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The Crystal and Molecular Structure of Magnesium Hexa-antipyrine Perchlorate

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The structure of magnesium hexa-antipyrine perchlorate, $Mg(C_{11}H_{12}ON_2)_6(ClO_4)_2$, has been solved by isomorphous difference-Patterson and trial-and-error methods. The compound crystallizes in the hexagonal system, space group $P\bar{3}$, with one formula unit in a unit cell of dimensions $a = 14{\cdot}06$, $c = 9{\cdot}76$ Å. The positional and anisotropic thermal parameters of the atoms were refined by the method of least squares to an R value of 0·132 for 1184 observed reflexions. In the structure, the six $\bar{3}$ equivalent antipyrine molecules are coordinated octahedrally to the central Mg^{2+} ion through their lone carbonyl oxygen atoms. The pyrazolone and the phenyl rings in the antipyrine group are planar and are inclined to each other by 62·3°. The non-equivalent Cl–O distances in the structure are 1·448 and 1·437 Å.

Introduction

Antipyrine is the trivial name for 1-phenyl-2,3-dimethyl-5-pyrazolone, an important keto derivative of pyrazoline which was first synthesized by Knorr (1884). Antipyrine receives its name from the antipyretic properties which are shared by several of its derivatives. The large dipole moment of antipyrine favours its coordination to different metal ions *via* the oxygen atom in the carbonyl group. Further, the proton accepting nature of the oxygen atom facilitates the formation of hydrogen bonded complexes with proton-donor molecules and groups. A large number (over 300) of metallic and molecular compounds of antipyrine have been synthesized. However, the only structural information so far reported in the literature concerning antipyrine compounds is about $Tb(C_{11}H_{12}ON_2)_6I_3$, which crystallizes in the space group $R\bar{3}$ (Van Uitert & Soden, 1961). No further details of this investigation are available. Hence, a programme of systematic X-ray investigation of some metal antipyrine complexes was initiated to study the nature of the metal–oxygen bonding in these and also to deduce the molecular geometry of antipyrine (Vijayan & Viswamitra, 1965*a*).

The first structure to be solved in this connexion was that of magnesium hexa-antipyrine perchlorate. A preliminary note on this investigation has already been published (Vijayan & Viswamitra, 1965*b*). A complete account of the solution and the refinement of the structure is given here. The structure determination of lead hexa-antipyrine perchlorate, taken up later, has also been reported (Vijayan & Viswamitra, 1966).

Experimental

Well developed, transparent crystals of magnesium hexa-antipyrine perchlorate were grown from a solution in water or methyl cyanide by slow evaporation at room temperature, using the sample kindly supplied

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to us by Dr C.C. Patel of the Inorganic and Physical Chemistry Department of this Institute.

Morphological and X-ray examination of the crystals showed that magnesium hexa-antipyrine perchlorate crystallizes in the space group $P\bar{3}$ with unit cell dimensions $a = 14{\cdot}06 \pm 0{\cdot}03$, $c = 9{\cdot}76 \pm 0{\cdot}03$ Å.

Other crystal data

$M = 1351{\cdot}81$, $U = 1670{\cdot}91$ Å^3

$D_m = 1{\cdot}375$ g.cm^{-3}, $Z = 1$, $D_x = 1{\cdot}343$ g.cm^{-3}

Absorption coefficient for X-rays,

$\lambda = 1{\cdot}5418$, $\mu = 16{\cdot}3$ cm^{-1}.

Intensity data were collected with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$), from a needle-like specimen having a nearly cylindrical cross-section of mean radius 0·23 mm, for reciprocal levels $hkil$, $l = 0$ to 8. $h0\bar{h}l$ zonal data were also recorded from a crystal cut along the a_2 axis and ground to an almost similar size and shape. Data were collected only for five levels to start with, *viz.* $hkil$, $l = 0$ to 3 and $h0\bar{h}l$ levels. However, during the final stages of refinement, the need for a larger number of observations in the least-squares analysis was felt and, hence, the additional $hkil$ levels, $l = 4$ to 8, were also recorded and measured. The well-known multiple film equi-inclination Weissenberg method was used for recording the data and the intensities were estimated visually by means of a time-exposure calibrated strip prepared from the same crystal, using a strong low-order reflexion. Out of the 2544 independent reflexions in the copper sphere, 2261 were recorded. Only 1184 were in the measurable range, the rest being too weak to be measured. The intensities were corrected for the Lorentz–polarization factor and the variation in spot shape in upper level Weissenberg pictures (Phillips, 1954) using a program devised by Nambudiri (Nambudiri, Kannan & Vijayan, 1966) for the National Elliott 803-B computer. Absorption errors were neglected ($\mu r = 0{\cdot}38$).

$hki0$ zonal data from the isomorphous zinc compound, $Zn(C_{11}H_{12}ON_2)_6(ClO_4)_2$, for which $a = 14{\cdot}14$, $c = 9{\cdot}61$ Å, were collected, using a nearly cylindrical specimen of mean radius 0·20 mm. The intensity data were processed as for the crystals of the magnesium compound, and again absorption corrections were not applied ($\mu = 19{\cdot}2$ cm^{-1}, $\mu r = 0{\cdot}38$). The data from the two compounds were then used to compute a difference Patterson projection on (0001).

Structure determination

The unit cell contains only one Mg^{2+} ion and hence it should occupy the $\bar{3}$ symmetry site at the origin. The two chlorine atoms in the cell could occupy either of the two twofold special positions, $\pm(0,0,z)$ or $\pm(\frac{1}{3},\frac{2}{3},z)$. In the former case, the magnesium ion, its coordination polyhedron (generally an octahedron) and the two perchlorate groups would all be stacked along the same hexagonal axis passing through the origin. When the normal ionic and van der Waals distances were considered, the above assignment seemed to require a c-axis length of about 15 Å. However, the observed value of c is only 9·76 Å, and hence packing requirements made this model unacceptable. Therefore the chlorine atoms had to be placed at the alternate locations $\pm(\frac{1}{3},\frac{2}{3},z)$. It follows that for each perchlorate ion, one oxygen atom must also lie on the same threefold axis as the corresponding chlorine atom, leaving six oxygen atoms (three for each perchlorate ion) to satisfy the requirements of general equivalent positions in space group $P\bar{3}$.

The structure was first solved in the $hki0$ projection by the interpretation of an isomorphous difference Patterson map prepared by using the intensity data from both the zinc and the magnesium compound. As the only replaceable atom, in the present case, is at a symmetry centre, this structure provides the most suitable example for the application of the difference Patterson method. Neglecting differential absorption and extinction effects between the crystals of the two compounds, the two sets of corrected $hki0$ zonal data were put on the same scale by Wilson's procedure. As the replaceable atom is at the origin, the difference Patterson map should, in theory, be a map of the crystal structure itself except for a broadening of the peaks. In fact, it was found that this diagram (Fig. 1) had a striking similarity to the later electron-density maps in its essential features. The difference Patterson diagram confirmed the positions of Mg^{2+} and Cl fixed earlier on elementary packing and symmetry considerations. The perchlorate oxygen atom O(2) occupying a general position was also identifiable from the map.

Divalent magnesium has normally an octahedral coordination of oxygen atoms. In the present case, the perchlorate oxygen atoms are beyond the coordination sphere of Mg^{2+} and therefore the coordination requirements of the metal ion in the structure can be fulfilled only by the carbonyl oxygens in the six $\bar{3}$ equivalent antipyrine groups. With the normal Mg–O distance of 2·1 Å, the oxygen peak in the $hki0$ difference Patterson map should be at a distance of 1·5 Å from the origin and a peak at almost this distance was actually observed in the map (O(1) in Fig. 1). Starting with this as the peak due to the antipyrine oxygen atom, a trial model (shown in Fig. 1) was proposed on packing and chemical considerations which explained the salient features of the difference Patterson map. This model gave an initial R index, defined by $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$, of 0·46 for the reflexions in the $hki0$ zone. The x,y coordinates and individual isotropic temperature factors were refined by the use of Bragg–Lipson structure-factor graphs (Bragg & Lipson, 1936) and successive Fourier and difference Fourier syntheses to $R = 0{\cdot}155$ for these reflexions. The Fourier syntheses and the structure-factor calculations were done on the Ferranti Sirius Computer at the National Aeronautical Laboratory, Bangalore, using a triclinic Fourier program written by Shankar (1964) of the computer group and a three-dimensional structure-factor program for the space group $P\bar{3}$ developed by one of the authors (M.V.).

The isomorphism of the zinc and magnesium compounds could not be utilized for deriving the z coordinates from zonal data as the crystals of the former were too tiny to be cut and ground along the a_1 or a_2 axis. An interpretation of the Patterson projection along the a_2 axis yielded the z coordinates of the atoms in the perchlorate group, but gave no indication of the z coordinates of the atoms in the antipyrine group. A careful examination revealed that the antipyrine group can be oriented in four different ways for a given set of x,y coordinates, and it was difficult to make a choice from among these four possibilities on chemical or packing considerations. Hence, the trial and error method was employed in arriving at the correct z coordinates, which were refined by difference Fourier and structure-factor least-squares methods to an R index of 0·22 for $h0\bar{h}l$ reflexions. Two more cycles of SFLS refinement from both $hki0$ and $h0\bar{h}l$ reflexions gave a combined projection R value of 0·164.

Refinement

The early cycles of three-dimensional refinement were carried out on the Elliott 803-B Computer at Hindustan Aeronautics Ltd., Bangalore, using the modified version of a SFLS program originally written by Nambudiri (Nambudiri *et al.*, 1966). Higher-layer data were successively introduced and the first SFLS cycle using all the 705 reflexions in the levels $hkil$, $l=0$ to 3, and $h0\bar{h}l$ gave an R value of 0·167. The discrepancy index was reduced to 0·156 in two more cycles of refinement on the CDC-3600 Computer installation at the Tata Institute of Fundamental Research, Bombay. At this stage, individual isotropic temperature factors were replaced by individual anisotropic temperature factors of the form

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

The R value was brought down to 0·117 in six cycles of anisotropic refinement on the IBM 1620 computer at the National Research Council, Ottawa, using a least-squares program written by Mair (Ahmed, Gabe, Mair & Pippy, 1963).

A calculation of bond lengths and bond angles and also of the mean plane of the phenyl ring revealed that the molecule was slightly distorted and adjustments were made to remove this distortion. It was felt that this distortion arose on account of the low reflexion to parameter ratio. Hence, equi-inclination Weissenberg photographs for five more reciprocal levels ($hkil$, $l=4$ to 8) were recorded and the intensities of 479 new independent reflexions were measured. All the 1184 observed reflexions, including the new ones, were used in further calculations.

The final cycles of anisotropic refinement were carried out on the CDC-3600 Computer at Bombay, using a general SFLS program originally written by Kannan (1965) for isotropic refinement and later modified by one of us (M.V.) to include anisotropic thermal parameters. In this program, the quantity minimized was $\Sigma w(F_o-F_c)^2$ and diagonal approximation was used in solving the normal equations. Reflexions with F_o values greater than six and less than 35 were given full weights and those with F_o values greater than 35 or less than six were given half weights (F_o values were scaled to correspond to half the contents of the unit cell). Four strong low-angle reflexions with F_o greater than 50

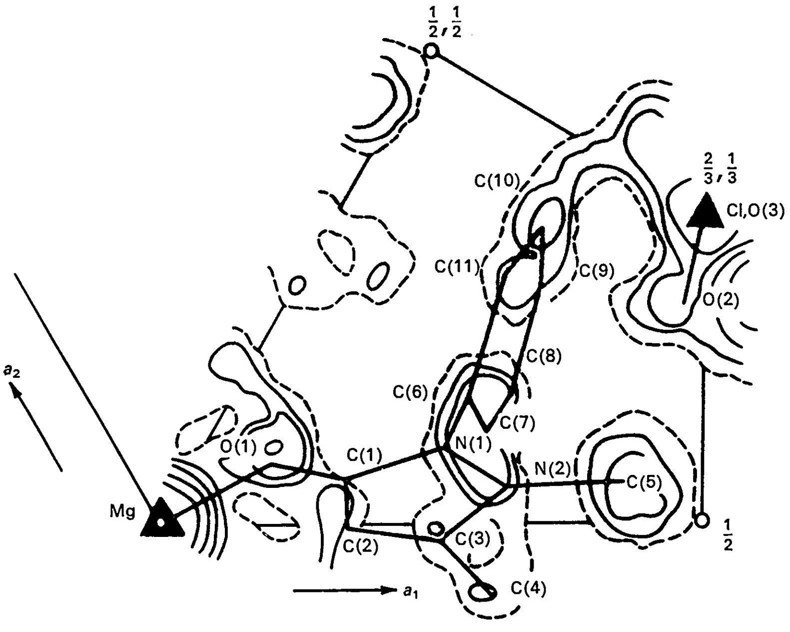

Fig. 1. (Zn–Mg) $(C_{11}H_{12}ON_2)_2$ $(ClO_4)_2$ difference Patterson map. $hki0$ projection.

were given zero weights as they were suspected to suffer from extinction errors. Atomic scattering factors used in these calculations were those computed from the nine-term analytical expressions given by Cromer & Waber (1965).

Further refinement of the structure was smooth and the discrepancy index was brought down from 0·164 to 0·132 in six SFLS cycles. The average and maximum shifts in positional coordinates indicated in the sixth cycles were $0{\cdot}20\sigma$ and $0{\cdot}96\sigma$ and the refinement was terminated. The R values quoted above are for observed reflexions alone.

Results

Table 1 lists the final positional parameters. The anisotropic thermal parameters and the corresponding equivalent isotropic temperature factors, defined as

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

(Hamilton, 1959), are given in Table 2. The magnitudes and direction cosines of the principal axes of the thermal vibration ellipsoids evaluated from the corresponding b_{ij} values are listed in Table 3. In Table 4 are listed the observed and calculated structure factors for all the measured reflexions. The bond lengths and valency angles in the structure are given in Table 5.

Table 1. *Final positional coordinates expressed as fractions of cell edges (e.s.d.'s* $\times 10^5$ *in parentheses)*

	x	y	z
Mg	0·00000 (0)	0·00000 (0)	0·00000 (0)
Cl	0·66667 (0)	0·33333 (0)	−0·50314 (49)
O(1)	0·13829 (46)	0·06358 (48)	−0·12120 (70)
O(2)	0·58655 (84)	0·22723 (83)	−0·55709 (107)
O(3)	0·66667 (0)	0·33333 (0)	−0·35591 (131)
N(1)	0·29916 (57)	0·07352 (58)	−0·18726 (75)
N(2)	0·34004 (59)	0·04532 (58)	−0·30318 (83)
C(1)	0·18901 (64)	0·03558 (64)	−0·20890 (98)
C(2)	0·16048 (72)	−0·01866 (71)	−0·33425 (102)
C(3)	0·25223 (72)	−0·01247 (72)	−0·38751 (93)
C(4)	0·26693 (95)	−0·06365 (93)	−0·52208 (116)
C(5)	0·44632 (80)	0·04669 (77)	−0·29472 (121)
C(6)	0·36818 (65)	0·14736 (67)	−0·08308 (95)
C(7)	0·34939 (83)	0·11091 (82)	0·05239 (102)
C(8)	0·41763 (84)	0·18423 (84)	0·15506 (117)
C(9)	0·49907 (84)	0·28867 (84)	0·12309 (117)
C(10)	0·51487 (86)	0·32361 (87)	−0·01219 (140)
C(11)	0·45001 (75)	0·25299 (75)	−0·12060 (116)

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

	Axis	B_i	g_{i1}	g_{i2}	g_{i3}
Mg	1	0·89 Å^2	1	0·5000	0
	2	0·89	0	0·8660	0
	3	1·01	0	0	1
Cl	1	4·00	1	0·5000	0
	2	4·00	0	0·8660	0
	3	1·98	0	0	1
O(1)	1	3·87	0·0953	−0·3830	0·8624
	2	2·80	−0·2293	0·6059	0·5051
	3	1·75	0·9687	0·6973	0·0347
O(2)	1	10·93	0·6300	−0·3540	0·0792
	2	7·78	−0·4876	−0·5159	0·8146
	3	5·67	0·6044	0·7801	0·5747
O(3)	1	8·07	1	0·5000	0
	2	8·07	0	0·8660	0
	3	1·46	0	0	1
N(1)	1	3·52	0·2726	0·8915	−0·4066
	2	2·26	−0·9474	−0·3269	−0·2715
	3	1·15	0·1678	−0·3138	−0·8723
N(2)	1	4·34	0·2905	0·7545	−0·6486
	2	2·48	−0·9464	−0·3769	−0·3032
	3	1·26	0·1411	−0·5373	−0·6982
C(1)	1	3·02	0·2299	−0·1928	0·9060
	2	1·41	−0·8649	−0·8667	0·0228
	3	1·06	0·4462	−0·4600	−0·4226
C(2)	1	3·05	0·4127	−0·5823	0·0155
	2	2·60	−0·9076	−0·8112	−0·0771
	3	1·86	0·0766	0·0537	−0·9969
C(3)	1	3·54	0·3832	−0·5633	0·3055
	2	2·62	−0·9078	−0·8146	−0·0499
	3	0·59	0·1708	−0·1382	−0·9509

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
Mg	150	150	265	150	0	0	0·93 Å^2
Cl	670	670	519	670	0	0	3·31
O(1)	308	413	944	220	−159	22	2·81
O(2)	1393	1162	1864	739	−435	−242	8·13
O(3)	1360	1360	382	1360	0	0	5·86
N(1)	391	532	426	504	−321	9	2·31
N(2)	440	537	700	586	−574	−97	2·69
C(1)	240	235	701	237	−147	169	1·83
C(2)	451	464	490	402	15	25	2·53
C(3)	454	484	228	390	−179	184	2·25
C(4)	891	1016	699	1158	−386	−249	4·39
C(5)	401	694	1324	875	−351	125	3·41
C(6)	324	344	420	470	−118	313	1·67
C(7)	517	775	362	429	39	132	3·30
C(8)	598	669	708	734	0	448	3·27
C(9)	668	692	911	821	47	38	3·66
C(10)	526	616	1573	296	11	−140	4·61
C(11)	463	375	1113	246	178	−135	3·30

Table 3 (*cont.*)

	Axis	B_i	g_{i1}	g_{i2}	g_{i3}
C(4)	1	6·39	0·6885	0·9371	−0·2394
	2	4·34	−0·7143	0·2467	−0·0604
	3	2·43	0·1256	0·2469	0·9690
C(5)	1	5·57	0·1463	0·4624	−0·8812
	2	3·93	−0·6937	−0·8565	−0·4153
	3	0·74	0·7053	−0·2294	−0·2257
C(6)	1	2·54	0·7039	0·2105	0·6912
	2	2·17	−0·5218	−0·9357	0·3472
	3	0·32	0·4819	−0·2831	−0·6337
C(7)	1	5·49	0·1266	−0·7954	0·0275
	2	3·08	−0·9762	−0·6002	−0·1742
	3	1·32	0·1763	0·0840	−0·9843
C(8)	1	4·27	0·8413	0·5019	0·5324
	2	3·88	−0·1275	−0·8628	0·3640
	3	1·67	0·5254	−0·0613	−0·7642
C(9)	1	4·33	0·8187	0·8926	0·1355
	2	3·46	−0·1388	−0·1011	0·9896
	3	3·19	0·5572	−0·4393	0·0476
C(10)	1	6·11	0·1724	−0·1330	−0·9520
	2	4·96	−0·3300	0·6107	−0·2979
	3	2·78	0·9281	0·7806	0·0700
C(11)	1	4·71	0·3050	−0·2298	−0·8439
	2	3·13	−0·6425	0·1626	−0·5244
	3	2·06	0·7030	0·9596	−0·1133

Superposed sections perpendicular to the *c* axis of the final electron density synthesis are shown, along with atomic positions, in Fig. 2. A three-dimensional difference Fourier synthesis was also made in an attempt to locate the hydrogen atoms in the structure. Although positive electron-density patches were observed around their expected positions, the hydrogen atoms could not be precisely located from the difference diagram. A view of the structure as a seen along the [0001] direction is shown in Fig. 3. Fig. 4 shows the contents of the unit cell projected along the a_2^* axis.

Discussion

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

The Mg^{2+} ion in the structure occupies a symmetry centre at the origin of the unit cell. The six $\bar{3}$ equivalent antipyrine ligands, disposed octahedrally about the metal ion, are coordinated to it through their lone oxygen atoms. The $\bar{3}$ axis of the coordination octahedron, thus formed, coincides with the $\bar{3}$ axis of the space group and hence the only distortion allowed by the symmetry of the space group is an elongation or a contraction along the *z* direction. However, in the present case, the coordination octahedron of antipyrine oxygen atoms around Mg^{2+} is quite regular within experimental error. The six Mg–O bonds are equivalent and have a length of 2·059 ± 0·006 Å, which compares very well with the values found in other compounds.

Geometry of the antipyrine molecule

The bond lengths and bond angles in the antipyrine molecule are shown in Fig. 5. 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 $Z' = z$ (Blow, 1960), together with the dis-

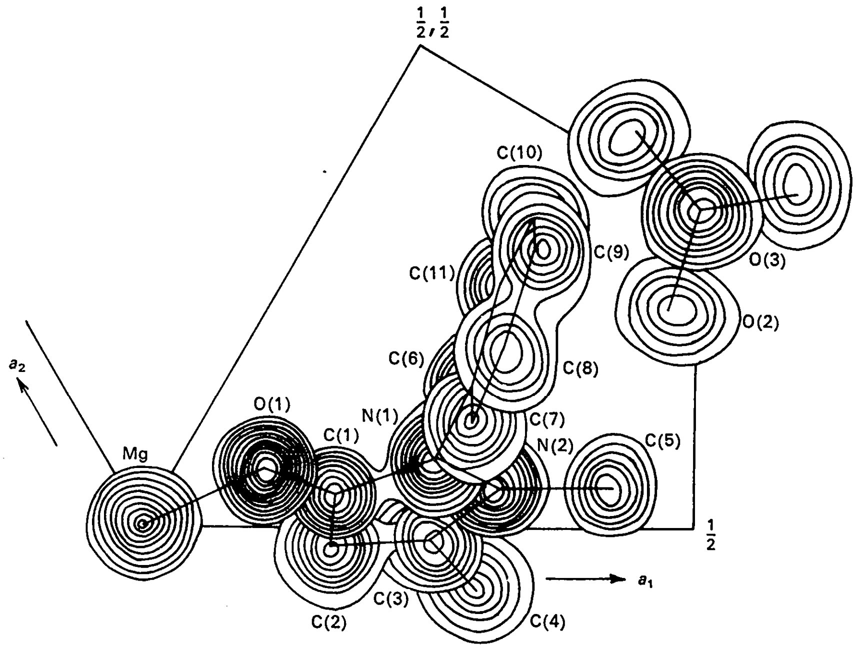

Fig. 2. Superposed sections of the final three-dimensional electron-density distribution, through atomic centres parallel to (0001). Contours start at 1e.Å^{-3} and are at intervals of 1e.Å^{-3} for C, N and O and 3 e.Å^{-3} for Mg. The position of the chlorine atom is below O(3).

placements of the ring atoms from their respective mean planes are given in Table 6. The estimated standard deviations normal to the planes are also indicated in the Table. The root mean square displacements of the atoms in the phenyl ring and the pyrazolone ring from their mean planes are 0·005 and 0·010 Å respectively.

The phenyl ring is tilted with respect to the pyrazolone ring by 62·3°. The length of the N–C bond (1·430 ± 0·011 Å) which connects the phenyl ring to the pyrazolone ring is not significantly different from the expected single-bond 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

Table 4. *Observed and calculated structure factors* (× 50)

h	k	F_{obs}	F_{calc}
		l = 0	
1	1	2035	1986
1	2	537	-755
1	3	3434	-1732
1	4	875	-419
1	5	711	346
1	6	1595	1500
1	7	303	346
1	8	691	-649
1	9	944	-767
1	10	1342	1124
1	11	780	687
1	13	865	925
1	14	427	446
1	15	388	380
2	1	1655	1464
2	2	447	625
2	3	1516	-1689
2	4	293	424
2	5	1448	1750
2	6	964	-698
2	7	681	553
2	8	591	456
2	9	303	193
2	13	398	488
2	14	273	434
3	1	1715	1639
3	2	3603	-3516
3	3	711	714
3	4	751	-1020
3	5	293	514
3	6	934	564
3	7	437	-273
3	8	368	-354
3	9	457	225
4	1	1108	1230
4	2	1004	-1048
4	3	2286	2194
4	4	378	430
4	6	1238	1122
4	7	1431	1378
4	8	517	575
4	9	780	-685
4	10	293	247
4	11	313	395
5	1	1958	-1567
5	2	4037	4118
5	4	875	832
5	5	1759	1642
5	6	855	854
5	7	974	1029
5	8	944	917
5	9	681	-686
5	11	497	579
5	12	254	-217
6	1	661	472
6	3	1342	1314
6	4	1292	1154
6	6	1332	1241
6	8	398	-304
7	1	2296	2461
7	2	1272	-1249
7	4	1461	1465
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9	-2	407	-389
9	-5	962	997
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12	-7	617	504
13	-2	570	680
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2	3	879	819
2	4	338	445
2	5	1322	-1301
2	7	1450	1611
3	1	1163	1265
3	2	1650	1686
3	4	720	826
3	5	1371	1584
3	6	556	361
3	8	457	436
3	9	308	-491
3	10	402	538
4	2	377	638
4	3	531	512
4	5	626	601
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5	8	740	-544
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1	7	781	738
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4	4	1623	1651
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7	-5	557	627
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10	-7	463	604
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12	-10	353	-335
13	-8	403	465

h	l	F_{obs}	F_{calc}
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0	3	2392	-2560
0	4	1561	-1735
0	5	2239	-2439
0	6,	2259	2465
0	8	556	444
0	10	1275	1212
1	2	1698	-2218
1	3	1265	1359
1	4	2800	-2862
1	5	1331	1358
1	6	658	-513
1	9	974	897
2	0	3891	-4375
2	1	1178	-1291
2	2	2162	-2360
2	3	1556	1445
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2	5	648	-669
2	6	1037	1030
2	7	1153	1161
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2	9	1403	1477
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3	0	2244	2499
3	1	5550	-6505
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3	10	704	755
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4	2	867	-529
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5	0	760	716
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5	2	1902	-1729
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5	4	342	272
5	5	1311	1299
5	6	1132	1150
5	9	755	769
6	0	1270	1336
6	1	1698	-1810
6	2	831	-659
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6	4	1433	1086
6	6	1672	1739
6	7	861	-843
6	8	571	521
6	9	535	526
7	0	1050	-1284
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7	2	703	-679
7	3	749	785
7	4	591	-801
7	6	596,	-478
8	0	1035	-944
8	2	1642	1737
8	3	1632	1614
8	4	535	-573
9	0	581	333
9	2	1213	1268
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9	4	1591	1416
9	5	668	-428
9	7	545	-373
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10	7	642	584
10	9	596	658
11	0	571	-373
11	2	1065	1117
11	3	1285	1062
11	4	652	-550
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12	2	963	1027
12	6	535	509
13	1	637	-627
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14	0	448	353
14	1	780	976
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-1	6	1076	844
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-2	1	1932	2360
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-3	6	1198	1117
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-5	11	759	786
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-6	2	2254	2457
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-6	7	749	-664
-6	8	703	527
-6	10	622	580
-6	11	244	101
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-7	2	1014	-952
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-7	4	504	701
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-7	7	571	433
-7	10	341	280
-8	1	1147	963
-8	2	790	668
-8	3	515	463
-8	5	1336	1411
-8	6	1519	-1522
-8	10	469	-178
-9	1	688	-530
-9	2	1535	1537
-9	3	739	-660
-9	5	668	625
-9	6	898	955
-9	9	566	-741
-10	2	566	309
-10	5	1127	1018
-10	6	805	796
-10	8	341	-60
-11	2	897	-709
-11	5	663	783
-11	8	367	442
-12	1	1020	-1067
-12	2	555	429
-12	6	739	723
-13	2	510	515
-13	4	341	-272
-14	1	341	381
-14	3	555	-583
-14	4	474	-694
-15	2	688	989

orientation of the phenyl group to be determined entirely by steric considerations. The steric hindrance between C(11) and the methyl group attached to the nitrogen atom on the one hand and that between C(7) and the carbonyl oxygen atom on the other rule out the possibility of the pyrazolone and the phenyl rings being coplanar, and the orientation that corresponds to the least steric hindrance would be the one with the phenyl ring perpendicular to the pyrazolone ring. However, the observed tilt deviates considerably from 90° and these deviations are probably due to intramolecular and intermolecular steric effects as can be inferred from Fig. 6 and Table 8.

The perchlorate ion

The perchlorate ion in the structure, which is close to a regular tetrahedron, occupies a position of threefold symmetry with the chlorine atom and one of the perchlorate oxygen atoms lying on the threefold axis. The other three threefold equivalent oxygen atoms lie

Table 5. *Bond lengths and bond angles and their standard deviations*

Bond	l	$\sigma(l)$	Angle	θ	$\sigma(\theta)$
Mg—O(1)	2·059 Å	0·006 Å	Mg—O(1)—C(1)	142·3°	0·6°
O(1)—C(1)	1·295	0·013	C(1)—C(2)—C(3)	107·4	1·0
C(1)—C(2)	1·390	0·013	C(2)—C(3)—C(4)	129·4	1·0
C(2)—C(3)	1·353	0·015	C(2)—C(3)—N(2)	110·9	0·9
C(3)—C(4)	1·560	0·016	C(4)—C(3)—N(2)	119·6	0·9
C(3)—N(2)	1·363	0·012	C(3)—N(2)—N(1)	106·1	0·8
N(2)—C(5)	1·487	0·014	C(3)—N(2)—C(5)	130·2	0·9
N(2)—N(1)	1·412	0·012	C(5)—N(2)—N(1)	119·9	0·8
N(1)—C(1)	1·379	0·013	N(2)—N(1)—C(6)	123·3	0·7
N(1)—C(6)	1·430	0·011	C(6)—N(1)—C(1)	127·8	0·8
C(6)—C(7)	1·395	0·014	N(2)—N(1)—C(1)	107·7	0·7
C(7)—C(8)	1·414	0·013	N(1)—C(1)—C(2)	107·9	0·8
C(8)—C(9)	1·372	0·013	N(1)—C(1)—O(1)	117·6	0·8
C(9)—C(10)	1·387	0·016	O(1)—C(1)—C(2)	134·2	0·9
C(10)-C(11)	1·425	0·016	N(1)—C(6)—C(11)	119·0	0·8
C(11)-C(6)	1·398	0·011	N(1)—C(6)—C(7)	118·2	0·8
Cl—O(2)	1·446	0·009	C(11)-C(6)—C(7)	122·9	0·9
Cl—O(3)	1·437	0·014	C(6)—C(7)—C(8)	118·0	1·0
			C(7)—C(8)—C(9)	121·2	1·1
			C(8)—C(9)—C(10)	119·7	1·1
			C(9)—C(10)-C(11)	121·8	1·1
			C(10)-C(11)-C(6)	116·5	0·8
			O(2)—Cl—O(3)	111·4	0·6

Table 6. *Equations of the mean planes and the displacements* (Å) *of atoms from, and their standard deviations* (Å) *normal to, the planes*

(1) Phenyl ring:
$0·9376X'-0·3290Y'-0·1126Z'-2·2806=0$

	Δ	σ_I
C(6)	0·003	0·009
C(7)	−0·007	0·011
C(8)	0·003	0·012
C(9)	0·005	0·012
C(10)	−0·008	0·012
C(11)	0·004	0·010

$\chi^2=1·42;\ n=3;\ P>0·70\ <0·80$

(2) Pyrazolene ring:
$-0·2493X'+0·8559Y'-0·4531Z'+3·7351=0$

	Δ	σ_I
N(1)	−0·013	0·008
N(2)	0·013	0·008
C(1)	0·007	0·009
C(2)	0·001	0·010
C(3)	−0·009	0·010

$\chi^2=6·78;\ n=2;\ P>0·02\ <0·05$

in a plane perpendicular to the *c* axis. The two non-equivalent Cl–O distances are 1·446 ± 0·009 and 1·437 ± 0·014 Å for Cl–O (2) and Cl–O (3) respectively.

Thermal vibrations

The atoms in the structure vibrate with widely different amplitudes, the equivalent isotropic B values varying from 0·93 Å^2 for Mg to 8·13 Å^2 for O(2). The motion of the magnesium ion at the origin is practically isotropic and its amplitude is as small as 0·11 Å. This is only to be expected when it is remembered that Mg^{2+} is at the centre of the octahedral environment produced by bulky antipyrine ligands.

All the atoms in the pyrazolone ring, except C(1), have thermal vibrations of the same order of magnitude. C(1), which is bonded to the coordinating oxygen atom, shows a lower temperature factor. The methyl carbon atoms single-bonded to the pyrazolone ring possess higher temperature factors. This is understandable as they are at the free ends of the molecule.

The phenyl carbon atoms except C(6), through which the group is linked to the pyrazolone ring, have comparatively greater amplitudes of thermal vibration. The single-bond character of the N–C link between the two rings facilitates rigid body oscillations of the phenyl group and, consequently, the atoms in this group have higher temperature factors. C(6) is comparatively unaffected by this type of motion, and hence has smaller vibration amplitude. However, the higher temperature factor of C(10) compared with those of the other phenyl carbon atoms is difficult to explain.

The equivalent isotropic B value of Cl, in spite of its being a heavier atom, is comparable to those of the peripheral carbon atoms in the phenyl ring. The perchlorate oxygen atoms are the ones with the highest temperature factors in the structure. As it is not directly bonded to the rest of the structure and as its structural role is to fill up the voids left in packing the metal hexa-antipyrine complex cations, the perchlorate group has more freedom of movement and hence the atoms in the group have greater temperature factors.

All the atoms in the structure, except the magnesium ion, are found to vibrate with significant anisotropy, the criterion used being that if at least one of the b_{ij} for the atom in question should differ by more than 2σ from the value it should have if the atom was actually vibrating isotropically with B equal to the mean principal axis B_i it is considered significantly anisotropic (Alden, Stout, Kraut & High, 1964).

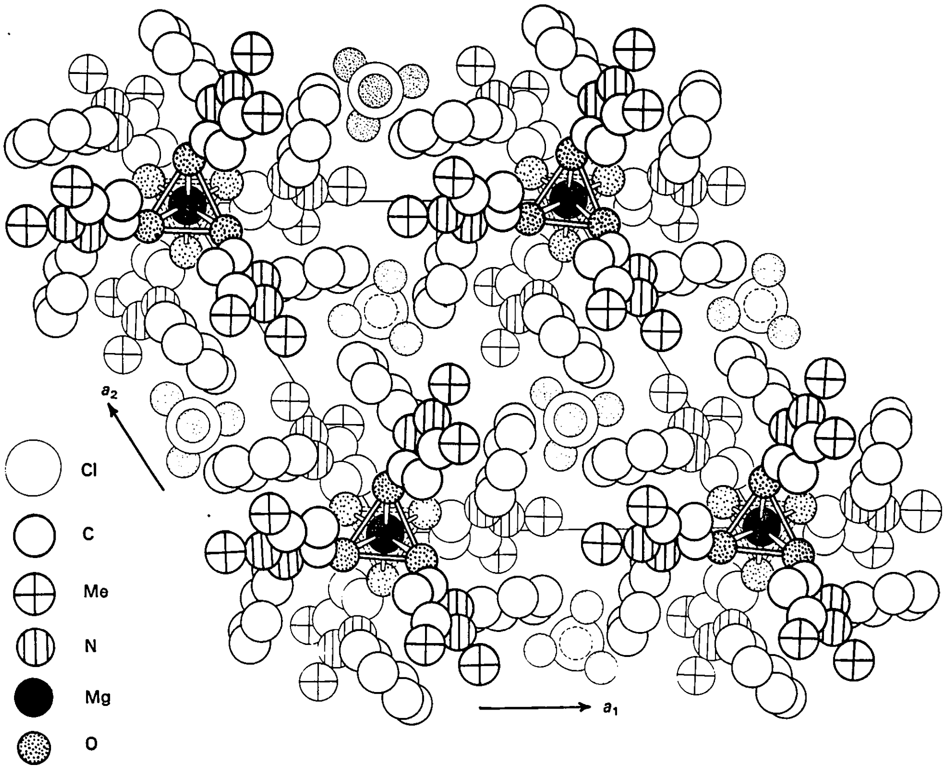

Fig. 3. The structure as seen along the [0001] direction.

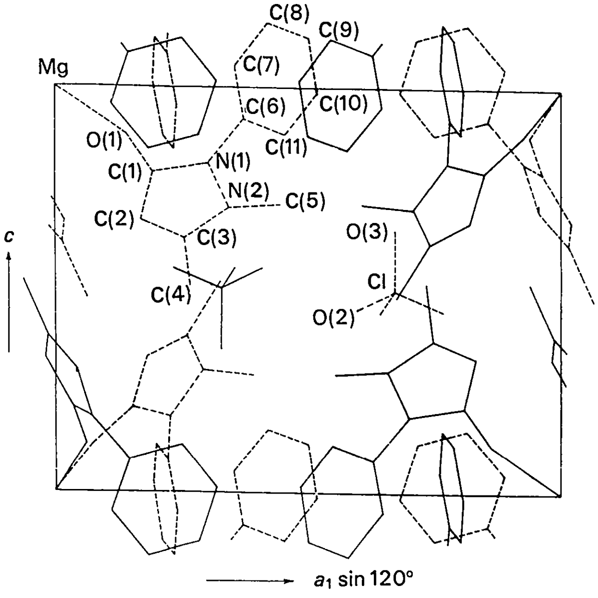

Fig. 4. The contents of the unit cell projected down the a_2* axis.

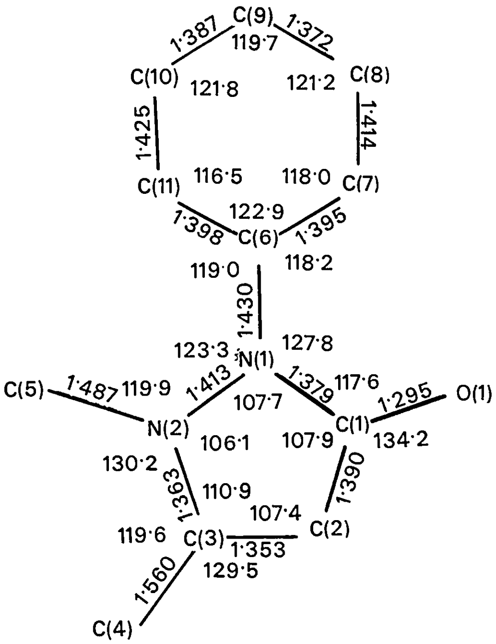

Fig. 5. Bond lengths (Å) and bond angles (°) in the antipyrine molecule.

Table 7. *Interionic contacts involving atoms in the antipyrine group with perchlorate oxygen atoms*

C(11)*A*–O(3)*A*	3·520 Å	(×3)
C(5)*A*—O(3)*A*	3·703	(×3)
C(10)*A*–O(3)*A*	3·942	(×3)
C(8)*E*—O(2)*A*	3·530	(×3)
C(9)*E*—O(2)*A*	3·615	(×3)
C(9)*E*—O(2)*C*	3·646	(×3)
C(4)*D*—O(2)*A*	3·856	(×3)
C(4)*D*—O(2)*B*	3·984	(×3)
C(5)*A*—O(2)*A*	3·447	(×3)

A: x, y, z
B: $\bar{y}+1, x-y, z$
C: $y-x+1, \bar{x}+1, z$
D: $\bar{x}+1, \bar{y}, \bar{z}$
E: $x, y, z-1$

Table 8. *Intramolecular and intermolecular contacts among antipyrine groups*

C(1)*A*—C(7)*B* C(7)*A*—C(1)*C*	3·762 Å	(×3)
C(1)*A*—C(8)*B* C(8)*A*—C(1)*C*	3·785	(×3)
C(2)*A*—C(7)*B* C(7)*A*—C(2)*C*	3·931	(×3)
C(2)*A*—C(8)*B* C(8)*A*—C(2)*C*	3·646	(×3)
C(3)*A*—C(8)*B* C(8)*A*—C(3)*C*	3·569	(×3)
N(1)*A*—C(8)*B* C(8)*A*—N(1)*C*	3·789	(×3)
N(1)—C(9)*B* C(9)*A*—N(1)*C*	3·970	(×3)
N(2)*A*—C(8)*B* C(8)*A*—N(2)*C*	3·696	(×3)
N(2)*A*—C(9)*B* C(9)*A*—N(2)*C*	3·734	(×3)
C(5)*A*—C(9)*B* C(9)*A*—C(5)*C*	3·574	(×3)
C(5)*A*—C(10)*D*	3·956	(×6)
C(8)*A*—C(9)*D*	3·971	(×6)
C(8)*A*—C(10)*D*	3·943	(×6)
C(9)*A*—C(9)*D*	3·661	(×6)
C(9)*A*—C(10)*D*	3·640	(×6)
C(10)*A*-C(10)*D*	3·584	(×6)
C(11)*A*-C(10)*D*	3·843	(×6)
C(10)*A*-C(5)*E*	3·953	(×6)
C(4)*A*—C(3)*F* C(3)*A*—C(4)*G*	3·619	(×3)
C(4)*A*—N(1)*F* N(1)*A*—C(4)*G*	3·799	(×3)
C(4)*A*—N(2)*F* N(2)*A*—C(4)*G*	3·612	(×3)
C(4)*A*—C(2)*F* C(2)*A*—C(4)*G*	3·769	(×3)
C(4)*A*—C(1)*F* C(1)*A*—C(4)*G*	3·868	(×3)

A: x, y, z
B: $y, y-x, \bar{z}$
C: $x-y, x, \bar{z}$
D: $\bar{y}+1, x-y, z$
E: $y-x+1, \bar{x}+1, z$
F: $y, y-x, \bar{z}-1$
G: $x-y, x, \bar{z}-1$

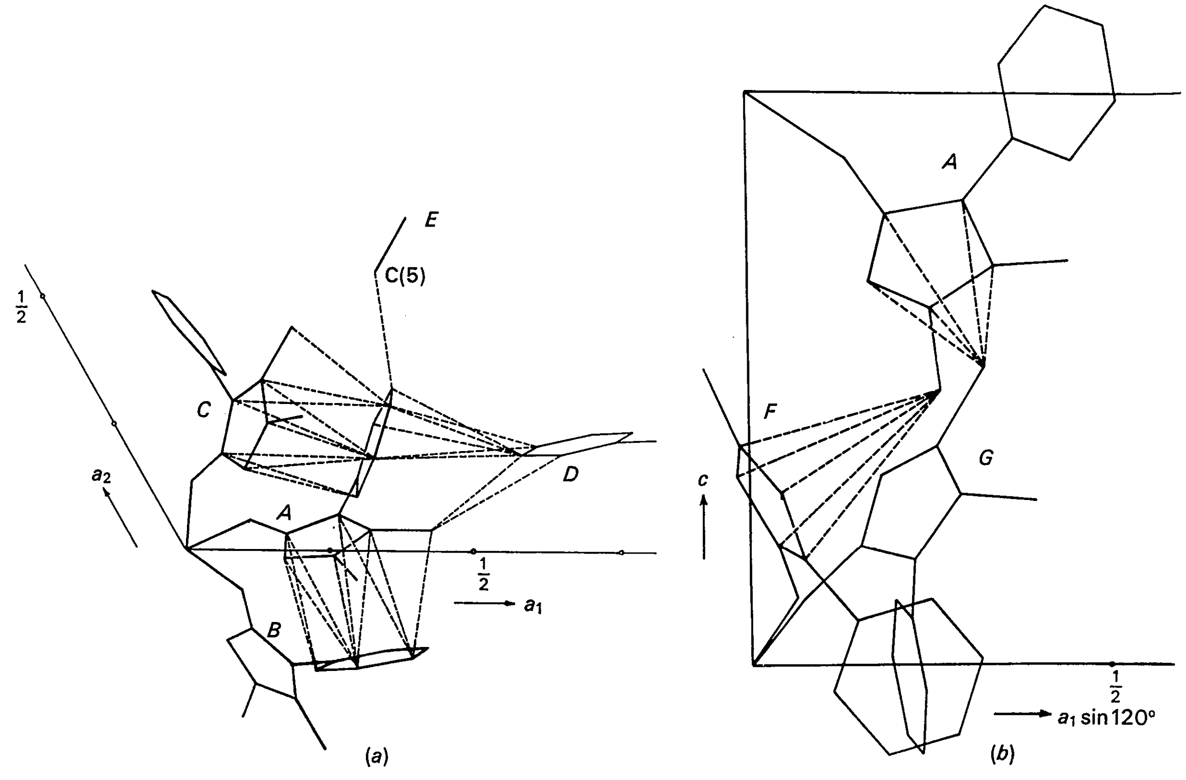

Fig. 6. (*a*) Intramolecular and intermolecular contacts involving antipyrine groups, as seen along the *c* axis. (*b*) Intermolecular approaches between metal hexaantipyrine complex cations related by *c* translation.

The distances involved in the contacts between the perchlorate ion and the surrounding antipyrine groups are listed in Table 7. The intramolecular and intermolecular approaches involving the atoms in the antipyrine groups are given in Table 8 and are indicated in Fig. 6. These correspond to the expected van der Waal interactions.

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The Crystal Structure of 2,6-Dimethylbenzoic acid

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Crystals of 2,6-dimethylbenzoic acid have been studied by three-dimensional X-ray methods. They are monoclinic, space group $P2_1/a$, with four molecules in a cell of dimensions $a=15{\cdot}24$, $b=4{\cdot}04$ $c=13{\cdot}16$ Å, $\beta=94°8'$. The structure was solved by Patterson methods and refined by Fourier and differential Fourier syntheses. R is 0·168 for 958 reflexions. The structure consists of hydrogen-bonded dimers. The carboxyl group is rotated, out of the benzene plane, through 53°31′ and there are bond-angle distortions.

Introduction

So far as we know little has been done about the molecular structure of methyl derivatives of benzoic acid. Ossorio (1960), has studied the ultraviolet absorption spectra of benzoic, toluic and dimethylbenzoic acids, and discussed the spectra in terms of the resonance theory and of steric inhibition of resonance. There is a close proximity of the methyl groups to the carboxyl group in 2,6-dimethylbenzoic acid. Thus interactions between these groups are expected. The angle between the carboxyl group and the benzene ring, estimated from ultraviolet absorption spectra, is close to 60°.

The study of related compounds was initiated by Sim, Robertson & Goodwin (1955), with the determination of the crystal structure of benzoic acid. Later, Ferguson & Sim (1961, 1962), studied the molecular overcrowding in isomorphous acids, *o*-chlorobenzoic acid and *o*-bromobenzoic acid. Finally, Brown & Marsh (1963), have described the molecular structure of 2-amino-3-methylbenzoic acid.

The present work gives an account of the crystal and molecular structure of 2,6-dimethylbenzoic acid.

Crystal data

A sample of highly purified 2,6-dimethylbenzoic acid was kindly furnished by Dr M. Colomina of our Institute. Colorless crystals of the acid were obtained by slow evaporation of a solution in an ethanol–chloro-