Acta Cryst. (1964). **17**, 472

The Crystal Structure of the Monoterpene Iridomyrmecin at −150 °C

By J. F. McConnell

School of Physics, University of New South Wales, Sydney, Australia

A. McL. Mathieson

Division of Chemical Physics, C.S.I.R.O., Chemical Research Laboratories, Melbourne, Australia

and B. P. Schoenborn*

School of Physics, University of New South Wales, Sydney, Australia

(*Received* 13 *May* 1963)

Iridomyrmecin, the C(8) epimer of isoiridomyrmecin, crystallizes in the monoclinic space group $P2_1$ with unit-cell dimensions $a=11\cdot96$, $b=5\cdot25$, $c=7\cdot48$ Å, $\beta=97\cdot1°$ at −150 °C. The density is 1·20 g.cm^{-3}, calculated for $Z=2$. From the Patterson b-axis projection and Harker sections, the alternative permissible orientations in the unit cell of the two probable molecular models were narrowed down to the correct selection by ϱ and $\Delta\varrho$ distributions of the zero-layer data about the b axis. Refinement by least-squares procedure using a block-diagonal approximation reduced the overall value of R to 0·14 for $h0l$–$h3l$ data.

The lactone group is shown to be planar, as in isoiridomyrmecin, and to restrain the six-membered ring to a boat conformation with the cyclopentanoid ring *endo* to the six-membered ring. Comparison of the molecular packing in this crystal with that in the closely related epimer permits consideration of the possible role of the oxygen atoms of the lactone group with regard to intermolecular packing forces.

Introduction

Iridomyrmecin, one of the monoterpenoid compounds of insect origin (for a review, see Cavill, 1960) is the C(8) epimer of isoiridomyrmecin, the crystal structure of which has been determined (McConnell & Schoenborn, 1962). The detailed structure of iridomyrmecin is of interest in relation to the overall shape of the molecule, the disposition of the lactone group and its influence on the conformation of the six-membered ring. Furthermore, comparison with the structure of isoiridomyrmecin has potential significance with regard to the intermolecular forces associated with the lactone group.

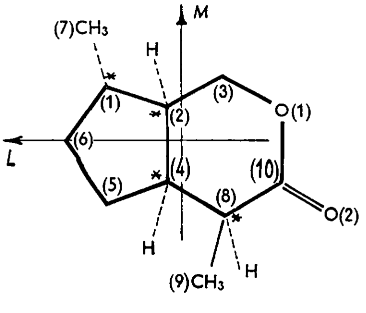


Fig. 1. The structure of iridomyrmecin. Atoms are numbered and asymmetric centres starred. The molecular axes L and M are indicated.

Brief comments concerning the structures of the epimeric compounds, iridomyrmecin (Fig. 1) and isoiridomyrmecin, have been presented earlier (McConnell, Mathieson & Schoenborn, 1962).

Experimental

Iridomyrmecin forms colourless crystals, m.p. = 58 °C, which are soluble in water and most organic solvents. For the X-ray measurements, a crystal was mounted in a fine quartz capillary which prevented loss by sublimation. The dimensions a and c of the monoclinic cell were determined from high-angle reflexions on a Weissenberg photograph, calibrated against a standard, Ag, $a=4\cdot0862$ Å (Fridrichsons, 1959), while the value of b was determined from a rotation photograph — $a=11\cdot96$, $b=5\cdot25$, $c=7\cdot48$ Å, $\beta=97\cdot1°$ at −150 °C. The density was not measured since only a minute amount of the material was available and it is very soluble in most solvents. It was therefore assumed to be similar to that of isoiridomyrmecin, *ca.* 1·1. From this estimate, it was deduced that $Z=2$, and since the material is optically active, $[\alpha]_D^{25\cdot5}=+210°$, the forbidden reflexions, $k=2n+1$, fix the space group as $P2_1$. Intensity data (582 observed reflexions) were collected at −150 °C (for details, see Fridrichsons & Mathieson, 1962) for 0–3 layers about the b axis. The intensities were estimated by eye with the aid of a calibration strip and corrected for Lorentz, polarization and equi-inclination factors

---

* Present address: Department of Pharmacology, School of Medicine, University of California, San Francisco 22, Calif., U.S.A.

(Löfgren, 1960). No correction for absorption was considered necessary.

Structure determination

Since iridomyrmecin is epimeric with respect to isoiridomyrmecin at C(8), its configurational details are well defined (Fig. 1). In addition, the planarity of the lactone group (Mathieson & Taylor, 1961; Fridrichsons & Mathieson, 1962) restricts the six-membered ring to a boat conformation (Mathieson,

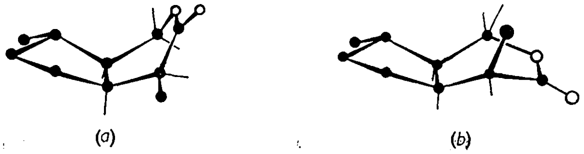


Fig. 2. The two possible molecular models, with the cyclopentanoid ring (*a*) *endo*, and (*b*) *exo* to the six-membered ring.

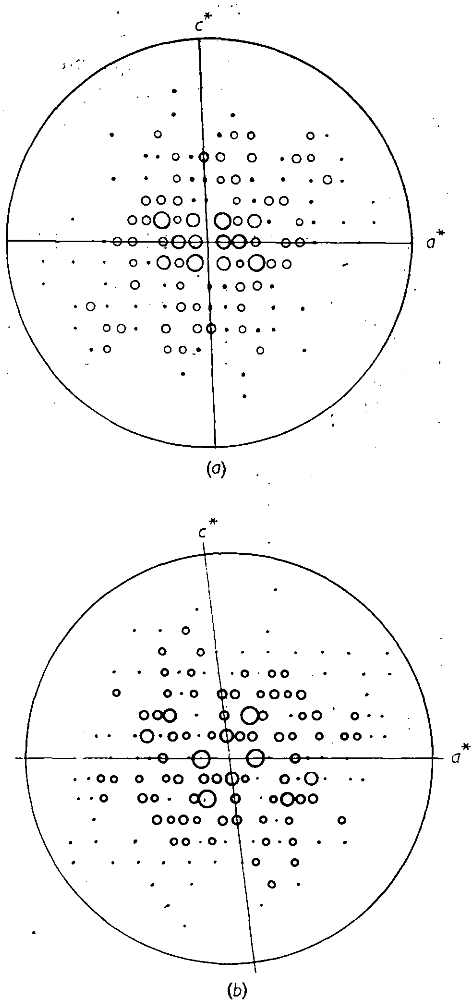


Fig. 3. Comparison of the weighted *h*0*l* reciprocal lattices for (*a*) isoiridomyrmecin and (*b*) iridomyrmecin.

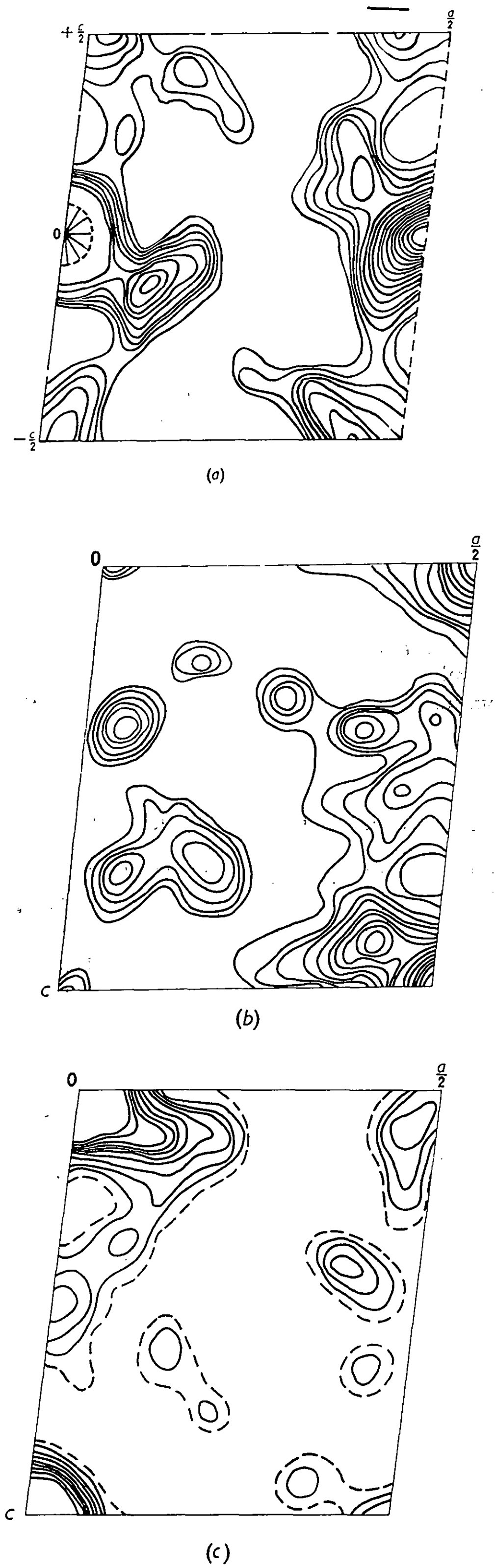


Fig. 4. (*a*) The vector distribution $P(x, z)$. (*b*) Harker section $P(x, \frac{1}{2}, z)$. (*c*) Harker section $P(x, 0, z)$.

1963) so that only two models are feasible for the structure of iridomyrmecin. The cyclopentanoid ring is either *endo* to the six-membered ring with the C(9) methyl equatorial (Fig. 2(*a*)) or *exo* with the methyl group axial (Fig. 2(*b*)). Because of the probable strong 1,4 interaction of C(9) with the axial hydrogen of C(3), model (*a*) is more likely but, for completeness, model (*b*) was also given consideration.

For the analysis, the zero-layer Patterson distribution $P(x, z)$ and the Harker sections, $P(x, \frac{1}{2}, z)$ and $P(x, 0, z)$ were calculated.

Before the analyses are considered in detail, certain general conclusions regarding the structure may be given. The b axis, 5·25 Å, is much smaller than that for isoiridomyrmecin, 6·41 Å, so that in the crystal the overall 'tilt' of the molecule relative to (010) is likely to be smaller. Furthermore, a comparison (Fig. 3) of the weighted $h0l$ reciprocal lattices (Lipson & Taylor, 1958) of the epimers disclosed that, despite the close similarity of chemical structure and cell dimensions and the identity of space group, the atomic arrangement in the unit cell must be very different although, as with isoiridomyrmecin, the b-axis projection of iridomyrmecin seems to correspond to relatively well-resolved atom groups. More specifically, the comparison suggested that the general orientation of the molecule must be approximately at right angles to that observed for isoiridomyrmecin in relation to the same definition of cell axes. Although indicative of the rough orientation of the molecule in the unit cell, the selection does not define the alignment of the $+L$ and $+M$ axes of the molecule relative to the cell axes and the mutual relationship to its symmetry-related neighbour.

Inspection of the vector distribution, $P(x, z)$ (Fig. 4(*a*)) reveals a strong peak at $x=a/2$, $z=0$ with an intense band extending with a small slope relative to z suggesting an approximation to a sub-periodicity which can be ascribed to the relative disposition of the two molecules. This is such that the two halves of each molecule bear an approximately centrosymmetric relationship which would place the centre of gravity of the molecule at $x=a/4$, $z=c/2$, a deduction in accord with the weak 100. This conclusion still leaves open the preferred alignment of the $+M$ axis, (the $+L$ axis being defined arbitrarily). Four possible molecular models require to be considered corresponding to the alternate alignments of the $+M$ axis for the two structures (Fig. 2). Owing to this approximation to internal symmetry, which is also supported by the Harker sections (Fig. 4(*b*), (*c*)), the four possibilities bear a somewhat close relation-

Table 1. *Comparison of observed and calculated structure amplitudes*

	F_o	F_c
00l		
1	30.6	-32.4
2	24.7	-29.6
3	17.1	-16.5
4	6.5	6.3
5	6.0	6.3
6	4.8	-5.0
7	3.8	3.3
10l		
$\bar{9}$	-	-1.4
$\bar{8}$	2.5	-2.0
$\bar{7}$	2.2	-3.0
$\bar{6}$	-	2.6
$\bar{5}$	2.6	5.0
$\bar{4}$	6.8	7.6
$\bar{3}$	18.1	-19.4
$\bar{2}$	10.5	-8.6
$\bar{1}$	20.9	24.5
0	5.5	-6.0
1	13.4	-16.1
2	1.7	-2.5
3	-	-1.3
4	7.5	9.7
5	10.1	10.6
6	4.0	-2.3
7	5.8	-7.0
8	-	-1.4
9	2.2	-3.0
20l		
$\bar{9}$	3.0	3.6
$\bar{8}$	-	-0.1
$\bar{7}$	-	-0.1
$\bar{6}$	4.5	-5.9
$\bar{5}$	5.7	5.2
$\bar{4}$	12.1	-15.8
$\bar{3}$	4.0	-4.4
$\bar{2}$	45.1	45.7
$\bar{1}$	21.2	21.1
0	50.6	-52.2
1	9.2	8.5
2	9.9	-8.4
3	16.1	17.7
4	10.8	-12.5
5	6.5	-7.2
6	11.5	12.5
7	4.9	-2.2
8	-	-0.3
9	2.6	-2.3
30l		
$\bar{9}$	-	-0.1
$\bar{8}$	4.2	-4.7
$\bar{7}$	2.7	4.2
$\bar{6}$	5.3	7.1
$\bar{5}$	1.9	-2.0
$\bar{4}$	5.9	-7.9
$\bar{3}$	15.7	12.5
$\bar{2}$	20.4	-20.4
$\bar{1}$	4.3	-6.9
0	7.1	7.0
1	3.2	3.6
2	11.9	13.6
3	7.7	4.5
4	6.0	-6.0
5	3.8	-3.7
6	-	-0.3
7	2.1	-2.3
8	-	1.6
9	1.6	2.4
40l		
$\bar{9}$	3.0	-5.0
40l		
$\bar{8}$	1.9	-3.1
$\bar{7}$	4.9	-5.3
$\bar{6}$	9.1	12.8
$\bar{5}$	6.6	-6.6
$\bar{4}$	14.2	13.0
$\bar{3}$	16.8	-15.9
$\bar{2}$	3.2	-0.9
$\bar{1}$	22.0	21.0
0	14.6	-13.6
1	17.1	17.5
2	30.5	-26.7
3	12.2	-11.6
4	11.1	12.0
5	13.3	13.1
6	7.0	-6.3
7	-	-1.2
8	-	0.5
50l		
$\bar{9}$	-	-1.0
$\bar{8}$	5.4	6.4
$\bar{7}$	2.2	-2.5
$\bar{6}$	3.1	3.3
$\bar{5}$	4.1	2.6
$\bar{4}$	11.2	-14.2
$\bar{3}$	11.0	-12.5
$\bar{2}$	7.4	9.5
$\bar{1}$	16.4	14.8
0	21.6	19.2
1	9.1	-11.0
2	18.4	-16.1
3	3.5	3.6
4	4.4	6.5
5	-	-1.6
6	2.2	-2.0
7	-	-1.3
8	1.9	-2.5
60l		
$\bar{9}$	1.6	-2.2
$\bar{8}$	-	1.9
$\bar{7}$	5.2	7.0
$\bar{6}$	3.5	-4.0
$\bar{5}$	6.4	-5.2
$\bar{4}$	1.9	-1.5
$\bar{3}$	18.6	21.2
$\bar{2}$	12.1	-10.4
$\bar{1}$	4.8	-4.0
0	5.7	1.5
1	29.1	-27.9
2	21.4	20.7
3	1.9	-0.8
4	8.9	11.7
5	4.9	-5.2
6	2.1	-1.9
7	3.0	-2.9
8	-	0.3
70l		
$\bar{9}$	-	0.6
$\bar{8}$	-	-0.3
$\bar{7}$	4.6	4.9
$\bar{6}$	6.5	-8.3
$\bar{5}$	4.1	-5.5
$\bar{4}$	4.1	3.2
$\bar{3}$	1.9	3.1
$\bar{2}$	17.3	17.3
$\bar{1}$	11.6	-12.4
0	7.3	-7.9
1	5.3	5.8
2	4.0	4.8
3	4.1	-3.9
4	-	-2.9
5	-	-0.6
70l		
6	2.0	-2.5
7	4.3	5.2
80l		
$\bar{8}$	-	0.5
$\bar{7}$	3.0	-1.2
$\bar{6}$	-	1.1
$\bar{5}$	8.9	11.4
$\bar{4}$	7.1	-10.2
$\bar{3}$	4.1	-4.6
$\bar{2}$	-	-2.2
$\bar{1}$	3.3	2.6
0	1.9	2.4
1	3.6	-2.3
2	-	0.0
3	12.1	13.4
4	7.5	-8.8
5	2.6	-3.2
6	-	0.7
7	-	1.1
90l		
$\bar{8}$	1.7	-2.6
$\bar{7}$	-	-0.2
$\bar{6}$	-	2.1
$\bar{5}$	-	-1.2
$\bar{4}$	-	0.7
$\bar{3}$	-	-1.0
$\bar{2}$	2.5	-1.0
$\bar{1}$	13.8	16.0
0	8.8	-9.1
1	7.1	-7.5
2	4.0	-4.6
3	5.0	5.0
4	2.2	2.1
5	-	1.8
6	-	0.5
10,0l		
$\bar{7}$	2.9	2.8
$\bar{6}$	-	0.3
$\bar{5}$	6.8	-9.6
$\bar{4}$	-	0.9
$\bar{3}$	2.7	-1.8
$\bar{2}$	12.7	15.6
$\bar{1}$	12.0	-12.4
0	2.2	-2.8
1	9.2	10.0
2	-	-1.2
3	3.8	-2.3
4	-	-0.4
5	2.9	2.1
6	3.4	-4.8
11,0l		
$\bar{7}$	2.7	-3.3
$\bar{6}$	-	0.2
$\bar{5}$	4.7	-4.6
$\bar{4}$	6.0	6.7
$\bar{3}$	7.5	9.9
$\bar{2}$	5.9	-6.1
$\bar{1}$	8.0	-10.5
0	-	-1.5
1	2.2	3.1
2	4.6	5.1
3	-	0.8
4	-	-1.0
5	-	-2.0
12,0l		
$\bar{6}$	3.7	-5.3
$\bar{5}$	-	-1.0
12,0l		
$\bar{4}$	4.4	6.2
$\bar{3}$	-	1.2
$\bar{2}$	8.3	-8.2
$\bar{1}$	8.0	6.6
0	-	0.6
1	-	-0.4
2	-	0.8
3	2.2	-3.1
4	1.9	1.1
13,0		
$\bar{6}$	0.8	-0.2
$\bar{5}$	6.0	7.5
$\bar{4}$	6.5	-7.2
$\bar{3}$	3.8	-2.8
$\bar{2}$	-	2.1
$\bar{1}$	2.0	-1.0
0	1.9	2.4
1	2.3	-2.7
2	3.9	3.8
3	-	-0.4
14,0l		
$\bar{5}$	-	1.1
$\bar{4}$	1.5	-2.1
$\bar{3}$	2.4	2.9
$\bar{2}$	-	0.7
$\bar{1}$	2.3	2.2
0	3.6	-4.1
1	-	-2.4
2	1.3	1.2
15,0l		
$\bar{3}$	1.5	-0.6
$\bar{2}$	1.6	-1.9
$\bar{1}$	1.9	-2.2
0	1.4	0.9
1	3.8	5.9
01l		
1	24.4	28.6
2	20.1	18.0
3	6.2	6.6
4	7.5	6.3
5	5.0	6.0
6	-	1.2
7	3.3	3.0
8	-	2.3
9	2.6	2.3
11l		
$\bar{9}$	-	0.3
$\bar{8}$	3.0	2.8
$\bar{7}$	4.7	5.0
$\bar{6}$	5.6	5.4
$\bar{5}$	5.4	6.3
$\bar{4}$	9.0	8.6
$\bar{3}$	22.2	18.4
$\bar{2}$	34.0	37.9
$\bar{1}$	32.3	36.6
0	40.7	56.3
1	14.8	17.8
2	22.0	20.2
3	4.4	4.2
4	9.5	9.1
5	6.2	6.9
6	9.7	12.7
7	5.2	4.6
8	4.1	3.0
9	4.2	4.6

	F_o	$\lvert F_c \rvert$
21l		
$\bar{9}$	2.1	2.2
$\bar{8}$	-	0.0
$\bar{7}$	5.7	7.3
$\bar{6}$	9.7	9.6
$\bar{5}$	7.6	8.7
$\bar{4}$	15.7	20.1
$\bar{3}$	14.7	16.4
$\bar{2}$	14.2	11.6
$\bar{1}$	20.5	21.4
0	15.0	11.4
1	17.3	19.2
2	12.7	10.4
3	15.5	14.4
4	4.9	3.8
5	3.7	3.7
6	5.2	6.2
7	4.6	4.0
8	-	2.2
9	2.5	4.3
31l		
$\bar{9}$	2.5	3.6
$\bar{8}$	-	2.1
$\bar{7}$	4.6	4.0
$\bar{6}$	6.9	7.9
$\bar{5}$	12.5	14.1
$\bar{4}$	5.4	5.2
$\bar{3}$	12.0	14.1
$\bar{2}$	17.1	19.4
$\bar{1}$	29.3	28.3
0	19.8	21.5
1	5.8	6.1
2	2.8	2.6
3	11.4	10.7
4	13.3	15.8
5	3.8	2.4
6	10.4	12.4
7	-	1.2
8	5.6	6.0
41l		
$\bar{9}$	2.8	2.7
$\bar{8}$	6.4	5.6
$\bar{7}$	3.3	4.9
$\bar{6}$	6.9	7.5
$\bar{5}$	9.0	10.5
$\bar{4}$	10.3	11.7
$\bar{3}$	1.6	2.2
$\bar{2}$	5.7	7.0
$\bar{1}$	12.8	13.5
0	10.2	6.4
1	11.4	10.2
2	6.0	2.8
3	5.0	4.0
4	9.0	10.9
5	6.7	5.9
6	-	1.5
7	3.1	4.2
8	3.5	4.3
51l		
$\bar{9}$	-	1.3
$\bar{8}$	-	2.0
$\bar{7}$	4.5	4.9
$\bar{6}$	7.4	7.7
$\bar{5}$	10.7	12.4
$\bar{4}$	-	1.8
$\bar{3}$	11.5	13.7
$\bar{2}$	24.6	22.9
$\bar{1}$	11.1	9.6
0	20.8	23.7
1	15.5	14.1
2	10.4	13.5
3	9.9	9.8
51l		
4	11.6	12.8
5	6.9	8.2
6	-	3.4
7	-	1.8
8	1.6	2.3
61l		
$\bar{9}$	1.5	1.8
$\bar{8}$	2.6	2.6
$\bar{7}$	6.6	7.1
$\bar{6}$	3.3	4.3
$\bar{5}$	3.9	5.1
$\bar{4}$	4.2	4.2
$\bar{3}$	-	2.1
$\bar{2}$	11.4	12.1
$\bar{1}$	8.5	9.0
0	13.7	12.6
1	10.2	10.7
2	8.4	10.5
3	11.2	3.8
4	4.5	3.4
5	-	1.7
6	5.1	4.9
7	-	2.3
8	2.2	2.7
71l		
$\bar{8}$	-	0.9
$\bar{7}$	2.0	2.0
$\bar{6}$	3.3	2.8
$\bar{5}$	6.1	5.3
$\bar{4}$	8.2	9.0
$\bar{3}$	5.0	3.4
$\bar{2}$	13.6	15.8
$\bar{1}$	8.3	9.3
0	14.3	14.4
1	3.8	2.4
2	5.0	5.8
3	11.8	13.2
4	9.8	11.1
5	4.7	5.2
6	4.3	3.7
7	-	1.7
81		
$\bar{8}$	1.5	1.7
$\bar{7}$	5.7	5.0
$\bar{6}$	3.3	2.3
$\bar{5}$	3.3	3.7
$\bar{4}$	6.9	7.9
$\bar{3}$	6.5	9.0
$\bar{2}$	11.0	11.3
$\bar{1}$	5.0	5.8
0	6.7	8.0
1	4.2	6.5
2	3.0	2.7
3	4.0	4.2
4	6.2	6.0
5	-	2.3
6	-	1.9
7	-	0.5
91l		
$\bar{8}$	-	1.5
$\bar{7}$	-	1.1
$\bar{6}$	-	0.8
$\bar{5}$	6.1	5.9
$\bar{4}$	8.1	9.2
$\bar{3}$	3.2	3.5
$\bar{2}$	3.9	2.2
$\bar{1}$	8.5	8.6
0	13.9	14.4
1	1.5	1.7
91l		
2	6.9	6.0
3	9.9	11.1
4	2.3	2.4
5	4.2	4.1
6	-	0.5
10,1l		
$\bar{7}$	-	2.2
$\bar{6}$	-	2.6
$\bar{5}$	-	1.2
$\bar{4}$	2.3	1.3
$\bar{3}$	7.4	9.3
$\bar{2}$	4.6	4.1
$\bar{1}$	6.9	6.0
0	5.7	5.5
1	5.2	5.0
2	4.7	3.5
3	5.1	4.1
4	-	1.1
5	-	1.6
6	3.6	3.6
11,1l		
$\bar{7}$	1.2	0.4
$\bar{6}$	2.5	3.4
$\bar{5}$	-	0.0
$\bar{4}$	3.1	3.7
$\bar{3}$	4.6	5.5
$\bar{2}$	6.2	7.0
$\bar{1}$	9.3	8.0
0	7.7	6.6
1	7.3	7.1
2	5.1	4.2
3	-	2.4
4	3.8	3.5
5	5.1	4.9
12,1l		
$\bar{6}$	2.0	2.7
$\bar{5}$	5.9	5.9
$\bar{4}$	2.8	2.6
$\bar{3}$	4.8	3.9
$\bar{2}$	3.1	2.7
$\bar{1}$	4.5	2.7
0	3.2	2.4
1	-	1.3
2	-	2.8
3	-	0.1
4	1.6	2.2
13,1l		
$\bar{5}$	3.7	5.5
$\bar{4}$	3.8	3.9
$\bar{3}$	-	1.8
$\bar{2}$	-	2.1
$\bar{1}$	-	1.7
0	4.5	3.7
1	-	1.7
2	-	0.3
3	1.5	1.3
14,1l		
$\bar{4}$	3.3	4.0
$\bar{3}$	3.0	3.1
$\bar{2}$	1.6	1.9
$\bar{1}$	2.9	3.7
0	2.4	2.5
1	3.4	2.7
2	4.3	5.6
15,1l		
$\bar{3}$	3.1	1.5
$\bar{2}$	1.5	1.6
$\bar{1}$	3.9	4.5
0	2.3	2.3
02l		
1	-	0.4
2	19.8	19.3
3	27.6	18.6
4	7.9	6.9
5	4.4	5.4
6	3.4	3.1
7	3.3	5.4
8	-	1.8
9	2.1	1.8
12l		
$\bar{9}$	3.3	3.3
$\bar{8}$	2.8	2.9
$\bar{7}$	6.2	2.7
$\bar{6}$	8.3	7.7
$\bar{5}$	-	1.1
$\bar{4}$	11.6	11.6
$\bar{3}$	12.1	12.0
$\bar{2}$	-	2.0
$\bar{1}$	5.8	5.9
0	13.4	15.4
1	5.4	7.4
2	9.0	7.6
3	11.8	12.6
4	14.9	15.5
5	9.0	8.0
6	4.2	3.0
7	8.1	6.7
8	1.9	0.2
9	1.8	2.8
22l		
$\bar{9}$	3.1	4.1
$\bar{8}$	-	1.7
$\bar{7}$	-	0.4
$\bar{6}$	9.3	8.6
$\bar{5}$	7.7	4.8
$\bar{4}$	4.8	3.8
$\bar{3}$	22.0	20.3
$\bar{2}$	14.0	10.9
$\bar{1}$	18.5	19.1
0	13.0	13.1
1	15.3	17.2
2	14.8	9.4
3	12.7	11.7
4	8.6	8.6
5	3.2	2.6
6	3.4	2.3
7	-	0.7
8	8.3	7.1
32l		
$\bar{8}$	3.4	2.9
$\bar{7}$	2.3	1.5
$\bar{6}$	11.5	11.3
$\bar{5}$	14.2	13.2
$\bar{4}$	2.8	2.4
$\bar{3}$	8.6	3.7
$\bar{2}$	15.3	10.5
$\bar{1}$	18.2	18.3
0	12.6	10.1
1	11.5	12.4
2	18.7	19.8
3	8.2	8.7
4	4.7	2.9
5	6.2	6.6
6	4.8	3.3
32l		
7	10.0	8.4
8	3.9	3.6
42l		
$\bar{8}$	5.1	4.2
$\bar{7}$	8.0	7.6
$\bar{6}$	12.1	11.7
$\bar{5}$	-	1.6
$\bar{4}$	11.7	11.6
$\bar{3}$	2.6	4.0
$\bar{2}$	5.1	4.5
$\bar{1}$	17.3	17.7
0	7.5	5.9
1	11.8	13.8
2	8.7	9.4
3	8.5	7.0
4	12.0	13.6
5	10.1	10.5
6	5.8	5.5
7	6.8	5.8
8	4.7	4.5
52l		
$\bar{8}$	2.6	1.7
$\bar{7}$	6.7	6.4
$\bar{6}$	-	0.9
$\bar{5}$	7.4	8.4
$\bar{4}$	5.3	3.7
$\bar{3}$	9.5	9.3
$\bar{2}$	5.0	5.7
$\bar{1}$	3.3	3.6
0	9.2	9.7
1	5.4	5.1
2	-	2.0
3	5.9	5.4
4	8.9	8.4
5	10.2	8.7
6	7.0	5.6
7	3.5	2.0
8	2.3	2.4
62l		
$\bar{8}$	7.2	6.4
$\bar{7}$	-	2.2
$\bar{6}$	8.3	8.1
$\bar{5}$	7.2	6.2
$\bar{4}$	6.4	6.4
$\bar{3}$	3.6	3.9
$\bar{2}$	6.7	6.7
$\bar{1}$	5.2	7.2
0	7.8	8.1
1	2.7	3.6
2	8.7	6.8
3	3.1	3.3
4	13.4	14.4
5	12.3	11.4
6	3.9	3.2
7	4.8	3.4
72l		
$\bar{8}$	2.1	2.2
$\bar{7}$	4.6	6.5
$\bar{6}$	-	0.3
$\bar{5}$	2.4	1.8
$\bar{4}$	6.6	7.6
$\bar{3}$	5.0	2.7
$\bar{2}$	4.7	3.9
$\bar{1}$	-	0.9
0	6.4	6.9
1	3.6	2.6
2	5.4	5.7
3	5.7	5.0
4	8.0	7.7
72l		
5	4.1	3.4
6	6.6	6.4
82l		
$\bar{8}$	3.0	3.2
$\bar{7}$	-	0.5
$\bar{6}$	-	1.7
$\bar{5}$	7.6	7.9
$\bar{4}$	6.8	5.3
$\bar{3}$	6.2	6.0
$\bar{2}$	14.3	15.7
$\bar{1}$	8.3	8.3
0	8.6	7.1
1	10.1	12.7
2	9.1	9.2
3	6.8	8.4
4	5.9	5.2
5	3.8	3.7
6	2.6	2.3
92l		
0	2.3	1.5
1	4.1	3.5
2	9.4	10.0
3	3.4	4.1
03l		
1	6.2	6.5
2	14.2	15.5
3	9.8	10.0
4	6.4	6.2
5	12.3	9.9
6	6.3	4.8
7	6.3	4.1
13l		
$\bar{6}$	6.3	3.3
$\bar{5}$	7.9	8.5
$\bar{4}$	5.6	2.8
$\bar{3}$	4.7	3.0
$\bar{2}$	13.9	10.6
$\bar{1}$	6.6	7.2
0	4.1	6.4
1	12.1	13.9
2	16.2	17.5
3	5.6	6.6
4	12.9	11.6
5	7.3	7.1
6	6.3	5.5
23l		
$\bar{6}$	-	3.9
$\bar{5}$	-	2.9
$\bar{4}$	7.6	7.0
$\bar{3}$	8.9	6.2
$\bar{2}$	4.6	4.0
$\bar{1}$	10.8	6.0
0	12.6	16.8
1	-	3.2
2	-	4.6
3	5.1	5.4
4	-	2.6
5	12.6	9.5
6	7.6	5.2
33l		
$\bar{6}$	-	1.6
$\bar{5}$	6.6	5.0
$\bar{4}$	16.6	13.4
$\bar{3}$	8.9	7.3
$\bar{2}$	7.8	4.3
33l		
$\bar{1}$	13.4	12.4
0	7.2	7.6
1	10.8	12.4
2	9.3	8.7
3	8.6	7.3
4	-	1.6
5	-	.7
6	-	2.3
43l		
$\bar{6}$	-	1.6
$\bar{5}$	-	2.5
$\bar{4}$	10.8	9.5
$\bar{3}$	15.7	9.5
$\bar{2}$	12.1	9.4
$\bar{1}$	6.3	5.6
0	6.0	5.4
1	4.4	3.7
2	7.1	4.0
3	5.6	2.8
4	12.9	9.3
5	6.3	5.5
53l		
$\bar{6}$	6.9	7.6
$\bar{5}$	10.7	9.0
$\bar{4}$	15.7	11.7
$\bar{3}$	11.9	9.9
$\bar{2}$	7.6	6.7
$\bar{1}$	8.9	7.5
0	6.9	7.4
1	-	1.4
2	11.8	10.4
3	12.7	8.8
4	6.3	6.1
5	-	2.8
63l		
$\bar{6}$	5.7	5.8
$\bar{5}$	-	1.8
$\bar{4}$	9.2	7.1
$\bar{3}$	-	2.3
$\bar{2}$	6.3	5.4
$\bar{1}$	11.5	10.3
0	-	1.3
1	-	2.3
2	13.5	12.4
3	7.2	6.7
4	8.9	9.4
5	7.3	6.6
6	-	3.7
73l		
$\bar{5}$	-	3.3
$\bar{4}$	-	4.1
$\bar{3}$	-	2.7
$\bar{2}$	6.0	4.6
$\bar{1}$	9.6	6.1
0	9.6	7.7
1	9.8	8.1
2	12.8	11.8
3	7.6	5.4
4	-	1.3
5	5.9	3.9
83l		
$\bar{3}$	6.3	5.5
$\bar{2}$	6.3	4.8
$\bar{1}$	-	1.8
0	6.3	6.6
1	4.8	3.3
2	6.2	6.2
83l		
3		3.2
93l		
$\bar{3}$	9.6	8.6
$\bar{2}$	10.4	9.5
$\bar{1}$	5.0	5.3
0	6.0	5.8
1	-	2.6
2	5.1	4.7

ship to each other and more specific allocations of atom sites were made in accord with the distribution of vectors in the Patterson and Harker sections.† The corresponding $h0l$ structure factors were computed. In the region $\sin\theta < 0{\cdot}60$, the values of the reliability indices R for the various models did not vary significantly from 0·60 and none showed any appreciable advantage at initial inspection. Attempts to improve the situation by inspection of the corresponding $\varrho(x, z)$ and $\Delta\varrho(x, z)$ distributions yielded little indication of improvement until an error synthesis intended to show major displacements of scattering matter rather than minor corrections in location was computed with terms for $\sin\theta < 0{\cdot}3$, and a fairly high discriminatory level such that terms were discarded if $F_c < \frac{3}{2}F_o$. This distribution also suggested certain shifts opposite to those indicated by earlier attempts using a more complete θ-range of data. Agreement dropped to 0·36 and after subsequent cycles to 0·20.

The y parameters were determined from the projection of the structure assuming bond lengths and angles normally expected for the atom types. Refinement of the atom parameters was then carried out by a least-squares procedure on UTECOM (≡ DEUCE) using Rollett's block-diagonal program, the first two cycles with unit weight and the next two with the w_1 weighting scheme and $F^* = 15$ (Rollett, 1961). The final agreement, R, for the layers was 0·12 ($k = 0$), 0·14 (1), 0·16 (2), 0·19 (3) with an overall value of 0·14. Comparison of individual F_c and F_o values is recorded in Table 1, the value for B (isotropic) being 2·4. The final electron-density projection down the b-axis is given in Fig. 5.

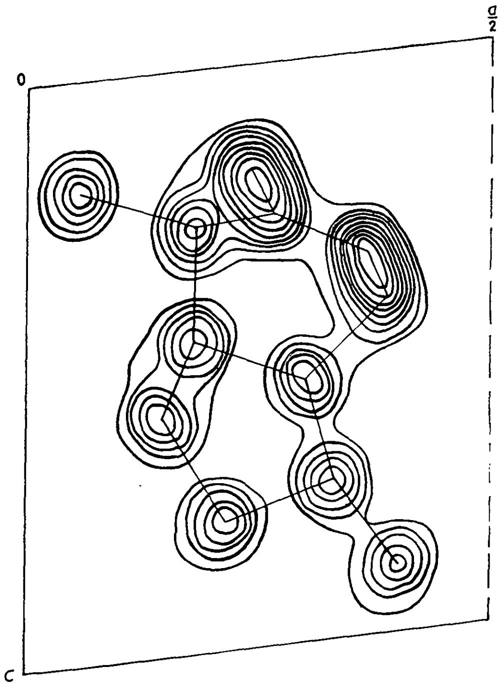


Fig. 5. The final electron-density distribution projected along the b axis.

Table 2. *Atomic coordinates of iridomyrmecin*

	x/a	y/b	z/c
C(1)	0·3293	0·2984	0·7266
C(2)	0·3038	0·1465	0·5483
C(3)	0·3841	0·1995	0·4248
C(4)	0·1802	0·2025	0·4632
C(5)	0·1411	0·3965	0·5879
C(6)	0·2055	0·3600	0·7742
C(7)	0·4009	0·1571	0·8795
C(8)	0·1767	0·2852	0·2646
C(9)	0·0582	0·3875	0·1910
C(10)	0·2615	0·4884	0·2598
O(1)	0·3645	0·4416	0·3445
O(2)	0·2424	0·7124	0·1828

The atom parameters are listed in Table 2 with the corresponding bond lengths and angles in Fig. 6.

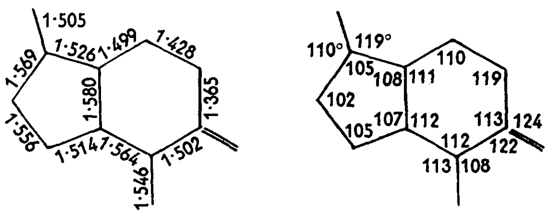


Fig. 6. Bond lengths and angles in the molecule.

Discussion

The average single C–C bond length, excluding C(8)–C(10), is 1·54 Å with a mean deviation of 0·03 Å. For the lactone group, the dimensions are consistent with earlier values (Fridrichsons & Mathieson, 1962), C(10)–O(1) being shorter than C(3)–O(1).

The relative configurations of the asymmetric atoms, C(1), C(2) and C(4), shown in Fig. 1, are in accord with the deductions by chemical means (Cavill & Locksley, 1957) from the relationship to nepetalactone and the nepetalinic acids. Further, the configuration of C(8) is in accord with that deduced by Dolejš, Mironov & Šorm (1960) through the relationship of guaiol to the nepetalinic acids and to bulnesol (see also Cavill, 1960).

With regard to the detailed shape of the molecule, the five-membered ring has four atoms near planar and one, C(6), out of this plane by approximately 0·6 Å. The cyclopentanoid ring is *endo* to the six-membered ring which is in the boat-conformation (Mathieson, 1963) because of the restriction imposed by the planarity and dimensions of the lactone group (Mathieson & Taylor, 1961). The molecule as a whole assumes the shape of a curved sheet (Fig. 2(*a*)).

---

† Around the screw axis regions, the short b axis permits the blocking-out of a considerable area for normal van der Waals approach distances and restricts location of atom sites (Fig. 7).

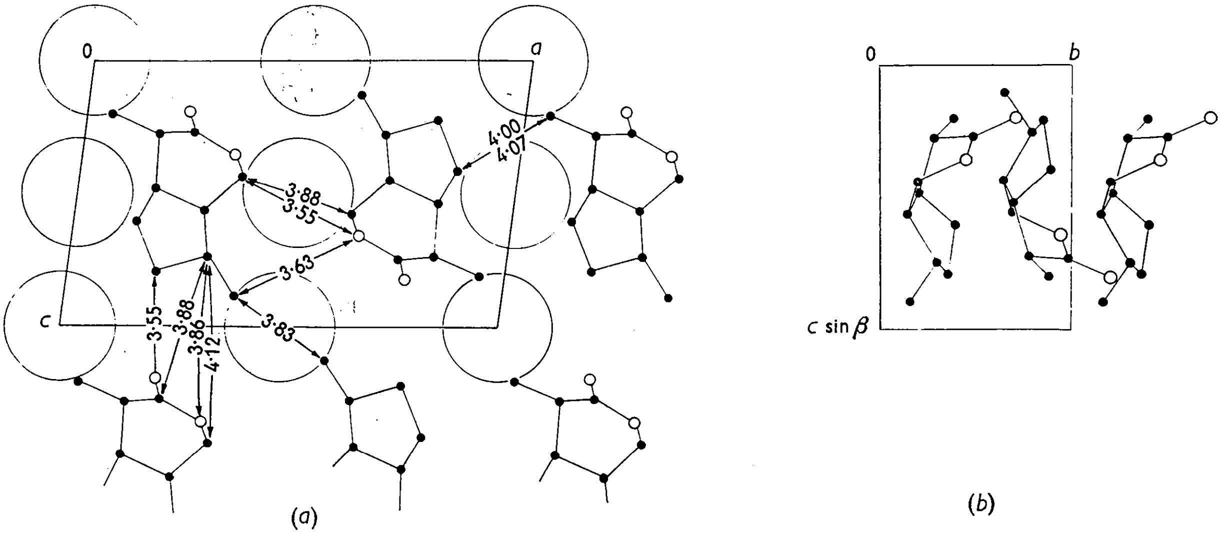
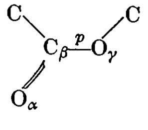


Fig. 7. The packing arrangement in the unit cell, (*a*) viewed along the *b* axis, (*b*) viewed along the *c* axis. In (*a*), areas around screw axes prohibited for normal van der Waals approach distances are outlined.

The packing of the molecules in the unit cell is shown in Fig. 7(*a*), (*b*). There appear to be no very short approach distances and hence no very strong intermolecular bonds in accord with the low melting point and high volatility of this compound. The mode of packing of the molecules appears to be mainly determined by its buckled shape, so that each molecule moulds itself in the concavity of its neighbours along *b*, (Fig. 7(*b*)). The shortest approach distances are of the order of 3·6 Å between oxygen and carbon atoms.

The availability of the structure analyses of the two epimers and the considerable difference in their packing habits provides the opportunity to examine the mode of packing of these molecules. It was of interest to determine whether the lactone group played a role of any significance in relation to packing. From studies of structures involving lactone groups, it has been concluded that this group is planar and that associated with this planarity is the shortening of the C–O bond adjacent to the C=O group. This may be interpreted as due to the hybridization character of O(γ) in the lactone group



and its interaction with C(β) or as a partial double bond character of bond *p*. From the first viewpoint, it may be presumed that O(γ) will be in a trigonal (sp^2) state with a 'lone pair' in the third location or from the alternative viewpoint as having a partial positive charge while O(α) bears a partial negative charge. It was worth considering whether the special states of the oxygen atoms make a sufficient contribution to permit these atoms to play some significant role in the complex of intermolecular forces. In isoiridomyrmecin and iridomyrmecin there are no gross ionic forces involved or any other strong bonds so that we have the possibility, through a comparison, of finding out whether the lactone group is active in this sense.

In these structures, the main factors involved in packing may be considered as (*a*) the shape of the molecules, (*b*) the possible influence of the lactone group and (*c*) van der Waals forces. Because the two molecules have a markedly different shape (*vide* Fig. 1(*a*), (*b*) in McConnell, Mathieson & Schoenborn, 1962), their packing might have been expected to be different, perhaps even to the extent of utilizing a different space group. In fact, the same space group was used but the similarity of cell dimensions is almost fortuitous, the orientations being completely different. Inspection of the two structures, isoiridomyrmecin (Fig. 7 in McConnell & Schoenborn, 1962) and iridomyrmecin (Fig. 7), reveals that the dominant factor determining the packing mode is the overall shape of the molecule, the former being in general extended and relatively flat whereas the latter is like a buckled sheet. Because of this difference it ought therefore to be more readily recognized whether the lactone groups in the two structures display some similarity of environment with respect to the oxygen atoms. Inspection of ball-on-spike models of both structures fails to reveal any obviously consistent pattern in the two structures. In iridomyrmecin, the keto O(2) makes a relatively close approach of 3·55 Å to C(6)(H) while O(1) makes a similar approach, 3·63 Å to C(7)(H). In isoiridomyrmecin O(2) approaches C(8)(H) at 3·17 Å while O(1) is at 3·42 Å from C(3)(H). In each case it is probable that a hydrogen atom is involved, and these observations may constitute evidence for what may be considered a weak hydrogen bond (Sutor, 1962). In this sense a certain measure of weak but not very specific interaction due to the lactone group may be considered to operate. However there is no clear distinction between the behaviour of the two oxygen atoms, O(1) and O(2), so that neither the lone pair of electrons or the partial charge appears to exert a specific bonding effect. The comparison of molecular packing in the two compounds therefore fails to reveal any direct evidence of the special states of O(1) and O(2) which would correlate with that suggested by the evidence of planarity of the lactone group and the dissymmetry of the C–O bond lengths.

We are grateful to Prof. G. W. K. Cavill of the University of New South Wales for his kindness in supplying a sample of iridomyrmecin. We also wish to thank Mr P. Jennings of the University of Western Australia for his assistance in constructing ball-on-spike models of the crystal structures of iridomyrmecin and isoiridomyrmecin.

References

Cavill, G. W. K. (1960). *Rev. Pure Appl. Chem.* **10**, 169.
Cavill, G. W. K. & Locksley, H. D. (1957). *Austr. J. Chem.* **10**, 352.
Dolejš, L., Mironov, A. & Šorm, F. (1960). *Tetrahedron Letters*, No. 11, 18.
Fridrichsons, J. (1959). *Amer. Min.* **44**, 200.
Fridrichsons, J. & Mathieson, A. McL. (1962). *Acta Cryst.* **15**, 119.
Lipson, H. & Taylor, C. H. (1958). *Fourier Transforms and X-ray Diffraction*. London: Bell.
Löfgren, T. (1960). *Acta Cryst.* **13**, 156.
McConnell, J. F. & Schoenborn, B. P. (1962). *Acta Cryst.* **15**, 779.
McConnell, J. F., Mathieson, A. McL. & Schoenborn, B. P. (1962). *Tetrahedron Letters*, No. 10, 445.
Mathieson, A. McL. (1963). *Tetrahedron Letters*, No. 2, 81.
Mathieson, A. McL. & Taylor, J. C. (1961). *Tetrahedron Letters*, No. 17, 590.
Rollett, J. S. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. p. 97. Symposium Publications Division, Pergamon Press.
Sutor, D. J. (1962). *Nature, Lond.* **193**, 68.

Acta Cryst. (1964). **17**, 477

X-ray Studies of the Bis-*N*-alkylsalicylaldiminates of Bivalent Metals. III. Structure of Bis-*N*-butylsalicylaldimine-palladium

By Edoardo Frasson, Carlo Panattoni and Luigi Sacconi

Centro di Strutturistica Chimica del C.N.R.-Sezione di Padova, Italy
Istituto di Chimica Generale ed Inorganica dell'Universita, Firenze, Italy

(*Received* 18 *March* 1963)

Following the examination of the metal complexes of *N*-alkylsalicylaldimines the crystal structure of bis-*N*-butylsalicylaldimine-palladium was determined by two-dimensional Fourier methods.

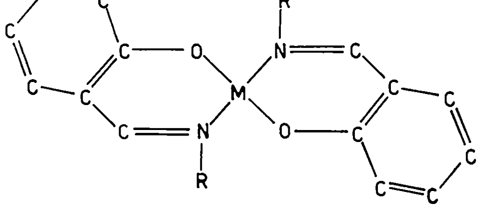
The unit cell is monoclinic with lattice constants

$$a=10\cdot99,\ b=7\cdot25,\ c=14\cdot72\ \text{Å};\ \beta=120^\circ;\ Z=2\ .$$

The space group is $P2_1/c$. The metal atoms are required to be at symmetry centers and the coordination bonds in a trans-planar arrangement. The form of the chelate ring in this compound will be discussed. The results of the structure determination of complexes of this series are compared.

Introduction

As a part of the study of the structures of complexes of *N*-alkylsalicylaldimines of bivalent metals with the general formula



the crystal structure of the palladium complex of the butyl derivative will be described in this paper.

The earlier studies of this series of complexes showed some curious features not only in the geometry of the coordination, but also in the shape of the chelate ring, exhibiting sensivity to steric hindrance.

Complexes of the butyl derivative with nickel, copper and palladium have been previously described (Frasson & Panattoni, 1962). The crystals are practically isometric and hence the differences in the radii of the coordinating metals can have no influence on the volume occupied by the different molecules. These have virtually identical volumes.