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Theoretical determination of molecular structure. Conformation of some benzo[10]-annulenes and [10]-annulene

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Summary. The AM1 method was used to carry out a theoretical study of optimized geometries and energies of some benzoannulenes. The transition state of the transformation of the benzo[10]annulene was also determined. The transition state has been located.

Key words: Benzoannulenes – Conformation – AM1 – Transition states

1 Introduction

The Hückel $4n + 2$ rule has been acknowledged as one of the most significant contributions of theoretical chemistry. It has at least proved its validity on application to annulenes, even though it is assumed to apply equally well to a much wider assembly of conjugated polycyclic systems. Among its most obvious successes is the observation of particularly stable 6π-electron species, namely benzene. For the $n = 2$ case, the success of the $(4n + 2)$ rule is less clear. Although the isoelectronic neutral [10]annulene is extremely reactive, the cyclononatetraenide anion $C_9H_9^-$ exhibits a certain measure of stability [1, 2].

Much of the experimental work on [10]annulenes has been carried out by the groups of van Tamelen [3, 4] and Masamune [5, 6]. Specifically, van Tamelen [7, 8] reported the synthesis of the bridged $C_{10}H_{10}$ molecule, which later on gave rise to an undetermined isomer of [10]annulene. Masamune et al. [9] managed to isolate isomers of [10]annulene in crystalline form. The annulenes, and their derivatives, benzannelated annulenes, are the subject of particular attention [10] since changes in the aromaticity and in the diatropicity of an annulene should have a much more pronounced magnetic resonance effect on internal groups.

The works of Nakagawa [11], Boekelheide [12], Mitchell [13, 14] on different families of nonbenzenoid annulenes have collectively led to a better understanding of various aspects of aromaticity. One of the most interesting areas studied by Mitchell [15] is the effect of the annelation, in particular benzannelation, on the diatropicity of annulenes.

This paper reports on a theoretical quantum-chemical study of four isomers of benzo[10]annulene and two of the isomers of [10]annulene (Figs. 1 and 2). These compounds feature a [10]annulene-like perimeter. The isomers, selected here as

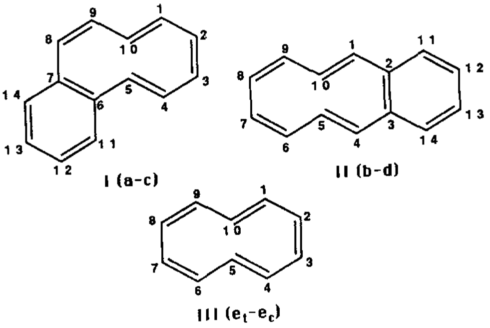

Fig. 1.

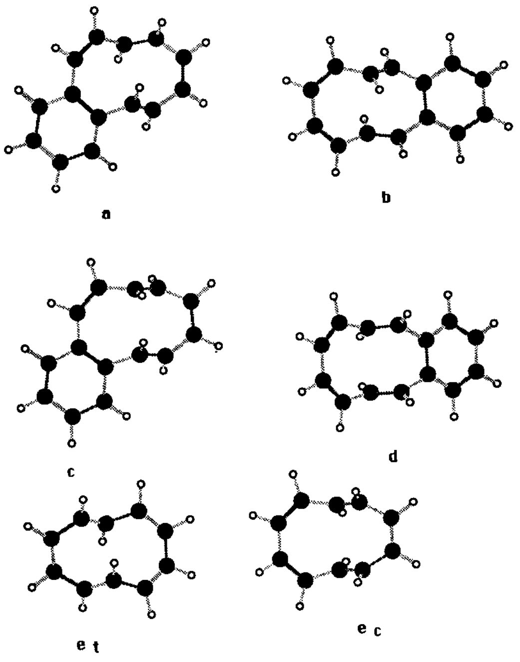

Fig. 2.

a common characteristic intramolecular repulsion of the two hydrogen atoms located inside the molecular ring. The *cis* isomers are more stable than the *trans* isomers.

2 Method of calculation

All computations were performed with an AM1 technique [16] contained in the MOPAC set of programs [17]. The unrestricted optimization method was used for all the geometric parameters of the molecule in order to minimize the energy.

The geometries of stationary points were optimized at SCF level employing the Davidon–Fletcher–Powell [18, 19, 20] algorithm for minima and gradient norm minimization for transition states. A force constant analysis was performed for AM1 stationary points. This method enables one to find an approximate point within the true transition state zone to be localized by starting from the geometries of the two minima situated on both sides of the saddle point.

3 Results and discussion

The calculated values of the most relevant geometric variables for the four isomers are listed in Tables 1–3 and the other parameters of interest are given in Tables 4, 5.

Larger differences between bond lengths are found, especially in the [10]perimeter. These differences in the [10]annulene provide results that are consistent with the available data [21]. The C–C bonds are considered as quasi-localized if the double bond is smaller than 1.37 Å and long bonds with more than 1.44 Å. Bonds with 1.37–1.44 Å can be considered as aromatic bonds. For the six-membered ring where all bonds are aromatic 1.39–1.40 Å are those common the adjacent in the [10]perimeter C–C (1–2, 3–4 in **b** and **d** or 5–6, 7–8 in **a** and **c**) bonds. This is due to a reduction in bond order by annelation. However, such bonds are still important since the π-conjugation cannot be considered as [14]perimeter systems. The C_5C_{10} distance is not significantly different 2.6 Å from the value cited by Hanson in [2,2]metacyclophane-1,9diene [22] and theoretical study in [23].

Table 2 lists the calculated bond angles. As shown below, the geometry obtained for isomers **a** and **c** has no symmetry (e.g. the angles formed by the bonds 6–7–8 and 7–8–9). However, these bond angles are equal in **b** and **d** and are very

Table 1

Bond lengths (Å)

				Isomer						
Bond	a	b	e_t	e_t^a	c	d	a–c	b–d	e_c	e_c^a
1–2	1.456	1.460	1.457	1.508	1.459	1.462	1.461	1.474	1.459	1.513
2–3	1.347	1.416	1.347	1.337	1.348	1.418	1.351	1.423	1.348	1.335
3–4	1.456	1.460	1.457	1.508	1.458	1.462	1.462	1.470	1.459	1.515
4–5	1.343	1.342	1.343	1.334	1.342	1.340	1.339	1.347	1.341	1.335
5–6	1.457	1.451	1.450	1.498	1.458	1.451	1.436	1.462	1.450	1.513
6–7	1.411	1.344	1.345	1.339	1.411	1.343	1.426	1.350	1.343	1.328
7–8	1.460	1.449	1.449	1.512	1.460	1.447	1.473	1.457	1.447	1.517
8–9	1.343	1.344	1.345	1.339	1.341	1.343	1.349	1.357	1.343	1.333
9–10	1.449	1.451	1.450	1.498	1.448	1.451	1.460	1.432	1.450	1.517
10–1	1.344	1.342	1.343	1.334	1.341	1.340	1.349	1.336	1.341	1.328
11–6	1.403	–	–	–	1.404	–	1.399	–	–	–
11–2	–	1.398	–	–	–	1.394	–	1.407	–	–
12–11	1.390	1.394	–	–	1.389	1.396	1.390	1.391	–	–
12–13	1.395	1.394	–	–	1.395	1.393	1.393	1.393	–	–
13–14	1.390	1.394	–	–	1.394	1.396	1.392	1.392	–	–
14–7	1.409	–	–	–	1.415	–	1.410	–	–	–
14–3	–	1.398	–	–	–	1.394	–	1.400	–	–

[a] Ref [21]

Table 2

Bond angles (°)

Angle	Isomer a	b	e_t	c	d	a–c	b–d	e_c
1–2–3	121.8	120.0	122.2	119.1	117.3	125.0	126.7	119.6
2–3–4	122.6	120.0	122.2	120.0	117.4	129.4	122.5	119.6
3–4–5	123.4	123.0	122.5	122.7	122.1	119.3	124.7	122.0
4–5–6	123.7	123.7	124.1	124.6	124.6	142.5	123.7	124.9
5–6–7	120.6	124.0	122.3	125.9	123.5	117.2	128.3	125.5
6–7–8	126.3	129.4	129.4	128.6	132.3	129.1	137.5	132.4
7–8–9	131.0	129.4	129.6	135.0	132.3	138.8	132.5	132.4
8–9–10	124.5	124.0	123.5	127.5	125.9	128.6	118.7	125.6
9–10–1	123.2	123.7	124.2	125.0	124.7	123.9	143.9	124.9
2–1–10	122.4	123.0	122.5	121.4	122.0	123.6	119.8	122.0
5–6–11	119.5	–	–	117.5	–	122.0	–	–
1–2–11	–	120.5	–	–	122.9	–	115.4	–
6–11–12	121.0	–	–	121.3	–	121.0	–	–
2–11–12	–	120.5	–	–	120.1	–	121.9	–
11–12–13	119.6	120.1	–	120.2	120.2	119.2	119.8	–
12–13–14	119.9	120.1	–	119.9	120.2	120.3	119.5	–
13–14–7	121.0	–	–	117.2	–	122.1	–	–

Table 3

Dihedral angles (°)

Dihedral	Isomer a	b	e_t	c	d	a–c	b–d	e_c
1–2–3–4	8.	353.	0.	359.	0.	6.	354.	353.
2–3–4–5	317.	46.	65.	62.	68.	8.	78.	44.
3–4–5–6	161.	198.	201.	198.	199.	176.	208.	201.
4–5–6–7	238.	116.	104.	112.	103.	179.	88.	118.
5–6–7–8	358.	1.	357.	357.	357.	359.	358.	1.
6–7–8–9	34.	331.	0.	358.	0.	18.	342.	330.
3–2–1–10	316.	46.	295.	294.	292.	291.	349.	44.
4–5–6–11	57.	–	–	291.	–	359.	–	–
5–6–11–12	181.	–	–	182.	–	179.	–	–
10–1–2–11	–	176.	–	–	183.	–	181.	–
1–2–11–12	–	184.	–	–	178.	–	0.	–
2–11–12–13	–	0.	–	–	359.	–		–
6–11–12–13	0.	–	–	0.	–	0.	–	–
11–12–13–14	0.	–	–	0.	0.	1.	0.	–

similar to the values that we have obtained for the [10]-annulene. The bond angles, in six-membered ring are significantly similar to the ideal value of 120° for an sp^2 carbon atom.

Molecules **b** and **d** have fairly precise C_2 and C_S symmetries, respectively, in a manner completely analogous to that seen for [10]annulene; in contrast, **a** and

Table 4

	a	b	c	d
Heat of formation (kcal mol^{-1})	98.751	96.371	103.510	99.584
Electronic energy (eV)	– 11605.54098	– 11527.96299	– 11559.16494	– 11507.11322
Core–core repulsion (eV)	9650.78830	9573.10714	9604.61865	9552.39667
μ(D)	0.060	0.234	0.150	0.213
Ionitation potential (eV)	8.596	8.641	8.780	8.971
HOMO (eV)	– 8.596	– 8.641	– 8.780	– 8.971
LUMO (eV)	– 0.105	– 0.033	– 0.116	0.145

Table 5

	a–c	b–d	e_t	e_c
Heat of formation (kcal mol^{-1})	121.902	121.512	86.800	90.345
Electronic energy (eV)	– 11492.04633	– 11454.68361	– 7185.49671	– 7157.03565
Core–core repulsion (eV)	9538.29755	9500.91791	5770.44186	5742.13451
μ(D)	0.331	0.328	0.109	0.152
Ionitation potential (eV)	8.392	8.322	8.632	8.887
HOMO (eV)	– 8.392	– 8.322	– 8.632	– 8.887
LUMO (eV)	– 0.533	– 0.568	0.127	0.182

c are not symmetric. However, the mutual repulsion between the atoms causes severe boat deformation of the rings. The deformation is greater in the dihedral angles 4–5–6–7 and 2–3–4–5 optimized to be AM1, for **a**, **b**, **c**, **d** respectively, (Table 3).

The stability of [10]-annulene is greater for the *trans* form than for the *cis* form (the formation heat is 86.800 and 90.345 kcal/mol by the *trans* form and *cis* form, respectively) Table 5.

The isomer **a**, is also that with the smallest electronic energy and the least marked alternancy of carbon–carbon bond lengths, which suggests **a** as having a somewhat more aromatic structure than that of its counterpart **b** (considering the two *trans* structures), with a relationship in the *cis* structure. Nuclear repulsion, obviously stronger in isomer **a**, compensates, although not completely, for the energetic implications of the above-mentioned effect, so that the calculated energy difference between the two *trans* isomers is 2.380 kcal/mol and between the *cis* isomers it is 3.926 kcal/mol.

The difference in energy between **a** and **c** is 4.759 kcal/mol and between **b** and **d** is 3.213 kcal/mol, the form in which the protons are in the *trans* position being more stable. Upon comparing, on one hand, the *cis*, and on the other, the *trans*, the lowest energy content corresponds to the isomer that has the greatest symmetry.

Thus, according to the formation heats, it can be stated that the order of stability would be: **b–a–d–c**; these are shown in Table 4. Regarding the amount of energy per clustered atom, in all cases this proves to be lower than that of the [10]-annulene, and the lowest of all corresponds to form **b**.

The dipole moments obtained for the four isomers allow one to state that isomers **b**, **a** and **c** will prevail in polar solvents.

The transition state is located on the AM1 potential hypersuperface. For each of the two above-mentioned potential peripheries of benzo[10]annulene, I and II, we located two minima on the respective potential energy hypersurface. In accordance with Fig. 1, we refer to the minima corresponding to I as **a** and **c**, and to those corresponding to II as **b** and **d**. We also located saddle points for the interconversions **a**$\rightleftharpoons$**c** and **b**$\rightleftharpoons$**d**. We calculated the activation barriers for each of the isomerization processes studied at 298.15 K and found them to be 121.902 kcal/mol, involving isomers with type I structure, and 121.512 kcal/mol for those involving type II structures. Analysis of the atomic components of its transition vector confirmed that this saddle point indicates the transition state corresponding to the interconversion process **b**$\rightleftharpoons$**d** permitted by conservation of symmetry. The interconversion is associated with a relaxation in the ring zone closest to the inner hydrogen atoms directly involved. Thus the bond angles 6–5–4, 8–7–6, 9–8–7, and 2–1–10 are larger than their counterparts in **a** and **c**. This is also the case with angles 4–5–6, 5–6–7, 8–9–10, and 9–10–1 in the transition state corresponding to the interconversion process **b**$\rightleftharpoons$**d**. In view of the values which appear in the transition state, it appears to be a truly intermediate situation, with a higher energy content, as corresponds to a transition state and as shown in Tables 1–3 and 5.

The geometries calculated in the present work by semiempirical methods of quantum mechanics are consistent with the experiments of Matusame et al. [5, 6] for 10-annulene and with those of Boekelheide [12] and Mitchell [14, 15] for benzo-annulenes.

The four investigated geometries of the benzo-annulenes show clear signals of aromaticity in the six-member ring, showing double bonds alternated on the other ring, as was the case of [10]-annulene. With the introduction of a six-atom ring a slight delocalization occurs along the other two carbon atoms contiguous to the bond. This delocalization does not occur in the [10]-annulene, such that there will be a greater degree of aromaticity than that present in this latter form apart from that appearing due to the benzene ring. As the number of benzene rings increases, one would expect that this would involve a greater degree of aromaticity and hence greater stability in the annulene ring. The diatropicity in this type of molecule continues to exist. The stability of these molecules is greater for the *trans* form than for the *cis* form, as shown by the energies obtained. From the analysis of all the structures obtained it can be deduced that the change of position of the benzene ring linked to [10]-annulene affects the geometry of the [10]-annulene but does not affect the benzene ring.

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