Acta Cryst. (1971). B**27**, 887

The Crystal Structure of 2-Acetyl-3,6-dihydroxy-3,7-dimethyl-6-phenyl-12-azatricyclo-[7,2,1,$0^{5,12}$]dodecane Methiodide

BY ANNE-MARIE PILOTTI

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

(*Received* 2 *June* 1970)

The crystal structure of 2-acetyl-3,6-dihydroxy-3,7-dimethyl-6-phenyl-12-azatricyclo[7,2,1,$0^{5,12}$]dodecane methiodide, $C_{22}H_{32}INO_3$, has been determined using three-dimensional X-ray diffraction data. The compound crystallizes in the monoclinic space group $P2_1$, with cell dimensions $a=15{\cdot}307$, $b=9{\cdot}198$, $c=7{\cdot}842$ Å and $\beta=97{\cdot}57°$. There are two molecules in the unit cell. The structure has been refined by the full-matrix least-squares technique to an R value of 0·044. The two six-membered rings A and B in the tricyclic system are chair-shaped and the five-membered ring C has an envelope conformation. The A/B and A/C ring junctions are both *cis* but the B/C ring junction is *trans*.

Introduction

An investigation of crepidine, $C_{21}H_{29}NO_3$, was started to obtain a better insight into the chemical constitution of various alkaloids isolated from *Dendrobium crepidatum* Lindl. (Leander, 1969). From this orchid five alkaloids have been isolated and crystallized. On the basis of spectroscopic analyses these compounds appear to be closely related. Such studies revealed some of the functional groups but not the molecular skeletons. Therefore, an X-ray analysis of crepidine methiodide, $C_{22}H_{32}INO_3$, was undertaken to establish its chemical structure and stereochemistry.

Experimental

Crystals suitable for X-ray analysis were kindly supplied by K. Leander (Institute of Organic Chemistry, University of Stockholm, Stockholm, Sweden).

Preliminary Weissenberg and rotation photographs indicated monoclinic symmetry. The space group is uniquely determined as $P2_1$ since the compound is optically active and systematic absences occur for $0k0$ with k odd.

Two crystals, measuring 0·266 (in the direction of **b**) ×0·058 (**c**) ×0·014 (**a**) mm and 0·206 (**b**) ×0·075 (**c**) ×0·014 (**a**) mm respectively, were used in the collection of three-dimensional X-ray diffraction data. The intensities of 1550 unique reflexions with $\sin\theta/\lambda<0{\cdot}45$ were measured by the θ–2θ scanning technique with a Siemens automatic diffractometer using Ni-filtered Cu K radiation. Each reflexion was measured twice, and stationary background measurements were made at both ends of the scan range of 1·2°. The crystals were oriented with the b-axis coincident with the φ axis. They were not stable to X-rays so test reflexions were therefore, measured periodically.

After a decay in intensity of about 15%, the crystal was exchanged for a fresh one. 1289 observed independent reflexions were used in the structure determination. Lorentz–polarization and absorption corrections ($\mu=120{\cdot}5$ cm^{-1}) were applied to the net intensity counts.

Crystal data

Lattice constants	$a=15{\cdot}307\pm5$, $b=9{\cdot}198\pm2$, $c=7{\cdot}842\pm5$Å; $\beta=97{\cdot}57\pm5°$
Cell volume	1094·4 Å^3
Density (X-ray)	1·471 g.cm^{-3}
Molecules per unit cell	2
Space group	$P2_1$

Structure determination and refinement

The structure was determined from Patterson and successive Fourier syntheses by the heavy-atom method. The x and z coordinates of the iodide ion were deduced from a three-dimensional Patterson synthesis. An arbitrary value of $\frac{1}{4}$ was assigned to the y coordinate, since there is no unique origin position along the b axis for the space group $P2_1$. The iodide ion position was refined by least-squares treatment until the R index 0·20 ($R=\sum||KF_o|-|F_c||/\sum|KF_o|$) was obtained.

The first Fourier synthesis was calculated with the structure amplitudes phased by the contributions of the iodide ions alone. There were as expected false-symmetry planes through the iodide peaks. Because of this, 50 peaks corresponding to 25 atoms were observed in the maps. It was found in a later stage of the structure analysis that two missing atoms were not resolved due to coincidental overlap of peaks from the two images. Since the molecular skeleton of the compound was unknown it was difficult to pick out the entire molecule from the double-image Fourier synthesis. Nuclear magnetic resonance data (Leander, 1969) indicated, however, that the molecule should contain a monosubstituted phenyl ring. A probable position for this group was found from the electron-density maps. Further atoms which had a high probability of belonging to the same molecular set were found from considerations of reasonable bond lengths and angles. In an attempt to locate the other atoms in the molecule, the relative heights of corresponding peaks in the Fourier syntheses were compared in order to select the correct member of each pair. The Fourier process was repeated several times, but the structure determination did not converge to a single molecule. The analysis was complicated by the fact that many of the light-atom peaks lay near the false mirror plane and their contribution to the phasing model reinforced rather than suppressed the false symmetry.

At this stage different structure alternatives had to be considered and models of the corresponding structures were built. Several steps of least-squares refinement followed by Fourier summation were calculated for the possible structure alternatives before the true structure was revealed. Spectroscopic and chemical evidence as well as differences in scattering power were used to differentiate between C, N and O atoms.

The atomic parameters were refined by the full-matrix least-squares method (Gantzel, Sparks & Trueblood, 1966) using isotropic temperature factors for the light non-hydrogen atoms and an anisotropic temperature factor for the iodide ion. The scattering factor curves used for oxygen, carbon and nitrogen were those given by Freeman (1959) and for the iodide ion that given by Cromer & Waber (1965). The scattering factors were corrected for the real part of the anomalous dispersion coefficient. 1289 reflexions were used in the refinement and Hughes's (1941) weighting procedure with $F_{o\min}=1{\cdot}56$ was applied. The R-value converged to 0·047. No extinction effects were observed and thus no correction for extinction was applied.

Up to this stage f_j'', the imaginary part of the anomalous dispersion factor for the iodide ion, was ignored. To decide upon the absolute configuration of the molecule, two sets of structure factors were calculated, one with $f_j''=6{\cdot}68$ (Cromer, 1965) and another with $f_j''=-6{\cdot}68$. The calculation with $f_j''=6{\cdot}68$ gave an R value of 0·044 after two cycles of full-matrix least-squares refinement whereas the calculation with $f_j''=-6{\cdot}68$ gave an R value of 0·054. According to the statistical theory discussed by Hamilton (1965), the configuration which has been assumed above should have a very high probability of being the real and absolute configuration (*cf.* Fig. 1). But for a statistical test to be relevant one must assume that there are no systematic errors present in the data which would favour one hypothesis over the other. As described above the crystals are not stable to X-rays. Furthermore, the intensities were not collected in a random sequence, but rather one layer after another. This could cause systematic errors and therefore the conclusion about the absolute configuration may not have the high significance indicated in the test. Comparison of observed and calculated intensities $I(h\,k\,l)$ and $I(\bar{h}\,\bar{k}\,\bar{l})$ would of course be valuable in deciding the absolute configuration. Because of the relatively small variation produced by anomalous dispersion, however, accurate intensity measurements are required. Since, as stated above, the crystals are damaged by X-rays and because no full-circle crystal orienter was available for measuring the Friedel pair reflexions directly after one another, this test was not performed.

The refinement was terminated when the shifts for all parameters but one where less than one tenth of the estimated standard deviations. The shift of the y parameter for the atom lying nearest to the false mirror plane was about twenty per cent of the corresponding standard deviation. The final difference synthesis yielded no thoroughly convincing H atom sites. They were therefore omitted from the calculation. Observed and calculated structure factors are given in Table 1.

Description and discussion of the structure

In the following discussion, atoms belonging to different asymmetric units are labelled as follows:

Superscript	Coordinates	Superscript	Coordinates
none	$x, \quad y, \quad z$	iv	$2-x,\ y-\frac{1}{2},\ 1-z$
i	$1-x,\ \frac{1}{2}+y,\ -z$	v	$x,\ y+1,\ z$
ii	$1-x,\ y-\frac{1}{2},\ 1-z$	vi	$1-x,\ y-\frac{1}{2},\ -z$
iii	$x,\ y,\ z+1$	vii	$x-1,\ y,\ z$

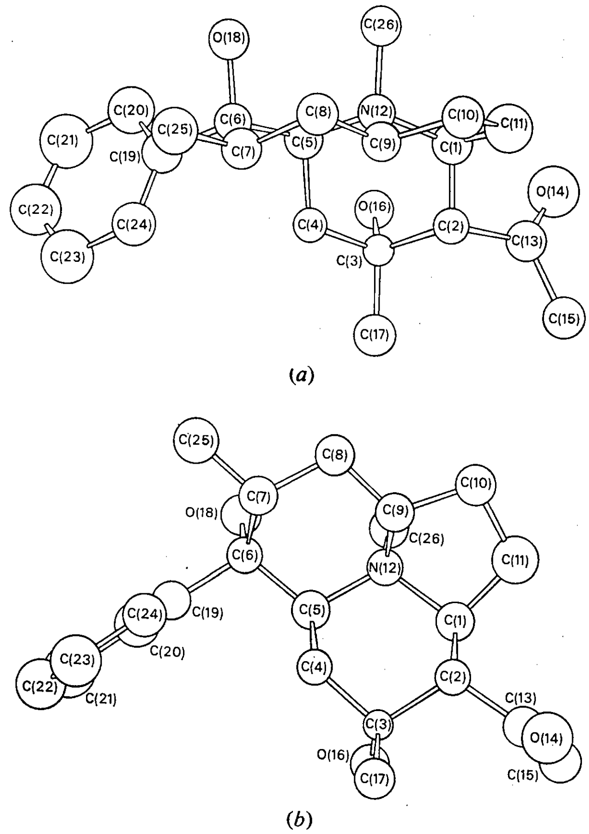

Fig. 1. Perspective views of the 2-acetyl-3,6-dihydroxy-6-phenyl-3,7,12-trimethyl-12-azatricyclo[7,2,1,$0^{5,12}$]dodecane ion. (*b*) is rotated 30° from (*a*).

Table 1. *Observed and calculated structure factors*

H K L	$10\|F_o\|$	$10\|F_c\|$
0 2 0	909	952
0 4 0	608	631
0 6 0	459	461
0 8 0	350	317
0 0 1	926	929
0 1 1	1006	1087
0 2 1	857	836
0 3 1	547	561
0 4 1	418	386
0 5 1	550	592
0 6 1	207	215
0 7 1	397	383
0 8 1	165	161
0 9 1	224	197
0 0 2	809	737
0 1 2	1204	1221
0 2 2	344	325
0 3 2	483	508
0 4 2	403	405
0 5 2	399	411
0 6 2	508	300
0 7 2	370	300
0 8 2	219	202
0 9 2	259	229
0 0 3	1011	1020
0 1 3	328	283
0 2 3	744	753
0 3 3	88	87
0 4 3	567	559
0 6 3	554	531
0 8 3	257	230
0 0 4	297	299
0 1 4	658	668
0 2 4	445	453
0 3 4	477	451
0 4 4	308	299
0 5 4	351	328
0 7 4	275	257
0 8 4	131	114
0 0 5	153	148
0 1 5	374	369
0 2 5	468	436
0 3 5	330	318
0 4 5	162	171
0 5 5	283	264
0 6 5	209	187
0 7 5	187	180
0 0 6	401	387
0 2 6	417	392
0 3 6	118	94
0 4 6	345	333
0 5 6	92	93
0 6 6	236	212
0 1 7	295	269
0 2 7	134	117
0 3 7	306	288
0 4 7	125	118
0 5 7	201	185
0 1 8	143	142
0 2 8	187	174
1 0 0	499	459
1 1 0	316	347
1 2 0	609	576
1 3 0	772	791
1 4 0	118	123
1 5 0	475	440
1 6 0	235	214
1 7 0	338	337
1 9 0	225	216
1 0 1	139	182
1 1 1	817	825
1 2 1	950	946
1 3 1	617	600
1 4 1	351	350
1 5 1	518	530
1 6 1	371	366
1 7 1	340	325
1 8 1	256	232
1 0 2	699	675
1 1 2	136	129
1 2 2	1115	1052
1 3 2	105	105
1 4 2	705	705
1 5 2	68	84
1 6 2	374	369
1 8 2	213	211
1 9 2	101	92
1 0 3	356	328
1 1 3	595	592
1 2 3	222	210
1 3 3	638	623
1 4 3	249	229
1 5 3	215	243
1 6 3	245	229
1 7 3	391	356
1 0 4	453	444
1 1 4	579	587
1 2 4	284	281
1 3 4	257	269
1 4 4	318	334
1 5 4	274	258
1 6 4	181	190
1 7 4	166	171
1 8 4	157	155
1 0 5	469	429
1 1 5	89	75
1 2 5	519	491
1 3 5	109	62
1 4 5	406	359
1 5 5	273	259
1 6 5	213	150
1 0 6	330	311
1 1 6	177	161
1 2 6	264	267
1 4 6	97	95
1 5 6	222	216
1 6 6	250	243
1 0 7	191	184
1 1 7	161	170
1 2 7	110	122
1 3 7	150	144
1 4 7	139	131
1 5 7	257	254
2 0 0	999	1052
2 1 0	747	812
2 2 0	712	706
2 3 0	386	383
2 4 0	712	700
2 5 0	376	362
2 6 0	270	280
2 7 0	215	228
2 8 0	251	235
2 9 0	151	163
2 0 1	516	596
2 1 1	991	592
2 2 1	739	800
2 3 1	461	452
2 4 1	639	652
2 5 1	234	188
2 6 1	349	356
2 7 1	191	170
2 8 1	379	359
2 0 2	139	157
2 1 2	646	681
2 2 2	158	178
2 3 2	779	715
2 4 2	565	544
2 5 2	298	285
2 7 2	355	274
2 0 3	501	314
2 1 3	330	313
2 2 3	752	705
2 3 3	183	178
2 4 3	668	651
2 5 3	193	104
2 6 3	335	323
2 7 3	206	197
2 8 3	178	151
2 0 4	439	450
2 1 4	272	280
2 2 4	453	442
2 3 4	260	263
2 4 4	574	497
2 5 4	305	278
2 6 4	332	307
2 7 4	130	115
2 8 4	274	208
1 5	414	432
2 5	164	162
3 5	451	450
5 5	344	347
7 5	233	224
0 6	370	370
1 6	103	95
2 6	348	335
3 6	161	155
4 6	303	278
5 6	141	115
6 6	212	197
0 7	262	255
1 7	175	173
2 7	295	282
3 7	165	142
4 7	193	172
1 8	163	163
0 0	890	999
1 0	211	196
2 0	951	940
3 0	225	241
4 0	811	820
5 0	132	153
6 0	373	366
7 0	167	171
8 0	188	198
9 0	138	130
1 1	1150	1147
2 1	176	140
3 1	575	573
4 1	212	203
5 1	496	489
3 7 1	394	369
3 8 1	114	84
3 9 1	171	182
3 0 2	629	673
3 1 2	478	482
3 2 2	622	569
3 3 2	765	690
3 4 2	520	509
3 5 2	252	231
3 6 2	370	354
3 7 2	242	251
3 8 2	211	217
3 0 3	470	466
3 1 3	237	255
3 2 3	751	783
3 3 3	255	255
3 4 3	563	591
3 5 3	204	184
3 6 3	362	377
3 7 3	147	157
3 8 3	211	201
3 0 4	170	171
3 1 4	517	529
3 3 4	355	351
3 4 4	588	570
3 5 4	105	95
3 6 4	265	245
3 7 4	493	486
3 0 5	230	232
3 1 5	514	492
3 2 5	246	226
3 3 5	205	192
3 4 5	223	212
3 6 5	389	367
3 0 6	168	177
3 1 6	292	293
3 2 6	157	158
3 3 6	220	214
3 4 6	129	110
3 5 6	191	194
3 6 6	277	276
3 1 7	192	166
3 3 7	162	174
4 0 0	810	815
4 1 0	127	145
4 2 0	403	518
4 3 0	510	474
4 4 0	517	530
4 5 0	136	125
4 6 0	352	344
4 7 0	204	180
4 0 1	974	901
4 1 1	439	427
4 2 1	845	853
4 3 1	250	235
4 4 1	516	502
4 5 1	136	120
4 6 1	341	361
4 7 1	151	133
4 8 1	273	255
4 0 2	623	789
4 1 2	472	450
4 2 2	212	248
4 3 2	185	135
4 4 2	346	407
4 5 2	426	419
4 6 2	338	335
4 7 2	214	216
4 8 2	121	124
4 9 2	117	120
4 0 3	156	145
4 1 3	660	644
4 2 3	268	287
4 3 3	529	496
4 4 3	90	84
4 5 3	323	331
4 6 3	188	131
4 7 3	193	188
4 0 4	543	540
4 1 4	185	185
4 2 4	311	293
4 3 4	142	136
4 4 4	441	425
4 5 4	141	325
4 6 4	342	335
4 0 5	195	194
4 2 5	420	439
4 3 5	243	229
4 4 5	100	180
4 5 5	170	171
4 6 5	256	257
4 7 5	212	216
4 0 6	119	118
4 1 6	164	166
4 3 6	262	215
4 5 6	133	132
4 0 7	287	280
4 2 7	230	277
5 0 0	186	169
5 1 0	252	249
5 2 0	436	432
5 3 0	283	261
5 4 0	573	590
5 5 0	184	167
5 6 0	702	699
5 8 0	331	313
5 0 1	503	462
5 1 1	246	250
5 2 1	519	530
5 3 1	602	604
5 4 1	428	394
5 5 1	596	577
5 6 1	457	441
5 7 1	300	311
5 8 1	276	224
5 9 1	124	137
5 0 2	200	218
5 1 2	133	125
5 2 2	163	145
5 3 2	405	447
5 4 2	368	348
5 5 2	606	533
5 6 2	212	213
5 7 2	440	447
5 8 2	288	290
5 0 3	103	99
5 1 3	666	664
5 2 3	242	239
5 3 3	638	656
5 4 3	362	379
5 5 3	153	132
5 6 3	352	339
5 8 3	212	225
5 0 4	141	147
5 1 4	332	346
5 2 4	326	377
5 3 4	412	406
5 4 4	160	164
5 5 4	292	293
5 6 4	272	272
5 7 4	118	105
5 0 5	121	109
5 1 5	470	451
5 2 5	245	260
5 3 5	332	334
5 4 5	163	164
5 5 5	175	176
5 6 5	79	72
5 0 6	394	373
5 1 6	94	90
5 2 6	345	341
5 3 6	115	110
5 4 6	250	246
5 0 7	214	224
5 1 7	208	208
5 2 7	165	158
5 3 7	185	181
6 0 0	174	142
6 1 0	500	509
6 2 0	577	557
6 3 0	485	499
6 4 0	289	292
6 5 0	352	354
6 6 0	198	203
6 7 0	291	266
6 0 1	134	123
6 1 1	439	478
6 2 1	587	604
6 3 1	238	247
6 4 1	667	652
6 5 1	180	158
6 6 1	322	309
6 7 1	144	176
6 8 1	203	206
6 0 2	197	182
6 1 2	536	553
6 2 2	408	459
6 3 2	91	97
6 4 2	472	476
6 5 2	144	147
6 6 2	380	366
6 7 2	117	89
6 8 2	208	218
6 0 3	166	159
6 1 3	382	378
6 2 3	301	322
6 3 3	400	404
6 4 3	209	271
6 5 3	203	191
6 6 3	198	189
6 7 3	123	113
6 8 3	215	204
6 0 4	275	263
6 1 4	180	177
6 2 4	347	343
6 3 4	176	162
6 4 4	288	280
6 5 4	107	84
6 7 4	118	124
6 0 5	291	307
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
2 6 -5	353	361
2 0 -6	280	250
2 1 -6	295	322
2 2 -6	247	249
2 3 -6	224	232
2 4 -6	223	210
2 5 -6	227	225
2 6 -6	140	149
2 0 -7	204	229
2 1 -7	249	244
2 3 -7	225	217
2 5 -7	180	168
2 0 -8	169	190
2 2 -8	205	231
3 0 -1	841	856
3 1 -1	599	564
3 2 -1	957	956
3 3 -1	710	704
3 4 -1	405	456
3 5 -1	203	296
3 6 -1	358	365
3 7 -1	187	147
3 8 -1	170	177
3 9 -1	115	105
3 0 -2	197	220
3 1 -2	892	920
3 3 -2	593	600
3 4 -2	228	201
3 5 -2	546	569
3 7 -2	230	252
3 8 -2	97	85
3 9 -2	151	167
3 0 -3	553	556
3 1 -3	180	166
3 2 -3	551	553
3 3 -3	379	374
3 4 -3	526	550
3 5 -3	125	111
3 6 -3	268	279
3 7 -3	104	115
3 8 -3	240	248
3 0 -4	546	578
3 1 -4	581	597
3 2 -4	466	450
3 3 -4	427	446
3 4 -4	315	321
3 5 -4	173	152
3 6 -4	214	209
3 8 -4	197	210
3 1 -5	509	507
3 3 -5	548	574
3 5 -5	307	309
3 7 -5	131	128
3 0 -6	357	354
3 1 -6	168	165
3 2 -6	345	300
3 3 -6	175	167
3 4 -6	203	315
3 6 -6	145	150
3 0 -7	249	263
3 1 -7	128	149
3 2 -7	201	210
3 3 -7	211	205
3 4 -7	161	166
3 5 -7	126	128
3 1 -8	237	236
4 0 -1	561	557
4 1 -1	761	751
4 3 -1	217	165
4 4 -1	295	299
4 5 -1	294	298
4 6 -1	354	374
4 7 -1	164	191
4 8 -1	258	225
4 9 -1	138	129
4 0 -2	393	420
4 1 -2	637	599
4 2 -2	666	692
4 3 -2	148	164
4 4 -2	621	595
4 5 -2	247	257
4 6 -2	319	333
4 7 -2	175	174
4 8 -2	260	263
4 0 -3	215	193
4 1 -3	697	646
4 3 -3	599	605
4 4 -3	78	83
4 5 -3	396	383
4 7 -3	294	303
4 0 -4	488	509
4 1 -4	219	204
4 2 -4	573	575
4 3 -4	276	277
4 4 -4	314	312
4 5 -4	249	244
4 6 -4	340	339
4 7 -4	142	135
4 8 -4	224	174
4 0 -5	278	286
4 1 -5	261	273
4 2 -5	431	440
4 3 -5	180	165
4 4 -5	308	332
4 5 -5	157	165
4 6 -5	287	296
4 7 -5	153	170
4 1 -6	374	360
4 2 -6	113	111
4 3 -6	398	401
4 5 -6	251	239
4 0 -7	343	335
4 1 -7	95	106
4 2 -7	217	210
4 3 -7	108	123
4 4 -7	244	236
4 5 -7	118	120
4 0 -8	176	164
4 1 -8	154	150
4 2 -8	212	190
5 0 -1	199	175
5 1 -1	717	746
5 2 -1	362	366
5 3 -1	652	601
5 4 -1	124	114
5 5 -1	446	437
5 6 -1	127	116
5 7 -1	316	327
5 9 -1	230	222
5 0 -2	524	525
5 1 -2	406	334
5 2 -2	436	447
5 3 -2	320	314
5 4 -2	467	472
5 5 -2	379	403
5 6 -2	254	259
5 7 -2	249	237
5 8 -2	105	111
5 9 -2	125	111
5 0 -3	869	874
5 2 -3	452	429
5 3 -3	256	241
5 4 -3	465	512
5 5 -3	227	225
5 6 -3	299	293
5 8 -3	207	170
5 1 -4	478	490
5 2 -4	121	127
5 3 -4	382	376
5 4 -4	120	125
5 5 -4	326	320
5 7 -4	250	249
5 0 -5	298	294
5 1 -5	344	361
5 2 -5	212	189
5 3 -5	121	151
5 4 -5	329	317
5 5 -5	197	180
5 6 -5	178	184
5 7 -5	90	96
5 0 -6	340	333
5 1 -6	131	136
5 2 -6	296	248
5 3 -6	99	106
5 4 -6	220	220
5 5 -6	121	113
5 6 -6	203	200
5 0 -7	105	119
5 1 -7	196	186
5 3 -7	196	182
5 0 -8	100	97
5 2 -8	206	209
6 0 -1	1074	1092
6 1 -1	470	417
6 2 -1	769	764
6 3 -1	159	166
6 4 -1	461	445
6 6 -1	373	359
6 7 -1	110	86
6 8 -1	191	194
6 0 -2	153	139
6 1 -2	745	732
6 2 -2	376	375
6 3 -2	470	526
6 4 -2	224	231
6 5 -2	403	308
6 7 -2	252	295
6 8 -2	119	129
6 0 -3	259	236
6 1 -3	565	613
6 2 -3	412	401
6 3 -3	268	282
6 4 -3	274	270
6 5 -3	261	256
6 6 -3	192	253
6 7 -3	239	223
6 8 -3	119	125
6 0 -4	494	465
6 1 -4	209	197
6 2 -4	513	533
6 4 -4	396	397
6 6 -4	386	366
6 8 -4	160	149
6 0 -5	90	77
6 1 -5	427	412
6 2 -5	259	264
6 3 -5	350	352
6 4 -5	145	139
6 5 -5	367	349
6 7 -5	149	161
6 0 -6	367	331
6 1 -6	227	211
6 2 -6	249	273
6 3 -6	255	246
6 4 -6	131	135
6 5 -6	215	192
6 6 -6	143	125
6 0 -7	362	353
6 1 -7	102	105
6 2 -7	251	251
6 4 -7	268	267
6 1 -8	239	233
7 0 -1	677	690
7 1 -1	299	[illegible]
7 2 -1	264	254
7 3 -1	555	571
7 4 -1	253	250
7 5 -1	307	306
7 6 -1	115	105
7 7 -1	204	[illegible]
7 8 -1	121	111
7 0 -2	490	417
7 1 -2	313	291
7 2 -2	634	635
7 4 -2	463	464
7 6 -2	245	255
7 8 -2	255	257
7 0 -3	277	317
7 1 -3	570	578
7 2 -3	234	210
7 3 -3	581	579
7 4 -3	203	195
7 5 -3	274	206
7 6 -3	105	75
7 7 -3	108	107
7 8 -3	110	99
7 0 -4	316	341
7 1 -4	258	231
7 2 -4	309	341
7 3 -4	367	392
7 4 -4	160	144
7 5 -4	137	143
7 6 -4	188	159
7 7 -4	223	219
7 0 -5	401	423
7 2 -5	415	415
7 3 -5	162	185
7 4 -5	332	331
7 6 -5	165	157
7 0 -6	156	168
7 1 -6	314	311
7 2 -6	119	95
7 3 -6	294	292
7 4 -6	136	144
7 5 -6	157	152
7 0 -7	116	110
7 1 -7	187	202
7 2 -7	155	132
7 3 -7	155	144
7 4 -7	127	137
8 0 -1	704	715
8 1 -1	313	328
8 2 -1	336	344
8 3 -1	305	398
8 4 -1	335	327
8 5 -1	222	213
8 6 -1	211	216
8 7 -1	209	211
8 8 -1	115	105
8 0 -2	122	126
8 1 -2	451	470
8 2 -2	95	97
8 3 -2	413	393
8 4 -2	125	141
8 5 -2	355	350
8 6 -2	105	106
8 7 -2	256	258
8 8 -2	105	26
8 0 -3	534	535
8 1 -3	93	82
8 2 -3	432	429
8 3 -3	132	148
8 4 -3	440	423
8 5 -3	96	97
8 6 -3	271	270
8 0 -4	293	287
8 1 -4	256	231
8 2 -4	362	384
8 3 -4	309	317
8 4 -4	[illegible]	[illegible]
8 5 -4	199	190
8 6 -4	226	210
8 7 -4	176	177
8 0 -5	95	90
8 1 -5	352	346
8 2 -5	108	92
8 3 -5	305	295
8 4 -5	136	133
8 5 -5	249	265
8 0 -6	147	150
8 2 -6	278	262
8 4 -6	198	200
8 1 -7	151	131
8 2 -7	152	151
8 3 -7	189	183
9 0 -1	606	595
9 1 -1	85	72
9 2 -1	464	481
9 3 -1	144	147
9 4 -1	497	495
9 5 -1	177	177
9 6 -1	234	215
9 7 -1	113	106
9 8 -1	171	157
9 0 -2	521	510
9 1 -2	303	294
9 2 -2	449	446
9 3 -2	316	286
9 4 -2	296	217
9 5 -2	214	232
9 6 -2	205	217
9 7 -2	191	199
9 1 -3	435	425
9 2 -3	197	171
9 3 -3	300	304
9 5 -3	367	373
9 6 -3	170	154
9 7 -3	166	161
9 0 -4	334	300
9 2 -4	377	354
9 4 -4	292	270
9 6 -4	274	276
9 0 -5	326	340
9 1 -5	357	357
9 2 -5	149	154
9 3 -5	235	225
9 4 -5	225	204
9 5 -5	149	140
9 6 -5	107	111
9 1 -6	306	306
9 2 -6	97	107
9 3 -6	203	199
9 5 -6	164	155
9 0 -7	265	268
9 2 -7	188	190
10 1 -1	301	308
10 2 -1	102	119
10 3 -1	232	231
10 5 -1	246	243
10 7 -1	207	199
10 0 -2	414	391
10 1 -2	156	172
10 2 -2	262	253
10 3 -2	178	182
10 4 -2	207	180
10 6 -2	220	206
10 7 -2	115	127
10 0 -3	271	246
10 1 -3	313	330
10 2 -3	291	300
10 3 -3	113	107
10 4 -3	190	180
10 5 -3	178	184
10 [illegible]	144	150
10 1 -4	321	300
10 2 -4	112	113
10 3 -4	287	285
10 4 -4	111	126
10 5 -4	171	160
10 0 -5	281	290
10 2 -5	165	162
10 3 -5	101	108
10 4 -5	205	202
10 [illegible] -6	97	97
10 1 -6	154	153
10 2 -6	100	158
10 3 -6	96	109
10 4 -6	160	152
10 1 -7	151	203
11 0 -1	344	364
11 1 -1	105	185
11 2 -1	317	280
11 3 -1	226	230
11 4 -1	447	445
11 6 -1	213	206
11 1 -2	341	331
11 2 -2	136	143
11 3 -2	468	466
11 4 -2	155	148
11 5 -2	244	245
11 7 -2	153	165
11 0 -3	252	212
11 1 -3	166	150
11 2 -3	315	312
11 3 -3	[illegible]	[illegible]
11 4 -3	207	[illegible]
11 5 -3	249	278
11 0 -4	294	307
11 1 -4	150	117
11 2 -4	316	306
11 3 -4	126	125
11 4 -4	252	245
11 6 -4	142	116
11 1 -5	307	298
11 3 -5	242	[illegible]
11 5 -5	[illegible]	156
11 1 -6	174	[illegible]
11 2 -6	166	[illegible]
11 3 -6	[illegible]	[illegible]
12 0 -1	231	[illegible]
12 1 -1	[illegible]	[illegible]
12 2 -1	195	[illegible]
12 3 -1	118	[illegible]
12 4 -1	175	[illegible]
12 5 -1	126	125
12 6 -1	117	[illegible]
12 0 -2	260	294
12 2 -2	332	336
12 3 -2	171	[illegible]
12 4 -2	147	141
12 5 -2	[illegible]	[illegible]
12 6 -2	162	[illegible]
12 1 -3	[illegible]	261
12 3 -3	202	205
12 5 -3	[illegible]	222
12 1 -4	157	170
12 2 -4	[illegible]	145
12 3 -4	[illegible]	142
12 4 -4	[illegible]	154
12 5 -4	[illegible]	[illegible]
12 0 -5	201	[illegible]
12 2 -5	[illegible]	[illegible]
12 3 -5	[illegible]	[illegible]
12 4 -5	[illegible]	[illegible]
12 1 -6	175	166
13 0 -1	225	229
13 1 -1	193	182
13 3 -1	141	137
13 4 -1	145	165
13 5 -1	130	199
13 0 -2	153	155
13 1 -2	158	156
13 2 -2	[illegible]	114
13 3 -2	[illegible]	[illegible]
13 5 -2	[illegible]	147
13 0 -3	250	236
13 2 -3	253	197
13 4 -3	[illegible]	[illegible]
13 1 -4	[illegible]	199
13 2 -4	184	194
13 0 -5	112	112
13 1 -5	128	126
13 2 -5	[illegible]	111
13 3 -5	[illegible]	165
14 0 -1	223	221
14 2 -1	233	229
14 4 -1	[illegible]	151
14 1 -2	[illegible]	216
14 2 -2	[illegible]	[illegible]
14 3 -2	165	[illegible]
14 4 -2	[illegible]	[illegible]
14 0 -3	127	118
14 1 -3	[illegible]	[illegible]
14 2 -3	94	70
14 3 -3	[illegible]	125
14 0 -4	242	250
14 2 -4	[illegible]	164
14 0 -5	[illegible]	103
14 1 -5	122	113
15 1 -1	138	142
15 2 -1	82	70
15 3 -1	101	[illegible]
15 0 -2	147	141
15 2 -2	191	180
15 1 -3	115	82
15 2 -3	133	141
15 1 -4	[illegible]	136
16 0 -1	153	[illegible]
16 1 -2	[illegible]	138

The bond lengths and bond angles, uncorrected for thermal motion, were computed from the refined coordinates given in Table 2 and are listed in Tables 3 and 4 (see Fig. 2).

Table 2. *Atomic parameters with their standard deviations*

	x	y	z	B
I	0·1922 (1)	0·2500	0·1705 (1)	–
C(1)	0·8903 (9)	0·4201 (18)	0·2534 (18)	4·0 (3)
C(2)	0·8382 (9)	0·5510 (14)	0·2708 (16)	3·2 (3)
C(3)	0·7493 (7)	0·5186 (12)	0·3427 (14)	2·5 (2)
C(4)	0·7008 (8)	0·4059 (15)	0·2193 (16)	3·2 (3)
C(5)	0·7487 (7)	0·2606 (26)	0·2034 (14)	4·0 (2)
C(6)	0·6931 (8)	0·1602 (14)	0·0753 (16)	3·4 (3)
C(7)	0·6915 (9)	0·2056 (15)	−0·1170 (18)	4·0 (3)
C(8)	0·7893 (9)	0·2277 (19)	−0·1540 (17)	4·5 (3)
C(9)	0·8332 (8)	0·3391 (16)	−0·0373 (16)	3·8 (3)
C(10)	0·9280 (10)	0·3808 (18)	−0·0549 (18)	4·5 (3)
C(11)	0·9599 (12)	0·4480 (21)	0·1298 (22)	5·7 (4)
N(12)	0·8395 (6)	0·2925 (11)	0·1502 (12)	3·5 (2)
C(13)	0·8983 (11)	0·6529 (19)	0·3885 (22)	4·2 (3)
O(14)	0·9517 (8)	0·6032 (15)	0·4997 (16)	6·3 (3)
C(15)	0·8888 (10)	0·8134 (19)	0·3672 (21)	4·4 (4)
O(16)	0·7646 (6)	0·4517 (11)	0·5061 (11)	3·9 (2)
C(17)	0·6942 (10)	0·6518 (18)	0·3491 (20)	4·4 (3)
O(18)	0·7397 (6)	0·0226 (11)	0·1015 (12)	4·2 (2)
C(19)	0·6022 (10)	0·1364 (17)	0·1325 (19)	4·0 (3)
C(20)	0·5933 (11)	0·0413 (21)	0·2546 (22)	5·4 (4)
C(21)	0·5080 (15)	0·0254 (27)	0·3169 (28)	7·1 (5)
C(22)	0·4393 (14)	0·1037 (24)	0·2387 (26)	6·6 (4)
C(23)	0·4457 (13)	0·2074 (22)	0·1124 (27)	6·8 (5)
C(24)	0·5326 (10)	0·2214 (18)	0·0545 (20)	5·0 (4)
C(25)	0·6414 (11)	0·1073 (19)	−0·2430 (21)	5·3 (4)
C(26)	0·8958 (9)	0·1582 (17)	0·1848 (19)	3·9 (3)

For I the anisotropic temperature factor T obtained was $T=\exp[-(0·0053h^2+0·0114k^2+0·0148l^2-0·0011hk+0·0024hl+0·0025kl)]$.

Table 3. *Bond distances with standard deviations*

C(1)—C(2)	1·46 (2) Å	C(13)–O(14)	1·20 (2) Å
C(2)—C(3)	1·57 (2)	C(13)–C(15)	1·49 (3)

Table 3 (*cont.*)

C(3)—C(4)	1·54 (2)	C(3)—O(16)	1·41 (2)
C(4)—C(5)	1·54 (3)	C(3)—C(17)	1·49 (2)
C(5)—C(6)	1·54 (2)	C(6)—O(18)	1·45 (2)
C(6)—C(7)	1·56 (2)	C(6)—C(19)	1·53 (2)
C(7)—C(8)	1·57 (2)	C(19)–C(20)	1·32 (3)
C(8)—C(9)	1·47 (2)	C(20)–C(21)	1·46 (3)
C(9)—C(10)	1·52 (2)	C(21)–C(22)	1·35 (3)
C(10)–C(11)	1·59 (3)	C(22)–C(23)	1·39 (3)
C(11)–C(1)	1·55 (2)	C(23)–C(24)	1·46 (3)
C(1)—N(12)	1·57 (2)	C(24)–C(19)	1·40 (2)
C(5)—N(12)	1·53 (2)	C(7)—C(25)	1·48 (2)
C(9)—N(12)	1·52 (2)	N(12)–C(26)	1·51 (2)
C(2)—C(13)	1·53 (2)		

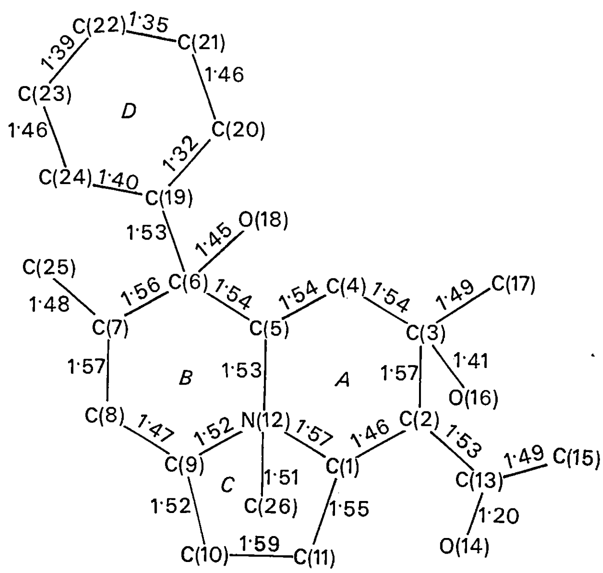

Fig. 2. Interatomic distances (in Å) in the 2-acetyl-3,6-dihydroxy-6-phenyl-3,7,12-trimethyl-12-azatricyclo[7,2,1,$0^{5,12}$]-dodecane ion.

Table 4. *Interatomic angles with standard deviations*

C(1)—C(2)—C(3)	112·8 (1·1)°	C(3)—C(2)—C(13)	112·4 (1·1)°
C(2)—C(3)—C(4)	105·7 (0·9)	C(2)—C(3)—O(16)	111·1 (0·9)
C(3)—C(4)—C(5)	116·1 (1·0)	C(2)—C(3)—C(17)	112·1 (1·0)
C(4)—C(5)—C(6)	110·3 (1·0)	O(16)–C(3)—C(17)	110·8 (1·0)
C(5)—C(6)—C(7)	114·0 (1·1)	C(4)—C(3)—O(16)	106·6 (0·9)
C(6)—C(7)—C(8)	108·6 (1·1)	C(4)—C(3)—C(17)	110·3 (1·0)
C(7)—C(8)—C(9)	110·0 (1·1)	C(5)—C(6)—O(18)	102·2 (1·1)
C(8)—C(9)—C(10)	118·7 (1·2)	C(5)—C(6)—C(19)	109·9 (1·1)
C(9)—C(10)–C(11)	101·4 (1·1)	C(18)–C(6)—C(19)	106·4 (1·1)
C(10)–C(11)–C(1)	110·5 (1·3)	C(6)—C(19)–C(20)	119·5 (1·4)
C(11)–C(1)—C(2)	110·5 (1·3)	C(19)–C(20)–C(21)	119·5 (1·7)
C(2)—C(1)—N(12)	115·1 (1·1)	C(20)–C(21)–C(22)	118·1 (2·0)
C(1)—N(12)–C(5)	114·1 (1·1)	C(21)–C(22)–C(23)	124·4 (2·0)
N(12)–C(5)—C(4)	108·4 (1·5)	C(22)–C(23)–C(24)	115·7 (1·7)
C(6)—C(5)—N(12)	112·4 (1·0)	C(23)–C(24)–C(19)	119·1 (1·5)
C(5)—N(12)–C(9)	111·9 (0·9)	C(24)–C(19)–C(20)	123·0 (1·5)
N(12)–C(9)—C(8)	111·6 (1·1)	C(24)–C(19)–C(6)	117·5 (1·3)
N(12)–C(9)—C(10)	102·6 (1·0)	C(19)–C(6)—C(7)	115·0 (1·1)
C(9)—N(12)–C(1)	104·5 (1·0)	C(18)–C(6)—C(7)	108·3 (1·0)
N(12)–C(1)—C(11)	97·8 (1·1)	C(6)—C(7)—C(25)	114·9 (1·2)
C(1)—C(2)—C(13)	105·6 (1·2)	C(25)–C(7)—C(8)	112·3 (1·2)
C(2)—C(13)–O(14)	120·0 (1·5)	C(1)—N(12)–C(26)	106·7 (1·0)
C(2)—C(13)–C(15)	119·7 (1·4)	C(5)—N(12)–C(26)	108·1 (1·2)
C(14)–C(13)–C(15)	120·3 (1·6)	C(9)—N(12)–C(26)	111·5 (1·0)

The deviations from normal values for carbon–carbon bonds of the type sp^3–sp^3, 1·53 Å, and for aromatic carbon–carbon bonds, 1·395 Å, are in accordance with the standard deviations calculated for the bond lengths in the molecule. The relatively large standard deviations may be explained by the presence of the iodide ion with its predominant scattering power and the fact that the crystals are not stable to X-rays.

The values of 1·49 Å for the C(13)–C(15) bond and 1·20 Å for the C(13)–O(14) double bond are in agreement with the generally assumed values of 1·50 Å for C(sp^2)–C(sp^3) bonds (Lide, 1962) and 1·23 Å for carbon–carbonyl oxygen double bonds (*International Tables for X-ray Crystallography*, 1962). Furthermore the carbon–oxygen single bond distances, 1·41 and 1·45 Å, are in accordance with the value 1·43 Å for such bonds (*International Tables for X-ray Crystallography*, 1962).

The C(sp^3)–N^+ bond lengths in this structure are not significantly different from the average value, 1·52 Å, deduced from a survey of alkaloids by Hamilton, Hamor, Robertson & Sim (1962). The iodide ion coordination is given in Table 5. All distances less than 3·8 Å between the cations are listed in Table 6. The distance between the iodide ion and the oxygen atom O(18^{i}) is 3·54 Å indicating a hydrogen bond O–H···I^-. This is in agreement with the average value 3·53 Å, reported by Clark (1962) for such bonds. No other hydrogen atoms available for normal hydrogen bondings have been found in the structure.

Table 5. *Distances to the iodide ion shorter than* 4·0 Å

I···C(22)	3·98 Å	I···O(16^{ii})	3·73 Å
I···C(23)	3·99	I···C(2^{vi})	3·89
I···O(18^{i})	3·54	I···C(9^{vi})	3·93
I···C(13^{ii})	3·99	I···C(10^{vi})	3·91
I···O(14^{ii})	3·85	I···C(11^{vii})	3·97

Table 6. *Intermolecular distances shorter than 3·8 Å between the cations*

O(16)···C(8^{iii})	3·35 Å	O(14)···C(15^{iv})	3·67 Å
O(16)···C(9^{iii})	3·74	C(15)···O(18^{v})	3·46
C(26)···O(14^{iv})	3·21	C(15)···C(26^{v})	3·49

The intermolecular packing arrangement viewed down the *b* axis is shown in Fig. 3. The ions are held together by a three-dimensional network of electrostatic forces. Perspective views of the molecule are shown in Fig. 1 (*a*) and (*b*). Rings *A* and *B* as well as *A* and *C* are *cis*-fused, but rings *B* and *C* are *trans*-fused (see Fig. 2). Least-squares planes have been calculated for these rings. The equations and deviations of atoms from the planes are given in Table 7. As is the case with most saturated five-membered rings, four atoms are coplanar in ring *C* and one is significantly out of the plane. Rings *A* and *B* are chair-shaped. Interplanar angles are also given in Table 7.

Table 7. *Least-squares planes and deviations*

The planes are described in terms of axes (m,n,p) having $m\|a^*$, $n\|b$ and $p\|c$.

Plane *A*	$0·0465m-0·1520n+0·9873p=\ 0·2398$
Plane *B*	$-0·2230m+0·9634n-0·1486p=-0·2050$
Plane *C*	$-0·3523m+0·9130n-0·2058p=-1·2354$
Plane *D*	$0·2341m+0·7122n+0·6618p=\ 2·9171$

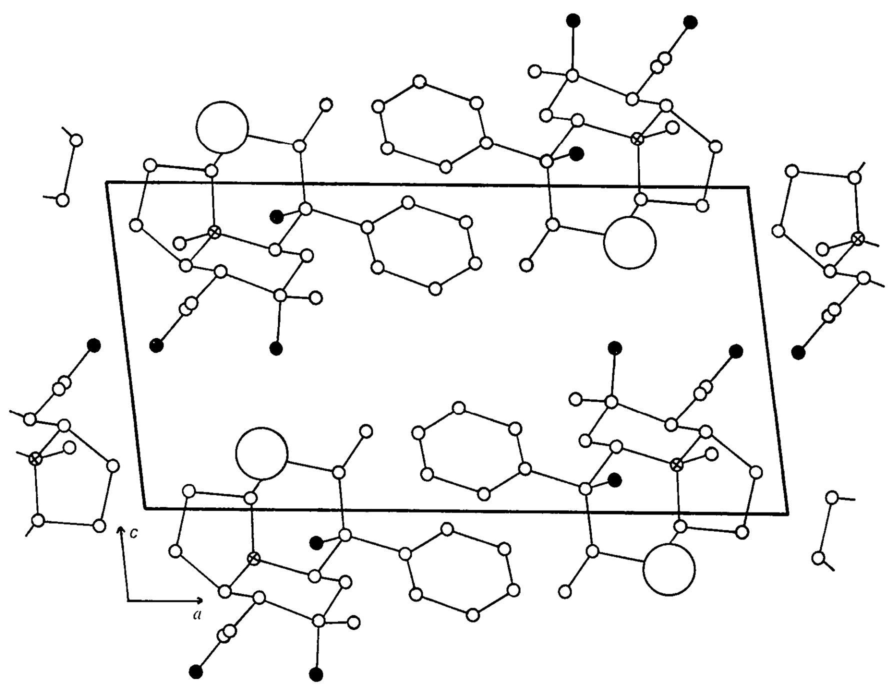

Fig. 3. The structure projected along the *b* axis. ⊗ nitrogen, ● oxygen, ○ carbon. The large open circles denote iodide ions.

Table 7 (*cont.*)

Plane *A*	Deviation	Plane *B*	Deviation
C(1)	−0·009 Å	C(5)	−0·031 Å
C(2)	0·010	C(6)†	−0·601
C(3)†	0·726	C(7)	0·031
C(4)	−0·009	C(8)	−0·032
C(5)	0·009	C(9)†	0·684
N(12)†	−0·564	N(12)	0·033

Plane *C*	Deviation	Plane *D*	Deviation
C(1)	−0·036 Å	C(19)	0·000 Å
C(9)	0·035	C(20)	−0·009
C(10)	−0·054	C(21)	0·021
C(11)	0·055	C(22)	−0·024
N(12)†	−0·691	C(23)	0·014
		C(24)	−0·002

† These atoms are not included in the least-squares planes.
Angles between planes: $A \wedge B$ 72·3° $A \wedge C$ 69·0° $B \wedge C$ 8·6°

Computer programs used for the calculations

Program name and function. Computer	Authors
SIP, Generation of steering paper tape for SIEMENS AED. IBM 360/75.	R. Norrestam, Stockholm, Sweden.
ABS, Calculation of absorption-, extinction- and Lp-factors. IBM 1800.	P.-E. Werner and M. Leijonmarck, Stockholm, Sweden.
DRF, Fourier summations and structure factor calculations. IBM 360/75.	A. Zalkin, Berkeley, USA. Modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg and A. G. Nord and B. G. Brandt, Stockholm, Sweden.
LALS, Full-matrix least-squares refinement of positional and thermal parameters and of scale factors. IBM 360/75.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, USA. Modified by A. Zalkin, Berkeley, USA and by J.-O. Lundgren, R. Liminga and C.-I. Brändén, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg and by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
DISTAN, Calculation of interatomic distances and bond angles with estimated standard deviations, IBM 360/75.	A. Zalkin, Berkeley, USA. Modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.
ORTEP, Thermal-ellipsoid plot. For crystal structure illustrations IBM 360/75.	C. K. Johnson, Oak Ridge, USA. Modified by I. Carlbom, Stockholm, Sweden.

The present investigation received financial support from the Tri-Centennial Fund of the Bank of Sweden and from the Swedish Natural Science Research Council.

The author is indebted to Professor Peder Kierkegaard for his active and stimulating interest in this work. Thanks are also due to Professor Arne Magnéli for all facilities placed at her disposal and to Dr Sven Westman for his correction of the English of this paper.

References

Clark, I. R. (1962). *Rev. Pure Appl. Chem.* **12**, 58.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.
Freeman, A. J. (1959). *Acta Cryst.* **12**, 261.
Gantzel, P. K., Sparks, R. A. & Trueblood, K. N. (1966). *IUCr World List of Crystallographic Computer Programs*. 2nd ed. Program 384.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502.
Hamilton, J. A., Hamor, T. A., Robertson, J. M. & Sim, G. A. (1962). *J. Chem. Soc.* p. 5061.
Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Leander, K. (1969). To be published.
Lide, D. R. (1962). *Tetrahedron*, **17**, 125.