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The Crystal Structure of Rimuene

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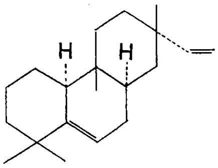
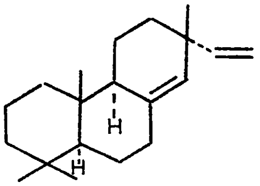
The crystal structure of the diterpene rimuene, $C_{20}H_{32}$, has been determined using three-dimensional photographic data. The crystals are orthorhombic, $a=7{\cdot}48$, $b=9{\cdot}49$, $c=24{\cdot}31$ Å, and the space group is $P2_12_12_1$. The structure was solved using the vector verification procedure for deconvolution of the Patterson function, and was refined by block-diagonal least squares to an R index of 0·132, with the mean standard deviation in position for a carbon atom 0·006 Å. The molecular structure is confirmed as

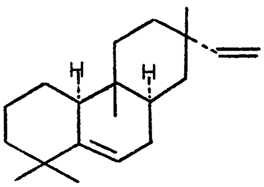


in agreement with other studies.

Rimuene is a diterpene hydrocarbon, $C_{20}H_{32}$, which is present in the essential oil of the New Zealand rimu tree (*Dacrydium cupressinum*), as well as in several other species (Aplin, Cambie & Rutledge, 1963). Chemical and infrared spectral studies (Briggs, Cain & Wilmshurst, 1958; Briggs, Cain & Cambie, 1959; Briggs, Cain, Davis & Wilmshurst, 1959) indicated the structure (I), but the four possible isomers of this (Church & Ireland, 1963) were synthesized and none of them was in fact, rimuene. At this stage the presently reported X-ray study was begun. Investigation by other techniques continued, until Fetizon (1964) proposed structure (II) on the basis of nuclear magnetic resonance and mass spectra. The same structure was demonstrated more or less simultaneously by other methods (Corbett & Wylie, 1964; Connolly, McCrindle, Murray & Overton, 1964) and a successful synthesis quickly followed (Ireland & Mander, 1964). The present investigation has confirmed structure (II).



(I)



(II)

Experimental

Rimuene, $C_{20}H_{32}$, m.p. 55·5 °C, was supplied by Professor L. H. Briggs as large clear crystals, from which small fragments suitable for X-ray photography were cut.

The crystals are orthorhombic, $a=7{\cdot}48 \pm 0{\cdot}03$, $b=9{\cdot}49 \pm 0{\cdot}02$, $c=24{\cdot}31 \pm 0{\cdot}03$ Å, D_m (by flotation in aqueous potassium nitrate), 1·055 g.cm^{-3}, D_c for 4 molecules per unit cell, 1·047 g.cm^{-3}; space group, $P2_12_12_1$ (h00, 0k0 and 00l absent for h, k or l odd).

Weissenberg photographs were taken of the layers 0kl–6kl and h0l–h1l, using the multiple-film pack technique and Cu $K\alpha$ radiation. Intensity data were measured visually. Crystals of square cross-section with dimensions of 0·5 mm were used. The absorption coefficient is 4·4 cm^{-1}, and no absorption corrections were made. In all, 1914 independent reflexions were defined after the data were placed on a common scale.

Structure solution

Although the molecular structure was not at this stage known, it was clear that it contained three fused rings with three methyl groups, at least one of which was axial. It was known that there was one endocyclic double bond, and although the distortion that might be consequent upon this was a complication, it was hoped that the vector patterns characteristic of at least the cyclohexane rings and quaternary carbon atoms would be discernible in the Patterson function. Considerable effort was then made to find such expected vectors and, by vector superposition and/or molecular packing techniques, to obtain the correct structure. Although these studies suggested, correctly, that rimuene must be a fairly planar molecule, more or less perpendicular to **a**, with many bonds parallel to **c**, no one of the many models that were tried led to successful refinement.

The approach which finally did succeed was the 'vector verification' technique of Mighell & Jacobson (1967). The first stage of this is effectively a systematic correlation of the three Harker sections, leading to a three-dimensional plot of those points in real space for which all three corresponding Harker values exceed a certain minimum value. This plot has much higher symmetry than the structure itself but must contain it. Attempts to recognize the molecule as such were unsuccessful, but a grouping of four peaks which formed a rectangle of sides 1·5 and 2·5 Å was correctly identified as being part of a cyclohexane ring [in fact atoms C(6), C(7), C(9) and C(10)]. Two of these atom sites were used in the second stage of vector verification, a systematic search in Patterson space for vectors from all points in real space to specified atoms. This is a variant on vector superposition which is particularly convenient to program. Seventeen atom positions were thus derived, although a subsequent difference Fourier synthesis calculated from reflexions corresponding to the 600 largest $|F_o|$ values showed that two of these were wrong. The largest peaks on this difference synthesis could not be related to the proposed structure, but five further atoms were obtained from the smaller maxima, and R then stood at 0·46 for the 1000 largest data terms. A further difference synthesis showed that three atoms were still not satisfactorily placed; two were repositioned and one, C(16), was removed. The R index was then 0·36 and was reduced to 0·25 by two further cycles and the subsequent replacing of C(16).

Refinement was continued by block-diagonal least squares, using all of the 1914 observed data. Isotropic temperature factors were assumed. The weights were calculated by the expression $w = 1/(1 + (|F_o| - b)^2/a^2)$, and a and b were adjusted between cycles such that $\langle w(\Delta F)^2 \rangle$ was constant for various ranges of F. The refinement converged with R at 0·21, with all atoms apparently well behaved except C(16) for which B was greater than 8 Å^2. Removal of this atom, followed by a difference synthesis, did not suggest that it was incorrectly placed, however. Assumption of anisotropic thermal parameters for all atoms, and further least-squares cycles, reduced R to 0·166. Again the thermal parameters for C(16) were very high, and again removal and calculation of a difference synthesis failed to reveal an alternative site for it. Six data which appear to have been affected by extinction were then removed, and a further difference synthesis was searched for hydrogen atoms. Peaks ranging in height from 0·77 to 0·41 e.Å^{-3} were successfully correlated with the 32 expected atoms, and following their inclusion and further least-squares cycles, R was 0·132. Hydrogen atom parameters were not refined; their isotropic temperature factors were taken as 1·5 times the mean temperature factor of the carbon to which they are attached.

At the conclusion, atom C(16) still appeared to be unsatisfactory, with an equivalent isotropic B along the major vibration axis of 23 Å^2. It was concluded that the atom may be disordered, and it was replaced by two half-atoms, separated along the above major vibration axis by the root-mean-square amplitude, *viz.* 0·54 Å. These half-atoms were given initial isotropic temperature factors corresponding to that of the smaller vibration axis, but were allowed to refine anisotropically. These adjustments to C(16) did not improve the agreement, the final R index being again 0·132.

Final atom parameters are listed in Tables 1 and 2, bond lengths and angles in Table 3, and observed and calculated structure factors in Table 4. The atom numbering system is shown in Fig. 1, the packing of the molecules in Fig. 2, and the pattern of thermal vibration in Fig. 3.

Table 2. *Hydrogen atom coordinates* (× 10^3) *and thermal parameters* (× 10)

	x/a	y/b	z/c	B
H(11)	379	338	227	88
H(12)	535	255	211	88
H(21)	502	141	295	101
H(22)	523	302	307	101
H(31)	221	267	344	89
H(32)	186	325	310	89
H(61)	−113	124	208	67
H(71)	−072	020	112	83
H(72)	030	162	106	83
H(81)	214	045	133	67
H(101)	372	054	197	60

Table 1. *Carbon atom coordinates and temperature factors* (× 10^4)

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
C(1)	4437 (11)	2438 (7)	2317 (2)	0333 (17)	−0104 (22)	−0002 (7)	0154 (7)	−0012 (5)	0019 (9)
C(2)	4361 (12)	2262 (9)	2933 (3)	0339 (18)	−0128 (25)	0009 (8)	0191 (9)	−0033 (5)	0020 (1)
C(3)	2465 (11)	2422 (7)	3119 (3)	0346 (17)	−0029 (21)	0032 (7)	0132 (6)	−0032 (5)	0022 (1)
C(4)	1228 (8)	1355 (6)	2868 (2)	0180 (10)	0037 (15)	0008 (5)	0129 (6)	−0005 (4)	0016 (7)
C(5)	1399 (7)	1321 (5)	2242 (2)	0146 (9)	0047 (12)	0024 (4)	0094 (4)	0008 (3)	0017 (7)
C(6)	0006 (7)	1161 (6)	1916 (2)	0155 (9)	0016 (15)	0009 (5)	0145 (6)	0007 (4)	0018 (8)
C(7)	0103 (8)	0905 (9)	1311 (2)	0180 (11)	−0020 (20)	0004 (5)	0211 (9)	0022 (5)	0017 (8)
C(8)	2011 (8)	0498 (7)	1137 (2)	0205 (11)	−0050 (17)	0000 (5)	0158 (7)	0008 (4)	0014 (7)
C(9)	3339 (8)	1543 (6)	1375 (2)	0188 (10)	0011 (15)	0024 (5)	0123 (5)	0016 (4)	0016 (7)
C(10)	3272 (7)	1373 (5)	2012 (2)	0196 (10)	0007 (13)	0008 (5)	0099 (4)	−0002 (3)	0017 (7)
C(11)	5212 (8)	1129 (8)	1167 (2)	0177 (10)	−0027 (19)	0011 (5)	0205 (9)	0012 (5)	0015 (7)
C(12)	5324 (9)	1019 (10)	0537 (2)	0238 (13)	−0017 (24)	0052 (6)	0255 (12)	0018 (6)	0016 (8)
C(13)	3985 (10)	−0039 (8)	0301 (2)	0269 (14)	−0017 (23)	0014 (6)	0213 (10)	0015 (5)	0014 (7)
C(14)	2119 (9)	0345 (9)	0507 (2)	0239 (13)	−0074 (22)	−0015 (5)	0224 (10)	0018 (5)	0013 (7)
C(15)	4603 (14)	−1530 (10)	0458 (3)	0466 (24)	−0012 (32)	0031 (9)	0199 (10)	−0018 (6)	0019 (1)
C(16)	3681 (28)	−2590 (12)	0597 (4)	1016 (65)	−0050 (59)	0068 (19)	0205 (12)	−0012 (8)	0027 (2)
C(17)	3989 (13)	0072 (12)	−0331 (2)	0389 (20)	0060 (37)	0029 (8)	0323 (17)	0022 (7)	0015 (9)
C(18)	2944 (11)	3064 (7)	1211 (3)	0301 (17)	−0012 (20)	0021 (8)	0134 (7)	0040 (5)	0028 (1)
C(19)	−0689 (9)	1695 (10)	3058 (3)	0204 (12)	0069 (23)	0053 (6)	0229 (11)	0012 (6)	0024 (1)
C(20)	1663 (10)	−0132 (7)	3088 (2)	0325 (16)	0023 (19)	0013 (6)	0135 (6)	0010 (4)	0016 (7)

Table 2 (*cont.*)

	x/*a*	*y*/*b*	*z*/*c*	*B*
H(111)	530	027	134	77
H(112)	639	163	137	77
H(121)	676	110	038	93
H(122)	554	195	030	93
H(141)	187	135	028	81
H(142)	130	−005	023	81
H(151)	639	−159	035	113
H(161)	424	−383	063	179
H(162)	276	−243	085	180
H(171)	387	099	−050	127
H(172)	524	−010	−039	127
H(173)	268	−067	−048	127
H(181)	436	301	117	95
H(182)	270	295	080	95
H(183)	206	334	144	95
H(191)	−088	188	341	94
H(192)	−164	124	288	94
H(193)	−117	244	300	94
H(201)	076	−082	287	80
H(202)	282	−042	293	80
H(203)	220	−014	347	80

Discussion

The molecule of rimuene, as deduced in this study, is shown in Figs. 1–3. It has a perhydrophenanthrene nucleus, with a double bond between C(5) and C(6), a *gem*-dimethyl grouping at C(4), a methyl group at C(9), and methyl and vinyl groups at C(13). Rings *A* and *C* are in chair conformation, with the former slightly distorted by the trigonal hybridization of atom C(5). The cyclohexene ring *B* is so folded that the perhydrophenanthrene nucleus is more or less planar overall. Methyl groups C(17) and C(19) are equatorial; methyl groups C(18) and C(20) and the vinyl group are axial. As deduced and depicted this is the mirror image of structure (II), but as the absolute configuration is not determined structure (II) is confirmed by this study.

No attempt has been made to correct bond lengths for the effects of thermal motion, as the pattern of motion is far from obvious. It is clear, however, that if the single atom description of C(16) is correct, and this atom is indeed undergoing the extreme vibration implied, the bond C(15)–C(16) will appear to be shortened, and thus the observed length of 1·27 Å is probably in tolerable agreement with the standard double-bond value of 1·337 Å. By contrast, the lengths of the same bond to the half-atoms used in the alternative description are both clearly impossible, at 1·15 and 1·42 Å respectively, and thus the former description is to be preferred in spite of the very high thermal parameters.

The other double bond, C(5)–C(6), is normal within

Table 3. *Bond lengths and bond angles*

Bond	*D*	*σ*
C(1)—C(2)	1·508 Å	0·008 Å
C(1)—C(10)	1·526	0·008
C(2)—C(3)	1·495	0·011
C(3)—C(4)	1·500	0·009
C(4)—C(5)	1·526	0·006
C(4)—C(19)	1·540	0·008
C(4)—C(20)	1·543	0·008
C(5)—C(6)	1·318	0·007
C(5)—C(10)	1·509	0·007
C(6)—C(7)	1·493	0·007
C(7)—C(8)	1·537	0·008
C(8)—C(9)	1·518	0·008
C(8)—C(14)	1·538	0·007
C(9)—C(10)	1·558	0·006
C(9)—C(11)	1·540	0·008
C(9)—C(18)	1·526	0·008
C(11)-C(12)	1·535	0·007
C(12)-C(13)	1·529	0·010
C(13)-C(14)	1·527	0·009
C(13)-C(15)	1·536	0·012
C(13)-C(17)	1·540	0·008
C(15)-C(16)	1·265	0·017

Angle	*θ*	*σ*
C(2)—C(1)—C(10)	112·7°	0·5°
C(1)—C(2)—C(3)	108·9	0·6
C(2)—C(3)—C(4)	113·1	0·5
C(3)—C(4)—C(5)	111·5	0·4
C(3)—C(4)—C(19)	108·1	0·5
C(3)—C(4)—C(20)	110·2	0·4
C(5)—C(4)—C(19)	112·3	0·4
C(5)—C(4)—C(20)	107·9	0·4
C(19)-C(4)—C(20)	106·5	0·5
C(4)—C(5)—C(6)	122·4	0·4
C(4)—C(5)—C(10)	116·5	0·4
C(6)—C(5)—C(10)	120·9	0·4
C(5)—C(6)-C(7)	124·9	0·5
C(6)—C(7)—C(8)	110·9	0·4
C(7)—C(8)—C(9)	109·7	0·5
C(7)—C(8)—C(14)	110·2	0·4
C(9)—C(8)—C(14)	113·9	0·4
C(8)—C(9)—C(10)	106·8	0·4
C(8)—C(9)—C(11)	107·6	0·4
C(8)—C(9)—C(18)	113·0	0·5
C(10)-C(9)—C(11)	109·2	0·4
C(10)-C(9)—C(18)	110·5	0·4
C(11)-C(9)—C(18)	109·3	0·5
C(1)—C(10)-C(5)	111·8	0·4
C(1)—C(10)-C(9)	113·2	0·4
C(5)—C(10)-C(9)	113·7	0·4
C(9)—C(11)-C(12)	113·2	0·4
C(12)-C(13)-C(14)	108·6	0·5
C(12)-C(13)-C(15)	108·2	0·6
C(12)-C(13)-C(17)	109·1	0·6
C(14)-C(13)-C(15)	114·3	0·6
C(14)-C(13)-C(17)	108·2	0·5
C(15)-C(13)-C(17)	108·1	0·6
C(8)—C(14)-C(13)	113·3	0·4
C(13)-C(15)-C(16)	129·3	1·1

error at 1·318 Å. The sixteen single bonds between sp^3-hybridized carbon atoms have a mean length of 1·530 Å and show a standard deviation of 0·016 Å. This is somewhat higher than the standard deviations derived from the inverse least-squares matrix, and the errors listed in Table 2 must be considered to be underestimates. The four single bonds involving one sp^2- and one sp^3-hybridized atom range in length from 1·494 to

Table 4. *Observed and calculated structure factors*

The four columns for each datum represent l, F_{obs} ($\times$ 10), F_{calc} ($\times$ 10), and the phase angle ($\times$ 100). Terms denoted * were assumed to be affected by extinction.

H= 0 K= 0			
4	13[illegible]	191	0
6	87	102	0
8	516	587	315
10	142	179	0
12*	893	1225	315
14	78	97	315
16	202	211	0
18	60	41	315
20	52	47	0
22	29	26	0
24	13	27	315
26	65	67	0
28	45	51	315
H= 0 K= 1			
2*	406	846	157
3	397	338	-157
4	515	550	157
5	541	589	-157
6	157	194	-157
7	439	479	157
8	142	176	157
9	567	521	157
10	359	380	157
11	400	360	-157
12	99	101	-157
13	45	53	157
14	233	227	-157
15	60	56	-157
16	173	163	-157
17	148	146	157
18	42	34	157
19	100	115	-157
20	30	30	157
21	22	7	157
22	13	31	157
23	13	15	-157
24	39	34	157
25	13	13	157
26	36	39	157
27	10	3	-157
28	23	19	157
29	26	24	-157
30	7	7	-157
31	16	18	157
H= 0 K= 2			
2*	557	834	0
3	182	140	0
4	65	27	315
5	93	78	0
6	179	182	0
7	39	32	315
8	105	133	0
9	201	209	0
10	160	143	315
11	358	366	315
12	142	123	315
13	314	360	0
14	260	267	315
15	46	42	0
16	76	77	315
17	74	73	315
18	44	45	315
19	17	14	315
20	13	19	315
21	54	46	315
22	22	21	315
23	29	27	315
24	25	16	0
25	12	7	315
26	35	32	0
27	10	10	315
28	26	18	0
29	17	11	0
H= 0 K= 3			
1	676	725	157
2	83	92	-157
3	579	485	-157
4	151	125	157
5	150	144	157
6	204	173	-157
7	220	224	-157
8	97	125	-157
9	80	93	-157
10	13	0	157
11	42	26	-157
12	45	60	157
13	321	324	-157
14	33	37	157
15	260	247	157
16	20	28	-157
17	71	78	157
18	12	6	-157
19	38	40	157
20	113	128	157
21	39	35	157
22	52	55	-157
23	35	34	-157
24	13	8	-157
25	12	3	-157
26	10	3	157
27	10	15	-157
28	5	11	-157
29	42	42	-157
H= 0 K= 4			
0	132	80	315
1	46	44	0
2	282	253	0
3	547	471	315
4	205	164	0
5	71	24	315
6	36	26	0
7	193	176	0
8	112	111	315
9	174	184	315
10	87	68	315
11	25	13	315
12	151	151	0
13	55	47	0
14	192	200	315
15	179	203	0
16	30	30	315
17	84	90	0
18	45	39	315
19	89	88	315
20	33	22	315
21	13	7	315
22	22	22	315
23	13	9	0
24	48	49	315
25	33	35	315
26	46	44	0
27	48	45	315
28	20	12	0
29	28	26	315
H= 0 K= 5			
1	9	6	-157
2	426	383	-157
3	195	171	157
4	234	204	157
5	65	64	-157
6	39	42	-157
7	68	42	-157
8	100	99	157
9	10	14	157
10	28	25	-157
11	39	41	-157
12	105	100	-157
13	48	38	-157
14	186	212	157
15	113	134	-157
16	13	12	-157
17	62	64	157
18	71	74	-157
19	61	61	157
20	17	18	157
21	13	3	-157
22	29	24	-157
23	12	11	157
24	32	24	157
25	35	32	157
26	17	16	-157
27	9	13	157
28	30	26	-157
H= 0 K= 6			
0	103	87	0
1	267	247	0
2	51	52	0
3	134	117	315
4	26	25	0
5	62	93	315
6	129	118	0
7	29	21	315
8	12	11	315
9	64	47	315
10	12	11	315
11	153	144	0
12	81	75	315
13	90	89	315
14	19	19	315
15	64	60	0
16	68	62	315
17	51	50	0
18	93	93	315
19	13	8	0
20	13	15	0
21	17	17	315
22	19	11	0
23	10	8	315
H= 0 K= 7			
1	45	42	157
2	81	87	157
3	12	12	-157
4	17	8	-157
5	57	51	-157
6	58	59	157
7	30	34	157
8	12	9	157
9	32	30	-157
10	52	47	157
11	22	15	157
12	13	13	-157
13	32	39	-157
14	22	22	-157
15	36	35	157
16	22	16	157
17	13	13	-157
18	12	13	-157
19	29	25	157
H= 0 K= 8			
0	263	223	0
1	13	10	315
2	145	130	315
3	13	8	0
4	153	149	0
5	22	24	0
6	17	9	0
7	61	54	0
8	129	113	315
9	13	12	315
10	51	53	0
11	13	16	315
12	70	68	315
13	28	25	0
14	30	23	0
15	41	36	315
16	35	26	315
17	29	24	0
18	29	26	315
19	12	5	315
20	10	0	315
21	9	8	315
22	7	18	0
23	16	1	0
H= 0 K= 9			
1	26	12	-157
2	32	26	-157
3	38	32	-157
4	13	6	-157
5	52	50	157
6	22	16	157
7	30	34	-157
8	17	8	-157
9	30	26	157
10	13	16	157
11	12	7	-157
12	12	3	-157
13	12	22	157
14	25	19	157
15	19	8	-157
16	10	2	157
17	10	5	-157
18	9	10	157
19	9	13	-157
20	7	9	-157
21	6	29	157
H= 0 K=10			
0	60	60	315
1	83	76	315
2	54	47	0
3	39	39	0
4	32	28	315
5	36	32	315
6	26	19	0
7	12	3	315
8	10	8	0
9	25	25	0
10	10	1	0
11	26	27	315
12	23	21	0
13	36	38	0
14	36	34	315
15	9	4	315
16	16	11	0
17	19	16	0
H= 0 K=11			
1	28	24	157
2	30	26	-157
3	17	16	-157
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16	96	103	0
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7	115	97	-14
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15	64	67	-251
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14	212	237	-200
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5	157	157	-311
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6	22	22	-171
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19	99	114	-245
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27	23	28	263
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16	48	55	-187
17	13	8	279
18	57	62	93
19	16	16	6
20	48	46	-207
21	14	17	95
H= 3 K= 7			
0	42	50	157
1	83	85	84
2	25	27	136
3	86	84	-295
4	77	71	249
5	51	54	72
6	38	40	1
7	38	32	-199
8	13	13	-215
9	30	32	117
10	51	53	-263
11	49	46	99
12	70	72	-27
13	60	68	-275
14	32	35	-286
15	48	53	26
16	48	51	-91
17	36	41	-235
18	10	15	209
19	10	12	181
20	29	28	-214
21	13	13	-57
22	19	21	62
23	28	27	-289
H= 3 K= 8			
0	39	37	157
1	45	42	-95
2	30	28	-294
3	30	24	112
4	17	13	-176
5	26	23	-249
6	17	15	161
7	33	37	143
8	13	11	-153
9	25	28	-181
10	17	21	302
11	12	11	312
12	20	19	-172
13	20	15	216
14	12	9	309
15	22	24	-260
16	26	30	42
17	30	32	82
18	41	37	-250
19	30	32	-154
20	30	30	94
21	28	30	152
H= 3 K= 9			
0	28	30	157
1	29	27	-114
2	17	17	-124
3	36	37	197
4	28	27	85
5	38	35	-38
6	20	22	-287
7	41	43	203
8	12	8	257
9	16	16	-254
10	28	29	81
11	36	32	-14
12	23	27	-220
13	42	44	274
14	16	19	15
15	33	31	-108
16	39	41	-269
17	25	23	178
18	30	32	-12
19	16	24	-178
H= 3 K=10			
0	14	10	-157
1	14	11	61
2	19	12	9
3	14	8	-304
4	12	12	-233
5	19	18	141
6	25	28	126
7	20	21	-169
8	28	32	-171
9	13	13	96
10	19	23	175
11	9	7	229
12	9	0	217
13	14	16	281
14	14	14	-201
15	14	17	-15
H= 3 K=11			
0	9	3	-157
1	9	4	-109
2	20	23	119
3	9	13	68
4	19	22	-156
5	10	10	282
6	7	9	186
7	17	15	-142
8	6	10	61
9	12	14	141
H= 4 K= 0			
0	62	85	0
1	28	31	157
2	86	106	0
3	452	379	-157
4	400	333	315
5	108	96	157
6	14	5	0
7	6	10	-157
8	6	6	0
9	10	16	157
10	10	19	315
11	100	117	157
12	17	10	315
13	102	104	-157
14	135	141	315
15	269	280	157
16	185	232	0
17	60	66	-157
18	36	46	0
19	9	7	-157
20	33	44	0
21	26	25	157
22	30	37	0
23	20	23	-157
24	7	3	0
25	19	7	157
26	23	28	0
27	16	49	-157
28	38	55	315
H= 4 K= 1			
0	14	1	0
1	119	113	92
2	298	271	226
3	58	39	-56
4	227	187	10
5	142	99	-96
6	42	39	242
7	51	50	-7
8	67	63	-310
9	51	65	199
10	67	72	30
11	57	57	-61
12	61	68	58
13	71	83	-99
14	147	176	-165
15	94	91	270
16	67	66	-239
17	52	43	253
18	17	17	-56
19	38	36	164
20	14	0	246
21	35	38	-150
22	19	17	178
23	14	11	-7
24	28	26	303
25	42	37	253
26	46	51	98
27	38	38	-51
H= 4 K= 2			
0	64	47	315
1	205	176	-137
2	176	148	-164
3	235	193	304
4	148	121	248
5	96	91	11
6	134	125	-230
7	32	28	-257
8	77	68	-51
9	52	41	-221
10	67	54	304
11	36	37	183
12	19	21	-258
13	138	143	205
14	126	145	93
15	129	168	-17
16	99	94	-126
17	73	91	257
18	73	80	40
19	38	42	-135
20	36	42	70
21	38	40	175
22	28	26	-122
23	7	8	269
24	16	21	4
25	26	21	-81
26	44	35	-247
27	30	37	311
H= 4 K= 3			
0	132	127	315
1	129	136	117
2	126	117	13
3	148	141	-98
4	89	70	-294
5	48	48	-308
6	61	55	-173
7	33	29	133
8	45	49	13
9	17	12	-94
10	7	12	258
11	33	21	78
12	64	58	-60
13	113	132	-188
14	62	60	301
15	52	63	194
16	9	21	-199
17	35	39	100
18	35	36	27
19	20	17	-246
20	29	33	-216
21	25	30	70
22	7	10	199
23	7	12	28
24	14	12	202
25	6	11	130
26	16	14	-53
H= 4 K= 4			
0	6	7	315
1	153	153	-244
2	185	195	272
3	96	92	300
4	94	87	-67
5	112	36	125
6	83	83	222
7	26	23	-126
8	23	13	-147
9	45	44	-286
10	42	45	-37
11	68	84	227
12	35	42	112
13	73	78	35
H= 4 K= 4			
14	103	126	-56
15	38	38	-45
16	61	67	288
17	9	9	-191
18	55	64	-58
19	20	17	149
20	7	7	-197
21	7	7	-272
22	41	36	106
23	16	15	169
24	9	8	-154
25	14	12	-273
26	20	23	287
H= 4 K= 5			
0	167	173	0
1	132	135	19
2	103	100	-162
3	49	47	112
4	19	29	267
5	54	55	-159
6	61	57	220
7	33	39	55
8	36	41	-70
9	49	41	306
10	35	35	-217
11	108	114	-88
12	94	107	-269
13	62	68	240
14	55	60	132
15	61	63	-272
16	12	18	-76
17	32	32	61
18	29	27	-92
19	7	14	236
20	17	21	8
21	23	24	35
22	14	9	224
23	14	16	205
24	12	17	19
25	9	11	-131
H= 4 K= 6			
0	125	145	315
1	58	63	-312
2	108	113	115
3	124	137	-93
4	35	25	163
5	71	67	277
6	60	54	-252
7	16	9	199
8	9	5	-72
9	32	35	150
10	32	35	236
11	30	32	225
12	52	57	34
13	35	35	-5
14	67	82	-149
15	60	72	251
16	30	22	-180
17	44	45	18
18	44	43	18
19	39	41	-197
20	20	17	88
21	33	28	99
22	19	18	222
23	20	19	-186
24	16	16	-77
H= 4 K= 7			
0	9	5	0
1	48	46	-265
2	36	34	0
3	30	27	197
4	29	24	-249
5	33	41	-2
6	22	25	176
7	36	38	-21
8	36	32	-288

Table 4 (*cont.*)

9	9	11	103
10	42	44	-116
11	36	38	302
12	41	43	187
13	30	37	48
14	32	37	-222
15	26	28	-168
16	20	17	-10
17	16	20	277
18	25	26	-66
19	6	2	128
20	26	22	64
21	23	26	-273
22	17	20	294
H= 4 K= 8			
0	36	44	315
1	54	60	10
2	15	22	-27
3	28	28	-228
4	35	40	280
5	14	11	300
6	22	27	33
7	9	12	-146
8	26	26	-251
9	10	9	-67
10	7	6	-206
11	33	32	119
12	30	33	-6
13	35	45	-232
14	29	30	-311
15	33	37	139
16	38	47	-48
17	13	9	-94
18	26	20	313
19	28	23	167
H= 4 K= 9			
0	7	6	0
1	16	12	-139
2	20	23	131
3	32	31	230
4	7	14	-122
5	7	8	-245
6	30	33	-292
7	10	9	-50
8	30	31	10
9	7	9	-128
10	20	21	-305
11	9	10	215
12	6	6	26
13	6	5	62
14	20	22	-187
15	20	17	-12
16	7	14	226
17	9	13	-67
H= 4 K=10			
0	30	29	0
1	13	13	123
2	16	22	-311
3	16	21	312
4	6	5	259
5	19	23	-67
6	4	6	278
7	14	17	-266
8	9	11	33
9	16	13	147
10	6	6	-79
11	20	8	-107
12	16	19	-267
H= 5 K= 0			
1	54	24	-157
2	33	69	0
3	29	46	157
4	7	29	315
5	9	27	-157
6	16	19	315
7	41	44	157
8	28	24	315
9	10	11	157
10	39	39	0
11	32	37	-157
12	36	44	315
13	55	63	157
13	55	63	157
14	30	12	315
15	55	55	-157
16	51	34	0
17	52	51	157
18	14	12	0
19	14	12	-157
20	46	39	0
21	13	5	-157
22	13	3	0
23	35	31	157
24	19	13	0
25	41	32	-157
H= 5 K= 1			
0	147	173	-157
1	110	164	48
2	74	105	145
3	42	29	145
4	57	43	-23
5	32	30	41
6	46	66	-310
7	25	26	126
8	29	32	149
9	30	19	89
10	62	73	-57
11	60	59	264
12	55	55	164
13	113	113	-245
14	36	33	-171
15	20	15	258
16	25	26	-193
17	25	24	-265
18	14	3	-101
19	35	24	-303
20	14	17	-6
21	22	19	298
22	13	17	283
23	12	11	214
24	30	24	173
H= 5 K= 2			
0	26	30	-157
1	119	141	71
2	80	85	216
3	93	103	141
4	97	101	-91
5	44	28	-202
6	51	38	256
7	29	29	309
8	30	25	224
9	41	30	98
10	52	47	-96
11	109	105	259
12	44	47	228
13	25	27	-177
14	97	79	-71
15	67	65	-139
16	74	75	212
17	25	34	47
18	32	29	-81
19	14	17	73
20	23	21	-56
21	13	11	39
22	22	18	180
23	12	2	203
24	22	20	-165
H= 5 K= 3			
0	116	131	157
1	174	188	103
2	105	114	-244
3	96	111	-48
4	33	46	-28
5	80	78	218
6	20	19	-66
7	12	22	16
8	25	34	94
9	33	33	-228
10	13	17	231
11	84	93	268
12	61	64	-192
13	67	63	-219
14	84	85	72
15	54	55	-301
16	14	19	-280
17	20	24	-135
18	20	19	240
19	30	27	119
H= 5 K= 4			
0	90	86	157
1	103	106	179
2	61	64	-268
3	22	11	-73
4	13	16	-173
5	87	63	134
6	13	5	175
7	23	28	288
8	44	37	-5
9	19	10	-236
10	64	58	291
11	78	81	105
12	77	73	-58
13	67	64	-178
14	14	9	172
15	14	8	256
16	36	41	48
18	32	30	-301
19	13	12	135
20	22	11	60
21	33	22	167
22	30	20	315
23	22	22	-240
H= 5 K= 5			
0	61	58	157
1	185	190	-129
2	60	58	-301
3	93	96	85
4	52	53	260
5	67	42	-246
6	84	85	-56
7	42	28	-127
8	14	12	-267
9	29	25	107
10	41	37	-291
11	67	68	-222
12	32	33	-117
13	86	79	203
14	36	37	38
15	55	51	-299
16	38	39	-22
17	13	5	-137
18	60	54	208
19	39	26	43
20	12	6	-283
21	39	29	271
22	10	7	-149
23	28	22	-159
H= 5 K= 6			
0	108	100	157
1	71	71	-201
2	29	27	305
3	14	11	109
4	35	26	-145
5	36	39	142
6	83	73	-253
7	25	24	116
8	35	29	151
9	14	19	295
10	68	47	40
11	64	57	-54
12	89	93	-224
13	61	52	179
14	70	55	5
15	13	9	-25
16	19	17	-10
17	55	40	-222
18	64	55	136
H= 5 K= 7			
0	109	102	-157
1	25	20	247
2	90	91	165
3	54	48	-46
4	45	35	-247
5	51	47	-29
6	14	21	-273
7	36	30	266
8	25	21	26
9	25	22	297
10	42	35	-165
11	13	10	-136
12	44	37	166
13	22	18	50
14	58	44	-130
15	30	30	284
16	38	31	7
17	36	33	263
18	32	26	63
H= 5 K= 8			
0	35	25	-157
1	14	8	-141
2	51	38	96
3	13	13	-284
4	61	21	272
5	13	9	-139
6	35	26	-116
7	36	30	100
8	13	17	287
9	13	6	-15
10	22	24	-114
11	29	24	-271
12	20	14	132
13	26	25	89
14	35	22	-210
15	10	8	-105
16	12	11	-135
17	28	27	195
H= 5 K=10			
0	20	19	-157
1	16	9	95
2	23	20	235
3	35	24	-251
4	25	19	-16
5	28	25	-18
6	7	6	147
7	35	30	230
H= 6 K= 0			
0	94	138	0
1	128	120	157
2	55	61	315
3	28	9	-157
4	132	119	315
5	14	11	-157
6	26	10	0
7	35	10	-157
8	35	50	0
9	25	22	-157
10	17	11	0
11	19	20	-157
12	70	66	315
13	85	97	-157
14	28	31	0
15	58	33	157
16	67	79	0
17	7	2	157
18	12	5	315
19	52	46	157
H= 6 K= 1			
0	0	46	0
1	69	95	161
2	170	174	241
3	212	220	-234
4	87	85	-74
5	81	92	137
6	28	15	-172
7	45	34	-76
8	32	35	-131
9	59	73	250
10	74	87	78
11	16	12	-145
12	14	10	-295
13	74	81	-148
14	67	68	-106
15	103	113	76
16	29	37	274
17	26	22	-163
18	10	13	193
19	35	25	-239
20	25	31	-293
21	36	40	244
H= 6 K= 2			
0	4	43	0
1	165	172	249
2	148	149	-224
3	35	37	251
4	42	41	-196
5	70	61	-81
6	5	10	41
7	23	21	-2
8	42	37	-287
9	51	41	284
10	70	72	-35
11	89	93	-229
12	16	13	-173
13	64	71	-71
14	83	92	160
15	36	36	-81
16	46	54	36
17	52	46	219
18	7	7	143
19	14	11	73
20	35	35	-111
H= 6 K= 3			
0	6	84	315
1	110	108	248
2	138	132	-195
3	78	75	-90
4	96	117	100
5	58	61	-305
6	77	75	-123
7	35	39	307
8	32	36	248
9	55	49	102
10	38	40	-91
11	55	55	-233
12	55	45	-52
13	33	43	-54
14	65	78	100
15	16	20	210
16	60	62	-257
17	38	37	55
18	33	30	313
19	17	15	-163
20	38	38	189
H= 6 K= 4			
0	182	176	315
1	22	16	290
2	55	47	-29
3	38	38	208
4	44	46	-161
5	23	23	126
6	30	27	229
7	7	8	315
8	7	9	-282
9	26	14	-93
10	25	18	-209
11	29	30	-288
12	77	78	20
13	7	11	-210
14	7	11	125
15	36	43	-79
16	35	36	187
17	19	18	-201
18	32	25	-22
19	6	8	-211
20	13	14	-127
H= 6 K= 5			
0	54	76	315
1	28	27	-167
2	60	69	-116
3	45	47	115
4	23	20	153
5	30	32	-185
6	17	19	-84
7	17	18	113
8	7	9	47
9	25	24	-187
10	39	39	-239
11	35	39	198
12	38	52	-46
13	19	9	-223
14	44	43	182
15	32	32	-260
16	6	4	185
17	23	21	62
18	20	26	-272
H= 6 K= 6			
0	20	14	0
1	73	78	-11
2	55	60	-267
3	20	22	286
4	17	10	13
5	35	42	199
6	7	3	24
7	29	28	-73
8	23	17	215
9	30	24	-299
10	19	17	-110
11	38	37	27
12	17	12	-55
13	35	29	278
14	35	34	28
15	28	24	-244
16	14	20	146
17	33	31	-70
18	0	8	-252
19	19	19	-272
H= 6 K= 7			
0	16	14	315
1	30	40	-40
2	20	23	73
3	20	21	186
4	42	40	-235
5	19	16	-107
6	23	19	52
7	22	21	246
8	14	19	-154
9	7	6	-208
10	13	14	149
11	29	25	-27
12	22	18	-140
13	33	35	233
H= 6 K= 8			
0	20	21	0
1	9	10	256
2	22	26	314
3	4	13	93
4	6	3	-140
5	20	12	-153
6	6	10	-79
7	12	17	136
8	22	17	-247
9	10	12	-244
10	22	22	1
H= 6 K= 9			
0	10	13	0
1	16	19	52
2	22	28	315
3	29	31	-201
4	23	27	-36
5	25	32	143
6	16	14	226
7	16	23	-201
H= 7 K= 0			
1	78	64	157
2	58	54	315
3	54	85	-157
4	76	55	0
5	14	20	157
6	14	2	315
7	14	10	-157
8	14	19	0
9	14	17	-157
10	45	24	315
11	14	10	157
12	14	18	0
13	13	24	-157
14	13	18	0
15	46	44	157
16	28	28	315
17	20	13	157
18	14	2	315
19	44	22	157
20	9	24	0
21	41	41	-157
H= 7 K= 1			
0	14	10	-157
1	44	24	-292
2	52	47	-194
3	25	24	245
4	45	60	-66
5	55	62	61
6	29	25	266
7	32	31	188
8	20	24	25
9	28	26	-161
10	28	21	165
11	28	17	-60
12	26	12	230
13	41	26	33
14	19	20	151
15	35	25	-125
16	36	33	150
17	33	29	-207
18	58	45	-260
19	62	54	273
20	36	35	56
H= 8 K= 0			
0	13	8	0
1	13	12	157
2	28	29	315
3	13	17	157
4	13	17	0
5	23	15	-157
6	13	13	0
7	13	8	157
8	12	14	0
9	28	22	157
10	12	12	0
11	26	21	-157
12	12	14	315
13	10	3	157
14	35	6	0
15	9	31	-157
16	32	31	315
H= 8 K= 1			
0	13	23	315
1	13	18	222
2	26	17	200
3	13	9	-76
4	26	27	-171
5	13	14	221
6	19	23	25
7	13	12	-131
8	17	10	245
9	12	12	-176
10	12	3	119
11	16	11	225
12	19	22	86
13	17	15	-165
14	16	9	-33
H= 9 K= 0			
1	35	56	157
H= 9 K= 1			
0	10	8	-157
1	48	28	-71
2	58	41	-209
3	74	47	214

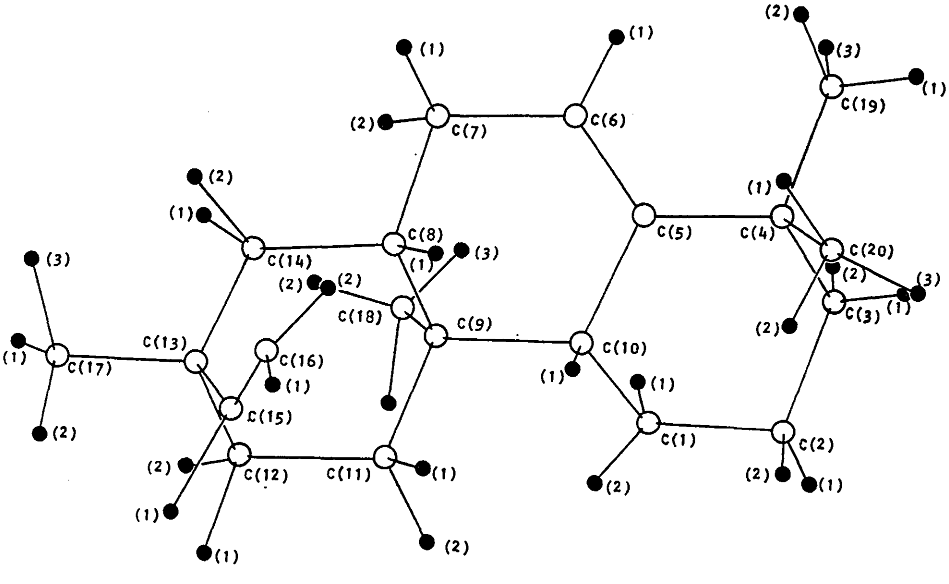


Fig. 1. The numbering system in the rimuene molecule. Hydrogen atoms are referred to the attached carbon atom.

1·537 Å, and thus are not in this study distinguishable from those above. The observed C–H bond lengths range from 0·84 to 1·36 Å. The majority of the intra-ring bond angles about sp^3-hybridized atoms are greater than tetrahedral (mean 111·2°), in evidence of the strain introduced by the endocyclic double bond.

Thermal parameters for most atoms are high, as expected for a hydrocarbon, and for many carbon atoms are distinctly anisotropic, as seen in Fig. 3. In general those atoms in the perhydrophenanthrene nucleus which have at least three carbon neighbours show the least vibration whereas the peripheral substituents are the most disturbed thermally, with their major vibration normal to the attaching bond.

The approximately planar molecules are inclined to the (010) plane at about 20°, and thus pack in layer fashion, as shown in Fig. 2. The closer intermolecular carbon–carbon approaches are indicated, but none are other than normal van der Waals approaches.

An interesting aspect of the structure is the placing of the vinyl group, in that in spite of the freedom of rotation about bond C(13)–C(15), atom C(16) adopts a position directly above ring *C*, such that the approach C(16)...C(14) is 3·03 Å. It is obvious from a model that this is by no means the optimum position, in so far as the minimization of internal repulsion is concerned. This may be no more than a result of the balance of crystal packing forces, as the vinyl group is the largest axial substituent on this approximately planar molecule, and the conformation adopted does make the molecule as compact as is possible. Nevertheless, it is notable that the vinyl group is ideally placed to undergo the ring closure which occurs during isomerization to isophyllocladene (III), a characteristic reac-

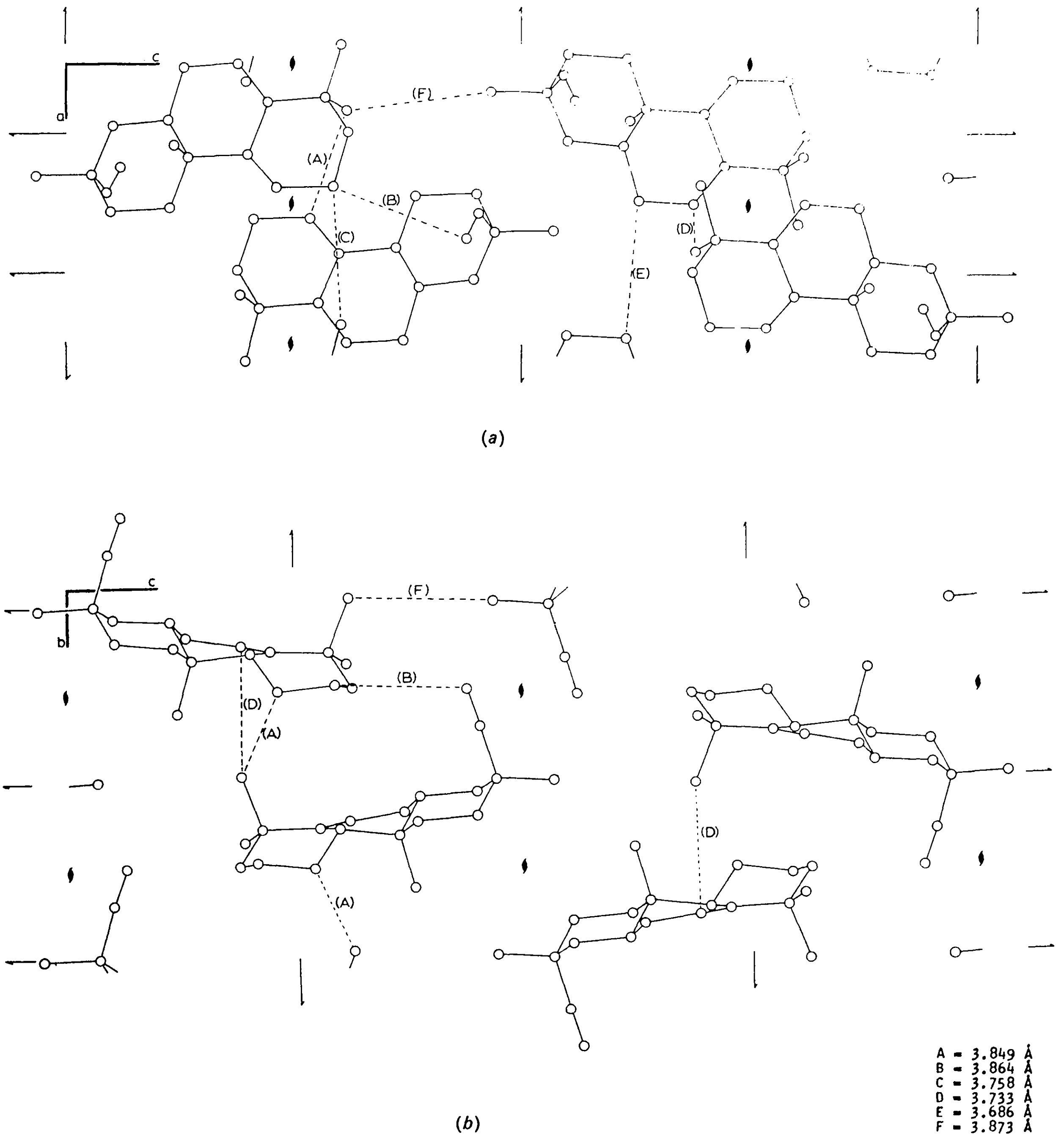


Fig. 2. The structure projected on (*a*) (010), (*b*) (100).

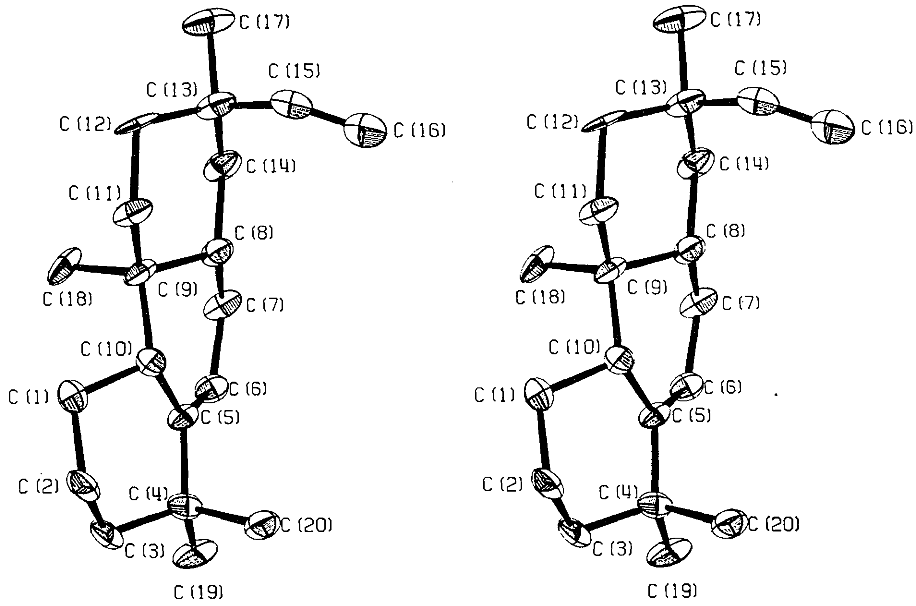
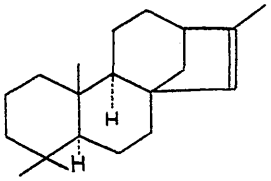


Fig. 3. A stereoscopic view of the rimuene molecule. The atoms are represented by ellipsoids whose principal axes were derived from the final anisotropic temperature factors.

tion of rimuene (Briggs, Cain & Wilmshurst, 1958). It is usually assumed that protonation of the endocyclic double bond and formation of a carbonium ion causes polarization of the vinylic double bond and thus attracts it into the correct position. It is interesting, if perhaps coincidental, that this required conformation is in fact that adopted in the crystalline state.



(III)

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