

## THE SESQUITERPENOID IRESIN

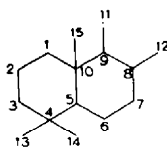
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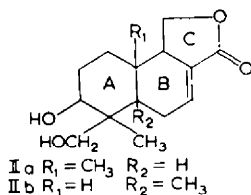
**Abstract**—The three-dimensional structure of the sesquiterpenoid iresin has been obtained from an X-ray diffraction study of the *p*-dibromobenzoate diester. The position of the angular methyl group is in agreement with the bicyclofarnesol skeleton, previously found only in higher terpenes.

DJERASSI *et al.*<sup>1</sup> isolated a new tricyclic sesquiterpenoid  $C_{15}H_{22}O_4$  from the Mexican plant "Iresine celosioides". This compound, named iresin, was shown to be tricyclic,<sup>2,3</sup> with the unique feature of possibly possessing the bicyclofarnesol(I), or a closely related, skeleton. If so, iresin would be the "long-sought-after missing link"<sup>2</sup> between



I

the higher and lower terpenes: this skeleton is present in all diterpenes, triterpenes and steroids, and its absence in the lower terpenes has been taken to indicate a fundamental difference between the biogenesis of the lower terpenes and the higher terpenes. We shall show that iresin is in fact based on the bicyclofarnesol skeleton.



At the time we started, the detailed stereochemistry and position of the angular methyl group were unknown. Classical organic procedures had not decided between Structures (IIa) and (IIb), but the OH group on C-3, the carbon atom bearing the primary hydroxyl function, and the 5-6 bond were thought to be all *cis*. The present X-ray diffraction study has confirmed these aspects of stereochemistry, established the position of the methyl group, and established all three-dimensional aspects of

<sup>1</sup> C. Djerassi, P. Sengupta, J. Herran and F. Walls, *J. Amer. Chem. Soc.* **76**, 2966 (1954).

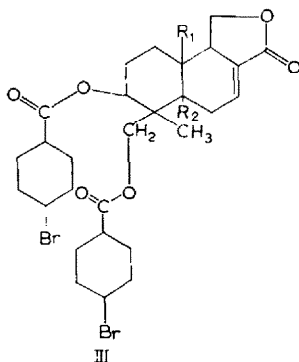
<sup>2</sup> C. Djerassi, W. Rittel, A. L. Nussbaum, F. W. Donovan and J. Herran, *J. Amer. Chem. Soc.* **76**, 6410 (1954).

<sup>3</sup> C. Djerassi and W. Rittel, *J. Amer. Chem. Soc.* **79**, 3528 (1957).

the molecular geometry except for the absolute configuration. Preliminary communications of the X-ray evidence<sup>4</sup> for the stereochemistry and presently available chemical evidence<sup>5</sup> for the stereochemistry and absolute configuration are in complete agreement.

#### EXPERIMENTAL DATA

A heavy atom derivative was prepared here by Dr. Paul Tomboulion who esterified the two OH groups by treating iresin with *p*-bromobenzoyl chloride in pyridine.



The product (III), recrystallized from a benzene-cyclohexane mixture, melted at 211.5–212° (corrected). Infrared spectra of iresin and this derivative indicated no changes in the iresin residue other than esterification.

Very thin crystals about 0.5 × 0.5 mm<sup>2</sup> were grown from benzene solution over a period of a month. Equi-inclination Weissenberg photographs were taken of levels 0, 1, 2, 3 and 4 about the *b* and *c* axes with CuK $\alpha$  radiation. The unit cell is monoclinic, with parameters *a* = 28.75, *b* = 7.41, *c* = 6.40 Å. and  $\beta$  = 92°, where the *a* axis is perpendicular to the plate. Our measured density of 1.526 g cm<sup>-3</sup> gives a molecular weight of 627 if two molecules are in the unit cell, in good agreement with the expected value of 632 for (III). The systematic absence only of 0*k*0 when *k* is odd indicates either *P*2<sub>1</sub> or *P*2<sub>1</sub>/*m*, but the molecule cannot be expected to have either a mirror plane or a centre of symmetry. Hence the space group *P*2<sub>1</sub>, later shown to be correct, was assumed.

Visual estimates of 1432 independent diffraction maxima were made with the multiple film technique in which account was taken of the variation of film factor with angle of incidence.<sup>6</sup> The usual Lorentz-polarization corrections were made, and corrections for absorption were estimated only on those very few reflections for which the incident or diffracted ray passed in the plane of the plate-like crystal. The very thin background band was used to indicate the magnitude of the correction for these few reflections. The use of reflections common to the several films allowed correlation to a single scale, later made absolute by comparison with trial structures.

#### STRUCTURE DETERMINATION

The Patterson projection along *c* yielded the Br positions which were so close to *P*2<sub>1</sub>/*m* symmetry that the remainder of the structure was obscured by a pseudo-mirror

<sup>4</sup> M. G. Rossmann and W. N. Lipscomb, *J. Amer. Chem. Soc.* **80**, 2592 (1958).

<sup>5</sup> C. Djerassi, F. W. Donovan, S. Burstein and R. Mauli, *J. Amer. Chem. Soc.* **80**, 2593 (1958).

<sup>6</sup> M. G. Rossmann, *Acta Cryst.* **9**, 819 (1956).

plane. Hence, the three-dimensional Patterson function was computed with sharpened coefficients  $[F_0^2/(\hat{f})^2] \exp [2(B - B^1)(\sin^2 \theta/\lambda^2)]$ , where  $B - B^1$  was chosen as  $1.0 \text{ \AA}^2$  and  $\hat{f} = \sum f_j/\sum Z_j$  in the usual notation. The only unusual features of the obvious  $\text{Br} \cdots \text{Br}$  peaks were the elongation of the non-Harker peaks (Fig. 1) along  $y$ , interpreted as displacement of  $0.14 \text{ \AA}$  from the pseudo-mirror plane, and the elongation of the Harker peaks which later was found to be due to pronounced anisotropy of the thermal motion of the Br atoms.

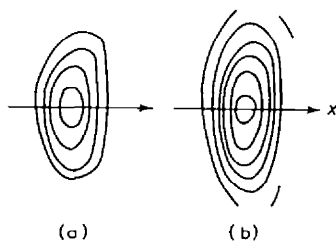


FIG. 1. (a) Single  $\text{Br} \cdots \text{Br}$  Harker peak. (b) General double  $\text{Br} \cdots \text{Br}$  peak. Contours are at  $400 \text{ e}^2/\text{\AA}^3$ .

The benzene rings were not obvious in the Patterson function, and hence only the positions of the Br atoms were used to compute phases for the first three-dimensional electron density map (F1). Had the Br atoms been placed exactly on the pseudo-mirror plane, the structure and its mirror image would have been superimposed, but the slight displacements of Br described above allowed the identification of the 7 C atoms (16–22) and O-1 and O-2 of one of the benzoate groups, as well as C-23, all of heights between 1 and  $3 \text{ e\AA}^{-3}$ . The effect of the pseudo-mirror plane was, however, still very evident. Four cycles of least-squares refinement of these atoms along with the Br atoms reduced  $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$  from 0.62 to 0.41, an improvement due mostly to small changes in the Br positions and scale factor. During the last cycle of this refinement, the new phases were inserted into the computation of a new electron density map (F2).

Nearly all of the light atoms were found in F2. Those found above in F1, and therefore included in F2, had heights between 5 and  $7 \text{ e\AA}^{-3}$ , and those not yet introduced had heights between 1 and  $3 \text{ e\AA}^{-3}$ . A search was made for peaks at a distance of  $1.5 \text{ \AA}$ , and at suitable bond angles from both the oxygen atoms that had so far been found. These peaks were marked and a similar search was then made of peaks  $1.5 \text{ \AA}$  away from these, and so forth. At the same time the chemical reasonableness of the emerging structure was taken into account. In this way the molecule could be fitted to peaks in the Fourier without undue imagination except that atom C-9 did not correspond to any real peak and the bonds in the five-membered ring required a good deal of "stretching" (see Fig. 2). All other peaks in the map could be accounted for by the pseudo-mirror plane. These false peaks were generally slightly smaller in height, larger in area and of more irregular outline than the real peaks. Some atoms had no "mirror atom". There was general confusion where the second benzene ring might have been expected to turn up. Thus in the next trial structure the whole of the first benzoate group, as well as the iresin molecule itself and atoms O-4 and C-29, were included. Atom C-23 was omitted at this stage. A revision of the scattering

curve for Br had been made. Unfortunately this contained an error. It effectively reduced the light atom contributions to high-order planes by a factor of three but left the low-order planes unchanged in structure factors used for F2.

Two cycles of least-squares refinement, in which  $R$  fell from 0.38 to only 0.37, were carried out, and then the third electron density map, F3, was computed. Examination of F3 indicated that atom C-23 had been incorrectly placed in F1, and atoms O-4 and C-29 had been incorrectly placed in F2. Moreover, the second benzoate

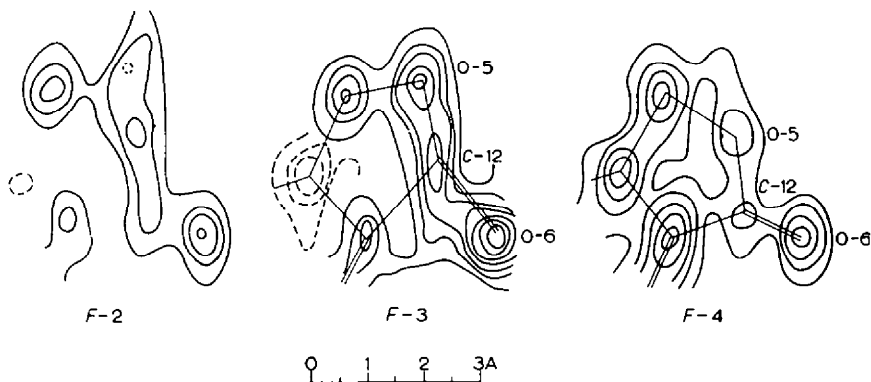


FIG. 2. Successive stages in determining the shape of the five-membered ring shown on section  $14/20c$ . Dotted lines show section  $13/20c$  and dashed line section  $15/20c$ . Contours are at intervals of  $1 e/\text{Å}^3$  upwards.

group was now clearly visible, but something was wrong with the five-membered ring. Atoms C-12 and O-5 (Fig. 2) did not give the expected well-resolved spherical peak, and the apparent temperature factor shifts indicated by least squares were unusually large. Therefore, only these two atoms were omitted from the next refinement.  $R$  was found to be 0.305. Computation of F4 only in the vicinity of the five-membered ring, with phases from all atoms except C-12 and O-5, showed clearly where these two atoms really were (Fig. 2), thus completing the structure. The difficulty had been caused by a "mirror peak" in F2 which was actually higher than the true peak.

#### REFINEMENT OF THE STRUCTURE

All atoms but hydrogen had been located, and hence three-dimensional least-squares refinement was tried but  $R$  fell only from 0.280 to 0.277 in three cycles. In an attempt to interpret this result, a three-dimensional difference electron density map D1 was computed. This map showed no variations higher than  $\pm 2.0 e\text{Å}^{-3}$ , all of which could be interpreted as shifts of light atoms, except for peaks up to  $3.5 e\text{Å}^{-3}$  around both bromines, indicating strong anisotropic thermal motion (Fig. 3). Six further cycles of least-squares refinement in which six thermal parameters were introduced for each of the two bromines, produced values of  $R = 0.182$  and  $r = \Sigma\omega(|F_0|^2 - |F_c|^2)^2 / \Sigma\omega F_0^4 = 0.183$ . The final electron density map F5 was now computed, composite sections of which are shown in Fig. 4. Except for a very few small peaks as high as  $1.5 e\text{Å}^{-3}$ , the background was below  $1 e\text{Å}^{-3}$ . Another three-dimensional difference electron density map D2 was also computed, which indicated

that the apparent thermal motions and termination of series effects around Br had been well accounted for (Fig. 3). This difference map showed no peaks higher than  $1.6 \text{ e}\text{\AA}^{-3}$ , but many peaks occurred at a height of about  $1 \text{ e}\text{\AA}^{-3}$ . When the expected parameters for hydrogen atom positions were evaluated, about three-fourths of these atoms fell on peaks greater than  $1 \text{ e}\text{\AA}^{-3}$ .

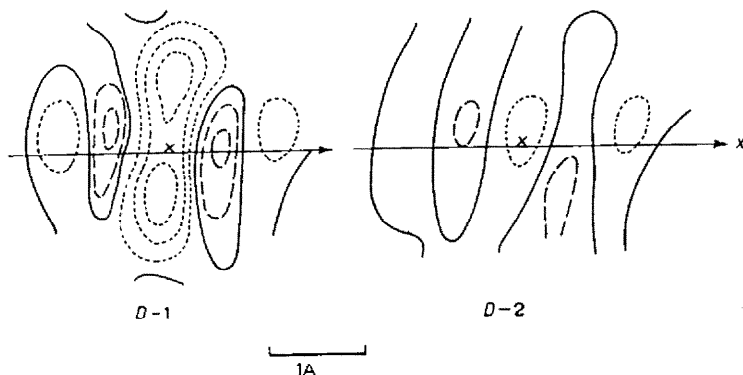


FIG. 3. Difference maps cut at  $9/20 \text{ c}$ . showing anisotropic motion of Br-2. Contours intervals of  $1 \text{ e}/\text{\AA}^3$ . Dashed lines are negative and dotted lines are positive contours.

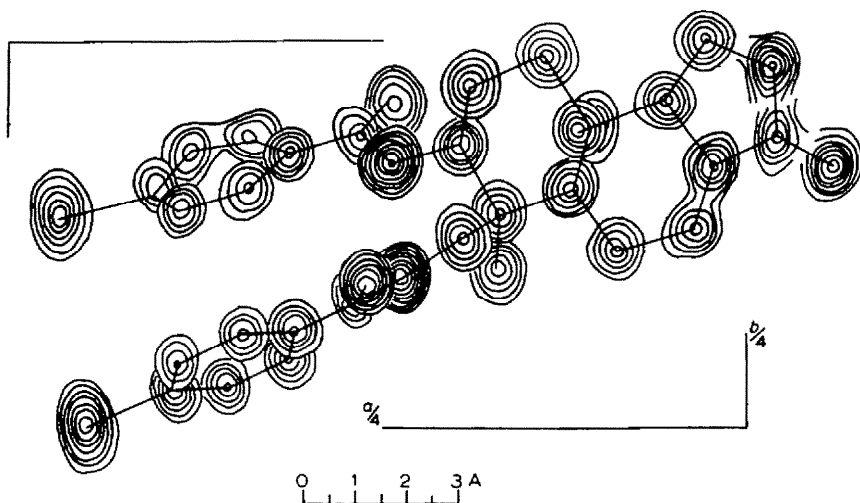


FIG. 4. Final electron density map. Contours are at intervals of  $1 \text{ e}/\text{\AA}^3$  (except near bromines). The lowest contour is at a height of  $2 \text{ e}/\text{\AA}^3$ . Contours around bromines are at intervals of  $5 \text{ e}/\text{\AA}^3$  upwards.

Further refinement of the structure is thus surely possible. The introduction of hydrogen atoms and possibly of anisotropic thermal parameters for other atoms than Br, especially atom O-3, would no doubt improve the already satisfactory agreement. In lieu of a complete table of the 1430 reflections, the agreement for different classes<sup>7</sup> of reflections is shown in Table 1. As a further check of the structure, a detailed examination was made of the 113 planes in Columns *a* and *b* of Table 1. Due to an error, we discovered that five of these planes, all having large indices, had

<sup>7</sup> R. E. Dickerson, P. J. Wheatley, P. A. Howell and W. N. Lipscomb, *J. Chem. Phys.* 27, 200 (1957).

been entered with either a wrong power of 10 or of 2 into the observed structure factor list used for refinements. However, the weighting factors for these five planes were small in the least-squares treatment, and we have shown that the maximum

TABLE 1. AGREEMENT FACTOR  $R$  FOR ALL CLASSES OF REFLECTIONS\*

Class	$R$	$n$	$a$	$b$
All	0.182	1430	94	19
$0kl$	0.143	29	2	0
$h0l$	0.207	268	31	2
$hk0$	0.175	186	9	6
$h$ odd	0.178	719	42	10
$k$ odd	0.167	649	28	12
$l$ odd	0.171	680	46	7
$h + k$ odd	0.180	710	42	10
$k + l$ odd	0.192	731	46	11
$h + l$ odd	0.180	721	54	13
$h + k + l$ odd	0.172	694	42	9

\* Two reflections were outside the range of  $\sin \theta$  for which computations were made. The number of reflections in each class is  $n$ . The number of planes showing  $|F_o| > 2|F_c|$  is in Column  $a$ , and the number showing  $|F_o| < (\frac{1}{2})|F_c|$  is in column  $b$ .

effect on the electron density maps is less than  $0.2 \text{ e}\text{\AA}^{-3}$ , even in the unlikely event that the errors are all at their maximum at a given point. Hence the effect of these errors is negligible, and their correction reduces  $R$  to 0.176. As an additional check on the over-all agreement, we have listed  $R$  as the scattering angle increases (Table 2).

TABLE 2. VARIATION OF  $R$  WITH  $\sin \theta$ 

Range of $\sin \theta$	$R$	$n$	$\Sigma  F_o $
0.00-0.15	0.249	14	606
0.15-0.30	0.136	91	4741
0.30-0.45	0.132	208	7283
0.45-0.60	0.140	361	7635
0.60-0.75	0.242	409	6574
0.75-0.90	0.244	242	2923
0.90-1.00	0.278	100	903

The five incorrectly listed planes were omitted. A final refinement in which all hydrogen atoms were included except those of the two methyl groups led to values of  $R = 0.163$  and  $r = 0.157$  and decreased the numbers in columns  $a$  and  $b$  of Table 1 by about a factor of two.

Isotropic temperature factor constants  $B$  in the formula  $\exp(-B \sin^2 \theta / \lambda^2)$  are shown in Fig. 7 for each atom. We have previously observed large least-square increases of  $B$  for atoms incorrectly placed in the structure<sup>8</sup> at early stages of the

<sup>8</sup> F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr. and W. N. Lipscomb, *J. Chem. Phys.* **28**, 56 (1958).

TABLE 3. CO-ORDINATES OF ATOMS IN 1 MOLECULE

Atom	$x/a$	$y/b$	$z/c$
Br-1	0.0318	0.0445	0.0274
Br-2	0.0507	0.4981	0.4427
C-1	0.3621	0.4561	0.5750
C-2	0.3096	0.3831	0.5504
C-3	0.3047	0.2312	0.4213
C-4	0.3301	0.0463	0.5190
C-5	0.3802	0.1158	0.5619
C-6	0.4105	0.9669	0.6603
C-7	0.4616	0.0127	0.7006
C-8	0.4738	0.1783	0.7002
C-9	0.4420	0.3465	0.6312
C-10	0.3915	0.2704	0.6824
C-11	0.4711	0.5038	0.7610
C-12	0.5210	0.2607	0.7655
C-13	0.3039	-0.0163	0.7209
C-14	0.3288	0.8996	0.3514
C-15	0.3857	0.2563	0.9257
C-16	0.0961	0.1007	0.0716
C-17	0.1140	0.0627	0.2924
C-18	0.1600	0.1192	0.3204
C-19	0.1873	0.2145	0.1579
C-20	0.1670	0.2416	-0.0253
C-21	0.1213	0.2226	-0.0471
C-22	0.2361	0.2631	0.1832
C-23	0.1101	0.6021	0.5485
C-24	0.1458	0.5978	0.4290
C-25	0.1884	0.6902	0.4962
C-26	0.1917	0.7543	0.6983
C-27	0.1556	0.7445	0.8273
C-28	0.1131	0.6716	0.7611
C-29	0.2342	0.8291	0.7784
O-1	0.2560	0.1850	0.3759
O-2	0.2592	0.3427	0.0611
O-3	0.2409	0.8611	0.9749
O-4	0.2630	0.8842	0.6400
O-5	0.5188	0.4308	0.7802
O-6	0.5586	0.1735	0.7956

refinement. In the present study we found that for atoms placed between 0.15 and 0.35 Å from their correct positions, the square of the full shift in temperature factor is roughly proportional to the full shift in position. Thus our earlier experience, that the behavior of temperature factors is a method of picking out incorrectly placed atoms, has been confirmed.

A list of co-ordinates for atoms in one molecule is given in Table 3. The observed amplitudes of scattering are listed in Table 4.

TABLE 4. OBSERVED STRUCTURE FACTORS ON ABSOLUTE SCALE

(h0l)

	$l = 3$	$l = 4$	$l = 3$	$l = 2$	$l = 1$	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$h = 0$	21.7	24.3	38.2	51.6	68.1	(640.0)	68.1	51.6	38.2	24.3	21.7
1	—	—	—	144.7	34.4	(cut off)	78.4	146.1	21.7	21.9	20.1
2	23.0	23.3	38.1	63.6	86.8	32.4	39.2	105.6	44.3	20.4	20.1
3	23.0	23.3	16.5	129.3	45.4	14.8	26.5	122.4	13.6	5.6	—
4	29.3	28.2	55.8	47.6	77.7	45.5	11.5	42.5	27.0	6.3	20.3
5	31.7	28.3	50.2	72.2	67.9	21.6	25.1	13.8	34.0	27.2	20.3
6	28.5	19.0	8.0	20.0	17.9	4.0	23.2	7.3	35.3	23.5	20.6
7	23.3	26.7	56.7	21.6	56.6	4.5	13.9	—	9.2	8.0	—
8	23.6	—	42.3	39.8	71.0	16.5	68.8	—	5.6	8.6	20.9
9	—	—	—	52.0	37.8	68.8	15.3	52.6	15.4	—	—
10	—	23.0	—	50.9	23.9	84.3	14.1	41.6	16.1	18.2	—
11	—	17.6	7.1	7.0	18.2	54.3	60.7	101.7	10.3	18.8	—
12	—	6.8	—	28.2	17.0	63.4	7.6	90.7	12.6	46.8	—
13	—	10.0	10.8	21.6	7.6	44.4	17.0	94.9	6.2	21.7	—
14	—	4.9	37.6	23.0	29.9	140.0	12.4	55.2	9.2	48.9	—
15	—	5.2	8.9	19.4	38.7	47.8	58.8	51.9	6.9	36.4	29.3
16	—	5.4	20.4	18.8	52.3	17.7	43.5	24.2	20.6	29.6	20.3
17	—	11.7	25.6	9.5	27.5	10.9	47.3	53.9	7.3	14.7	28.2
18	—	8.5	21.7	—	50.4	11.4	25.6	—	16.5	—	27.6
19	—	—	27.8	8.7	44.9	26.1	77.2	—	22.2	10.9	26.8
20	—	—	—	—	54.5	23.2	28.9	21.7	15.8	17.2	—
21	—	6.1	29.2	15.5	16.7	23.9	43.5	18.7	25.0	25.8	—
22	—	12.7	—	—	28.2	8.0	22.0	48.5	25.1	—	—
23	—	15.2	10.1	—	—	13.2	20.8	8.3	—	17.2	—
24	—	15.1	18.9	—	—	12.5	—	35.8	7.8	16.6	—
25	—	5.4	—	29.7	29.9	7.7	—	19.1	—	22.7	—
26	—	8.6	—	14.1	16.7	7.7	—	22.2	7.5	21.4	—
27	—	7.1	—	16.1	—	15.7	19.1	10.1	7.2	14.0	—
28	—	—	9.7	—	24.1	11.0	21.3	16.7	8.7	12.7	—
29	—	—	—	8.3	23.4	—	27.7	14.7	11.4	7.5	—
30	—	—	—	—	20.1	—	32.0	—	21.5	8.9	—
31	—	—	11.5	—	12.4	—	29.6	—	12.3	—	—
32	—	—	9.4	8.1	12.7	—	28.7	—	16.2	—	—
33	—	—	—	—	11.5	—	21.7	—	3.4	—	—
34	—	—	—	7.0	9.1	9.8	20.3	4.1	—	—	—
35	—	—	—	—	—	—	12.7	—	—	—	—
36	—	—	—	—	—	14.5	6.9	—	—	—	—

(h1l)

$h = 0$	16.6	15.2	17.5	44.5	20.6	—	20.6	44.5	17.5	15.2	16.6
1	—	30.0	48.4	69.0	60.0	58.0	90.3	37.5	20.9	33.3	—
2	—	17.5	30.3	70.1	150.6	38.1	94.9	56.0	18.4	19.0	16.8
3	16.6	9.0	29.6	29.7	114.0	33.8	73.9	37.8	47.4	29.5	—
4	14.0	14.8	54.9	41.9	102.3	34.6	64.3	27.4	30.7	30.7	17.0
5	—	18.9	35.6	9.9	106.4	1.0	69.1	28.8	54.6	21.9	14.2
6	16.8	8.3	3.9	42.2	67.2	22.3	115.2	17.1	36.8	7.9	14.4
7	—	19.3	6.9	37.6	85.1	10.1	70.7	20.2	45.7	12.3	—
8	—	18.3	30.4	34.7	24.1	37.4	88.4	13.0	30.7	19.7	—
9	—	19.0	22.5	67.5	25.6	28.8	74.8	30.0	52.1	—	—
10	—	23.8	5.8	50.2	16.7	41.5	67.6	22.2	38.5	11.1	—
11	—	20.3	13.9	42.1	18.2	45.5	45.6	12.4	26.4	13.4	—
12	—	9.9	11.5	57.2	7.4	30.0	54.5	20.3	17.6	16.9	—
13	—	10.3	8.7	47.0	31.5	87.0	36.1	26.0	13.4	17.2	—
14	—	14.4	12.5	49.0	9.6	37.0	39.0	28.8	8.7	7.2	—
15	—	12.4	9.5	11.0	10.5	46.1	39.7	25.9	32.1	12.7	—
16	—	—	6.6	33.0	36.3	22.8	65.7	24.0	26.8	8.3	—
17	—	13.4	10.3	—	19.1	15.3	33.9	—	28.1	26.2	—
18	—	16.4	14.5	18.8	16.5	—	33.0	22.8	36.5	23.1	—



Table 4 (Cont'd.).

(h1) contd.

	$l = 3$	$l = 4$	$l = 3$	$l = 2$	$l = 1$	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$h = 19$	—	8.3	7.3	21.0	19.8	—	40.9	12.2	39.3	8.6	—
20	—	12.0	15.4	29.2	15.5	25.9	42.1	24.0	10.3	8.6	—
21	—	13.3	15.8	37.3	—	36.0	27.0	24.3	24.6	12.5	—
22	—	—	11.7	27.5	16.0	39.9	22.5	17.7	23.9	—	—
23	—	13.1	16.2	35.8	18.4	49.0	26.8	34.4	13.6	8.2	—
24	—	—	8.0	26.2	—	40.3	11.7	29.5	13.4	11.0	—
25	—	—	—	13.6	19.8	20.6	15.8	33.5	9.8	5.8	—
26	—	—	12.3	16.2	28.0	28.8	10.5	24.3	9.5	9.2	—
27	—	—	10.0	22.3	12.9	14.5	—	30.4	7.0	9.2	—
28	—	—	9.7	—	17.9	16.6	—	23.0	8.6	8.3	—
29	—	—	12.8	8.3	9.6	12.7	—	11.6	10.8	7.2	—
30	—	—	12.2	—	9.8	10.5	—	8.3	13.4	—	—
31	—	—	10.0	—	11.5	6.3	—	—	8.1	—	—
32	—	—	9.2	—	9.8	8.5	—	9.2	9.8	—	—
33	—	—	—	7.2	7.6	5.6	—	8.1	4.2	—	—
34	—	—	—	—	—	14.5	—	19.3	—	—	—
35	—	—	—	—	—	14.5	6.7	—	—	—	—
36	—	—	—	—	—	10.9	—	—	—	—	—

(h2)

	$l = 4$	$l = 3$	$l = 2$	$l = 1$	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$h = 0$	17.1	11.7	54.2	50.9	44.7	50.9	54.2	11.7	17.1	—
1	17.3	27.5	77.4	49.0	87.0	26.5	61.8	16.1	11.8	—
2	—	33.9	34.1	77.7	104.8	60.7	67.6	31.8	17.9	—
3	21.3	36.7	42.8	47.8	92.9	56.2	56.9	38.2	16.9	21.3
4	8.2	26.4	28.3	56.9	45.2	38.0	25.9	10.9	24.0	—
5	21.9	41.5	—	16.7	22.7	48.0	70.8	25.0	13.1	—
6	13.1	26.1	56.8	57.6	29.6	19.8	17.6	23.2	—	—
7	—	43.5	45.9	21.5	30.6	35.9	24.0	27.0	25.5	21.7
8	6.9	14.0	35.8	33.5	38.5	64.3	46.2	22.2	14.5	21.7
9	9.6	22.6	23.4	30.8	26.5	26.1	40.5	22.8	6.5	21.7
10	4.7	8.4	40.9	37.8	52.1	32.7	48.5	—	16.8	21.7
11	15.5	6.7	21.9	31.3	61.4	21.3	60.6	17.9	21.6	—
12	—	20.3	19.0	6.9	63.1	28.4	45.7	15.8	24.4	—
13	10.4	15.3	11.5	25.3	41.5	13.6	61.8	12.2	24.8	—
14	—	—	—	26.1	24.7	15.8	41.3	—	22.7	—
15	—	22.2	—	25.8	25.8	18.2	33.5	21.4	—	—
16	—	22.8	21.9	27.0	32.8	31.1	27.2	13.6	13.1	—
17	12.3	19.3	22.5	45.4	15.1	26.3	32.1	13.9	25.9	—
18	5.2	22.9	—	47.3	—	39.0	24.9	24.0	9.4	—
19	8.0	13.6	13.6	28.7	18.1	59.5	27.7	27.8	12.7	—
20	10.2	11.5	31.1	37.0	—	19.1	—	—	13.1	—
21	—	10.1	14.2	19.6	—	40.2	38.9	8.0	13.0	—
22	8.2	10.3	28.3	12.7	19.0	27.0	33.0	8.0	8.2	—
23	8.9	14.2	20.2	12.9	—	10.0	24.8	14.0	15.7	—
24	—	—	16.2	15.1	16.1	—	9.9	9.4	21.3	—
25	12.5	—	—	—	—	—	25.4	—	14.2	—
26	—	13.7	17.9	15.1	12.0	10.5	12.7	—	9.3	—
27	8.2	9.0	—	18.2	11.9	14.1	24.6	7.3	19.0	—
28	—	—	7.7	17.7	11.7	15.1	23.6	8.1	16.8	—
29	—	6.9	—	24.1	—	15.1	8.4	15.0	—	—
30	—	7.3	—	13.4	—	25.6	6.4	9.5	—	—
31	—	5.9	—	12.7	—	22.5	9.5	10.6	—	—
32	—	—	—	18.6	7.0	20.6	—	11.9	—	—
33	—	—	6.4	—	—	17.7	—	—	—	—
34	—	—	—	—	—	6.0	—	—	—	—
35	—	—	—	—	7.8	—	—	—	—	—

Table 4 (Cont'd.).

(h3l)

	<i>l</i> = 5	<i>l</i> = 4	<i>l</i> = 3	<i>l</i> = 2	<i>l</i> = 1	<i>l</i> = 0	<i>l</i> = 1	<i>l</i> = 2	<i>l</i> = 3	<i>l</i> = 4	<i>l</i> = 5
<i>h</i> = 0	17.0	33.7	13.7	58.9	15.3	—	15.3	58.9	13.7	33.7	17.0
1	17.0	20.3	23.9	15.0	26.5	16.5	9.6	6.6	—	33.8	18.6
2	17.0	4.2	20.7	26.2	—	28.7	46.4	33.1	32.6	9.3	—
3	17.0	13.0	23.9	50.3	35.9	25.2	19.4	44.4	25.7	10.4	—
4	—	15.1	21.7	53.4	48.3	26.7	77.9	23.1	—	24.7	—
5	—	6.8	12.3	23.9	62.4	14.8	62.4	23.6	26.5	20.4	—
6	—	—	24.0	33.2	44.7	33.5	65.0	47.6	27.8	9.9	—
7	—	10.6	12.6	23.9	30.1	40.0	39.2	24.9	31.8	20.4	—
8	—	8.0	9.0	19.4	23.9	14.1	99.7	19.4	36.5	23.5	—
9	—	13.1	9.4	15.1	32.7	21.3	71.2	18.5	11.9	17.3	—
10	—	8.5	—	27.4	17.2	34.3	44.9	32.9	24.8	12.0	—
11	—	13.7	13.4	34.0	17.0	35.4	22.9	15.0	36.8	9.0	—
12	—	14.0	12.9	22.0	16.3	45.8	19.8	19.1	26.2	—	—
13	—	18.6	10.3	29.5	19.4	16.8	20.1	27.2	17.0	23.5	—
14	—	—	10.6	14.5	23.7	35.6	16.5	14.4	—	23.8	—
15	—	—	7.3	21.6	12.9	15.8	22.2	15.9	—	17.2	—
16	—	—	—	—	9.1	25.1	21.7	25.9	15.3	—	—
17	—	—	—	10.7	—	—	22.5	15.9	24.0	9.4	—
18	—	—	10.0	—	25.3	—	30.6	14.4	17.3	10.0	—
19	—	7.6	—	—	21.0	—	28.0	—	24.3	9.9	—
20	—	—	—	18.1	20.3	14.7	22.2	16.5	31.5	—	—
21	—	—	10.3	13.6	—	13.7	27.5	28.8	27.0	—	—
22	—	—	—	—	—	26.1	25.6	9.3	18.9	—	—
23	—	5.2	9.7	13.2	10.5	16.6	—	9.3	13.7	—	—
24	—	5.2	9.5	13.0	19.8	26.5	10.0	—	13.3	—	—
25	—	—	—	15.9	—	24.8	18.9	19.9	14.5	—	—
26	—	9.9	9.0	7.8	—	25.1	14.3	19.3	12.0	8.2	—
27	—	—	—	7.7	—	15.1	9.8	18.4	11.2	—	—
28	—	6.8	10.1	7.3	—	6.6	—	8.7	7.3	—	—
29	—	4.5	—	—	—	6.3	—	9.5	6.6	—	—
30	—	—	—	—	9.8	7.3	—	7.3	7.8	—	—
31	—	—	—	—	7.6	6.9	—	—	6.9	—	—
32	—	—	—	—	—	—	—	—	—	—	—
33	—	—	—	—	—	8.9	—	4.6	—	—	—
34	—	—	—	—	—	7.8	—	—	—	—	—
35	—	—	—	—	9.8	—	—	—	—	—	—

(h4l)

	<i>l</i> = 4	<i>l</i> = 3	<i>l</i> = 2	<i>l</i> = 1	<i>l</i> = 0	<i>l</i> = 1	<i>l</i> = 2	<i>l</i> = 3	<i>l</i> = 4
<i>h</i> = 0	11.7	14.2	28.2	31.1	33.4	31.1	28.2	14.2	11.7
1	24.8	12.6	18.5	20.3	37.6	28.0	36.1	21.4	23.7
2	8.6	15.8	28.0	20.6	37.8	28.7	27.8	21.5	23.8
3	11.7	8.7	7.3	38.0	30.0	21.0	33.0	7.8	11.8
4	—	6.7	33.7	43.0	12.8	44.5	21.4	30.3	16.9
5	15.8	33.7	7.5	30.8	22.8	30.4	20.8	15.4	12.1
6	7.2	11.1	6.6	37.3	17.0	7.9	21.3	—	17.2
7	7.2	24.0	6.1	17.9	21.5	37.0	14.2	19.8	—
8	7.3	—	18.5	21.0	37.3	22.5	—	20.3	12.4
9	—	—	15.5	18.2	28.9	23.2	15.0	22.6	17.8
10	—	14.8	—	17.4	20.0	17.2	36.3	20.9	14.8
11	—	8.4	10.1	12.7	27.3	20.3	15.8	—	14.8
12	10.0	11.4	8.4	—	35.8	—	12.9	21.7	14.9
13	—	8.7	8.6	—	—	15.1	35.0	15.9	9.4
14	10.1	—	10.7	18.6	16.2	—	17.6	—	—
15	14.9	11.9	8.9	12.0	16.9	15.8	19.3	22.8	—
16	—	—	7.8	19.4	17.4	—	28.0	—	11.3

Table 4 (Cont'd.).

(h4l) contd.

	$l = 4$	$l = 3$	$l = 2$	$l = 1$	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
$h = 17$	—	—	14.5	12.4	23.0	19.4	8.7	—	11.1
18	—	—	17.9	—	—	15.8	—	—	8.9
19	—	12.2	—	15.8	13.6	15.8	8.1	—	7.1
20	—	—	8.1	15.8	9.9	19.8	18.1	12.5	6.8
21	—	—	10.4	11.7	7.0	12.9	8.0	9.7	7.9
22	—	7.6	10.4	—	—	11.7	—	—	6.2
23	—	7.5	—	—	—	11.7	—	—	11.1
24	6.1	11.1	7.8	—	9.8	—	17.7	10.1	14.4
25	7.2	7.0	—	—	—	—	26.0	—	—
26	—	8.6	7.3	—	9.3	—	6.7	—	7.3
27	—	6.2	6.9	—	9.0	—	—	—	—
28	5.4	—	—	—	10.1	9.6	20.0	—	—
29	4.4	—	—	8.4	11.5	8.8	9.6	—	—
30	—	—	—	8.6	6.6	9.3	10.3	—	—
31	—	—	—	7.6	—	—	7.8	—	—
32	—	—	—	—	—	9.3	—	—	—

(h5l)

	$l = 4$	$l = 3$	$l = 2$	$l = 1$	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
$h = 0$	7.6	—	—	10.3	—	10.3	—	—	7.6
1	12.7	9.8	8.4	—	12.6	—	25.1	16.8	7.6
2	9.3	9.8	13.3	17.2	5.0	—	14.7	16.8	12.1
3	8.5	9.8	—	12.2	20.6	—	18.2	—	10.2
4	—	—	—	8.8	17.0	15.1	12.5	10.8	10.2
5	8.6	—	11.3	8.8	13.6	15.3	15.0	15.8	10.2
6	8.6	—	29.8	29.9	24.2	35.6	18.5	—	14.9
7	8.6	—	27.5	10.8	—	25.6	26.2	15.9	7.8
8	—	11.9	15.3	25.6	7.7	25.8	34.6	9.0	—
9	—	11.9	7.7	9.8	10.0	26.1	—	14.4	9.4
10	—	9.0	—	10.0	22.0	26.5	18.1	8.0	14.8
11	—	12.0	13.2	10.0	6.6	16.0	—	8.0	9.3
12	—	8.0	8.6	—	6.7	—	—	8.0	—
13	—	11.2	13.5	11.5	6.7	—	—	—	—
14	—	8.0	8.7	11.7	13.6	12.9	—	—	—
15	—	—	8.7	11.7	11.9	24.4	—	—	—
16	—	—	—	—	—	10.0	—	—	—
17	—	—	8.1	—	14.0	—	—	—	—
18	—	—	—	—	8.6	14.1	—	9.5	—
19	—	—	—	10.0	7.0	—	9.0	11.9	8.3
20	—	—	—	11.7	7.0	—	—	9.0	—
21	—	—	—	—	6.9	—	8.6	—	6.5
22	—	—	7.7	—	—	—	—	11.5	4.8
23	—	—	—	—	8.2	—	8.0	7.6	4.2
24	—	—	7.0	—	9.7	17.2	—	7.0	—
25	—	—	—	—	13.0	—	—	7.5	—
26	—	—	—	—	6.0	—	—	5.5	—
27	—	—	—	—	5.7	6.9	—	3.6	—
28	—	—	—	—	4.5	6.0	—	—	—
29	—	—	—	—	—	6.9	6.0	—	—

Table 4 (Cont'd.).

(h6l)

	$l=4$	$l=3$	$l=2$	$l=1$	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
$h=0$	—	8.0	—	14.1	—	14.1	—	8.0	—
1	—	—	8.0	—	13.2	10.3	—	—	—
2	—	—	8.0	9.8	13.2	10.3	13.2	16.2	—
3	—	—	—	9.8	—	28.9	—	11.2	7.5
4	8.5	11.9	—	16.5	23.0	10.3	16.2	8.0	9.9
5	7.5	—	—	16.5	—	11.7	18.1	11.2	8.3
6	7.5	—	10.4	—	18.7	11.7	13.2	16.2	—
7	—	—	10.4	19.6	6.8	16.5	16.2	11.1	—
8	—	—	—	—	13.8	10.5	18.1	—	—
9	—	12.9	10.6	—	13.8	10.5	—	7.8	—
10	—	11.1	—	—	14.0	16.7	—	7.8	—
11	—	9.0	8.1	12.0	—	12.0	—	7.6	—
12	—	8.9	—	—	7.0	16.0	—	—	—
13	—	10.9	9.3	—	9.5	10.5	—	8.6	—
14	—	—	8.0	10.5	8.6	—	—	—	—
15	—	—	7.2	—	—	—	—	—	—
24	—	—	—	—	—	—	—	3.4	—

(h7l)

	$l=3$	$l=2$	$l=1$	$l=0$	$l=1$	$l=2$
$h=0$	—	—	—	—	—	—
1	—	—	—	—	—	—
2	—	—	10.5	—	12.9	—
3	—	—	—	—	—	—
4	—	—	—	—	—	—
5	—	—	—	—	—	9.0
6	—	—	—	7.0	—	11.0
7	—	—	—	—	—	9.0
8	—	—	—	—	—	—
9	—	—	9.8	8.6	—	—
10	8.1	—	—	7.0	—	—
11	—	8.7	—	8.5	—	—
12	—	10.7	—	—	—	—
13	—	8.4	—	—	—	—
14	—	—	—	9.2	—	—

## DISCUSSION

The iresin molecule (IV) was found to have the angular methyl attached to C-10. Rings A and B are fused *trans*. The fact that the OH group on C-3, the methylene group on C-4 and the 5-6 bond are all *cis* has been confirmed. Ring A is in chair form. Rings B and C are very roughly in the same plane, except for atom C-5. However, the H on C-9 and the methyl C-15 are *trans* (Fig. 5), in agreement with the chemical results of Djerassi *et al.*<sup>5</sup> The shape of the molecule and its packing in the crystal can be seen in Figs. 5 and 6.

The standard deviations of the atomic position parameters, calculated from the residuals in the least-squares refinement, were essentially isotropic. Their values (Fig. 7) led to estimated standard deviations of 0.035, 0.050, 0.042 Å in the Br-C, C-C and C-O bond lengths, respectively. As an independent estimate, the mean

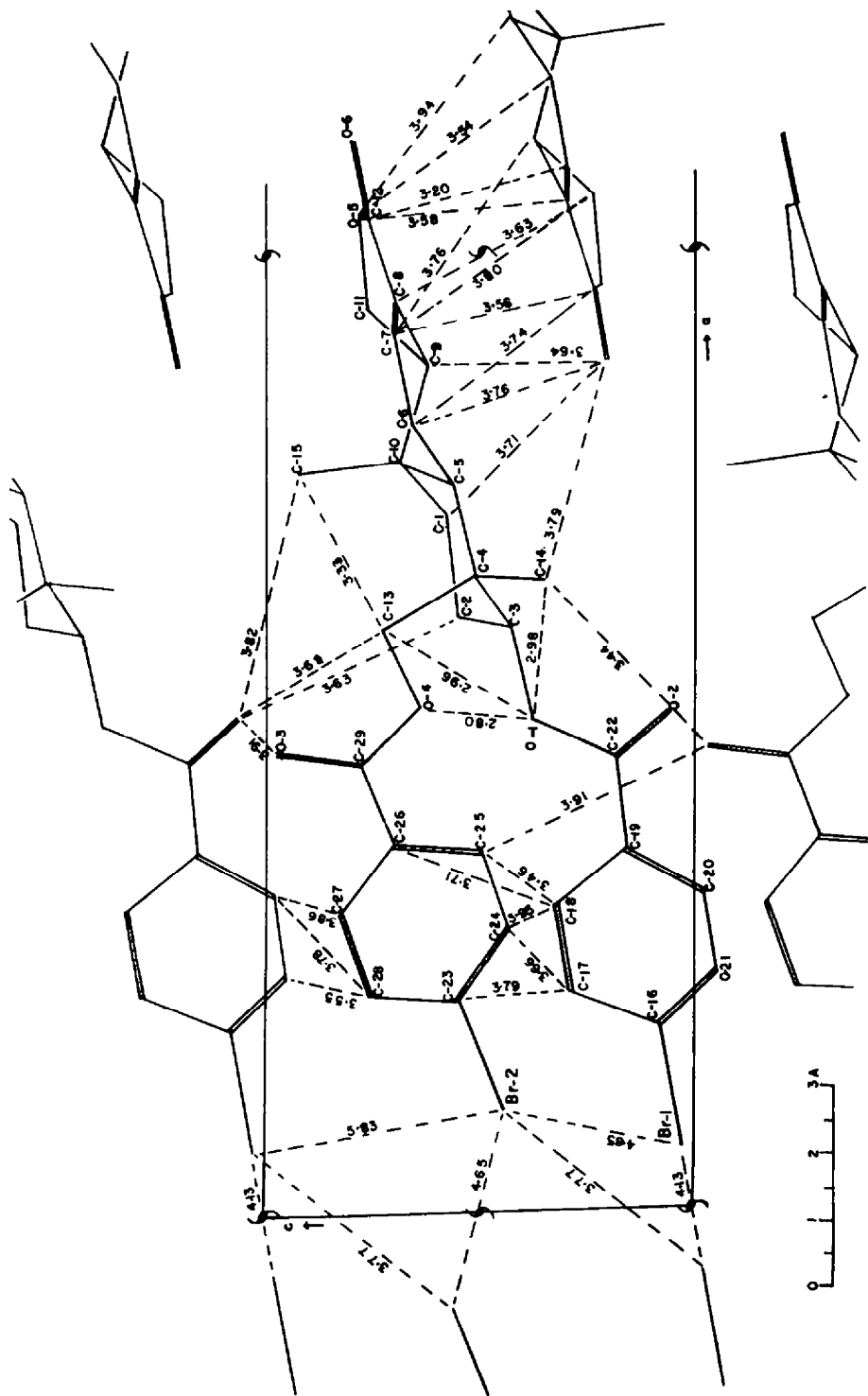


Fig. 5. Diagram showing projection of the molecule along the *b* axis, its packing and intermolecular distances.

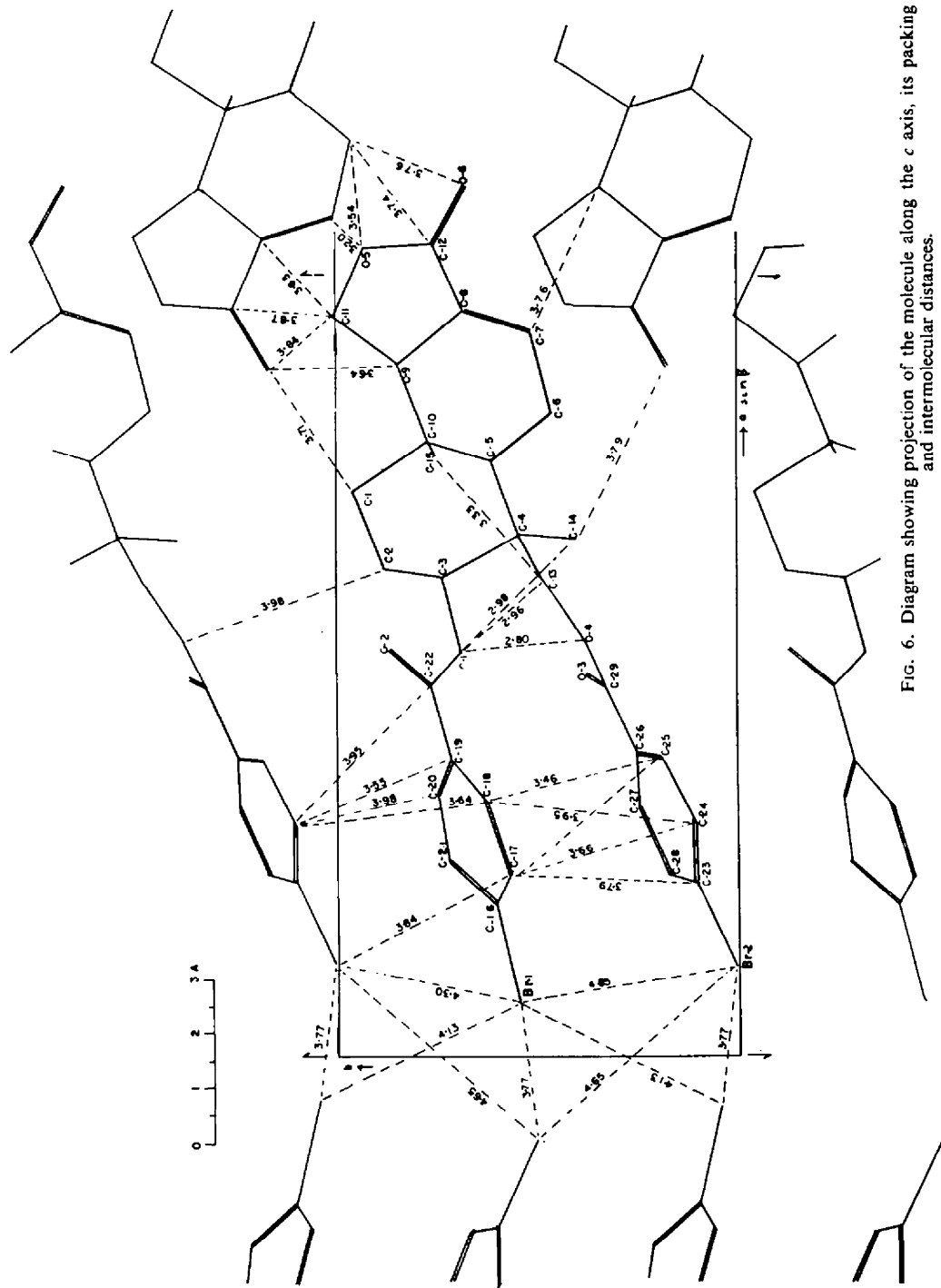
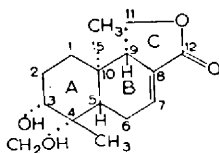


FIG. 6. Diagram showing projection of the molecule along the *c* axis, its packing and intermolecular distances.

distance of 1.395 Å for the twelve C–C bonds in the two benzene rings gave a standard deviation of 0.068 Å, quite reasonably a bit higher than the least-squares value of 0.050 Å obtained by neglect of off-diagonal terms in solving the normal equations.



IV

Standard deviations in bond angles (Fig. 7) were about 4°. The fact that bonds C-22...O-2, C-29...O-3, C-29...O-4, C-12...O-6 and C-12...O-5 are significantly shorter than a single C...C bond of 1.54 Å, establishes that O-2, O-3, O-4, O-5 and O-6 are oxygen atoms. Also, their higher electron density (Fig. 4) and yet sensible temperature factors (Fig. 7) further confirms this point. The shortness of the bond C-8...C-7, as well as the general planarity of ring B establishes the position of the double bond in ring B.

The benzene ring attached to Br-1 and the corresponding carboxyl group and atom C-3 all lie in the same plane. The maximum distance of any one atom from this plane is 0.2 Å. In contrast, the benzene ring attached to Br-2 does not lie in the same plane as its corresponding carboxyl group. The maximum distance of any one atom from the best plane representing the benzene ring was 0.10 Å. The carboxyl group, methylene group and atom C-4 are roughly co-planar to within 0.5 Å. The angle between the normal to the benzene ring attached to Br-2 and the plane through the corresponding carboxyl group is 59°. The five-membered ring and atom O-6 was planar to within 0.09 Å, except for atom C-9, which is 0.44 Å from this mean plane. Exactly the same degree of non-planarity is found in similar five-membered rings.<sup>9</sup> As a general rule, one of the two carbon atoms furthest away from the oxygen is displaced by about 0.4 Å from the plane of the other four atoms. Atoms C-6, C-7 and C-10 lie on the same side of and between 0.25 to 0.35 Å away from the five membered ring plane.

Inter-molecular distances less than 4.0 Å, shown in Figs. 5 and 6, indicate no contacts significantly less than Van der Waals distances. All close C...C contacts are just greater than 3.4 Å, the recognized Van der Waals C...C distance. The close C...O contact of 3.20 Å between molecules related by a twofold screw is also just greater than the C...O Van der Waals contact distance of 3.1 Å. Within the molecule the methylene group C-13 and the methyl C-15 approach to 3.33 Å, and the oxygen O-1 approaches the methylene C-13 and methyl C-14 to 2.96 and 2.98 Å, respectively. Similarly, the two ether oxygens O-1 and O-4 approach to exactly the limit set by the sum of their radii, presumably because they are unhindered by hydrogen atoms. The angle between the normals of the two benzene rings is 50½°, which compares very favourably with about 52° in naphthalene and anthracene. Had it not been so difficult to obtain good single crystals, we would marvel at how well Nature is able to pack such an awkwardly shaped molecule.

<sup>9</sup> F. Jellinek, *Acta Cryst.* **10**, 277 (1957); S. Furberg, *Ibid.* **3**, 325 (1950); and L. A. Beevers and W. Cochran, *Proc. Roy. Soc. A* **190**, 257 (1947).

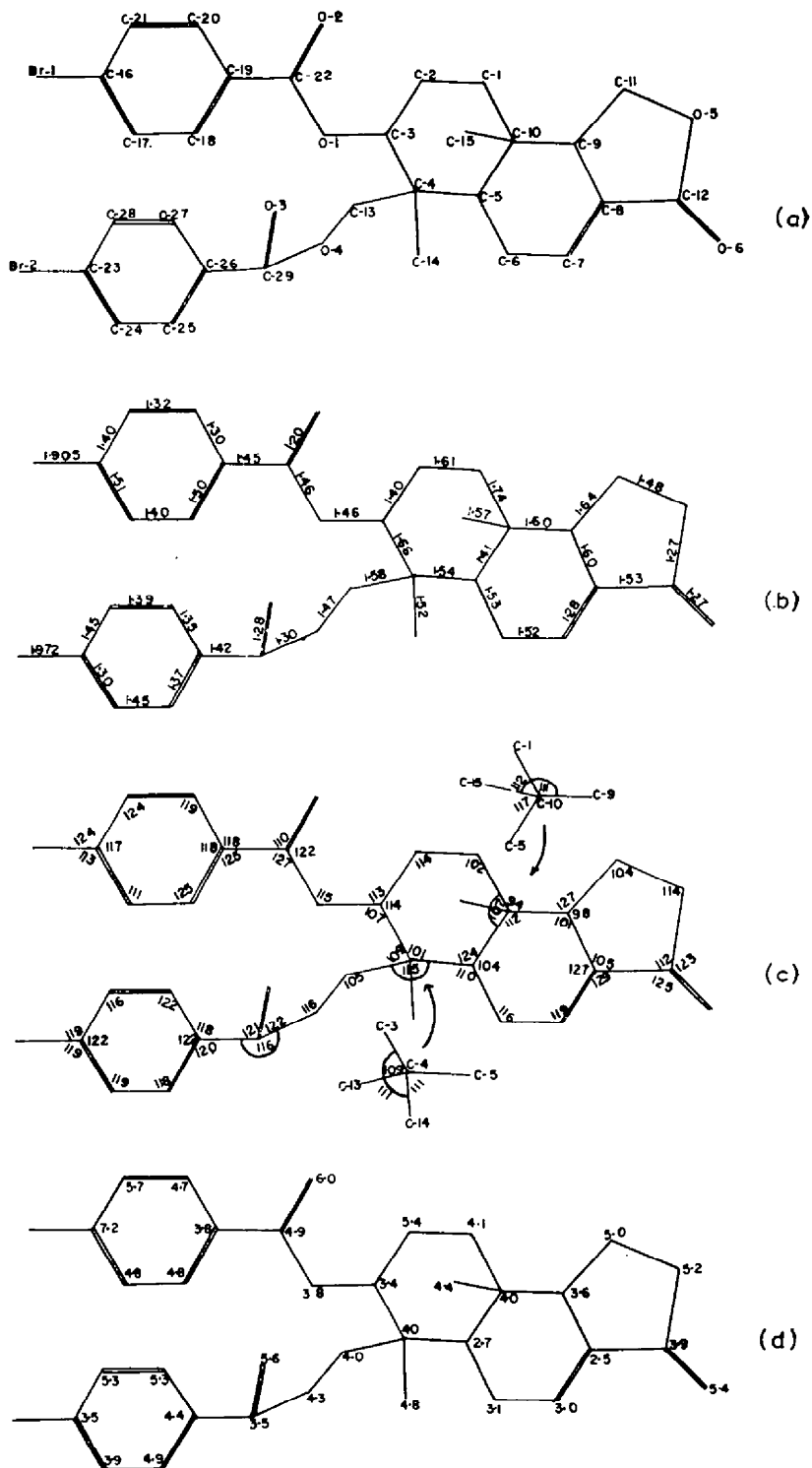


FIG. 7. Diagram (a) gives the atomic names. Diagram (b) shows bond length. Diagram (c) shows bond angles. Diagram (d) shows final isotropic temperature factors.



## ANISOTROPIC THERMAL MOTION OF THE Br ATOMS

The determination of amplitudes of vibration by least-squares methods for individual atoms<sup>10,11</sup> is adopted here as being more suitable than the analysis of the motion of a rigid molecule<sup>12</sup> and to the analysis of electron density gradients in difference projections<sup>13</sup> or three-dimensional difference maps.<sup>14</sup> For an isotropic atom the atomic amplitude of scattering is reduced by  $\exp(-\mathbf{B} \sin^2 \theta/\lambda^2)$  where  $\mathbf{B}$  is related to the mean square amplitude of vibration by  $\mathbf{B} = 8\pi^2\mu^2$ , and is usually expressed in units of  $\text{\AA}^2$ . When the motion is anisotropic, the usual form is  $\exp[-(\beta_1 h^2 + \beta_2 k^2 + \beta_3 l^2 + \beta_4 hk + \beta_5 kl + \beta_6 hl)]$  where the  $\beta$ 's are determined from the experimental data by the least-squares treatment. If we substitute  $A = 4\beta_1/a^{*2}$ ,  $B = 4\beta_2/b^{*2}$ ,  $C = 4\beta_3/c^{*2}$ ,  $D = 4\beta_4/a^*b^*$ ,  $E = 4\beta_5/b^*c^*$  and  $F = 4\beta_6/c^*a^*$ , then in an orthogonal system of axes, where  $2\phi$ ,  $2\psi$ ,  $2\omega$  is a point in reciprocal space and  $\phi^2 + \psi^2 + \omega^2 = 1$ , we can express  $\mathbf{B}$  as

$$\mathbf{B} = A\phi^2 + B\psi^2 + C\omega^2 + D\phi\psi + E\psi\omega + F\omega\phi \quad (1)$$

The values of  $\phi$ ,  $\psi$  and  $\omega$  which define the directions of the principal axes of the ellipsoid of vibration are given by the simultaneous solutions of

$$\left. \begin{aligned} (2A - \lambda)\phi + D\psi + F\omega &= 0 \\ D\phi + (2B - \lambda)\psi + E\omega &= 0 \\ F\phi + E\psi + (2C - \lambda)\omega &= 0 \end{aligned} \right\} \quad (2)$$

when  $\lambda$  is a root of

$$\lambda^3 + p\lambda^2 + q\lambda + r = 0$$

where

$$\begin{aligned} p &= -2(A + B + C) \\ q &= 4(AB + BC + CA) - (D^2 + E^2 + F^2) \\ r &= -2[4ABC - (AE^2 + BF^2 + CD^2) + DEF] \end{aligned} \quad (3)$$

Then the three solutions of the cubic equation correspond to the three principal directions of the ellipsoid of vibration.\*

The experimental data are the  $\beta$ 's listed in Table 5 corresponding to the bromine

TABLE 5. ANISOTROPIC THERMAL PARAMETERS FOR BROMINE ATOMS

	Br-1	Br-2		Br-1	Br-2
$\beta_1$	0.0012	0.0012	$A$	3.9	3.9
$\beta_2$	0.0522	0.0467	$B$	11.5	10.3
$\beta_3$	0.0636	0.0553	$C$	10.4	9.0
$\beta_4$	-0.0002	-0.0036	$D$	-0.2	-3.0
$\beta_5$	-0.0108	-0.0193	$E$	-2.0	-3.6
$\beta_6$	-0.0055	-0.0050	$F$	-4.0	-3.6

\* In the monoclinic system ( $b$  unique),  $A$ ,  $B$  and  $D$  remain as defined above, but  $C = (\csc \beta^*)[4\beta_3/c^{*2} - 4\beta_6(\cos \beta^*)/c^*a^* + 4\beta_1(\cos^2 \beta^*)/a^{*2}]$ ,  $E = (\csc \beta^*)[4\beta_5/b^*c^* - 4\beta_4(\cos \beta^*)/a^*b^*]$ , and  $F = (\csc \beta^*)[4\beta_6/c^*a^* - 8\beta_1(\cos \beta^*)/a^{*2}]$ .

when  $a$ ,  $b$  and an axis perpendicular to  $a$  and  $b$  are chosen as orthogonal axes.

<sup>10</sup> J. S. Rollett and D. R. Davies, *Acta Cryst.* **8**, 125 (1955).

<sup>11</sup> J. Waser, *Acta Cryst.* **8**, 731 (1955).

<sup>12</sup> D. W. J. Cruickshank, *Acta Cryst.* **9**, 754 (1956).

<sup>13</sup> W. Cochran, *Acta Cryst.* **4**, 81 (1951); *Ibid.* **4**, 408 (1951).

<sup>14</sup> Y. C. Leung, R. E. Marsh and V. Schomaker, *Acta Cryst.* **10**, 650 (1957).

co-ordinates given in Table 3. These values were converted to  $A \cdots F$  with the use of the unit cell parameters. The procedure, probably to be found useful in other similar cases, is as follows. For a given Br, substitute  $A \cdots F$  into (3), solve for the roots  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  by convenient graphical procedures, then substitute each root into (2) in order to find the proportions  $\phi : \psi : \omega$ , and then divide these final results by  $\sqrt{\phi^2 + \psi^2 + \omega^2}$  to obtain the actual direction cosines (Table 6) which can be inserted into equation (1) to find the magnitude of the temperature factor in the direction of each principal axis (Table 6).

TABLE 6. DIRECTION AND MAGNITUDE OF PRINCIPAL AXES OF ELLIPSOID OF VIBRATION

	$\lambda$	$\phi$	$\psi$	$\omega$	<b>B</b>	
Br-1	6.7	0.963	0.042	0.265	3.3	<i>L</i>
	20.7	0.230	-0.597	-0.769	10.3	<i>M</i>
	24.4	0.128	0.814	-0.571	12.1	<i>N</i>
Br-2	5.6	0.910	0.263	0.328	2.8	<i>L</i>
	17.7	0.426	-0.498	0.758	8.9	<i>N</i>
	23.1	0.034	-0.839	0.547	11.6	<i>M</i>

If we label these principal axes (Table 6) by *L*, *M*, *N* and if we name the direction of the  $\text{Br} \cdots \text{C}$  bond as *P*, the normal to the benzene ring as *Q*, and an axis in the plane of each benzene ring and perpendicular to *P* and *Q* as *R*, then the angles which *L*, *M* and *N* make with *P*, *Q* and *R* are shown in Table 7.

TABLE 7. THE ANGLES BETWEEN THE PRINCIPAL AXES OF VIBRATION WITH GIVEN DIRECTIONS IN THE CORRESPONDING BENZENE RING

Angle	Br <sub>1</sub>	Br <sub>2</sub>
$\angle L, P$	14°	8°
$\angle M, Q$	27°	20°
$\angle N, R$	30°	20°

Thus we see that a fairly "normal" amplitude of vibration exists in a direction parallel to the  $\text{Br} \cdots \text{C}$  bonds, while the motion perpendicular to this bond is extraordinarily large. There is apparently no correlation between the plane of the benzene rings and the direction of the major axes. It does seem surprising that there is no conclusive evidence of anisotropic thermal motion in the atoms of the benzene ring in D2, as one would expect from the apparent anisotropic motion of the Br atoms, or from possible randomness in the position of the benzoate groups by about 0.35 Å perpendicular to the  $\text{Br} \cdots \text{C}$  bond. From this analysis it would seem that the short  $\text{Br} \cdots \text{Br}$  contact of 3.77 Å, just over the Van der Waals contact distance, is a very important feature of the molecular packing.

The standard deviation of  $B$  in any given direction is  $0.4 \text{ \AA}^2$  for the bromine atoms and  $0.6 \text{ \AA}^2$  for the isotropic atoms.

#### CALCULATIONS

All calculations were carried out on the Remington Rand UNIVAC 1103 high-speed digital computer. Phases used to compute Fourier summations were written onto magnetic tape during a least-squares calculation. These were then read back into the computer and sorted in such a way as to be suitable for our Fourier program. The  $a$ ,  $b$  and  $c$  axes were divided into 160, 40 and 20 parts so that the intervals in these directions measured  $0.18$ ,  $0.19$  and  $0.32 \text{ \AA}$ , respectively. The time required to punch the electron density at all the 64,000 points in the asymmetric unit was  $2\frac{1}{2}$  hr. One least-squares refinement cycle, when all atoms were included, and the bromine atoms were given six thermal parameters each, took 64 min. 1430 reflections were included in all Fourier summations and least-squares calculations. The Thomas-Fermi<sup>15</sup> scattering curve was used for bromine but McWeeny<sup>16</sup> curves were used for oxygen and carbon. A total of 39 hr of computing was used in this study.

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<sup>15</sup> *Internationale Tabellen* p. 572. Zweiter Band, Berlin (1935).

<sup>16</sup> F. McWeeny, *Acta Cryst.* **4**, 513 (1951).