

AROMATIC AND NON-AROMATIC BRIDGED ANNULENES

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Abstract - The geometry of a number of $|10|$ -, $|12|$ -, $|14|$ -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.

$|14|$ -ANNULENES

The idea of producing a $|14|$ -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-diylidene $|14|$ annulene, shown in Fig. 1.

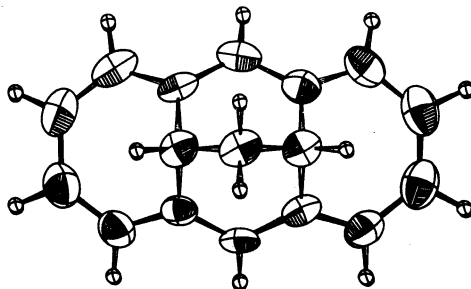


Fig. 1. The geometry of 1,6:8,13-propane-1,3-diylidene $|14|$ annulene

At the time of this study we had not yet at hand efficient direct method programs, so the crystal structure has been solved by means of a force field

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_2 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-cyclopentanediyliidene|14|annulene (7) have been solved. The experimental geometries are shown in Figs. 2-5.

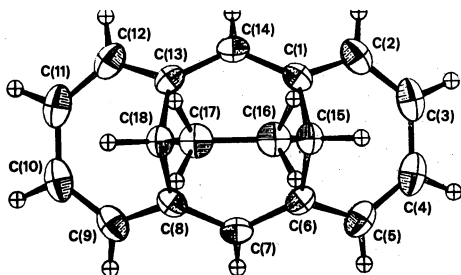


Fig. 2. The geometry of 1,6:8,13-butane-1,4-diylidene|14|annulene

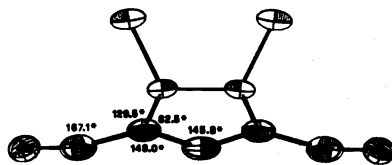
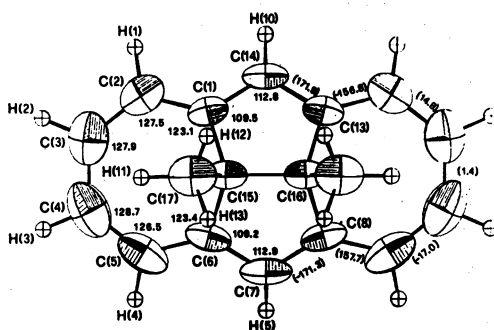
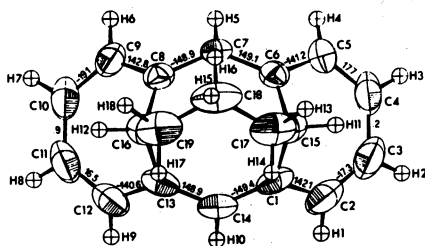
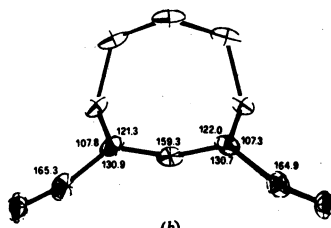


Fig. 3. The geometry of 15,16-dimethyl-1,6:8,13-ethanediylidene|14|annulene



(a)



(b)

Fig. 4. The geometry of 1,6:8,13-pentane-1,5-diylidene|14|annulene

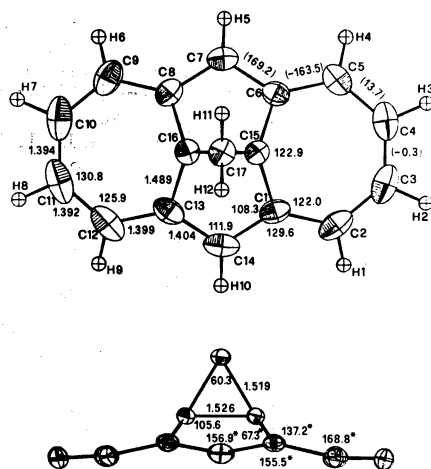


Fig. 5. The geometry of 1,6:8,13-cyclopropanediylidene|14|annulene

Interestingly enough the force field calculation for the butane derivative predicted the molecular 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):

$$\sigma = \left| \sum_i (r_i - \bar{r})^2 \right|^{\frac{1}{2}}, \quad \phi = \sum_i \phi_i / 14, \quad \Delta = \sum_i |d_i| / 14$$

where r_i are the observed bond lengths in the perimeter, \bar{r} is the corresponding average value, ϕ_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 σ values ranged from 0.019 to 0.090 Å, ϕ values from 12° to 25°, and Δ 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).

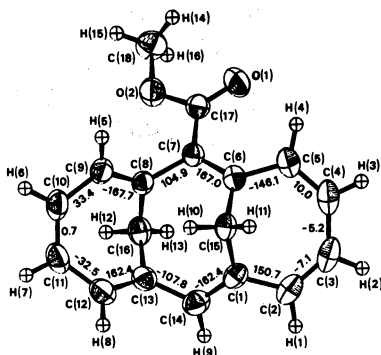


Fig. 6. The geometry of 7-methoxycarbonyl-anti-1,6:8,13-dimethano|14|annulene

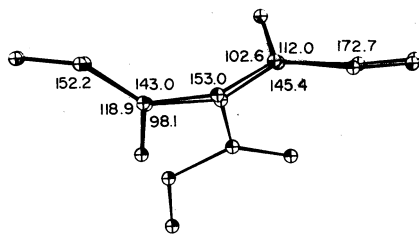


Fig. 7. Side view of the molecule shown in Fig. 6

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 \AA) and experimental torsion angles ϕ_i . The resonance integral was

$$\beta_{ij} = 6.3119 |\exp(-1.31876r_{ij})| \cos \phi_i$$

in β_0 units, where β_0 is the resonance integral for two parallel $2p_z$ carbon orbitals centered at a distance of 1.397 \AA . The standard procedure gave π -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.

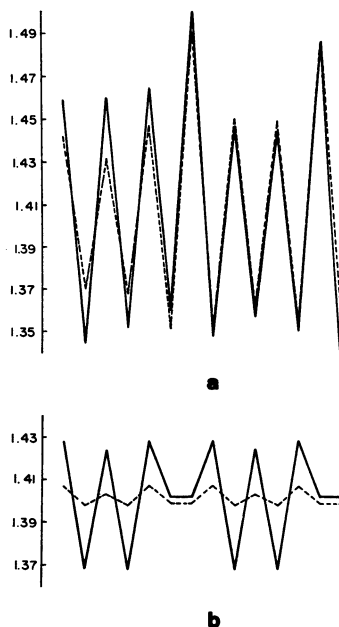


Fig. 8. Experimental (solid line) and calculated (dashed line) bond lengths (\AA) along the ring for anti (a) and butano (b) derivatives

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.

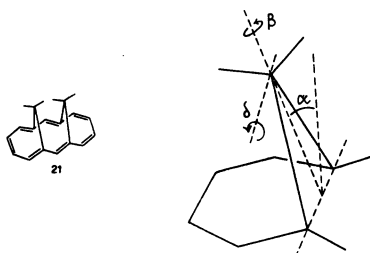


Fig. 9. Degrees of freedom allowed to methylene groups in syn-1,6:8,13-bismethano[14]annulene

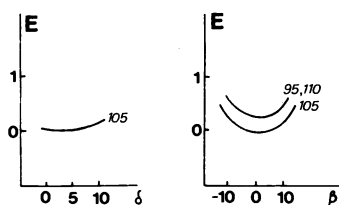


Fig. 10. Energy as a function of degrees of freedom shown in Fig. 9.

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).

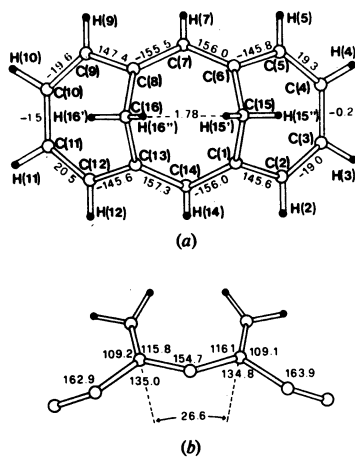


Fig. 11. The molecule syn-1,6:8,13-bismethano[14]annulene seen along two principal axes of inertia

I would like to mention here that in the synthesis of syn-bismethano[14]annulene, 3,5,8,11-tetrabromo-tricyclo(5,4,1,0^{3,5})dodeca-1,6,9 triene, C₁₂H₁₀Br₄ was isolated as an intermediate. It was of relevance to an understanding of the reaction to know if in this compound the two CH₂ 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-biscarbonyl[14]annulene (15).

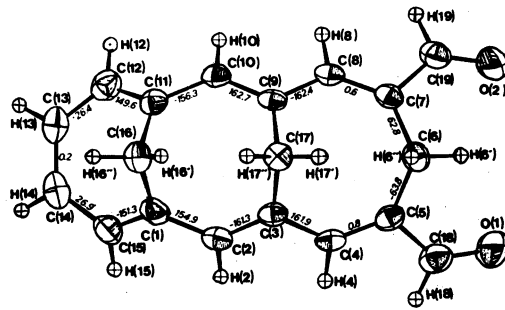


Fig. 15. The geometry of syn-5,7-diformyltricyclo(9.4.1.1^{3,9})heptadeca-2,4,7,9,11,13,15-heptaene

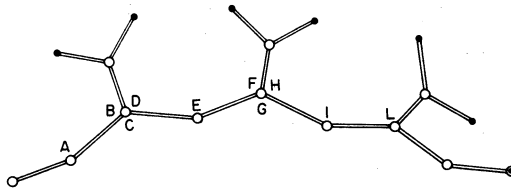


Fig. 16. Schematic side view of the molecule shown in Fig. 15

Even four CH₂ groups are stable in the syn position as shown in Fig. 17 (18).

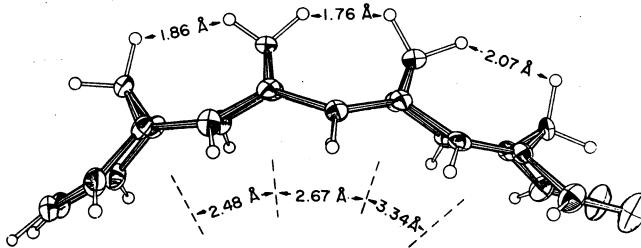


Fig. 17. Geometry of C₂₄H₂₀O₂

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.

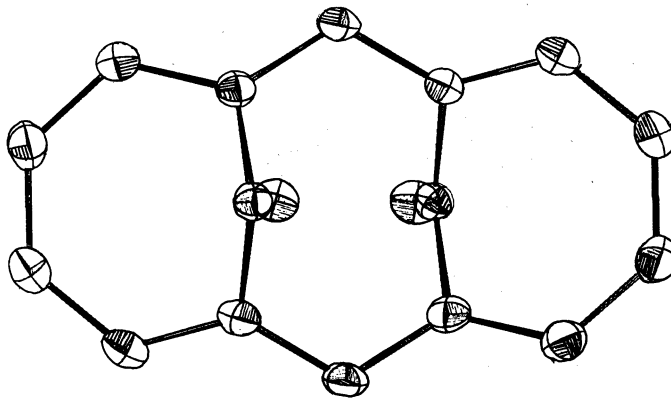


Fig. 18. Geometry of anti-1,6:8,13-biscarbonyl|14|annulene

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.

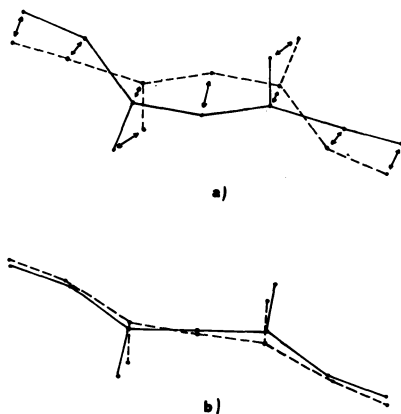


Fig. 19. a) Side view of anti-1,6:8,13-bismethano|14|annulene before (full line) and after (broken line) rotation by 180°. b) Average of the position of atom pairs shown in Fig. 19 a) (full line) and side view of anti-1,6:8,13-biscarbonyl|14|annulene

|12|-ANNULENES

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

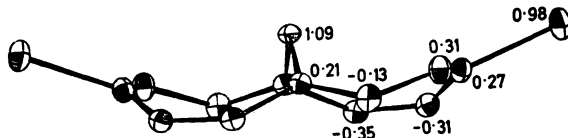


Fig. 20. Side view of 4,10-dibromo-1,7-methano|12|annulene

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 butano|14|annulene are also shown.

|10|-ANNULENES

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-methano|10|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-methano|10|annulene (24) gave a C₁-C₆ 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.

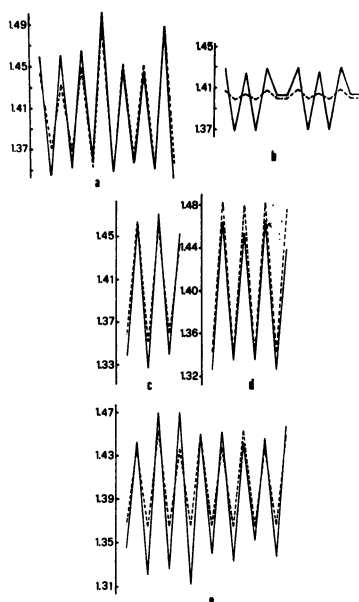


Fig. 21. Experimental (full lines) and calculated (broken lines) bond lengths in annulenes: a) syn-1,6;8,13-bismethanoannulene; b) butano|14|annulene; c) 1,7-methano|12|annulene; d) cyclooctatetraene (21); e) |16|annulene (22)

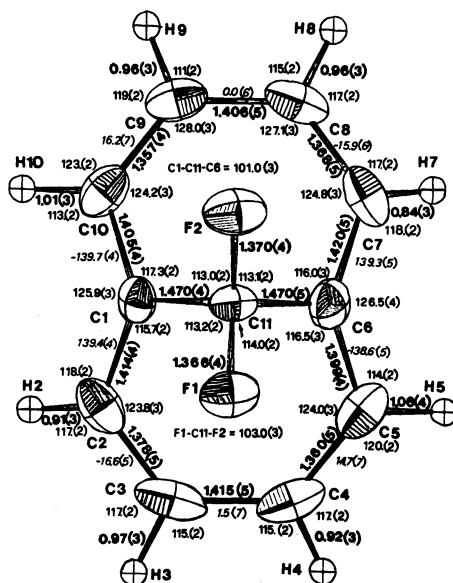


Fig. 22. The geometry of 11,11-difluoro-1,6-methano|10|annulene

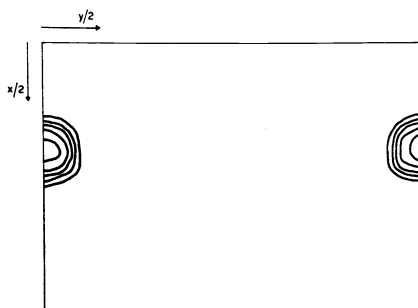


Fig. 23. Map of packing energy for the molecule shown in Fig. 22

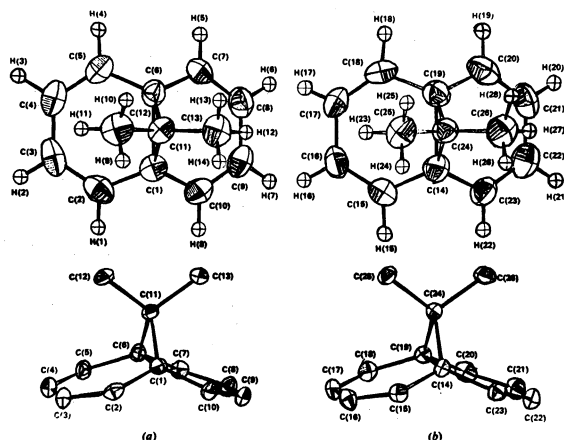


Fig. 24. Geometry of the two molecules in the asymmetric unit of a crystal of 11,11-dimethyltricyclo(4.4.1.0^{1,6})undeca-2,4,7,9-tetraene

The C₁-C₆ 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

First molecule							Second molecule							
Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃	Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃	U (Å ²)
C(1)	calc. 161	247	91	89	45	55	C(14)	149	191	85	54	35	30	
	obs. 187	212	97	111	28	34		147	231	86	80	11	34	
C(2)	178	272	144	85	77	74	C(15)	170	232	109	62	61	35	
	205	248	134	124	81	74		178	264	101	111	44	43	
C(3)	148	305	180	58	50	40	C(16)	158	250	145	36	59	34	
	122	269	189	67	42	32		143	268	144	61	47	52	
C(4)	158	361	140	97	0	5	C(17)	185	227	137	25	30	5	
	156	310	159	110	-11	13		174	203	127	35	5	0	
C(5)	182	138	94	132	12	58	C(18)	213	229	105	68	36	4	
	184	308	82	141	2	21		247	242	86	132	26	1	
C(6)	151	243	84	94	32	47	C(19)	168	225	87	77	43	35	
	135	259	81	99	18	25		147	215	94	93	31	34	
C(7)	172	320	106	120	58	88	C(20)	191	309	134	122	77	71	
	163	255	96	93	55	49		229	277	140	158	94	76	
C(8)	156	380	141	127	62	113	C(21)	154	372	170	105	55	98	
	140	309	129	99	44	52		145	343	183	119	52	92	
C(9)	172	394	136	143	39	111	C(22)	156	327	134	47	6	82	
	159	305	125	133	0	38		171	309	134	75	-16	40	
C(10)	197	331	108	131	44	95	C(23)	179	240	92	42	17	30	
	203	265	98	129	12	56		176	239	85	61	5	19	
C(11)	177	229	91	91	32	34	C(24)	174	232	94	81	34	51	
	168	203	82	105	16	21		141	208	81	88	22	27	
C(12)	247	315	130	172	41	39	C(25)	222	362	134	142	14	75	
	240	290	128	179	51	36		195	293	120	131	-10	46	
C(13)	231	246	134	65	9	16	C(26)	236	262	135	87	63	95	
	214	212	121	96	13	4		232	247	118	101	36	63	
Molecular vibration tensors (x 10 ³)							Molecular vibration tensors (x 10 ³)							
T(A ²)	calc. 0	35		obs. 359	40	7	T(A ²)	calc. -51	40		obs. 365	34	4	
	350	420	13		351	-8		354	421	-11		373	-29	
			384			357							353	
L(rad ²)	51	-10	-7		44	-9	L(rad ²)	53	9	-7		40	11	-3
		53	-5			7			53	0			62	-4
			43			34								36
B(A rad)	0	-4	-8		(2)	7	B(A rad)	0	13	0		(-4)	-3	-5
	10	-25	11		18	(-6)			-15	-18		-18	(-7)	-12
		-11	-5	19		-11			-2	3	13		1	0

The different behaviour of the difluoro and dimethyl derivatives can be understood by examination of Walsh orbitals in cyclopropane. The introduction of π -electron acceptor substituents at carbon 1 makes the C₂-C₃ bond stronger and the C₁-C₂ and C₁-C₃ bonds weaker, while the introduction of π -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^{1,6})undeca-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.

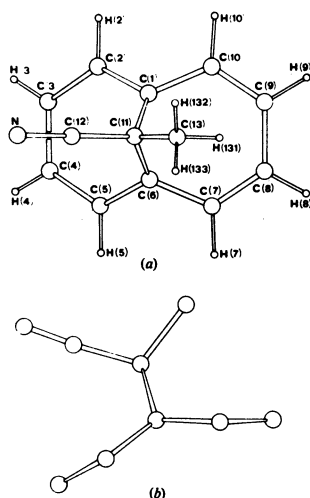


Fig. 25. The geometry of 11-methyltricyclo(4.4.1.0^{1,6})undeca-2,4,7,9-tetraene-11-carbonitrile

The C₁-C₆ distance in the two molecules is 1.85 and 1.78 Å. The C₁-C₆ bond can be described as a weak oscillator, as suggested by examination of the electron difference map for the plane C₁-C₆-C₁₁ shown in Fig. 26.

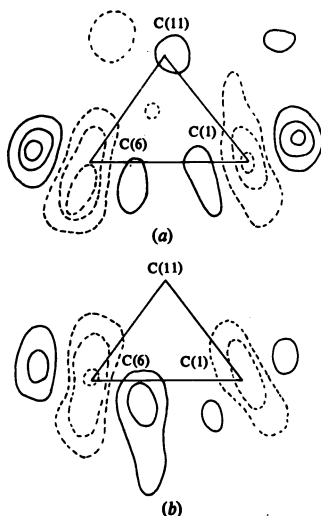


Fig. 26. Difference map for the C₁-C₆-C₁₁ plane of the two molecules A and B in the asymmetric unit of the compound shown in Fig. 25. Solid line positive, dashed lines negative

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]annulenium cation on the base 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 C₁-C₆ 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 K

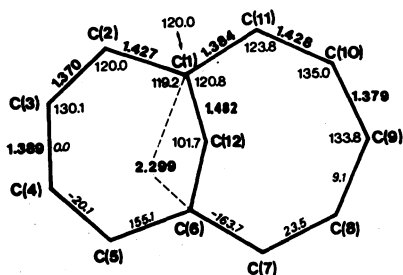


Fig. 27. A schematic representation of the |11|annulenium cation geometry

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).

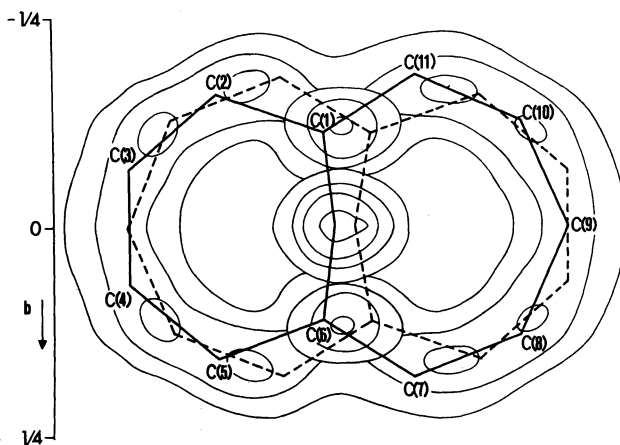


Fig. 28. Electron density map for the |11|annulenium cation in the plane of the ring

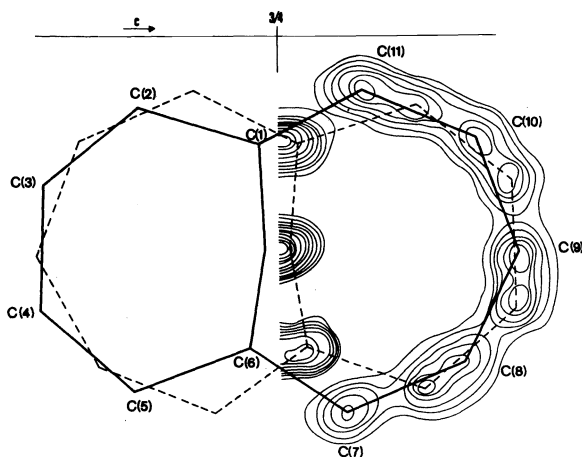


Fig. 29. Same as in Fig. 28, after refinement with constrains

The value of the C_1-C_6 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.

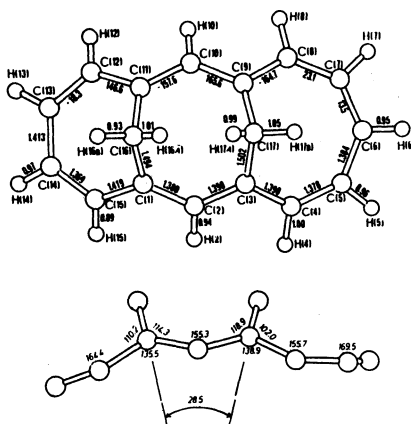


Fig. 30. The geometry of the |15|annulenium cation

The C₁-C₁₁ and C₃-C₉ interactions are negligible, since the related distances are 2.321 and 2.43 Å.

In Table 3 a comparison of the geometrical parameters \bar{r} , ϕ , and τ 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

Compound				
\bar{r} (Å)	1.389	1.397	1.404	1.411
ϕ (Å)	0.016	0.024	0.042	0.052
τ (°)	20.4	18.7	26.2	30.2

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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