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11,11-Difluoro-1,6-methano[10]annulene at −100°C

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Abstract. $C_{11}H_8F_2$, orthorhombic, $Pna2_1$, $a=9{\cdot}111$ (1), $b=13{\cdot}203$ (2), $c=6{\cdot}981$ (1) Å at −100°C. $C_{11}H_8F_2$; $M=178{\cdot}17$, $Z=4$; $F(000)=368$.

Introduction. The room-temperature determination of the structure of 11,11-difluoro-1,6-methano[10]annulene (Gramaccioli & Simonetta, 1971) has led to geometrical parameters showing an unexpected lack of molecular symmetry which might be only apparent, owing to unusually high values for r.m.s. atomic thermal displacements. Consequently, a low-temperature redetermination was thought to be appropriate, since knowledge of the precise geometry of the molecule is essential for the interpretation of its chemical behaviour (Vogel, 1967, 1968*a*,*b*). Experimental (Taylor, 1975) and theoretical (Gavezzotti & Simonetta, 1975) studies of the reactivity of this molecule are in progress.

Experimental. The lattice parameters were obtained by the fitting of $\sin^2\theta$ values of 50 reflexions. Intensities were collected on a Syntex $P\overline{1}$ diffractometer. The experimental conditions are given in Table 1. The 17 most intense reflexions ($|F_o|>35$) and the unobserved ones were excluded from the refinement. Standard deviations were obtained according to Peterson & Levy (1957). Intensities and their standard deviations were corrected for Lorentz and polarization factors but not for absorption. The full-matrix least-squares refinement included 149 parameters: scale factor, coordinates for the 21 atoms, anisotropic thermal parameters for the 13 heavy atoms and isotropic B's for the 8 H atoms. Since there are no phase transitions between room temperature and −100°C, the starting point was the room-temperature geometry with thermal parameters reduced to 50%. The function minimized was $\sum w(|F_o|-|F_c|)$, with weights $w=4F_o^2/\sigma^2(F_o^2)$. The minimization was carried out with a modified *ORFLS* program (Busing, Martin & Levy, 1962). The final results were $R=0{\cdot}048$ for 1003 reflexions > 0 and $R_w=0{\cdot}039$ for the 986 reflexions used in the refinement. The final difference map did not reveal any special feature; positional and thermal parameters are reported in Table 2.*

Table 1. *Experimental data*

Source Mo $K\alpha$; $\lambda=0{\cdot}71069$, graphite monochromator, $\mu=1{\cdot}22$ cm^{-1}, $\theta/2\theta$ scan, $\Delta 2\theta$ variable, $2\theta_{\max}=54{\cdot}9°$. Total number of independent reflexions: 1042. Total number observed: 1003

Discussion. Bond lengths, angles and torsional angles are shown in Fig. 1, with the numbering of atoms and thermal ellipsoids. Rigid-body tensors are given in Table 3; they are referred to a Cartesian coordinate system whose origin and directions of axes coincide with the crystallographic axes. The rigid-body approximation (Schomaker & Trueblood, 1968) leads to good agreement between calculated and experimental B_{ij}'s for each atom, the difference exceeding 3σ only for B_{22} of C(11) and B_{33} of F(2). Bond distances corrected for thermal libration are reported in Table 4. The variation of C–C lengths (1·357 to 1·420 Å) along the annulene ring is considerably reduced compared with the room-

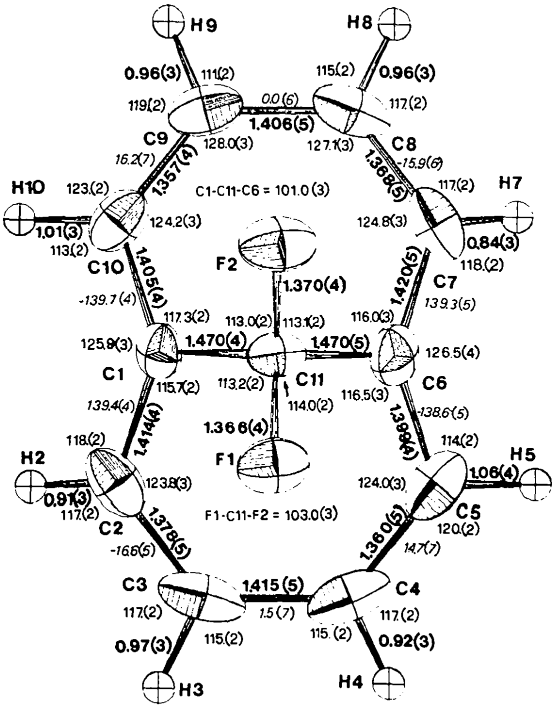

Fig. 1. The molecule viewed along the direction corresponding to the maximum moment of inertia. Numbering of atoms, temperature ellipsoids for heavy atoms, bond distances (Å), bond angles (°), and torsional angles (°) (in italics) along the ring are shown.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31685 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final atomic parameters and standard deviations* (*in parentheses*)

All the parameters of heavy atoms are multiplied by 10^4. Coordinates of hydrogen atoms are multiplied by 10^3 and their isotropic B's by 10. The anisotropic temperature coefficients are in the form: $T_i = \exp\ [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	1001 (3)	298 (2)	1145 (0)	78 (3)	44 (1)	90 (5)	7 (2)	14 (3)	7 (2)
C(2)	70 (3)	−549 (2)	905 (5)	83 (4)	72 (2)	136 (6)	−16 (2)	−9 (4)	34 (3)
C(3)	550 (4)	−1488 (2)	314 (5)	157 (5)	46 (2)	201 (7)	−41 (3)	−85 (5)	41 (3)
C(4)	1901 (4)	−1723 (2)	−584 (6)	194 (6)	32 (1)	208 (7)	14 (3)	−72 (6)	−18 (3)
C(5)	3022 (3)	−1083 (2)	−1019 (6)	127 (4)	54 (2)	206 (8)	32 (2)	−18 (5)	−14 (3)
C(6)	3165 (3)	−105 (2)	−271 (6)	61 (3)	50 (2)	204 (7)	11 (2)	−7 (4)	−5 (3)
C(7)	3606 (3)	775 (3)	−1290 (6)	74 (3)	82 (3)	214 (8)	−20 (2)	13 (5)	13 (4)
C(8)	2992 (3)	1713 (2)	−1073 (6)	131 (4)	49 (2)	226 (8)	−33 (2)	−43 (5)	39 (3)
C(9)	1646 (3)	1947 (2)	−194 (5)	155 (5)	33 (1)	171 (7)	6 (2)	−44 (5)	7 (3)
C(10)	672 (3)	1300 (2)	622 (5)	122 (4)	46 (2)	124 (5)	23 (2)	−13 (4)	−10 (3)
C(11)	2534 (3)	67 (2)	1639 (5)	88 (3)	28 (1)	159 (5)	−2 (2)	−26 (3)	3 (2)
F(1)	2672 (1)	−737 (1)	2855 (4)	127 (2)	42 (1)	179 (4)	3 (1)	−56 (3)	15 (2)
F(2)	3210 (2)	836 (1)	2620 (4)	133 (2)	44 (2)	222 (4)	−12 (1)	−77 (3)	−4 (2)

Table 2 (*cont.*)

	x	y	z	B
H(2)	−92 (3)	−44 (2)	92 (4)	38 (6)
H(3)	−17 (3)	−203 (2)	32 (5)	54 (7)
H(4)	197 (3)	−237 (2)	−105 (5)	58 (7)
H(5)	370 (3)	−123 (2)	−221 (5)	61 (7)
H(7)	420 (3)	70 (2)	−221 (5)	45 (7)
H(8)	344 (3)	226 (2)	−178 (5)	65 (8)
H(9)	135 (3)	263 (2)	−46 (5)	52 (6)
H(10)	−39 (3)	147 (3)	81 (6)	64 (8)

temperature values. In 1,6-methano[10]annulene-2-carboxylic acid (Dobler & Dunitz, 1965) the variation was 1·378–1·426 Å at room temperature. The C(1)–C(6) distance (2·269 Å) is virtually unchanged compared with the room-temperature value (2·25 Å), confirming a very small interaction between C(1) and C(6). The C_2 molecular symmetry is very well satisfied; some discrepancy from $mm2$ symmetry is observed: this is however greatly reduced compared with the room-temperature geometry; at this level the geometry of the annulene ring is very similar to that found in 1,6-methano[10]annulene-2-carboxylic acid (Dobler & Dunitz, 1965). The aromatic ring appears to be slightly perturbed and a 'flavour' of the bisnorcaradiene structure can be detected.

The volume thermal expansion coefficient α observed between −100°C and room temperature is 0·000032 K^{-1}, within the usual range for organic crystals.

Table 3. *Rigid-body tensors for the molecule, referred to a Cartesian coordinate system, whose origin and directions of axes coincide with the crystallographic axes*

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

T (Å^2)	262 (13)	−31 (10)	15 (15)
		516 (17)	102 (17)
			287 (23)
L (rad^2)	34 (3)	−6 (3)	38 (3)
		43 (6)	−18 (3)
			85 (3)
S (Å rad)	12 (4)	−61 (7)	−24 (6)
	12 (5)	38 (7)	32 (12)
	21 (3)	−138 (7)	−50 (6)

Table 4. *Bond distances* (Å) *after correction for thermal libration*

C(1)–C(2)	1·423	C(8)—C(9)	1·416
C(2)–C(3)	1·387	C(9)—C(10)	1·366
C(3)–C(4)	1·426	C(10)–C(1)	1·412
C(4)–C(5)	1·369	C(1)—C(11)	1·478
C(5)–C(6)	1·407	C(11)–C(6)	1·479
C(6)–C(7)	1·428	C(11)–F(1)	1·371
C(7)–C(8)	1·376	C(11)–F(2)	1·378

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