

Acta Cryst. (1972). B28, 1733

The Crystal and Molecular Structure of 1,1,2,2,9,9,10,10-Octafluoro-[2.2]paracyclophane and a Reinvestigation of the Structure of [2.2]Paracyclophane*

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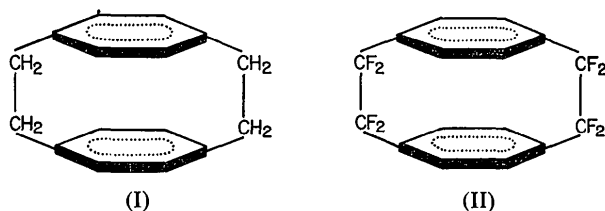
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(Received 23 August 1971)

[2.2]Paracyclophane (I), $C_{16}H_{16}$, crystallizes in the tetragonal system with $a=7.781$ (1), $c=9.290$ (2) Å, space group $P4_2/mnm$, and two molecules per unit cell. 1,1,2,2,9,9,10,10-Octafluoro-[2.2]paracyclophane (II), $C_{16}H_8F_8$, crystallizes in the monoclinic system with $a=7.994$ (2), $b=7.986$ (2), $c=10.855$ (3) Å, $\beta=97.84$ (1)°, space group $P2_1/n$, and two molecules per unit cell. The known structure of (I) was refined with new three-dimensional diffractometer data by full-matrix least-squares methods to $R=0.029$ (360 reflections). The structure of (II) was solved by direct methods with three-dimensional diffractometer data and was refined by full-matrix least-squares to $R=0.037$ (956 reflections). In the initial refinement of each molecule, the substituent atoms on the bridging carbon atoms showed high anisotropy of apparent thermal motion normal to the bridge-substituent bond, this pattern being remarkably similar in the two molecules. Final refinement was done with a model in which each molecule is statistically disordered, to simulate a dynamic disorder that occurs by a twist of the aromatic rings in opposite directions about their common normal; this model is in accord with spectroscopic and thermodynamic measurements on the hydrocarbon. The amplitude of this motion is found to be about 3° for each molecule. The carbon skeletons of (I) and (II) are very similar. The bridge C–C distance is about 1.59 Å. The average C–F distance is 1.35 Å and the average F–C–F angle is 106°. The planes of the four unsubstituted C atoms of each ring are 3.09 Å apart. The *para* carbon atoms are bent about 12° out of the plane of the other four atoms of the aromatic ring.

Introduction

The crystal structure of the unusual strained hydrocarbon, [2.2]paracyclophane (I), was first determined by Brown (1953) and was later reinvestigated by Lonsdale, Milledge & Rao (1960), whose results were considerably at variance with those of Brown. Lonsdale *et al.* attempted a detailed analysis of the molecular motion in the crystal, but their analysis was limited by the quality of their experimental data and the available computational facilities. A re-examination of the structure, with new diffractometer data, was begun some time ago (Bekoe & Trueblood, 1964), but the data were not sufficiently precise to give us confidence in an analysis of the thermal motion. Consequently, we undertook the present study, using data of much great precision. (The results are in fact quite similar to those based on the 1964 work.)



(I)

(II)

* Supported in part by NSF Grants GP-10949 and GP-10622.

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‡ Contribution No. 2777.

Recently, the crystalline 1,1,2,2,9,9,10,10-octafluoro derivative (II) of [2.2]paracyclophane became available (Chow, Pilato & Wheelwright, 1970), and we have determined the structure of that compound as well. These two analyses are reported together because certain features of the molecular structures are remarkably similar, particularly with respect to the very large apparent anisotropy of the motion of the atoms (H and F respectively) attached to the bridging carbon atoms. The best model we have found to explain this anisotropy corresponds to a disorder of these atoms in the crystal.

Throughout this paper we use the names 'hydrocarbon' and 'fluoro derivative' to refer to (I) and (II) respectively.

Experimental

The fluoro derivative

The compound was supplied by Dr Donald Stewart. Suitable crystals were grown from a 1:1 dichloromethane–diethyl ether solution. Oscillation and Weissenberg photographs showed monoclinic symmetry. The systematic absence of $h0l$ reflections with $h+l$ odd and $0k0$ with k odd uniquely establishes the space group $P2_1/n$.

Cell dimensions were determined by a least-squares fit to χ , φ , 2θ angles for 10 reflections measured on a Picker four-circle diffractometer, giving $a=7.994$ (2), $b=7.986$ (2), $c=10.855$ (3)Å and $\beta=97.84$ (0.01)° (λ Cu $K\alpha_1=1.54051$ Å, $t=24^\circ\text{C}$). The density observed by

flotation is 1.704 g.cm^{-3} , the same as that calculated for a two-molecule unit cell. The centers of the molecules are required to lie on centers of symmetry, with one half-molecule constituting the asymmetric unit. All atoms occupy the general fourfold set of positions: $\pm(x, y, z)$ and $\pm(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

With the diffractometer in automatic mode, two separate data sets were collected, for reasons given below. The first set was measured with Zr-filtered Mo $K\alpha$ radiation using a crystal measuring about $0.3 \times 0.3 \times 0.3$ mm. All unique reflections below $2\theta = 50^\circ$ were measured with the $\theta-2\theta$ scan technique, a scan speed of 1° min^{-1} (2θ), and the scan range [$2\theta(\alpha_1) - 1^\circ$] to [$2\theta(\alpha_2) + 1^\circ$]. Background was measured for 40 sec at each end of the scan range. Three reflections, $20\bar{2}$, 305 , and $30\bar{1}$, were used to monitor the stability of the crystal. The intensity of the strongest of these, $20\bar{2}$, increased by about 3% during the first 24 hours of exposure, and then decreased gradually to about 96% of its original value. In contrast, the other two intensities remained constant for about 24 hours and then, during the remaining four days, declined to about 91% of their initial values. The difference in behavior of $20\bar{2}$ is thought to be caused by decreased secondary extinction arising from radiation damage.

In conjunction with the Lorentz and polarization correction, a decay correction was applied, corresponding to the decay curve for reflections 305 and $30\bar{1}$. No absorption correction was made ($\mu R \sim 0.03$). Altogether 1460 reflections were measured; for 956 of these the net intensity exceeded twice the estimated standard deviation and was recorded as 'observed'. No further use was made of 'unobserved' reflections. The e.s.d. of a recorded number of counts, N , was taken to be $[N + (0.01 N)^2]^{1/2}$. Although the range of 'observed' intensities determined is 3×10^4 to 1, about one-third of the measured reflections were recorded as 'unobserved', mainly because of an unusually rapid decline in intensity with increasing diffraction angle.

For the second set of data, collected with Ni-filtered Cu $K\alpha$ radiation, a crystal of approximate dimensions $0.15 \times 0.15 \times 0.35$ mm was used. The crystal was mounted with the long direction (**b**) nearly coincident with the diffractometer φ axis. Intensity measurements of 1188 unique reflections accessible below $2\theta = 133^\circ$ were made, as described for the first data set. Again, the check reflections showed a gradual decline, the final intensities for each amounting to about 93% of the initial value. In order to obtain an approximate absorption correction the intensity of 040 was measured as a function of φ . The maximum relative correction was indicated to be 10%. The intensity data were corrected for decay effects and for absorption, on the basis of the measured correction curves. The intensities of 1010 reflections exceeded 3 e.s.d.'s and were recorded as 'observed'.

The hydrocarbon

The space group ($P4_2/mnm$) and cell dimensions for

[2.2]paracyclophane were known (Brown, 1953). A re-determination of the cell dimensions gave $a = 7.781(1)$ and $c = 9.290(2) \text{ \AA}$, based on eight measurements of $\pm h00$ and $0 \pm k0$ and four measurements of $00 \pm l$ with Cu $K\alpha_1$ radiation ($\lambda = 1.54051 \text{ \AA}$, $t = 24^\circ \text{C}$).

The crystal selected for intensity measurements was a slightly elongated irregular polyhedron with 10 faces. The longest dimension, which was mounted within 5° of the diffractometer φ axis, was 0.28 mm, and the largest cross-section perpendicular to it had dimensions 0.18×0.20 mm. All reflections ($2\theta < 160^\circ$) within one quadrant (hkl ; khl ; $\bar{k}hl$; hkl) were measured with Ni-filtered Cu $K\alpha$ radiation, at a scan speed of 1° min^{-1} (2θ) and with 40 sec background counts taken at each end of the scan range, defined by [$2\theta(\alpha_1) - 1^\circ$] to [$2\theta(\alpha_2) + 1^\circ$]. The intensities of two check reflections showed no systematic variation throughout the run. Lorentz and polarization corrections were applied in the usual manner. Each recorded number of counts (N) was assigned a standard deviation equal to $[N + (0.005N)^2]^{1/2}$. (The constant 0.005 corresponds to the actual variation of check reflections during data collection.) With very few exceptions (see below), the intensities of equivalent reflections were equal within the estimated errors. Equivalent intensities were averaged, resulting in 360 unique data. All reflections were recorded as 'observed'.

From the dimensions of the crystal the maximum and minimum absorption correction factors were calculated to be about 1.14 and 1.10 respectively ($\mu = 5.3 \text{ cm}^{-1}$ for Cu $K\alpha$). The intensities of $\bar{h}0h$ for $h = 2, 3, 4$ ($\chi \sim 85^\circ$ for $\bar{h}0h$) were measured as a function of φ and were found to vary within about $\pm 2\%$. Since most relative absorption errors in I_o would be less than 2%, we did not apply absorption corrections. The largest discrepancy between equivalent reflections was observed for $\{101\}$, with deviations from the mean amounting to about $\pm 3.5\%$ in $|F|$. The eight most intense reflections were also the ones that showed much larger discrepancies between equivalents than were expected from counting statistics. These discrepancies may result from anisotropic secondary extinction (Coppens & Hamilton, 1970).

Solution and initial refinement of the fluoro derivative structure

The structure of the fluoro derivative was solved readily by direct methods. A total of 174 E 's greater than 1.5 (from the Mo data set) was used as input for Long's (1965) program for sign determination. The solution with the highest consistency index, which also was the one that converged most rapidly, resulted in an E map that clearly revealed the positions of eleven atoms. A twelfth peak, identified as a fluorine atom, was only slightly above background. Four of the 174 signs later proved to be incorrect. Three cycles of full-matrix least-squares refinement, based on 590 reflections with $\sin \theta/\lambda$ below 0.50 \AA^{-1} and isotropic temperature fac-

tors for all atoms, converged with an R index of 0.31. The sharp drop-off of intensities with increasing 2θ was now manifest in very large isotropic temperature factors, especially for the fluorine atoms (9 to 12 \AA^2). Least-squares refinement was then continued in stages.

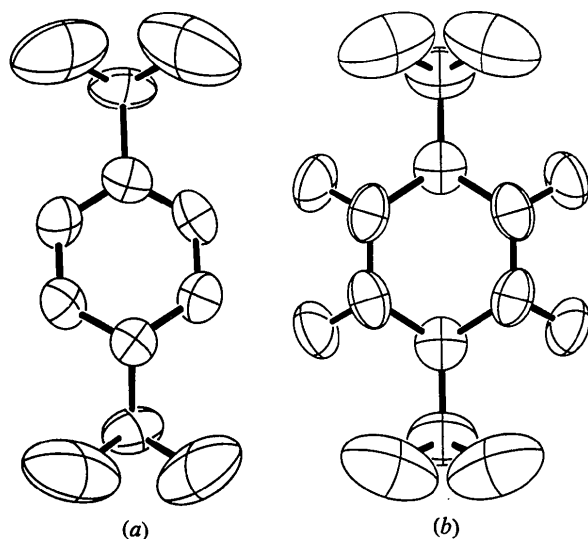


Fig. 1. (a) Thermal ellipsoids for the half-molecule of the fluoro derivative before introduction of disorder ($R=0.11$). (b) Thermal ellipsoids for the half-molecule of the hydrocarbon before introduction of disorder ($R=0.031$).

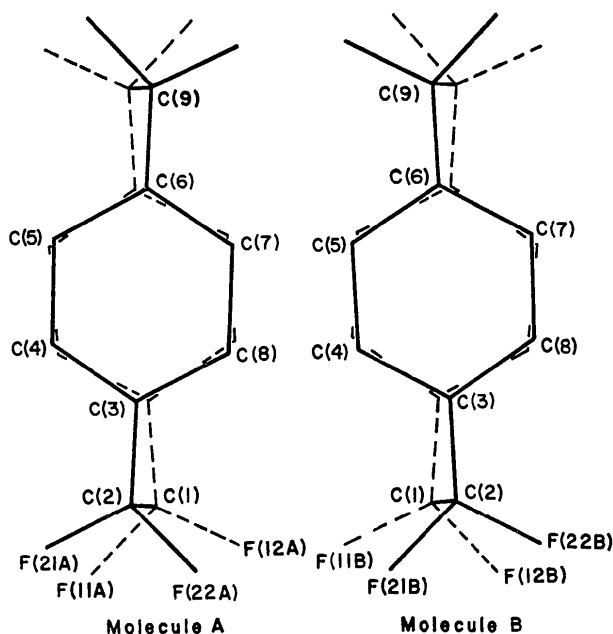


Fig. 2. Model for the disorder. The molecular center of symmetry is preserved only on the average in the disorder structures, e.g. the top half of molecule *A* is related to the bottom half of molecule *B* by the center of symmetry. C(9) is related to C(1) by the center of symmetry in the ordered molecule; in the disorder structure, C(9A) is so related to C(1B) and C(9B) to C(1A).

The limit for $\sin \theta/\lambda$ was increased, first to 0.55 \AA^{-1} and then to the limit of the data, and anisotropic temperature factors for all atoms were introduced. The refinement converged at $R=0.132$. The hydrogen atoms were then found on a difference map near their predicted positions. They were assigned isotropic temperature parameters of 5.5 \AA^2 , which were not permitted to vary, and further least-squares refinement converged in two cycles to $R=0.11$.

A difference map calculated at this stage showed three regions of residual electron density with maxima of approximately 0.5 e. \AA^{-3} , two of which were situated between geminal fluorine atoms, indicating that the anisotropic temperature factors did not adequately account for the motion of the fluorine atoms. The third region was not near any atom.

The results so far obtained were puzzling. The data set was estimated to be of a quality that would normally give an R index of less than 0.05. The R index at convergence was more than twice this value, yet no systematic discrepancies between F_o and F_c could be found. The molecular geometry showed some anomalies, which also indicated that the model was inadequate. For example, the formal e.s.d.'s for C-C and C-F bonds were about 0.01 \AA or less, whereas some chemically equivalent bonds differed in length by as much as $0.08\text{--}0.12 \text{ \AA}$.

The problems appeared to be related to the large temperature factors of the fluorine atoms. The anisotropy indicated by the ellipsoidal approximation is shown in Fig. 1(a). The largest axes in the fluorine thermal ellipsoids correspond to B values of about 25 \AA^2 ; for ring and methylene carbon atoms, the corresponding values are 8 and 9 \AA^2 , respectively.

We felt that an explanation of these problems might be found more easily if a data set containing more data at higher $\sin \theta/\lambda$ values could be obtained; as a result, the Cu data set was collected. Although it did yield a larger number of 'observed' reflections, the results of a least-squares refinement were essentially the same as those described above. The problem was temporarily set aside, and attention was directed towards the refinement of the hydrocarbon.

Refinement of the structures

The hydrocarbon

The crystallographically required molecular point symmetry is mmm and as in the previous studies of the hydrocarbon, the asymmetric unit was taken to consist of two 'half' carbon atoms at a mirror plane, and one carbon and two hydrogen atoms in general positions. The starting parameters were those of Bekoe & Trueblood (1964), who had obtained an R index of 0.062. Hydrogen atoms were included with isotropic temperature factors. Three cycles of full-matrix least-squares refinement with the complete data set converged to $R=0.061$, after insignificant parameter changes. A comparison of F_o and F_c indicated serious secondary

extinction effects. Application of two cycles of secondary extinction corrections (Zachariasen, 1963) and subsequent least-squares refinement gave an R of 0.039. Although this is a quite respectable agreement, the overall quality of the data seemed sufficiently good to warrant attempts to find an improved model.

Inspection of the results revealed one unusual feature: the temperature parameters for the H atoms were quite large, about 8 \AA^2 (ring) and 11 \AA^2 (bridge), respectively. This observation, combined with results from the fluoro derivative study, led us to attempt refinement of the hydrocarbon with anisotropic temperature factors for the hydrogen atoms. The R index improved to 0.031, and the resulting pattern of thermal ellipsoids, Fig. 1(b), was strikingly similar to that obtained for the fluoro derivative.

The high anisotropy of the methylene substituents in both compounds suggested that the thermal ellipsoid approximation was not adequate for either molecule. A model that seemed more reasonable is indicated in Fig. 2. We assume that the carbon skeleton of each half of the molecule is a rigid body and that the C-C-X and X-C-X (X=H, F) angles are essentially constant. The two halves of the molecule can then be twisted in opposite directions, with the two possible conformations shown in Fig. 2 having equal probability. It also seemed reasonable to assume that the energy barrier is so low that at room temperature rapid interconversion takes place (see 'Discussion').

A motion of this type is compatible with the pattern of thermal ellipsoids shown in Fig. 1. The root-mean-square displacements along the major axes of the thermal ellipsoids for the methylene substituents in both

Table 1. Positional parameters for [2.2] paracyclophane

E.s.d.'s are in parentheses. The carbon atoms are numbered to correspond to the system used in the fluoro derivative and in the conventional chemical numbering system. The 'half' hydrogen atoms attached to C(2) are numbered 21 and 22.

	x	y	z
C(2)	0.07098 (13)	0.07098 (13)	0.29926 (15)
C(3)	0.12618 (9)	0.12618 (9)	0.15060 (12)
C(4)	0.24773 (10)	0.03326 (11)	0.07459 (9)
H(4)	0.3238 (10)	-0.0503 (11)	0.1264 (8)
H(21)	0.1923 (27)	-0.0165 (24)	0.3391 (21)
H(22)	0.0621 (21)	0.1566 (24)	0.3688 (16)

Table 2. Thermal parameters for [2.2]paracyclophane

Anisotropic temperature factors are of the form: $\exp(-h^2\beta_{11} - \dots - k^2\beta_{33})$, and isotropic ones are of the form: $\exp(-B \sin^2 \theta/\lambda^2)$. $10^4\beta_{ij}$ are given. B 's are in \AA^2 . E.s.d.'s in parentheses apply to the least significant figures.

	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(2)	298 (2)	298 (2)	144 (2)	-164 (6)	-28 (3)	-28 (3)
C(3)	177 (1)	177 (1)	151 (2)	-77 (3)	-30 (2)	-30 (2)
C(4)	149 (1)	182 (2)	190 (1)	-7 (2)	-53 (2)	28 (2)
H(4)	178 (16)	293 (21)	212 (14)	167 (34)	101 (29)	95 (29)
H(21)	6.6 (5)					
H(22)	5.4 (5)					

compounds exceed 0.5 \AA . An 'in-plane' twist of each ring in the hydrocarbon in opposite directions by only 4° leads to a displacement of about 0.8 \AA for a methylene hydrogen atom. Hence, it seemed reasonable to attempt further refinement with a statistically disordered model, each of the two twisted conformations having half weight. The separation of 0.8 \AA was chosen as the starting value. A twist angle of 4° separates the ring 'half' carbon atoms by less than 0.2 \AA and the methylene 'half' carbon atoms by less than 0.4 \AA ; since these separations are smaller than the resolution afforded by

Table 3. Observed and calculated structure factors for [2.2]paracyclophane

The columns are l , $100F_o$, $100F_c$, $1/\sigma(F_o)$, in that order.

h	k	l	$100F_o$	$100F_c$	$1/\sigma(F_o)$
0	0	0	3 312	-307	33
0	0	1	2 411	255	23
0	1	0	5 436	435	25
0	1	1	6 795	-607	25
0	1	2	8 919	959	25
0	1	3	0 28	10	5
0	1	4	0 24	-7	8
0	1	5	10 24	-7	8
0	1	6	11 72	-98	25
0	1	7	10 24	-7	8
0	1	8	11 72	-98	25
0	1	9	10 24	-7	8
0	1	10	11 72	-98	25
0	1	11	10 24	-7	8
0	1	12	11 72	-98	25
0	1	13	10 24	-7	8
0	1	14	11 72	-98	25
0	1	15	10 24	-7	8
0	1	16	11 72	-98	25
0	1	17	10 24	-7	8
0	1	18	11 72	-98	25
0	1	19	10 24	-7	8
0	1	20	11 72	-98	25
0	1	21	10 24	-7	8
0	1	22	11 72	-98	25
0	1	23	10 24	-7	8
0	1	24	11 72	-98	25
0	1	25	10 24	-7	8
0	1	26	11 72	-98	25
0	1	27	10 24	-7	8
0	1	28	11 72	-98	25
0	1	29	10 24	-7	8
0	1	30	11 72	-98	25
0	1	31	10 24	-7	8
0	1	32	11 72	-98	25
0	1	33	10 24	-7	8
0	1	34	11 72	-98	25
0	1	35	10 24	-7	8
0	1	36	11 72	-98	25
0	1	37	10 24	-7	8
0	1	38	11 72	-98	25
0	1	39	10 24	-7	8
0	1	40	11 72	-98	25
0	1	41	10 24	-7	8
0	1	42	11 72	-98	25
0	1	43	10 24	-7	8
0	1	44	11 72	-98	25
0	1	45	10 24	-7	8
0	1	46	11 72	-98	25
0	1	47	10 24	-7	8
0	1	48	11 72	-98	25
0	1	49	10 24	-7	8
0	1	50	11 72	-98	25
0	1	51	10 24	-7	8
0	1	52	11 72	-98	25
0	1	53	10 24	-7	8
0	1	54	11 72	-98	25
0	1	55	10 24	-7	8
0	1	56	11 72	-98	25
0	1	57	10 24	-7	8
0	1	58	11 72	-98	25
0	1	59	10 24	-7	8
0	1	60	11 72	-98	25
0	1	61	10 24	-7	8
0	1	62	11 72	-98	25
0	1	63	10 24	-7	8
0	1	64	11 72	-98	25
0	1	65	10 24	-7	8
0	1	66	11 72	-98	25
0	1	67	10 24	-7	8
0	1	68	11 72	-98	25
0	1	69	10 24	-7	8
0	1	70	11 72	-98	25
0	1	71	10 24	-7	8
0	1	72	11 72	-98	25
0	1	73	10 24	-7	8
0	1	74	11 72	-98	25
0	1	75	10 24	-7	8
0	1	76	11 72	-98	25
0	1	77	10 24	-7	8
0	1	78	11 72	-98	25
0	1	79	10 24	-7	8
0	1	80	11 72	-98	25
0	1	81	10 24	-7	8
0	1	82	11 72	-98	25
0	1	83	10 24	-7	8
0	1	84	11 72	-98	25
0	1	85	10 24	-7	8
0	1	86	11 72	-98	25
0	1	87	10 24	-7	8
0	1	88	11 72	-98	25
0	1	89	10 24	-7	8
0	1	90	11 72	-98	25
0	1	91	10 24	-7	8
0	1	92	11 72	-98	25
0	1	93	10 24	-7	8
0	1	94	11 72	-98	25
0	1	95	10 24	-7	8
0	1	96	11 72	-98	25
0	1	97	10 24	-7	8
0	1	98	11 72	-98	25
0	1	99	10 24	-7	8
0	1	100	11 72	-98	25

the data, these atoms were treated as 'whole' in the first calculations with this model.

Refinement with isotropic temperature factors for the 'half' hydrogen atoms converged in three least-squares cycles to an R index of 0.0295. The maximum shift in the final cycle did not exceed 1% of the corresponding e.s.d. Since this disorder model employs one less parameter than the ordered one and results in a lower R index, it appears to provide a better description of the structure. The methylene-hydrogen temperature factors are normal. The final parameters from this refinement are listed in Tables 1 and 2. A list of F_o 's and F_c 's is given in Table 3.

Since the separation of the two 'half' methylene carbon atoms approaches the experimental resolution, a refinement was also attempted with these atoms disordered. The convergence was very sluggish, and the correlation between shifts in positional and thermal parameters for the disordered C atom was high, as anticipated. Nevertheless, when the process was interrupted (because convergence did not seem within reach) an R index of 0.028 had been attained, and the molecular geometry was reasonable.

The fluoro derivative

The success of the disordered model for the hydrocarbon led us to try a corresponding model for the fluoro derivative. Positions for the disordered fluorine atoms were estimated, assuming a twist angle of 3° . Refinement with the Cu data set, after correction for secondary extinction effects, converged with $R=0.053$. All parameters, including isotropic temperature parameters for hydrogen, were refined. The Mo data set was then corrected for secondary extinction, and subsequent least-squares refinement converged with $R=0.037$. The last shifts were less than 10% of their corresponding e.s.d.'s. The residual electron density in a final difference Fourier synthesis at no point reached $0.2 \text{ e.}\text{\AA}^{-3}$. The final positional and thermal parameters for both data sets are listed in Tables 4 and 5. A comparison of F_o and F_c for the Mo data set is given in Table 6.

Computing procedures

The calculations were performed on IBM 7044, 360/75, and 360/91 computers. The least-squares program (UCLALS-1, written by R. A. Sparks, P. K. Gantzel & K. N. Trueblood) minimizes $\sum w(K \cdot F_o - |F_c|)^2$ by full-matrix methods. The weights, w , were inversely proportional to the variances of the intensities; values of $1/w$ are given in Tables 3 and 6. Estimated standard deviations were obtained from the expression $(a_{ii}S/m)^{1/2}$, where a_{ii} is the diagonal element in the inverse normal equation matrix, and m is the difference between the number of observations and the number of parameters refined.

The atomic form factors for fluorine and carbon are those given by Hanson, Herman, Lea & Skillman (1964). For hydrogen we used the form factor of Stewart, Davidson & Simpson (1965).

Table 4. Positional parameters for fluoro derivative

Parameters are from the least-squares refinement of the disordered structure. For each atom, the results from the Mo data set are given on the first line and those from the Cu data set are given on the second line. E.s.d.'s (in parentheses) apply to the least significant digits. The first digit of the identifying number assigned to each fluorine atom denotes the carbon atom to which it is attached (see Fig. 2).

	x	y	z
C(1)	-0.2374 (3)	0.2481 (3)	0.0509 (2)
	-0.2379 (5)	0.2491 (5)	0.0499 (4)
C(2)	-0.0864 (3)	0.2600 (3)	0.1595 (2)
	-0.0856 (5)	0.2605 (6)	0.1603 (4)
C(3)	0.0539 (2)	0.1393 (2)	0.1495 (1)
	0.0542 (4)	0.1400 (4)	0.1491 (3)
C(4)	0.1750 (2)	0.1746 (2)	0.0739 (2)
	0.1757 (4)	0.1761 (4)	0.0741 (3)
C(5)	0.2557 (2)	0.0469 (2)	0.0215 (2)
	0.2562 (4)	0.0484 (4)	0.0220 (3)
C(6)	0.2162 (2)	-0.1167 (2)	0.0438 (2)
	0.2153 (4)	-0.1176 (4)	0.0435 (3)
C(7)	0.1230 (2)	-0.1506 (3)	0.1387 (2)
	0.1222 (4)	-0.1519 (5)	0.1391 (3)
C(8)	0.0428 (2)	-0.0228 (3)	0.1916 (2)
	0.0428 (5)	-0.0231 (5)	0.1915 (3)
F(11A)	-0.2965 (8)	0.3881 (9)	0.0151 (7)
	-0.2969 (14)	0.3886 (16)	0.0141 (13)
F(12A)	-0.3632 (8)	0.1838 (8)	0.1281 (6)
	-0.3615 (12)	0.1884 (14)	0.1285 (9)
F(11B)	-0.2126 (8)	0.4074 (9)	-0.0122 (8)
	-0.2147 (15)	0.4054 (15)	-0.0108 (14)
F(12B)	-0.3860 (9)	0.2577 (8)	0.0769 (7)
	-0.3883 (13)	0.2573 (15)	0.0756 (11)
F(21A)	-0.0236 (10)	0.4301 (8)	0.1302 (5)
	-0.0245 (18)	0.4270 (15)	0.1310 (10)
F(22A)	-0.1260 (9)	0.2785 (7)	0.2666 (6)
	-0.1255 (18)	0.2773 (15)	0.2674 (12)
F(21B)	-0.0450 (10)	0.4009 (8)	0.1972 (6)
	-0.0451 (19)	0.4044 (17)	0.1968 (11)
F(22B)	-0.1797 (9)	0.1930 (8)	0.2598 (7)
	-0.1777 (18)	0.1954 (16)	0.2593 (13)
H(4)	0.1891 (18)	0.2860 (21)	0.0504 (14)
	0.1854 (37)	0.2930 (42)	0.0585 (28)
H(5)	0.3294 (19)	0.0716 (18)	-0.0424 (15)
	0.3044 (55)	0.0934 (58)	-0.0421 (42)
H(7)	0.0996 (19)	-0.2616 (21)	0.1589 (14)
	0.1115 (40)	-0.2677 (47)	0.1690 (31)
H(8)	-0.0330 (19)	-0.0432 (19)	0.2460 (15)
	-0.0226 (51)	-0.0614 (50)	0.2426 (38)

Discussion

The outcome of the refinements of the models involving disorder for each molecule clearly indicates that this description should be preferred to one with ordered molecules. The more dramatic difference is seen with the fluoro derivative because of the high proportion of the scattering power contributed by the fluorine atoms.

The disorder is essentially the same for both compounds. In ordered (mmm) molecules, the dimethylene bridge joining the rings would be in the eclipsed conformation, corresponding to a maximum in the potential-energy function for rotation about this bridge bond. The exact alignment of the aromatic rings relative to one another presumably also corresponds to an energy maximum. When the molecules are twisted as described these repulsive interactions are relieved, but other

strains are introduced and act as restoring forces. Either the rings are forced closer together or the C-C bridge bond is stretched, or both, and bond angles are also deformed. The potential function for these restoring forces has a minimum at the eclipsed position and rises steeply as the angle of twist increases. The total potential energy function for the molecule, representing the sum of these opposing effects, is presumably rather broad, with a relatively flat bottom and steep sides. The exact shape of the bottom will depend on the relative widths and curvatures of the individual potential functions for the different interactions present, but, whatever its shape, the corresponding vibrational motion would presumably be nearly classical at room temperature so that the molecule would exist most of the time near the extremes of its motion. This is consistent with what we found. In the absence of any evidence to rule out equal probabilities for twisting in opposite directions, an equal distribution between the two positions is assumed. Packing forces might play a minor

role in altering the distribution, but intramolecular rather than intermolecular forces appear to dominate the disordering described.

A distortion of the type discussed here has been proposed for the hydrocarbon by Ron & Schnepf (1962,) on the basis of spectral data. They estimated a static twist angle of about 3°. Our data do not permit us to distinguish explicitly between a static and a dynamic disorder. However, after we had reported the present results (Hope, Bernstein & Trueblood, 1970) a thermodynamic study of the hydrocarbon appeared (Andrews & Westrum, 1970), which contains the information needed to settle this question with reasonable confidence. An anomaly in the heat capacity (C_p) near 50°K led Andrews & Westrum to suggest that at this temperature the majority of the molecules have acquired sufficient energy to permit the twisting motion to become an active vibrational mode, whereas at lower temperatures this is not the case. The transition temperature for the fluoro derivative may be somewhat higher, but

Table 5. *Thermal parameters for fluoro derivative*

See captions of Tables 2 and 4 for clarifying notes.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	221 (4) 218 (7)	235 (5) 247 (8)	194 (3) 200 (5)	68 (7) 92 (13)	51 (6) 43 (10)	-87 (6) -103 (11)
C(2)	289 (4) 295 (8)	282 (5) 316 (10)	152 (3) 150 (5)	1 (8) 23 (15)	81 (6) 83 (10)	-173 (6) -195 (11)
C(3)	204 (3) 206 (6)	217 (4) 240 (7)	88 (2) 89 (3)	-56 (6) -48 (10)	-5 (4) 15 (6)	-75 (4) -83 (7)
C(4)	208 (3) 212 (6)	177 (3) 183 (6)	121 (2) 126 (3)	-116 (6) -124 (10)	2 (4) -1 (7)	-19 (5) -31 (8)
C(5)	159 (3) 163 (5)	234 (4) 269 (7)	111 (2) 118 (3)	-82 (6) -78 (10)	30 (4) 44 (7)	-25 (4) -18 (8)
C(6)	157 (3) 167 (5)	194 (3) 208 (6)	116 (2) 116 (3)	12 (5) 29 (9)	-16 (4) -11 (6)	-7 (4) 6 (7)
C(7)	235 (4) 234 (7)	211 (4) 226 (7)	116 (2) 124 (4)	-33 (7) -25 (12)	-35 (5) -22 (8)	81 (5) 75 (9)
C(8)	224 (4) 228 (7)	308 (5) 321 (10)	78 (2) 81 (3)	-70 (7) -86 (13)	30 (4) 30 (7)	15 (5) 10 (8)
F(11A)	427 (14) 402 (24)	253 (11) 253 (19)	270 (9) 259 (14)	290 (24) 256 (41)	7 (16) 24 (28)	-58 (14) -79 (25)
F(12A)	256 (10) 214 (15)	407 (15) 387 (22)	230 (7) 229 (12)	-88 (17) -39 (25)	234 (14) 211 (22)	-181 (12) -144 (20)
F(11B)	613 (19) 559 (33)	170 (6) 170 (10)	252 (6) 268 (11)	147 (23) 155 (39)	94 (20) 158 (36)	40 (8) 35 (15)
F(12B)	215 (6) 217 (11)	433 (19) 428 (31)	306 (11) 275 (16)	58 (22) 123 (34)	122 (16) 60 (25)	-321 (20) -263 (31)
F(21A)	336 (7) 338 (13)	164 (5) 185 (11)	343 (10) 333 (19)	-79 (9) -68 (17)	125 (20) 167 (36)	-122 (16) -223 (30)
F(22A)	414 (15) 415 (27)	502 (20) 517 (38)	152 (4) 170 (9)	77 (23) 42 (43)	176 (11) 201 (23)	-234 (20) -262 (38)
F(21B)	405 (14) 412 (27)	270 (13) 306 (22)	262 (9) 270 (17)	-51 (9) -48 (34)	2 (18) 44 (34)	-310 (19) -374 (37)
F(22B)	457 (16) 463 (31)	482 (15) 493 (31)	199 (6) 201 (13)	90 (19) 51 (37)	357 (18) 377 (36)	-63 (16) -32 (29)

Table 5 (cont.)

	Isotropic B values for the hydrogen-atoms	
	Mo Data	Cu Data
H(4)	5.8 (4)	5.5 (7)
H(5)	5.8 (4)	10.0 (13)
H(7)	5.9 (4)	6.5 (8)
H(8)	5.8 (4)	8.5 (11)

it seems likely to be still well below room temperature. We can therefore conclude that the disorder found for both crystals in our X-ray study is dynamic. From the shape of the C_p curve near the transition temperature, Andrews & Westrum conclude that the disordering is only weakly cooperative, in accord with the suggested twisting mechanism. Thus all the available evidence

establishes the reality of the proposed motion. The convergence of ideas based on results from widely different methods is most reassuring.

The least-squares positional parameters for the carbon skeleton and the hydrogen atoms on the rings are, as a consequence of the computational model, averages over the positions attained when the molecules are twisted to the two positions prescribed by the disordering model. A proper determination of the molecular geometry must take into account the disordering of the carbon atoms. Reasonable positions for these atoms were obtained by calculating displacements arising from appropriate twist angles. Two independent estimates of these angles were made: in one calculation, all C(bridge)-C-F angles were assumed to be equal, and in the other all C-F bond distances were assumed to be the same. Individual parameters of both categories are sensitive to the calculated positions of the bridge carbon atoms. The 'best' twist angle based on the equal-angle criterion was taken to be that which led to a minimum in the expression $\sum_i (u_i - \bar{u})^2$, where u_i represents an individual C-C-F angle and \bar{u} the mean of the eight crystallographically independent angles, the summation being taken over these same eight an-

Table 7. Positional parameters derived from twist-angle calculations

These values were derived from the parameters of Tables 1 and 4, with the twist angles of 3.2 and 3.0° determined for the hydrocarbon and the fluoro derivative respectively (see text).

Table with 3 columns: Parameter, x, y, z. Rows include Hydrocarbon (C(2A) to H(4A)) and Fluoro derivative (C(1A) to C(8B)).

Table 6. Observed and calculated structure factors for 1,1,2,2,9,9,10,10-octafluoro-[2.2]paracyclophane (Mo Kα data)

The columns are l, 10F0, 10F6, 1/σ(F0), in that order.

Large grid of numerical data representing structure factors, organized in columns corresponding to the variables l, 10F0, 10F6, and 1/σ(F0).

gles. The minimum was obtained for a 'half' (individual ring) twist angle of 2.8° , or a displacement of the bridge C atom by 0.14 \AA from the least-squares position. A similar least-squares fit of the C-F distances led to a 'best' half twist angle of 3.2° . We chose the mean, 3.0° , for subsequent calculations.

The corresponding treatment for the hydrocarbon is quite simple, since there are only two independent C-C-H angles or C-H distances involving the bridge atoms. Unfortunately, however, because the calculations are based on 'half-hydrogen' positions, the uncertainties are much larger. Equal C-C-H angles were indicated for a half twist of 2.6° , equal C-H distances for 3.8° , and a mean of 3.2° for the half twist.

We then calculated disorder positions for all carbon atoms in each molecule, and for the single unique ring hydrogen atom in the hydrocarbon, assuming the twist angles just described and a rigid carbon skeleton. Each carbon position found in the least-squares refinements was assumed to represent the midpoint of a line connecting the two disorder positions. The displacement was therefore calculated to take place along a direction perpendicular to the radius from the twist axis to the least-squares atomic position and in a plane perpendicular to the twist axis. (The twist axis for each molecule passes through the centers of the aromatic rings.) The coordinates so derived are given in Table 7, and the corrected bond distances and angles corresponding to them are shown in Table 8. This analysis is related to that used in correction for librational motion, when there is only one mode of libration (Cruickshank, 1956; Schomaker & Trueblood, 1968). Although these molecules are not rigid, the eight carbon atoms of each half-molecule [C(2) to C(9) in Fig. 2] form a framework that may, to a first approximation, be considered rigid. Application of the rigid-body model to the thermal parameters of Tables 2 and 5 for these eight-atom skeletons indicated a fair fit for each molecule; neither half-molecule librates very anisotropically, the r.m.s. amplitudes for each varying from 4 to 6° . These motions imply librational corrections to the bond distances, as indicated in Table 8.

The most interesting of the bond lengths is that for the bridging C-C bond. The increases in this distance, indicated by the twist-angle calculations, are 0.025 to 0.030 \AA ; those from the rigid-body analysis are only about one fourth as large, but they do not take into account the nonrigidity manifested in the motion of the bridging atoms and especially, their substituents. The uncertainty in the twist-angle results is indicated by a calculation of the corresponding increases for each of the two hydrocarbon twist angles mentioned above (2.6 and 3.8°), which are 0.017 and 0.042 \AA respectively. Perhaps the most that should be said about the bridging C-C distance is that each molecule exists most of the time in a form in which this distance is about 1.59 \AA .

The twist-angle calculations leading to the parameters of Table 7 underestimate the corrections needed for the aromatic and exocyclic C-C distances because

Table 8. *Some bond distances and bond angles*

Carbon atoms are identified only by their numbers. When only a single value is given, it was calculated with the parameters of Table 1 or 4. The C-C-C angles are not significantly affected by either of the corrections. The C-C-H angles on the aromatic nuclei are all close to 120° , ranging from 117 to 122° . The C-H distances in the fluoro derivative range from 0.92 to 0.99 \AA .

Fluoro derivative	Parameters of Table 4	Parameters of Table 7	After libration correction
1-2	1.571 Å	1.597 Å	1.577 Å
2-3	1.494	1.496	1.502
3-4	1.381	1.382	1.391
4-5	1.371	1.373	1.380
5-6	1.373	1.375	1.384
6-7	1.378	1.381	1.388
7-8	1.372	1.374	1.381
8-3	1.380	1.382	1.391
1-F(11A)	1.26	1.34	
1-F(11B)	1.47	1.34	
1-F(12A)	1.49	1.36	
1-F(12B)	1.26	1.35	
2-F(21A)	1.50	1.37	
2-F(21B)	1.23	1.31	
2-F(22A)	1.26	1.35	
2-F(22B)	1.50	1.37	
Angles			
F-C-F			
Average:	103°	106°	
Range:	103-104	105-107	
C _{bridge} -C-F			
Average:	107°	107°	
Range:	96-119	104-110	
C _{ring} -C-F			
Average:	111	111	
Range:	105-119	109-115	
	2-3-4	120.4°	
	2-3-8	119.9	
	3-4-5	120.2	
	4-5-6	120.1	
	5-6-7	118.6	
	6-7-8	119.9	
	7-8-3	120.3	
	8-3-4	118.1	
	5-6-9	119.8	
	7-6-9	120.0	
Hydrocarbon			
	Parameters of Table 1	Parameters of Table 7	After libration correction
1-2	1.562 Å	1.593 Å	1.569 Å
2-3	1.509	1.511	1.514
3-4	1.384	1.386	1.394
4-5	1.386	1.387	1.394
4-H(4)	1.00	1.00	
2-H(21)	1.22	1.08	
2-H(22)	0.93	1.02	
Angles			
H-C-H	104°	109°	
C _{bridge} -C-H	99	110	
	117	106	
C _{ring} -C _{bridge} -H	102	107	
	117	112	
	2-3-4	120.9°	
	3-4-5	120.7	
	8-3-4	117.0	

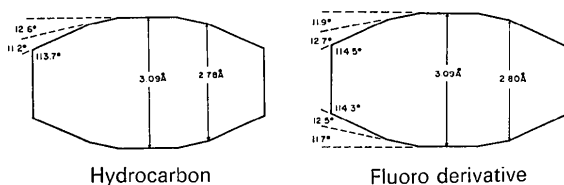


Fig. 3. Molecular profiles of the carbon skeletons, calculated with the parameters of Tables 1 and 4. The parameters of Table 7 give results not greatly different; the largest change is a decrease of about 1° in the internal angle at each of the bridging carbon atoms, as a consequence of the increase in the bridge C-C bond lengths.

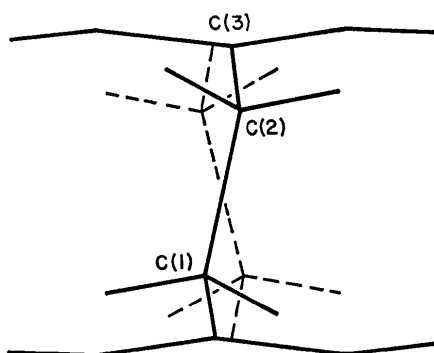


Fig. 4. End view of the hydrocarbon, illustrating the effect of the disorder and the bending of the aromatic hydrogen atoms below the ring plane. These hydrogen atoms are also bent below the ring plane in the fluoro derivative (see Table 9).

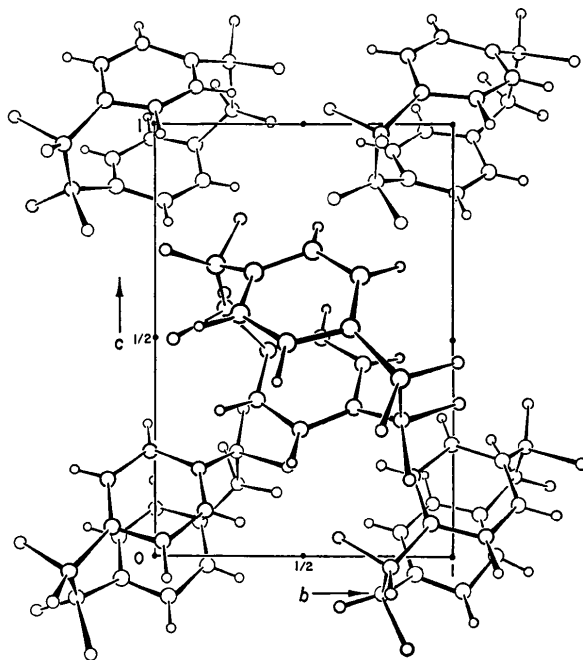


Fig. 5. View of the structure of the fluoro derivative down a . For clarity, only one set of fluorine positions has been shown; thus the disorder is not illustrated. The viewing distance is about 25 \AA .

they consider only one mode of motion. The librational corrections give values more in accord with those found in other benzene derivatives. However, the uncertainties in the corrections are such that no great credence should be placed in the values derived by either method.

Because of the difficulty in the exact positioning of the fluorine and bridging carbon atoms, only a brief discussion of the geometric parameters involving these atoms is warranted. The C-F bond distances for the 'half' fluorine atoms and the (ordered) carbon positions of Table 4 fall into two groups, as a result of the disorder, and they range from 1.23 to 1.26 \AA and from 1.47 to 1.50 \AA (Table 8). The average C-F distance for the two unique bridging atoms is, however, the same; 1.37 \AA . The parameters of Table 7 lead to C-F bond distances in the range 1.31 to 1.37 \AA and average 1.35 \AA . These distances generally agree well with the distance found in methylene fluoride (Lide, 1952), 1.358 \AA , and in 1,2-diphenyltetrafluoroethane (Cruickshank, Jeffrey & Nyburg, 1959), 1.374 \AA . Our F-C-F bond angles, averaging 106° after correction, also agree with those found in earlier work.

The deformation of the aromatic rings is very similar in the two molecules, as shown in the molecular profiles in Fig. 3. The *para* carbon atoms are bent about 12° out of the plane of the other four atoms in the

Table 9. *Some least-squares planes*

Deviations of the atoms used to define the plane are shown in bold face. l_1, l_2, l_3 are direction cosines relative to $a, b,$ and c^* . D is the distance of the plane from the origin. The atomic parameters used are those of Tables 1 and 4.

	I	II	III	IV	V
$l_1 \times 10^4$	6720	6032	7294	7071	6074
$l_2 \times 10^4$	0655	-0141	1460	7071	7944
$l_3 \times 10^4$	7377	7974	6684	0000	0000
$D(\text{\AA})$	-1.546	-1.392	-1.391	-1.546	-1.377

Deviations of atoms ($\text{\AA} \times 10^3$)

Fluoro derivative				
C(2)	-767	-613	-617	
C(3)	-146	000	-001	
C(4)	-002	-001	284	
C(5)	002	001	286	
C(6)	-142	000	001	
C(7)	-002	283	-002	
C(8)	002	288	002	
H(4)	-031	-126	353	
H(5)	-033	-138	354	
H(7)	-045	338	-145	
H(8)	-039	343	-131	
Hydrocarbon†				
C(2)			-765	-602
C(3)			-157	000
C(4)			000	000
H(4)			-041	-157

† Plane IV is defined by atom C(4) and the other three atoms equivalent to it in the same ring. Plane V is defined by the sequence of four atoms in the hydrocarbon, analogous to atoms 3, 4, 5, 6 of the fluorocarbon, that is C(3), C(4), and the two atoms equivalent to them at $x, y, -z$.

ring. In each molecule, the hydrogen atoms substituted on the aromatic ring are also displaced slightly inward from the least-squares plane of the four essentially coplanar atoms to which they are bonded (Fig. 4 and Table 9). Although the effect is small (about 0.04 Å), it has been observed in other similar molecules (Coulter & Trueblood, 1963; Gantzel & Trueblood, 1965; Bernstein & Trueblood, 1971) and in earlier studies on the present hydrocarbon (Bekoe & Trueblood, 1964). The effect can be rationalized either by postulating a shift in electron density towards the outside of each molecule (this shift in turn causing a displacement of the hydrogen atoms by repulsion), or by invoking a bent-bond model, which, together with a requirement of coplanar bonds at each ring atom, would lead to the observed effect.

The packing seems normal in each structure. A view of the structure of the fluoro derivative is shown in Fig. 5; for simplicity, the disorder has not been illustrated. The shortest interatomic distances between molecules are listed in Table 10. None of these distances in either structure is significantly smaller than the sum of the corresponding van der Waals radii, and only two are about equal to this sum: the two shortest H...F contacts. None of the distances in Table 10 varies by more than 0.05 Å when the disorder in the carbon positions is taken into account, and most of the variations are much smaller.

The twisting of the aromatic rings that we found was one of the two principal kinds of molecular distortion deduced for the hydrocarbon by Lonsdale *et al.* (1960). On the other hand, we found no evidence for the other mode which they described in some detail, a concertina-like motion. Indeed, their principal evidence for that

motion, a markedly greater vibration amplitude parallel to *c* for C(2) than for C(3), is completely absent in our analysis of the present data, as well as in our independent analyses of the earlier set of diffractometer intensities (Bekoe & Trueblood, 1964) and of Brown's (1953) data.

We are grateful to Dr Donald Stewart and Dr S. W. Chow of the Union Carbide Corporation for supplying us with a sample of the fluoro derivative and information about it, to Professor D. J. Cram for a sample of the hydrocarbon, to the National Science Foundation for their support, and to Donna Davis, Keith Parker, and Krista Black for their assistance with the calculations and drawings.

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Table 10. Intermolecular distances

Atom 1 is at position of Table 1 or 4; position of atom 2 is indicated by a serial number denoting the position relative to Table 1 or 4, as in footnotes, and by a triple of numbers denoting translations parallel to *a*, *b*, and *c*.

The distances listed include all C-F ≤ 3.40 Å, F...F ≤ 3.20 Å, C...H ≤ 3.0 Å, F...H ≤ 2.9 Å, and H...H ≤ 2.7 Å. There are no intermolecular C...C ≤ 3.40 Å in either structure.

Fluoro derivative*			Hydrocarbon†		
Atom 1	Atom 2		Atom 1	Atom 2	
C(5)	F(12A), 1, 100	3.30 Å	C(4)	H(21), 16	2.93 Å
C(5)	F(12B), 1, 100	3.31	H(22)	H(22), 6, 001	2.44
C(5)	F(22A), 3, 00I	3.35	H(22)	H(4), 7	2.45
F(11B)	F(21A), 2, 010	2.75	H(21)	H(4), 16	2.52
F(12A)	F(21B), 4, 110	3.10	H(22)	H(22), 14, 001	2.65
F(21A)	F(21A), 2, 010	3.11			
F(22A)	H(5), 3, 100	2.46			
F(11B)	H(4), 2, 010	2.50			
F(12B)	H(8), 4, 100	2.64			
F(21A)	H(7), 1, 010	2.65			
F(12A)	H(8), 4, 100	2.76			
F(22B)	H(5), 3, 100	2.85			
F(11A)	H(4), 2, 010	2.86			
F(12B)	H(5), 1, 100	2.87			

* Fluoro derivative: 1, x, y, z ; 2, $-x, -y, -z$; 3, $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; 4, $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

† Hydrocarbon: 6, $x, y, -z$; 7, $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; 14, $y, x, -z$; 16, $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$.

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The Structure of Desoxycholic Acid *p*-Bromoanilide

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(Received 22 July 1971 and in revised form 17 November 1971)

The crystal and molecular structure of the *p*-bromoanilide derivative of desoxycholic acid has been determined from three-dimensional X-ray diffraction data. The molecule crystallizes in the space group $P2_12_12_1$, with four molecules in the unit cell. The cell constants are $a=11.942$ (8), $b=30.62$ (2), $c=7.585$ (4) Å. Acentric direct-method phasing techniques successfully avoided pseudosymmetry difficulties generated from phases based on the bromine atom. A cage-like dimeric structure, with a polar interior cavity and a nonpolar exterior surface, characterizes the molecular association found in the crystal. With the aid of the anomalous scattering properties of the bromine atom, the absolute configuration of the ten chiral centers is determined.

Introduction

The bile acids have received little attention in the area of X-ray crystallography. Although the physiological and chemical properties of this steroid system have been extensively studied, little is known concerning the crystal structures of these biologically important compounds. Many possible hydrogen bonding schemes can be formulated involving the various potential hydrogen bonding sites in these molecules (Fieser & Fieser, 1959).

Desoxycholic acid plays a very important role in many biological systems. It is found, combined with glycine or taurine, as a minor component in bile fluids of most mammals. It is generally believed that these compounds are involved as emulsifying agents useful in the solubilization of fats. However, the mechanism of this process is not clearly understood, since it is uncertain if these compounds act alone or in conjunction with enzymes.

Desoxycholic acid is unique among bile acids in its ability to form molecular inclusion compounds, termed choleic acids. Other bile acids retain solvent molecules such as water or alcohol in the crystal lattice, but do not form complexes with the wide variety of substrates that comprise the choleic acids. A recent X-ray study of the cholic acid-ethanol complex (Johnson & Schaefer, 1971) has revealed a complex hydrogen-bonding scheme involving three molecules of cholic acid and five hydrogen bonds.

The choleic acids commonly show remarkable

stability. Indeed, these complexes often remain intact even when the crystal lattice is destroyed. In certain instances, the guest molecule can only be removed by chemically altering the desoxycholic acid molecule, or by adding a suitable substrate that can displace the original guest molecule.

The structure of the interaction between the desoxycholic acid molecule and various substrate molecules in the solid choleic acids still remains to be investigated. In an attempt to gain some preliminary information on choleic acids, the molecular structure of the *p*-bromoanilide derivative of desoxycholic acid has been determined. This derivative is similar to the naturally occurring form of this bile acid, and shows a very simple type of solid-state molecular association compared with cholic acid.

Experimental

The *p*-bromoanilide derivative of desoxycholic acid, $3\alpha,12\alpha$ -dihydroxycholan-3-yl *p*-bromobenzoate (I), was prepared by methods outlined in the literature (Ruzicka, Plattner & Engle, 1944; Julian, Cole, Magnani & Meyer, 1945).

