(for simplicity the Cl^- ions have been omitted). Reaction 2 indicates the reaction of a detrapped electron with the ethanol monoradical, after or accompanying the diffusing apart of the biradical. The resultant excited anion would be the chain propagator, as shown in reaction 3. Reactions 4a and 4b are both possible termination reactions. The first re-forms a choline cation; the second forms the two stable products. Both seem equally possible.

Summary

This work has added to our knowledge of the radicals that appear in γ-irradiated choline chloride and has added further evidence of the important role of free electrons in the radiolysis mechanism. The irradiated crystalline compound has been shown to exhibit the following characteristics.

1. The changes with temperature of the esr spectra appear to reflect a diffusing apart of an initially-formed $(CH_3)_3N^+\cdot\cdot CH_2CH_2OH\text{---}Cl^-$ biradical. At −196° the distance between the coupled spins is about 6 Å.
2. Thermoluminescence observations have shown the release of trapped electrons from two principal trap depths and have also shown that higher doses of radiation create larger numbers of trapped electrons in the crystals. The electrons released from the lower temperature (lower energy) trap appear to play no part in the radiolysis.
3. It was confirmed that the photoelectron-emitting dye, Brilliant Green, enhances the radiolysis; it also speeds the rate of radical decay.
4. The radical decay rate is extremely slow below 10°, and, at a given temperature, this rate diminishes with time. The reduced rate appears to be a result of a diminishing availability of free (detrapped) electrons.
5. The decay of radical signals in high-dose samples can continue to be faster than that in a low-dose sample even after a point of equal radical concentrations is reached. Thermoluminescence observations have shown that, at this "cross-over" point, the higher-dose samples still have available a higher concentration of trapped electrons.

Acknowledgment. We wish to express our thanks to Drs. Amar Nath and Micha Tomkiewicz for stimulating discussions about the choline problem.

Crystal and Molecular Structure of 7-Methoxycarbonyl-*anti*-1,6:8,13-dimethano[14]annulene

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Abstract: The molecular conformation in the crystal phase of 7-methoxycarbonyl-*anti*-1,6:8,13-dimethano[14]-annulene (**6**) accounts for its chemical olefinic reactivity. The crystals are monoclinic, space group $P2_1/c$, $a = 13.888$, $b = 13.186$, $c = 7.575$ Å, $\beta = 103.06°$, $Z = 4$. The symmetry of the annulene nucleus is close to m (C_s); misalignments as high as 70° between adjacent $2p_z$ orbitals along the annulene ring prevent aromatic behavior. Simple Hückel molecular orbital calculations for syn- and anti-[$4n + 2$] bridged annulenes agree with the crystal structure results.

In recent years, interest has been devoted to the synthesis and chemical behavior of bridged [14]annulenes; work in this field is being carried on extensively by Vogel and coworkers.[1-6] An important feature of these compounds is the change in reactivity in passing from syn- to anti-bridged annulenes: syn derivatives maintain aromatic behavior in spite of the distortion imposed by the bridges to the annulene ring,[1-5] whereas anti compounds show a definite polyenic character.[6] This difference must be reflected in the molecular geometry of the two types of compounds and should be connected with values of bond lengths and torsion angles along the annulene perimeter. Previous X-ray crystal structure determinations on bridged [10]annulenes[7,8] and on syn-bridged [14]annulenes[9-12] afforded results which could be correlated with the retention of aromatic behavior. We considered it worthwhile therefore to determine by X-ray analysis the crystal structure of an anti-bridged [14]-annulene. Because of the low melting point (41–42°) of the hydrocarbon,[6] we used its 7-methoxycarbonyl derivative, a well-crystallized substance which was kindly supplied to us by Professor E. Vogel. In the meanwhile, when crystallographic work was already at an advanced stage, a communication on *anti*-1,6:8,13-

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dimethano[14]annulenetricarbonylchromium[13] was published showing the molecular geometry of these anti-bridged [14]annulenes. The presence, however, of a heavy atom, such as Cr, and its influence on the molecular conformation suggested to us that it would be worthwhile to carry out an accurate investigation on our compound. Preliminary results have been collected in a short communication.[14]

Experimental Section

Collection and Reduction of X-Ray Data. Crystals of 7-methoxycarbonyl-*anti*-1,6:8,13-dimethano[14]annulene are in the form of yellow needles, elongated along the *c* axis. Weissenberg photographs showed them to be monoclinic, with space group $P2_1/c$ from systematic absences. The unit cell dimensions (see Table I) were obtained by a least-squares fit to measurements of $\sin^2 \vartheta$ for 37 $hk0$ and 37 $h0l$ reflections on zero-level Weissenberg photographs taken at 21° with Cu Kα radiation on a double-radius camera; the film was held in the asymmetric position, following the Straumanis technique. No corrections for eccentricity or absorption were introduced in the least-squares calculations, and weights were assumed as inversely proportional to $\sin^2 2\vartheta$. Standard deviations, as obtained from the inverse matrix of the least-squares fit, are considerably lower than the reported values; however, no significance is given to further digits. The density was measured by flotation in a dilute Thoulet (K_2HgI_4) solution.

Table I. Crystal Data for $C_{18}H_{16}O_2$

$a = 13.888 \pm 0.001$ Å	$D_m = 1.302$ g cm^{-3}
$b = 13.186 \pm 0.001$ Å	$D_x = 1.299$ g cm^{-3} ($Z = 4$)
$c = 7.575 \pm 0.001$ Å	λ (Cu Kα_1) = 1.54051 Å
$\beta = 103.06 \pm 0.01°$	λ (Cu Kα_2) = 1.54433 Å
Monoclinic, $P2_1/c$	λ (Cu Kα) = 1.5418 Å

For determination of the structure, intensity data were collected on a Philips linear equiinclination diffractometer (PAILRED) in the automatic mode, using the ω-scan technique. Mo Kα radiation (monochromatized by a graphite (0001) single crystal) and a scintillation detector with pulse height analyzer were used. The scan range varied from ± 0.5 to $\pm 1.6°$ (the larger values being used in the higher layers for low values of the Υ angle). The scan speed was 1 deg min^{-1}; background counts were taken for 1 to 2 min at both ends of the scan, with crystal and counter stationary (the larger values of time for these counts were used for higher layers, where on the average the intensities were low). Scanning was automatically repeated for each reflection (up to a maximum of three times) until the number of scan counts reached at least the value of 1000. The layers 0 to 9 about the *c* axis were obtained from a crystal whose diameter was about 0.3 mm; the layers 0 and 1 about the *b* axis were collected from another crystal, whose diameter was about 0.3 mm. A total of 3128 reflections were measured (of which 270 were unobserved reflections, *i.e.*, with peak intensity inferior to the background); the total number of independent reflections within the copper sphere is 3080 for this compound.

All the collected data were corrected for Lorentz and polarization factors. No correction either for extinction or for absorption ($\mu_{\text{Mo K}\alpha} = 0.9$ cm^{-1}) was applied.

Solution and Refinement of the Structure. The approximate absolute scale and the overall temperature factor were obtained by Wilson's method. For the solution of the phase problem by direct methods, the structure factors were converted to the normalized amplitudes $|E_{hkl}|$.[16] The values of the statistical averages $\langle|E|\rangle$ and $\langle|E^2 - 1|\rangle$ are 0.796 and 1.011, in good agreement with the values expected for a centrosymmetric structure. The Σ_2 form[15] of inequality (34) of Karle and Hauptman[16] was employed in the phase determination of 220 reflections with $|E| > 1.85$. The whole process was performed using a Fortran IV computer program.[17] The E map[18] obtained with the phases corresponding to the highest con-

$$C = \frac{\langle|E_h \sum_k E_k E_{h-k}|\rangle}{\langle|E_h| \sum_k |E_k||E_{h-k}|\rangle} = 0.83$$

sistency index revealed all the carbon and oxygen atoms. The structure factor calculation including all the three-dimensional data gave an index $R = 46.5\%$; for data with $(\sin^2 \vartheta)/\lambda^2$ less than 0.10, the R index was 35.5%, which suggested the essential correctness of the structure.

Refinement was performed by a block-diagonal least-squares process, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, by means of a Fortran IV computer program.[19] The atomic scattering factors of Cromer and Waber[20] for C and O atoms, and those of Stewart, *et al.*,[21] for H atoms were used in all structure factor calculations. After 16 cycles of least-squares refinement carried on 2090 reflections for which $F^2/\sigma(F^2) > 2$, the R index was 4.7%, with anisotropic temperature factors assigned to all the C and O atoms. The initial coordinates of all H atoms except those in the methyl group were derived from geometrical considerations at an early stage of the refinement; the remaining H atoms were revealed by a difference Fourier synthesis. During all these cycles, weights (w) were chosen equal to $1/\bar{f}^2$, where $\bar{f}$ is the average scattering factor for all the atoms at the calculated value of $(\sin \vartheta)/\lambda$.

Although the R index was low, the set of weights used was not yet fully satisfactory as the weighted mean quadratic error $w(\Delta F)^2$ showed considerable differences (up to 50%) over the range of $|F_o|$. Accordingly, in the last three refinement cycles weights were calculated according to the expression

$$w' = 1/(A + B|F_o| + C|F_o|^2)$$

where A, B, and C were deduced from a least-squares fit of $(|F_o| - |F_c|)^2$ as a function of $|F_o|$ in two different intervals, one for $|F_o| \leq 8$ and the other for higher $|F|$'s. Correspondingly, constancy of $w'(\Delta F)^2$ within 9.3% was reached. This last part of the refinement led to a slightly higher R index (5.1%); however, since the weighting scheme is more satisfactory, we consider the corresponding structural results as more significant.

At the end of the refinement, the shifts in atomic parameters were less than 0.25σ for heavier atoms (with the exception of B_{23} for C(18), the shift being $<0.3\sigma$) and less than 0.3σ for hydrogen atom parameters (with the exception of B for H(14) and H(15), the shift being $<0.5\sigma$). Observed and calculated structure factors are listed in Table II;[22] the final parameters of the heavier atoms are given in Table III and of the hydrogen atoms in Table IV. The numbering of atoms is shown on the thermal ellipsoids plot[23] of Figure 1.

The standard deviations for the coordinates correspond to positional uncertainties of the order of 0.002 Å for the carbon and oxygen atoms and of 0.025 Å for the hydrogen atoms. The corresponding standard deviations for the bond distances involving only heavier atoms are about 0.003 Å, for the bond angles 0.2°, and for the torsion angles[24] 0.3°; for the C–H bonds they are about 0.03 Å and for the bond angles involving hydrogen atoms they are between 1 and 2°.

Corrections for Thermal Libration. The tensors **T**, **L**, and **S**[25] were derived from a least-squares procedure.[26] A first treatment including all carbon and oxygen atoms clearly showed that C(17),

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Table III. The Heavy Atom Parameters and Their Standard Deviations[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3755 (1)	−520 (1)	5407 (2)	48 (1)	44 (1)	157 (2)	2 (1)	40 (1)	9 (1)
C(2)	3992 (1)	−1320 (1)	4253 (2)	67 (1)	52 (1)	198 (2)	10 (1)	60 (1)	8 (1)
C(3)	3331 (1)	−1817 (1)	2985 (2)	92 (1)	45 (1)	199 (2)	3 (1)	75 (1)	−13 (1)
C(4)	2257 (1)	−1786 (1)	2556 (2)	91 (1)	50 (1)	158 (2)	−14 (1)	48 (1)	−23 (1)
C(5)	1620 (1)	−1308 (1)	3378 (2)	65 (1)	53 (1)	141 (2)	−10 (1)	20 (1)	−15 (1)
C(6)	1922 (1)	−555 (1)	4813 (2)	46 (1)	38 (1)	125 (2)	3 (1)	10 (1)	1 (1)
C(7)	1516 (1)	−384 (1)	6253 (2)	40 (1)	36 (1)	144 (2)	0 (0)	15 (1)	−6 (1)
C(8)	2064 (1)	265 (1)	7770 (2)	42 (1)	40 (1)	132 (2)	−6 (0)	30 (1)	−7 (1)
C(9)	1837 (1)	1228 (1)	8097 (2)	48 (1)	46 (1)	181 (2)	−3 (1)	35 (1)	−18 (1)
C(10)	2481 (1)	1892 (1)	9347 (2)	70 (1)	46 (1)	204 (2)	−9 (1)	47 (1)	−33 (1)
C(11)	3479 (1)	1899 (1)	9699 (2)	69 (1)	58 (1)	183 (3)	−22 (1)	27 (1)	−33 (1)
C(12)	4090 (1)	1251 (1)	8879 (2)	49 (1)	70 (1)	157 (2)	−15 (1)	15 (1)	−11 (1)
C(13)	3848 (1)	292 (1)	8348 (2)	43 (1)	62 (1)	124 (2)	2 (1)	5 (1)	2 (1)
C(14)	4280 (1)	−320 (1)	7079 (2)	46 (1)	63 (1)	177 (2)	10 (1)	21 (1)	6 (1)
C(15)	2818 (1)	50 (1)	4638 (2)	53 (1)	38 (1)	112 (2)	1 (1)	24 (1)	4 (1)
C(16)	2985 (1)	−190 (1)	8939 (2)	58 (1)	45 (1)	123 (2)	−3 (1)	21 (1)	1 (1)
C(17)	632 (1)	−939 (1)	6531 (2)	41 (1)	39 (1)	174 (2)	1 (1)	15 (1)	−4 (1)
C(18)	−447 (1)	−1148 (1)	8514 (2)	60 (1)	61 (1)	263 (3)	−16 (1)	56 (1)	4 (1)
O(1)	174 (1)	−1568 (1)	5542 (2)	63 (1)	82 (1)	259 (2)	−28 (1)	36 (1)	−58 (1)
O(2)	394 (1)	−655 (1)	8061 (1)	61 (0)	60 (1)	203 (2)	−20 (0)	50 (1)	−21 (1)

[a] All the values in this table have been multiplied by 10^4. The temperature factor is in the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

Table IV. Parameters for the Hydrogen Atoms

	x	y	z	$10B$, Å^2
H(1)	0.468 (1)	−0.149 (1)	0.451 (2)	58 (4)
H(2)	0.357 (1)	−0.231 (1)	0.231 (2)	59 (4)
H(3)	0.195 (1)	−0.221 (1)	0.158 (2)	62 (4)
H(4)	0.090 (1)	−0.146 (1)	0.299 (2)	56 (4)
H(5)	0.119 (1)	0.151 (1)	0.742 (2)	47 (4)
H(6)	0.218 (1)	0.244 (1)	0.987 (2)	61 (4)
H(7)	0.380 (1)	0.244 (2)	1.042 (2)	65 (5)
H(8)	0.470 (1)	0.155 (1)	0.865 (3)	56 (4)
H(9)	0.491 (1)	−0.068 (1)	0.750 (3)	62 (4)
H(10)	0.283 (1)	0.071 (1)	0.527 (2)	34 (3)
H(11)	0.278 (1)	0.019 (1)	0.336 (2)	35 (3)
H(12)	0.303 (1)	−0.003 (1)	1.024 (2)	46 (4)
H(13)	0.300 (1)	−0.094 (1)	0.884 (2)	46 (3)
H(14)	−0.098 (2)	−0.118 (2)	0.741 (3)	88 (6)
H(15)	−0.065 (2)	−0.076 (2)	0.942 (3)	85 (6)
H(16)	−0.026 (2)	−0.182 (2)	0.889 (3)	84 (6)

C(18), O(1), and O(2), as might reasonably have been expected, did not fit at all to a rigid-body molecular motion; for this reason, these atoms were excluded from our calculations. For all other heavy atoms, thermal factors were included with equal weights. With the exception of C(7), the differences between observed and calculated B_{ij}'s for the annulene nucleus C(1)–C(16) rarely exceeded 3σ and then only slightly. For C(7) the difference amounted to eight standard deviations. On the whole, considering that the standard deviations are very low, this was taken as proof of essential rigid-body motion for the annulene nucleus. The results relative to C(7) can be explained by the influence of the independent motion of the "heavy" methoxycarbonyl group directly bonded to this atom.

Table V. Rigid-Body Tensors[a]

T (Å^2)	1321 (72)	58 (55)	−523 (43)
("unreduced")		1259 (65)	−34 (30)
			610 (24)
L (rad^2)	25 (2)	5 (1)	−12 (1)
		40 (3)	12 (3)
			36 (4)
S (Å rad)	−28 (6)	139 (8)	19 (4)
	−195 (15)	−19 (11)	110 (9)
	−52 (13)	−142 (13)	47 (8)

[a] Tensors are referred to a Cartesian coordinate system defined by unit vectors **a**, **b**, **a** × **b**. All values have been multiplied by 10^4. The annulene nucleus alone is considered, excluding the methoxycarbonyl group.

The mean-square rotational displacements of the annulene nucleus amount to 17, 12, and 4 (deg)^2 about the principal axes of the tensor **L**. The rigid-body parameters are given in Table V.

Bond distances involving carbon and oxygen atoms are reported in Table VI. The corrected values were derived by using the rigid-body parameters[25] of Table V. Corrections to bond and torsion angles are small ($\leq 0.1°$) and have been neglected. In Table VI, the calculated values refer to semiempirical calculations (see next paragraph). Bond angles for heavier atoms are given in Table VII. Torsion angles[27] along the perimeter ring are reported in Figure 1. Dihedral angles between subsequent least-squares planes[28] in the annulene ring, *e.g.*, C(2)C(3)C(4)C(5), C(1)C(2)C(5)C(6), etc., are shown in Figure 2. The highest deviation from these planes is 0.026 Å.

Table VI. Bond Lengths (Å)

	Found[a]	Cor[b]	Calcd
C(1)–C(2)	1.455 (2)	1.459	1.442
C(2)–C(3)	1.340 (2)	1.345	1.370
C(3)–C(4)	1.455 (3)	1.460	1.432
C(4)–C(5)	1.348 (2)	1.352	1.368
C(5)–C(6)	1.462 (2)	1.465	1.447
C(6)–C(7)	1.355 (2)	(1.36)[c]	1.351
C(7)–C(8)	1.496 (2)	(1.50)[c]	1.491
C(8)–C(9)	1.344 (2)	1.348	1.350
C(9)–C(10)	1.443 (2)	1.447	1.450
C(10)–C(11)	1.352 (3)	1.357	1.360
C(11)–C(12)	1.440 (2)	1.444	1.448
C(12)–C(13)	1.347 (2)	1.350	1.351
C(13)–C(14)	1.482 (2)	1.486	1.486
C(14)–C(1)	1.337 (2)	1.341	1.354
C(1)–C(15)	1.502 (2)	1.509	
C(6)–C(15)	1.510 (2)	1.515	
C(8)–C(16)	1.506 (2)	1.512	
C(13)–C(16)	1.511 (2)	1.516	
C(7)–C(17)	1.485 (2)		
C(17)–O(1)	1.199 (2)		
C(17)–O(2)	1.329 (2)		
O(2)–C(18)	1.444 (2)		

[a] C–H bond distances range from 0.94 to 1.00 Å. [b] After rigid-body correction. [c] Lack of strict rigid body behavior for atom C(7).

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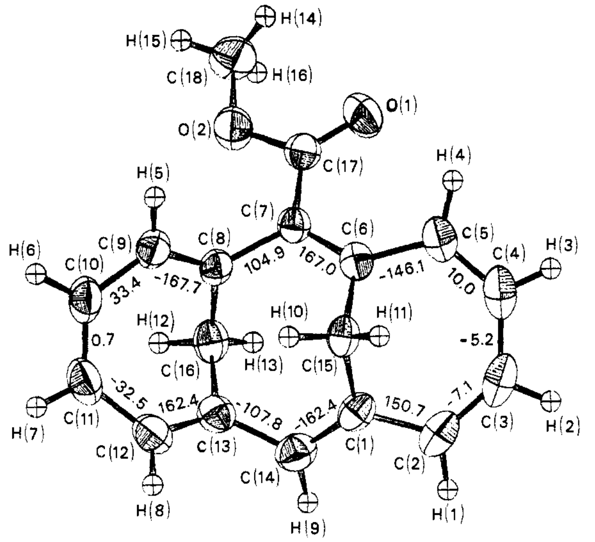

Figure 1. The molecule seen along the direction corresponding to the maximum moment of inertia of the annulene nucleus. Thermal ellipsoids are drawn at a probability 0.50. Hydrogen atoms, treated as isotropic, are on an arbitrary scale. Torsion angles along the perimeter ring are reported.

Table VII. Bond Angles[a] (deg)

C(1)–C(2)–C(3)	125.1 (1)	C(2)–C(1)–C(15)	115.1 (1)
C(2)–C(3)–C(4)	130.4 (2)	C(5)–C(6)–C(15)	113.4 (1)
C(3)–C(4)–C(5)	131.1 (2)	C(7)–C(6)–C(15)	118.9 (1)
C(4)–C(5)–C(6)	123.6 (2)	C(1)–C(15)–C(6)	111.1 (1)
C(5)–C(6)–C(7)	127.6 (1)	C(7)–C(8)–C(16)	116.2 (1)
C(6)–C(7)–C(8)	118.8 (1)	C(9)–C(8)–C(16)	118.1 (1)
C(7)–C(8)–C(9)	125.6 (1)	C(12)–C(13)–C(16)	117.9 (1)
C(8)–C(9)–C(10)	123.9 (1)	C(14)–C(13)–C(16)	115.3 (1)
C(9)–C(10)–C(11)	126.1 (2)	C(8)–C(16)–C(13)	106.5 (1)
C(10)–C(11)–C(12)	126.1 (2)	C(6)–C(7)–C(17)	122.6 (1)
C(11)–C(12)–C(13)	123.6 (1)	C(8)–C(7)–C(17)	117.8 (1)
C(12)–C(13)–C(14)	126.5 (1)	C(7)–C(17)–O(1)	126.3 (1)
C(13)–C(14)–C(1)	120.5 (1)	C(7)–C(17)–O(2)	111.2 (1)
C(14)–C(1)–C(2)	124.3 (1)	O(1)–C(17)–O(2)	122.6 (1)
C(14)–C(1)–C(15)	120.5 (1)	C(17)–O(2)–C(18)	117.0 (1)

[a] The C–C–H, O–C–H, and H–C–H bond angles range from 109 to 121, 108 to 109, and 107 to 113°, respectively.

Calculated Geometry for Isolated Bridged Annulene Molecules. To check the dependence of bond lengths on torsion angles along the annulene ring, simple Hückel molecular orbital (HMO) calculations were made for the π-electron systems in annulene molecules. Input data were the bond distances, r_{ij} (which at the beginning were chosen to be all equal to 1.40 Å), and torsion angles, τ_{ij} (which were kept fixed at the experimental values for different compounds). The misalignment angle φ_{ij} between the p_z orbitals of two adjacent carbon atoms i and j in the ring was considered to be $|\tau_{ij}|$ for $|\tau_{ij}| \leq 90°$, and $180° - |\tau_{ij}|$ for $|\tau_{ij}| > 90°$.

The resonance integral, β_{ij} was calculated from the formula[29]

$$\beta_{ij} = 6.3119[\exp(-1.31876 r_{ij})] \cos \varphi_{ij} \qquad (1)$$

in β_0 units, where β_0 is the resonance integral between two parallel $2p_z$ carbon orbitals centered at a distance 1.397 Å.

The standard procedure gave π-electron energy and bond orders, n_{ij}. New bond distances were evaluated by use of Coulson's formula[30]

$$r_{ij} = s - \frac{s - d}{1 + k[(1 - n_{ij})/n_{ij}]} \qquad (2)$$

where the following values were employed: s = 1.517 Å, d = 1.333 Å, k = 1.06 as an average value to fit accepted values for ben-

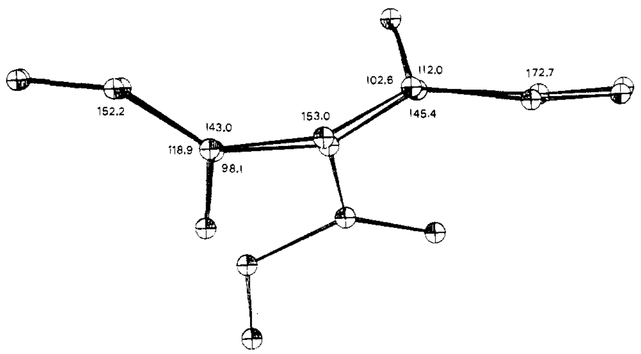

Figure 2. Side view of the molecule showing restricted deviation from planarity of the annulene ring and dihedral angles between least-squares planes.

zene (r_{ij} = 1.397 Å, n_{ij} = 0.667) and graphite (r_{ij} = 1.421 Å, n_{ij} = 0.535).[31]

From the set of new r_{ij} values and the fixed φ_{ij} angles, new values for the resonance integrals were calculated through eq 1; the process was repeated until the absolute change of every β value in two subsequent cycles was less than $0.001|\beta_0|$. The corresponding bond distances for the annulene ring in 7-methoxycarbonyl-*anti*-1,6:8,13-dimethano[14]annulene are reported in the last column of Table VI.

Discussion

The molecule as viewed along the direction corresponding to the maximum moment of inertia of the annulene nucleus is shown in Figure 1. The symmetry of the annulene nucleus C(1)–C(16) in the crystal is fairly close to m (C_s); the highest differences between m-symmetry-related bond distances, bond angles, and absolute values of torsion angles are found to be 0.02 Å, 3.3°, and 5.3°, respectively. These maximum differences are observed between C(6)–C(7), C(5)–C(6)–C(7), C(7)–C(8)–C(9)–C(10) and their m-symmetry-related bonds and angles. Since all the highest deviations are distributed around atom C(7), the distortion from ideal m-molecular symmetry could be ascribed, at least in part, to the methoxycarbonyl group and to packing forces exerted on it by the environment.

A striking feature of our molecule, as well as of *anti*-1,6:8,13-dimethano[14]annulenetricarbonylchromium,[13] besides the nonplanarity of the ring, is the systematic succession of long and short bond distances in the annulene perimeter. These distances correspond to localized single and double bonds, thus explaining the observed polyenic behavior.[6] By contrast, syn-bridged [14]annulenes show aromatic character.[1–5] An interesting comparison can be made considering the following compounds, whose crystal-structure results are at hand: *syn*-1,6:8,13-diepoxy[14]annulene (**1**),[9] 1,6:8,13-propane-1,3-diylidene[14]annulene (**2**),[11] 1,6-methano[10]annulene-2-carboxylic acid (**3**),[7] 1,6:8,13-butane-1,4-diylidene[14]annulene (**4**),[12] 11,11-difluoro-1,6-methano[10]annulene (**5**),[8] and 7-methoxycarbonyl-*anti*-1,6:8,13-dimethano[14]annulene (**6**). Differences between bond lengths in the annulene perimeter increase markedly through compounds **1** to **6**; for this last compound, which is the object of the present paper, there is a sharp split around the mean values of 1.47 and 1.35 Å (for libration-corrected distances).

A single figure which could express numerically the dispersion of bond lengths in the ring around the (gen-

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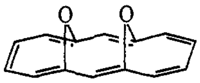
eral) mean value $\bar{r}$, is the sample standard deviation

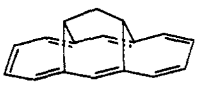
$$\sigma_S = \left[\frac{\sum_{i=1}^{n}(r_i - \bar{r})^2}{n-1}\right]^{1/2}$$

where n is the number of bonds in the ring and r_i the observed bond distances. Here σ_S is calculated as if all the bonds along the perimeter were equivalent; the results are given in column 2 of Table VIII for various compounds.

Table VIII. Comparison between Geometrical Parameters of the Annulene Ring in Related Compounds



1



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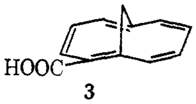

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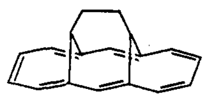

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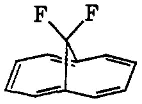

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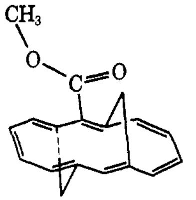

6

Compd	σ_S	$D_{\max}$, Å[a]	$\varphi_{\max}$, deg[a]	Molecular symmetry
1	0.006	0.49	24	*mm2*
2	0.013	0.57	28	*mm2*
3	0.016	0.46	34	*mm2*
4	0.025	0.75	35	*mm2*[b]
5	0.047	0.50	41	*mm2*
6	0.062	0.69	74	*m*

[a] Mean of symmetry related values. [b] Crystallographic symmetry.

With reference to the C(2), C(5), C(9), C(12) plane for bridged [14]annulenes and to the C(2), C(5), C(7), C(10) plane for bridged [10]annulenes, the highest deviation $D_{\max}$ for a perimeter atom is given in the third column of Table VIII. As one can see, the largest value for $D_{\max}$ (**4**) does not correspond to the largest deviations in bond lengths.

The olefinic or aromatic behavior (and the corresponding split in bond length values) can be referred back to the misalignment angles φ_{ij} between the directions of adjacent $2p_z$ carbon orbitals in the ring, rather than to the extent of the deviation of the annulene ring from planarity. The maximum value $\varphi_{\max}$ is reported for the different compounds in column 4 of Table VIII. The jump in $\varphi_{\max}$ from compound **5** to **6** is accompanied by the change from *mm2* (C_{2v}) to *m* (C_s) symmetry. The connection between observed φ_{ij} values and calculated bond distances in the ring can be investigated by means of calculations of the type reported in the preceding paragraph. The same calculation was performed for all the six considered compounds, starting always with all distances equal to 1.40 Å.

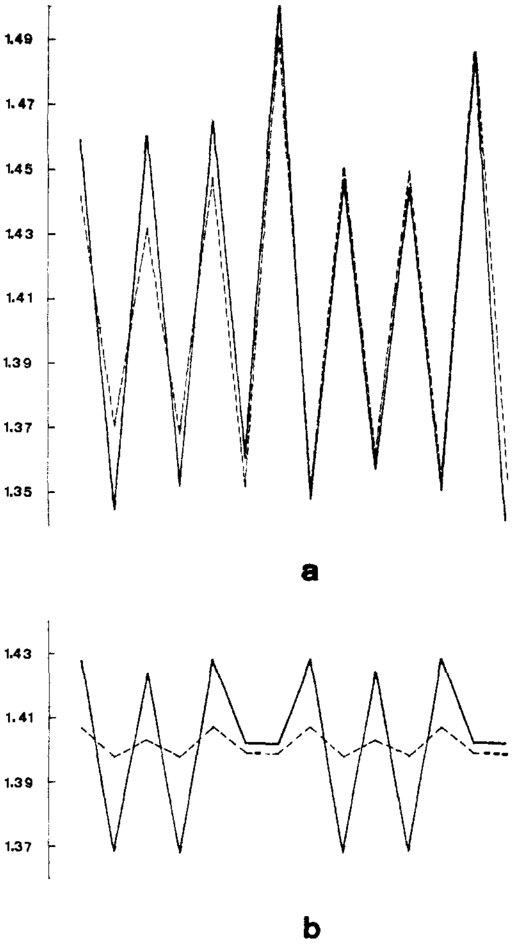

Figure 3. Experimental (solid line) and calculated (dashed line) bond lengths (Å) for bonds C(1)–C(2) to C(14)–C(1) in the annulene ring: (a) compound **6**; (b) compound **4**.

For compounds **1–5** the resulting bond lengths at convergence remain in the range expected for C–C (aromatic) bonds, with mean value (and σ_S) 1.402 (2), 1.402 (2), 1.401 (3), 1.402 (4), 1.401 (6) Å, respectively. For compound **6**, the results are given in the fourth column of Table VI; experimental torsion angles cause a succession of long and short bond distances around mean values of 1.46 and 1.36 Å, in agreement with the experimental results. Because of the succession of different bond lengths in compound **6**, a better evaluation of the agreement between observed and calculated bond distances r could be expressed through a reliability index

$$R_r = \frac{\sum |r_{\text{obsd}} - r_{\text{calcd}}|}{\sum r_{\text{obsd}}}$$

where r_{obsd}'s are the observed bond distances in the ring after rigid-body correction. For compound **6**, the R_r value results in the low figure of 0.8%. The good agreement between calculated and experimental bond distances for compound **6** is also clearly evident from Figure 3a. Not only are long and short experimental distances calculated as long and short, but the quantitative agreement between the two sets of values is extraordinarily good. The results for compounds **1–5** are qualitatively satisfactory in the sense that the calculation predicts all bond distances to be close to the aromatic value. Experimental deviations from the mean value are however higher than the calculated ones. As an example, in Figure 3b the results for compound **4** are reported. The higher value of the experimental deviations as compared to the calculated ones could be in part accounted for by considering the effect of intermolecular forces in the crystal. Besides, the Hückel

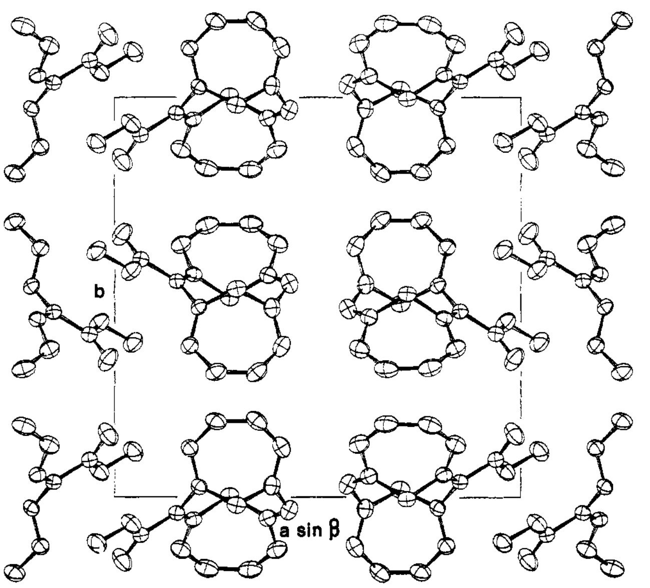

Figure 4. Packing of molecules as viewed along the *c* axis.

method used in our computation is very crude and is more apt to afford qualitative rather than quantitative interpretations. Nevertheless, we are confident that it may be concluded that the internal strain in this series of molecules imposes the aromatic or olefinic behavior through the influence of torsion angles.

(The geometry of the examined compounds **1–6** is considerably different from that of some related compounds, like [14]annulene, 2,7-diacetoxy-*trans*-15,16-dimethyl-15,16-dihydropyrene, and *trans*-15,16-diethyldihydropyrene, which have been the object of recent crystallographic research.[32–34] In all these cases the configuration of the molecular perimeter is not too far from that of pyrene,[35] and misalignment angles φ_{ij} between adjacent $2p_z$ orbitals do not exceed 18° for [14]-annulene[32] and 9° for the other two compounds.[33,34] This is in agreement with the absence of systematic alternation of shorter and longer bonds as found in these compounds on the basis of X-ray diffraction evidence.)

Carbon–hydrogen bond distances are in the range 0.94–1.00 Å (σ 0.03 Å). The nonbonded distances C(1). . .C(6) and C(8). . .C(13) are 2.48 and 2.42 Å (libration corrected values, 2.49 and 2.43 Å), respectively. The range of intermolecular distances is normal. There are only four contacts appreciably shorter than the sum of van der Waals radii (C 1.7, CH_2 2.0, CH_3 2.0, O 1.4, H 1.2 Å).[36]

Atom in *x*, *y*, *z*	With atom	In position	Distance, Å
C(9)	C(18)	$-x, -y, 2 - z$	3.54
C(18)	C(18)	$-x, -y, 2 - z$	3.81
C(15)	H(14)	$-x, -y, 1 - z$	3.05
O(1)	H(16)	$x, -\frac{1}{2} - y, -\frac{1}{2} - z$	2.47

A plotter output of the packing of molecules in the crystal is shown in Figure 4.

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Triethylammonium Tris(*o*-phenylenedioxy)phosphate. Crystal and Molecular Structure[1]

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Abstract: Triethylammonium tris(*o*-phenylenedioxy)phosphate (III) was isolated from the reaction of tris(*o*-phenylenedioxy)cyclotriphosphazene (I) with catechol and triethylamine. Crystals of III are trigonal, space group $P\bar{3}$, with lattice constants of a = 12.046 (13) Å, c = 8.744 (12) Å, and with Z = 2. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to an R value of 0.043 for 529 unique reflections. The phosphorus atom within each spirophosphate anion is bonded octahedrally to six oxygen atoms. A hydrogen atom was unambiguously located within bonding distance of the nitrogen atom in the cation. Important molecular parameters are: P–O = 1.723 (4), 1.706 (4) Å; N–H = 0.94 (8), H . . . O = 2.36 (7) Å, O–P–O(ring) = 91.4 (2)°. The nonbonding transannular O . . . O distance is 2.454 (5) Å.

The unusual ring degradations of spirocyclophosphazenes to spirophosphoranes or spirophosphates in the presence of *o*-aminophenol or catechol and triethylamine have been described previously.[2–6] In one such reaction, tris(*o*-phenylenedioxy)cyclotriphosphazene (I) reacts rapidly with catechol and triethylamine to yield ammonia and a white, crystalline spirophosphorane (II) or spirophosphate (III) anion.[2,3] Some uncertainty existed with respect to the correct

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