

Fig. 1. Pseudo-monoclinic F -cell (fine line) and triclinic P -cell (heavy line). (a) Each of the full and empty triangles represents the asymmetric unit (two molecules) at x and $\frac{1}{2}+x$ respectively, referred to the F -cell. (b) Here each triangle represents a single molecule. Two types of dashed triangles stand for molecules at $-x$ and at $\frac{1}{2}-x$ respectively (always referred to the F -cell).

and of 11,11-difluoro-1,6-methano[10]annulene (*Ib*) (Gramaccioli & Simonetta, 1971) confirmed the presence of an aromatic perimeter ring, in agreement with chemical and spectroscopic (n.m.r.) results. The situation seemed quite different for the corresponding 11,11-dimethyl derivative, for which the n.m.r. data (Vogel, 1969) clearly favoured the bisnorcaradiene structure (*II*).

The present structure determination of compound (*II*), 11,11-dimethyltricyclo[4,4,1,0^{1,6}]undeca-2,4,7,9-tetraene (hereafter DIM), has been undertaken in order to study to what extent the substitution of the hydrogen or fluorine atoms of (*I*) by methyl groups can affect the molecular geometry of the nucleus [atoms C(1) to C(11)].* Preliminary results have been reported in a short communication (Bianchi, Mugnoli & Simonetta, 1972).

Preliminary considerations on the symmetry

Crystals of DIM (m.p. 88°C) are in the form of colourless parallelepipeds which decompose rapidly in air;

* We wish to thank Professor Emanuel Vogel for suggesting this problem and for supplying the crystals.

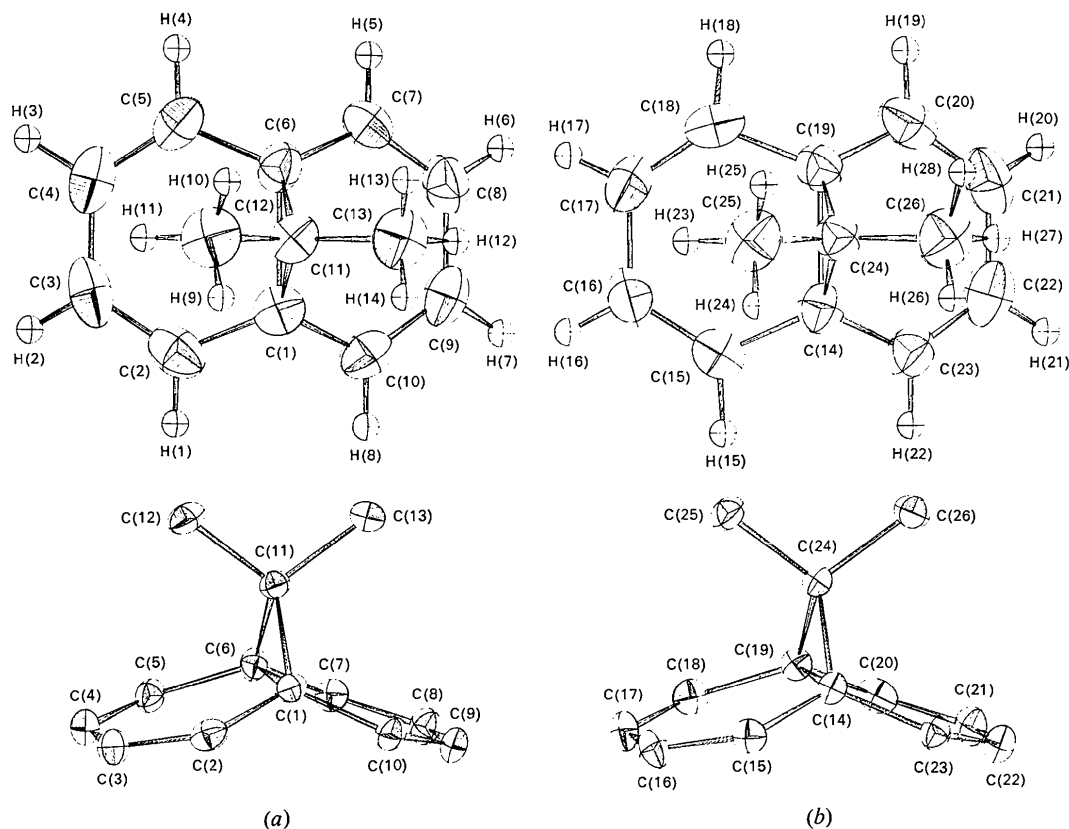


Fig. 2. Numbering of atoms and temperature ellipsoids for (a) molecule *A* and (b) molecule *B*. The ellipsoids for carbon atoms are drawn at probabilities 0.50 and 0.20 in the upper and lower part of the Figure, respectively. Hydrogen atoms are on an arbitrary scale.

for the X-ray analysis, crystals sealed in Lindemann glass tubes were used. Weissenberg and precession photographs taken with several crystals exhibited unusual features: the nkl layers with n odd showed no symmetry related intensities, whereas for n even the symmetry of the layer was very near to mm (for $n=0$) and to m (for higher levels), thus simulating monoclinic symmetry. On the basis of the corresponding pseudo-monoclinic unit cell ($a \sim 14.6$, $b \sim 7.0$, $c \sim 38.9$ Å, $\beta \sim 102^\circ$) reflexions were found to be present according to the following laws: for $h=2n$, $h+k=2n$ and $k+l=4n$; for $h=2n+1$, $h+k=2n$ and $k+l=4n+2$. All the reflexions are sharp; no systematic intensity changes were found between subsequent layers. For an observed density $D_m = 1.157$ g cm⁻³, the described pseudo-monoclinic face-centered unit cell (hereafter briefly F -cell) contains 16 molecules of C₁₃H₁₄. Besides the F lattice, the observed extinctions suggest a further lattice translation: since for all layers $3k+l=4n$, repetition must take place also at $(0, \frac{3}{4}, \frac{1}{4})$. In the absence of further symmetry operations, the asymmetric unit contains therefore two molecules of C₁₃H₁₄ [see Fig. 1(a)].

A monoclinic symmetry $I_{hkl} = I_{\bar{h}\bar{k}l}$ for $h=2n$ in the F -cell can be justified by assuming the presence of a twofold screw axis with a shift of $\frac{1}{4}$ along \mathbf{b} relating the two molecules of the asymmetric unit. Following Dornberger-Schiff (1966) and Dornberger-Schiff & Grell-Niemann (1961), such partial operator (P.O.) of symmetry is a $2_{1/2}$ axis in an O.D.-structure. In this case it is easy to show that, if Friedel's law holds, $A_{hkl} = A_{\bar{h}\bar{k}l}$, $B_{hkl} = -B_{\bar{h}\bar{k}l}$ for $k=4n$, and $A_{hkl} = -A_{\bar{h}\bar{k}l}$, $B_{hkl} = B_{\bar{h}\bar{k}l}$ for $k=4n+2$; in particular for both cases $|F_{hkl}| = |F_{\bar{h}\bar{k}l}|$. For $h=2n+1$, if the hkl reflexion is observed, the corresponding $\bar{h}\bar{k}l$ is missing, thus interrupting the 'monoclinic symmetry'. Therefore from the observed data only ($I_{hkl} \sim I_{\bar{h}\bar{k}l}$ for $h=2n$) the second molecule of the asymmetric unit is expected to be related to the first one by a twofold screw axis, the shift being about $\pm 0.250 \mathbf{b}$. The presence of a $2_{1/2}$ axis at $x_F=0$, $z_F=0$,

implies also a 2 axis at $x_F=0$, $z_F=\frac{1}{8}$ as a P.O. between two adjacent layers of the structure [see Fig. 1(b)].

For the solution of the structure however a triclinic primitive cell (hereafter P -cell) was chosen, as obtained from the F -cell by the transformation matrix

$$\mathbf{S} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 1 & 0 \\ 0 & -\frac{1}{4} & \frac{1}{4} \end{pmatrix}$$

This cell, which contains two molecules of C₁₃H₁₄, preserves the \mathbf{b} vector of the F -cell, which lies along the elongation axis of the crystals. Hereafter, if not explicitly quoted, reference will be made always to the triclinic P -cell.

Collection and reduction of X-ray data

The unit-cell dimensions (see Table 1) were obtained by a least-squares fit to measurements of $\sin^2 \theta$ for 35, 20, and 55 reflexions on zero-level Weissenberg photographs taken at 21 °C with Cu $K\alpha$ radiation about the [010], [001] and [210] axes respectively; the film was held in the asymmetric position, following the Straumanis technique. No correction for eccentricity or absorption was introduced in the least-squares calculations and weights were assumed to be inversely proportional to $\sin^2 2\theta$. The density was measured by flotation in a dilute Thoulet (K₂HgI₄) solution. The space group $P1$ was assumed in agreement with the intensity statistic (see later) and confirmed by the structure solution.

Intensity data were collected with Mo $K\alpha$ radiation and a silicon (111) single-crystal monochromator on a PAILRED linear equi-inclination diffractometer in the automatic mode using the ω -scan technique, with a scan speed of 1° min^{-1} . The scan range varied from $\pm 0.6^\circ$ to $\pm 1.5^\circ$ (the larger values being used in the higher layers for low values of the Y angle); correspondingly, background counts were taken for 60 to 100 sec at both ends of the scan, with crystal and counter stationary. Scanning was automatically repeated for each reflexion if the number of scan counts did not reach the value of 1000. A crystal with dimensions $0.35 \times 0.50 \times 0.52$ mm, sealed in a Lindemann glass capillary, was mounted along the b axis, but after the collection of the second layer the capillary cracked causing decomposition of the crystal by air infiltration. A second crystal of dimensions $0.37 \times 0.44 \times 0.47$ mm was then mounted along the b axis and the layers

Table 1. Crystal data for C₁₃H₁₄

In parentheses with the lattice constants are the estimated standard deviations referred to the last decimal place.

$a = 8.089$ (1) Å	Triclinic, space group $P1$
$b = 7.007$ (1)	$D_m = 1.157$ g cm ⁻³
$c = 9.886$ (1)	$D_x = 1.161$ g cm ⁻³ ; $Z = 2$
$\alpha = 100.47$ (1)°	$\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å
$\beta = 95.91$ (1)	$\lambda(\text{Cu } K\alpha_2) = 1.54433$
$\gamma = 115.46$ (1)	$F(000) = 184$

Table 2. Statistical averages

	Theor. centric	Theor. non-centric	hkl	Experimental		
				$0kl$	$h0l$	hko
$\langle E \rangle$	0.798	0.886	0.867			
$\langle E ^2 \rangle$	1.000	1.000	1.000			
$\langle E ^2 - 1 \rangle$	0.968	0.736	0.767			
$\langle E ^2 - 1 \rangle$	0.000	0.000	-0.02	0.09	0.15	0.06
$\langle (E ^2 - 1)^2 \rangle$	1.891	0.964	1.10	1.22	2.39	1.63
$\langle (E ^2 - 1)^3 \rangle$	6.748	1.788	2.73	2.36	12.00	8.13

2 to 8 were collected. With both crystals some check reflexions were periodically remeasured, which gave no significant changes in the intensities. Scaling between the two sets of data was achieved through the reflexions of the second layer.

A total of 2232 independent reflexions were collected, of which 103 (the 'unobserved reflexions') had peak intensity less than the background; the total number of independent reflexions within the copper sphere is 2230. All the collected data were corrected for Lorentz and polarization factors. No correction either for extinction or for absorption ($\mu_{\text{MoK}\alpha} = 0.7 \text{ cm}^{-1}$) was applied.

Solution and refinement of the structure

Preliminary values for the absolute scale constant and the overall temperature factor ($B = 3.65 \text{ \AA}^2$) were ob-

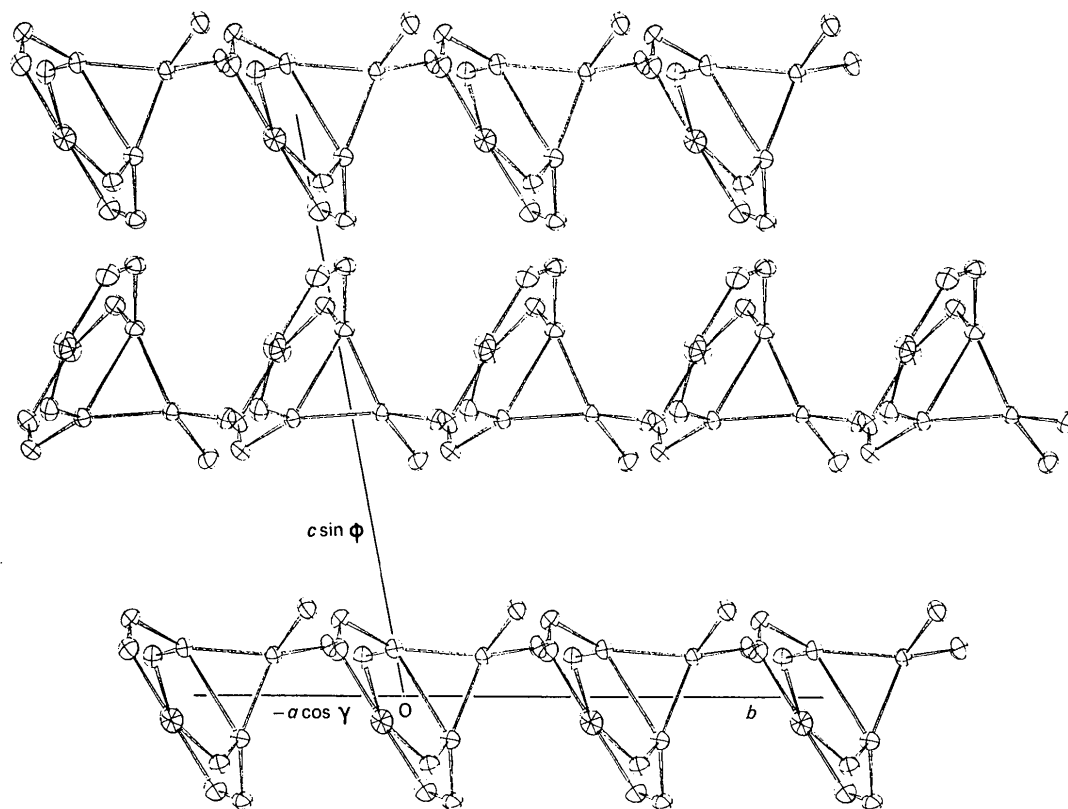
Table 3. *Observed and calculated structure factors*

All F values have been multiplied by 10. Reflexions omitted from the least-squares calculations are indicated by an asterisk.

h	k	l	F_o	F_c	F_o/F_c	$F_o - F_c$	$F_o + F_c$	$F_o - F_c$	$F_o + F_c$
1	0	0	100	100	1.00	0	200	0	200
2	0	0	400	400	1.00	0	800	0	800
3	0	0	900	900	1.00	0	1800	0	1800
4	0	0	1600	1600	1.00	0	3200	0	3200
5	0	0	2500	2500	1.00	0	5000	0	5000
6	0	0	3600	3600	1.00	0	7200	0	7200
7	0	0	4900	4900	1.00	0	9800	0	9800
8	0	0	6400	6400	1.00	0	12800	0	12800
9	0	0	8100	8100	1.00	0	16200	0	16200
10	0	0	10000	10000	1.00	0	20000	0	20000
11	0	0	12100	12100	1.00	0	24200	0	24200
12	0	0	14400	14400	1.00	0	28800	0	28800
13	0	0	16900	16900	1.00	0	33800	0	33800
14	0	0	19600	19600	1.00	0	39200	0	39200
15	0	0	22500	22500	1.00	0	45000	0	45000
16	0	0	25600	25600	1.00	0	51200	0	51200
17	0	0	28900	28900	1.00	0	57800	0	57800
18	0	0	32400	32400	1.00	0	64800	0	64800
19	0	0	36100	36100	1.00	0	72200	0	72200
20	0	0	40000	40000	1.00	0	80000	0	80000
21	0	0	44100	44100	1.00	0	88200	0	88200
22	0	0	48400	48400	1.00	0	96800	0	96800
23	0	0	52900	52900	1.00	0	105800	0	105800
24	0	0	57600	57600	1.00	0	115200	0	115200
25	0	0	62500	62500	1.00	0	125000	0	125000
26	0	0	67600	67600	1.00	0	135200	0	135200
27	0	0	72900	72900	1.00	0	145800	0	145800
28	0	0	78400	78400	1.00	0	156800	0	156800
29	0	0	84100	84100	1.00	0	168200	0	168200
30	0	0	90000	90000	1.00	0	180000	0	180000
31	0	0	96100	96100	1.00	0	192200	0	192200
32	0	0	102400	102400	1.00	0	204800	0	204800
33	0	0	108900	108900	1.00	0	217800	0	217800
34	0	0	115600	115600	1.00	0	231200	0	231200
35	0	0	122500	122500	1.00	0	245000	0	245000
36	0	0	129600	129600	1.00	0	259200	0	259200
37	0	0	136900	136900	1.00	0	273800	0	273800
38	0	0	144400	144400	1.00	0	288800	0	288800
39	0	0	152100	152100	1.00	0	304200	0	304200
40	0	0	160000	160000	1.00	0	320000	0	320000
41	0	0	168100	168100	1.00	0	336200	0	336200
42	0	0	176400	176400	1.00	0	352800	0	352800
43	0	0	184900	184900	1.00	0	369800	0	369800
44	0	0	193600	193600	1.00	0	387200	0	387200
45	0	0	202500	202500	1.00	0	405000	0	405000
46	0	0	211600	211600	1.00	0	423200	0	423200
47	0	0	220900	220900	1.00	0	441800	0	441800
48	0	0	230400	230400	1.00	0	460800	0	460800
49	0	0	240100	240100	1.00	0	480200	0	480200
50	0	0	250000	250000	1.00	0	500000	0	500000
51	0	0	260100	260100	1.00	0	520200	0	520200
52	0	0	270400	270400	1.00	0	540800	0	540800
53	0	0	280900	280900	1.00	0	561800	0	561800
54	0	0	291600	291600	1.00	0	583200	0	583200
55	0	0	302500	302500	1.00	0	605000	0	605000
56	0	0	313600	313600	1.00	0	627200	0	627200
57	0	0	324900	324900	1.00	0	650800	0	650800
58	0	0	336400	336400	1.00	0	675800	0	675800
59	0	0	348100	348100	1.00	0	701200	0	701200
60	0	0	360000	360000	1.00	0	728000	0	728000
61	0	0	372100	372100	1.00	0	755200	0	755200
62	0	0	384400	384400	1.00	0	782800	0	782800
63	0	0	396900	396900	1.00	0	810800	0	810800
64	0	0	409600	409600	1.00	0	839200	0	839200
65	0	0	422500	422500	1.00	0	868000	0	868000
66	0	0	435600	435600	1.00	0	897200	0	897200
67	0	0	448900	448900	1.00	0	926800	0	926800
68	0	0	462400	462400	1.00	0	956800	0	956800
69	0	0	476100	476100	1.00	0	987200	0	987200
70	0	0	490000	490000	1.00	0	1018000	0	1018000
71	0	0	504100	504100	1.00	0	1049200	0	1049200
72	0	0	518400	518400	1.00	0	1080800	0	1080800
73	0	0	532900	532900	1.00	0	1112800	0	1112800
74	0	0	547600	547600	1.00	0	1145200	0	1145200
75	0	0	562500	562500	1.00	0	1178000	0	1178000
76	0	0	577600	577600	1.00	0	1211200	0	1211200
77	0	0	592900	592900	1.00	0	1244800	0	1244800
78	0	0	608400	608400	1.00	0	1278800	0	1278800
79	0	0	624100	624100	1.00	0	1313200	0	1313200
80	0	0	640000	640000	1.00	0	1348000	0	1348000
81	0	0	656100	656100	1.00	0	1383200	0	1383200
82	0	0	672400	672400	1.00	0	1418800	0	1418800
83	0	0	688900	688900	1.00	0	1454800	0	1454800
84	0	0	705600	705600	1.00	0	1491200	0	1491200
85	0	0	722500	722500	1.00	0	1528000	0	1528000
86	0	0	739600	739600	1.00	0	1565200	0	1565200
87	0	0	756900	756900	1.00	0	1602800	0	1602800
88	0	0	774400	774400	1.00	0	1640800	0	1640800
89	0	0	792100	792100	1.00	0	1679200	0	1679200
90	0	0	810000	810000	1.00	0	1718000	0	1718000
91	0	0	828100	828100	1.00	0	1757200	0	1757200
92	0	0	846400	846400	1.00	0	1796800	0	1796800
93	0	0	864900	864900	1.00	0	1836800	0	1836800
94	0	0	883600	883600	1.00	0	1877200	0	1877200
95	0	0	902500	902500	1.00	0	1918000	0	1918000
96	0	0	921600	921600	1.00	0	1959200	0	1959200
97	0	0	940900	940900	1.00	0	2000800	0	2000800
98	0	0	960400	960400	1.00	0	2042800	0	2042800
99	0	0	980100	980100	1.00	0	2085200	0	2085200
100	0	0	1000000	1000000	1.00	0	2128000	0	2128000
101	0	0	1020100	1020100	1.00	0	2171200	0	2171200
102	0	0	1040400	1040400	1.00	0	2214800	0	2214800
103	0	0	1060900	1060900	1.00	0	2258800	0	2258800
104	0	0	1081600	1081600	1.00	0	2303200	0	2303200
105	0	0	1102500	1102500	1.00	0	2348000	0	2348000
106	0	0	1123600	1123600	1.00	0	2393200	0	2393200
107	0	0	1144900	1144900	1.00	0	2438800	0	2438800
108	0	0	1166400	1166400	1.00	0	2484800	0	2484800
109	0	0	1188100	1188100	1.00	0	2531200	0	2531200
110	0	0	1210000	1210000	1.00	0	2578000	0	2578000
111	0	0	1232100	1232100	1.00	0	2625200	0	2625200
112	0	0	1254400	1254400	1.00	0	2672800	0	2672800
113	0	0	1276900	1276900	1.00	0	2720800	0	2720800
114	0	0	1299600	1299600	1.00	0	2769200	0	2769200
115	0	0	1322500	1322500	1.00	0	2818000	0	2818000
116	0	0	1345600	1345600	1.00	0	2867200	0	2867200
117	0	0	1368900	1368900	1.00	0	2916800	0	2916800
118	0	0	1392400	1392400	1.00	0	2966800	0	2966800
119	0	0	1416100	1416100	1.00	0	3017200	0	3017200
120	0	0	1440000	1440000	1.00	0	3068000	0	3068000
121	0	0	1464100	1464100	1.00	0	3119200	0	3119200
122	0	0	1488400	1488400	1.00	0	3170800	0	3170800
123	0	0	1512900	1512900	1.00	0	3222800	0	3222800
124	0	0	1537600	1537600	1.00	0	3275200	0	3275200
125	0	0	1562500	1562500	1.00	0	3328000	0	3328000
126	0	0	1587600	1587600	1.00	0	3381200	0	3381200
127	0	0	1612900	1612900	1.00	0	3434800	0	3434800
128	0	0	1638400	1638400	1.00	0	3488800	0	3488800
129	0	0	1664100	1664100	1.00	0	3543200	0	3543200
130	0	0	1690000	1690000	1.00	0	3598000	0	3598000
131	0	0	171						

Table 4. *The carbon atom parameters and their standard deviations*All the values in this table have been multiplied by 10⁴.The temperature factor is in the form $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C(1)	-53 (0)	-40 (0)	816 (0)	187 (7)	212 (9)	97 (4)	111 (6)	28 (4)	34 (4)
C(2)	-1943 (7)	-1777 (8)	664 (5)	205 (8)	248 (10)	134 (5)	124 (7)	81 (5)	74 (5)
C(3)	-3371 (7)	-2324 (8)	-418 (6)	122 (7)	269 (11)	189 (6)	67 (7)	42 (5)	32 (7)
C(4)	-3132 (7)	-1460 (8)	-1630 (5)	156 (7)	310 (12)	139 (5)	110 (7)	-11 (5)	13 (6)
C(5)	-1487 (7)	-38 (8)	-1814 (5)	184 (7)	308 (11)	82 (4)	141 (8)	2 (4)	21 (5)
C(6)	220 (6)	1029 (7)	-744 (5)	135 (6)	259 (9)	81 (3)	99 (6)	18 (3)	25 (4)
C(7)	1948 (6)	1293 (8)	-1181 (5)	163 (7)	255 (9)	96 (4)	93 (7)	55 (4)	49 (5)
C(8)	3290 (6)	1022 (8)	-432 (5)	140 (7)	309 (11)	129 (5)	99 (7)	44 (4)	52 (6)
C(9)	3070 (7)	184 (8)	788 (5)	159 (7)	305 (11)	125 (4)	133 (7)	0 (4)	38 (6)
C(10)	1494 (7)	-429 (8)	1316 (5)	203 (8)	265 (10)	98 (4)	129 (7)	12 (4)	56 (5)
C(11)	241 (6)	2198 (7)	698 (5)	168 (6)	203 (8)	82 (3)	105 (6)	16 (4)	21 (4)
C(12)	-1350 (7)	2772 (8)	858 (5)	240 (9)	290 (11)	128 (5)	179 (8)	51 (5)	36 (6)
C(13)	2075 (7)	4122 (7)	1497 (5)	214 (8)	212 (9)	121 (5)	96 (7)	13 (5)	4 (5)
C(14)	7998 (6)	4194 (7)	6284 (5)	147 (6)	231 (9)	86 (4)	80 (6)	11 (4)	24 (4)
C(15)	6250 (7)	2959 (7)	6694 (5)	178 (7)	266 (10)	101 (4)	111 (7)	44 (4)	43 (5)
C(16)	4905 (6)	1021 (8)	5920 (5)	143 (7)	268 (10)	144 (5)	61 (7)	47 (5)	52 (6)
C(17)	5149 (7)	-173 (8)	4701 (5)	174 (7)	203 (9)	127 (5)	35 (7)	5 (5)	0 (5)
C(18)	6712 (7)	544 (8)	4202 (5)	247 (9)	242 (10)	86 (4)	132 (8)	26 (5)	1 (5)
C(19)	8301 (6)	2717 (7)	4758 (5)	147 (6)	215 (8)	94 (4)	93 (6)	31 (4)	34 (4)
C(20)	10181 (7)	2900 (8)	4905 (5)	229 (9)	277 (11)	140 (5)	158 (8)	94 (5)	76 (6)
C(21)	11589 (7)	4254 (8)	5994 (6)	145 (7)	343 (13)	185 (6)	119 (8)	52 (5)	92 (7)
C(22)	11328 (7)	5446 (9)	7201 (5)	171 (8)	309 (12)	134 (5)	75 (8)	-16 (5)	40 (6)
C(23)	9687 (7)	5329 (8)	7381 (5)	176 (7)	239 (10)	85 (4)	61 (7)	5 (4)	19 (5)
C(24)	8007 (6)	4719 (7)	4867 (4)	141 (6)	208 (8)	81 (3)	88 (6)	22 (3)	27 (4)
C(25)	6185 (7)	4480 (8)	4061 (5)	195 (8)	293 (11)	120 (4)	131 (8)	-10 (5)	46 (5)
C(26)	9615 (7)	6808 (8)	4750 (5)	232 (9)	247 (10)	118 (5)	101 (8)	36 (5)	63 (5)

Fig. 3. Packing of molecules as seen along the [210] axis. Twofold screw axes 2_p ($|p| < 1$) run parallel to *b*. ϕ is the angle between [210] and [001] axes.

made by one of us (R.B.). The starting coordinates corresponded to an *mm2*-symmetrized molecular model having the twofold axis coincident with the x_0 axis of a right-handed Cartesian coordinate system, and the elongation direction of the molecule parallel to the z_0 axis. The rotation range was 0 to 180° for θ_1 (around x_0), -90 to 90° for θ_2 (around y_0), 0 to 360° for θ_3 (around z_0). Two of the highest peaks in the sum function occurred at $\theta_1=75$, $\theta_2=30$, $\theta_3=90^\circ$ and $\theta_1=75$, $\theta_2=-30$, $\theta_3=90^\circ$ respectively, giving the approximate orientations of the two molecules in the unit cell.

The position of the two molecules was then found by means of systematic structure factor calculations, using a Fortran IV program written by C. M. Gramaccioli. The contributions of the first molecule (oriented, and kept fixed at the origin) were added to those of the second molecule, oriented and shifted along the x and y axes of the triclinic cell. In the region of minimum R , a last search was performed by moving the second molecule also along the z axis; the three-dimensional minimum (for $\Delta x=0.81$, $\Delta y=0.31$, $\Delta z=0.58$) was $R=0.20$ for 118 reflexions having $\sin^2 \theta/\lambda^2 \leq 0.07$. A subsequent structure factor calculation on about 450 reflexions having $\sin^2 \theta/\lambda^2 \leq 0.15$ gave $R=0.25$.

Refinement of the two molecules of the asymmetric unit was performed by a least-squares process, minimizing the function $\sum w(|F_{\text{obs}}| - |F_{\text{cal}}|)^2$. The coordinates of atom C(1) were held constant, owing to the polarity of space group *P1* along the three axes. During the first thirteen cycles (ten with isotropic, three with anisotropic carbon atoms) the block-diagonal approximation was applied, using a program written by Albano, Domenicano & Vaciago (1966). The limit in $\sin^2 \theta/\lambda^2$ was gradually extended from 0.15 to 0.35; initial weights were chosen as $w=1/f^2$ (where f is the scattering factor for the carbon atom at the calculated value of $\sin \theta/\lambda$), whereas after the tenth cycle the weights were calculated according to the expression

$$w' = 1/(A + B |F_{\text{obs}}| + C |F_{\text{obs}}|^2);$$

A , B and C were deduced from a least-squares fit of $(|F_{\text{obs}}| - |F_{\text{cal}}|)^2$ as a function of $|F_{\text{obs}}|$. Zero weight was given to reflexions having intensity $I < 2\sigma(I)$. The R index fell to about 0.10 but the convergence was very slow. A three-dimensional difference Fourier synthesis indicated the positions of the hydrogen atoms, with some uncertainty in the positions of the hydrogen atoms of two methyl groups.

At this stage, refinement was continued by an anisotropic full-matrix process using a modified version of the *ORFLS* program written by Busing, Martin & Levy (1962). Initially, the hydrogen atoms were included only in structure factor calculations; then, after a second difference Fourier synthesis (which gave better details of the methyl hydrogen positions, but showed broad peaks for some of them), they were refined isotropically. Because of computer-core size limitation, hydrogen and carbon atoms were refined in subsequent separate cycles. Weights were of the same form as w' ;

however, after examining the distribution of the average $(\Delta F)^2$ for various intervals of $|F_{\text{obs}}|$, it was considered profitable to use two different expressions, one parabolic in the $|F_{\text{obs}}|$ for $|F_{\text{obs}}| < 7$, and one linear for $7 \leq |F_{\text{obs}}| \leq 30$. Correspondingly, constancy of $w'(\Delta F)^2$ within 10% was reached. Zero weight was given to $|F_{\text{obs}}| > 30$ and to reflexions having $I < 2\sigma(I)$, as before. After 7 cycles of refinement on carbon atoms and 5 cycles on hydrogen atoms all the shifts were less than 0.1 times and 0.5 times the standard deviation of the corresponding parameter for the carbon and the hydrogen atoms respectively. The final R index over all the 2129 observed reflexions was 0.056, and that over the 1845 non-zero weight observations was 0.048.

Precision of the results

The observed and final calculated structure factors are listed in Table 3; the atomic scattering factors of Cromer & Waber (1965) for carbon atoms, and those of Stewart, Davidson & Simpson (1965) for hydrogen atoms were used. The final parameters of the carbon atoms are given in Table 4 and those of the hydrogen atoms in Table 5.

The standard deviations of the coordinates, derived from the residuals and the diagonal elements of the least-squares inverse matrix, correspond to positional uncertainties of the order of 0.006 Å for the carbon atoms and of 0.04 Å for the hydrogen atoms. The corresponding standard deviations in the bond distances, bond angles and torsion angles involving only carbon

Table 5. *Parameters for the hydrogen atoms*
Fractional coordinates are $\times 10^3$.

	x	y	z	B (Å ²)
H(1)	-210	-253	136	4.1
H(2)	-451	-356	-41	5.8
H(3)	-421	-203	-245	6.4
H(4)	-137	32	-271	4.7
H(5)	211	167	-200	5.4
H(6)	437	130	-79	6.0
H(7)	405	-22	116	5.7
H(8)	136	-115	203	5.9
H(9)	-134	313	183	8.1
H(10)	-101	394	56	6.3
H(11)	-253	167	40	8.4
H(12)	313	382	144	5.2
H(13)	224	520	111	6.0
H(14)	198	456	247	6.8
H(15)	624	360	772	4.9
H(16)	382	32	625	4.6
H(17)	425	-151	435	5.5
H(18)	704	-27	354	5.4
H(19)	1038	192	424	6.9
H(20)	1273	423	603	7.2
H(21)	1235	633	797	7.1
H(22)	957	599	824	5.9
H(23)	514	326	408	6.1
H(24)	587	568	444	6.6
H(25)	625	458	312	6.2
H(26)	939	806	505	8.2
H(27)	1074	699	525	6.8
H(28)	987	686	377	7.1

atoms are around 0.008 Å, 0.4 and 0.8° respectively; in the C-H bonds they are around 0.05 Å and in the C-C-H and H-C-H angles around 2.7 and 3.6°, respectively.

Corrections for thermal libration

The rigidity of the molecule C₁₃H₁₄ suggests the interpretation of thermal parameters in terms of rigid-body

Table 6. *Rigid-body tensors*

The tensors are referred to a Cartesian coordinate system defined by unit vectors $\mathbf{b} \times \mathbf{c}^*$, \mathbf{b} , $(\mathbf{b} \times \mathbf{c}^*) \times \mathbf{b}$. For each molecule, the origin is at the centre of gravity. All values have been multiplied by 10⁴.

		Molecule <i>A</i> [atoms C(1) to C(13)]		
T (Å ²) (‘unreduced’)	359 (9)	40 (9)	7 (9)	
		351 (12)	-8 (10)	357 (12)
L (rad ²)	44 (5)	-9 (3)	1 (3)	
		58 (3)	7 (3)	
			34 (3)	
S (Å rad)	2 (4)	7 (4)	-5 (4)	
	18 (3)	-6 (3)	16 (3)	
	-11 (3)	0 (3)	4 (3)	
		Molecule <i>B</i> [atoms C(14) to C(26)]		
T (Å ²) (‘unreduced’)	365 (11)	24 (10)	4 (10)	
		373 (14)	-29 (12)	353 (14)
L (rad ²)	40 (6)	11 (3)	-3 (3)	
		62 (4)	-6 (3)	
			36 (4)	
S (Å rad)	-6 (4)	-3 (4)	-5 (5)	
	-18 (4)	-7 (4)	-12 (3)	
	1 (4)	0 (3)	13 (4)	

motion. Accordingly, the tensors **T**, **L**, **S** (Schomaker & Trueblood, 1968) were derived for both molecules of the asymmetric unit from a least-squares treatment, using a Fortran IV program written by G. Filippini. In these calculations, equal weights were assigned to all thermal factors; the results are shown in Table 6. The agreement between observed and calculated values of B_{ij} for each atom is good, the differences exceeding 3σ only for 8 cases over a total of 156, and in most cases being of the order of 1σ . The mean square rotational displacements about the principal axes of the tensor **L** are 21, 14, and 10 (°)² for molecule *A*, and 22, 12, and 11 (°)² for molecule *B*. The numbering of atoms and the temperature ellipsoids for molecule *A* and *B* are shown in Fig. 2.

Bond distances (uncorrected and corrected for rigid-body motion), bond angles, and torsion angles, with their standard deviations, are collected in Tables 7, 8, and 9, respectively. The correction for distances have been derived under the rigid-body assumption from the tensor **L**, according to Schomaker & Trueblood (1968). Corrections for bond and torsion angles (less than 0.1°) were neglected. Signs for the torsion angles are given following the convention of Klyne & Prelog (1960). The standard deviations of the torsion angles along the perimeter ring were calculated according to Huber (1961). The mean planes, calculated following Schomaker, Waser, Marsh & Bergman (1959) are given in Table 10.

Are the two molecules symmetry-related?

The presence of two molecules as the asymmetric unit in space group *P1* is quite unusual; therefore the question arises whether a higher symmetry has been over-

Table 7. *Bond distances (Å)*

The ‘mean’ value is that of *mm*2-related bonds, averaged over the two molecules.

	Observed	Corrected*		Observed	Corrected*
C(1)—C(2)	1.459	1.466	C(3)—C(4)	1.432	1.440
C(5)—C(6)	1.452	1.459	C(8)—C(9)	1.430	1.437
C(6)—C(7)	1.451	1.457	C(16)—C(17)	1.420	1.427
C(1)—C(10)	1.449	1.455	C(21)—C(22)	1.417	1.424
C(14)—C(15)	1.451	1.458	Mean		1.432
C(18)—C(19)	1.463	1.469	C(1)—C(6)	1.827	1.836
C(19)—C(20)	1.460	1.467	C(14)—C(19)	1.771	1.780
C(14)—C(23)	1.457	1.464	Mean		1.808
Mean		1.462			
C(2)—C(3)	1.357	1.363	C(1)—C(11)	1.510	1.516
C(4)—C(5)	1.331	1.338	C(6)—C(11)	1.504	1.511
C(7)—C(8)	1.350	1.356	C(14)—C(24)	1.511	1.518
C(9)—C(10)	1.353	1.360	C(19)—C(24)	1.507	1.513
C(15)—C(16)	1.340	1.346	Mean		1.515
C(17)—C(18)	1.329	1.336	C(11)—C(12)	1.520	1.526
C(20)—C(21)	1.343	1.350	C(11)—C(13)	1.515	1.522
C(22)—C(23)	1.327	1.333	C(24)—C(25)	1.527	1.535
Mean		1.348	C(24)—C(26)	1.518	1.524
			Mean		1.527

* After rigid-body correction.

Table 8. *Bond angles*

The 'mean' value is that of *mm*2-related angles averaged over the two molecules.

C(1)—C(2)—C(3)	123.9°	C(2)—C(1)—C(11)	119.9°
C(4)—C(5)—C(6)	124.1	C(5)—C(6)—C(11)	120.1
C(6)—C(7)—C(8)	123.9	C(7)—C(6)—C(11)	120.9
C(9)—C(10)—C(1)	123.3	C(10)—C(1)—C(11)	121.6
C(14)—C(15)—C(16)	124.0	C(15)—C(14)—C(24)	120.8
C(17)—C(18)—C(19)	124.2	C(18)—C(19)—C(24)	119.9
C(19)—C(20)—C(21)	123.8	C(20)—C(19)—C(24)	120.7
C(22)—C(23)—C(14)	123.6	C(23)—C(14)—C(24)	120.2
Mean	123.9	Mean	120.5
C(2)—C(3)—C(4)	123.4	C(11)—C(1)—C(6)	52.5
C(3)—C(4)—C(5)	123.6	C(11)—C(6)—C(1)	52.9
C(7)—C(8)—C(9)	123.7	C(24)—C(14)—C(19)	54.0
C(8)—C(9)—C(10)	123.7	C(24)—C(19)—C(14)	54.2
C(15)—C(16)—C(17)	123.0	Mean	53.4
C(16)—C(17)—C(18)	123.4		
C(20)—C(21)—C(22)	122.7	C(1)—C(11)—C(6)	74.6
C(21)—C(22)—C(23)	124.0	C(14)—C(24)—C(19)	71.8
Mean	123.4	Mean	73.2
C(2)—C(1)—C(6)	111.3	C(12)—C(11)—C(1)	118.0
C(5)—C(6)—C(1)	112.6	C(12)—C(11)—C(6)	117.2
C(7)—C(6)—C(1)	111.9	C(13)—C(11)—C(1)	117.0
C(10)—C(1)—C(6)	112.8	C(13)—C(11)—C(6)	117.1
C(15)—C(14)—C(19)	112.7	C(25)—C(24)—C(14)	117.8
C(18)—C(19)—C(14)	112.1	C(25)—C(24)—C(19)	118.7
C(20)—C(19)—C(14)	112.3	C(26)—C(24)—C(14)	117.8
C(23)—C(14)—C(19)	112.6	C(26)—C(24)—C(19)	118.2
Mean	112.3	Mean	117.7
C(2)—C(1)—C(10)	117.7	C(12)—C(11)—C(13)	109.5
C(5)—C(6)—C(7)	117.9	C(25)—C(24)—C(26)	108.9
C(15)—C(14)—C(23)	117.5	Mean	109.2
C(18)—C(19)—C(20)	118.1		
Mean	117.8		

Table 9. *Torsion angles*

The 'mean' value is that of the absolute values of *mm*2-related angles, averaged over the two molecules.

C(1)—C(2)—C(3)—C(4)	8.6°
C(3)—C(4)—C(5)—C(6)	—8.3
C(6)—C(7)—C(8)—C(9)	8.0
C(8)—C(9)—C(10)—C(1)	—8.4
C(14)—C(15)—C(16)—C(17)	8.8
C(16)—C(17)—C(18)—C(19)	—5.9
C(19)—C(20)—C(21)—C(22)	8.2
C(21)—C(22)—C(23)—C(14)	—8.7
Mean	8.1
C(2)—C(3)—C(4)—C(5)	0.0
C(7)—C(8)—C(9)—C(10)	0.2
C(15)—C(16)—C(17)—C(18)	—1.6
C(20)—C(21)—C(22)—C(23)	0.8
Mean	0.7
C(10)—C(1)—C(2)—C(3)	—140.3
C(4)—C(5)—C(6)—C(7)	139.9
C(5)—C(6)—C(7)—C(8)	—140.1
C(9)—C(10)—C(1)—C(2)	139.3
C(23)—C(14)—C(15)—C(16)	—141.0
C(17)—C(18)—C(19)—C(20)	138.5
C(18)—C(19)—C(20)—C(21)	—140.8
C(22)—C(23)—C(14)—C(15)	140.6
Mean	140.1

looked and the two molecules are related by some kind of crystallographic operation. In a preceding paragraph it has been pointed out that the presence of a

particular symmetry operator (a twofold screw axis with a translation of $\sim \frac{1}{2}\mathbf{b}$) can be inferred from the raw intensity data. To study the correlation between the two molecules *A* (carbon atoms 1 to 13) and *B* (carbon atoms 14 to 26) in a more quantitative way, the following procedure was applied.

Final coordinates were referred to a Cartesian system by means of an orthogonalization matrix, **O**, using the following convention: $\mathbf{a}_o = \mathbf{b}_c \times \mathbf{c}_c^*$; $\mathbf{b}_o = \mathbf{b}_c$; $\mathbf{c}_o = \mathbf{a}_o \times \mathbf{b}_o$, where **a**, **b**, **c** are unit vectors, and the subscripts *o* and *c* refer to orthogonal and crystal axes respectively. Then both molecules, *A* and *B*, were translated in order to have their centres of gravity on the origin of the coordinate system, and the direction of the principal axes of inertia were determined both for molecule *A* and *B*. Let us call \mathbf{x}_{cA}^0 , \mathbf{x}_{cB}^0 the crystal (fractional) coordinates referred to the centre of gravity of the molecule *A* and *B* respectively. If one assumes that the two molecules are not independent, their coordinates on the inertial axes must be equal, thus

$$\begin{aligned} \mathbf{x}_{iA} &= \mathbf{x}_{iB} \\ \mathbf{V}_A \mathbf{O} \mathbf{x}_{cA}^0 &= \mathbf{V}_B \mathbf{O} \mathbf{x}_{cB}^0 \\ \mathbf{x}_{cB}^0 &= \mathbf{O}^{-1} \mathbf{V}_B^{-1} \mathbf{V}_A \mathbf{O} \mathbf{x}_{cA}^0 = \mathbf{R} \mathbf{x}_{cA}^0 \end{aligned}$$

where \mathbf{V}_A and \mathbf{V}_B are transformation matrices from our initial Cartesian system to the inertial system of each molecule. In this case **R** should express the point-group symmetry operation relating molecule *B* to *A*.

However, the matrix **R** is not unequivocally defined, because the normalized eigenvectors of the inertia moment matrices (the rows of \mathbf{V}_A and \mathbf{V}_B) can be either positive or negative. Calling x_i the inertial axis coincident with the twofold molecular axis of symmetry, we have four possible sign combinations for the second and third rows of \mathbf{V}_B (with respect to \mathbf{V}_A) to define the directions of the y_i and z_i inertial axes, resulting in four possible matrices **R**. Among these, a choice can be made by comparing the values obtained for trace (**R**), which must be very near to a whole number. Another criterion of choice for **R**, suitable for symmetry operators 2 and $\bar{2}$, is that if we apply the operation **R** to an arbitrary lattice vector **u**, and calculate the sum (for 2) or the difference (for $\bar{2}$) between the original and the 'rotated' vector, the resulting vector $\mathbf{u} \pm \mathbf{R}\mathbf{u}$ must have whole components except for a common factor, because the symmetry axis must lie along a lattice direction. The same argument can obviously be applied to test the presence of an axis 3, $\bar{3}$, 6, $\bar{6}$, by inspection of the sum vector $\mathbf{u} + \mathbf{R}^2\mathbf{u} + \mathbf{R}^4\mathbf{u}$.

The results for the four sign combinations and the type of vectors (**s**=sum, **d**=difference) verifying the preceding conditions are:

Signs	Trace	Determinant	Axis	Vectors
+ +	2.012	1.	6	$\mathbf{s} \simeq [210]$
+ -	0.098	—1.	$\bar{3}$	no
- +	0.915	—1.	$\bar{2}$	no
- -	—1.000	1.	2	$\mathbf{s} \simeq [010]$

The first possibility is the presence of an axis 6 parallel to the [210] vector in the *P*-cell; this direction coincides with that of the [100] axis of the *F*-cell and of the Cartesian reference system used. In effect, the solution of the structure was achieved for orientation angles $\theta_1, \theta_2, \theta_3$ which implied repetition of molecule *A* in molecule *B* by a rotation of 60° around the x_0 axis. Sixfold symmetry however is not found in the diffraction data,* and the value of trace (\mathbf{R}_4) is appreciably different from a whole number.

The only other possibility concerns the fourth case, for which the matrix is

$$\mathbf{R}_4 = \begin{pmatrix} -1.0135 & 0.0203 & 0.0194 \\ -0.9822 & 1.0109 & -0.5012 \\ -0.0158 & 0.0040 & -0.9971 \end{pmatrix}$$

leading to a very good value for the trace. For arbitrary lattice vectors, the resulting sum vectors $\mathbf{u} + \mathbf{R}_4\mathbf{u}$ are of the type [010] (except for a common factor) within a good approximation. While confirming the presence of a twofold rotation axis (as a point-group symmetry operator), this direction is also defined as parallel to the \mathbf{b} vector of the *P*-cell.

This symmetry operation however is incompatible with the lattice defined by the *P*-cell, because \mathbf{R}_4 has one element which is not identifiable with zero or with a whole number. It is possible to construct a number of pseudo-monoclinic cells, having the [010] translation corresponding to the \mathbf{b} vector in the *P*-cell. Considering vectors of the *P*-lattice with components u, v, w between -5 and $+5$, and choosing pairs of vectors normal to \mathbf{b} within 0.3°, ten pseudo-monoclinic unit

* On the zero-layer Weissenberg photograph taken around [210], only the two dominant reflexions, T21 and T22, are related by approximate sixfold symmetry.

cells (including the *F*-cell) could be defined. For these cells the matrices corresponding to \mathbf{R}_4 are all near to $(\bar{1}00/010/00\bar{1})$. In particular, for the *F*-cell parameters ($a=14.607, b=7.007, c=38.886$ Å, $\alpha=90.26, \beta=101.77, \gamma=89.80^\circ$, as obtained from the data of Table 1), \mathbf{R}_4 becomes

$$\begin{pmatrix} -1.0033 & 0.0101 & 0.0490 \\ 0.0563 & 0.9997 & -0.0462 \\ -0.0069 & 0.0010 & -0.9961 \end{pmatrix}$$

thus a nearly exact rotation matrix for a twofold crystallographic axis along \mathbf{b} . However the structure is not monoclinic; for instance, oscillation photographs taken around \mathbf{b} show m_x symmetry (Stout & Jensen, 1968) only for even layer lines.

The difference of the origin to centre of gravity vectors for molecules *A* and *B*, referred back to the *F*-cell, has components (0.4035, $-0.2433, 0.1371$), thus expressing a shift of -0.243 \mathbf{b} in good agreement with the value expected from the analysis of the raw intensity data. If we consider the molecule *A* in $x_A, y_A, 1 + z_A$ and the molecule *B* in x_B, y_B, z_B in the *P*-cell, the difference of the origin to centre of gravity vectors in the *F*-cell becomes (0.4035, 0.0067, -0.1129).

In conclusion, on the basis of the inertia moment matrices, the structure possesses nearly exact twofold screw axes $2_m, 2_n$ parallel to y , at $\Delta x_F=0$ and $\Delta z_F=\frac{1}{8}$, with $m=-0.487$ and $n=0.013$, which relate the molecules *A* and *B*.

Provided the [010] translation is the same in the *P*- and *F*-cell, and the periodicity along \mathbf{b} is confirmed by a rotation photograph, the space group *P1* is proved; the twofold screw axes do not correspond to (total) symmetry operations of the structure, but behave as proper P.O.'s in an O.D. structure. Because of the succession of the $2_{0.013}$ and $2_{-0.487}$ axes, which

Table 10. Some least-squares planes through groups of atoms

The coefficients q_i are the direction cosines relative to the crystallographic axes a, b and c , multiplied by 10^4 . The distance of the defining atoms from the mean plane involving four atoms is always less than 0.006 Å.

Plane		q_1	q_2	q_3	D
<i>A</i>	C(2), C(3), C(4), C(5)	-5934	8533	3352	0.090 Å
<i>B</i>	C(1), C(2), C(5), C(6)	-6938	8369	3104	0.254
<i>C</i>	C(1), C(6), C(11)	9253	-1355	668	0.018
<i>D</i>	C(1), C(6), C(7), C(10)	154	7266	3568	0.265
<i>E</i>	C(7), C(8), C(9), C(10)	-1125	7791	3639	0.104
<i>F</i>	C(15), C(16), C(17), C(18)	5562	-7958	6335	5.351
<i>G</i>	C(14), C(15), C(18), C(19)	6311	-7501	6127	5.688
<i>H</i>	C(14), C(19), C(24)	8049	1334	394	5.844
<i>I</i>	C(14), C(19), C(20), C(23)	195	-8460	5891	1.296
<i>J</i>	C(20), C(21), C(22), C(23)	1339	-8637	6235	2.372

Dihedral angles between planes			
<i>A</i> ∧ <i>B</i>	172.5	<i>B</i> ∧ <i>C</i>	111.7
<i>E</i> ∧ <i>D</i>	172.7	<i>D</i> ∧ <i>C</i>	113.1
<i>F</i> ∧ <i>G</i>	173.4	<i>G</i> ∧ <i>H</i>	112.1
<i>J</i> ∧ <i>I</i>	172.4	<i>I</i> ∧ <i>H</i>	112.2
Mean	172.8	Mean	112.3
<i>B</i> ∧ <i>D</i>	135.2		
<i>G</i> ∧ <i>I</i>	135.7		
Mean	135.5		

are both $_{pq}Q$ P.O.'s (Dornberger-Schiff & Grell-Niemann, 1961), there are two sets of pairs of adjacent layers in the structure (see Fig. 3): the layers (L_{p-1} , L_p) are 'equivalent' to the (L_{q-1} , L_q) only for p, q both odd or both even. The only $_{pq}T$ P.O., which is present for $p-q=2n$ is the stacking vector c of the P -cell. According to Dornberger-Schiff & Grell-Niemann (1961), these features characterize the O.D. structures of category III.

The structure refinement however led us to conclude that the observed P.O.'s between molecules A and B are only approximate operators. The two molecules A and B do indeed differ significantly in the geometry of the central cyclopropane ring: the C(1)–C(6) bond distance is 1.836 Å and the C(1)–C(11)–C(6) angle 74.7°, as compared with a C(14)–C(19) bond distance of 1.780 Å and a C(14)–C(24)–C(19) angle of 71.9° (values corrected for rigid-body motion). The e.s.d.s for these bonds and angles are 0.007 Å and 0.3° respectively.

The refinement was carried out holding fixed the position of atom C(1). In the light of earlier experience in the refinement of polar structures (Karle & Karle, 1968; Colman & Medlin, 1970), where it was found not sufficient to keep constant the coordinate of one atom, two pieces of refinement were repeated, starting with the initial model of the solved structure [C(1)–C(6)–C(14)–C(19)=1.55 Å], the first time keeping constant the position of atom C(1), and the second time the position of atom C(16). Five cycles of full-matrix least-squares calculations led to exactly the same geometry, with C(1)–C(6)=1.84, C(14)–C(19)=1.77 Å.

As another test, we printed out the correlation matrix for the 232 variable parameters in an intermediate full-matrix refinement cycle on the 26 carbon atoms. Correlation coefficients referring to the same coordinate axis for different atoms [e.g. $z_{C(i)}$, $z_{C(j)}$] were always rather high (ca. 0.5) but did not increase by more than 10 to 15% when considering 'P.O. related' atoms. Such rather high values indeed should depend

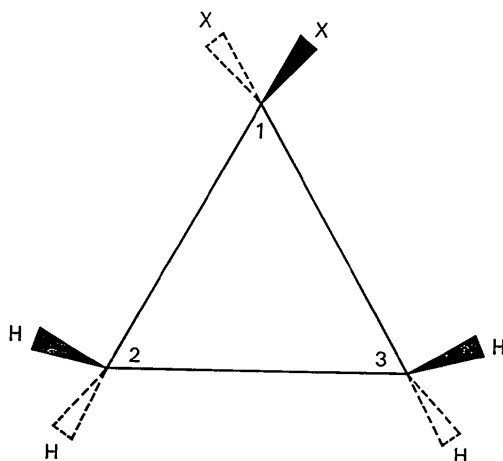


Fig. 4. Numbering of disubstituted cyclopropanes (X=F, CH₃).

on the polarity of axes in space group $P1$. Other cases of coefficients of the order of 0.5 were found for different parameters concerning the same atom, but these were related to considerable departures of unit-cell angles from 90°. Most correlation coefficients had values less than 0.1.

To test the numerical errors in the least-squares procedure for a possibly ill-conditioned normal equation matrix M because of the polarity of axes and the presumed presence of P.O.'s of symmetry, the product of the 232×232 matrix M by its inverse was calculated. Resulting values were different from those expected by less than $3 \cdot 10^{-6}$.

As a last test, packing energy calculations were made for different cases. Because of the relevant uncertainty in the experimental parameters of the hydrogen atoms, their positions were calculated at fixed distances along the bisectrix of the appropriate C–C–C angle for the perimeter ring, and in tetrahedral arrangement for the methyl groups. Here the atoms H(11), H(12), and H(23), H(27) were placed in the planes through atoms C(11), C(12), C(13) and C(24), C(25), C(26) respectively and pointing towards the perimeter rings. The situation corresponding to the experimental case (molecule A at centre of gravity 1, molecule B at centre of gravity 2) was compared with other situations (see Table 11). The change in orientation, when required, was obtained through matrix R_4 for the P -cell; the shift of coordinates was applied through the difference between the origin to centre of gravity vectors. The packing energy was calculated by means of formulae given by Kitaigorodskii (1966) and Jacob, Thompson & Bartell (1967) for C···C, C···H and H···H interactions, summing the contributions for all intermolecular distances within 5.5 Å from each atom. This value was chosen according to Pawley (1967); there are about 1370 contributions for each case within this distance. As Table 11 shows, the situation corresponding to the experimental case lies always in a minimum of energy. Because the C(1)–C(6) and the C(14)–C(19) bonds are very long, and therefore weak, even a little difference in energy could be effective in stretching the two bonds to different lengths. Our results show that packing energy contributes to this effect.

Table 11. Differences in packing energy (cal.mole⁻¹)

A and B are the two molecules of the asymmetric unit, 1 and 2 their centres of gravity. Differences ΔE are referred to the minimum packing energy for each type of calculation.

Situation	ΔE		ΔE
	(Jacob, Thompson & Bartell, 1967)	(Jacob, Thompson & Bartell, 1967)	(Kitaigorodskii, 1966)
	$d_{C-H}=1.0 \text{ \AA}$	$d_{C-H}=1.1 \text{ \AA}$	$d_{C-H}=1.09 \text{ \AA}$
A at 1, B at 2	0	0	0
B at 1, A at 2	209	364	483
A at 1, A at 2	117	209	333
B at 1, B at 2	74	134	91

We feel entitled to conclude that in the crystal the two molecules A and B are different, and that the

observed hypersymmetry corresponds to the presence of approximate P.O.'s in the structure.

Molecular orbital calculations

The shifting of the equilibrium bisnorcaradiene \rightleftharpoons 1,6-methano[10]annulene towards bisnorcaradiene implies the formation of a cyclopropane ring, so that information on the influence of substituents at C(11) on this equilibrium may be obtained through the study of the influence of the same substituents in cyclopropane.

On the basis of orbital symmetry arguments it has been shown (Hoffmann, 1971; Hoffmann & Davidson, 1971) that in cyclopropane the introduction of π -electron acceptor substituents at carbon C(1) makes the C(2)–C(3) bond stronger and the C(1)–C(2) and C(1)–C(3) bonds weaker while the introduction of π -electron donating substituents should weaken all the bonds in the ring. This argument would afford a qualitative explanation of the fact that the introduction of two methyl groups at C(11) of 1,6-methano[10]annulene shifts the equilibrium towards the formation of 11,11-dimethylbisnorcaradiene, while the annulene structure is favoured by fluoro-substitution at the same position.

To check this result we decided to carry out *ab initio* molecular orbital calculations for 1,1-difluoro- and 1,1-dimethylcyclopropane and to compare the results with those found in the literature for cyclopropane. Many *ab initio* M.O. calculations have been performed on this molecule, using different basis sets and assuming the experimental geometry or varying some of or all the geometrical parameters. The treatment by Radom, Lathan, Hehre & Pople (1971) using a STO-3G basis set has proved to give an overall good agreement between calculated and experimental geometries and is simple enough to allow geometry optimization of disubstituted cyclopropanes. Therefore this treatment was chosen by us when performing our calculations, using the program GAUSSIAN 70 written by W. J. Hehre, W. A. Lathan and J. A. Pople.*

* We are grateful to Dr W. J. Hehre for a copy of this program.

In the geometry optimization of 1,1-difluorocyclopropane and 1,1-dimethylcyclopropane (see Fig. 4) we assumed *mm2* (C_{2v}) symmetry, and for the hydrogen atoms bonded to the ring we assumed a fixed bond length (1.081 Å) and a fixed bond angle (H–C–H = 113.8°), the plane of these three atoms bisecting the internal ring angle: these values correspond to the optimized geometrical parameters in cyclopropane (Radom, Lathan, Hehre & Pople, 1971). Furthermore we assumed for the methyl group a C–H bond length of 1.09 Å and tetrahedral bond angles; the methyl groups are both in a conformation with a C–H bond bisecting the internal ring angle C(2)–C(1)–C(3).

The remaining geometrical parameters [C(1)–C(2) and C(1)–X bond lengths and C(2)–C(1)–C(3) and X–C(1)–X bond angles] were optimized varying one parameter at a time: cycling was continued until no variation was found on the third decimal place for bond distances and on the first decimal place for bond angles.

Results are reported in Table 12. All features predicted by the qualitative treatment are reproduced, even if the effects are smaller than might have been expected.

Discussion

The geometry of the two molecules of the asymmetric unit of DIM is described in Tables 7 to 10. For each molecule the observed geometry fits as a whole the *mm2* symmetry within experimental error. By considering all the corresponding *mm2*-related bond lengths and bond angles in the perimeter ring for the two molecules [*e.g.* the eight bond lengths of the type C(1)–C(2)], the χ^2 -test shows that for each group the bonds (or angles) are all equivalent at a significance level $\alpha \geq 0.25$; only one exception was found, namely for the eight bonds of the type C(2)–C(3), where the differences are more noticeable and become possibly significant ($\alpha \sim 0.05$). Torsion angles are equivalent at a level $\alpha \geq 0.10$.

There is no doubt about the bisnorcaradiene structure of the compound examined: the mean values (over the two molecules) of bond lengths along the perimeter ring, corrected for rigid-body motion, are 1.462, 1.348

Table 12. *Ab initio* calculated geometries for isolated molecules

Molecule	Symmetry constraint		
Cyclopropane (Radom, Lathan, Hehre & Pople, 1971)	$\bar{3}m2$ (D_{3h})	C–C	1.502 Å
		C–H	1.081
		H–C–H	113.8°
1,1-Difluorocyclopropane	<i>mm2</i> (C_{2v})	C(1)–C(2)	1.511 Å
		C(2)–C(1)–C(3)	60.3°
		C(1)–F	1.368 Å
		F–C(1)–F	110.2°
1,1-Dimethylcyclopropane	<i>mm2</i> (C_{2v})	C(1)–C(2)	1.509 Å
		C(2)–C(1)–C(3)	59.7°
		C(1)–C(methyl)	1.536 Å
		C(methyl)–C(1)–C(methyl)	114.0°

and 1.432 Å for bonds of the type C(1)–C(2), C(2)–C(3) and C(3)–C(4) respectively.

An outstanding feature of the molecular geometry is the extraordinary length found for the central bonds, C(1)–C(6) and C(14)–C(19): 1.827 and 1.771 Å ($\sigma = 0.007$ Å) for uncorrected, 1.836 and 1.780 Å for libration corrected coordinates respectively. For the sake of comparison, in cyclopropane-1,1-dicarboxylic acid (Meester, Schenk & MacGillavry, 1971) the C–C bond lengths in the ring are in the range 1.456 to 1.540 Å. A few very long carbon–carbon bond distances have been previously found, such as 1.65 Å in tricarbonyl(tricyclo[4,3,1,0^{1,6}]deca-2,4-diene)chromium (Beddoes, Lindley & Mills, 1970); 1.72 Å in a homoaromatic structure, tricarbonyl(bicyclo[4,4,1]undeca-1,3,5-triene)chromium (Barrow & Mills, 1971); and 1.77 Å in bi(anthracene-9,10-dimethylene) photo-isomer (Ehrenberg, 1966). The central distance C(1)–C(6) becomes

2.25 Å in 11,11-difluoro-1,6-methano[10]annulene (Ib) (Gramaccioli & Simonetta, 1971), and 2.257 Å in 1,6-methano[10]-annulene-2-carboxylic acid (Ia) (Dobler & Dunitz, 1965), thus corresponding to a non-bonded separation.

The possibility of the presence of both annulene- and bisnorcaradiene-type molecules in the crystals of DIM* is in contrast with the quite 'normal' features of thermal parameters (see Fig. 2 and Table 13). In particular, the anisotropy directions for atoms C(1), C(6), C(14) and C(19) do not support the hypothesis of a mixture. Instead, the experimental carbon atom thermal parameters result in good agreement with those calculated for rigid-body motion of the bisnorcaradiene-type molecules, giving rise to mean square rotational displacements which are notably smaller than those found for compound (Ib). The presence of a C–C central bond is also in agreement with the observed geometry along the perimeter ring, C(1) to C(10) and C(14) to C(23).

In conclusion, the experimental evidence is in favour of the existence of a real, very long C–C bond distance, to which the results of M.O. calculations also lend support.

The difference between the bond lengths C(1)–C(6) and C(14)–C(19), and the bond angles C(1)–C(11)–C(6) and C(14)–C(24)–C(19) (74.6 and 71.8° respectively, $\sigma = 0.3^\circ$) could be interpreted at least in part in terms of packing energy, as seen before.

The bonds of the bridge, C(1)–C(11) *etc.*, are all equivalent (at a level $\alpha > 0.90$), with a mean length of 1.515 Å. Corresponding bond distances are 1.477 in (Ia) and 1.455 in (Ib), in complete agreement with the change in electronegativity of the substituents (–CH₃, –H, –F), as pointed out by Walsh (1947) and Bent (1961). Even the C(1)–C(6) distance, on the basis of the same arguments, is expected to increase in going from the 11,11-dimethyl derivative to the 11,11-difluoro compound.

The bonds of the type C(11)–C(12) are all equivalent ($\alpha > 0.50$) with a mean (libration corrected) length of

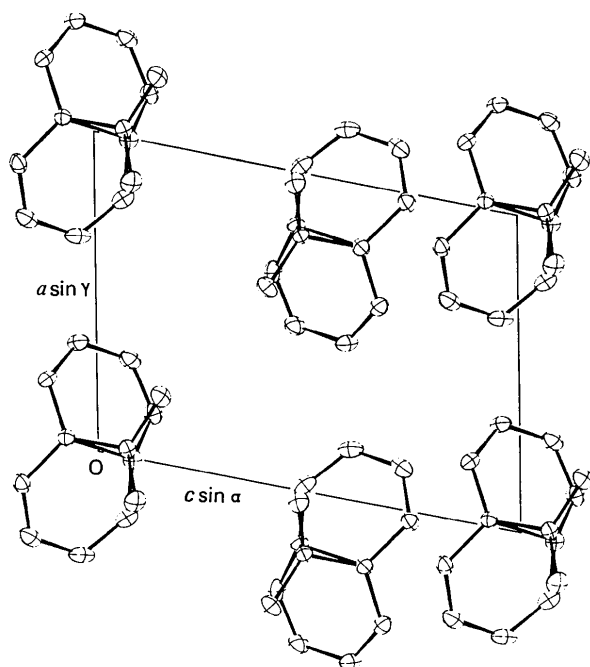


Fig. 5. Packing of molecules as seen along the y axis.

* We are grateful to Professor J. D. Dunitz for drawing our attention to this possibility.

Table 13. Magnitudes of the temperature ellipsoids and 'equivalent' isotropic factor $B = (B_1 B_2 B_3)^{1/3}$

	B_1	B_2	B_3	B		B_1	B_2	B_3	B
C(1)	2.73	3.55	3.88	3.35	C(14)	2.78	3.40	3.70	3.27
C(2)	2.87	3.27	5.64	3.75	C(15)	3.01	3.92	4.06	3.63
C(3)	2.39	4.30	7.24	4.21	C(16)	2.65	4.63	5.35	4.03
C(4)	2.72	4.38	6.31	4.22	C(17)	2.47	4.90	5.41	4.03
C(5)	2.57	3.35	5.16	3.54	C(18)	2.41	4.27	5.14	3.75
C(6)	2.51	2.92	4.06	3.10	C(19)	2.65	3.28	3.47	3.11
C(7)	2.39	3.86	4.10	3.36	C(20)	2.61	3.65	6.19	3.89
C(8)	2.58	4.69	4.78	3.86	C(21)	2.61	4.71	6.82	4.38
C(9)	2.35	4.40	5.32	3.80	C(22)	2.94	4.95	6.15	4.47
C(10)	2.56	4.09	4.51	3.62	C(23)	2.74	3.82	4.66	3.65
C(11)	2.51	2.96	3.77	3.04	C(24)	2.63	2.93	3.25	2.93
C(12)	2.55	4.86	5.37	4.05	C(25)	2.64	4.37	5.60	4.01
C(13)	2.87	4.37	5.23	4.03	C(26)	3.29	4.44	4.98	4.17

1.527 Å. Experimental methyl hydrogen atoms lie in the staggered arrangement with respect to the adjacent carbon, C(11) or C(24) (see Fig. 2). Carbon-hydrogen bond distances are in the range 0.86–1.03 Å ($\sigma = 0.05$ Å).

The range of intermolecular distances is normal. There are no contacts shorter than the sum of van der Waals radii, $r(\text{C}) = 1.7$, $r(\text{CH}_3) = 2.0$, and $r(\text{H}) = 1.2$ Å (Pauling, 1960). The molecular packing seen along **b** is represented in Fig. 5. Figs. 2, 3 and 5 were obtained by use of the program *ORTEP* (Johnson, 1965).

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