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The Structure of 11,11-Difluoro-1,6-methano[10]annulene

By Carlo Maria Gramaccioli and Massimo Simonetta

Istituto di Chimica Fisica, Università, Via Saldini 50, 20133 *Milano, Italy*

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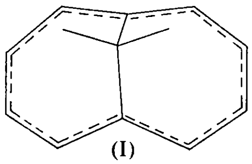
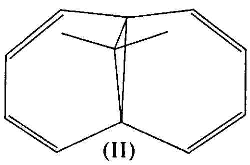
The crystal and molecular structure of 11,11-difluoro-1,6-methano[10]annulene has been determined and refined by least-squares methods. The crystals are orthorhombic, space group $Pna2_1$, with $a=9{\cdot}233$, $b=13{\cdot}235$, $c=7{\cdot}055$ Å and four molecules per unit cell. Intensity data were collected visually from Weissenberg photographs. The solution of the phase problem was readily obtained by finding the orientation of a plausible molecular model with respect to the crystallographic axes through a systematic search of the Patterson synthesis around the origin; the position of the molecule in the unit cell was then found by molecular packing energy calculations. After refinement by least-squares, the final R index is 0·080. The presence of fluorine atoms does not seem to affect the conformation of 1,6-methano[10]annulene; the distance C(1)–C(6) is 2·25 Å, excluding any 'double norcaradiene' character for this compound, in agreement with chemical and spectroscopic evidence.

Introduction

In line with a recent interest in aromatic systems with $4n+2$ π-electrons (n greater than 1) the chemistry of aromatic compounds with 10 π-electrons has been extensively developed by Vogel and co-workers (Vogel, 1967; 1968*a*,*b*). An interesting property of 1,6-methano[10]annulene is the influence of substituents in the bridge (position 11) on the stability of the aromatic system (I). Chemical and spectroscopic (n.m.r.) evidence are in favour of the existence of a direct C(1)–C(6) bond for the 11,11-dimethyl derivative which is consequently non-aromatic and has the so-called bisnorcaradiene structure (II).

The situation for the 11,11-difluoro derivative seems to be the opposite and the substance has the chemical character of an aromatic compound. An investigation of the structure of these two substances by X-ray diffraction has been suggested to us by Prof. Vogel.* As a first result, the structure of 11,11-difluoro-1,6-methano[10]annulene has been solved and refined. Although the extensive thermal vibration does not permit a very high precision in determining the molecular geometry at room temperature, it is felt that the method here adopted for solving the structure might be interesting and the results are anyway fully adequate to prove the aromaticity of this compound.


(I)


(II)

Experimental

Crystals of 11,11-difluoro-1,6-methano[10]annulene are in the form of greenish needles, elongated along **c**.

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* We wish to thank Prof. Emmanuel Vogel for having suggested this problem and for having supplied us with good crystals of the substance.

Weissenberg photographs indicated them to be orthorhombic, with space group either *Pnam* or *Pna*2_1 (the systematic absences are: $0kl$ with $k+l$ odd and $h0l$ with h odd); the latter space group was confirmed by solution of the structure.* The unit-cell dimensions (see Table 1) were obtained from a least-squares fit to measurements of $\sin^2\theta$ for 27 $h0l$ and 25 hhl reflexions on zero-level Weissenberg photographs taken at 21 °C with Cu $K\alpha$ radiation; the film was held in the asymmetric position, essentially following the Straumanis technique. No corrections for eccentricity or absorption were included in least-squares calculations and weights were assigned as inversely proportional to $\sin^2 2\theta$. The density was measured by flotation in a dilute Thoulet (K_2HgI_4) solution.

Table 1. *Crystal data for* 11,11-*difluoro*-1,6-*methano*[10]*annulene*

$a = 9{\cdot}233 \pm 0{\cdot}003$ Å	$C_{11}F_2H_8$
$b = 13{\cdot}235 \pm 0{\cdot}005$	M.W. = 178·17
$c = 7{\cdot}055 \pm 0{\cdot}002$	$Z = 4$
$D_m = 1{\cdot}38$ g.cm^{-3}	$D_x = 1{\cdot}376$ g.cm^{-3}

$\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051$ Å
$\lambda(\text{Cu } K\alpha_2) = 1{\cdot}54433$
$\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$

For determination of the structure, intensity data were collected from multiple-film equi-inclination Weissenberg photographs and measured visually. The layers 0–6 along **c** were obtained from one crystal, almost square in section, whose diameter was about 0·3 mm. The zero level about [110] was obtained from a larger crystal (diameter = 0·5 mm), almost square in section. Of 985 reflexions within the effective sphere of copper radiation, 856 were collected, of which 220 were too weak to be observed ('less than'). The intensities were corrected for Lorentz and polarization factors; no corrections either for absorption or extinction were made.

Previously, data (layers 0–7 along **c**) had been obtained from the first crystal using an equi-inclination Philips diffractometer (Pailred) and Mo $K\alpha$ radiation, monochromatized by a silicon [111] crystal. Owing to very large peak breadths, an ω-scan range of $\pm 1{\cdot}5$ to $\pm 1{\cdot}6°$ was adopted: this fact and the abundance of weak reflexions rendered our measurements rather unsatisfactory. Consequently, these data were only used in determining the coefficients for inter-layer scaling, and then discarded.

The processing of the observed intensities was first carried on within the single layers, obtaining film and time factors by minimizing $\sum(\ln I_i - \ln KI_j)^2$, as indicated by Rae (1965). Standard deviations were assigned to single observations by means of an analysis of the residuals (Gramaccioli & Mariani, 1967). The evaluation of relative scale factors for all the layers and subsequent averaging of the observed F^2 values were performed according to the method proposed by Rollett & Sparks, modified to account for the dependence of the weights upon the final scale factors (Hamilton, Rollett & Sparks, 1965; Duchamp, 1964).

Determination and refinement of the structure

In recent years, several structures have been solved by a systematic search of the best conditions for packing (Williams, 1966; Rabinovitch & Schmidt, 1966). These methods are obviously most efficient either when the parameters to be examined are limited in number, as for rigid molecules, when a plausible model can be assumed, or for particular situations. Our feeling is, however, that, in spite of various claims, the calculations involved in a general case are rather lengthy, even for a rigid molecule, especially when the efficiency of other structure-solving procedures, such as direct methods, is considered.

It is well known that orientation can be easily deduced for a rigid molecular group by a systematic search of the Patterson synthesis (Nordman & Nakatsu, 1963; Huber, 1965; Nordman, 1966; Hoppe & Paulus, 1967; Braun, Hornstra & Leenhouts, 1969). A program written in this laboratory in FORTRAN language for orthorhombic crystals (Filippini & Gramaccioli, 1969) has been successfully applied to the solution of two structures (Destro, Filippini, Gramaccioli & Simonetta, 1969; Casalone, Gavezzotti, Mugnoli & Simonetta, 1970). The method is essentially close to the procedure adopted by Nordman (1966): the sharpened Patterson function (not necessarily on the absolute scale or with manipulations at the origin), evaluated at intervals of about 0·1 Å along the three crystallographic axes, is considered for this purpose only within 3·2 Å of the origin (this excludes all intermolecular vectors) and stored in the memory of the computer. A map of the 'sum function' (Buerger, 1959) is calculated for intervals of 7·5° in the rotation angles of the model. The correct orientation corresponds to the highest or next highest peak and no serious trouble is encountered even in cases of some complexity; the computing time has never exceeded one minute for the UNIVAC 1108 or fifteen minutes for the IBM 7040.

In our case, this procedure was adopted using a starting model derived from the structure of 1,6-methano[10]annulene-2-carboxylic acid, as found by Dobler & Dunitz (1965). A couple of high values of

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* Whereas a test for piezoelectricity gives a positive result, it may be interesting to remark that the mean values of the normalized structure factor $|E|$ (Hauptman & Karle, 1953), of E^2 and $|E^2-1|$ are 0·705, 1·00 and 1·01 respectively, in marked agreement with the expected values for a centrosymmetric crystal; the $N(z)$ test is also in favour of a centrosymmetric case, except for the region of high θ, where the situation is less clear. The E values for these statistics were deduced from the intensities scaled by a Wilson plot, following exactly the procedure indicated by Rogers (1965). The reasons for this anomalous behaviour can be connected with the high symmetry ($mm2$) of the molecule, or with the high percentage of 'less thans', whose treatment in the Wilson plot might not be fully adequate.

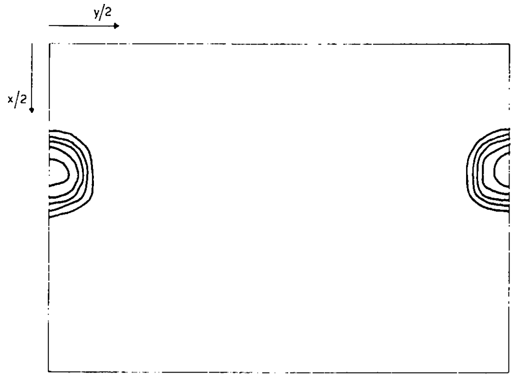

Fig. 1. Map of packing energy for the molecule of 11,11-difluoromethanoannulene as a function of x and y (fractional) coordinates of its centre of gravity, for a fixed molecular orientation, as found by rotational search on the Patterson. Contours are drawn from zero downwards at intervals of 0·2 kcal.mole^{-1}.

the sum function corresponded to possible orientations of the molecule; the highest peak was regarded as of little significance, because in this case many vectors fell on the section $w=0$, between symmetrically related maxima lying close to each other. The other peak corresponded to a general angular orientation, thereby excluding any coincidence between symmetry elements in the molecule and in the crystal. This orientation is compatible with the non-centric space group $Pna2_1$.

The packing energy, as a function of molecular position in the unit cell, was calculated at intervals of 0·025 (fractional) in x and y using a program written for non-centrosymmetric orthorhombic space groups by Rovere, Filippini & Gramaccioli (1970); interaction energies between non-bonded atoms were evaluated according to Bartell (1960) for C–C, C–H and H–H. For the other contacts, involving fluorine atoms, Kitaigorodskii's (1961) formula was applied, assigning 'van der Waals' radii of 1·7, 1·4 and 1·5 Å to carbon, fluorine and hydrogen respectively. In order to save computing time, all situations having at least one contact shorter than 0·65 times the sum of van der Waals radii were automatically discarded; for the remaining points, the corresponding energy was reported in a map (Fig. 1). A clear minimum ($-0\cdot8$ kcal. mole^{-1} with respect to the isolated molecule) appeared, corresponding to the correct structure. The calculation time for this stage was about thirteen minutes for the IBM 7040 computer.

Starting with the coordinates corresponding to this minimum energy, the R value was 0·35 for observed three-dimensional data with $\sin^2\theta/\lambda^2 \le 0\cdot10$; small shifts in positional coordinates ($\Delta x=0\cdot020$, $\Delta y=0\cdot010$) reduced R to 0·27.

Refinement of the positions of the heavier atoms by block-diagonal least squares was then initiated, minimizing the function $\sum w(|F|_{\rm obs}-|F|_{\rm cal})^2$ and using for this purpose a program written by Albano, Domenicano & Vaciago (1966). In the first cycles, weights of the form $w=1/\bar{f}^2$ were used, where $\bar{f}$ is the average scattering factor for all the atoms at the calculated value of $\sin\theta/\lambda$; later, and throughout the subsequent refinement, weights were taken as $w=1/(a+b|F|_{\rm obs}+cF^2_{\rm obs})$ where $a\,(=1\cdot25)$, $b\,(=2\cdot5)$, $c\,(=0\cdot07)$ were chosen so as to give the average of $w(|F|_{\rm obs}-|F|_{\rm cal})^2$ approximately constant (within 5% of the average) for various significant intervals of F (Cruickshank, 1961). Unobserved ('less than') reflexions were always excluded from the least-squares analysis.

In the last cycles, performed by full-matrix least squares, using a program written by Busing, Martin & Levy (1962), anisotropic temperature factors were assigned to the C and F atoms, hydrogen atoms were included in the structure factor calculations only, with positional coordinates derived from the presumed geometry of the molecule (C–H bond lengths = 1·00 Å; C–C–H bond angles = 120°) and isotropic temperature factors $B=5\cdot0$ Å^2. An attempt to localize the hydrogen atoms better by a three-dimensional difference Fourier synthesis did not result in a reasonable geometry for at least some of them (C–C–H bond angles from 80° to 150°). Including these 'Fourier' H atoms in the least-squares calculations led to a consistent increase of their thermal factors (B's up to 14 Å^2) and to a better value of the R index (down to 7·2%) without, however, any significant improvement in the molecular geometry. Starting from geometrically calculated H atom coordinates did not lead to a better situation.

For these reasons, the final stage of the refinement was performed with the H atoms included only in structure-factor calculations, with positional coordinates derived from the presumed molecular geometry and isotropic thermal factors B of 10 Å^2. Because the larger observed F values were systematically lower than the corresponding calculated values (with the exception of the reflexion 020, which was the only one remaining from diffractometer data and therefore was poorly measured), a secondary extinction coefficient g for which $F_{\rm cal}=F_{\rm cal}(1+g\beta F^2_{\rm cal})^{-1/2}$ (Zachariasen, 1963; Larson, 1967) was considered at this stage, the reflexion 020 being excluded from the least squares. After four cycles, nearly all parameter shifts were below 0·1 times the standard deviation; the largest shift, 0·12 σ, occurred for B_{11} of C(1). The final R index is 0·080; the extinction coefficient g is $(28\pm5)\,.\,10^{-6}$.

Precision of the structure

The observed and calculated structure factors are listed in Table 2; the final parameters of the heavier atoms are given in Table 3 and of the hydrogen atoms in Table 4. The standard deviations in the coordinates of the heavier atoms, derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties of the order of 0·01 Å. The corresponding standard deviations in the bond distances are around 0·015 Å and in the bond angles around 1°.

Table 2. *Observed and calculated structure factors*

All $|F|$ values have been multiplied by 10. 'Less than' reflexions are indicated as negative $|F|_{obs}$. Form factors for heavier atoms were taken from Cromer & Waber (1965) and for H atoms from Stewart, Davidson & Simpson (1965).

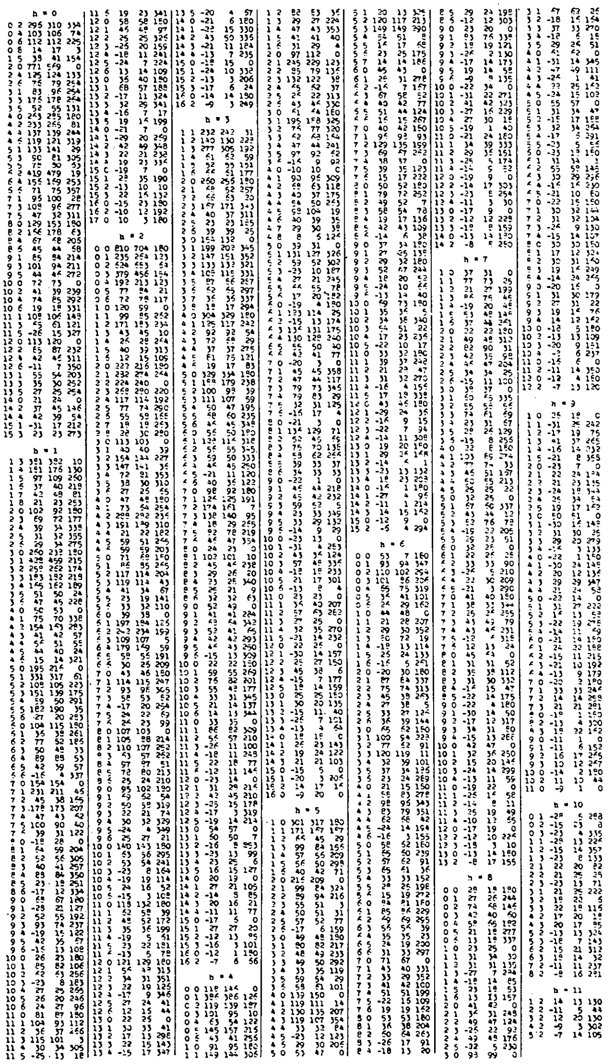

Table 4. *Parameters for the hydrogen atoms*

	x	y	z	B(Å^2)
H(2)	−0·097	−0·047	0·118	10·0
H(3)	−0·002	−0·209	0·053	10·0
H(4)	0·211	−0·243	−0·092	10·0
H(5)	0·377	−0·129	−0·193	10·0
H(7)	0·441	0·077	−0·220	10·0
H(8)	0·339	0·232	−0·163	10·0
H(9)	0·136	0·267	−0·008	10·0
H(10)	−0·029	0·156	0·095	10·0

Corrections for thermal libration

The molecule of 11,11-difluoro-1,6-methano[10]annulene is substantially rigid and is therefore expected to behave as a rigid body in undergoing thermal libration. Accordingly, the tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968) were derived from a least-squares treatment, using a FORTRAN program written by G. Filippini. In these calculations, equal weights were assigned to all thermal factors; the results are shown in Table 5. The agreement between observed and calculated values of B_{ij} for each atom is fairly good, the differences being significant (exceeding 3σ) only for B_{11} of C(2), where the discrepancy amounts to 5 times the standard deviation. The temperature ellipsoids are shown in Fig. 2.

Table 5. *Rigid-body tensors for* 11,11-*difluoro*-1,6-*methano*[10]*annulene, referred to a Cartesian coordinate system, whose origin and directions of axes coincide with crystallographic axes*

Standard deviations are given in brackets; all the value have been multiplied by 10^4.

T (Å)^2	543 (35)	−72 (27)	−45 (40)
		969 (46)	192 (46)
			571 (63)
L (rad^2)	69 (9)	−9 (8)	58 (7)
		90 (17)	−37 (8)
			147 (9)
S (Å.rad)	22 (10)	−102 (19)	−38 (16)
	−1 (14)	74 (20)	83 (32)
	42 (7)	−252 (18)	−96 (17)

Table 3. *The heavy atom parameters and their standard deviations*

All the values in this table have been multiplied by 10^4. The temperature factor is in the form

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right]$$

	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	1038 (8)	296 (5)	1145 (**)	123 (9)	83 (4)	212 (15)	13 (5)	−6 (10)	11 (7)
C(2)	98 (12)	−558 (8)	933 (16)	238 (16)	129 (7)	216 (18)	−48 (9)	−15 (14)	60 (10)
C(3)	654 (12)	−1501 (7)	301 (18)	266 (16)	87 (6)	389 (27)	−72 (8)	−137 (19)	86 (11)
C(4)	1956 (16)	−1699 (6)	−546 (21)	340 (22)	62 (4)	389 (30)	25 (9)	−124 (24)	−35 (10)
C(5)	3015 (13)	−1055 (8)	−991 (19)	262 (17)	89 (7)	363 (28)	58 (9)	−13 (19)	−32 (11)
C(6)	3138 (8)	−92 (6)	−212 (17)	125 (8)	98 (6)	318 (22)	29 (6)	−14 (12)	−1 (10)
C(7)	3568 (9)	809 (8)	−1267 (20)	155 (10)	127 (8)	403 (29)	−26 (7)	31 (15)	21 (14)
C(8)	2878 (11)	1734 (6)	−1032 (19)	226 (14)	81 (5)	411 (30)	−49 (8)	−51 (18)	52 (12)
C(9)	1632 (13)	1940 (6)	−151 (18)	326 (19)	61 (5)	328 (26)	5 (7)	−60 (20)	0 (10)
C(10)	721 (8)	1306 (7)	658 (17)	186 (10)	81 (5)	267 (19)	41 (7)	−28 (12)	−15 (9)
C(11)	2535 (7)	67 (5)	1629 (16)	134 (8)	59 (4)	272 (17)	−5 (4)	−69 (10)	1 (7)
F(1)	2679 (5)	−722 (3)	2848 (13)	212 (6)	80 (3)	326 (13)	−3 (3)	−103 (9)	37 (5)
F(2)	3198 (6)	842 (4)	2594 (14)	257 (8)	86 (3)	398 (17)	−20 (4)	−174 (11)	−3 (6)

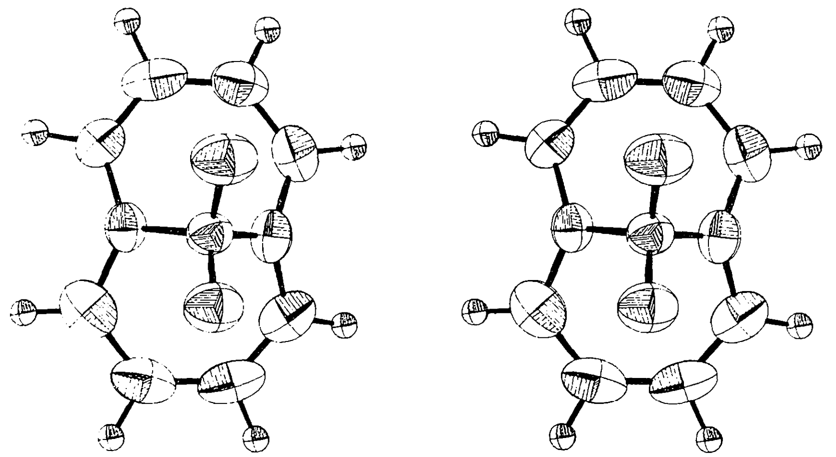

Fig. 2. A stereo pair showing the temperature ellipsoids of the heavy atoms.

Considering the approximations involved in the method and in using the B_{ij}'s themselves, especially when thermal motion is large, it is not quite certain whether we really have evidence for non-rigid libration. The mean-square rotational displacements of the molecule amount to 63, 26 and 12(°)^2 about the principal axes of the tensor **L**.

The correction for distances have been derived under the rigid-body assumption from the tensor **L**, according to Schomaker & Trueblood (1968). This procedure resulted in a substantial increase (around 0·015 Å) in all of them; a negligible correction of the bond angles (within 0·1°) was found. Values for all bond distances after corrections for thermal libration are given in Fig. 3, and torsion angles in Table 6.

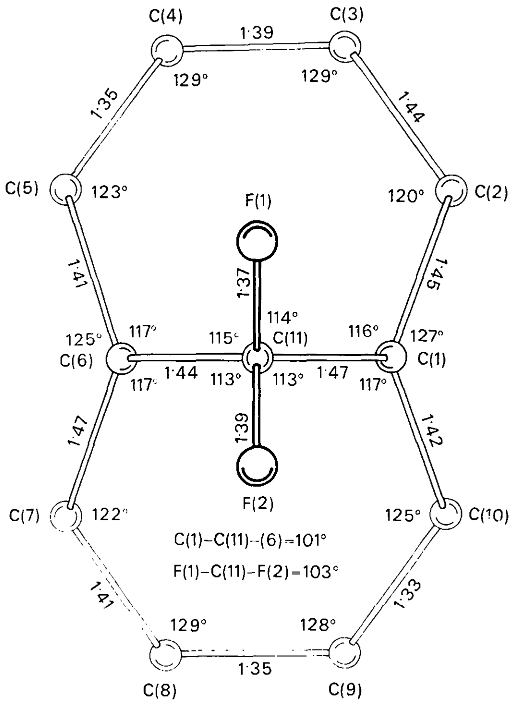

Fig. 3. The molecule of 11,11-difluoro-1,6-methano[10]annulene viewed along the direction corresponding to the maximum moment of inertia. Bond distances are corrected for thermal libration.

Table 6. *Torsion angles*

The convention of Klyne & Prelog (1960) is adopted.

C(1)—C(2)—C(3)—C(4)	−15°
C(2)—C(3)—C(4)—C(5)	−0
C(3)—C(4)—C(5)—C(6)	18
C(4)—C(5)—C(6)—C(7)	−140
C(5)—C(6)—C(7)—C(8)	137
C(6)—C(7)—C(8)—C(9)	−13
C(7)—C(8)—C(9)—C(10)	−3
C(8)—C(9)—C(10)-C(1)	16
C(9)—C(10)-C(1)—C(2)	−140
C(10)-C(1)—C(2)—C(3)	140

Discussion

The molecular structure

The molecule as viewed along the direction corresponding to the maximum moment of inertia is shown in Fig. 3. The conformation of the 1,6-methano[10]annulene group is in essential agreement with the results of previous crystallographic work (Dobler & Dunitz, 1965) relative to 1,6-methano[10]annulene-2-carboxylic acid, no substantial difference being found in the C(1)–C(6) distance (2·25 Å in our compound against 2·257 Å in the acid), a fact which excludes any 'double norcaradiene' character for our difluoro derivative. It is also in complete agreement with the chemical behaviour of the substance and with nuclear magnetic resonance data (Vogel, 1967; Vogel, 1968*a*, *b*). As in similar compounds (Dobler & Dunitz, 1965; Casalone, Gavezzotti, Mugnoli & Simonetta, 1970; Ganis & Dunitz, 1967) the atoms within the two 'halves' of the annulene ring (*i.e.* C(1) to C(6) through C(2) or C(1) to C(6) through C(10)) are not coplanar, the situation being most conveniently expressed in Table 7.

Whereas the *mm*2 point group is to be expected for the isolated molecule, here significant deviations from this symmetry can be observed, the most striking case occurring for the C(9)–C(10) bond which is 0·1 Å shorter than the C(2)–C(3) bond. It can be noticed that these distortions are not quite random, being consistent with the conservation of the twofold axis.

Molecular packing

If we assume as van der Waals radii for carbon, fluorine and hydrogen the values 1·7, 1·4 and 1·5 Å, respectively, as we used in our calculations of molecular packing energy, we see that in a few cases two atoms belonging to different molecules lie at a distance smaller than the sum of the corresponding van der Waals radii; among these, one [F(2)–H(4)] contact of 2·53 Å seems to be particularly short. The molecular packing seen along **c** is represented in Fig. 4.

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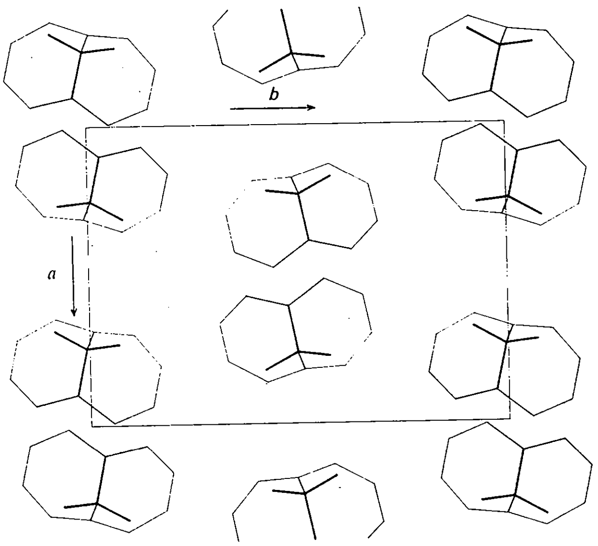

Fig. 4. Molecular packing seen along **c**.

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Table 7. *Some planes of interest*

The coefficients q_j are the direction cosines relative to the crystallographic axes **a**, **b** and **c**. In the least-squares treatment, the method described by Schomaker, Waser, Marsh & Bergman (1959) was adopted, with weights inversely proportional to the positional standard deviation along the normal to the plane. Atoms marked with an asterisk were omitted from least squares.

Plane *A*		Plane *A′*		Plane *A″*		Plane *B*		Plane *B′*		Plane *B″*	
C(1)	0·03 Å	C(1)	−0·01 Å	*C(1)	0·33 Å	C(1)	0·02 Å	C(1)	−0·01 Å	*C(1)	0·27 Å
C(2)	−0·09	C(2)	0·01	C(2)	0·00	C(6)	0·04	C(6)	0·01	*C(6)	0·31
C(3)	0·07	*C(3)	0·27	C(3)	−0·00	C(7)	−0·09	C(7)	−0·01	C(7)	0·00
C(4)	0·06	*C(4)	0·26	C(4)	0·00	C(8)	0·04	*C(8)	0·21	C(8)	−0·01
C(5)	−0·11	C(5)	−0·01	C(5)	−0·00	C(9)	0·07	*C(9)	0·23	C(9)	0·01
C(6)	0·04	C(6)	0·01	*C(6)	0·35	C(10)	−0·08	C(10)	0·01	C(10)	0·00

Plane *C* defined by C(1), C(11), C(6)

Plane *D* defined by C(11), F(1), F(2)

	q_1	q_2	q_3	D
Plane *A*:	0·3636	−0·2952	0·8835	−0·913 Å
Plane *B*:	0·4882	0·2500	0·8362	−1·222
Plane *A′*:	0·3335	−0·3833	0·8613	−0·872
Plane *A″*:	0·4156	−0·1485	0·8974	−0·737
Plane *B′*:	0·4927	0·3251	0·8072	−1·258
Plane *B″*:	0·4816	0·1214	0·8679	−0·936
Plane *C*:	0·2283	0·9718	−0·0593	−0·552
Plane *D*:	0·8733	−0·2390	−0·4245	−1·535

Dihedral angles:

$A \wedge B$	32·6°	$A' \wedge B'$	42·7°	$A' \wedge A''$	14·4°
$B' \wedge B''$	12·2°	$C \wedge D$	89·6°		

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The Crystal Structure of L-Isoleucine

BY KAZUO TORII AND YOICHI IITAKA

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan

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The crystal structure of L-isoleucine has been determined by X-ray analysis. L-Isoleucine crystallizes in the monoclinic space group $P2_1$, $Z=4$, with lattice constants $a=9{\cdot}75$, $b=5{\cdot}32$, $c=14{\cdot}12$ Å, $\beta=95{\cdot}8°$. Final refinement was carried out for 1387 observed structure factors by the full-matrix least-squares method including anisotropic thermal parameters. The R value was 0·117. Two crystallographically independent molecules have different rotational angles about the C^{α}–C^{β} bond. The crystal structure is formed by hydrogen-bonded double layers of molecules stacked in such a way that their terminal groups of the side chain face each other. The molecular and crystal structures are closely related to those in L-valine. Crystal data for other L-α-amino acids having similar hydrocarbon side chains are given indicating that they also have closely related crystal structures.

Introduction

On the basis of infrared spectroscopic study, the crystal of L-isoleucine was assumed to belong to a rather unusual type in which the molecules take two kinds of conformation (Tsuboi, Takenishi & Iitaka, 1959). L-Valine also crystallizes into the same type of crystal. The crystal structure of L-valine was investigated by X-ray diffraction methods; it contains two crystallographically independent molecules having different rotational angles about the C^{α}–C^{β} bond: *trans* and *gauche* I forms (Torii & Iitaka, 1970). The present study of the crystal structure of L-isoleucine was undertaken to compare its structure with that of L-valine and to establish a typical structure of L-α-amino acids having hydrophobic side chains.

Experimental

Crystals of L-isoleucine were grown from a warm saturated aqueous solution by slow cooling. They are colourless thin plates elongated along the b axis with well developed {001} faces.

Unit-cell dimensions were measured on $0kl$ and $h0l$ precession photographs. The crystal density was measured by the flotation method using benzene-carbon tetrachloride mixture. Crystal data are as follows:

L-Isoleucine, $C_6H_{13}O_2N$, M.W. 131·2
Monoclinic
$a=9{\cdot}75\pm0{\cdot}02$, $b=5{\cdot}32\pm0{\cdot}02$, $c=14{\cdot}12\pm0{\cdot}02$ Å
$\beta=95{\cdot}8\pm0{\cdot}2°$
$U=723{\cdot}0$ Å^3
$D_m=1{\cdot}202$ g.cm^{-3}, $D_x=1{\cdot}196$ g.cm^{-3}
$Z=4$
Systematic absences, $0k0$ when $k\neq2n$
Space group, $P2_1$.

Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photographs. For both the a and b axes, five layers from zero to the 4th layer were taken with Cu $K\alpha$ radiation.