Tetrahedron Vol. 38, No. 10, pp. 1443 to 1446, 1982
Printed in Great Britain.

0040-4020/82/101443-04$03.00/0

ON THE POLYENIC CHARACTER OF *ANTI*-BRIDGED[14]ANNULENE. THE STRUCTURE OF *ANTI*-1,6:8,13-BIS(DIFLUOROMETHANO) [14]ANNULENE AT 200K

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(*Received in U.K.* 3 *August* 1981)

Abstract—The X-ray crystal structure determination of *anti*-1,6:8,13-bis(difluoromethano) [14]annulene (1) at 200 K is described. The structure has been solved by direct methods, and least-squares refinement based on 1716 reflections of non-zero weight yielded a final *R* index of 0.046. The molecular structure of 1 appears to be polyenic, as expected from a comparison with the structures of previously studied *anti*-bridged[14]annulenes, and in particular confirms conclusions previously reported from a study of the structure of *anti*-1,6:8,13-biscarbonyl [14]annulene.

The series of bridged [14]annulenes has been the object of extensive structural investigation.[1] So far X-ray diffraction structure determinations have revealed that all compounds with syn-related bridges have aromatic character, in the sense that there is no bond alternation around the 14-membered ring. A molecular orbital discussion of the connection between non-planarity in the ring and twisting around the sp^2–sp^2 carbon–carbon bonds has been given.[2] However a different situation arises when the bridges are *anti*. In 7-methoxycarbonyl-*anti*-1, 6: 8, 13-dimethano [14]annulene (2) alternate long and short ring bonds were found.[3] The same geometrical feature was found in *anti*-1, 6: 8, 13-dimethano [14]annulenetricarbonylchromium.[4] Yet, when the geometry of *anti*-1, 6: 8, 13-biscarbonyl [14]annulene (3) was determined,[5] the results suggested an aromatic structure. After careful examination, however, it was concluded that the apparent aromaticity was due to disorder in the crystal, and the possibility that the disorder was dynamic rather than static was discussed.[5] Recently a new *anti* derivative became available, namely *anti*-1, 6: 8, 13-bis(difluoromethano) [14]annulene (1).[6] The crystal structure of this compound has been determined to check whether it obeys the rule syn/aromatic, anti/polyenic. To reduce the likelihood of disorder in the crystal the data were collected at 200K.

EXPERIMENTAL

A sample of 1, in the form of yellow-brown crystals, was kindly supplied by Prof. E. Vogel. Preliminary investigations were made at room temp on a prismatic crystal of approximate dimensions $0.38 \times 0.35 \times 0.18$ mm^3. The same crystal was subsequently used for data collection at low-temperature. The density was measured by flotation in a dilute K_2HgI_4 solution.

Crystal data. For $C_{16}H_{10}F_4$: M = 278.26; m.p. 122°; orthorhombic, space group *Cmc*2$_1$ (No. 36), $Z = 4$, $F(000) = 568$; Mo *Kα* radiation (graphite monochromatized), $\lambda_\alpha = 0.71069$ Å, μ((Mo *Kα*) = 1.44 cm^{-1}. At 293(2)K: $a = 9.723(2)$, $b = 17.795(4)$, $c = 7.041(2)$ Å, $V = 1218.2(5)$ Å^3 at room T; $\rho_{obs} = 1.51$ gcm^{-3}, $\rho_{calc.} = 1.517$ gcm^{-3}. At 200(5)K: $a = 9.691(1)$, $b = 17.769(1)$, $c = 6.989(1)$ Å, $V = 1203.5(3)$ Å^3 at low T; $\rho_{calc.} = 1.535$ gcm^{-3} at low T.

Data Collection. Data were collected on a computer-controlled Syntex Pl diffractometer equipped with the low-temperature LT-1 device (Syntex Analytical Instruments). The temperature was measured, before and after data collection, by placing the junction of an accurately calibrated thermocouple in the same position as the crystal. The temperature variation in reproducing the same cooling conditions was less than 1K, and variations in the gas stream did not exceed 2 K within a cubic volume of 2 mm side. An inclusive error of ± 5 K may be safely associated with the temperature measurements.

Accurate cell dimensions at 200 K were obtained by a least-squares fit to the $\sin^2\theta$ values of 64 reflections. The systematic absences, *hkl* with $(h + k)$ odd and *h*0*l* with *l* odd, are common to three space groups, namely *Cmc*2$_1$, *Cmcm*, and *C*2*cm*. (The latter is conventionally reported[7] as space group *Ama*2, which implies the interchange of the *a* and *c* axes). There being four molecules per cell, the centrosymmetric space group *Cmcm* —with 16 equivalent positions—would imply a disordered structure, since the isolated molecule of 1 exhibits only an *m* symmetry, with the six atoms of the two CF_2 groups lying on the mirror plane. On the other hand, a molecular *m* symmetry is consistent with the two noncentrosymmetric space groups *Cmc*2$_1$ and *C*2*cm*, both having 8 equivalent general positions, and therefore requiring half a molecule as the asymmetric unit. No evidence of disorder was given by the preliminary photographic investigation.

Intensities were measured by variable rate θ–2θ scans to a maximum 2θ value of 75°. Three standard reflections were monitored after every 47 intensity measurements; they showed no significant drift in intensity. Of the 1769 independent reflections collected, a total of 1716 with $I > 0$ were retained and were corrected for Lorentz, polarization, and background effects. No absorption correction was deemed necessary. The 53 reflections with $I < 0$ were given zero weight; all other reflections were assigned variances, $\sigma^2(I)$, based on counting statistics plus the additional term $(0.03 \text{ scan count})^2$.

Solution and refinement of the structure. The results of several statistical tests were consistent with an acentric structure, and the space group *Cmc*2$_1$ was tentatively assumed on the basis of packing considerations. Direct methods[8] led to an *E* map from which the positions of eight non-hydrogen atoms were recovered. The eight peaks observed in the asymmetric unit include six lying on a crystallographic mirror plane. These were easily interpreted as the atoms of the two difluoromethano groups, while the other two were taken to be the C atoms directly bound to the CF_2 groups. A subsequent electron-density map revealed the position of the five remaining non-symmetry-related C atoms of the annulene ring. After a few cycles of isotropic refinement by full-matrix least-squares, ($R = 0.153$ on all the 1716 observed reflections), the 10 H atoms were introduced at calculated positions, and the model was complete. At the end of the anisotropic refinement (which was by minimization of the quantity $\Sigma w(|F_0| - |F_c|)^2$, with weights $w = 4\ F_0^2/\sigma^2(F_0^2)$) the shifts in atomic parameters were less than 0.33σ for the heavier atoms, and less than 1σ for H atom parameters.

Table 1. Final atomic coordinates[a]

Atom	x	y	z
C(1)	7606(17)	4010(8)	41000
C(2)	16604(16)	9697(7)	43213(34)
C(3)	12908(12)	17535(7)	46997(32)
C(4)	19263(12)	23437(7)	38653(34)
C(5)	12591(13)	30936(7)	36660(33)
C(6)	15974(16)	37253(7)	46518(36)
C(7)	7063(18)	43561(8)	49949(37)
C(8)	0	31094(11)	24162(40)
C(9)	0	18535(9)	58682(36)
F(1)	0	37396(8)	12697(35)
F(2)	0	25194(8)	11670(33)
F(3)	0	25312(6)	68086(32)
F(4)	0	13399(7)	73417(31)
H(1)	1147(19)	-73(13)	3728(38)
H(2)	2625(20)	873(11)	4158(33)
H(4)	2792(19)	2252(9)	3266(31)
H(6)	2507(18)	3737(12)	5347(36)
H(7)	1143(20)	4793(12)	5567(39)

[a]Multiplied by 10^5 for C and F, by 10^4 for H. Estimated standard deviations in the least significant digit are given in parentheses.

Hydrogen atoms are numbered according to the C atom to which they are bonded.

In the final cycles 120 parameters were simultaneously adjusted: non fixed coordinates and anisotropic temperature coefficients for 13 heavy atoms, coordinates and isotropic B's for 10 H atoms, a scale factor and a secondary extinction parameter g.[9] The final results are $R = 0.046$ and $R_w = 0.045$ for 1716 reflections ($R = 0.050$ including unobserved). The goodness-of-fit, defined as $(\Sigma w(\Delta F)^2/(m-s))^{1/2}$, where m is the number of observations and s is the number of parameters, is 1.44. Atomic scattering factors for C and F were from Ref. 10 and for H from Ref. 11. The final atomic parameters are given in Table 1.* The successful refinement of the structure and a close survey of the final positional parameters confirm the correctness of space-group assignment.

Correction for thermal libration. The tensors **T**, **L** and **S** were derived from a least-squares procedure.[12] The thermal factors of the C atoms of the annulene perimeter were included with equal weights, and their treatment showed that the entire annulene nucleus, including the C atoms of the CF_2 groups, behaves essentially as a rigid body, the difference between observed and calculated B_{ij}'s rarely exceeding 2σ. At 200 K, the mean-square rotational displacements of the annulene nucleus amount to 9,6, and 6 $(deg)^2$ about the principal axes of the tensor L, and implied corrections to the interatomic distances are in the range 0.003-0.004 Å.

A different treatment of the thermal parameters, according to the procedure proposed by Hirshfeld,[13,14] clearly confirms the essential rigid-body motion of the C atom skeleton.

DISCUSSION

The molecule as viewed along the direction corresponding to the maximum moment of inertia is shown in Fig. 1, where the calculated geometry and the adopted numbering scheme are also reported. A striking feature of **1**, besides the nonplanarity of the ring, is the systematic succession of long and short bond distances in the annulene perimeter (Table 2). These distances correspond to localized single and double bonds, thus indicating the polyenic character of the molecule. In Table 2 a comparison of C–C bond distances in **1** and **2** is also shown, confirming the close similarity between the two geometries. Another striking difference in the geometry of aromatic and polyenic [14]annulenes is that the transannular distance, (i.e. the distance between bridgehead C atoms) are practically equal in syn derivatives and significantly different in anti compounds. A number of examples are given in Table 3, where the simulation of aromatic character in *anti*-1, 6: 8, 13-biscarbonyl [14]annulene can be noticed. In polyenic derivatives the larger distance appears when a double bond is missing in the hypothetical Kekulé structure of an external hexagon, the shorter one when a single bond is missing. This finding can be rationalized as follows. The span between atoms C(4) and C(4′) is made up differently on the two sides of the central ring. On one side C(3)...C(3′) has to be long to compensate for the two short bonds, C(3)...C(4′) and C(3′)...C(4′) whereas on the other side C(5)...C(5′) must be short to compensate for the two long bonds C(4)...C(5)

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*A list of thermal parameters and calculated structure factors has been deposited with Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW.

Table 2. Comparison of bond lengths around the annulene ring in compound **1** and in 7-methoxycarbonyl-*anti*-1,6:8,13-dimethano [14]annulene (**2**)

	1		**2**[a]	
	Found	Corr[c]	Found[b]	Corr[c]
C(1)-C(1')	1.474(2)	1.478	1.455(2)	1.459
C(1)-C(2)	1.344(2)	1.347	1.344(2)	1.348
C(2)-C(3)	1.462(2)	1.465	1.458(2)	1.462
C(3)-C(4)	1.349(2)	1.352	1.346(2)	1.351
C(4)-C(5)	1.488(2)	1.491	1.489(2)	1.493
C(5)-C(6)	1.357(2)	1.360	1.346(2)	1.349
C(6)-C(7)	1.435(2)	1.438	1.441(2)	1.445
C(7)-C(7')	1.369(3)	1.372	1.352(3)	1.357
C(5)-C(8)	1.501(2)	1.504	1.508(2)	1.514
C(3)-C(9)	1.504(2)	1.508	1.506	1.512

[a] Averaged assuming *m* symmetry.
[b] At room temperature.
[c] After rigid-body treatment (Ref. 12).

Table 3. Comparison of transannular distances in the annulene ring of related compounds

Compound	C(3)...C(3')	C(5)...C(5')	Ref.
1	2.502Å	2.440Å	this work
2	2.483	2.417	3
3	2.452	2.457	5
(**4**)[a]	2.359	2.360	15
(**5**)[b]	2.470	2.472	16

[a] syn-1,6:8,13-bismethano [14]annulene
[b] syn-1,6.8,13-biscarbonyl [14]annulene

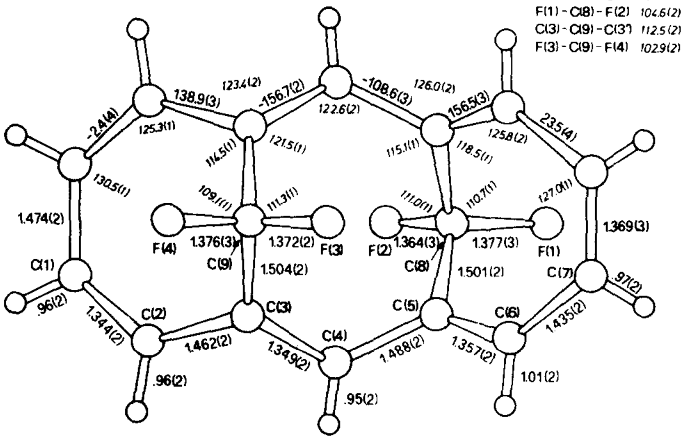
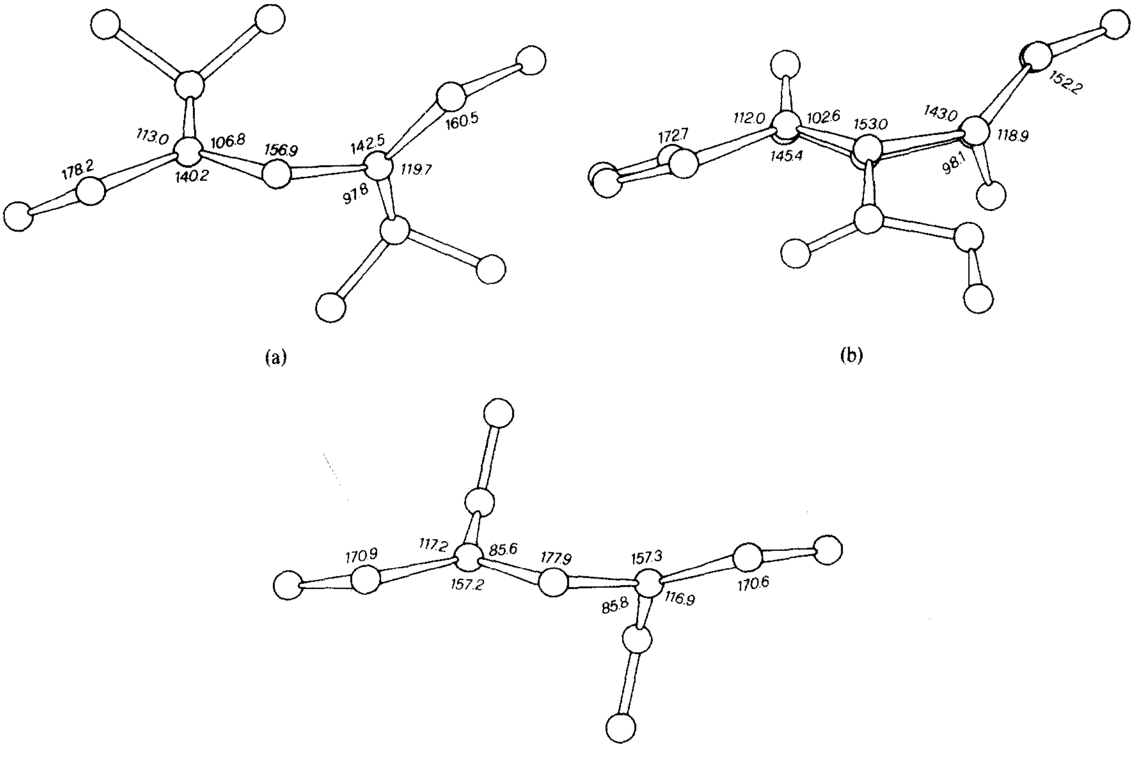


Fig. 1. The molecule of **1** as seen along the maximum inertial axis, with numbering scheme, bond distances, bond angles and torsion angles around the annulene perimeter.



(a) (b)

(c)

Fig. 2. Side view and dihedral angles for molecules **1** (a), **2** (b), and **3** (c).

and C(4′)...C(5′). The difference in transannular bond lengths between **4** and **5** is easily explained if one recalls that the bridged carbon atoms in the two molecules are in different hybridisation.

It has been pointed out[3] that polyenic behaviour is related to the presence of a remarkably high value for at least one misalignment angle between 2p orbitals of adjacent carbon atoms in the ring. In **1** the maximum value of such an angle is 71.4(3)°, more than enough to prevent aromaticity. In Fig. 2 side views and dihedral angles of molecules **1**, **2**, and **3** are shown. A striking similarity for the first two compounds is apparent, while once again **3** shows a marked anomaly. The close similarity of **1** and **2** supports the anti/polyenic rule and also the interpretation of the results for **3** previously offered.[5] If the necessary material were to become available, the present work indicates that a redetermination of the crystal structure of **3** at low temperature would be highly desirable.

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