318. Extended *Hückel* Molecular Orbital Calculations for the Bridged Annulenes

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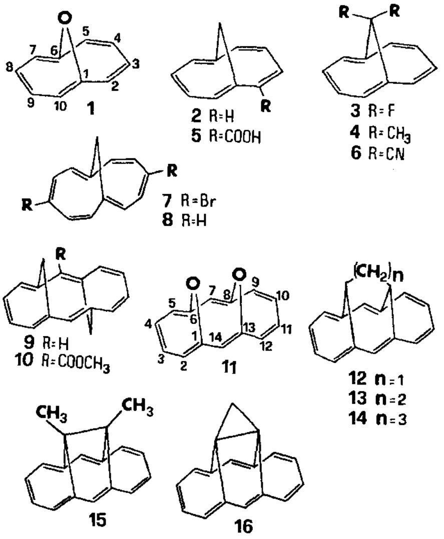
Summary. Extended *Hückel* molecular orbital calculations have been performed for bridged [10], [12] and [14]annulenes. Orbital energies and wave functions were used to investigate the relative stabilities of different geometries. The theoretical results were also used to reinforce and complement available experimental information about aromaticity and reactivity of this series of molecules. Some spectroscopic properties are also discussed.

As an increasing body of experimental evidence of various kinds is being collected about the bridged annulenes (see *Scheme 1*), we thought it interesting to calculate the extended *Hückel* [1] molecular orbitals of these compounds, to obtain informations about aromaticity and reactivity. Theoretical studies can support the experimental investigations, and become more and more important as experiment becomes more and more arduous. The merits of Extended *Hückel* Theory (EHT) in calculating molecular properties from known geometries, and in the field of chemical reactivity have been explored [2] and reviewed [3]. Moreover, due to the size of these molecules, more sophisticated MO methods become extremely expensive.

Standard parameters were used in the calculations: Table 1 collects them. The geometries of all the compounds have been obtained starting from X-ray crystal data; where needed, small geometrical adjustments were made to impose to each molecule the symmetry to which it was closer. For the compounds whose crystal

Scheme 1



structures were not available, the geometries have been obtained starting from those of closely related compounds. Table 2 collects the symmetry information for each compound. The positions of the hydrogen atoms were calculated using distances of 1.0 Å for the ring hydrogen atoms, and 1.1 Å for other hydrogen atoms. The ring C–H bonds pointed along the bisector of the C–C–C angle, other C–H bonds along directions reasonably chosen for each case (see [4] for more details).

Table 1. *EHT parameters*

Atomic species	Exponent	α_s	α_p
H	1.0	−13.6	—
C	1.625	−21.4	−11.4
N	1.95	−27.5	−14.49
O	2.275	−35.3	−17.76
F	2.6	−34.5	−12.96
Cl	2.033	−25.29	−13.99
Br	2.054	−24.05	−12.52

Table 2. *General data for the compounds considered* (see *Scheme 1*)

Compound number	Name	Molecular symmetry	Ref. for crystal structure	Ref. for synthesis and properties
1	1,6-epoxy[10]annulene	C_{2v}	[8]	[10]
2	1,6-methano[10]annulene	C_{2v}	—	[11] [12]
3	11,11-difluoro-1,6-methano[10]annulene	C_{2v}	[5]	[12]
4	11,11-dimethyl-1,6-methano[10]annulene	C_{2v}	[6]	[12]
5	1,6-methano[10]annulene-2-carboxylic acid	C_{2v}	[7]	—
6	11,11-dicyano-1,6-methano[10]annulene	C_{2v}	—	[12]
7	4,10-dibromo-1,7-methano[12]annulene	C_2	[22]	—
8	1,7-methano[12]annulene	C_2	—	[21]
9	*anti*-1,6:8,13-dimethano[14]annulene	C_s	—	[32]
10	7-methoxycarbonyl-derivative of **9**	none	[23]	—
11	*syn*-1,6:8,13-diepoxy[14]annulene	C_{2v}	[24]	[33]
12	1,6:8,13:15,16-Trimethano[14]annulene	C_{2v}	[25]	[34]
13	1,6:8,13-Dimethano-15,16-ethano[14]annulene	C_{2v}	[26]	[35]
14	1,6:8,13-Dimethano-15,16-propano[14]annulene	C_{2v}a)	[27]	[36]
15	15,16-Dimethyl-1,6:8,13-dimethano-15,16-nullo[14]annulene b)	C_{2v}	[28]	[37]
16	1,6:8,13:15,16-Trimethano-15,16-nullo[14]annulene	C_{2v}	[29]	[38]

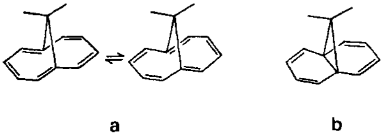
a) For **14**, the symmetry does not include the atoms of the bridge.

b) The editorial board would like to suggest for this case the following innovation of nomenclature: with the purpose of maintening the analogy to annulenes the bridge inthe compounds **15** and **16** is called 'nullo' (in analogy to methano, ethano a.s.a.). Otherweise this compounds should be named as tricyclohexadecaheptaen resp. as tetracycloheptadecaheptaen derivatives, wich name does not permit direct correlation to annulenes.
If this suggestion should be accepted from IUPAC, the prefixe 'nulla' would also be of some advisability for naming complicated compounds, for example for 'nido' compounds as derivatives of the corresponding 'closo' compounds, the latter having often a trivial name.

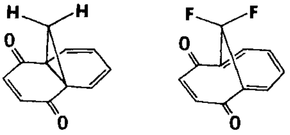
1. The [10]annulenes. – 1.1. *Geometries.* The X-ray crystal structures of **3**, **4** and **5** are available [5–7]. A communication on the unrefined crystal structure of **1** confirms its annulenic structure [8]. Therefore, good data are available to model the geometries of all the [10]annulenes shown in *Scheme 1*, both in the annulenic and norcaradienic form.

1.2. *Annulene-bisnorcaradiene equilibrium.* The bridged [10]annulenes can in principle exist in two forms (*Scheme 2*, **a** and **b**). Which of the two forms is more stable depends on the nature of the substituents at C_{11}. In keeping with the substituents effects on the strength of a cyclopropane bond [2] [9], the annulenic form **a** is more stable when the bridge hydrogen atoms are replaced by π-electron-releasing groups; on the contrary, π-electron-withdrawing substituents stabilize the norcaradienic form **b**. Discussion of this point has been given by *Vogel et al.* for compounds **1**–**4**, in the papers describing their synthesis and properties [10–12]. For **2**, further spectroscopic evidence has been given [13] [14] in favour of the annulenic form. All the available experimental data on the relative stability of the two forms in various compounds is given in Table 3. Another example comes from the structural assignments [15] shown in *Scheme 3*. A calculation of the relative energies of the two forms for some representative compounds seemed interesting. The X-ray ring geometries of **3** and **5** are quite similar, so that either of them can be used to model the annulenic form of the 10-membered ring. The X-ray geometry of **4** was used to model the norcaradienic, or tetraenic, form of the ring. The substituents were then placed on the bridging carbon atom for each of the two forms. Table 3 collects the results of the calculations.

Scheme 2



Scheme 3



The substituents effect is evident in what concerns the strength of the 1–6 bond (see below); agreement with experiment in what concerns the relative stabilities of the two forms is obtained in all cases, except for the parent hydrocarbon. It is not likely that the reasons of this failure lie in a different geometry for the compound, since both **3** and **5** confirm the same structure for the 10-membered ring, and the energy difference between the two forms was tested to be scarcely sensitive to small

Table 3. *Stability of the annulenic and norcaradienic forms in the bridged [10]annulenes*

Substituents at C_{11}	Experimentally more stable	Calculated Relative Energies (eV)	
		annulenic	norcaradienic
H, H	annulenic[a][b][c]	0.0	−0.73
H, CH_3	annulenic[a]	—	—
CH_3, CH_3	norcaradienic[a][d]	0.0	−1.82
H, CN	annulenic[a]	—	—
CN, CN	norcaradienic[e]	0.0	−0.74
CH_3, CN	norcaradienic[c]	–	–
F, F	annulenic[a][f]	0.0	+0.42
Cl, Cl	mixture[a]	—	—
Br, Br	mixture[a]	—	—

[a] NMR. spectra and general discussion: see [12a].
[b] PE. spectroscopy: see [14].
[c] Spectroscopic evidence: see [13].
[d] Crystal structure: see [6].
[e] Most probable isomer; see [12a].
[f] Crystal structure: see [5].

geometrical distortions. The hydrocarbon is however correctly predicted to be intermediate in behaviour between the difluoro and dimethyl derivatives.

Table 4 collects some more calculated properties of the bridged [10]annulenes. Since overlap populations [16] between atoms 1 and 6 are of particular interest, they are collected separately in Table 5. In this Table are also reported the 1–6 overlap populations for the cation of [11]annulene, a 10-π-electron system that behaves like an aromatic [10]annulene.

1.3. *Reactivity.* It is known [12b] that **2** gives 2-derivatives upon electrophilic substitution. A quantitative kinetic study [17] for the protiodetritiation of **3** is clearly in favour of reaction at position 2. It has also been stated that this result is rationalizable on the basis of reaction in the norcaradienic form, judging from the different number of resonance formulae that can be written for the cations in the two cases [17].

A discussion of reactivity towards electrophilic substitution in terms of the EHT charges on the perimeter carbon atoms reported in Table 4 cannot be attempted. However, although some well known shortcomings of EHT when dealing with charged

Table 4. *Some calculated properties of the bridged [10]annulenes*

Compound number[a]	Bond overlap populations			Charges		
	1–2	2–3	3–4	q_1	q_2	q_3
1	1.06	1.05	1.01	0.68	−0.18	−0.16
2a	1.03	1.08	1.00	0.18	−0.19	−0.19
2b	0.93	1.18	0.94	0.17	−0.17	−0.20
3a	0.99	1.12	0.96	0.13	−0.15	−0.20
3b	0.91	1.18	0.93	0.13	−0.15	−0.21
4a	1.01	1.12	0.96	0.14	−0.18	−0.17
4b	0.93	1.18	0.93	0.13	−0.17	−0.20
6a	1.01	1.11	0.96	0.23	−0.16	−0.19
6b	0.93	1.17	0.94	0.23	−0.16	−0.19

[a] a means annulenic, b norcaradienic form (see *Scheme 2*).

Table 5. *Some EHT bond overlap populations*

Atoms	Compound a)	Overlap population	Bond distance
1 and 6	**2a**	0.04	2.26
	3a	0.04	2.27
	4a	0.05	2.27
	6a	0.06	2.27
	2b	0.32	1.83
	3b	0.30	1.83
	4b	0.32	1.83
	6b	0.34	1.83
	cation of 1,6-methano-[11]annulene b)	0.02	2.30
C–C	ethane	0.67 c)	1.54 c)
C–C	cyclopropane	0.63 c)	1.54 c)
1 and 11	**2a**	0.77	1.51
	2b	0.70	1.51
9 and 10	naphthalene	1.02 c)	1.34 c)

a) See Footnote a) of Table 4.

b) Geometry from *R. Destro, T. Pilati & M. Simonetta,* J. Amer. chem. Soc. *98,* 1999 (1976).

c) See [1].

species [3] [18] disallow energy comparisons between charged and uncharged species, so that no idea of the activation energy for protonation can be obtained, the relative stabilities of the various cations arising from protonation at various positions can be computed. Table 6 reports the results.

The geometries of the substrates have been obtained from those of **2**, **3** and **4**. The two C-H bonds involving the protonated carbon atom have been placed along directions determined according to the previously mentioned rules [4]. From inspection of Table 6, it is seen that protonation at position 2 is unfavourable for **2a** and **3b**; this is in contrast with the resonance argument mentioned above. No general conclusions about the reactivity of the two compounds can be drawn, since the most favourable intermediates for protonation at position 2 or 3 differ by only 0.04 and 0.06 eV for **2** and **3** respectively.

Table 6. *Relative stabilities of various cations arising from protonation of the bridged [10]annulenes* **2** and **3** (**a** and **b**). No formal double bonds have been drawn. The zero has been taken as the energy of the most stable cation for each compound, so that there is no relationship between zeroes for different compounds

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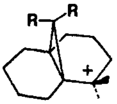
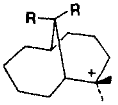
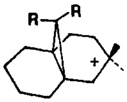
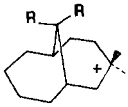
	0.04	0.42		0.49	0.06
	0.11	0.10		0	0

The discussion of reactivity by considering the relative stabilities of the intermediate cations has some connections with the older theories on localization energies [19], *i. e.* the energies needed to localize two electrons of the π-system to form the bond with the electrophile in the activated complex. However, the enlargement of the basis set to all valence orbitals implies that the perturbation is not traced back to a perturbation of the π-system only, and energy differences between the various cations are smeared over a large number of MO's, including σ-type MO's. In this way, care is taken of the puckering in the bridged annulenes, that reduces the σ–π separation.

1.4. *Orbital shapes.* Fig. 1 shows the shapes and energies of some frontier MO's of the [10]annulenes. The LUMO for all compounds is a pure *Hückel* MO of the perimeter. For **2a**, **2b**, **1** and **6b** the HOMO is an almost pure bonding *Hückel* MO. The HOMO for **3a** and **4b**, on the contrary, includes significant contributions from the atoms of the bridge: for **4b**, it is a combination of an antibonding *Hückel* orbital of the perimeter with a ($\pi_{CH_3} - p + \pi_{CH_3}$) MO of the CH_3CCH_3 fragment (see Fig. 1), while for **3a** it is a combination of the same *Hückel* orbital with the highest-lying π orbital of

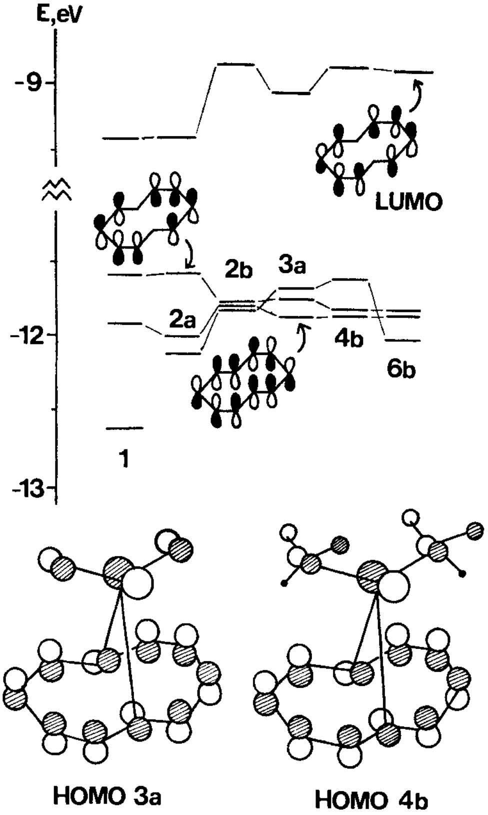


Fig. 1. *Energies and shapes of some MO's in the bridged [10]annulenes.* The thin lines correlate MO's with the same sequence of signs in the perimeter p_z orbitals.

the CF_2 fragment. A similar MO, including a contribution from the p orbital of the CH_2 group, is present in **2** at lower energies.

These results can be compared with a *Hückel*-MO investigation of the ordering of the π-orbitals of the bridged [10]annulenes [20].

2. The non-aromatic [12]annulenes. – As predicted by *Hückel's* rule, the [12]annulene **8** is an olefinic compound [21], with a barrier of 5 kcal/mol for the interconversion between the two possible alternant forms. The crystal structure of **7**, the 4,10-dibromo derivative of **8**, confirms this [22]. The EHT bond overlap populations alternate as expected along the perimeter. Halogen substitution has no significant effect on the π-system, and replacing hydrogen by F, Cl or Br produces only the expected charge shift between carbon and halogen. Thus, the dibromo derivative **7** is representative of the properties of the hydrocarbon **8**.

3. The [14]annulenes. – 3.1. *Geometries.* The crystal structures of compounds **10–16** are known [23–29]. The geometry of **9** has been obtained from that of **10**.

3.2. *Aromaticity.* It has been pointed out that aromaticity is often an elusive concept [30]. Various criteria have been proposed to define it: a) the amount of resonance energy; b) the chemical reactivity; c) the appearance of a diamagnetic ring current [31]; d) conformational criteria. We shall discuss these last first, since a satisfactory amount of evidence is available from X-ray crystal data. It will be shown that there are some EHT quantities that reflect these conformational criteria of aromaticity.

From the standpoint of molecular conformation, the relevant parameters that influence aromaticity are bond alternation and the misalignment angles between adjacent orbitals, this last factor being related to the deviation of the π-system from planarity. To quantify these concepts on the basis of the available structural data we define

$$\sigma = \left[\sum_i (r_i - \bar{r})^2\right]^{1/2}, \quad \varphi = \sum_i \varphi_i/14, \quad \Delta = \left[\sum_i d_i^2\right]^{1/2}$$

in which r_i are the observed bond lengths in the annulene perimeter, and $\bar{r}$ is the corresponding average value; φ_i are the misalignment angles, as measured by the torsion angles in the annulene perimeter; d_i is the distance of each atom from the least-squares plane through all the atoms in the perimeter.

EHT allows the calculation of the bond overlap populations through *Mulliken's* population analysis [16]. These quantities are sensitive to both bond length variations and misalignment angles, through their dependence from the involved overlap integrals. We define

$$\Delta P = \left[\sum_i (P_i - \bar{P})^2\right]^{1/2}$$

where the P_i's are the overlap populations between each couple of bonded atoms in the perimeter, and $\bar{P}$ is the corresponding average value. Furthermore, since conjugation of double bonds is enhanced by the alignment of adjacent p orbitals and since one can expect the frequency of the first electronic transition to be sensitive to the amount of conjugation, the experimental values of the wavelengths of these transitions have been also considered in assessing the possible indexes of aromaticity for the [14]annulenes.

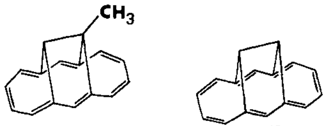
Table 7 collects the values of all the above-mentioned quantities for the bridged [14]annulenes. The order of aromaticity that introduces the smallest number of contradictions in the sequences of σ, ΔP, φ and λ_{obs} is **16** > **11** > **15** > **12** > **14** > **13** > **9**. **15** and **12** are slightly out of sequence in ΔP, the discrepancy being however as small as 0.04. In the sequence of φ, **11** and **15** are out of sequence by the scarcely significant amount of 2°, and **14** and **13** by 3°. It is not surprising, on the contrary, that the sequence of Δ is contradictory, since closeness of the atoms to the least-squares plane can be achieved also by alternant systems, as demonstrated by the anomalous place of **9** in the sequence. The Δ's are therefore to be rejected as a criterion of aromaticity, at least in this context. Although it is well known that EHT is not suited for the calculation of the spectroscopic properties of molecules, an unexpected good correlation is found between the sequences of observed λ's and of the HOMO-LUMO gaps for the *syn*-hydrocarbons (see Table 7). This is not so for the bis(oxido) compound and the *anti*-hydrocarbon; the comparisons can evidently be made only among strictly similar compounds.

Table 7. *Indexes of aromaticity for the bridged [14]annulenes* (see text)

Compound number	σ	φ	Δ	ΔP	λ_{calc} nm	λ_{obs} nm
16	0.019	12	0.12	0.052	747	600
11	0.024	16	0.21	0.065	659	555
15	0.041	14	0.15	0.097	704	530
12	0.050	19	0.26	0.093	663	480–513
14	0.086	25	0.49	0.165	642	—
13	0.090	22	0.40	0.177	602	467–492
9	0.409	26	0.27	0.340	639	350

The synthesis and physico-chemical properties of the [14]annulenes **9** and **11**–**16** have been described by *Vogel et al.* [32–38]. The general trend that can be derived for the aromaticity from the qualitative arguments of ring puckering and conformational strain, as well as from the results of UV. and ^{1}H- and ^{13}C-NMR. spectroscopy, agrees with our derived order of aromaticity. The sequence of planarity in the bridged [14] annulenes, as inferred from inspection of molecular models, has been found to agree with the sequence obtained from a study of the ESR. spectra of the corresponding anions [39]: **16** > **17**[1]) > **11** > **12** > **13** > **9**.

Scheme 4



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Photoelectron spectroscopy studies [40] of the orbital sequences of some annulenic compounds were consistent with the following order of planarity: **16** > **18**[1]) > **12** > **13**. If **17** and **18** are considered to be similar, and representative of the properties of **15**, the sequences are in agreement with the one we have given above.

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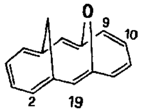
[1]) See *Scheme 4*.

It is not possible at present to compare our derived order of aromaticity with orders derived from different definitions of the term, *i. e.* from resonance energies or chemical behaviour. The energy of these molecules is too much dependent on the strain imposed by the bridges to allow enucleation of resonance energies. The chemical reactivity studies are hampered by arduous experimental conditions. However, conformational, molecular orbital, and ESR. and PE. spectroscopy results are in agreement, and therefore support each other.

3.3. *Reactivity.* For **11** and **12** it is known that the first electrophilic substituent enters at position 2 [34]. *Friedel-Crafts* acylation of **19** gave the results given in *Scheme 5.*

Scheme 5



19

2	14%
9	40%
10	12%

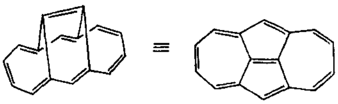
It is also known [32] that for **9** selective protonation at position 7 takes place, and the resulting cation is unusually stable. Both oxygen and methylene bridging groups should therefore drive the electrophilic attack towards the ring carbon atoms adjacent to the bridges, oxygen more than methylene. The EHT charges (see Table 8) are in agreement with this, and in particular the charges at position 7 reflect the fact that the effect is doubled. However, no 7-substituted derivatives are obtained from *syn*-compounds, except for the probably very planar compound **20** [42] (see *Scheme 6*).

Table 8. *Charge distributions in the bridged [14]annulenes.* (The atom numbering is shown in *Scheme 1*)

Compound number	q_1	q_2	q_3	q_7	q_{11}	q_{12}	q_{13}
9	0.08	−0.14	−0.18	−0.21	−0.17	−0.26	0.16
10	0.15	−0.14	−0.16	−0.15	−0.17	−0.26	0.16
11	0.68	−0.20	−0.15	−0.25			
12	0.11	−0.20	−0.17	−0.22			
13	0.11	−0.18	−0.18	−0.22			
14	0.12	−0.18	−0.19	−0.21			
15	0.08	−0.20	−0.17	−0.18			
16	0.08	−0.20	−0.15	−0.23			

Therefore, other factors must play a role in determining the reaction rates: a) steric factors; b) the fact that in molecules with C_{2v}-symmetry the chances of addition at position 2 or 3 are twice those of addition at position 7, and c) different stabilities of the intermediate cations. *Scheme 7* shows the spreading of the charge and the rela-

Scheme 6



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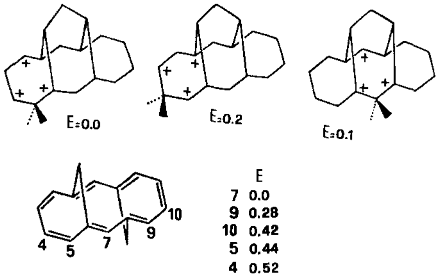
Scheme 7. *Relative energies* (eV) *of the cations of* **12** *and* **9**. See also the captions to Table 6. The plus signs indicate the positions at which positive charge increases with respect to the neutral compound.



tive energies of the cations of **12** and **9**, taken to be good examples of the behaviour of *syn*- and *anti*-compounds respectively. In each case, the cation calculated to be more stable leads to the experimentally found products; for **9**, the very large stabilization of the 7-protonated intermediate relative to the others reflects the observed selectivity of the protonation reaction. The order or reactivity, as obtained from the relative stabilities of the cations is (pos. = position):

syn-compounds: pos. 2 > pos. 7 > pos. 3;

anti-compounds: pos. 7 > pos. 9 > pos. 10 > pos. 5 > pos. 4.

This is in agreement with experimental findings.

3.4. *Orbital shapes*. The frontier orbitals of the bridged [14]annulenes are *Hückel* orbitals of the perimeter, with various degrees of interaction with the orbitals of the bridging groups (see Fig. 2). **16** has a high-lying *Walsh*-type orbital of the cyclo-

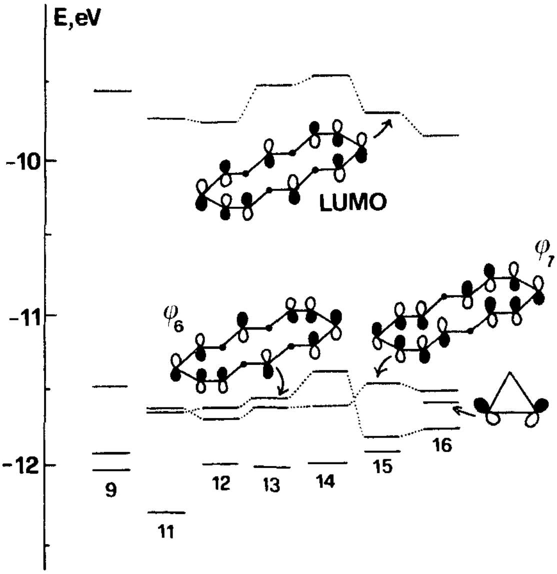


Fig. 2. *Energies* (eV) *of some MO's in the bridged [14]annulenes* **9** *and* **11–16**. The drawings refer only to the relative signs of the p_z AO's in the perimeter. See Fig. 3 for more detail.

propane ring just below the HOMO, as already inferred by PE. spectroscopy [40]. The approximate MO drawings of Fig. 2 are detailed in Fig. 3 to include the contributions of AO's other than the p_z of the perimeter carbon atoms. The *Hückel* MO φ_6 (Fig. 2) is almost pure in **15** and **16**; on going to **12**, **13** and **14** the increasing distortion of the perimeter allows an increasing amount of p_x contributions to come in (notice specially the substantial growth of the p_x contributions on atoms 1, 6, 8 and 13, Fig. 3). This allows also the bridge orbitals to mix in. The *Hückel* MO φ_7 is the HOMO in planar compounds; in **16**, it is strongly coupled with a σ-type orbital of cyclopropane, and in **15** with an orbital of the bridging group. The interactions between π-orbitals of the perimeter and σ-orbitals of the saturated bridges have been invoked in the analysis of spectroscopic results for **16**, **18**, **12** and **13** [43]. EHT, as has been shown, can be of valuable help in sketching out and ordering the complex MO's of these compounds.

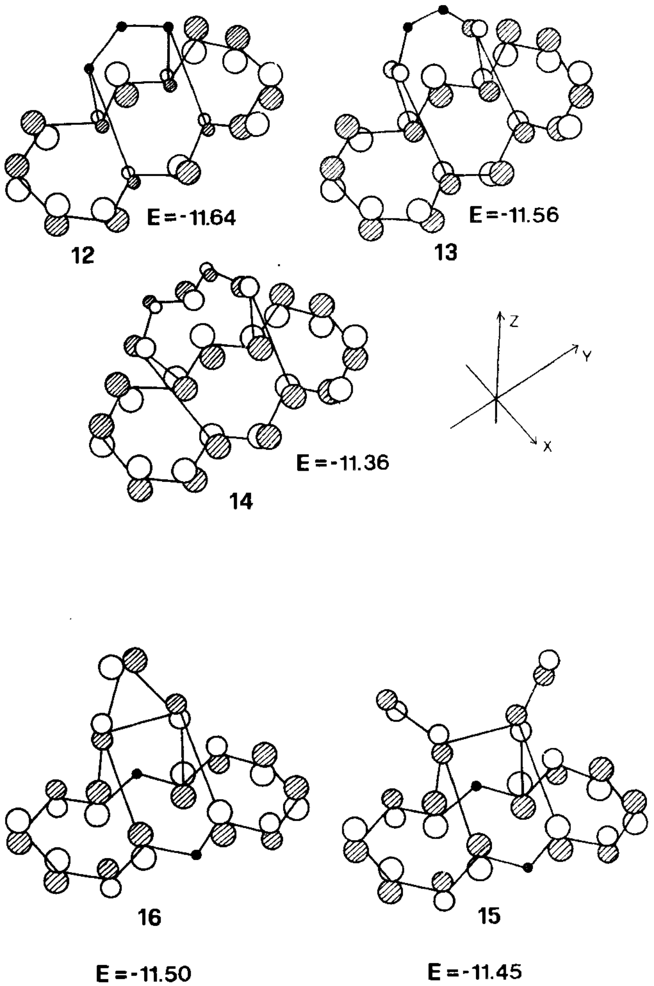
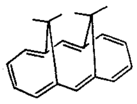


Fig. 3. *Full shapes of the HOMO's for the bridged [14]annulenes* **12–16** *with their energies* (eV).

3.5. *The strain in* syn-*1,6:8,13-dimethano[14]annulene* (**21**). This extremely interesting compound has recently been synthesized [44], after considerable effort due to the high strain of the two methylene bridging groups. An X-ray crystal structure determination is being carried out in our laboratory, and preliminary results [45] for the ring geometry are in agreement with evidence coming from spectroscopic studies [44] that this compound is aromatic and closely resembles the propano-bridged analog **12**. EHT calculations have been carried out using the ring frame of **12** and allowing the methylene bridges the degrees of freedom sketched in Fig. 4. The angle α was given the fixed value of 13°, as resulting from the preliminary X-ray results. The relevant H ... H distance is only 1.7 Å in the energy minimum (see the curves in Fig. 5), but still the twisting motion resulting from $\beta \neq 0$ is clearly unfavourable. Instead, a small tilt resulting from $\delta \simeq 5°$ is predicted. A reasonable HCH angle is obtained (105°). These results await for confirmation from a refined structure determination.



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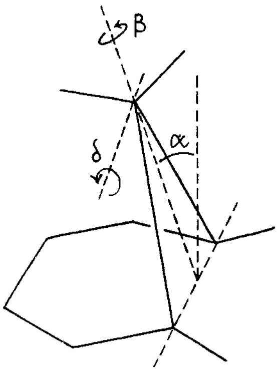

Fig. 4. *Degrees of freedom allowed to the methylene groups in* syn-*1,6:8,13-bismethano[14]annulene in the energy calculations.*

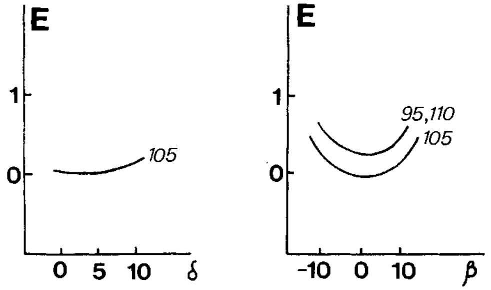

Fig. 5. *Energy* (eV) *of* **21** *as a function of the degrees of freedom shown in Fig. 4.* The numbers near each curve refer to the value of the HCH angle (degrees).

4. The ^{1}H and ^{13}C-chemical shifts in the bridged annulenes. – It is generally accepted that the values of δ for ^{1}H and ^{13}C can give information about the shielding of the nucleus, and hence about its conformational environment. Charge distributions can be calculated by EHT, and a good correlation has been found between δ values and EHT charges in the five- and six-membered *N*-heterocycles

[46]. But factors other than total charges are effective in the annulenes [47] [48], namely, ring-current effects of various intensity and direction, and strain effects, these last being particularly important in the case of the ^{13}C-shifts [48]. This is evident from the scatterplot of the observed shifts versus total EHT charges for the ring carbon atoms in the annulenes (Fig. 6). If a rough charge dependence is assumed, as the dotted line in Fig. 6, the effects of the strain to which the bridgehead carbon atoms are subject in **12**, **2** and **4** are evident. It is known, for instance, that **2** shows an *upfield* shift of the signal of C_1 with respect to its 2,3,4,5-tetrahydro-analog [48]. Since EHT charges are known to be qualitatively reliable, our results confirm that the charges are only one of the many factors influencing the shifts in the bridged annulenes.

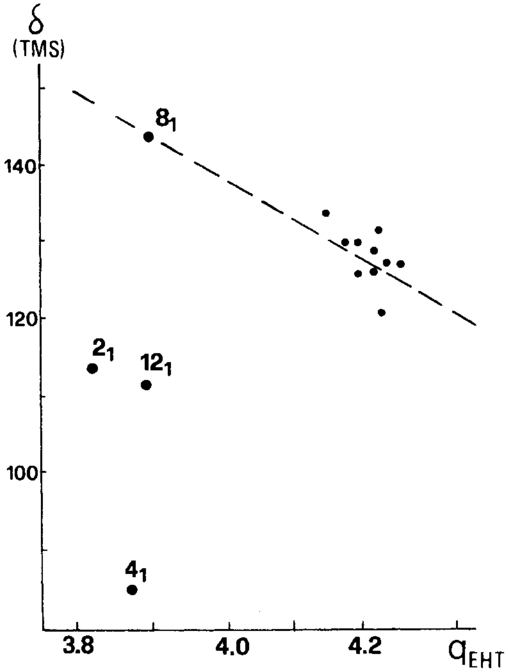

Fig. 6. *Scatterplot of the values of δ* versus *EHT charges* (electrons) *for C atoms in the annulenes.* Boldface numbers near each point refer to the compound (see *Scheme 1*), lower case indices to the position in the annulene ring. The dotted line is no more than a roughly expected trend.

The calculation of δ from molecular wavefunctions is feasible, by the use of approximate expressions such as the *Karplus-Das* formula [49] [50]. Such empirical treatments met considerable success with EHT wavefunctions for the *N*-heterocycles [51–54]. Our results for the bridged annulenes are summarized in Table 9, together with the available experimental data. As can be seen, the agreement can be considered good only for those cases in which the magnitude of the shift is chiefly influenced by charge effects, the ones that most strongly are at work in the formulas used. As expected, the most prominent discrepancies are for those carbon atoms that deviate the most from the charge dependence sketched in Fig. 6.

Table 9. *Observed and calculated ^{13}C chemical shifts in the bridged annulenes.* (Calculated using benzene as reference and then scaled to TMS using the experimental TMS shift of benzene, 128). ppm [55])

Compound number	Position in the ring	Experimental shift[a])	Calculated shift	Total EHT charge
2a	1	114	146	0.18
	2	129	122	−0.19
	3	126	122	−0.19
4b	1	80–90	145	0.13
	2	126	123	−0.17
	3	121	121	−0.20
8	1	146	142	0.11
	2	132	121	−0.17
	3	134	127	−0.12
	4	130	125	−0.16
9	1	136	147	0.1
	2	124	121	−0.2
	3	129	123	−0.2
	7	—	121	−0.21
12	1	112	143	0.11
	2	127	121	−0.20
	3	130	123	−0.17
	7	127	120	−0.22
15	1	131	140	0.08
	2	123	122	−0.20
	3	127	124	−0.17
	7	132	122	−0.18
3	1	—	144	0.13
	2	—	125	−0.15
	3	—	121	−0.20
6	1	—	151	0.23
	2	—	125	−0.16
	3	—	122	−0.19

[a]) Values from [13] [47] [48]. For **9**, the experimental values refer to the 1,7-dihydroderivative.

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