Acta Cryst. (1957). **10**, 498

The Crystal Structure of Hydroxydihydroeremophilone

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(*Received* 7 *November* 1956 *and in revised form* 4 *February* 1957)

Hydroxydihydroeremophilone (HDE) ($C_{15}H_{24}O_2$) crystallizes in the orthorhombic space group $P2_12_12_1$–D_2^4, with $a = 7{\cdot}526 \pm 0{\cdot}004$, $b = 10{\cdot}086 \pm 0{\cdot}008$, $c = 19{\cdot}699 \pm 0{\cdot}012$ Å. The structure has been determined by the solution of the (100) projection by means of a new method of applying the sign relation $S(\mathbf{h}')S(\mathbf{h}+\mathbf{h}') \approx S(\mathbf{h})$ to the plane group *pgg*; and also by the solution of the (010) projection, by means of Taylor's Fourier transform method. The stereochemical details of HDE have been completely determined and the molecule is shown to consist essentially of two *cis*-fused chair-shaped rings with the substituents in the equatorial positions. Bond lengths and angles and intermolecular distances are given and the principal chemical implications of the structure are summarized.

1. Introduction

Hydroxydihydroeremophilone (HDE) is a sesquiterpenoid which occurs naturally together with its closely related crystalline ketones, eremophilone and hydroxyeremophilone; these latter two, however, oxidize readily on exposure to air and only HDE is stable. The chemical constitution of HDE (Fig. 1) has been deduced from the investigations of Simonsen and others (Simonsen & Barton, 1952), and is the first known terpenoid to violate the 'isoprene rule' (Ruzicka, 1953) in that the angular methyl is at C_{10} and not C_9. Furthermore, the two rings are highly substituted, and evidence as to whether they are *cis*- or *trans*-fused in this state is of considerable chemical interest.

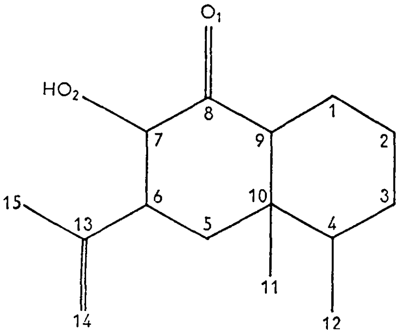

Fig. 1. The chemical constitution of HDE.

From a crystallographic point of view HDE represents a class of organic molecules the structures of which have been least successfully solved by conventional methods. The molecule is of moderate size (17 light atoms), contains no heavy atom, and is certainly not planar or approximately planar. Furthermore, the unit-cell dimensions are such that no considerations of packing are likely to determine the structure unambiguously, even if it were known which of the 16 stereochemically different ways of arranging the proposed chemical constitution was correct.

2. Crystal data

Hydroxydihydroeremophilone, $C_{15}H_{24}O_2$; molecular weight 236; m.p. 102–3° C.

The space group was determined by means of oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation; accurate lattice parameters were determined by means of photographs taken with a van Arkel mounting. The unit cell is orthorhombic with

$$a = 7{\cdot}526 \pm 0{\cdot}004,\ b = 10{\cdot}086 \pm 0{\cdot}008,$$
$$c = 19{\cdot}699 \pm 0{\cdot}012 \text{ Å},$$

and volume 1495 Å^3. The density, calculated on the basis of 4 molecules of HDE per cell, is 1·049 g.cm.$^{-3}$; that measured by flotation was 1·049 g.cm.$^{-3}$. The number of electrons per unit cell, $F(000)$, is 520. The absorption factor for Cu $K\alpha$ radiation is 6·35 cm.$^{-1}$.

Absent spectra were found to be ($h00$) for h odd, ($0k0$) for k odd and ($00l$) for l odd; hence the space group is determined uniquely as $P2_12_12_1$–D_2^4.

3. Intensity data

Multiple-film Weissenberg photographs taken with Cu $K\alpha$ radiation were used to record the intensities of the ($h0l$) and ($0kl$) reflexions. The crystals used were of approximate dimensions 0·1×0·02×0·02 cm. Only 90 of the possible 200 ($h0l$) reflexions and 148 of the 254 ($0kl$) reflexions were observed. Most of the accidentally absent reflexions are those of large sin θ value; this rapid fade-off of the high-order terms is a characteristic of most of the terpenes studied in this laboratory.

The relative intensities of the reflexions were obtained by visual comparison with a scale constructed from one of the crystal reflexions. Corrections for polarization and Lorentz factors were made in the usual way; no correction was made for absorption. The intensities for each zone were put on an approximate absolute scale by the method of Wilson (1942).

4. Structure determination

The (100) projection was solved by means of a systematic application of the sign relation $S(\mathbf{h}')S(\mathbf{h}+\mathbf{h}') \approx S(\mathbf{h})$ by a method the details of which are described in a previous paper (Grant, Howells & Rogers, 1957). The intensities of the $(0kl)$ reflexions were converted to the unitary structure factors, and the method was applied to the 55 terms for which $|U| \geq 0{\cdot}15$. (The largest unitary structure factor was 0·38, and only 7 had $|U| \geq 0{\cdot}30$.) A self-consistent set of signs was deduced for 54 of these terms, including two signs which may be chosen arbitrarily, and the electron density projected on (100) was calculated from these signs (Fig. 2(a)). The method was then extended to a further 38 terms for which $0{\cdot}1 \leq |U| \leq 0{\cdot}15$, and it was possible to give signs to 24 of these with a fair degree of confidence. The electron density projected on (100), using all 78 terms, was then calculated (Fig. 2(b)). A comparison of these two maps shows that they are essentially the same in appearance.

At this stage, of course, it was impossible to know whether or not the set of signs converged upon by this method was substantially correct; only successful interpretation and refinement could show that. It was argued, therefore, that if the electron-density maps (Fig. 2(a) and (b)) were reasonably correct, then it would appear that the molecule is being viewed edge-on in this projection, and an investigation of the (010) projection would give a map capable of easier interpretation.

The method was therefore tried on the (010) projection. Only 28 terms had $U \geq 0{\cdot}15$, and it was found possible to give a sign to them all. The electron density projected on (010) (Fig. 2(c)) was then calculated from these terms. This map could not be interpreted in terms of any of the arrangements of the chemical constitution; this is not surprising if the peak positions are compared with the correct atomic positions found later and marked in Fig. 2(c). It would appear that this method did not give a satisfactory set of signs because the number of independent products available was not very much greater than the number of signs to be determined. Consequently, many of the deductions towards a self-consistent set of signs were insufficiently confirmed.

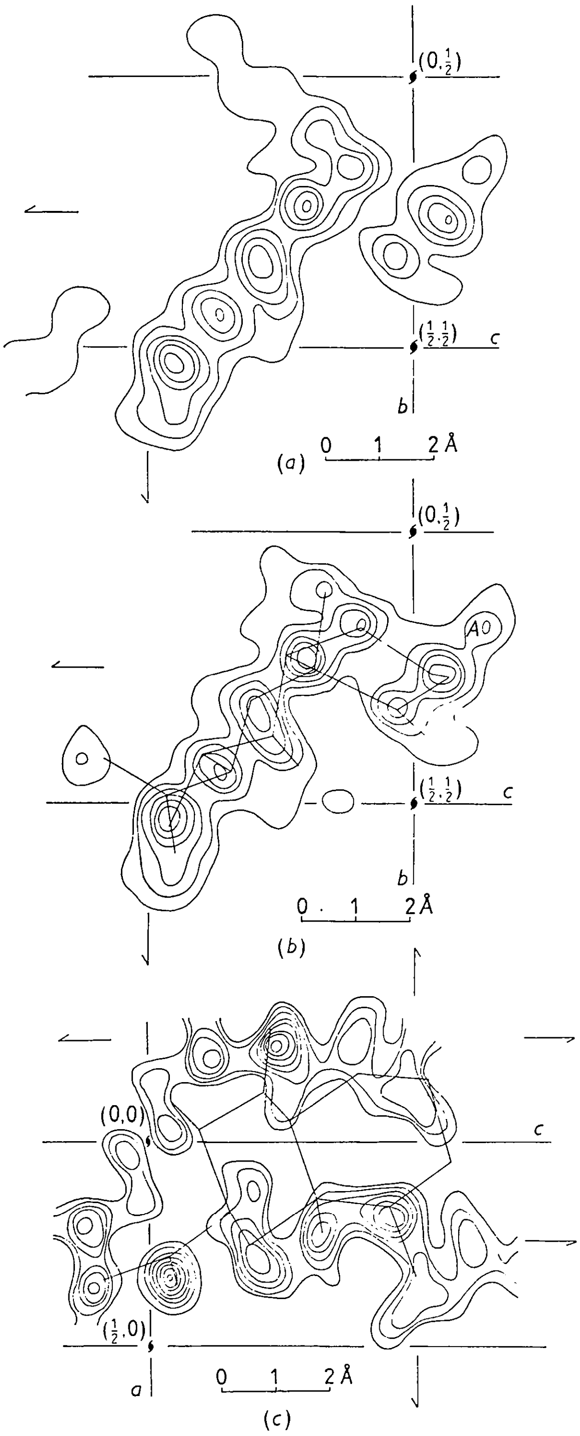

Fig. 2. (a) Electron density projected on (100). In this synthesis 54 terms are included. (b) Electron density projected on (100). In this synthesis 78 terms are included. The position of the molecule is indicated, showing how the map was interpreted. (c) Electron density projected on (010). In this synthesis 28 terms are included. The final position of the molecule is shown for comparison.

Attention was, therefore, re-directed to the (100) projection, and a systematic trial of all sixteen stereoisomers of HDE showed that it was possible to fit the molecule to the electron-density maps (Fig. 2(a) and (b)) when the rings were *cis*-fused and all substituents are in the equatorial positions. Even so, it was uncertain whether C_{12} was as indicated and as Simonsen suggested, or attached to C_2 and appearing at A in the map. Two error syntheses, calculated with C_{12} in each position, indicated that the Simonsen position is the correct one and that the peak A is spurious. Structure factors were then calculated from the Hartree scattering curve for carbon, and the carbon and oxygen contributions were included with weights in the ratio 6:8. The reliability index $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ obtained was 0·53 for the observed reflexions. Four stages of (F_o-F_c) refinement were carried out, and during the last stage McWeeny scattering curves were introduced. Between each stage a plot of $\log[\Sigma|F_o|\div\Sigma|F_c|]$ against $\sin^2\theta$ gave revisions of the scaling and temperature factors. The electron-density map at this stage is shown in Fig. 4 for which R is 0·27. The considerable overlap in this projection made interpretation of the difference synthesis difficult, but it appeared that the z coordinates of the atoms were now sufficiently well known to be used as an aid to the solution of the (010) projection.

If a molecule is referred to some arbitrary origin, the Fourier-transform method of Taylor (1954) can be used to locate this arbitrary origin with respect to a centre of symmetry. In the application of the method to the plane group *pgg* it is preferable to choose terms which are observed zero and which have the additional property that the Fourier transform of one pair of centrosymmetrically related molecules is very much smaller than that for the other pair of centrosymmetrically related molecules. The solution of the simultaneous equations for the fractional distances X and Z of the arbitrary origin from the centre of symmetry reduces to the places of intersection of families of bands.

In this case, therefore, the shape of the molecule in the (010) projection was calculated from its position in the (100) projection and, assuming an ideal structure (i.e. C–C bond lengths of 1·54 Å, tetrahedral angles of 109° etc.), this molecule was then referred to an arbitrary origin, chosen on the x axis, and nine reflexions were chosen on the principles outlined above, together with four axial observed reflexions. The problem was now reduced to locating the place of intersection of the bands with the x axis, since Z had been made zero. The axial reflexions and the 202 and $\bar{1}08$ reflexions were used to locate likely regions between $X = -0·25$ and $X = +0·25$, and indicated the region $X = -0·12$ to $X = -0·22$. The seven other reflexions were used to try and limit further the position of the arbitrary origin (Fig. 3). It will be apparent that two positions are indicated, one at $X = -0·150$ and the other at $X = -0·175$, a difference in the position of the molecule of only 0·19 Å. However, the calculation of a few low-order structure factors, in particular for the 102 reflexion which is not observed, indicated that the arbitrary origin must be placed $X = -0·150$ from the origin of the cell. The reflexions were about equally divided in their preference for one or other of these positions, and some (e.g. 407) did not favour either position. This is, of course, due to the inaccuracies involved in calculating the Fourier transform from an idealized molecule. Structure factors calculated on this position of the molecule gave an R value of 0·38. Four stages of (F_o-F_c) refinement reduced R to 0·21 for the observed reflexions. It was found necessary to introduce separate temperature factors for the oxygens and C_{15} (Table 1); these were estimated by the method of Hamilton (1955). Further refinement of the (100) projection reduced R to 0·24. The electron-density maps at this stage are shown in Fig. 4.

Table 1. *Temperature factors*

(100) projection	C_1 to C_{15}	3·44 Å^2
	O_1	7·10
	O_2	3·44
(010) projection	C_1 to C_{14}	2·84
	C_{15}	8·60
	O_1 and O_2	7·10

Only the observed reflexions are included in the R values quoted, as the very large number of unobserved

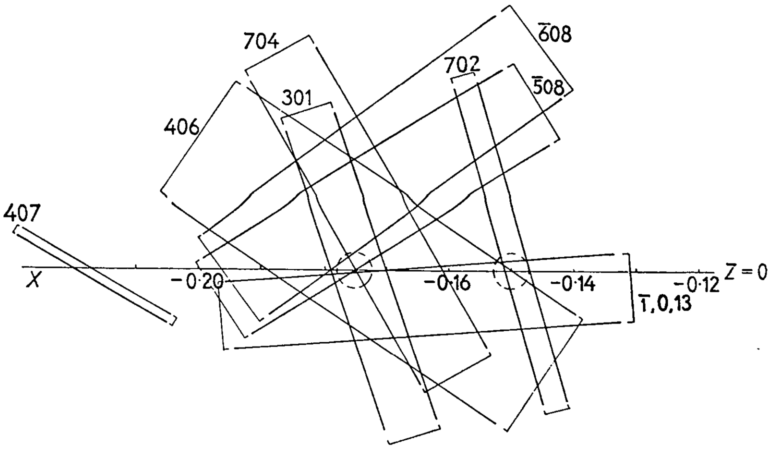

Fig. 3. Taylor's bands for the region from $X = -0·12$ to $X = -0·22$. The two possible positions of the arbitrary origin of the molecule are ringed.

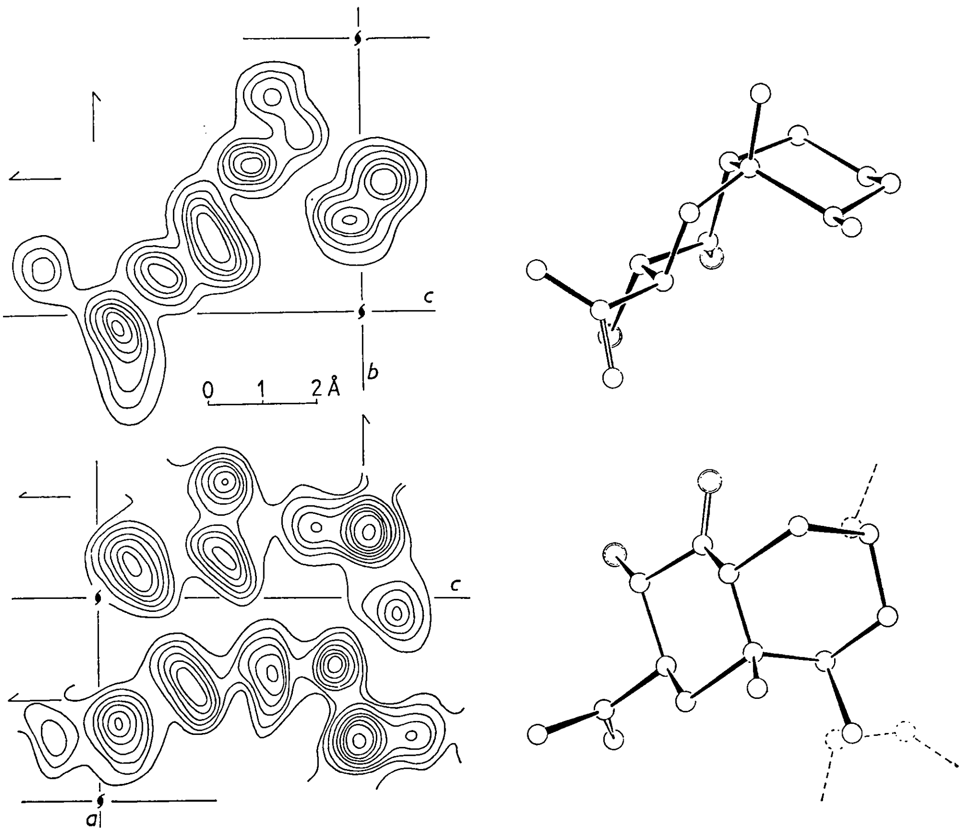

Fig. 4. Final electron-density maps projected on (100) (above) and (010) (below). The contours are shown at intervals of 1 e.Å^{-2}, starting at 2 e.Å^{-2}. In the skeleton molecules the oxygen atoms are shown as double circles.

reflexions tends to mask the progress of the refinement. However, after the last stages of refinement, the F_c's of only 6 of the 110 unobserved (*h*0*l*) reflexions and only 11 of the 106 unobserved (0*kl*) reflexions were greater than the minimum observable F value for the particular point in the reciprocal lattice. The observed and calculated structure factors at this stage are shown in Table 4.

An attempt was made to carry the refinement further by introducing the effect of the hydrogen atoms into the calculation of the structure factors. The difference syntheses gave little indication of the positions of the hydrogens. Of the 24 hydrogens, 12, which are attached to carbons in the ring system, could be placed with fair accuracy. The hydrogen in the OH group could not be placed at all. The remaining 11 hydrogens, in the methyl and isopropenyl groups, could be placed only by guess-work, using the positive regions of the difference syntheses as a guide.

The structure factors were recalculated, using these

Table 2. *Atomic coordinates*

	x/a	*x* (Å)	*y/b*	*y* (Å)	*z/c*	*z* (Å)
C_1	−0·167	−1·253	+0·175	+1·750	+0·450	+8·765
C_2	−0·148	−1·108	+0·251	+2·513	+0·516	+10·060
C_3	+0·055	+0·412	+0·264	+2·642	+0·534	+10·409
C_4	+0·161	+1·210	+0·324	+3·244	+0·474	+9·237
C_5	+0·260	+1·949	+0·314	+3·145	+0·343	+6·690
C_6	+0·175	+1·313	+0·444	+4·439	+0·324	+6·324
C_7	−0·028	−0·212	+0·412	+4·115	+0·300	+5·850
C_8	−0·121	−0·909	+0·371	+3·705	+0·360	+7·018
C_9	−0·051	−0·383	+0·221	+2·211	+0·385	+7·506
C_{10}	+0·141	+1·060	+0·233	+2·332	+0·406	+7·915
C_{11}	+0·226	+1·697	+0·099	+0·987	+0·410	+7·993
C_{12}	+0·336	+2·523	+0·345	+3·450	+0·500	+9·742
C_{13}	+0·282	+2·114	+0·494	+4·938	+0·266	+5·189
C_{14}	+0·354	+2·653	+0·619	+6·194	+0·276	+5·374
C_{15}	+0·344	+2·578	+0·419	+4·186	+0·203	+3·959
O_1	−0·276	−2·070	+0·400	+4·000	+0·367	+7·157
O_2	−0·096	−0·718	+0·544	+5·443	+0·277	+5·392

hydrogen atom positions. The result was that for the (010) projection R increased by 0·005 to 0·21 and for the (100) projection R decreased by 0·02 to 0·22. The first of these changes is regarded as being not significant, and the second as being of small importance; for, in this projection, the molecule is viewed nearly edge on and the effect of adding in the hydrogens is simply to increase the electron density of the ridge representing the molecule. Thus the decrease in R cannot be regarded as confirming the positions assigned to the hydrogens.

It is probable, therefore, that the limit of useful refinement based on two-dimensional work has been reached. Since the two primary objects of this structure determination—the verification of the Simonsen formula and the successful use of the sign relations—have been achieved, no further work is proposed.

5. Results

5·1. *Atomic coordinates*

The atomic coordinates for the asymmetric unit of one molecule of HDE referred to an origin at (0, $\frac{1}{4}$, 0) from the origin given in the *International Tables* are given in Table 2.

The coordinates have standard deviations of $\sigma(x)$ = 0·020 Å, $\sigma(y)$ = 0·027 Å, $\sigma(z)$ = 0·018 Å (Cruickshank, 1949).

5·2. *Bond lengths and angles*

Table 3 shows the bond lengths and angles for one molecule of HDE. The mean standard deviation for the bond lengths is 0·031 Å, and for the bond angles 1·5°. There is a significant difference between C_{13}–C_{14} and C_{13}–C_{15}, indicating that C_{13}–C_{14} is the double bond in the isopropenyl group. Several other bonds deviate considerably from the ideal length of 1·54 Å, and several of the tetrahedral angles differ considerably from the ideal angle of 109°. It is obvious also that C_7, C_8, C_9 and O_1 do not lie in the same plane: the oxygen atom is displaced considerably towards the equatorial position. Even at the stage of refinement reached it is apparent that the *cis*-decalin ring system has been considerably distorted from its ideal configuration by the presence of the substituents. It is hoped to give a detailed discussion of the distortions introduced and their chemical implications elsewhere.

Table 3. *Bond lengths and angles*

C_1–C_2	1·51 Å	C_9–C_1–C_2	118·5°
C_1–C_9	1·60	C_1–C_2–C_3	109·3
C_2–C_3	1·57	C_2–C_3–C_4	111·5
C_3–C_4	1·54	C_3–C_4–C_{10}	110·7
C_4–C_{10}	1·61	C_3–C_4–C_{12}	105·5
C_4–C_{12}	1·43	C_{10}–C_4–C_{12}	117·3
C_5–C_{10}	1·72	C_4–C_{10}–C_{11}	115·3
C_5–C_6	1·49	C_4–C_{10}–C_9	111·0
C_6–C_7	1·64	C_5–C_{10}–C_4	105·7
C_6–C_{13}	1·48	C_5–C_{10}–C_{11}	104·1
C_7–C_8	1·42	C_5–C_{10}–C_9	110·1
C_8–C_9	1·66	C_9–C_{10}–C_{11}	110·6
C_9–C_{10}	1·50	C_{10}–C_5–C_6	111·7
C_{10}–C_{11}	1·49	C_7–C_6–C_5	107·3
C_{13}–C_{15}	1·51	C_7–C_6–C_{13}	110·8
		C_5–C_6–C_{13}	104·3
C_{13}–C_{14}	1·38	C_6–C_7–C_8	106·0
		C_6–C_7–O_2	103·1
C_7–O_2	1·49	C_8–C_7–O_2	110·1
		C_8–C_9–C_{10}	108·3
C_8–O_1	1·21	C_1–C_9–C_{10}	109·3
		C_8–C_9–C_1	108·6
		C_7–C_8–C_9	110·3
		C_7–C_8–O_1	119·7
		C_9–C_8–O_1	119·6
		C_6–C_{13}–C_{15}	128·5
		C_{14}–C_{13}–C_{15}	116·2
		C_6–C_{13}–C_{14}	114·3

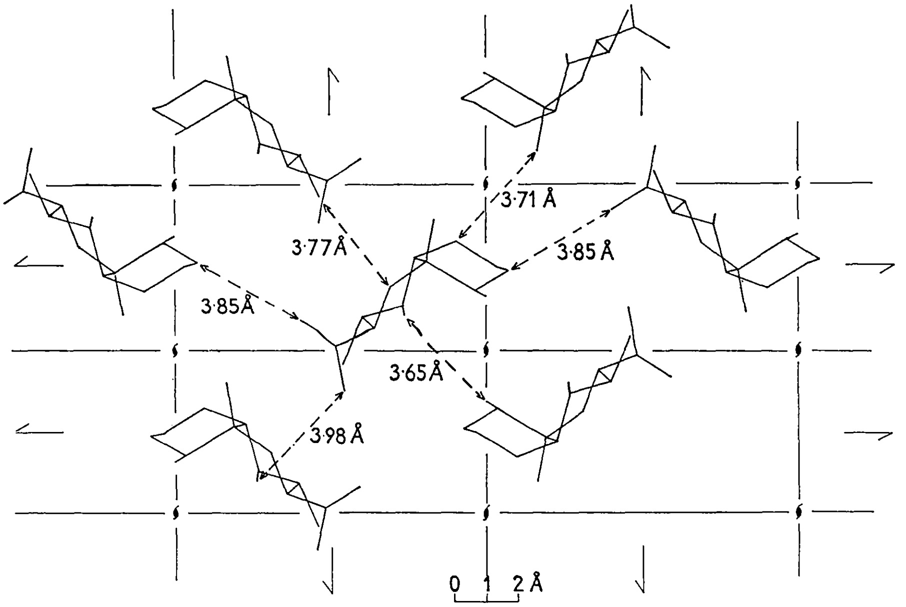

Fig. 5. The structure viewed along the a axis and showing the shortest intermolecular distances.

Table 4. *Observed and calculated structure factors for 0kl and h0l reflexions*

h	k	l	F_o	F_c
0	0	2	4	14-
0	0	4	47	33
0	0	6	28	20
0	0	8	34	33
0	0	10	13	16
0	0	12	11	15-
0	0	14	9	8
0	0	16	9	16-
0	0	18	<6	1
0	0	20	<6	1-
0	0	22	<5	6
0	0	24	<4	1-
0	1	1	33	45
0	1	2	96	107
0	1	3	55	65-
0	1	4	20	15
0	1	5	71	70
0	1	6	72	61-
0	1	7	24	15
0	1	8	6	8
0	1	9	39	27
0	1	10	13	14-
0	1	11	33	31-
0	1	12	4	1
0	1	13	15	20
0	1	14	6	5-
0	1	15	6	5-
0	1	16	<6	2-
0	1	17	8	9
0	1	18	8	6-
0	1	19	8	7-
0	1	20	<6	3-
0	1	21	<5	0
0	1	22	5	3
0	1	23	<4	1
0	1	24	<3	0
0	2	0	39	28-
0	2	1	30	38
0	2	2	114	132-
0	2	3	9	2-
0	2	4	12	17
0	2	5	76	77-
0	2	6	38	26-
0	2	7	42	39
0	2	8	23	17-
0	2	9	29	18
0	2	10	6	2
0	2	11	13	6
0	2	12	9	2-
0	2	13	<5	5-
0	2	14	<5	13
0	2	15	<5	1
0	2	16	12	5
0	2	17	14	16
0	2	18	<6	2
0	2	19	9	7-
0	2	20	6	4-
0	2	21	<5	6
0	2	22	5	5
0	2	23	<4	5-
0	2	24	<3	1-
0	3	1	28	22-
0	3	2	20	22
0	3	3	14	13-
0	3	4	27	11
0	3	5	29	20-
0	3	6	4	10-
0	3	7	60	54-
0	3	8	42	47
0	3	9	<4	3
0	3	10	<5	6-
0	3	11	<5	5-
0	3	12	11	12
0	3	13	9	5-
0	3	14	5	3-
0	3	15	8	10-
0	3	16	12	11
0	3	17	17	11
0	3	18	8	5
0	3	19	<6	1-
0	3	20	6	7-
0	3	21	<5	2
0	3	22	4	0
0	3	23	<4	1
0	3	24	<3	1
0	4	0	4	11-
0	4	1	17	17
0	4	2	9	13
0	4	3	6	14
0	4	4	22	22
0	4	5	10	10-
0	4	6	10	16-
0	4	7	12	11
0	4	8	16	3
0	4	9	28	14-
0	4	10	9	0
0	4	11	15	10
0	4	12	9	5
0	4	13	6	7-
0	4	14	19	18-
0	4	15	22	19-
0	4	16	7	5-
0	4	17	9	5
0	4	18	6	4
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0	4	20	<5	6-
0	4	21	<5	3
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0	4	23	<3	1-
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0	5	2	5	6-
0	5	3	17	19
0	5	4	5	8-
0	5	5	18	17
0	5	6	27	26-
0	5	7	6	6-
0	5	8	28	20-
0	5	9	7	3-
0	5	10	22	24-
0	5	11	8	8
0	5	12	16	8
0	5	13	16	10
0	5	14	9	3-
0	5	15	13	11-
0	5	16	11	8-
0	5	17	8	6-
0	5	18	<5	2
0	5	19	5	2-
0	5	20	<5	1-
0	5	21	<4	1-
0	5	22	<3	1-
0	5	23	<2	2-
0	6	0	21	23-
0	6	1	8	9-
0	6	2	<5	8
0	6	3	10	11-
0	6	4	18	16
0	6	5	<5	0
0	6	6	5	4
0	6	7	17	12
0	6	8	11	7
0	6	9	9	9-
0	6	10	34	21-
0	6	11	10	9-
0	6	12	10	8
0	6	13	8	10
0	6	14	10	2
0	6	15	<6	1
0	6	16	<6	3
0	6	17	<5	1-
0	6	18	7	8
0	6	19	<5	2
0	6	20	<4	0
0	6	21	<3	0
0	6	22	<2	2
0	7	1	5	9
0	7	2	5	5-
0	7	3	<5	0
0	7	4	5	5
0	7	5	12	7-
0	7	6	14	21
0	7	7	<5	0
0	7	8	34	25
0	7	9	14	17
0	7	10	<6	3
0	7	11	<6	0
0	7	12	6	3
0	7	13	9	6
0	7	14	<6	4
0	7	15	<5	2
0	7	16	<5	4-
0	7	17	<5	2
0	7	18	<5	2
0	7	19	<4	1
0	7	20	<3	4
0	7	21	<2	4
0	8	0	8	3
0	8	1	6	4-
0	8	2	6	5
0	8	3	14	16
0	8	4	<6	1
0	8	5	<6	1
0	8	6	13	9-
0	8	7	6	7-
0	8	8	16	15
0	8	9	<6	3
0	8	10	<6	1
0	8	11	<6	0
0	8	12	6	1
0	8	13	12	13
0	8	14	<5	2
0	8	15	<5	0
0	8	16	<5	1-
0	8	17	<4	4-
0	8	18	<3	3-
0	8	19	<2	0
0	9	1	10	7-
0	9	2	8	6-
0	9	3	6	2
0	9	4	<6	2-
0	9	5	<6	3
0	9	6	10	9-
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0	9	13	<5	1-
0	9	14	5	5-
0	9	15	<4	3
0	9	16	<4	0
0	9	17	<3	0
0	9	18	<2	0
0	10	0	6	2-
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0	10	2	<6	8-
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0	10	4	<6	7-
0	10	5	<5	2-
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0	10	7	<5	2-
0	10	8	<5	2-
0	10	9	<5	3
0	10	10	<5	2-
0	10	11	9	9-
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0	10	13	<4	4-
0	10	14	<3	0
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0	11	5	<5	4-
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0	11	7	<4	3
0	11	8	<4	2
0	11	9	6	2
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0	12	2	5	6
0	12	3	4	2
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0	12	5	<3	0
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0	12	9	<2	3
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1	0	2	<2	7-
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1	0	7	11	17
1	0	8	<4	9-
1	0	9	16	16-
1	0	10	17	18
1	0	11	5	5-
1	0	12	19	18
1	0	13	<5	4-
1	0	14	46	44-
1	0	15	<6	6
1	0	16	<6	5-
1	0	17	<6	0
1	0	18	<6	4-
1	0	19	<6	4
1	0	20	<6	0
1	0	21	<5	3
1	0	22	<5	0
1	0	23	<4	1-
1	0	24	<3	1
1	0	25	<2	2
2	0	0	74	75-
2	0	1	14	15
2	0	2	<3	8
2	0	3	7	4-
2	0	4	19	12
2	0	5	34	32
2	0	6	10	9
2	0	7	8	3-
2	0	8	9	14-
2	0	9	30	31
2	0	10	8	13-
2	0	11	22	28
2	0	12	17	23-
2	0	13	24	20
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2	0	15	12	13-
2	0	16	6	5
2	0	17	15	14
2	0	18	<6	3
2	0	19	7	8-
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2	0	23	<4	1
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3	0	4	16	16
3	0	5	11	8-
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3	0	7	25	18
3	0	8	6	7
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3	0	10	7	7
3	0	11	10	12-
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3	0	17	6	5
3	0	18	6	4-
3	0	19	6	9-
3	0	20	<5	4
3	0	21	7	7
3	0	22	<4	0
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3	0	24	<2	5
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4	0	1	6	3
4	0	2	9	13
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4	0	5	13	15-
4	0	6	<5	4
4	0	7	<5	5
4	0	8	7	6-
4	0	9	5	6
4	0	10	6	6
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4	0	12	7	2
4	0	13	14	11-
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5	0	8	<6	1
5	0	9	12	13-
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5	0	16	<6	1-
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6	0	1	8	7-
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6	0	17	<4	4
6	0	18	<4	3-
6	0	19	<3	4-
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7	0	2	<6	5
7	0	3	<6	4-
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7	0	5	<6	0
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7	0	9	<6	6
7	0	10	<6	1-
7	0	11	<5	3
7	0	12	<5	1-
7	0	13	<5	0
7	0	14	<4	4-
7	0	15	<4	2
7	0	16	<3	2
7	0	17	<2	1-
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8	0	1	<5	5
8	0	2	<5	5
8	0	3	<5	3-
8	0	4	<5	5-
8	0	5	<5	1
8	0	6	<5	1
8	0	7	6	1
8	0	8	<5	2
8	0	9	<5	5
8	0	10	<4	0
8	0	11	<4	3-
8	0	12	<3	3
8	0	13	<3	1-
8	0	14	3	7-
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9	0	3	<4	0
9	0	4	<4	4
9	0	5	<4	0
9	0	6	<3	1-
9	0	7	<3	1
9	0	8	<3	0
9	0	9	<2	1-

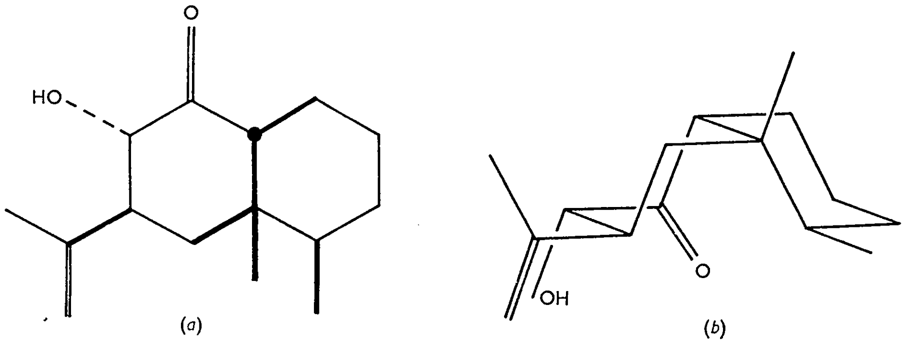
5·3. *Intermolecular distances*

The shortest distances between the atoms of one molecule and the atoms in its nearest neighbours are shown in Fig. 5. There are no approach distances smaller than 3·65 Å.

6. Conclusions

6·1. *Chemical conclusions*

The chemical implications of the structure of HDE have been set out fully elsewhere (Grant & Rogers,



(a) (b)

Fig. 6. Two representations of the absolute configuration of HDE.

1956), and here it will suffice to summarize the conclusions:

(*a*) Simonsen's chemical constitution is confirmed and HDE is, as it stands, a violator of the 'isoprene rule'.

(*b*) The rings are *cis*-fused, and HDE is, therefore, based on *cis*-decalin together with the substituents in the equatorial positions. This is despite the fact that *trans*-fusion is the more stable configuration when the rings are unsubstituted.

(*c*) From optical rotation considerations Klyne (1954) has established the absolute configuration of part of eremophilone, and this in turn determines the absolute configuration of HDE, as illustrated in the paper by Grant & Rogers mentioned above. However, recent work by Djerassi (private communication) on the dispersion of the optical rotation has shown that Klyne's conclusions are probably incorrect. The absolute configuration of HDE is that based on Djerassi's work, and is shown in Fig. 6.

6·2. *Crystallographic conclusions*

(*a*) The structure of HDE was primarily determined through the application to the plane group *pgg* of a new method of using sign relations. The signs of a number of terms were determined without any previous knowledge of the signs of any other terms or of the stereochemistry of the molecule.

(*b*) The method failed to give a satisfactory set of signs for the (010) projection, probably because of the relatively small number of independent products available for consideration. It is interesting to note that, if the correct set of signs is put back into the products considered, then these are also a self-consistent set. That is, the correct set is another solution that might have been converged upon.

(*c*) Taylor's Fourier-transform method seems to be very useful when the location of a molecule in one projection is to be found from its known position in another projection, especially when packing considerations or heavy-atom positions are not available.

The author's thanks are due to Prof. A. J. C. Wilson for encouragement and for the use of equipment purchased with a Royal Society grant, and to Dr D. Rogers for many helpful conversations and criticisms.

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A Detailed Refinement of the Crystal and Molecular Structure of Naphthalene

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(*Received* 25 *March* 1957)

A detailed refinement of Abrahams, Robertson & White's data for naphthalene has been carried out. The many calculations needed were performed on the Manchester University electronic computer. As for anthracene, the difference map indicates some channelling of the electrons along the lines of the bonds. The anisotropic vibrations of the carbon atoms can be interpreted in terms of anisotropic translational and rotational oscillations of the molecules. The magnitudes of the angular oscillations (~ 4°) agree well with those inferred from Raman spectra. C–C bond lengths with e.s.d.'s of about 0·005 Å are obtained.

1. Introduction

A very considerable extension of Ahmed & Cruickshank's (1952) refinement of Mathieson, Robertson & Sinclair's (1950) data for anthracene was recently described (Cruickshank, 1956*a*, 1957*a*). The present paper describes a similar extension of Ahmed & Cruickshank's refinement of Abrahams, Robertson & White's (1949*a*) data for naphthalene.

The experience gained in the work on anthracene has enabled the analysis of naphthalene to be carried through with appreciably less effort, though, as before, very large calculations were involved. These were