AROMATIC AND NON-AROMATIC BRIDGED ANNULENES

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Abstract - The geometry of a number of $\text{[10]}$, $\text{[12]}$, $\text{[14]}$-annulenes of the bridged kind and of related cations has been determined by means of X-ray diffractometry. The results are discussed with respect to physical and chemical properties of these compounds.

INTRODUCTION

Aromaticity is a very controversial concept and quite a number of papers, books and symposia devoted to its definition can be quoted (1). The main source of all difficulties is perhaps the fact that experimentalists have used different properties, such as geometrical features, heats of formation, ring currents, chemical reactivity, to be taken as measure of the aromatic character of molecules. The variety of theoretical approaches to the same problem has contributed to the blurring of our views on this subject. In the present paper the geometries of a number of molecules as determined by X-ray crystal structure analysis are reported.

A few geometrical features can be abstracted from the data, such as planarity of the rings, constancy or variation (with particular attention to alternation) of bond lengths, torsional angles along the rings or others: these quantities can offer some arguments in a discussion of aromaticity. The compounds we have examined belong to one class, that I would like to call annulenes of the Köln type, from the name of the university where they have been synthesized. It is a pleasure here to thank prof. E. Vogel who sent us samples of all the compounds we studied. In some occasions he was kind and capable enough to synthesize a particular molecule at our request.

$\text{[14]}$-ANNULENES

The idea of producing a $\text{[14]}$-annulene with the anthracene-like configuration is confronted with the problem of strong repulsion between the hydrogens replacing the C-C bonds internal to the ring. This difficulty was overcome by replacing each couple of hydrogen atoms with a CH$_2$ bridge, and then connecting the two bridges with another CH$_2$ bridge (2). The resulting molecule is 1,6:8,13-propane-1,3-diyldene$\text{[14]}$annulene, shown in Fig. 1.

![Fig. 1. The geometry of 1,6:8,13-propane-1,3-diyldene$\text{[14]}$annulene](image-url)
calculation of the geometry of an isolated molecule, following by a minimization of the packing energy in the experimental unit cell (3). The two CH bridges could be connected in a number of different ways, and the crystal structure of 1,6:8,13-butane-1,4-diylidene|14|annulene (4), 15,16-dimethyl-1,6:8,13-ethanediylidene|14|annulene (5), 1,6:8,13-pentane-1,5-diylidene|14|annulene (6), 1,6:8,13-cyclopentanediylidene|14|annulene (7) have been solved. The experimental geometries are shown in Figs. 2-5.
Interestingly enough the force field calculation for the butane derivative predicted the molecular \( \text{mm}^2 \) symmetry that was found by experiment. All carbon atoms in the bridges of the five compounds were found in the symmetry plane with respect to the rings, except for the central atom in the pentane bridge. No regular alternation of bond lengths in the C-C bonds along the molecular perimeters was found. The following quantities were defined (8):

\[
\sigma = \left| \sum_i \frac{(r_i - \bar{r})^2}{2} \right|, \quad \phi = \sum_i \phi_i / 14, \quad \Delta = \sum_i d_i / 14
\]

where \( r_i \) are the observed bond lengths in the perimeter, \( \bar{r} \) is the corresponding average value, \( \phi_i \) are the misalignment angles, as measured by torsion angles in the perimeter, \( d_i \) is the distance of each atom from the least squares plane through all the atoms in the perimeter. In the five \( 14 \)-annulenes \( \sigma \) values ranged from 0.019 to 0.090 Å, \( \phi \) values from 12° to 25°, and \( \Delta \) values from 0.54 to 1.98 Å.

THE SYN-, ANTI- PROBLEM

A second way to avoid the repulsion between the internal hydrogen atoms of the two bridges is to place the bridges on opposite sides of the 14-carbon atoms ring, that is in anti position. The hydrocarbon had been prepared by Vogel and coworkers (9), but since it had a low melting point we preferred to investigate its 7-methoxy carbonyl derivative. The geometry and a side view of the molecule are shown in Figs. 6 and 7 (10).
In the anti derivative, in contrast with previously mentioned \(14\) annulenes alternation of carbon-carbon bond length along the perimeter is evident. In a closer examination of its geometrical features it was found that the main difference from the other \(14\) annulenes is not the deviation from planarity, which for example is more pronounced in the butano derivative, but the torsion angles, that go up to 75°. A calculation of bond length along the perimeter was made by means of simple Hückel theory. Input data were bond distances (at the start all were assumed to be equal to 1.40 Å) and experimental torsion angles \(\phi_i\). The resonance integral was

\[
\beta_{ij} = 6.3119 \exp(-1.31876r_{ij})\cos \phi_i
\]

in \(\beta\) units, where \(\beta\) is the resonance integral for two parallel \(2p\) carbon orbitals centered at a distance of 1.397 Å. The standard procedure gave \(\pi\)-electron energies and bond orders. From bond orders the bond lengths were obtained through the Coulson relationship (11). With the new values of bond distances and the fixed experimental values of torsion angles the calculation was repeated, and so forth till consistency was obtained. The final results for the butano and the anti derivative are shown in Fig. 8, where the agreement with the experimental data is more than satisfactory.

The stability shown by the \(14\) annulenes with anthracene-like configuration suggests that this ring can resist the strong repulsion present in syn-bis-methano derivatives. In fact Vogel and coworkers succeeded in the synthesis of syn-1,6:8,13-bismethano\(14\) annulene (12). The geometry of this molecule was calculated by means of Extended Hückel Theory (EHT) (8). The geometry of the ring was thought to be close to that found for the butano derivative and assumed to be equal to that one. The HCH angles were calculated from the
C-C-C angle at the top of the bridges and orthogonality conditions and the total energy was minimized with respect to the geometrical parameters shown in Fig. 9. The results are shown in Fig. 10.

![Fig. 9. Degrees of freedom allowed to methylene groups in syn-1,6:8,13-bisethanoj14|annulene](image)

Fig. 9. Degrees of freedom allowed to methylene groups in syn-1,6:8,13-bisethanoj14|annulene

![Fig. 10. Energy as a function of degrees of freedom shown in Fig. 9.](image)

Fig. 10. Energy as a function of degrees of freedom shown in Fig. 9.

When the crystal structure analysis was performed (13) the experimental geometry turned out to be in a surprisingly excellent agreement with the calculated one (see Fig. 11).

![Fig. 11. The molecule syn-1,6:8,13-bisethanoj14|annulene seen along two principal axes of inertia](image)

Fig. 11. The molecule syn-1,6:8,13-bisethanoj14|annulene seen along two principal axes of inertia

I would like to mention here that in the synthesis of syn-bisethanoj14|annulene, 3,5,8,11-tetrahydro-tricyclo(5,4,1,0^2,7)decac-1,6,9 triene, C_{12}H_{10}Br_{4} was isolated as an intermediate. It was of relevance to an understanding of the reaction to know if in this compound the two CH_{2} groups were syn or anti. A quick crystal structure determination was performed (14) and the anti isomer was found. Other examples of syn derivatives are available. Fig. 12 shows the geometry of syn-1,6:8,13-biscarbonyl14|annulene (15).
In Table 1, Figs. 13 and 14 give geometrical data for syn-4,13:6,11-dimethano15|annulene, a 14π-analog of tropone and Figs. 15 and 16 show geometrical features for syn-5,7-diformyltricyclo(9.4.1.1^3,9)heptadeca-2,4,7,9,11,13,15-heptaaene.

Fig. 12. The geometry of syn 1,6:8,13-biscarbonyl14|annulene

Bond lengths along the ring range between 1.376 and 1.413 Å. A comparison between geometrical parameters of the annulene ring in this and related compounds is shown in Table 1.

**TABLE 1. Comparison between geometrical parameters of the annulene ring in related compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>r(A)</th>
<th>p(A)</th>
<th>τ(A)</th>
<th>D(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn-1,6:8,13-biscarbonyl14</td>
<td>annulene</td>
<td>1.396</td>
<td>0.013</td>
<td>0.20</td>
</tr>
<tr>
<td>syn-4,13:6,11-dimethano15</td>
<td>annulene</td>
<td>1.394</td>
<td>0.012</td>
<td>0.20</td>
</tr>
<tr>
<td>syn-5,7-diformyltricyclo(9.4.1.1^3,9)heptadeca-2,4,7,9,11,13,15-heptaaene</td>
<td>1.393</td>
<td>0.017</td>
<td>0.20</td>
<td>0.024</td>
</tr>
</tbody>
</table>

In Table 1, \( r = \langle r_1 \rangle, \rho = \langle (r_1 - r)^2 \rangle^{\frac{1}{2}}, \tau = \langle \tau_1 \rangle^{\frac{1}{2}}, D = \langle d_1 \rangle^{\frac{1}{2}} \).

Figs. 13 and 14 give geometrical data for syn-4,13:6,11-dimethano15|annulene, a 14π-analog of tropone and Figs. 15 and 16 show geometrical features for syn-5,7-diformyltricyclo(9.4.1.1^3,9)heptadeca-2,4,7,9,11,13,15-heptaaene.

Fig. 13. Bond lengths and angles in syn-4,13:6,11 dimethano15|annulene

Fig. 14. Side view of the molecule shown in Fig. 13
Aromatic and non-aromatic bridged annulenes

Fig. 15. The geometry of syn-5,7-diformyltricyclo(9.4.1.1^3,9)heptadeca-2,4,7,9,11,13,15-heptaene

Fig. 16. Schematic side view of the molecule shown in Fig. 15
Even four CH₂ groups are stable in the syn position as shown in Fig. 17 (18).

Fig. 17. Geometry of C₂₄H₂₀O₂
An interesting problem arises in the case of anti-1,6:8,13-biscarbonyl|₁⁴|annulene (19). The geometry of the molecule is shown in Fig. 18.

Fig. 18. Geometry of anti-1,6:8,13-biscarbonyl|₁⁴|annulene
Apparently there is no bond length alternation along the 14 atoms ring. However there is evidence that the structure could be disordered and that we have in each crystallographic position a 1:1 mixture of a polyenic molecule in two different orientations. The situation is illustrated in Fig. 19. Fig. 19 a) shows in full line the skeleton of anti-1,6:8,13-dimethano 14|annulene as found in the work of Ref. 10. The broken line shows the same molecule rotated by 180°. Fig. 19 b) shows in full line the atomic positions obtained averaging each atom pair and in broken line the skeleton obtained for the bis-carbonyl derivative.

Fig. 19. a) Side view of anti-1,6:8,13-bismethano14|annulene before (full line) and after (broken line) rotation by 180°. b) Average of the position of atom pairs shown in Fig. 19 a) (full line) and side view of anti-1,6:8,13-biscarbonyl14|annulene

Only one example of a 12|annulene will be shown here, namely 4,10-dibromo-1,7-methano12|annulene. The geometry of this molecule is shown in Fig. 20 (20).

Fig. 20. Side view of 4,10-dibromo-1,7-methano12|annulene

In Fig. 21 we report the results for experimental and calculated (by Hückel theory) bond distances in the present molecule and in a number of related cyclic polyenes. The agreement is more than satisfactory. For sake of comparison the same data for butano14|annulene are also shown.

In the field of 10|annulenes a most interesting problem arises, that is the 1-6 interaction. In fact from the spectroscopic study of 1,6-methano10|annulene in solution (23) the existence of a bisnorcaradiene-10|annulene equilibrium was suggested. However the X-ray analysis of a crystal of 11,11-difluoro-1,6-methano10|annulene (24) gave a C-C distance of 2.27 Å, that hardly supports the presence of a significant direct electronic interaction between the two carbon atoms. The geometry of the molecule is shown in Fig. 22; the structure was solved by minimization of the packing energy, and Fig. 23 shows the energy map, where a clear minimum appears. On the other hand when the corresponding 11,11 dimethyl derivative was analyzed a different result came out (25) and the compound had to be described as 11,11-dimethyltricyclo(4,4,1,0^1,6)undeca-2,4,7,9-tetraene. Two molecules were present in the asymmetric unit and their geometries are shown in Fig. 24.
Fig. 21. Experimental (full lines) and calculated (broken lines) bond lengths in annulenes: a) syn-1,6:8,13-bismethanoannulene; b) butano14|annulene; c) 1,7-methano12|annulene; d) cyclooctatetraene (21); e) 16|annulene (22)

Fig. 22. The geometry of 11,11-difluoro-1,6-methano10|annulene

Fig. 23. Map of packing energy for the molecule shown in Fig. 22
The $C_1-C_6$ distance is now 1.83 and 1.77 Å in the two molecules. These are very long and unusual carbon-carbon bond lengths and particular consideration has been given to the thermal parameters of the two bonded atoms. The thermal parameters have quite normal features and no evidence whatsoever is present of the existence of a mixture of annulene and bisnorcaradiene type molecules in the crystal. The reliability of our thermal parameters has also been checked by a lattice dynamic calculation (26). The agreement between calculated and experimental values is shown in Table 2.

**Table 2. Comparison between calculated and observed values of thermal vibration tensors**

<table>
<thead>
<tr>
<th>Compound</th>
<th>First molecule</th>
<th>Second molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3H9</td>
<td>$\Delta A_0$</td>
<td>$\Delta A_1$</td>
</tr>
<tr>
<td>C3H9</td>
<td>$\Delta A_2$</td>
<td>$\Delta A_3$</td>
</tr>
<tr>
<td>C3H9</td>
<td>$\Delta A_4$</td>
<td>$\Delta A_5$</td>
</tr>
<tr>
<td>C3H9</td>
<td>$\Delta A_6$</td>
<td>$\Delta A_7$</td>
</tr>
<tr>
<td>C3H9</td>
<td>$\Delta A_8$</td>
<td>$\Delta A_9$</td>
</tr>
</tbody>
</table>

The different behaviour of the difluoro and dimethyl derivatives can be understood by examination of Walsh orbitals in cyclopropane. The introduction of $\pi$-electron acceptor substituents at carbon 1 makes the $C_2-C_3$ bond stronger and the $C_1-C_2$ and $C_1-C_3$ bonds weaker, while the introduction of $\pi$-electron donating substituents weakens all the bonds in the ring. Ab initio molecular orbital calculations for the model molecules cyclopropane, 1,1-difluorocyclopropane, and 1,1-dimethylcyclopropane with geometry optimization confirmed the qualitative trend. EHT calculations for the difluoro and dimethyl derivatives with both experimental geometries have shown the annulenic form to be more stable than the norcaradienic form in the case of the difluoro compound and vice versa for the dimethyl compound (8). Further evidence of the existence of a bisnorcaradienic structure was obtained from the analysis of 11-methyltricyclo[4.4.1.0^2,5]undec-2,4,7,9-tetraene-11-carbonitrile (27). Again there are two independent molecules in the asymmetric unit. The
geometry of one of them is shown in Fig. 25.

![Fig. 25. The geometry of 11-methyltricyclo(4.4.1.0^1,6)undeca-2,4,7,9-tetraene-11-carbonitrile](image)

The C-C distance in the two molecules is 1.85 and 1.78 Å. The C-C bond can be described as a weak oscillator, as suggested by examination of the electron difference map for the plane C_1-C_6-C_11 shown in Fig. 26.

![Fig. 26. Difference map for the C_1-C_6-C_11 plane of the two molecules A and B in the asymmetric unit of the compound shown in Fig. 25. Solid line positive, dashed lines negative](image)

ANNULENIUM CATIONS

A controversial subject is the structure of bicyclo(5.4.1)dodecapentaenylium ion synthesized by Vogel and coworkers (28). The compound has been considered a perturbed [11]annuleniunm cation on the basis of its U.V. spectrum (29) or a perturbed benzohomotropenylium ion, after the analysis of its N.M.R. spectrum (30). A preliminary crystal structure determination of the hexafluorophosphate of the cation gave a C_6-C_9 distance of about 2.30 Å (see Fig. 27), in favour of the annulenic structure (31). It seemed however that the problem deserved a very careful study of the geometry. Three salts of the same cation have been examined, namely the hexafluorophosphate, the tetrafluoroborate and the hexafluoroantimonate at room temperature and at 110°C.
All these crystals were affected by disorder and use had to be made of a special program for refinement with constrains (32). The disorder is due to the two possible orientations of the cation, rotated by 180°. Figs. 28 and 29 in which the electron density maps viewed in the direction perpendicular to the ring plane are reported for the tetrafluoroborate and the hexafluorophosphate salts respectively, show very clearly the improvement in the resolution (33).

The value of the C-C₆ distance has been completely confirmed and also the conclusions about the structure of the cation.
Recently an analog of the previously mentioned compound was synthesized (34), tricyclo(9.4.1.1^3,9)heptadecaheptaenylium tetrafluoroborate. No disorder was present in the crystal of this derivative and so the geometry of the 15|annulenium cation was quickly determined (35). It is reported in Fig. 30.

Fig. 30. The geometry of the 15|annulenium cation

The C1-C11 and C-C0 interactions are negligible, since the related distances are 2.32 and 2.43 Å.

In Table 3 a comparison of the geometrical parameters $\tau$, $\phi$, and $\tau$ previously defined for the two cations and two annulenes with bond length alternation is reported.

TABLE 3. A comparison of geometrical parameters of the annulene ring in related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau(\AA)$</th>
<th>$\phi(\AA)$</th>
<th>$\tau(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.389</td>
<td>0.016</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>1.397</td>
<td>0.034</td>
<td>18.7</td>
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<td></td>
<td>1.404</td>
<td>0.042</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>1.411</td>
<td>0.052</td>
<td>30.2</td>
</tr>
</tbody>
</table>

CONCLUSIONS

A number of geometries for annulenic compounds of the Köln type has been reported. They show quite a variety of situations. Different geometrical parameters can be derived and used as a definition of aromaticity. The choice of a particular parameter and its limiting value for aromatic compounds can be a matter of preference. Of course other physical properties could be measured by different experimental techniques and used to the same purpose. It is regrettable that at the moment such very interesting compounds have been prepared in small amounts so that very little is known about their chemistry. It can be expected that to the different geometrical situations very diversified chemical behaviour would correspond.

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