

ANOTHER AROMATICITY VS NON-AROMATICITY DILEMMA

THE STRUCTURE OF *ANTI*-1,6:8,13-BISCARBONYL[14]ANNULENE

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Abstract—The X-ray crystal structure determination of *anti*-1,6:8,13-bis-carbonyl[14]annulene (**1**) is described. The structure has been solved by direct methods and refined to an R of 0.046 for 1074 reflections with $I > 2\sigma(I)$. The molecular structure of **1** appears to be aromatic, at least from geometrical parameters. This is in contrast with the great tendency of the compound to polymerize and also with the structure of the *anti*-bridged [14]annulenes previously studied, having polyenic character. It is possible that the geometry of the compound appears to be 'aromatic' due to disorder in the crystal.

Aromaticity is a very controversial concept in chemistry and the topic has been the object not only of an impressive number of papers and books, but also of numerous and rather debated symposia in recent years.^{1,2}

The main source of disagreement may be found in the fact that definition of aromaticity was based on different experimentally accessible properties, such as geometrical features, heats of formation, ring currents, chemical reactivity, or on different theoretical

approaches. In the case of bridged annulenes a systematic discussion could be offered, based on geometrical data provided by X-ray diffraction crystal structure analysis.³ However, *anti*-1,6:8,13-biscarbonyl[14]annulene (**1**), recently synthesized by Vogel,⁴ represents a situation where bond length alternation in the ring may be difficult to prove by means of X-ray diffraction data. We also found worthwhile to compare the conformation of **1** with those of its *syn*-isomer **2**,⁵ of 7-methoxycarbonyl-*anti*-

Table 1. Final atomic coordinates^a

Atom	X	Y	Z
C(1)	68676(32)	46337(49)	65718
C(2)	64523(36)	60807(60)	60104(38)
C(3)	55476(42)	57421(64)	54240(37)
C(4)	47590(44)	41010(72)	53308(38)
C(5)	45937(38)	23313(64)	57998(36)
C(6)	53727(32)	16549(48)	64275(34)
C(7)	51900(43)	2550(65)	70847(39)
C(8)	58976(31)	4610(52)	78063(25)
C(9)	63445(35)	-10007(57)	83551(37)
C(10)	72750(50)	-6939(82)	89300(41)
C(11)	80695(44)	9410(79)	90244(37)
C(12)	82046(38)	27324(64)	85502(36)
C(13)	74033(34)	34357(47)	79519(34)
C(14)	75539(47)	48828(59)	73048(40)
C(15)	66076(33)	24448(49)	63541(34)
C(16)	61699(34)	26319(48)	80410(35)
O(1)	74026(25)	13319(36)	61114(29)
O(2)	53850(24)	37255(41)	83140(30)
H(2)	670(5)	757(8)	607(4)
H(3)	535(4)	684(6)	505(3)
H(4)	415(4)	426(7)	491(3)
H(5)	389(4)	164(6)	576(3)
H(7)	463(4)	-56(7)	706(3)
H(9)	593(4)	-247(6)	824(3)
H(10)	733(6)	-183(8)	930(5)
H(11)	872(4)	73(7)	948(3)
H(12)	901(5)	357(7)	864(3)
H(14)	821(6)	607(9)	735(5)

^aMultiplied by 10⁵ for C and O, by 10³ for H.

Estimated standard deviations in the least significant digit are given in parentheses.

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

Table 2. Bond angles ($^{\circ}$) involving heavy atoms^a

C(1)–C(14)–C(13)	117.8	C(1)–C(2)–C(3)	124.8
C(6)–C(7)–C(8)	117.9	C(4)–C(5)–C(6)	124.4
C(2)–C(1)–C(14)	130.1	C(8)–C(9)–C(10)	125.7
C(5)–C(6)–C(7)	130.4	C(11)–C(12)–C(13)	125.2
C(7)–C(8)–C(9)	131.0	C(2)–C(3)–C(4)	130.7
C(12)–C(13)–C(14)	130.4	C(3)–C(4)–C(5)	131.6
C(2)–C(1)–C(15)	115.7	C(9)–C(10)–C(11)	130.8
C(5)–C(6)–C(15)	114.7	C(10)–C(11)–C(12)	130.3
C(9)–C(8)–C(16)	114.7	C(1)–C(15)–C(6)	119.6
C(12)–C(13)–C(16)	114.8	C(8)–C(16)–C(13)	120.0
C(14)–C(1)–C(15)	114.1	C(1)–C(15)–O(1)	120.1
C(7)–C(6)–C(15)	114.9	C(6)–C(15)–O(1)	120.3
C(7)–C(8)–C(16)	114.3	C(8)–C(16)–O(2)	119.8
C(14)–C(13)–C(16)	114.7	C(13)–C(16)–O(2)	120.2

^aEstimated standard deviations range between 0.3 and 0.5 $^{\circ}$.

1,6:8,13-dimethano[14]annulene 3,⁶ and of *anti*-1,6:8,13-dimethano[14]annulene tricarbonylchromium 4.⁷

EXPERIMENTAL

The crystals of 1, kindly supplied to us by Professor E. Vogel, are red prisms or thin needles, the first being often polycrystalline, the second too small to be examined by X-rays. All crystals are covered with a film of polymer, that rapidly reforms after peeling. After a number of unsuccessful attempts, an acceptable crystal was obtained from a relatively large prism by partial dissolution in acetone. This crystal, sealed in a thin-walled glass capillary, was used for all data collection.

Crystal data. For C₁₆H₁₀O₂: Mol wt 234.3; orthorhombic, $a = 11.2011(5)$, $b = 6.5077(2)$, $c = 15.9458(5)$ Å, $V = 1162.3(1)$ Å³; $\rho_{\text{obs}} = 1.33$ g cm⁻³, $\rho_{\text{calcd}} = 1.339$ g cm⁻³, $Z = 4$; $F(000) = 488$; space group $Pca2_1$; K_{α} Cu radiation (graphite monochromatized), $\lambda_{\alpha} = 1.5418$ Å, $\mu(K_{\alpha}\text{Cu}) = 7.17$ cm⁻¹.

Data collection. Accurate cell dimensions were obtained by a least-squares fitting of $\sin^2\theta$ values for 52 reflections. Systematic absences okl with l odd and hol with h odd indicate the space groups $Pca2_1$ or $Pcam$. Intensities were collected by variable rate θ - 2θ scans on a Syntex P1 diffractometer to a maximum 2θ value of 148 $^{\circ}$. Background measurements were taken at both ends of the scan range, each for a time equal to one-half the scan time. Two standard reflections were checked after every 50 intensity measurements. They showed no unusual variations over the course of the experiment, the maximum deviation of each standard from its mean intensity being about 3% ($<3\sigma$). More than two thirds (67.3%) of the accessible reflections were recorded twice in succession, at different ψ values. For all but three of these reflections the agreement between the two observations was within the statistics associated with the assigned standard deviations. Observational variances $\sigma^2(I)$ included counting statistics plus an additional term $(0.03S)^2$, where S is the scan count. Weighted averages of the equivalent measurements led to a list of 1212 independent intensities, of which 138 had $I < 2.0\sigma(I)_{\text{c.s.}}$ and were classed as unobserved. Weights of the averaged values were taken as averages, rather than sums, of the individual weights. Intensities and their standard deviations were corrected for Lorentz and polarization effects, but not for absorption.

After data collection, equi-inclination Weissenberg photographs were taken on the same crystal mounted along a . They showed that the quality of the specimen was rather poor: the crystal was composed of several slightly displaced blocks that gave the reflection spots on the film an uneven appearance. Moreover, the diffraction pattern showed various degrees of continuous streaking along reciprocal-lattice rows parallel to c .^{*} The diffuse lines were particularly pronounced along festoons with odd h , rather faint for even $h > 0$, and undetectable on the okl photograph. It is well known that the appearance of diffuse streaks is indicative of possible structural disorder, often in form of microsynthetic twinning resulting from mistakes in crystal growth of layer structures. Diffuse lines may also arise from thermal diffuse scattering, particularly for structures involving large planar molecules.

Solution and refinement of the structure. Statistical tests showed clearly that the structure is acentric, and the space group $Pca2_1$ was assumed. The structure was solved by direct methods.⁸ The positions of all non-H atoms were derived from an E map and the H atoms were initially introduced at calculated positions. A modified version of ORFLS⁹ was used for the full-matrix least-squares refinement by minimization of the quantity $\sum w[(F_o - |F_c|)^2]$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$, except for the 138 unobserved reflections, for which $w = 0.0$. In the final cycles 202 parameters were simultaneously adjusted: coordinates and anisotropic temperature coefficients for 18 heavy atoms, coordinates and isotropic B's for 10 H atoms, and a scale factor. The final results are $R = 0.046$ and $R_w = 0.052$ for 1074 reflections. The goodness-of-fit defined as $[\sum w(\Delta F)^2/(m - s)]^{1/2}$, where m is the number of observations and s the number of parameters, is 2.00. Form factors for C and O were from Ref. 10 and for H from Ref. 11. The final atomic parameters are given in Table 1. A final difference map showed no unusual features, with a maximum peak at 0.27 eÅ⁻³. Figure 1 shows two views of the heavy atom skeleton together with the numbering scheme, bond distances, torsion angles along the anthracene perimeter and dihedral angles between least-squares planes. Thermal ellipsoids are drawn at the 0.20 probability level. Table 2 gives bond angles involving heavy atoms. The C–H bond lengths range between 0.82 and 1.07 Å and the C–C–H angles between 110 and 124 $^{\circ}$.[†]

[†]A list of thermal parameters and calculated structure factors has been deposited. Tetrahedron should deposit the list with the British library and give the details.

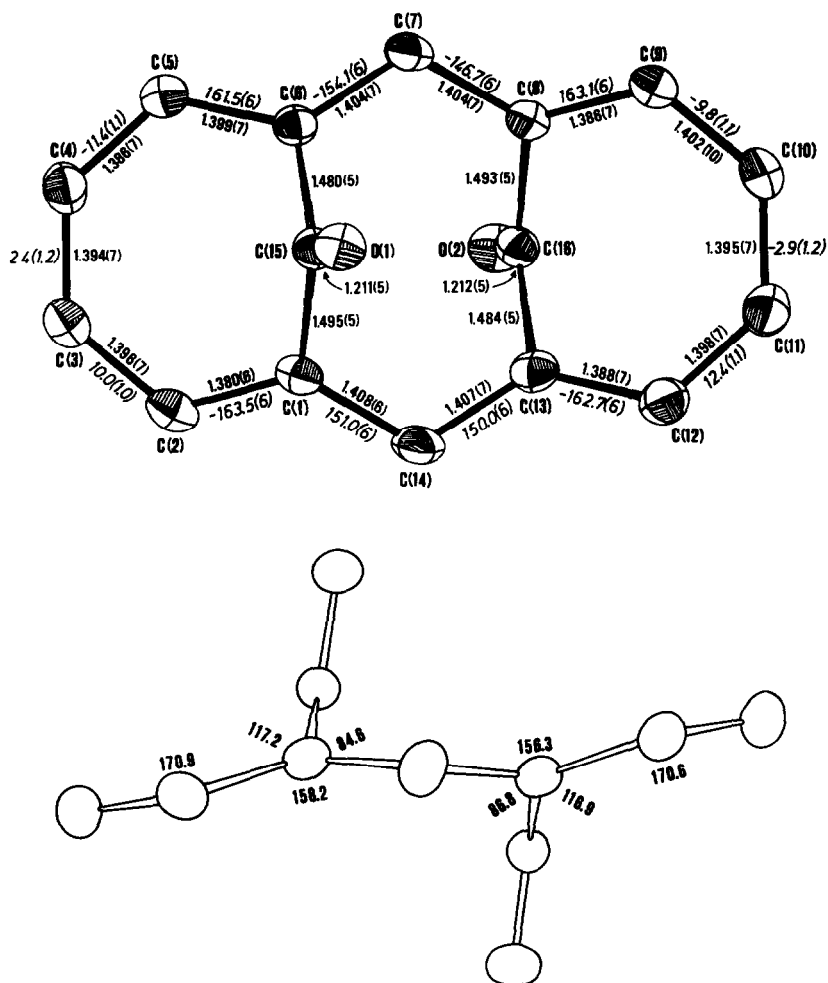


Fig. 1. (a) The molecule of **1** as seen along the maximum inertial axis, with numbering scheme, bond distances, and torsion angles (italics) along the annulene perimeter.

(b) The same rotated by 90°. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at a probability level of 0.20.

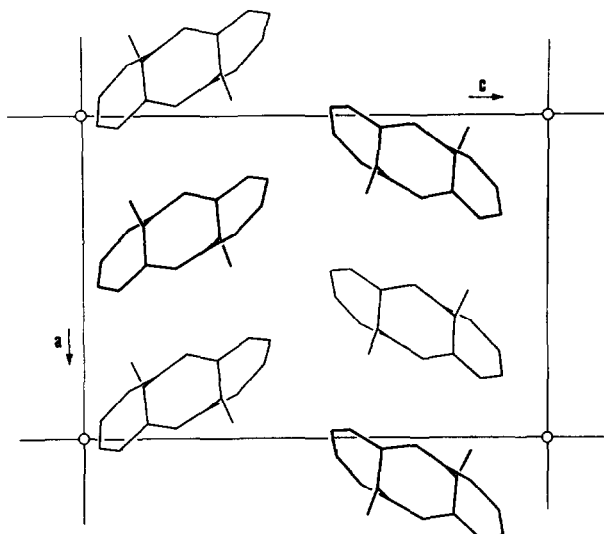


Fig. 2. A drawing of the structure as viewed down the b axis.

DISCUSSION

A "prima vista" analysis of the X-ray results suggests an aromatic structure for **1**: the molecule exhibits a rough $2/m$ symmetry with no single bond—double bond alternation, and the angles between pairs of p orbitals on adjacent C atoms along the ring are smaller than 34° . To quantify these concepts we have calculated $\rho = \langle (r_i - \bar{r})^2 \rangle^{1/2} = 0.008 \text{ \AA}$ and $\tau = \langle \tau_i^2 \rangle^{1/2} = 19.3^\circ$, where r_i are the observed bond lengths in the annulene perimeter and τ_i are the misalignment angles, as measured by the torsion angles ϕ , when $|\phi_i| \leq 90^\circ$ and $180 - |\phi_i|$ for $|\phi_i| > 90^\circ$. Both values of ρ and τ fall in the range representative of an aromatic structure, according to Gavezzotti and Simonetta.¹² However the following considerations are against this interpretation: (i) The ease of polymerization is quite unexpected for an aromatic annulene. (ii) The two *anti*-bridged [14] annulenes (**3** and **4**) for which the crystal structures have been reported^{6,7} are clearly polyenic. (iii) The previous studies of bridged [14] annulenes have indicated that these molecules can be described as rigid bodies to a good approximation, at least as far as the annulenic skeleton is concerned. The derived model implies large displacements at the end atoms but small displacements at the atoms close to the centre of the molecule. In the present case, a close analysis of the thermal parameters indicated that the motion is largest at the central atoms, especially at C(14), decreases significantly at the bridge atoms, and becomes large again at the outer atoms (this is also evident from a look to thermal ellipsoids reported in Fig. 1(b)). This behaviour is well documented also by the unusually large values of the isotropic temperature factors of some hydrogens, up to 9.8 and 13.5 \AA^2 for H(10) and H(14), respectively (to be compared with the overall B, at the end of the isotropic refinement, 4.4 \AA^2) (iv) The diffraction pattern shown on the Weissenberg films (Experimental) might be consistent with partial crystal disorder.

All these arguments suggest two alternative interpretations of the experimental data, both consistent with a polyenic structure.

(A) The crystal structure may be affected by static disorder:¹³ in each crystallographic position we may have a 1:1 mixture of a polyenic molecule in two different orientations. Following this hypothesis, we have performed a constrained refinement of a model consisting of two annulene systems (whose geometry was derived from compound **3** with slight modifications), rotated by 180° with respect to each other, and translated in such a way as to minimize distances between the corresponding atom pairs. It is worth noting that for such a model the largest separations between atoms in the same pair occur both at the central and at the end pairs. Refinement with TLS and m symmetry constraints converged at $R = 0.060$ and $R_w = 0.076$ (lower values could have been obtained if the H atoms had not been included in the thermal constraint). It has been pointed out¹⁴ that statistical worsening of the agreement between observed and calculated structure factors does not

necessarily imply that the constrained model is less reliable on chemical or physical grounds. In the present case, however, the molecular pattern obtained at the end of the constrained refinement is not totally satisfactory: the single bond—double bond alternation along the annulene perimeter is maintained, but the anthracene skeleton appears much flatter than in compounds **3** and **4**. A typical feature of *anti*-bridged [14] annulenes, that is the presence of two torsion angles $|\phi| > 60^\circ$, is here missing.

(B) Dynamical disorder might be invoked as well to explain the observations. It has been reported¹⁵ that the NMR spectra of *anti*-1,6:8,13-bismethano-[14]annulene excluded an aromatic structure with a delocalized 14 π electron system, and yet a polyenic structure with fixed double bonds could not be reconciled with the paucity of lines actually observed. Low-temperature measurements indicated that above -60° a dynamic process, consisting of a double-bond migration, occurs in the molecule. The activation energy was estimated to be about 7 kcal mole⁻¹. In view of this low value, and since in our case the packing arrangement of the molecules (Fig. 2) is rather loose,¹⁶ it seems not unrealistic to think of a similar dynamic process occurring also in the crystal phase of **1**. If so, the results of the X-ray analysis would represent the averaged structure of the two valence tautomers.

In retrospect it would appear that the use of other techniques, such, e.g. NMR spectroscopy or the investigation of the structures of appropriately substituted compounds, would be necessary to find a definitive answer to the problem.

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