Tableau 8. *Angles* (O–K–O) *faisant intervenir deux oxygènes voisins dans les polyèdres de coordination des cations* K^+

Ecarts-type sur les angles 0,1°

$O(6^{ii})-K(1)-O(6^{i})$	87,7°	$O(6^{i})-K(2)-O(5^{iv})$	105,7°
$O(6^{ii})-K(1)-O(7^{vii})$	101,0	$O(6^{i})-K(2)-O(1^{v})$	147,6
$O(6^{ii})-K(1)-O(2^{vii})$	72,1	$O(6^{i})-K(2)-O(3^{ii})$	75,5
$O(6^{ii})-K(1)-O(3^{i})$	79,0	$O(6^{i})-K(2)-W^{vi}$	80,4
$O(4)-K(1)-O(7^{vii})$	82,7	$O(3^{v})-K(2)-O(1^{v})$	51,2
$O(4)-K(1)-O(6^{i})$	95,6	$O(3^{v})-K(2)-O(5^{iv})$	80,0
$O(4)-K(1)-O(3^{i})$	97,5	$O(3^{v})-K(2)-W^{vi}$	74,2
$O(4)-K(1)-O(5)$	50,0	$O(3^{v})-K(2)-O(3^{ii})$	81,2
$O(5)-K(1)-O(7^{vii})$	105,5	$O(5^{iv})-K(2)-O(1^{v})$	102,6
$O(5)-K(1)-O(2^{vii})$	73,7	$O(5^{iv})-K(2)-W^{vi}$	68,5
$O(5)-K(1)-O(3^{i})$	76,7	$O(3^{ii})-K(2)-O(1^{v})$	92,9
$O(7^{vii})-K(1)-O(6^{i})$	103,3	$O(3^{ii})-K(2)-W^{vi}$	71,8
$O(7^{vii})-K(1)-O(2^{vii})$	68,7		
$O(3^{ii})-K(1)-O(6^{i})$	73,8		
$O(3^{ii})-K(1)-O(2^{vii})$	114,0		

déduisent par l'axe d'ordre 2 et des polyèdres de coordination différente ont toujours une arête commune.

Nous remercions Monsieur le Professeur Maurin de nous avoir suggéré cette étude.

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The Crystal Structure of Fulvine: A Pyrrolizidine Alkaloid

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The structure of fulvine, a pyrrolizidine alkaloid which is a potent hepatoxin, has been determined. It crystallizes in space group $P2_12_12_1$, with unit-cell dimensions $a = 10{\cdot}17\ (1)$, $b = 11{\cdot}60\ (1)$, $c = 13{\cdot}18\ (1)$ Å; and the unit-cell content is $4(C_{16}H_{23}O_5N)$. X-ray analysis was based on data collected by the multiple-film equi-inclination Weissenberg technique. The films were scanned on a drum microdensitometer, and integrated intensities were obtained by processing on a computer with programs written in Fortran. The structure was determined by means of symbolic addition followed by application of the tangent procedure, and refined by the method of least squares to an R index of 0·062. Structural features of fulvine are noted and compared with those of two other pyrrolizidine alkaloids, in an attempt to understand the structure-function relationship.

Introduction

The pyrrolizidine alkaloids are a large family of compounds present in a variety of plants throughout the world. Their main structural feature is that they are mono or di-esters of a pyrrolizidine diol with an acid moiety (see Fig. 1). Evidence regarding their chemical structure has been extensively reviewed (Bull, Culvenor & Dick, 1968; McLean, 1970).

Many members of the pyrrolizidine alkaloids are known to cause severe lesions in the liver and lungs of man and other mammals. The predominant biological effect is a halt in cell division; thus pyrrolizidine alkaloids have been investigated as antitumor agents (McLean, 1970). Correlation between the lesions and cancer has also been studied and is currently disputed (Schoental, 1968).

The molecular mechanism by which the pyrrolizidine alkaloids damage organs is unknown, although involvement of biochemical intermediates is suggested (Schoental, 1970; Culvenor, Edgar, Smith, Jago & Peterson, 1971). Not all pyrrolizidine alkaloids produce

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lesions, rather only those that simultaneously have the following three chemical features (McLean, 1970):

(1) The presence of a double bond between C(1) and C(2) [see numbering scheme, Fig. 1(*d*)];

(2) The presence of at least one ester linkage, *i.e.* esterification of the hydroxyl group on either C(9) or C(7).

(3) The acid moiety has to contain a branched hydrocarbon chain.

The potency varies widely within this subgroup of biologically active pyrrolizidine alkaloids, but lesions produced are similar. A thorough comparison of the three-dimensional structure of different biologically active pyrrolizidine alkaloids is needed to elucidate the structure-function relationship. We present here a preliminary comparison of the structure of fulvine and two previously determined crystal structures: the potent di-ester jacobine (Fridrichsons, Mathieson & Sutor, 1963) and the mild monoester heliotrine (Wodak, 1972).

The structure determination was also undertaken as a test of the accuracy of digital film-scanning methods. Fulvine was judged suitable for such a test, being small enough for a full-matrix least-squares refinement on the final atomic parameters to be performed.

Table 1. *Crystal data*

$C_{16}H_{23}O_5N$	M.W. 309·37
Orthorhombic	Space group $P2_12_12_1$
Unit-cell parameters*	$Z=4$
$a=10\cdot17$ (1) Å	Copper radiation (Cu $K\alpha$) = 1·5418 Å
$b=11\cdot60$ (1)	$\mu=8\cdot079$ cm^{-1}
$c=13\cdot18$ (1)	

Measured density = 1·302 g cm^{-3}
Calculated density = 1·319

* Unit-cell parameters were measured on a Syntex computer-controlled diffractometer.

Experimental

Crystals of fulvine, grown from an acetone/water solution, were kindly given to us by Dr R. Schoental (Schoental, 1963.) Three-dimensional intensity data were collected with the multiple-film equi-inclination Weissenberg technique (Buerger, 1942), using Ni-filtered Cu radiation. Two roughly cubic crystals were used, each about 0·3 mm on a side. One was mounted along **a** with data collected through the 6th level, the other along **c** from which were collected only zero-level data (for crystal data see Table 1.)

The films were scanned on an Optronics drum microdensitometer (Street, 1971) interfaced to an Adage model 50 computer. In this paper we present only an outline of the film-scanning technique, as illustrated in Fig. 2. For a full description of the system see Sussman (1972) and Pearson (1973).

Once all the films were processed, the data were brought to a common scale by the method of Hamilton, Rollett & Sparks (1965). The overall reliability of the data based on a comparison of symmetrically related spots on a single film and the same spots on different films of a film pack is between 4 to 6% from the following formula for average relative deviation:

$$D=\sum_{\substack{\text{all}\\ hkl}} \frac{\sum_{i=1}^{n}|\bar{F}_{hkl}-\text{Sc}\,F^{i}_{hkl}|}{n\bar{F}_{hkl}},$$

where:

$\bar{F}_{hkl}$ is the average F for all the observations of a particular reflection,

F^{i}_{hkl} is the value of an individual observation, i of a particular reflection hkl before scaling,

Sc is the appropriate scale factor to bring an observation on one film to that of the first film in a film pack,

Table 2. *Initial values of phases derived from symbolic addition and their values after repeated application of the tangent formula*

u stands for ungerade (odd), *g* stands for gerade (even).

Type of Reflection	Parity	*h*	*k*	*l*		Value derived from symbolic addition	Value after tangent formula refinement
Origin determining	(*ugg*)	5	8	0		$\pi/2$	$\pi/2$ (held constant)
	(*ggu*)	0	12	1		0	0 ″ ″
	(*gug*)	0	3	6		$\pi/2$	$\pi/2$ ″ ″
Enantiomorph determining	(*ugg*)	3	0	16		π	π ″ ″
Symbols	(*guu*)	0	9	5	*m*	$3\pi/2$	$3\pi/2$
	(*ggg*)	4	10	0	*s*	0	0
	(*ggg*)	4	4	0	*p*	0	0
Phases derived from symbolic addition	(*gug*)	0	11	6		$3\pi/2$	$\pi/2$
	(*ggg*)	8	0	0		0	0
	(*ggg*)	10	0	0		0	0
	(*ggg*)	8	6	0		0	0
	(*guu*)	0	1	5		$\pi/2$	$3\pi/2$

n is the number of observations of a particular reflection.

We found the film-scanning method quite satisfactory. The reasonable bond distances and bond angles in fulvine and the ease with which the hydrogen positions were found in the difference-Fourier synthesis, as well as the final agreement index between calculated and observed structure factors indicate that sufficient accuracy in the data-processing system has been achieved. It is clear, however, that some improvements are necessary; these include increasing the linearity range of the system, so that fewer films per pack are required, and automating the determination of the alignment parameters of the film on the scanner. Such a system would be especially efficient when applied to data processing of large molecules.

Structure determination and refinement

The structure of fulvine was determined by application of the symbolic addition and tangent formula procedure (Karle & Karle, 1966). Normalized structure fac-

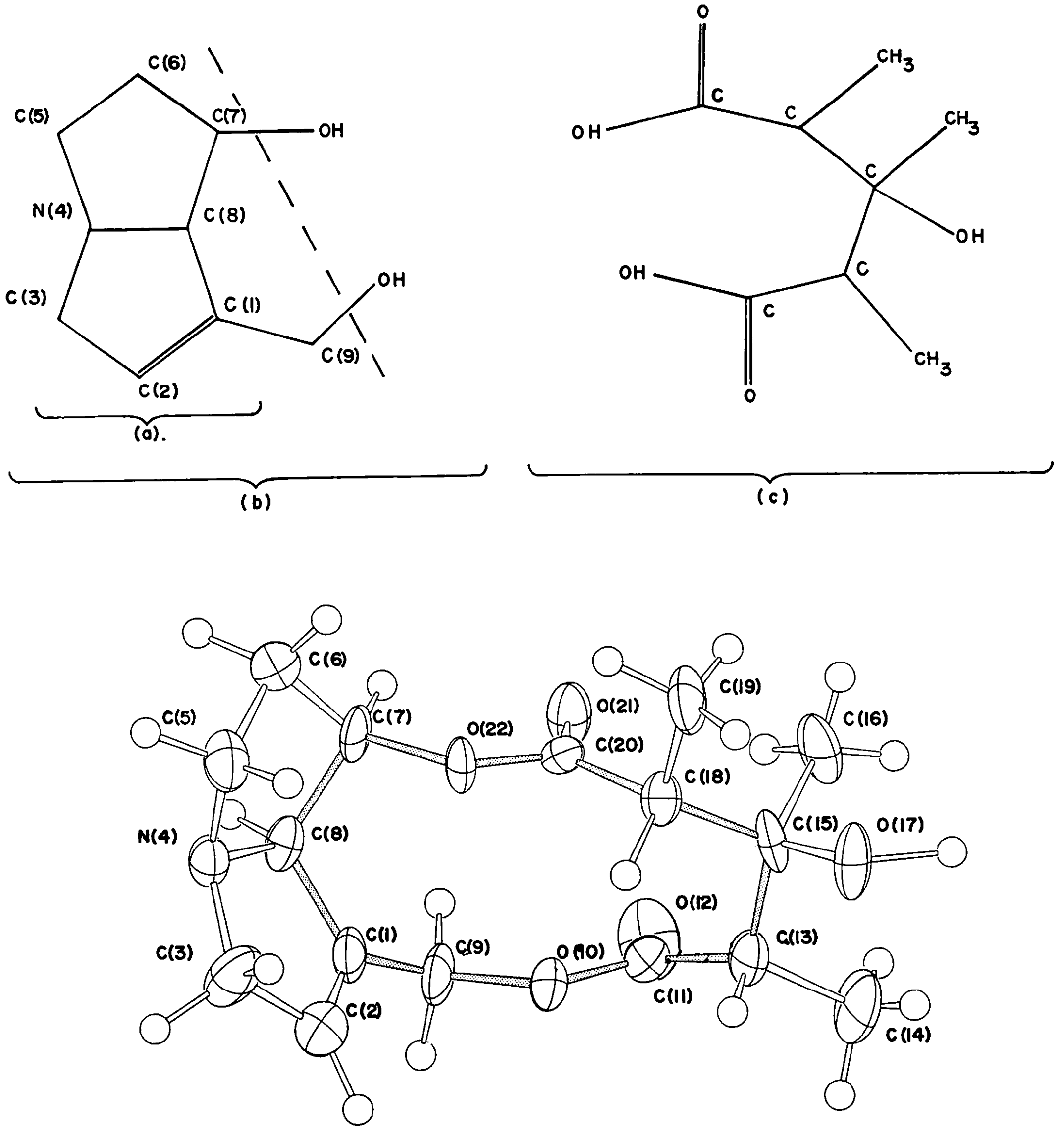


Fig. 1. Fulvine component parts and numbering schemes. (*a*) The chemical formula and numbering scheme of a pyrrolizidine nucleus, retronecine. Note the double bond between C(1) and C(2). (*b*) A pyrrolizidine diol. (*c*) Fulvinic acid, a typical acid moiety of a pyrrolizidine alkaloid. (*d*) An *ORTEP* plot (Johnson, 1965) of the structure of fulvine, showing the numbering scheme. The 11-membered macro-ring is shaded.

tors, E, were calculated from a Wilson plot. Three origin reflections and an enantiomorph were chosen. In addition, three reflections were assigned symbols. Phases for these reflections as well as five others were derived *via* the symbolic addition procedure; see Table 2.

These phases were then used in the tangent formula and refinement program (Hall, 1967), holding only the phases of the three origin and enantiomorph reflections fixed.

Of the 246E's greater than 1·3, 245 had their phases determined and an E map was calculated, which revealed all 22 nonhydrogen atoms of fulvine as the largest 22 peaks. The initial R value, $R=\sum||F_o|-|F_c||/\sum|F_o|$, based on all the F's for these 22 atoms was 0·35.

Full matrix least-squares refinement (Busing, Martin & Levy, 1962) of the positional parameters and isotropic temperature factors, using weights equal to $1/\sigma$ [where σ was determined in the film processing program to be approximately proportional to the error in the estimate of the background value for each reflection (Pearson, 1971)] reduced the R value to 0·13.

When temperature factors of the nonhydrogen atoms were allowed to vary anisotropically, the R index was further reduced to 0·096. Successive difference Fourier

Table 3. *Observed and calculated structure factors*

(* indicates that the reflection was not used in the last cycle of least-squares refinement.)

K = 0

H	L	FO	FC
0	2	3017	2769
0	4	4975*	5275
0	6	1126*	1327
0	8	455	496
0	10	774	727
0	12	1097*	738
0	14	840	800
0	16	279*	170
1	1	2553	2466
1	2	400	452
1	3	1783	1736
1	4	2571	2578
1	5	1203	1075
1	6	1536	1491
1	7	1860	1837
1	8	2293	2250
1	9	188	140
1	10	373	457
1	11	32	254
1	12	531	495
1	13	719	655
1	14	419	416
1	15	694	715
1	16	32	56
2	0	5087*	6011
2	1	3070*	3391
2	2	1693	1423
2	3	371*	501
2	4	3098	3072
2	5	875	888
2	6	948	1065
2	7	1724	1876
2	8	1949	2005
2	9	341	295
2	10	446	495
2	11	32	11
2	12	216	195
2	13	1526	1419
2	14	319	106
2	15	291	149
2	16	81	86
3	1	2092	2095
3	2	646	428
3	3	374*	79
3	4	1040	1035
3	5	1522	1499
3	6	1022	976
3	7	1865	1823
3	8	1236*	1015
3	9	891*	749
3	10	32	5
3	11	1704*	2005
3	12	290	139
3	13	223	199
3	14	164	99
3	15	39	357
3	16	765*	1237
4	0	3384	3336
4	1	748	744
4	2	2145	2196
4	3	252*	122
4	4	4602*	5008
4	5	3440*	3849
4	6	145*	31
4	7	711	797
4	8	1706	1729
4	9	607	597
4	10	982	999
4	11	650	672
4	12	1802	1871
4	13	294	248
4	14	892	820
4	15	478	492
4	16	32	90
5	1	1180	1241
5	2	1318	1209
5	3	2004	2027
5	4	611*	356
5	5	1417	1416
5	6	2159	2163
5	7	1057*	1019
5	8	773*	716
5	9	922	905
5	10	646	626
5	11	605	621
5	12	406	421
5	13	520	518
5	14	725	815
5	15	349*	488
6	0	377*	130
6	1	1277	1307
6	2	830	823
6	3	1480*	1403
6	4	2289	2273
6	5	1755	1727
6	6	439*	190
6	7	217	132
6	8	279	304
6	9	332	328
6	10	1012	1048
6	11	244	251
6	12	178	155
6	13	32	72
6	14	795	852
8	0	4426	4551
10	0	2222	2030
12	0	721	652

K = 1

H	L	FO	FC
0	1	5616*	5162
0	2	8290*	14545
0	3	4435*	5230
0	4	3455*	3727
0	5	5501*	6161
0	6	622	616
0	7	833	824
0	8	597	574
0	9	2092	1936
0	10	464	448
0	11	1051	1033
0	12	204	155
0	13	32	138
0	14	491	511
0	15	277	276
0	16	391	424
1	0	3744*	3958
1	1	2924	2789
1	2	4322*	4911
1	3	1379	1222
1	4	4833	4905
1	5	2014	1887
1	6	2565	2551
1	7	2848	2830
1	8	874	903
1	9	1599	1526
1	10	930	845
1	11	1175	1154
1	12	513	449
1	13	635	630
1	14	808	737
1	15	236	148
1	16	76	216
2	0	515*	610
2	1	4431*	5254
2	2	2363	2400
2	3	2641*	2910
2	4	1818	1852
2	5	1134	1136
2	6	3106	2971
2	7	1658	1612
2	8	894	952
2	9	991	900
2	10	394	346
2	11	1898	1922
2	12	1279	1276
2	13	237	146
2	14	539	539
2	15	243	349
2	16	396	470
3	0	4975*	5790
3	1	3732*	3972
3	2	1527	1591
3	3	2609	2677
3	4	3403*	3673
3	5	1844	1837
3	6	2314	2420
3	7	1198	1114
3	8	1306	1355
3	9	1283	1339
3	10	1317	1315
3	11	225	375
3	12	684	695
3	13	1019	1085
3	14	280	335
3	15	578	581
3	16	288*	478
4	0	3724*	4238
4	1	1436	1435
4	2	2834	2884
4	3	2473	2662
4	4	2116	2145
4	5	796	768
4	6	1446	1090
4	7	2353	2501
4	8	248	244
4	9	1385	1452
4	10	1819	1987
4	11	587	613
4	12	740	705
4	13	598	563
4	14	608	601
4	15	278	318
4	16	91*	458
5	0	769	778
5	1	531	494
5	2	1787	1798
5	3	1825*	1994
5	4	1103	1000
5	5	2169	2220
5	6	1546	1398
5	7	920*	1059
5	8	1568	1564
5	9	233*	68
5	10	796	806
5	11	864	758
5	12	912*	1035
5	13	403	415
5	14	211	300
5	15	421	444
6	0	346	324
6	1	309	325
6	2	500	517
6	3	684	671
6	4	1738*	1598
6	5	722*	532
6	6	914*	804
6	7	628	639
6	8	1083	1226
6	9	1250	1274
6	10	883	814
6	11	534	609
6	12	1077	1132
6	13	603	601
6	14	410*	579
7	0	1592	1458
8	0	879	877
9	0	576	592
10	0	1145	1130
11	0	733	734
12	0	1039	1047

K = 2

H	L	FO	FC
0	0	6406*	9411
0	1	5329*	6290
0	2	6183*	8076
0	3	4529*	5138
0	4	3218	3308
0	5	3082	3095
0	6	464	404
0	7	224*	7
0	8	277	206
0	9	203	269
0	10	1084	1066
0	11	2226	2182
0	12	670	683
0	13	1338	1354
0	14	274*	140
0	15	165	103
0	16	47	76
1	0	2476	2482
1	1	5385*	6417
1	2	1984	1942
1	3	4488	4698
1	4	6709*	7570
1	5	1526	1469
1	6	726	619
1	7	1069	631
1	8	1422	1268
1	9	893*	673
1	10	1204	1132
1	11	394	415
1	12	984	1004
1	13	348	232
1	14	479	500
1	15	663	617
1	16	36	220
2	0	2912*	2529
2	1	3135	3179
2	2	3560	3684
2	3	1950	1860
2	4	1993	2007
2	5	1569	1647
2	6	1627	1640
2	7	2068	2121
2	8	2467	2651
2	9	1214	1254
2	10	1066	977
2	11	114	164
2	12	1006	994
2	13	406	378
2	14	284	242
2	15	304	382
2	16	316	560
3	0	2140	2215
3	1	4448*	4746
3	2	1688	1610
3	3	3109	3226
3	4	1397*	1222
3	5	2398	2402
3	6	793	794
3	7	1347	1239
3	8	1527	1513
3	9	407	369
3	10	1443	1430
3	11	1532	1618
3	12	662	541
3	13	368	309
3	14	687	704
3	15	240	246
3	16	211*	453
4	0	571*	222
4	1	5655*	6303
4	2	375*	259
4	3	644	634
4	4	1867	2015
4	5	1470	1437
4	6	2151	2227
4	7	419	425
4	8	508	505
4	9	824	841
4	10	423	404
4	11	865	877
4	12	1474	1508
4	13	937	849
4	14	248	216
4	15	649	663
4	16	85*	617
5	0	3393	3360
5	1	935	913
5	2	749*	556
5	3	876	803
5	4	1995	1984
5	5	1220	1060
5	6	1671	1720
5	7	1159	1141
5	8	1450	1463
5	9	1395	1442
5	10	220	214
5	11	658	664
5	12	716	752
5	13	501	526
5	14	650	769
5	15	182*	255
6	0	872*	905
6	1	1466*	1318
6	2	1190	1173
6	3	678	677
6	4	382	428
6	5	1387	1405
6	6	894	756
6	7	1476	1472
6	8	1053	1042
6	9	675	645
6	10	397	375
6	11	717	745
6	12	539	521
6	13	751	794
6	14	350	375
7	0	514*	353
8	0	328*	154
9	0	1724	1719
10	0	1207	1223
11	0	971	1015
12	0	32	22

K = 3

H	L	FO	FC
0	1	552	539
0	2	3999*	4605
0	3	4264	4396
0	4	1583	1691
0	5	1412	1465
0	6	4733	4802
0	7	2221	2219
0	8	3910	3984
0	9	172	172
0	10	2436	2513
0	11	1119	1229
0	12	203	27
0	13	654	583
0	14	32	3
0	15	94	238
0	16	32	66
1	0	422	419
1	1	1382	1287
1	2	4603	4895
1	3	3574	3480
1	4	1408	1358
1	5	4183	4284
1	6	2767	2693
1	7	693	677
1	8	1140	1069
1	9	294	263
1	10	1169*	1020
1	11	295	242
1	12	794	708
1	13	584	527
1	14	79	66
1	15	102	214
1	16	32	131
2	0	2450	2472
2	1	2602*	2789
2	2	3379	3561
2	3	2714	2721
2	4	2769	2910
2	5	559	520
2	6	2431	2625
2	7	1080	1104
2	8	1228	1230
2	9	972	948
2	10	918	803
2	11	503	515
2	12	1613	1661
2	13	790	747
2	14	192	132
2	15	32	132
2	16	100	531
3	0	1082*	907
3	1	528*	400
3	2	1970	1855
3	3	2001	1976
3	4	1094	1065
3	5	1332*	1156
3	6	1813*	1686
3	7	912	864
3	8	1340	1371
3	9	2013	1997
3	10	672	661
3	11	1098	1012
3	12	534	502
3	13	714	699
3	14	781	752
3	15	979	1014
3	16	143	112
4	0	2483	2500
4	1	4478*	4769
4	2	5461*	5972
4	3	1705	1743
4	4	3867	4099
4	5	1253	1130
4	6	1123	1126
4	7	1121	1156
4	8	568	473
4	9	700	705
4	10	469*	351
4	11	114	293
4	12	609	545
4	13	612	596
4	14	768	795
4	15	285	313
5	0	1748	1755
5	1	2295	2257
5	2	1741	1696
5	3	1616	1651
5	4	2019	1977
5	5	1119	1118
5	6	2023	2128
5	7	1164	1108
5	8	492*	417
5	9	1924	2244
5	10	369	374
5	11	740	727
5	12	612	616
5	13	895*	1117
5	14	743*	859
5	15	247	255
6	0	2068	2095
6	1	824	831
6	2	2402	2368
6	3	1586*	1480
6	4	963	953
6	5	2167	2154
6	6	1529	1491
6	7	770	707
6	8	907	931
6	9	604*	486
6	10	793*	661
6	11	613	620
6	12	252	294
6	13	166	264
6	14	379	393
7	0	1239	1162
8	0	1336	1261
9	0	908*	1084
10	0	487	478
11	0	85	80
12	0	272	269

K = 4

H	L	FO	FC
0	0	1680	1742
0	1	1845	1911
0	2	4138*	4398
0	3	4849*	5287
0	4	3282	3379
0	5	2014	2033
0	6	51	125
0	7	1268	1249
0	8	1695	1683
0	9	1787	1734
0	10	1200	1305
0	11	533	486
0	12	943	984
0	13	552	542
0	14	493	472
0	15	300	304
0	16	32	312
1	0	1126*	795
1	1	557*	463
1	2	3226	3218
1	3	2863	2709
1	4	3965	3854
1	5	1111	1011
1	6	2350	2401
1	7	1719	1581
1	8	572	575
1	9	2400	2328
1	10	1282	1119
1	11	1363	1288
1	12	870	841
1	13	444	479
1	14	360	367
1	15	713	709
1	16	558	632
2	0	3398	3365
2	1	2102	2051
2	2	1528	1513
2	3	1478	1368
2	4	999*	811
2	5	1608	1688
2	6	1469	1452
2	7	2019	2083
2	8	1082	1077
2	9	788	889
2	10	1377	1439
2	11	1088	1048
2	12	584	538
2	13	687	660
2	14	682	751
2	15	32	151
3	0	3440	3504
3	1	1946	1986
3	2	1557	1436
3	3	1989*	1716
3	4	2093*	1852
3	5	1494*	1352
3	6	1088	1112
3	7	805	787
3	8	1210	1109
3	9	972	901
3	10	799	710
3	11	1616	1630
3	12	624	581
3	13	992	960
3	14	287	170
3	15	310	314
4	0	7180*	7679
4	1	1560	1546
4	2	3777	4006
4	3	2739	2787
4	4	1510	1514
4	5	802	696
4	6	1256	1207
4	7	102	154
4	8	387	360
4	9	577*	438
4	10	1226	1167
4	11	806*	721
4	12	339	337
4	13	435	448
4	14	688	701
4	15	631	683
5	0	717*	644
5	1	1509	1461
5	2	2179	2107
5	3	2508	2491
5	4	193	143
5	5	552	403
5	6	1373	1487
5	7	943	1002
5	8	1059	1085
5	9	2030*	2257
5	10	518	523
5	11	809	861
5	12	309	273
5	13	225	269
5	14	589*	727
6	0	941*	819
6	1	2126	2068
6	2	990*	887
6	3	1562	1623
6	4	558	580
6	5	702	725
6	6	1507	1490
6	7	1047	1013
6	8	1686	1686
6	9	798	801
6	10	539	562
6	11	247	293
6	12	243	248
6	13	156	191
6	14	420*	493
7	0	726	742
8	0	1957	1951
9	0	660	673
10	0	205	298
11	0	619*	362
12	0	395	394

K = 5

H	L	FO	FC
0	1	680*	795
0	2	1993	1954
0	3	1158	1142
0	4	2069	2010
0	5	2689	2660
0	6	2162	2023
0	7	466	442
0	8	872*	613
0	9	1538	1549
0	10	874	894
0	11	912	897
0	12	254	177
0	13	1384	1413
0	14	167	199
0	15	69	179
1	0	206*	9
1	1	611*	436
1	2	2026	1915
1	3	1307	1237
1	4	934*	786
1	5	1999	1858
1	6	1936	1745
1	7	3423	3471
1	8	1213*	1021
1	9	1885	1778
1	10	930	838
1	11	657	648
1	12	461	313
1	13	607	577
1	14	1169	1163
1	15	245	217
2	0	1440*	1356
2	1	3047	3050
2	2	2403	2404
2	3	328	288
2	4	771	775
2	5	1457	1494
2	6	641	561
2	7	1047	986
2	8	1775	1749
2	9	1384	1414
2	10	538	562
2	11	721	669
2	12	649	629
2	13	558	589
2	14	212	352
2	15	212	289
3	0	1904	1920
3	1	978*	840
3	2	2747	2642
3	3	1733	1634
3	4	1236	1162
3	5	1453*	1311
3	6	1685	1650
3	7	558	498
3	8	902*	758
3	9	1688	1788
3	10	1392	1409
3	11	571	542
3	12	417*	281
3	13	1018	911
3	14	576	589
3	15	177	112
4	0	792*	634
4	1	1324	1174
4	2	1560*	1338
4	3	647*	472
4	4	1401	1364
4	5	3521	3657
4	6	1088	1073
4	7	1970	2068
4	8	350	399
4	9	1972	2067
4	10	1010	993
4	11	524	532
4	12	510	462
4	13	503	471
4	14	394	446
4	15	274	386
5	0	1153*	1021
5	1	1604	1561
5	2	1482	1512
5	3	1157	1167
5	4	1427	1323
5	5	1409	1331
5	6	933*	833
5	7	1434	1476
5	8	1619	1736
5	9	1091	1045
5	10	349	401
5	11	1212*	1398
5	12	187	328
5	13	264	289
5	14	399	428
6	0	1052*	861
6	1	1628*	1540
6	2	636	660
6	3	2926	2864
6	4	263	191
6	5	1407	1335
6	6	1738	1790
6	7	1024	1003
6	8	1153	1172
6	9	592	618
6	10	418	363
6	11	442	440
6	12	517	524
6	13	376	478
7	0	575	554
8	0	457	419
9	0	589	575
10	0	684	672
11	0	117	117
12	0	370	279

K = 6

H	L	FO	FC
0	0	3380	3317
0	1	543	496
0	2	2036	1975
0	3	815	674
0	4	791	809
0	5	2279	2293
0	6	646*	480
0	7	676	705
0	8	723	647
0	9	354	291
0	10	1337	1409
0	11	582	547
0	12	977	969
0	13	233	176
0	14	331	398
0	15	233	240
1	0	384*	251
1	1	1761	1666
1	2	1095	1023
1	3	1380	1295
1	4	1750	1611
1	5	942	875
1	6	1248	1092
1	7	1376	1398
1	8	1039*	864
1	9	1432	1271
1	10	884	866
1	11	1036	958
1	12	976	947
1	13	550	511
1	14	327	399
1	15	667	717
2	0	1324*	1246
2	1	1454	1473
2	2	1865	1798
2	3	1774	1777
2	4	1132	1085
2	5	1436	1363
2	6	1765	1766
2	7	1842	1942
2	8	1429	1335
2	9	837	828
2	10	911	897
2	11	440	449
2	12	498	502
2	13	497	503
2	14	242	278
2	15	146	241
3	0	750*	659
3	1	2382	2315
3	2	1626	1604
3	3	2145*	1910
3	4	3032	2980
3	5	1783	1810
3	6	1380	1316
3	7	2082	2083
3	8	939	891
3	9	969	949
3	10	557	557
3	11	1024	999
3	12	232	35
3	13	252	219
3	14	346	354
4	0	2148	2082
4	1	575*	374
4	2	1183	1059
4	3	1983	1998
4	4	2485	2610
4	5	537	511
4	6	892	929
4	7	1050	1122
4	8	652	614
4	9	1452	1445
4	10	1029	978
4	11	682	667
4	12	536	484
4	13	197	118
4	14	128*	309
5	0	1602	1593
5	1	1841	1748
5	2	1813	1782
5	3	3336*	3647
5	4	2540	2550
5	5	838	776
5	6	578	551
5	7	440	448
5	8	668	646
5	9	669	736
5	10	1019	1043
5	11	695	726
5	12	375	350
5	13	276	302
6	0	1780*	1573
6	1	1147	1089
6	2	798	718
6	3	797	749
6	4	751	894
6	5	546	537
6	6	1562	1572
6	7	544	502
6	8	1260	1266
6	9	288	285
6	10	175*	81
6	11	114	100
6	12	660	669
6	13	299	325
7	0	541	538
8	0	1587	1601
9	0	769	745
10	0	897	926
11	0	1020*	1225

K = 7

H	L	FO	FC
0	1	458	466
0	2	2357	2300
0	3	252	284
0	4	179	58
0	5	694	678
0	6	1023	1009
0	7	1277	1171
0	8	233*	13
0	9	522	538
0	10	662	606
0	11	1530	1549
0	12	363	364
0	13	271	266
0	14	344*	447
1	0	181	28
1	1	1601	1545
1	2	1156	1105
1	3	2334	2142
1	4	909*	731
1	5	1207*	945
1	6	1324*	1118
1	7	1375	1173
1	8	964	918
1	9	1676	1613
1	10	697	630
1	11	190	219
1	12	1204	1148
1	13	601	599
1	14	522*	649
2	0	1408	1398
2	1	1385	1413
2	2	1863	1875
2	3	1676	1728
2	4	403	352
2	5	708	649
2	6	1229	1186
2	7	1189	1203
2	8	483	608
2	9	1178	1178
2	10	907	899
2	11	526	528
2	12	295	281
2	13	551	557
2	14	32	164
3	0	1433*	1265
3	1	197	154
3	2	557*	334
3	3	239	72
3	4	291*	99
3	5	1632	1528
3	6	1438	1385
3	7	420*	234
3	8	2152	2205
3	9	1283	1263
3	10	230	90
3	11	770*	618
3	12	155	72
3	13	393*	261
3	14	118	223
4	0	192	183
4	1	770	612
4	2	1511	1527
4	3	1009	997
4	4	2068	2182
4	5	1294	1250
4	6	2141	2426
4	7	1300	1380
4	8	1689	1823
4	9	84	146
4	10	885	780
4	11	795	836
4	12	277	277
4	13	438	512
4	14	32	92
5	0	1453	1440
5	1	653	617
5	2	2200	2231
5	3	213	296
5	4	1053	961
5	5	2077	2177
5	6	1518	1544
5	7	1062	1169
5	8	634	636
5	9	525	541
5	10	807	780
5	11	510	531
5	12	479	508
5	13	281	301
6	0	210	207
6	1	1442	1462
6	2	606	644
6	3	451*	304
6	4	525	583
6	5	627	639
6	6	1444	1503
6	7	973	932
6	8	1039	1034
6	9	517	558
6	10	284	292
6	11	429	439
6	12	171	201
7	0	450	335
8	0	1086*	906
9	0	174	130
10	0	173	183
11	0	195	187

K = 8

H	L	FO	FC
0	0	2475	2446
0	1	1809	1818
0	2	819	790
0	3	222	203
0	4	239	256
0	5	1546	1605
0	6	32	85
0	7	456	398
0	8	1231	1200
0	9	410	300
0	10	656	667
0	11	321	248
0	12	462	491
0	13	260	244
1	0	263	198
1	1	1947	1846
1	2	859*	725
1	3	511*	327
1	4	904	845
1	5	1534	1468
1	6	1033	930
1	7	367	288
1	8	1301*	1129
1	9	1016	969
1	10	717	693
1	11	797*	676
1	12	472	427
1	13	32	150
1	14	358	421
2	0	483*	382
2	1	835	857
2	2	369	228
2	3	1349	1262
2	4	760	594
2	5	959	899
2	6	748	706
2	7	2025	2148
2	8	939	920
2	9	380	294
2	10	199	190
2	11	1089	1090
2	12	304	264
2	13	256	296
3	0	595*	408
3	1	796	766
3	2	765	704
3	3	1005	963
3	4	1458	1383
3	5	491	414
3	6	961	952
3	7	1607	1607
3	8	370	412
3	9	463	480
3	10	812	795
3	11	762	763
3	12	574	569
3	13	441	453
4	0	2792	2935
4	1	2461	2700
4	2	585	550
4	3	937*	819
4	4	1199	1325
4	5	1586	1641
4	6	1067	1065
4	7	1013	1063
4	8	542	497
4	9	718	772
4	10	428	387
4	11	497	510
4	12	356	305
4	13	301	325
5	0	3740*	4110
5	1	947	908
5	2	538	501
5	3	1052*	924
5	4	737	711
5	5	1693	1836
5	6	585	574
5	7	507	460
5	8	555	557
5	9	357	371
5	10	522	535
5	11	429*	532
5	12	440	441
6	0	209*	287
6	1	534	526
6	2	249	318
6	3	562*	416
6	4	829	817
6	5	680*	541
6	6	487	472
6	7	1319	1321
6	8	143	183
6	9	347	340
6	10	314	290
6	11	113	87
7	0	576	600
8	0	116	19
9	0	415*	224
10	0	603	624

K = 9

H	L	FO	FC
0	1	427	435
0	2	2188	2186
0	3	1196	1204
0	4	517*	279
0	5	1958	1995
0	6	32	161
0	7	1179	1224
0	8	182	53
0	9	748	728
0	10	1017	1043
0	11	105	84
0	12	622	650
0	13	32	51
1	0	346*	5
1	1	812	678
1	2	1236	1160
1	3	1423	1289
1	4	1421	1308
1	5	1402	1294
1	6	630*	382
1	7	1339	1175
1	8	177	71
1	9	253	254
1	10	783	724
1	11	720	708
1	12	228	120
1	13	276	333
2	0	400	332
2	1	581*	382
2	2	1417	1379
2	3	439	450
2	4	705	672
2	5	1210	1252
2	6	1490	1440
2	7	243	265
2	8	862	828
2	9	591	588
2	10	32	163
2	11	438	373
2	12	403	440
3	0	351*	252
3	1	1262	1230
3	2	640	469
3	3	1623	1568
3	4	1047	1047
3	5	1106	1073
3	6	938	921
3	7	594	552
3	8	978*	846
3	9	814	750
3	10	235	253
3	11	634	658
3	12	148	159
4	0	1252	1275
4	1	1605	1684
4	2	2664*	3148
4	3	1180	1310
4	4	711	660
4	5	810	745
4	6	965	882
4	7	308*	157
4	8	194	100
4	9	209	262
4	10	211	86
4	11	128	121
4	12	402	382
5	0	815	819
5	1	1023*	933
5	2	1729	1843
5	3	1012	995
5	4	702*	594
5	5	172	152
5	6	597	599
5	7	1387	1365
5	8	574	572
5	9	268	275
5	10	251	287
5	11	695*	837
6	0	693	700
6	1	184	174
6	2	1114	1125
6	3	349*	246
6	4	322	306
6	5	307	267
6	6	278	281
6	7	295*	206
6	8	447	418
6	9	498	493
6	10	278	259
7	0	595	568
8	0	766	805
9	0	486	502
10	0	326	313

K = 10

H	L	FO	FC
0	0	744	792
0	1	519*	628
0	2	198	29
0	3	663	578
0	4	1459	1495
0	5	240*	102
0	6	609	516
0	7	1241	1162
0	8	273	348
0	9	96	157
0	10	193	28
0	11	327	327
0	12	655*	798
1	0	675*	586
1	1	1331	1292
1	2	520	423
1	3	898	807
1	4	241	272
1	5	1227*	1146
1	6	1336	1194
1	7	575	558
1	8	831	770
1	9	310*	151
1	10	217	151
1	11	350	322
1	12	438	464
2	0	822	822
2	1	335	332
2	2	705	684
2	3	383	381
2	4	1223	1186
2	5	1535	1500
2	6	1221	1207
2	7	885	885
2	8	867	879
2	9	696	639
2	10	663	690
2	11	703	752
3	0	1282	1288
3	1	1339	1251
3	2	1458	1447
3	3	1347	1335
3	4	837	775
3	5	682	594
3	6	771	741
3	7	685	619
3	8	350	353
3	9	214	171
3	10	617	592
3	11	32	184
4	0	2556	2630
4	1	895	939
4	2	650	669
4	3	1342	1388
4	4	876	964
4	5	937	960
4	6	626	633
4	7	429	394
4	8	186	113
4	9	167	133
4	10	250	305
4	11	364	381
5	0	327	314
5	1	762	681
5	2	1297	1317
5	3	828	820
5	4	938	826
5	5	978	893
5	6	417	431
5	7	178	149
5	8	126	176
5	9	179	231
5	10	409*	484
6	0	696	715
6	1	313	293
6	2	661	630
6	3	599	568
6	4	1003	973
6	5	398	410
6	6	605	645
6	7	860	879
6	8	273	229
6	9	445*	529
7	0	110	73
8	0	159	258
9	0	324	320

K = 11

H	L	FO	FC
0	1	481	515
0	2	456	393
0	3	1480	1581
0	4	802	785
0	5	959	943
0	6	1659	1628
0	7	535	533
0	8	367	353
0	9	327	339
0	10	406	431
1	0	292*	76
1	1	1399	1259
1	2	869	842
1	3	1060	962
1	4	900	819
1	5	1024	1015
1	6	1149*	1054
1	7	621	604
1	8	512	438
1	9	800	737
1	10	676	701
1	11	32	40
2	0	642	697
2	1	767	703
2	2	350	258
2	3	800	758
2	4	275	232
2	5	819	814
2	6	517	549
2	7	260	140
2	8	169	84
2	9	209	312
2	10	567	575
3	0	144	39
3	1	1057	1046
3	2	1275	1210
3	3	1102	1091
3	4	585	605
3	5	813	811
3	6	372	336
3	7	336	310
3	8	309	268
3	9	419	392
3	10	418	447
4	0	721	696
4	1	1186	1365
4	2	767	785
4	3	544	619
4	4	1054	1112
4	5	363	320
4	6	482	498
4	7	207*	58
4	8	207	198
4	9	138	203
4	10	207	186
5	0	194*	75
5	1	357	377
5	2	856	850
5	3	1029	957
5	4	92	194
5	5	589	596
5	6	611	610
5	7	343	377
5	8	232	264
6	0	215	215
6	1	687	643
6	2	449	512
6	3	738	703
6	4	100	60
6	5	718	741
6	6	157	111
6	7	415	445
7	0	426	424
8	0	177	82

K = 12

H	L	FO	FC
0	0	250*	22
0	1	2219	2258
0	2	1506	1516
0	3	168	145
0	4	1220	1249
0	5	283	368
0	6	322	331
0	7	32	176
0	8	79	10
0	9	557	555
1	0	1020	1010
1	1	339	266
1	2	369	343
1	3	929*	840
1	4	947	923
1	5	118	59
1	6	901	845
1	7	668	648
1	8	381	424
1	9	308	316
2	0	284	308
2	1	259	248
2	2	745	737
2	3	509	489
2	4	876	849
2	5	419	347
2	6	360	387
2	7	508	548
2	8	574	597
2	9	286	264
3	0	332	367
3	1	821	839
3	2	339	240
3	3	98	176
3	4	183	201
3	5	370	401
3	6	618	635
3	7	407	410
3	8	144	42
4	0	921	934
4	1	1175	1332
4	2	788	837
4	3	402	338
4	4	638	713
4	5	178*	63
4	6	442	482
4	7	99	210
4	8	32	187
5	0	247*	362
5	1	146	88
5	2	710	712
5	3	734	773
5	4	559	577
5	5	244	255
5	6	414	428
5	7	325*	390
6	0	119	85
6	1	836	872
6	2	800	424
6	3	735	768
6	4	57	54
6	5	514*	623
7	0	645	635

K = 13

H	L	FO	FC
0	1	651	585
0	2	507	575
0	3	364	366
0	4	1195	1182
0	5	301	286
0	6	149	294
0	7	302*	376
1	0	166	157
1	1	477	494
1	2	417	388
1	3	672	627
1	4	491	389
1	5	720	655
1	6	585	624
1	7	477	469
2	0	249	364
2	1	382	472
2	2	1125	1149
2	3	464	538
2	4	474	494
2	5	381	381
2	6	357	417
2	7	155	166
3	0	897	926
3	1	226	291
3	2	467	450
3	3	299	334
3	4	391	401
3	5	192	114
3	6	229	346
4	0	600	641
4	1	303	166
4	2	749	774
4	3	401	377
4	4	205	263
4	5	376*	518
4	6	458*	559
5	0	577	580
5	1	458*	575
5	2	128	203
5	3	259	317
6	0	502	500

K = 14

H	L	FO	FC
0	0	228	268
0	1	118	96
0	2	659	718
0	3	700	726
1	0	250*	387
1	1	367	357
1	2	696	668
1	3	657	680
1	4	427	467
1	5	248	237
2	0	180	263
2	1	59	206
2	2	205	101
2	3	390	431
3	0	502	521
3	1	32	72
3	2	610*	710
3	3	207	255
4	0	32	253

Table 4. *Atomic coordinates and their estimated standard deviations*

Positional parameters are expressed in fractional coordinates. Anisotropic temperature factors are expressed as:

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

The b_{ij}'s are multiplied by 10^4. The isotropic temperature factors are of the form $\exp\left(-B\sin^2\theta/\lambda^2\right)$ with B values expressed in Å^2. The temperature factors assigned to the hydrogen atoms are the same as the isotropic temperature factor of the atoms to which they are bonded, based on the last cycle of isotropic refinement. The estimated standard deviations are given in parentheses and correspond to the last significant decimal place. An asterisk (*) indicates that the hydrogen atom was not clearly defined in the difference Fourier synthesis, and therefore its coordinates were calculated.

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	−0·8505 (4)	−0·1370 (3)	−0·2921 (2)	22 (4)	48 (2)	42 (2)	−5 (2)	−2 (2)	7 (2)
C(2)	−0·8834 (4)	−0·0772 (3)	−0·2105 (3)	58 (6)	83 (3)	36 (2)	0 (3)	−3 (2)	2 (2)
C(3)	−0·9817 (5)	0·0173 (4)	−0·2351 (3)	74 (6)	87 (4)	33 (2)	28 (4)	−17 (3)	−20 (2)
N(4)	−1·0071 (3)	0·0006 (2)	−0·3446 (2)	34 (5)	42 (2)	32 (1)	4 (1)	1 (2)	−3 (1)
C(5)	−0·9852 (4)	0·1039 (3)	−0·4089 (3)	43 (4)	45 (2)	51 (2)	4 (2)	3 (3)	5 (2)
C(6)	−0·9279 (4)	0·0553 (3)	−0·5064 (3)	52 (5)	64 (3)	35 (2)	3 (3)	0 (2)	12 (2)
C(7)	−0·8394 (4)	−0·0409 (3)	−0·4686 (2)	21 (4)	48 (2)	36 (2)	−7 (2)	−11 (2)	−10 (2)
C(8)	−0·9219 (4)	−0·0938 (3)	−0·3834 (3)	32 (5)	32 (2)	37 (2)	8 (2)	−7 (2)	−6 (2)
C(9)	−0·7500 (3)	−0·2301 (3)	−0·2966 (3)	23 (5)	51 (2)	53 (2)	−12 (2)	−11 (3)	11 (2)
O(10)	−0·6245 (2)	−0·1752 (2)	−0·2727 (2)	29 (3)	50 (1)	35 (1)	8 (2)	−2 (2)	1 (1)
C(11)	−0·5138 (4)	−0·2256 (3)	−0·3072 (2)	44 (4)	50 (2)	31 (1)	5 (2)	−3 (2)	10 (1)
O(12)	−0·5106 (3)	−0·3185 (2)	−0·3482 (3)	79 (4)	38 (2)	84 (2)	11 (2)	11 (2)	−8 (2)
C(13)	−0·3977 (4)	−0·1491 (3)	−0·2875 (3)	34 (5)	55 (3)	42 (2)	14 (3)	1 (2)	7 (2)
C(14)	−0·2757 (5)	−0·2235 (4)	−0·2608 (4)	47 (5)	106 (5)	82 (3)	38 (4)	−5 (3)	32 (3)
C(15)	−0·3690 (3)	−0·0585 (2)	−0·3708 (2)	20 (4)	37 (2)	43 (2)	−9 (2)	11 (2)	−17 (2)
C(16)	−0·3132 (4)	−0·1130 (3)	−0·4675 (3)	40 (5)	64 (3)	50 (2)	2 (3)	19 (3)	−22 (2)
O(17)	−0·2783 (3)	0·0220 (2)	−0·3308 (2)	29 (3)	47 (2)	67 (2)	−6 (2)	−7 (2)	−24 (1)
C(18)	−0·4940 (4)	0·0171 (2)	−0·3915 (2)	35 (5)	29 (2)	37 (2)	8 (2)	1 (2)	−4 (1)
C(19)	−0·4621 (4)	0·1267 (3)	−0·4523 (3)	31 (4)	53 (2)	69 (2)	−10 (3)	2 (3)	16 (2)
C(20)	−0·6049 (3)	−0·0414 (2)	−0·4470 (2)	40 (5)	40 (2)	18 (1)	−4 (2)	−5 (2)	4 (1)
O(21)	−0·5963 (3)	−0·1235 (2)	−0·5041 (2)	40 (3)	55 (2)	43 (1)	−3 (2)	−3 (2)	−18 (1)
O(22)	−0·7199 (2)	0·0094 (2)	−0·4264 (2)	19 (2)	39 (1)	35 (1)	5 (2)	2 (1)	−9 (1)

Table 4 (*cont*.)

	x/a	y/b	z/c	B
H(2)	−0·8438	−0·0878	−0·1397	3·3
H(3*A*)*	−0·9417	0·1013	−0·2201	2·9
H(3*B*)*	−1·0716	0·0059	−0·1915	2·9
H(5*A*)*	−0·9165	0·1627	−0·3737	3·5
H(5*B*)*	−1·0763	0·1489	−0·4242	3·5
H(6*A*)	−0·8696	0·1094	−0·5345	2·8
H(6*B*)	−1·0149	0·0250	−0·5452	2·8
H(7)	−0·8083	−0·0919	−0·5248	1·8
H(8)	−0·9816	−0·1517	−0·4255	2·3
H(9*A*)*	−0·7467	−0·2685	−0·3712	2·3
H(9*B*)*	−0·7712	−0·2968	−0·2410	2·3
H(13)	−0·4170	−0·0983	−0·2260	2·7
H(14*A*)	−0·2972	−0·2491	−0·1876	4·1
H(14*B*)	−0·2510	−0·2700	−0·3113	4·1
H(14*C*)	−0·2106	−0·1675	−0·2475	4·1
H(16*A*)	−0·2295	−0·1391	−0·4669	3·2
H(16*B*)*	−0·3750	−0·1854	−0·4857	3·2
H(16*C*)	−0·2890	−0·0670	−0·5204	3·2
H(17)	−0·1655	−0·0002	−0·3438	2·8
H(18)	−0·5359	0·0467	−0·3148	1·8
H(19*A*)*	−0·4082	0·1869	−0·4057	2·8
H(19*B*)	−0·4149	0·1060	−0·5039	2·8
H(19*C*)*	−0·5519	0·1672	−0·4784	2·8

syntheses revealed the positions of all 23 hydrogen atoms, although 9 were not clearly resolved. For these hydrogens, the positions were calculated.

A final cycle of refinement was performed in which the positions of the hydrogen atoms remained fixed; they were assigned the same isotropic temperature factors as those of the atoms to which they are bonded, based on the last cycle of isotropic refinement.

The R value was then 0·082 for all 1396 reflections, and 0·062 for the 1131 reflections whose intensities where greater than 3σ.

The observed and calculated structure factors are given in Table 3, and the positional and temperature parameters of the atoms are given in Table 4.

Discussion

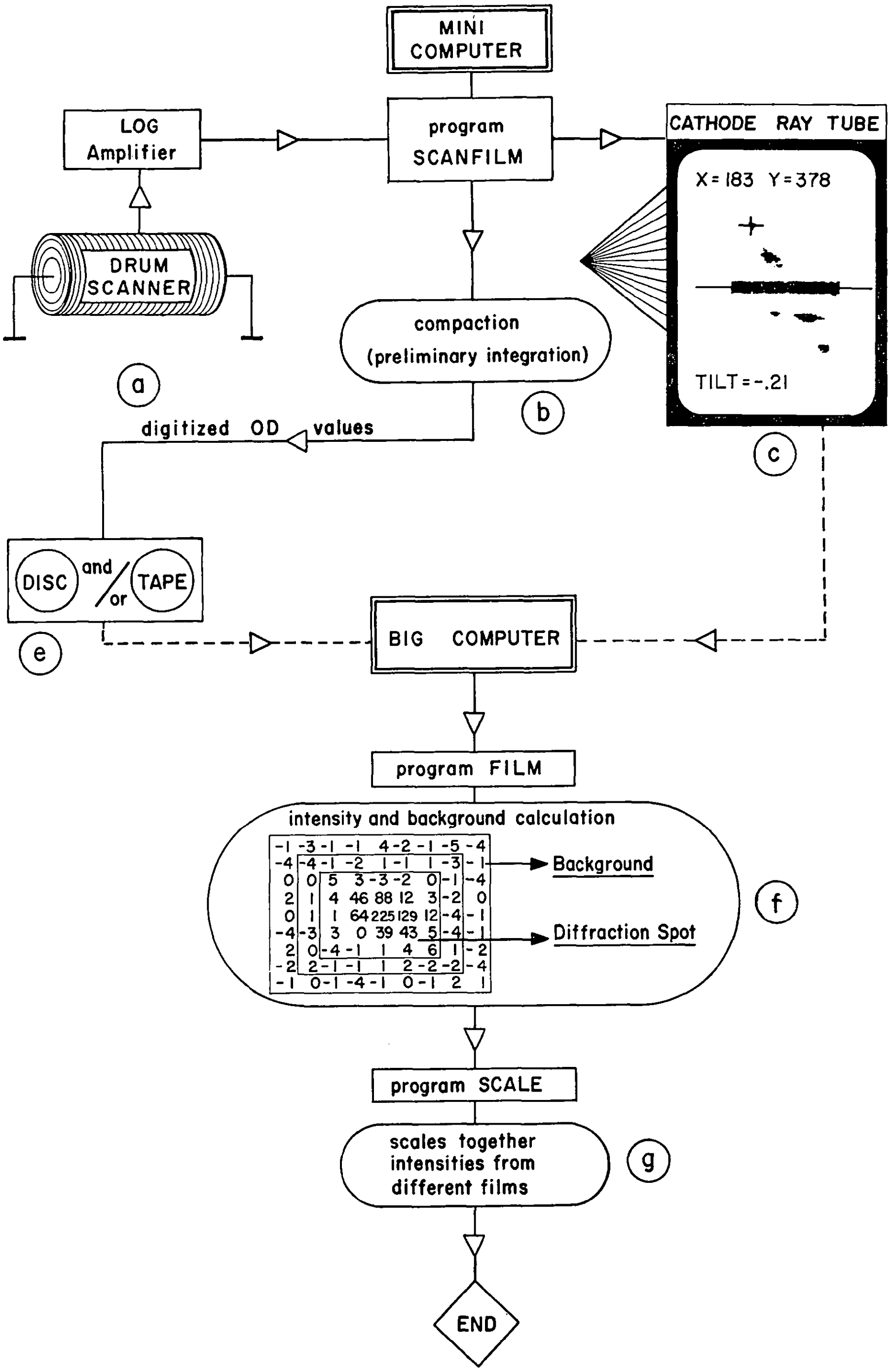
Description of the structure

(1) The observed bond lengths and angles of fulvine (see Fig. 1, Table 5 and Table 6) were found to differ

Table 5. *Bond angles in the crystal structure of fulvine*

The estimated standard deviations are given in parentheses and correspond to the least significant figure.

C(2)—C(1)—C(9)	125·9 (3)°	O(12)–C(11)–C(13)	125·8 (2)°
C(2)—C(1)—C(8)	110·9 (2)	O(10)–C(11)–C(13)	110·0 (2)
C(9)—C(1)—C(8)	123·1 (2)	C(11)–C(13)–C(15)	115·3 (2)
C(1)—C(2)—C(3)	111·8 (3)	C(11)–C(13)–C(14)	109·9 (3)
N(4)—C(3)—C(2)	103·2 (2)	C(15)–C(13)–C(14)	112·8 (2)
C(3)—N(4)—C(5)	115·2 (2)	O(17)–C(15)–C(16)	109·9 (2)
C(3)—N(4)—C(8)	109·3 (2)	O(17)–C(15)–C(13)	107·9 (2)
C(5)—N(4)—C(8)	108·1 (2)	O(17)–C(15)–C(18)	103·0 (2)
N(4)—C(5)—C(6)	103·9 (2)	C(16)–C(15)–C(13)	112·3 (2)
C(7)—C(6)—C(5)	102·9 (2)	C(16)–C(15)–C(18)	112·7 (2)
O(22)–C(7)—C(6)	109·0 (2)	C(13)–C(15)–C(18)	110·5 (2)
O(22)–C(7)—C(8)	109·7 (2)	C(20)–C(18)–C(19)	106·1 (2)
C(6)—C(7)—C(8)	102·2 (2)	C(20)–C(18)–C(15)	116·1 (2)
N(4)—C(8)—C(1)	104·7 (2)	C(19)–C(18)–C(15)	112·5 (2)
N(4)—C(8)—C(7)	106·0 (2)	O(21)–C(20)–O(22)	122·2 (2)
C(1)—C(8)—C(7)	117·4 (2)	O(21)–C(20)–C(18)	126·8 (2)
O(10)–C(9)—C(1)	106·0 (2)	O(22)–C(20)–C(18)	111·0 (2)
C(11)–O(10)–C(9)	117·9 (2)	C(20)–O(22)–C(7)	118·4 (2)
O(12)–C(11)–O(10)	124·1 (3)		



-1	-3	-1	-1	4	-2	-1	-5	-4
-4	-4	-1	-2	1	-1	1	-3	-1
0	0	5	3	-3	-2	0	-1	-4
2	1	4	46	88	12	3	-2	0
0	1	1	64	225	129	12	-4	-1
-4	-3	3	0	39	43	5	-4	-1
2	0	-4	-1	1	4	6	1	-2
-2	2	-1	-1	1	2	-2	-2	-4
-1	0	-1	-4	-1	0	-1	2	1

Fig. 2. Film-scanning system. Top: a mini-computer (an Adage model 50) controls the operation of the film-scanner including converting the analog signal after it has been logarithmically amplified to a digital value (*a*) and simultaneously performs a preintegration (or compaction) of the data, *i. e.* adjacent data points on the same line are summed and the resultant data are again summed with corresponding data from adjacent lines. Once the entire film is scanned, it can be played back on a cathode ray tube (CRT) (*c*) attached to the computer so that one can determine the alignment of the film on the scanner. The specific parameters required are: (1) the *x*, *y* coordinates of an origin spot (such as where one of the axis crosses the horizontal), and (2) the 'tilt' of the film relative to the axis of the scanner. These are found by moving a cross on the CRT to different points of the picture and reading the *x*, *y* values directly from the scope; and by adjusting a line to match the black direct-beam line and reading the tilt in degrees. About 20 films are stored on one tape (*e*) and then carried to the main computer. Bottom: A larger computer (an IBM 360) is used for further processing. The program *FILM* determines for each spot an integrated intensity after subtracting an appropriate estimate of the background (*f*). After all the films are processed they are brought to a common scale by the program *SCALE* (Hamilton, Rollett & Sparks, 1965) in order to obtain a set of *F*'s.

insignificantly from those in jacobine (Fridrichsons, Mathieson & Sutor, 1963), which has 12 atoms in its macro-ring while fulvine has only 11 atoms.

Table 6. *Bond lengths* (Å) *in the crystal structure of fulvine*

The estimated standard deviations are given in parentheses and correspond to the least significant figure.

C(1)–C(2)	1·323 (4)	O(10)–C(11)	1·348 (3)
C(1)–C(8)	1·492 (4)	C(11)–O(12)	1·206 (4)
C(1)–C(9)	1·488 (4)	C(11)–C(13)	1·500 (4)
C(2)–C(3)	1·519 (5)	C(13)–C(14)	1·552 (4)
C(3)–N(4)	1·479 (4)	C(13)–C(15)	1·548 (4)
N(4)–C(5)	1·484 (3)	C(15)–C(16)	1·532 (3)
N(4)–C(8)	1·487 (3)	C(15)–O(17)	1·414 (3)
C(5)–C(6)	1·519 (4)	C(15)–C(18)	1·568 (3)
C(6)–C(7)	1·518 (4)	C(18)–C(19)	1·537 (4)
C(7)–C(8)	1·530 (4)	C(18)–C(20)	1·506 (3)
C(7)–O(22)	1·458 (3)	C(20)–O(21)	1·217 (3)
C(9)–O(10)	1·461 (3)	C(20)–O(22)	1·337 (3)

(2) The pyrrolizidine nucleus of fulvine exists in the *exo*-puckered form, with a puckering angle of 46° between the planes defined by atoms C(5)C(6)C(7) and C(5)N(4)C(8). The sense of the puckering is defined by the relative position of the C(6) atom and the unsaturated ring C(1)C(2)C(3)N(4)C(8) with respect to the plane defined by the atoms N(4)C(5)C(7). If they are on the same side of this plane, the puckering is *endo*- and if they are on the opposite sides, *exo*-.

(3) The atoms C(1)C(2)C(3)N(4)C(8)C(9) are planar with the largest deviation from the least-squares plane determined by them being 0·04 Å.

(4) The dihedral angle between the two five-membered rings of the pyrrolizidine nucleus is 115°.

(5) The two lactone planes

[C(9)–O(10)–C(11)=O(12)

and

C(7)–O(22)–C(20)=O(21)]

are roughly parallel, with a 9° angle between them. The distance between the carbonyl groups is 2·97 Å, which is within the range of π–π interactions.

(6) The absolute configuration of fulvine was assigned by comparison with that of jacobine, as both are derived from the same pyrrolizidine nucleus retronecine (Bull, Culvenor & Dick, 1968).

(7) The O(17) hydroxyl group is pointing in the opposite direction with respect to the C(8) hydrogen (see Fig. 1). This determines unambiguously the stereo-

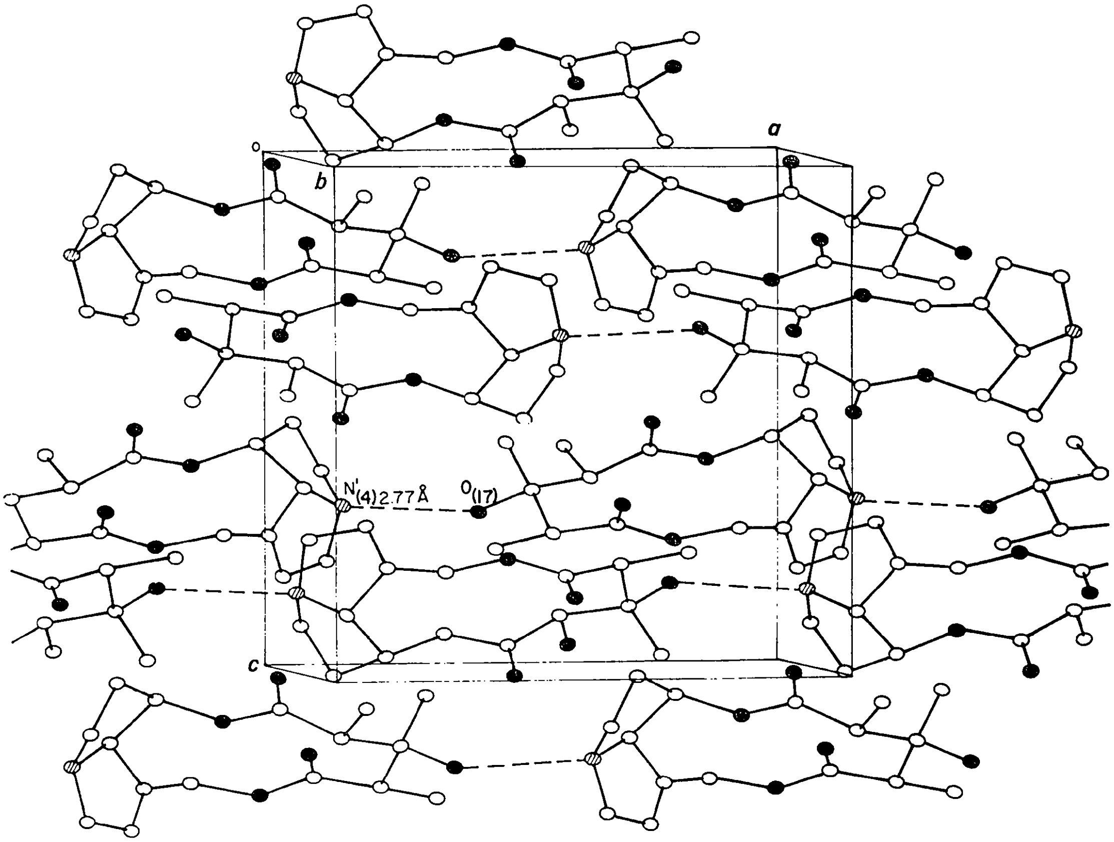


Fig. 3. Molecular packing diagram (Johnson, 1965) of the crystal structure of fulvine, without hydrogens, as viewed down the *b* axis. ● represents oxygen. ⊛ represents nitrogen. ○ represents carbon. Note the hydrogen bond between O(17) and N(4).

chemistry of the asymmetric carbon C(15) distinguishing fulvine from its stereoisomer crispatine.

Packing

The packing of fulvine molecules seems to be mainly dominated by hydrophobic forces. Although hydrogen pockets are clearly visible in the packing diagram, no H–H distances are less than 2·2 Å. The only hydrogen bond formed in this crystal is the one between the hydrogen of O(17) in one molecule and the nitrogen of the molecule translated one unit cell away in the **a** direction. The distance between the oxygen and the nitrogen atoms is 2·7 Å, and the angle O(17)–H(17)–N(4) is 165° (see Fig. 3).

Possible structure–function relationship

It has been shown that the di-esters fulvine and jacobine are about seven times more potent than the mono-ester heliotrine (Schoental, 1968). The potency in these compounds is believed to be correlated to the reactivity of the C(1)–C(2) double bond (Schoental, 1957; Schoental, 1970; McLean, 1970; Culvenor *et al.*, 1971).

According to this study, the double bond in fulvine is readily accessible to attack if we consider such access to depend on the dihedral angle between the bonds C(1)C(2) and C(9)C(10). In fulvine these atoms are 'locked' in a 'half-*trans*' position, the dihedral angle is 64° and thus O(10) points away from the C(1)–C(2) double-bond (see Fig. 4). They have virtually no freedom of movement because of the tightness of the structure. The value of the same dihedral angle in jacobine is 114°, almost completely *trans* and thus also accessible to attack.

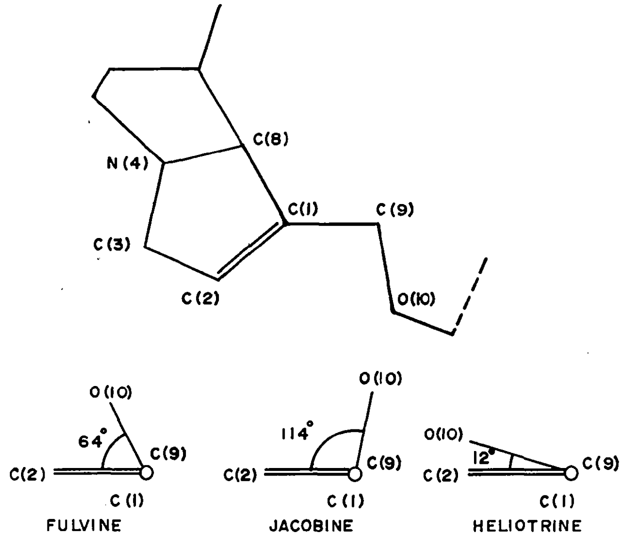


Fig. 4. Accessibility of the C(1)C(2) double bond in pyrrolizidine alkaloids. Top: Diagram of the pyrrolizidine nucleus and the rotatable bond adjacent to the saturated ring. Bottom: View down the C(1)C(9) bond in the pyrrolizidine alkaloids fulvine, jacobine, and heliotrine. Note how much closer O(10) is to C(2) in heliotrine than in the other two structures.

However, a *cis* position would correspond to a hindered access where the O(10) oxygen is brought into close contact with the double bond. This has been observed in the mono-ester heliotrine (Wodak, 1972).

Before a final statement about the relationship between accessibility of the C(1)–C(2) bond and potency can be made, several other pyrrolizidine alkaloid structures should be studied. Of special interest would be the biologically active mono- or di-esters having separate bulky acid moieties, *i.e.* not forming a covalent macro-ring. For such a structure the number of assumed conformations in solution would be restricted because of interactions between non-bonded atoms. In a potent hepatoxin of this kind, the three-dimensional structure should reveal an accessible double-bond and supply information about the forces applying the constraints.

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The Crystal Structure of Stoichiometric $CoIn_3$

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The compound $CoIn_3$ prepared at 400°C is stoichiometric. Its crystal structure has been determined by single-crystal X-ray analysis. $CoIn_3$ crystallizes in the tetragonal system, space group $P4/mbm$. The unit cell, which contains eight atoms, has the dimensions $a=6{\cdot}830$ and $c=3{\cdot}547$ Å. The structure was refined by the least-squares method, using the positional parameters and isotropic temperature parameters. The structure is based on layers of square-triangular nets and is related to $CoGa_3$ and Si_2U_3 in that it is a disordered variant of the former and a defect structure of the latter. Whereas the geometry of the known compounds with the Si_2U_3 structure is closely tied to the conditions of spherical packing, $CoGa_3$ and $CoIn_3$ are characterized by a short bond distance Co–Ga and Co–In.

Introduction

Until quite recently, the information on phases in the cobalt–indium binary system was sparse. Some clarification of the phase equilibria and the composition of the intermetallic compounds was provided by Schöbel & Stadelmaier (1970). In looking over the preliminary structural information that we had on $CoIn_3$, we detected a relationship to tetragonal $CoGa_3$ (Schubert, Lukas, Meissner & Bhan, 1959) suggesting that our unit cell was essentially that of tetragonal $CoGa_3$ with half the cell constant c. Since a unit cell to be obtained by merely cutting the cell of the $CoGa_3$ type in half in this manner did not appear compatible with the tetragonal lattice actually observed, we believed that a full structure determination would shed some light on this problem.

Sample preparation and chemical composition

$CoIn_3$ was formed by reacting solid cobalt (99·74 wt.% purity) with liquid indium (99·99 wt.% purity) for 200 h at 400°C and quenching to room temperature. The reaction layer consisted of a single phase sandwiched between the cobalt and the solidified indium. Although the grains in the reaction layer were mostly columnar, equiaxed crystals suitable for X-ray work could be isolated by digesting the reaction layer in dilute HCl.

The chemical composition was determined by electron-probe analysis, using a Hitachi XMA-5 microprobe. The compound layer was analyzed against standards of elemental cobalt and indium. Corrections for atomic number, absorption, and fluorescence effects were made using a computer program developed by Colby (1968). The composition, averaged from six independent and separately corrected determinations, was 24·9 ± 1·2 at.% Co and 75·1 ± 1·2 at.% In. A microprobe line scan through the compound layer showed that its composition was uniform. Therefore the microprobe evidence supports the assumption of stoichiometric $CoIn_3$.

Experimental

Approximate cell constants were obtained from 001 and 110 rotation patterns (camera diameter 10 cm, filtered Co $K\alpha$ radiation). The final cell constants were measured with a Straumanis-type powder camera (diameter 114·59 mm) extrapolating to $\theta=90°$ and using Co $K\alpha_1$, $\lambda=1{\cdot}78892$ Å and Co $K\alpha_2$, $\lambda=1{\cdot}79278$ Å. The single-crystal integrated intensities of 194 reflections were collected with a manually operated Picker four-circle diffractometer using crystal-monochrom-

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