

## 3 $\beta$ -Acetoxy-16 $\beta$ -methyl-5-pregnen-20-one: an Example of Rotamers in a Crystal

BY H. CAMPSTEYN, O. DIDEBERG, L. DUPONT AND J. LAMOTTE

Université de Liège au Sart Tilman, Laboratoire de Cristallographie, Institut de Physique B5, B-4000 Liège, Belgium

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### Abstract

Crystals of C<sub>24</sub>H<sub>36</sub>O<sub>3</sub>,  $M_r = 373.0$ , are triclinic with  $a = 6.414(3)$ ,  $b = 28.426(5)$ ,  $c = 6.290(3)$  Å,  $\alpha = 99.68(2)$ ,  $\beta = 107.92(2)$ ,  $\gamma = 83.74(2)^\circ$ ,  $Z = 2$ ,  $V = 1073.69$  Å<sup>3</sup>,  $d_x = 1.115$  Mg m<sup>-3</sup>, space group  $P1$ . The structure was determined by direct least-squares methods to a final  $R$  of 0.059 for 3616 independent reflexions. The side chains of the non-equivalent molecules are in quite different conformations; this rotation seems to be due to a broad minimum in the conformational potential surface.

### Introduction

This compound was studied in our research on corticosteroid side-chain conformations. Crystals of the title compound (Steraloid, Q 5201) were grown from an ethyl acetate solution.

Intensities were measured on a four-circle Hilger & Watts diffractometer with Cu  $K\alpha$  radiation ( $\mu = 0.568$  mm<sup>-1</sup>). Among the 3750 independent reflexions collected, 90 were considered as unobserved [ $I < 2\sigma(I)$ ]. Only Lorentz and polarization corrections were applied.

### Solution and refinement

The structure was solved using the *MULTAN* program (Main, Lessinger, Woolfson, Germain & Declercq, 1977). All the heavy atoms were found on Fourier maps. Atomic positions and anisotropic thermal parameters were refined by full-matrix least-squares methods. The H atoms were introduced in the structure factor calculations at unrefined positions corresponding to the theoretical values of the bond lengths, valency and torsion angles. The final conventional  $R$  indices were 6.4% for all data (3750 reflections) and 5.9% for 3616 reflections. Table 1 gives the final atomic coordinates.\*

\* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34716 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

### Description of the structure and discussion

The numbering scheme, bond lengths, bond angles and torsion angles are given in Fig. 1, Tables 2, 3 and 4 respectively, while Figs. 2 and 3 show views of the two independent molecules.

A striking observation concerns the side-chain conformation. In the discussion, we shall refer to three rotamers around the C(17)–C(20) bond:

CF1: the 'normal' rotamer as is found, for instance, in progesterone (Campsteyn, Dupont & Dideberg, 1972),

CF2: a slightly distorted rotamer as in  $\Delta^6$ -6-azidobetamethasone-21-acetate (Nassimbeni, Sheldrick & Kennard, 1974),

CF3: a strongly rotated rotamer as in 16 $\beta$ -methylprogesterone (Weeks, Strong & Osawa, 1976).

Table 5 gives a number of parameters which differ from one conformation to another. The 'mean corticoid' is a hypothetical structure resulting from the averaging of atomic positions of some corticosteroids (unpublished results).

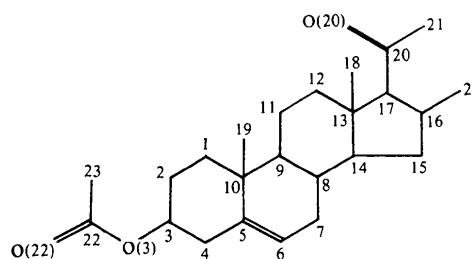


Fig. 1. Numbering scheme of molecule A. For molecule B, 50 is added to all indices.

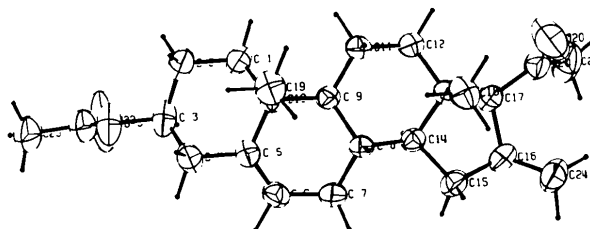


Fig. 2. View of molecule A.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters, with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
C(1)	-11718 (8)	11214 (2)	10684 (10)	5.8
C(2)	-12389 (9)	11742 (2)	11020 (11)	6.0
C(3)	-10882 (11)	11975 (2)	13242 (9)	5.9
C(4)	-8532 (9)	11912 (2)	13196 (9)	5.4
C(5)	-7842 (8)	11390 (2)	12817 (7)	4.4
C(6)	-6073 (8)	11206 (2)	14247 (7)	5.5
C(7)	-5253 (8)	10698 (2)	14092 (8)	4.7
C(8)	-6293 (7)	10404 (1)	11782 (6)	3.9
C(9)	-8768 (7)	10549 (1)	10956 (7)	3.8
C(10)	-9292 (7)	11087 (1)	10760 (7)	3.7
C(11)	-9915 (8)	10219 (2)	8776 (8)	5.9
C(12)	-9512 (8)	9689 (2)	8988 (10)	5.2
C(13)	-7037 (7)	9545 (1)	9771 (7)	3.6
C(14)	-6029 (6)	9873 (1)	11968 (5)	3.8
C(15)	-3754 (7)	9629 (2)	12887 (8)	5.2
C(16)	-4122 (7)	9086 (2)	12361 (8)	5.3
C(17)	-6512 (7)	9061 (2)	10646 (7)	5.4
C(18)	-5954 (9)	9580 (2)	7930 (7)	5.5
C(19)	-8897 (9)	11217 (2)	8637 (7)	4.9
C(20)	-6914 (9)	8601 (2)	9033 (13)	7.4
C(21)	-7068 (11)	8172 (2)	10051 (17)	7.1
C(22)	-12456 (10)	12644 (2)	15148 (10)	6.8
C(23)	-12861 (12)	13177 (2)	15400 (11)	8.2
C(24)	-2309 (8)	8786 (2)	11592 (11)	5.6
C(51)	-795 (8)	4814 (1)	1196 (6)	4.7
C(52)	-644 (10)	4289 (2)	260 (7)	6.2
C(53)	1468 (8)	4054 (2)	1608 (9)	6.0
C(54)	1534 (8)	4104 (2)	4069 (8)	4.9
C(55)	1345 (6)	4626 (1)	5028 (7)	4.6
C(56)	2869 (6)	4806 (1)	6882 (7)	5.2
C(57)	2874 (6)	5309 (2)	7957 (7)	4.4
C(58)	681 (6)	5593 (1)	7103 (5)	4.1
C(59)	-260 (6)	5468 (1)	4530 (6)	4.0
C(60)	-609 (6)	4926 (1)	3739 (5)	4.2
C(61)	-2316 (7)	5792 (1)	3602 (7)	4.1
C(62)	-1975 (7)	6325 (1)	4315 (6)	4.6
C(63)	-1123 (6)	6446 (1)	6902 (6)	3.8
C(64)	984 (6)	6126 (1)	7682 (6)	3.7
C(65)	2005 (7)	6348 (2)	10127 (7)	4.7
C(66)	1662 (6)	6893 (1)	10049 (6)	5.5
C(67)	-199 (6)	6949 (1)	7782 (6)	4.3
C(68)	-2876 (6)	6369 (1)	7973 (7)	5.2
C(69)	-2692 (6)	4784 (1)	4119 (7)	4.6
C(70)	-1957 (8)	7351 (1)	7826 (7)	5.7
C(71)	-2594 (11)	7646 (2)	5940 (10)	7.1
C(72)	3177 (9)	3387 (2)	-188 (8)	6.6
C(73)	3198 (11)	2863 (2)	-870 (11)	7.2
C(74)	1374 (9)	7170 (2)	12246 (7)	9.1
O(3)	-11462 (7)	12483 (1)	13608 (6)	10.8
O(20)	-7150 (11)	8571 (2)	7031 (8)	10.1
O(22)	-12934 (13)	12394 (2)	16169 (12)	6.0
O(53)	1634 (6)	3551 (1)	776 (7)	7.8
O(70)	-2863 (7)	7427 (2)	9290 (7)	9.8
O(72)	4443 (11)	3643 (2)	-373 (12)	10.2

The side-chain conformation of 16 $\alpha$ ,17 $\alpha$ -epoxy-pregnenolone monohydrate (Hazel, Weeks & Osawa, 1976) is CF3. This compound is not included in Table 5 because of the strong distortions introduced in the *D* ring by the epoxy group. Non-equivalent molecules *A*

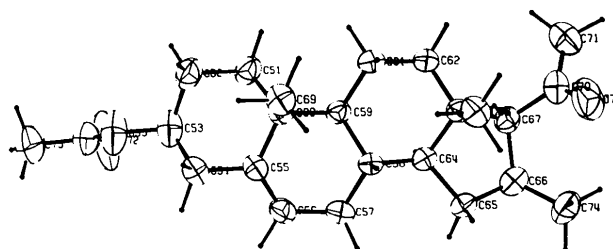


Fig. 3. View of molecule *B*.

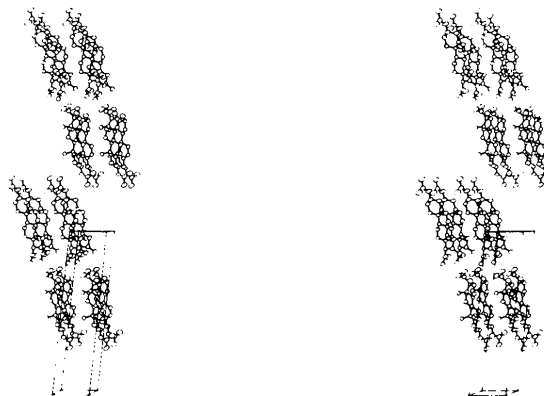


Fig. 4. Stereoscopic view of the crystal packing.

and *B* of the title compound are respectively of types CF3 and CF2.

The first remark we can make about Table 5 is the very weak transmission of conformation: all the modifications are localized in the *D* ring and the side chain. If we compare other regions of molecules *A* and *B*, all geometrical parameters are equal within the limits of experimental error. The conformations of the rings are the same: chair for the *A* and *C* rings, *C*<sub>2</sub> half-chair for the *B* rings [with the symmetry axis perpendicular to the C(5)–C(6) and C(8)–C(9) bonds]; even the *D* ring keeps the same *C*<sub>2</sub> half-chair conformation with the symmetry axis passing through the C(16) atom [ $\varphi$  parameters (Cremer & Pople, 1975) are equal to 15.7 and 23.3° for molecules *A* and *B* instead of the theoretical value of 18°]. Moreover, the angles between the mean planes of the rings do not vary significantly (*cf.* Table 6). An internal program (*CSCS*, unpublished) which allows a direct comparison of corresponding atomic positions, shows that the methyl C(18) is very slightly displaced.

We will now consider the intramolecular geometrical effects of the substitution (*S*) at C(16) and of the rotation (*R*) of the chain (see Table 5), on

(1) bond lengths: *S* increases C(16)–C(17) but *R* causes a shortening of C(13)–C(17),

Table 2. Bond lengths (Å)

	A	B		A	B		A	B
C(1)–C(2)	1.514 (8)	1.513 (6)	C(8)–C(9)	1.543 (6)	1.537 (5)	C(14)–C(15)	1.530 (6)	1.528 (5)
C(1)–C(10)	1.546 (7)	1.547 (5)	C(8)–C(14)	1.520 (5)	1.519 (5)	C(15)–C(16)	1.550 (7)	1.546 (6)
C(2)–C(3)	1.524 (9)	1.512 (8)	C(9)–C(10)	1.546 (6)	1.556 (5)	C(16)–C(17)	1.581 (6)	1.572 (5)
C(3)–C(4)	1.507 (9)	1.519 (7)	C(9)–C(11)	1.549 (6)	1.540 (6)	C(16)–C(24)	1.517 (8)	1.524 (6)
C(3)–O(3)	1.448 (6)	1.441 (6)	C(10)–C(19)	1.542 (6)	1.533 (6)	C(17)–C(20)	1.508 (8)	1.519 (6)
C(4)–C(5)	1.503 (7)	1.512 (6)	C(11)–C(12)	1.521 (7)	1.526 (6)	C(20)–C(21)	1.494 (10)	1.497 (7)
C(5)–C(6)	1.331 (7)	1.335 (6)	C(12)–C(13)	1.541 (7)	1.540 (5)	C(20)–O(20)	1.211 (9)	1.211 (7)
C(5)–C(10)	1.531 (6)	1.526 (5)	C(13)–C(14)	1.531 (5)	1.538 (5)	C(22)–C(23)	1.500 (9)	1.477 (8)
C(6)–C(7)	1.480 (7)	1.476 (6)	C(13)–C(17)	1.534 (6)	1.555 (5)	C(22)–O(3)	1.312 (7)	1.319 (7)
C(7)–C(8)	1.541 (6)	1.533 (6)	C(13)–C(18)	1.543 (7)	1.529 (6)	C(22)–O(22)	1.153 (9)	1.191 (9)

Table 3. Valency angles (°)

	A	B		A	B		A	B
C(2)–C(1)–C(10)	116.0 (4)	115.6 (4)	C(10)–C(9)–C(11)	113.2 (4)	113.4 (3)	C(8)–C(14)–C(15)	120.7 (3)	120.3 (3)
C(1)–C(2)–C(3)	108.9 (5)	109.6 (4)	C(1)–C(10)–C(5)	108.4 (4)	108.5 (3)	C(13)–C(14)–C(15)	103.0 (3)	103.2 (3)
C(2)–C(3)–C(4)	110.2 (5)	110.1 (4)	C(1)–C(10)–C(9)	108.7 (4)	108.6 (3)	C(14)–C(15)–C(16)	104.9 (4)	104.0 (3)
C(2)–C(3)–O(3)	110.4 (5)	110.8 (4)	C(1)–C(10)–C(19)	109.6 (4)	109.4 (3)	C(15)–C(16)–C(17)	103.5 (4)	105.1 (3)
C(4)–C(3)–O(3)	108.1 (5)	107.9 (4)	C(5)–C(10)–C(9)	110.4 (3)	110.3 (3)	C(15)–C(16)–C(24)	113.5 (4)	111.9 (3)
C(3)–C(4)–C(5)	110.4 (5)	110.2 (4)	C(5)–C(10)–C(19)	107.7 (4)	108.4 (3)	C(17)–C(16)–C(24)	116.5 (4)	118.7 (3)
C(4)–C(5)–C(6)	120.7 (4)	120.1 (4)	C(9)–C(10)–C(19)	112.1 (4)	111.5 (3)	C(13)–C(17)–C(16)	105.6 (3)	105.5 (3)
C(4)–C(5)–C(10)	116.8 (4)	116.5 (3)	C(9)–C(11)–C(12)	113.7 (4)	113.9 (3)	C(13)–C(17)–C(20)	120.7 (4)	113.8 (3)
C(6)–C(5)–C(10)	122.5 (4)	123.3 (4)	C(11)–C(12)–C(13)	111.3 (4)	111.0 (3)	C(16)–C(17)–C(20)	114.6 (4)	117.7 (3)
C(5)–C(6)–C(7)	125.9 (5)	125.0 (4)	C(12)–C(13)–C(14)	107.3 (4)	106.8 (3)	C(17)–C(20)–C(21)	115.5 (6)	117.5 (4)
C(6)–C(7)–C(8)	113.4 (4)	113.4 (3)	C(12)–C(13)–C(17)	113.6 (4)	115.0 (3)	C(17)–C(20)–O(20)	123.7 (6)	122.0 (4)
C(7)–C(8)–C(9)	109.5 (3)	110.4 (3)	C(12)–C(13)–C(18)	110.9 (4)	110.5 (3)	C(21)–C(20)–O(20)	120.8 (6)	120.5 (5)
C(7)–C(8)–C(14)	110.5 (3)	110.5 (3)	C(14)–C(13)–C(17)	99.5 (3)	100.3 (3)	C(23)–C(22)–O(3)	112.1 (5)	112.9 (5)
C(9)–C(8)–C(14)	108.4 (3)	108.9 (3)	C(14)–C(13)–C(18)	112.1 (4)	112.5 (3)	C(23)–C(22)–O(22)	125.5 (7)	125.6 (6)
C(8)–C(9)–C(10)	114.2 (3)	113.3 (3)	C(17)–C(13)–C(18)	112.7 (4)	111.4 (3)	O(3)–C(22)–O(22)	122.4 (6)	121.5 (6)
C(8)–C(9)–C(11)	110.8 (4)	111.2 (3)	C(8)–C(14)–C(13)	115.1 (3)	114.9 (3)	C(3)–O(3)–C(22)	118.4 (5)	119.1 (4)

Table 4. Torsion angles (°) ( $\sigma \simeq 0.5^\circ$ )

	A	B		A	B		A	B
C(10)–C(1)–C(2)–C(3)	–55.5	–55.7	C(16)–C(17)–C(13)–C(14)	–39.9	–34.5	C(6)–C(5)–C(10)–C(19)	–108.3	–109.0
C(1)–C(2)–C(3)–C(4)	60.0	59.7	C(2)–C(1)–C(10)–C(9)	166.8	167.2	C(8)–C(9)–C(10)–C(19)	76.7	78.0
C(2)–C(3)–C(4)–C(5)	–59.2	–58.5	C(4)–C(5)–C(10)–C(9)	–164.4	–165.1	C(11)–C(9)–C(10)–C(19)	–51.3	–49.9
C(3)–C(4)–C(5)–C(10)	53.6	53.5	C(3)–C(4)–C(5)–C(6)	–125.1	–125.0	C(12)–C(13)–C(17)–C(20)	74.4	80.9
C(4)–C(5)–C(10)–C(1)	–45.4	–46.2	C(6)–C(5)–C(10)–C(1)	133.2	132.2	C(14)–C(13)–C(17)–C(20)	–171.9	–165.0
C(5)–C(10)–C(1)–C(2)	46.7	47.3	C(6)–C(7)–C(8)–C(14)	–160.3	–162.3	C(18)–C(13)–C(17)–C(20)	–52.9	–45.7
C(10)–C(5)–C(6)–C(7)	–0.1	0.9	C(7)–C(8)–C(14)–C(13)	179.1	–179.9	C(13)–C(17)–C(20)–C(21)	–160.4	–100.7
C(5)–C(6)–C(7)–C(8)	14.2	13.9	C(7)–C(8)–C(14)–C(15)	–56.3	–55.7	C(16)–C(17)–C(20)–C(21)	71.5	135.1
C(6)–C(7)–C(8)–C(9)	–40.9	–41.8	C(9)–C(8)–C(14)–C(15)	–176.3	–177.0	C(15)–C(16)–C(17)–C(20)	152.2	138.4
C(7)–C(8)–C(9)–C(10)	57.4	57.8	C(7)–C(8)–C(9)–C(11)	–173.4	–173.1	C(16)–C(17)–C(13)–C(18)	79.1	84.8
C(8)–C(9)–C(10)–C(5)	–43.2	–42.5	C(14)–C(8)–C(9)–C(10)	178.1	179.2	C(8)–C(14)–C(13)–C(18)	62.3	61.0
C(9)–C(10)–C(5)–C(6)	14.3	13.4	C(11)–C(9)–C(10)–C(1)	70.0	70.8	C(15)–C(14)–C(13)–C(18)	–71.1	–71.8
C(14)–C(8)–C(9)–C(11)	–52.7	–51.7	C(11)–C(9)–C(10)–C(5)	–171.2	–170.4	C(11)–C(12)–C(13)–C(18)	–67.9	–66.8
C(8)–C(9)–C(11)–C(12)	53.4	52.5	C(1)–C(10)–C(9)–C(8)	–162.0	–161.3	C(20)–C(17)–C(16)–C(24)	26.9	12.4
C(9)–C(11)–C(12)–C(13)	–54.8	–55.3	C(12)–C(11)–C(9)–C(10)	–176.9	–178.4	C(13)–C(17)–C(16)–C(24)	–108.4	–115.9
C(11)–C(12)–C(13)–C(14)	54.9	55.9	C(11)–C(12)–C(13)–C(17)	163.9	166.1	C(14)–C(15)–C(16)–C(24)	140.3	148.7
C(12)–C(13)–C(14)–C(8)	–59.7	–60.3	C(12)–C(13)–C(14)–C(15)	166.9	166.9	C(1)–C(2)–C(3)–O(3)	179.3	179.0
C(13)–C(14)–C(8)–C(9)	59.1	58.7	C(17)–C(13)–C(14)–C(8)	–178.3	179.5	C(5)–C(4)–C(3)–O(3)	–180.0	–179.5
C(17)–C(13)–C(14)–C(15)	48.3	46.7	C(12)–C(13)–C(17)–C(16)	–153.6	–148.6	C(16)–C(17)–C(20)–O(20)	–110.0	–46.6
C(13)–C(14)–C(15)–C(16)	–38.8	–41.2	C(8)–C(14)–C(15)–C(16)	–168.9	–170.8	C(13)–C(17)–C(20)–O(20)	18.1	77.5
C(14)–C(15)–C(16)–C(17)	13.2	18.6	C(2)–C(1)–C(10)–C(19)	–70.5	–70.8	C(3)–O(3)–C(22)–O(22)	–2.2	0.5
C(15)–C(16)–C(17)–C(13)	16.8	10.2	C(4)–C(5)–C(10)–C(19)	73.0	72.5	C(3)–O(3)–C(22)–C(23)	177.5	177.7

Table 5. *Effects of different side-chain conformations on some geometrical parameters*

	CF1	CF2		CF3	
	Mean corticoid	$\Delta^6$ -Azido-betamethasone	Molecule B	16 $\beta$ -Methylprogesterone	Molecule A
C(13)—C(17)	1.568 Å	1.569 Å	1.555 Å	1.543 Å	1.534 Å
C(16)—C(17)	1.546	1.572	1.572	1.576	1.581
C(17)—C(13)—C(18)	108.9°	110.1°	111.4°	112.8°	112.7°
C(15)—C(16)—C(17)	107.0	105.8	105.1	104.0	103.5
C(13)—C(17)—C(20)	113.6	112.0	113.8	120.1	120.7
C(16)—C(17)—C(20)	113.8	117.7	117.7	114.0	114.6
C(13)—C(17)—C(20)—C(21)	-80.6°	-96.7°	-100.7°	-162.7°	-160.4°
C(16)—C(17)—C(20)—C(21)	161.0	142.4	135.1	70.7	71.5
C(13)—C(17)—C(20)—O(20)	99.0	80.6	77.5	18.6	18.1
C(16)—C(17)—C(20)—O(20)	-19.5	-40.3	-46.7	-108.0	-110.0
C(15)—C(16)—C(17)—C(20)	143.1	138.9	138.4	151.5	152.2
C(12)—C(21)	3.51 Å	3.61 Å	3.73 Å	4.57 Å	4.51 Å
C(16)—O(20)	2.85	3.04	3.06	3.46	3.48
C(18)—C(20)	2.90	2.91	2.94	3.14	3.15
C(18)—C(21)	3.78	4.04	4.09	4.62	4.61
C(18)—O(20)	3.23	2.97	2.98	2.95	2.97
(C <sub>3</sub> O <sub>3</sub> , C <sub>20</sub> O <sub>20</sub> )	145.2°	149.2°	111.6°	62.3°	96.5°

Table 6. *Angles between rings (°)*

Ring 1	Ring 2	Molecule A	Molecule B
A	B	25.8	26.1
B	C	7.5	7.5
C	D	43.9	44.5

Table 7. *Intermolecular distances (<3.7 Å);  $\bar{\sigma} \sim 0.007 \text{ Å}$* Symmetry code: (i)  $x - 2, y + 1, z + 2$ .

C(21) ... O(70)	3.346 Å
C(23) ... O(72 <sup>i</sup> )	3.600
O(22) ... O(73 <sup>i</sup> )	3.562

(2) valency angles: the more spectacular effect of *R* is the 'opening' of C(13)—C(17)—C(20) (from 113 to 120°). *S*, alone, causes a lesser effect on C(16)—C(17)—C(20),

(3) torsion angles: as mentioned above, only angles involving the side chain are modified by *R* and *S*,

(4) intramolecular contacts: as the geometries of the *D* rings and the positions of atoms C(18) and C(24) do not change, one could expect CF3 to be more probable than CF2, but one intramolecular distance does not fit such a hypothesis [only C(18)—C(20) is longer upon *R*, but, simultaneously, an opening of angle C(13)—C(17)—C(20) is observed]. It thus seems that the rotation is not related just to short intramolecular contacts.

The only other factor affecting geometry in a crystalline compound is the packing energy. A stereoview of the packing in the present compound is given in Fig. 4. No hydrogen bonds appear in the crystal, and very few short van der Waals interactions can be measured (*cf.* Table 7), but, if we put the molecule *A* side chain in the CF2 conformation, intermolecular contacts become much too short. The same calculation with 16 $\beta$ -methylprogesterone leads to an identical conclusion. At this point, one could explain

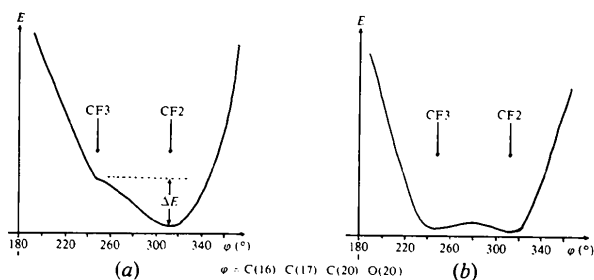


Fig. 5. Possible intramolecular-energy variations associated with side-chain rotation.

the existence of rotamers in two ways. Firstly, intermolecular forces can rotate the side chain from CF2 to CF3 [Fig. 5(a)], but the intramolecular energy  $\Delta E$  would be compensated by a lower packing energy. Secondly, in the 16 $\beta$ -methyl compounds the molecular-energy curve changes, with two minima or a broad valley [Fig. 5(b)]. Energy calculations using the Westheimer model are in agreement with the latter explanation (Schmit & Rousseau, 1978). Thus, we have a new example, where the crystalline and lowest-molecular-energy conformations are very close.

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## Neutron Structure Refinement of Orthorhombic Hexachloroethane

By D. HOHLWEIN, W. NÄGELE AND W. PRANDL

*Institut für Kristallographie der Universität Tübingen, Charlottenstrasse 33, D-7400 Tübingen, Federal Republic of Germany*

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#### Abstract

The structure of orthorhombic hexachloroethane has been refined at 294 and 140 K. At room temperature 983 symmetry-independent reflections were measured on a four-circle neutron diffractometer. The final  $R(F)$  was 0.066 including an isotropic extinction parameter. At 140 K 793 symmetry-independent reflections refined to  $R(F) = 0.056$ . The temperature parameters have been analyzed in terms of the tensors  $T$ ,  $L$  and  $S$  describing the rigid-body movement of the  $C_2Cl_6$  molecule. The temperature variation of the  $T$  and  $L$  tensors can be understood with the assumption of strong anharmonic contributions. There is, however, no indication of rotational disorder in the orthorhombic phase.

#### Introduction

Hexachloroethane is known in three modifications:

orthorhombic  $\xleftrightarrow{318\text{ K}}$  monoclinic  $\xleftrightarrow{344.4\text{ K}}$  cubic (plastic)

(Sasada & Atoji, 1953; Atoji, Oda & Watanabé, 1953; Koga & Miura, 1978). The cubic modification shows the characteristics of a plastic phase: high symmetry and Bragg intensities which rapidly decrease with the scattering angle. Crystallographic data for the monoclinic (or perhaps triclinic) phase are not known. Neutron powder diagrams of all three phases together

with neutron and X-ray single-crystal photographs (Gerlach, Hohlwein & Prandl, 1978) have shown considerable diffuse scattering in the intermediate and even in the low-temperature orthorhombic phase. The investigation reported here was started, therefore, with the aim of finding out whether the crystals are rotationally or otherwise disordered at room temperature.

A structure determination at room temperature based on visually estimated intensities from X-ray film data has been reported (Sasada & Atoji, 1953). Only positional parameters could be refined at that time. Therefore, four-circle measurements on a neutron diffractometer were performed to obtain precise data for a full structure refinement. Neutrons are advantageous for the study of soft materials because the scattering length does not decrease with  $\sin \theta/\lambda$ . Also, the difference in the scattering lengths of C and Cl is less pronounced. The relatively large librations of the molecules at room temperature are the reason for a second measurement at 140 K.

#### Experimental

Crystals were grown from solution (acetone + methyl alcohol). The large crystal faces were (210) planes, giving a plate-like appearance. The crystals are very volatile and were kept in a closed aluminum cylinder during the measurements.

The experiments were performed at the FR2-reactor in Karlsruhe on the P110 (294 K) and P32 (140 K)