.98	0.4002	0.0657	-0.9032
	2	5.56	-0.8224	-0.8405	-0.2792
	3	4.91	0.4045	-0.5378	0.3260
C(11)	1	5.83	0.1855	-0.1625	-0.9374
	2	4.83	-0.4336	-0.9794	0.1911
	3	3.99	0.8818	0.1196	0.2911

The mean C—C distance and the average C—C—C angle in the phenyl ring are 1.401 Å and 120.0° respectively. The N—C and C—C distances in the pyrazolone ring lie between the corresponding single-bond and double-bond values. The N—CH₃ and C—CH₃ bond distances in the molecule are 1.494 ± 0.016 and 1.539

± 0.015 Å respectively and the length of the C—O bond in the carbonyl group is 1.284 ± 0.012 Å.

The perchlorate ion

The threefold axis of the tetrahedral perchlorate ion in the structure coincides with the threefold axis in the

Table 4. *Interatomic distances, valency angles and their standard deviations*

Bond	<i>l</i>	$\sigma(l)$	Angle	θ	$\sigma(\theta)$
Ca—O(1)	2.304 Å	0.006 Å	Ca—O(1)—C(1)	146.2°	0.6°
O(1)—C(1)	1.284	0.012	C(1)—C(2)—C(3)	107.0	0.9
C(1)—C(2)	1.392	0.013	C(2)—C(3)—C(4)	128.6	1.0
C(2)—C(3)	1.357	0.016	C(2)—C(3)—N(2)	111.4	0.9
C(3)—C(4)	1.538	0.015	C(4)—C(3)—N(2)	120.0	0.9
C(3)—N(2)	1.368	0.011	C(3)—N(2)—N(1)	106.2	0.8
N(2)—C(5)	1.494	0.016	C(3)—N(2)—C(5)	128.8	0.9
N(2)—N(1)	1.407	0.012	C(5)—N(2)—N(1)	119.7	0.8
N(1)—C(1)	1.401	0.011	N(2)—N(1)—C(6)	123.7	0.7
N(1)—C(6)	1.424	0.010	C(6)—N(1)—C(1)	127.4	0.8
C(6)—C(7)	1.392	0.013	N(2)—N(1)—C(1)	107.4	0.7
C(7)—C(8)	1.420	0.014	N(1)—C(1)—C(2)	107.9	0.8
C(8)—C(9)	1.383	0.013	N(1)—C(1)—O(1)	118.2	0.8
C(9)—C(10)	1.393	0.016	O(1)—C(1)—C(2)	133.5	0.9
C(10)—C(11)	1.413	0.015	N(1)—C(6)—C(11)	120.2	0.8
C(11)—C(6)	1.404	0.011	N(1)—C(6)—C(7)	117.8	0.9
Cl—O(2)	1.428	0.008	C(11)—C(6)—C(7)	122.0	0.9
Cl—O(3)	1.424	0.014	C(6)—C(7)—C(8)	118.1	1.0
			C(7)—C(8)—C(9)	120.5	1.1
			C(8)—C(9)—C(10)	120.9	1.1
			C(9)—C(10)—C(11)	119.8	1.1
			C(10)—C(11)—C(6)	118.7	1.0
			O(2)—Cl—O(3)	110.6	0.8

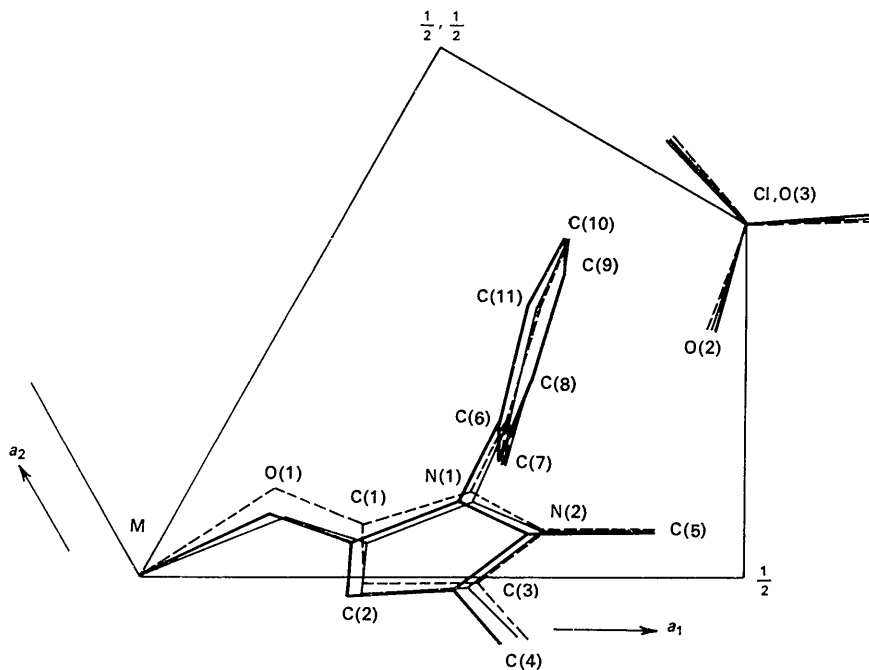


Fig. 3. Atomic positions in magnesium (heavy line), calcium (light line) and lead (broken line) hexa-antipyrine perchlorates as seen along the *c* axis.

Table 5 (cont.)

h k		F _{obs}	F _{calc}	h k		F _{obs}	F _{calc}	h k		F _{obs}	F _{calc}	h k		F _{obs}	F _{calc}
1	9	1270	1186	-5	4	584	648	5	1	108	150	-8	13	275	358
1	10	457	-421	-5	5	370	391	5	2	725	807	-9	12	391	409
1	14	209	224	-5	7	235	-355	5	4	116	516	-9	15	328	450
2	2	205	-524	-5	8	725	794	5	5	1459	1504	-10	11	637	565
2	5	445	-4155	-5	11	1195	1038	5	6	516	531	-11	13	379	424
2	8	516	598	-5	15	107	189	5	9	264	281	-11	14	271	274
2	9	272	261	-4	5	1265	1328	5	11	59	127	-11	14	154	215
2	13	251	277	-4	6	850	875	6	1	506	648	-4	5	287	-172
3	1	1661	1581	-5	7	1118	1175	6	3	979	1056	-4	6	305	439
3	2	1586	1575	-4	8	654	-708	6	4	916	814	1	2	580	714
3	5	1608	-1518	-4	13	505	289	4	5	373	404	1	5	1044	1115
3	4	1146	1010	-5	6	743	674	6	6	358	334	1	4	924	-994
3	5	1276	1039	-5	7	1057	1056	6	9	189	261	1	4	459	-482
3	6	664	-595	-5	8	975	853	7	1	549	562	1	6	275	59
3	7	750	550	-5	12	408	448	7	2	793	796	1	11	226	459
3	8	924	800	-5	16	772	-25	7	3	452	404	2	1	1292	1158
3	10	272	296	-6	8	991	1002	7	7	272	483	2	2	625	-671
4	1	399	505	-6	10	1060	1053	8	1	452	-533	2	5	275	504
4	2	706	734	-6	11	951	954	8	2	641	567	2	4	603	427
4	3	1142	1188	-6	12	999	320	8	3	541	434	2	5	359	-374
4	4	586	592	-6	13	581	580	8	4	299	515	2	6	419	324
4	5	429	-392	-6	14	452	452	8	8	195	287	2	7	867	881
4	6	1104	900	-7	10	691	666	9	2	506	-278	2	10	291	396
4	7	697	535	-7	11	223	458	9	3	264	281	2	11	228	121
4	8	267	414	-7	13	512	335	9	4	272	164	2	12	146	182
4	9	408	565	-7	14	408	480	9	6	268	237	1	1	257	450
4	12	288	162	-7	15	506	550	10	1	525	-521	1	2	1045	1125
5	1	1205	1373	-7	16	180	518	10	4	212	417	1	4	79	860
5	1	715	618	-9	6	625	564	10	5	484	504	1	5	1505	1496
5	5	755	624	-9	10	274	-775	11	2	236	251	1	6	456	29
5	7	454	589	-8	11	161	178	12	1	210	319	1	6	226	400
6	1	760	604	-8	15	311	420	15	1	260	598	1	10	172	447
6	2	862	928	-9	10	505	363	-1	7	741	693	4	1	504	-61
6	3	490	-422	-9	11	612	565	-1	8	459	456	4	2	260	455
6	4	272	-255	-9	13	249	251	-1	6	283	153	-12	15	266	309
6	5	1038	788	-10	11	555	-288	-1	7	402	429	4	4	462	426
7	2	383	596	-10	15	272	396	-1	8	811	842	4	5	422	376
7	3	615	751	-10	16	156	205	-1	8	452	441	4	6	245	372
7	6	512	524	-11	14	512	400	-1	10	596	521	5	2	245	-860
7	7	261	340	-11	15	203	505	-1	11	268	-176	5	3	279	260
7	8	732	-768	-12	14	281	291	-1	14	701	-719	5	4	578	572
8	5	824	912	-11	15	242	286	-2	1	1128	-1445	5	5	277	-235
8	4	505	227	-13	16	87	234	-2	4	412	488	5	9	197	153
8	5	563	-523	-14	15	174	192	-2	6	594	-189	6	1	500	393
8	7	516	404	l = 6				-2	7	569	528	6	2	817	783
9	1	410	-349	1	1	1574	1366	-2	8	815	729	6	4	550	468
9	2	766	665	1	2	1669	1718	-2	10	670	576	6	4	510	562
9	3	557	652	1	3	539	-436	-2	11	457	265	6	5	435	484
9	4	584	554	1	4	452	402	-2	13	552	390	6	8	518	541
9	7	196	518	1	4	452	402	-2	14	178	184	7	2	966	857
10	1	592	736	1	5	511	496	-3	4	214	-180	7	5	706	624
10	2	516	527	1	7	567	587	-3	5	469	522	7	6	245	362
10	3	746	800	1	8	815	651	-1	6	1418	1215	7	8	285	224
10	4	247	277	1	9	719	839	-3	7	531	-159	8	1	551	548
10	5	216	252	1	11	295	429	-3	8	535	-206	8	4	441	446
11	1	505	265	1	14	214	154	-3	9	764	803	8	6	243	275
11	3	347	462	2	1	542	580	-3	15	151	144	8	4	147	122
11	4	181	332	2	2	778	772	-4	5	1210	1110	9	5	178	265
12	2	222	214	2	3	544	406	-4	6	867	848	11	1	257	261
12	4	211	314	2	7	275	-105	-4	7	504	581	12	1	196	244
-1	2	1575	1660	2	5	1261	1155	-4	8	446	464	12	2	148	222
-1	3	74	-688	2	7	578	580	-4	9	1990	1479	-1	2	486	612
-1	4	2520	2305	2	8	1024	953	-4	11	371	450	-1	3	812	764
-1	5	438	475	2	11	559	416	-5	7	1648	1458	-1	4	341	-514
-1	6	563	-233	3	2	623	-565	-5	8	457	741	-1	6	294	298
-1	7	419	537	3	5	483	561	-5	9	498	477	-1	7	751	634
-1	8	538	507	3	5	586	-437	-5	11	606	613	-1	8	481	748
-1	10	773	697	3	6	909	884	-5	12	614	619	-1	10	445	446
-1	15	194	258	3	7	404	199	-5	11	479	582	-1	11	514	-224
-2	3	1035	1101	3	8	419	-153	-6	9	511	662	-1	12	259	236
-2	5	1037	968	3	10	171	460	-6	12	713	700	-1	13	310	339
-2	6	882	934	3	12	511	161	-6	13	531	451	-2	1	1699	1964
-2	7	559	-484	4	1	1211	1203	-7	8	561	647	-2	4	255	-136
-2	8	1072	1172	4	2	422	416	-7	9	338	-277	-2	5	536	-679
-2	9	514	464	4	3	435	-469	-7	10	621	-771	-2	6	415	442
-2	11	586	419	4	4	619	471	-7	11	596	602	-2	10	454	540
-2	14	222	523	4	5	314	109	-7	14	246	249	-1	5	1638	1761
-2	15	146	250	4	10	207	505	-8	11	510	515	-1	6	652	541

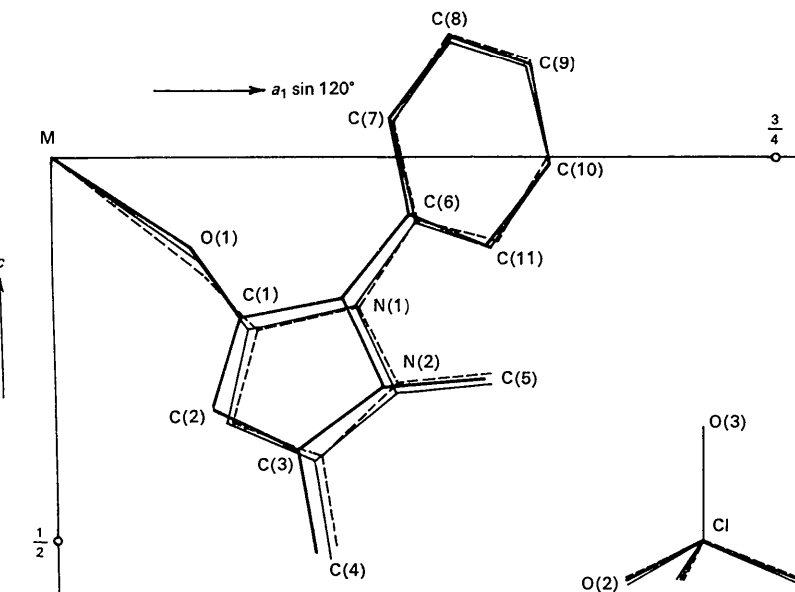


Fig. 4. Atomic positions in magnesium (heavy line), calcium (light line) and lead (broken line) hexa-antipyrene perchlorates as seen along a_2^* axis.

Table 6. Equations of the mean planes of the phenyl and pyrazolone rings

The displacements (Å) of the atoms from, and their standard deviations (Å) normal to, the planes are also indicated.

Phenyl ring:

$$0.9488 X' - 0.3055 Y' - 0.0798 Z' - 2.8470 = 0.$$

	Δ	σ_{\perp}
C(6)	0.001	0.010
C(7)	-0.002	0.011
C(8)	-0.002	0.013
C(9)	0.007	0.012
C(10)	-0.008	0.011
C(11)	0.004	0.011

$$\chi^2 = 1.08; \quad \nu = 3, \quad P < 80\% \text{ and } > 70\%$$

Pyrazolone ring:

$$-0.2458 X' + 0.8623 Y' - 0.4428 Z' + 3.6334 = 0.$$

	Δ	σ_{\perp}
N(1)	-0.020	.007
N(2)	0.021	.008
C(1)	0.012	.009
C(2)	0.001	.010
C(3)	-0.014	.011

$$\chi^2 = 18.37; \quad \nu = 2; \quad P < 0.1\%$$

nearly the same in the structures although individual atomic positions show appreciable deviations. As is to be expected, deviations are maximum for the coordinating oxygen atom and are quite considerable for the other atoms in the pyrazolone group. The differences in the atomic positions of the phenyl carbon atoms in the three compounds, though not as large as those in the case of the pyrazolone ring, are not insignificant.

Coordination of the metal ion

In these compounds, the $\bar{3}$ equivalent antipyrine molecules are coordinated to the central metal ion through the lone oxygen atom in the carbonyl group. As mentioned earlier, the octahedral coordination of these oxygen atoms about the metal ion is hence determined essentially by the symmetry of the space group. The $\bar{3}$ axis of this octahedron coincides with that of the space group and the only permissible departure from a perfect symmetrical arrangement is an elongation or a contraction in the direction of the z axis.

The principal distances and angles involved in the arrangement of oxygen atoms around the metal ion

are given in Table 7. For this arrangement to be a regular octahedron, all the OMO angles ($M = \text{Mg}^{2+}$, Ca^{2+} or Pb^{2+}) should be exactly 90° and all the O-O distances should be equal, and any departure from these conditions is a measure of the distortion of the regular figure. Further, for a regular octahedron, $c/a = \sqrt{2}$ where c is the height of the octahedron along the z axis and a is the centroid-to-apex distance of the triangular face perpendicular to it. This ratio is greater or less than the ideal value of $\sqrt{2}$ according as the polyhedron is elongated or contracted along the $\bar{3}$ axis. The c/a ratios in the three cases are also listed in Table 7. An examination of this Table reveals that the octahedron is regular within experimental error in the magnesium compound but becomes elongated in the z direction as the size of the metal ion increases. In the absence of any chemical reason warranting such an elongation, it may be considered as due to packing requirements resulting from the increase in the size of the central metal ion, and it takes place in the z direction probably because of the less dense packing of molecules along the c axis on either side of the octahedron than in other directions.

The coordination polyhedron of oxygen atoms around divalent magnesium is almost invariably octahedral whereas the number of oxygen atoms that coordinate divalent calcium varies from 6 to 12. However, in both cases, the coordination is determined essentially by geometrical and packing considerations and the binding forces are predominantly electrostatic in character. The plumbous ion, on the other hand, is known to exhibit a wide variety of coordination numbers ranging from 3 to 12 and it is generally rec-

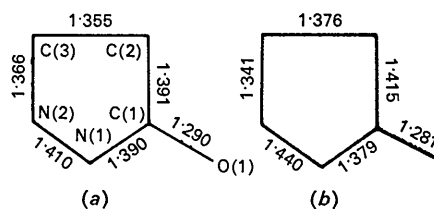


Fig. 6. (a) Observed bond lengths (Å) in the pyrazolone ring. (b) Bond lengths (Å) calculated from the estimated relative contributions of the canonical structures.

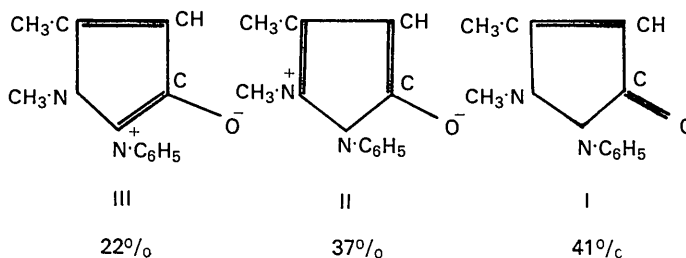


Fig. 5. Canonical structures of antipyrine and their relative contributions.

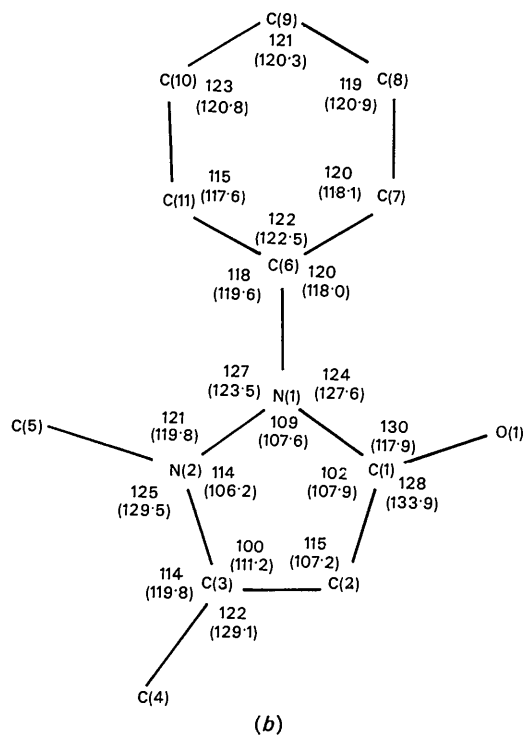
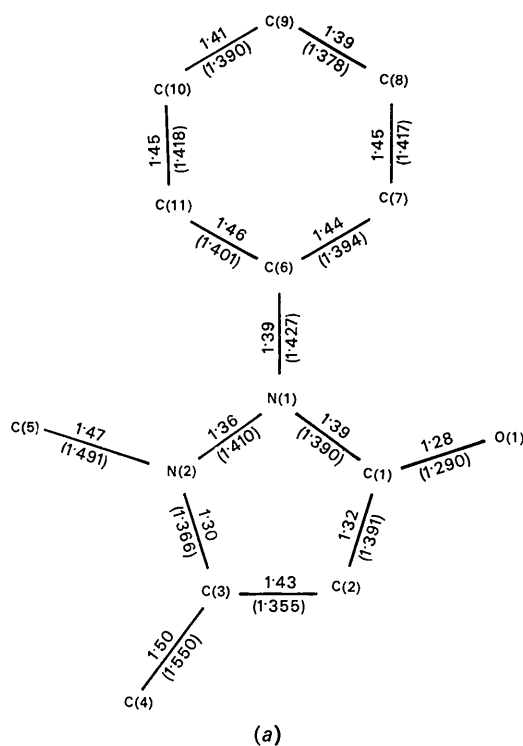


Fig. 7. (a) Bond lengths (Å) and (b) bond angles (°) in 4-bromoantipyrine. The corresponding values obtained from the present analysis are given in parentheses.

Table 7. Principal lengths (Å) and angles (°) in the coordination polyhedron around the metal ion in $M(C_{11}H_{12}ON_2)_6(ClO_4)_2$

	Mg	Ca	Pb
M—O(1 ⁱ)	2.059	2.304	2.446
O(1 ⁱⁱ)—O(1 ⁱⁱⁱ)	2.920	3.215	3.319
O(1 ⁱ)—O(1 ⁱⁱ)	2.905	3.310	3.595
O(1 ⁱ)—M—O(1 ⁱⁱⁱ)	90.3	88.1	85.4
O(1 ⁱ)—M—O(1 ⁱⁱ)	89.7	91.9	94.6
c/a	1.403	1.480	1.588

i x, y, z
ii y, y-x, z̄
iii x-y, x, z̄

ognized that the $Pb^{II}-O$ bond has an appreciable covalent nature (Vijayan & Viswamitra, 1966).

The approximate amount of ionic character of a bond between atoms A and B with electronegativity coefficients x_A and x_B can be estimated by use of the equation

$$\text{Amount of ionic character} = 0.16(x_A - x_B) + 0.035(x_A - x_B)^2$$

(Hanny & Smyth, 1946). The ionic character of the $Mg^{II}-O$, $Ca^{II}-O$ and $Pb^{II}-O$ bonds, derived from the above equation and the known electronegativity coefficients of the relevant atoms (Pauling, 1960; Gordy & Thomas, 1956), are 56.3%, 61.8% and 43% respectively. These values suggest that the first two bonds are predominantly ionic whereas the third is predominantly covalent.

The antipyrine group

The orientation of the antipyrine group and its dimensions are similar in all three compounds. However, the estimated bond lengths and valency angles in the lead compound are much less accurate than those in the other two and hence the dimensions of the antipyrine group used in the following discussion are, unless otherwise stated, the average values of those obtained from the analysis of the magnesium and the calcium compounds.

The antipyrine molecule can be considered as a resonance hybrid, the three important canonical structures of which are given in Fig. 5 (Knorr, 1887; Michaelis, 1902; Kitamura, 1940; Valyashko & Bliznyukov, 1941; Brown, Hukins, Le Fevre, Northcott & Wilson, 1949). The estimates of their relative contributions which explain most satisfactorily the observed bond lengths are also indicated. The relevant bond lengths calculated on the basis of these contributions and the corresponding observed values are shown in Fig. 6. The C-C distances were calculated by means of the semi-empirical formula

$$D_n = D_1 - (D_1 - D_2) \frac{1.84(n-1)}{0.84n + 0.16}$$

(Pauling, 1960) in which D_n is the value of the interatomic bond distance of intermediate type, D_1 that for a single bond, D_2 that for a double bond and n the bond number. The C-N and C-O distances were obtained from the curves given by Donohue, Lavine & Rollett (1956) and Curl (1959) respectively. Calculations based on the C-N and the C-O distances given in Table 6 of Marsh, Bierstedt & Eichhorn (1962) resulted in slightly different relative contributions of the canonical structures (37% of I, 39% of II and 24% of III). However, the values of Donohue *et al.* and Curl were thought to be more reliable as they have used a larger number of observations in drawing up the bond length-bond order curves. The N(1)-N(2) bond is single in all the three canonical structures and the relatively high discrepancy between its observed and calculated lengths may be due to the neglect of other less important resonance structures.

The bond length-bond order curves used in the above calculations have no firm theoretical basis and the estimated contributions of the canonical forms cannot be considered to be accurate. However, they are of interest as they give a semi-quantitative idea of the relative importance of the different structures proposed. The preponderance of the phenylhydrazine structure by Knorr (I) is expected since it does not involve charge separation. The phenol betaine structure of Michaelis (II) is second in importance whereas the contribution of the third structure proposed by Kitamura (III) is substantial. However, it might be mentioned that the association of the metal ion at the carbonyl oxygen favours the development of the ionic forms and hence the contribution of Knorr's structure can be expected to be larger in free antipyrine than in its complexes.

The pyrazolone ring and the phenyl ring are tilted with respect to each other by 62.3, 62.5 and 68.6° in the magnesium, the calcium and the lead compounds respectively. The respective distances of the N(1)-C(6) bonds which connect the phenyl ring to the pyrazolone ring, *viz.* 1.430 ± 0.011, 1.424 ± 0.010 and 1.414 ± 0.024 Å, are not significantly different from the expected N-C distance of 1.440 Å for sp^2 hybridized carbon (Dewar & Schmeising, 1959). The single-bond character of the N-C link permits the orientation of the phenyl group to be determined entirely by steric considerations. The actual tilts are probably determined, as was shown in the communication on the structure of the magnesium compound (Vijayan & Viswamitra, 1967), by intramolecular and intermolecular steric effects.

The only X-ray investigation on the derivatives of antipyrine so far reported is the determination of the structure of 4-bromoantipyrine by two-dimensional methods (Romain, 1957) and it is of interest to compare the molecular geometry of antipyrine deduced from this analysis with that obtained from our studies. The molecular dimensions of 4-bromoantipyrine are shown in Fig. 7. The corresponding lengths and angles obtained from the present analysis are also indicated for comparison. Even a cursory look at these values

reveals that the dimensions obtained by Romain are substantially different from those obtained by us. It is rather improbable that the substitution of bromine in the 4-position on the one hand and the association of the metal ion on the other are responsible for such drastic changes in bond lengths in the pyrazolone group. It is felt that these differences are probably due to the fact that the structure of 4-bromoantipyrine, determined from two-dimensional data, merits further refinement.

The authors are grateful to Professor R. S. Krishnan for his kind interest and encouragement. They are indebted to Dr C. C. Patel for providing them with the material used in this investigation. Their thanks are also due to Dr N. V. Mani for the useful discussions they had with him.

References

- BROWN, R. D., HUKINS, A. A., LE FEVRE, R. J. W., NORTH-COTT, J. & WILSON, I. R. (1949). *J. Chem. Soc.* p. 2812.
 BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 CURL, R. F. (1959). *J. Chem. Phys.* **30**, 1529.
 DEWAR, M. J. & SCHMEISING, H. N. (1959). *Tetrahedron*, **5**, 166.
 DONOHUE, J., LAVINE, L. R. & ROLLETT, J. S. (1956). *Acta Cryst.* **9**, 655.
 GORDY, W. & THOMAS, W. J. O. (1956). *J. Chem. Phys.* **24**, 439.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609.
 HANNY, N. B. & SMYTH, C. P. (1946). *J. Amer. Chem. Soc.* **68**, 171.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KANNAN, K. K. (1965). Ph. D. Thesis, Indian Institute of Science, Bangalore.
 KITAMURA, R. (1940). *J. Pharm. Soc. Japan*, **60**, 45.
 KNORR, L. (1887). *Liebig's Ann.* **238**, 137.
 MARSH, R. E., BIERSTEDT, R. & EICHHORN, E. L. (1962). *Acta Cryst.* **15**, 310.
 MICHAELIS, A. (1902). *Liebig's Ann.* **320**, 1.
 NAMBU DIRI, M. M. G., KANNAN, K. K. & VIJAYAN, M. (1966). *A Unified Set of Crystallographic Programs for the National Elliott 803-B Computer* (Unpublished).
 PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
 ROMAIN, P. (1957). *Bull. Soc. Chim. France*, p. 1417.
 VALYASHKO, N. A. & BLIZNYUKOV, V. I. (1941). *J. Gen. Chem. (USSR)*, **11**, 559.
 VIJAYAN, M. (1966). Ph. D. Thesis, Indian Institute of Science, Bangalore.
 VIJAYAN, M. & VISWAMITRA, M. A. (1965). *Z. Kristallogr.* **122**, 153.
 VIJAYAN, M. & VISWAMITRA, M. A. (1966). *Acta Cryst.* **21**, 522.
 VIJAYAN, M. & VISWAMITRA, M. A. (1967). *Acta Cryst.* **23**, 1000.
 WELLS, A. F. (1962). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.