

## Theoretical Study of the Effect Exerted on the Periphery of 10-Annulene by Two Benzenoid Rings

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A conformational study of the energies and geometries of two dibenzo [10]-annulenes, their methylated derivatives and their corresponding bridged valence isomers has been carried out by the semiempirical molecular orbital method AM1. The relative energies of these compounds are strongly dependent on the relative positions of the two benzenoid rings. Interconversions into the corresponding dehydroannulenes were studied. The respective transformations into the corresponding polycyclic benzenoid hydrocarbons were also analyzed.

### INTRODUCTION

Annulenes<sup>1</sup> form a broad group of molecules that have been addressed in numerous theoretical and experimental studies. Among these is the work performed by F. Sondheimer.<sup>2,3</sup>

Among the annulenes that fulfil the Hückel rule with  $4n+2$  electrons, the second in the series corresponds to [10]-annulene. Five different geometries of this compound are known,<sup>4,5</sup> some of them with strong strain owing to the existence of clustered hydrogen atoms. Most of the studies conducted on this molecule and its derivatives referred to the geometry in which the clustered hydrogen atoms are in the *trans* position, since the molecule can readily be transformed into the corresponding dehydroannulene and later into a polycyclic benzenoid hydrocarbon compound.<sup>6,7</sup>

The present paper reports on a theoretical study of the effect exerted on the periphery of [10]-annulene by two benzenoid rings appended to it. Two dibenzo [10]-annulenes and their methylated derivatives were chosen. The respective conversions into the corresponding bridged valence isomers were

also studied. It should be stressed that these compounds display  $C_{2h}$  symmetry and that the appended benzo groups have been situated in such a way that they occupy, respectively, the closest and most distant positions possible with regard to the clustered hydrogen atoms or methyl group.

The molecules studied are shown in Figure 1. In the case of molecule **Ia** ( $R=H$ ), experimental work has shown that this compound undergoes a thermally allowed valence isomerization into **Ib** ( $R=H$ ), and that it is finally transformed by dehydrogenation into a more stable molecule, called pyrene.<sup>8</sup> The 10-annulene **III** may cyclize too rapidly (into **IV**)<sup>9,10</sup>, to be experimentally observable. In the case of molecule **Ic** ( $R=H$ ), it is expected that it would likewise be transformed into a more stable compound, tetracene naphthacene. Accordingly, it was also taken to be of interest to study this possible transformation.

### CALCULATION METHOD

The semiempirical method AM1<sup>11</sup> included in the MOPAC package<sup>12</sup> was used. The Davidson<sup>13</sup> algorithm was used to calculate the minimum energy

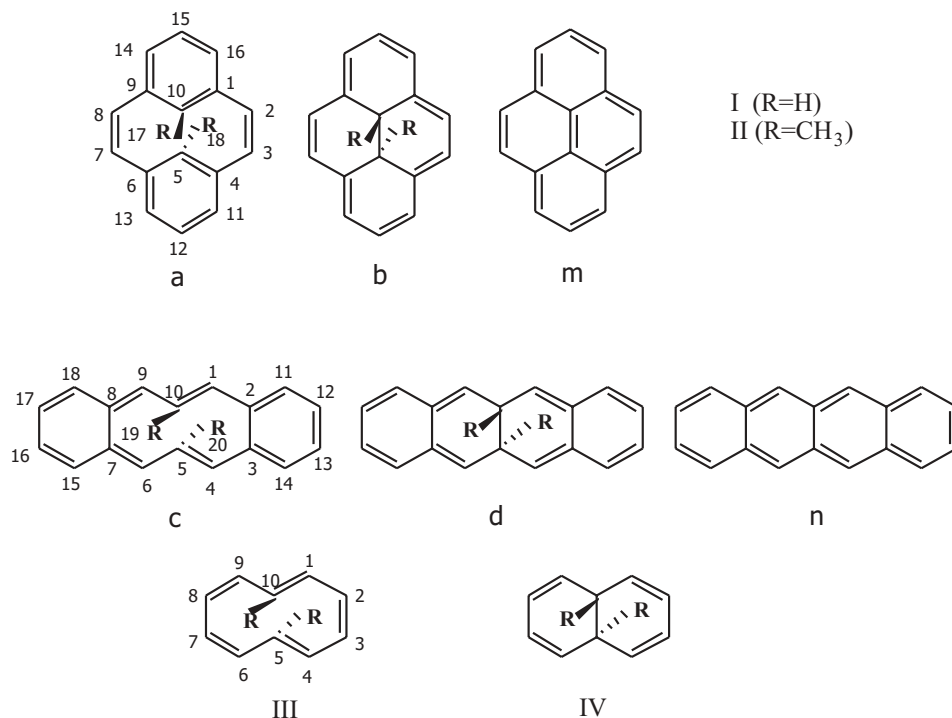


Figure 1.

geometries. In all the cases, we started from the flat molecule while for the C–C bonds and the bonding angles standard values of 1.39 Å and 120° were taken, respectively. Initially, no symmetry constraints were imposed on the molecules. In all the cases, the gradient was  $1.10^{-5}$  eV.

To calculate the transition states, two previously calculated minimum energy geometries, **a** and **c**, were used, followed by the reaction coordinate furnished by the AM1 program.

## RESULTS AND DISCUSSION

The geometries of each of the studied compounds display clear differences in the bond lengths obtained.

The four bridged valence isomers (**Ib**, **Id**, **IIb**, **IIc**) exhibit a clear alternation in all their  $sp^2$  type C–C bond lengths, ranging from 1.349 Å to 1.474 Å. The bond lengths of the  $C_5$ – $C_{10}$  carbon atoms are 1.532 Å for compound **Ib** and 1.552 Å for the methylated compound **IIb**. In the **d** type compounds, the  $C_5$ – $C_{10}$  bond length of the methylated compound has again a greater distance: 1.553 Å versus 1.534 Å for the unmethylated compound. The values calculated for the **d** type are slightly higher in some bonds than the **b** type (these variations of the bond lengths of these molecules are smaller than 0.03 Å), as it may be seen from Tables I–IV.

In the case of the type **a** and type **c** meta-cyclophanes, the differences in bond lengths are more pronounced. Whereas the ten-membered ring conserves an alternance similar to that indicated for the corresponding valence isomers **b** and **d**, the benzenoid rings are very different. In type **a** molecules, the two benzenoid rings have delocalized bonds, with the bond length values between 1.394 Å and 1.403 Å. However, the type **c** molecules have one six-membered ring that can be considered delocalized whereas the other one indicates ortho-quinoid alternance since its bond lengths values range from 1.348 Å to 1.466 Å. The difference in the  $C_5$ – $C_{10}$  bond lengths is more marked in the methylated compounds. This would be consistent with the larger size of the methyl groups bound to these carbons as compared with the size of the hydrogen atom. Additionally, of the studied type **a** cyclophanes, whose benzene rings form part of the clustered hydrogen atoms, display a lower separation between atoms  $C_5$ – $C_{10}$ . This separation is 2.471 Å for **Ia** and 2.661 Å for **IIa** versus 2.553 Å and 2.782 Å for **Ic** and **IIc**, respectively.

The study of the bond angles and dihedral angles reveals that the type **a** and type **b** molecules show higher symmetry than the type **c** and type **d** molecules. In the type **a** molecules, the bond angles of  $sp^2$  carbon atoms that differ most from 120° are 1–2–3 and 2–3–4, with a deviation from that value

of about  $5^\circ$ . In the type **c** molecules, it is in the angles 7–8–9 and 8–9–10 that the greatest deviations appear and these may reach  $8^\circ$ . These greater deviations are in agreement with the fact that the bond of the benzenoid

TABLE I

Relative energy, geometry, dipole moment and heat of formation at several points along the AM1 concerted reaction pathway

	Isomer			
	Ia	Ib	R <sup>d</sup> (Ia)	Transition state
Bond lengths (Å)				
2–1	1.460	1.448	1.483	1.455
3–2	1.348	1.349	1.341	1.347
5–4	1.403	1.498	1.404	1.447
11–4	1.403	1.355	1.396	1.376
12–11	1.395	1.440	1.383	1.418
10–5	2.471	1.532	2.570	1.904
Bond angles ( $^\circ$ )				
3–2–1	125.4	122.2	125.3	123.0
4–3–2	125.4	122.2	126.6	122.9
5–4–3	120.7	116.0	121.1	118.1
6–5–4	119.7	114.6	119.2	117.3
11–4–3	120.0	123.0	119.9	121.1
12–11–4	119.8	121.0	120.2	120.6
13–12–11	120.3	121.1	120.7	120.5
Dihedral angles ( $^\circ$ )				
4–3–2–1	348	2		351
5–4–3–2	36	13		27
6–5–4–3	211	194		199
7–6–5–4	149	163		159
11–4–3–2	227	190		215
12–11–4–3	163	179		169
13–12–11–4	353	355		356
Heat of formation (kcal mol <sup>-1</sup> )				
	108.183	100.377		146.850
Relative energy (kcal mol <sup>-1</sup> )				
	7.806	0.000		46.473
Dipole moment ( <i>D</i> )				
	0.002	0.247		0.277

<sup>d</sup>Ref. <sup>20</sup>

TABLE II

Relative energy, geometry, dipole moment and heat of formation at several points along the AM1 concerted reaction pathway

	Isomer		
	IIa	IIb	Transition state
Bond lengths (Å)			
2-1	1.461	1.450	1.409
3-2	1.348	1.350	1.388
5-4	1.413	1.508	1.456
11-4	1.403	1.355	1.422
12-11	1.394	1.441	1.372
17-5	1.480	1.537	1.499
10-5	2.661	1.552	1.992
Bond angles (°)			
3-2-1	124.8	122.1	122.6
4-3-2	124.8	122.1	122.6
5-4-3	122.2	115.8	120.4
11-16-7	117.7	113.7	117.0
11-4-3	118.1	123.0	120.9
12-11-4	120.2	121.1	121.0
13-12-11	119.6	121.1	120.5
17-5-4	121.2	107.2	116.1
Dihedral angles (°)			
4-3-2-1	345	2	358
5-4-3-2	44	14	339
6-5-4-3	215	194	156
7-6-5-4	145	161	202
11-4-3-2	235	191	153
12-11-4-3	161	178	195
13-12-11-4	352	355	2
17-5-4-3	37	76	299
Heat of formation (kcal mol <sup>-1</sup> )			
	108.173	104.807	149.222
Relative energy (kcal mol <sup>-1</sup> )			
	3.366	0.000	44.415
Dipole moment ( <i>D</i> )			
	0.005	0.220	0.113

TABLE III

Relative energy, geometry, dipole moment and heat of formation at several points along the AM1 concerted reaction pathway

	Isomer		
	Ic	Id	Transition state
Bond lengths (Å)			
2-1	1.459	1.355	1.405
3-2	1.417	1.470	1.443
8-7	1.469	1.470	1.467
9-8	1.357	1.355	1.353
10-1	1.344	1.487	1.415
10-9	1.446	1.487	1.457
11-2	1.399	1.451	1.421
12-11	1.394	1.351	1.373
13-12	1.394	1.444	1.416
17-16	1.443	1.444	1.445
18-17	1.349	1.351	1.350
18-8	1.463	1.451	1.454
10-5	2.553	1.534	1.935
Bond angles (°)			
3-2-1	120.1	119.7	119.9
9-8-7	127.1	119.8	122.5
10-1-2	123.3	119.7	120.8
10-9-8	125.3	119.7	122.6
11-2-1	120.4	122.6	121.4
12-11-2	120.5	121.3	120.9
13-12-11	120.0	120.7	120.4
18-17-16	120.0	120.8	120.5
17-18-8	122.1	121.2	121.2
18-8-9	117.0	122.5	120.5
Dihedral angles (°)			
4-3-2-1	9	14	0
5-4-3-2	315	3	335
9-8-7-6	28	-12	21
10-1-2-3	315	5	336
10-9-8-7	1	-6	1
12-11-2-1	176	171	180
13-12-11-2	0	1	359
14-13-12-11	1	3	2
18-17-16-15	7	-3	7
17-18-8-9	161	188	166
Heat of formation (kcal mol <sup>-1</sup> )			
	128.035	117.207	169.587
Relative energy (kcal mol <sup>-1</sup> )			
	10.828	0.000	52.380
Dipole moment ( <i>D</i> )			
	0.083	0.014	0.211

TABLE IV

Relative energy, geometry, dipole moment and heat of formation at several points along the AM1 concerted reaction pathway

	Isomer		
	IIc	IIId	Transition state
Bond lengths (Å)			
2-1	1.458	1.355	1.400
3-2	1.418	1.471	1.446
8-7	1.469	1.471	1.467
9-8	1.355	1.355	1.352
10-1	1.348	1.497	1.422
10-9	1.459	1.497	1.466
11-2	1.396	1.451	1.422
12-11	1.395	1.351	1.372
13-12	1.393	1.444	1.418
17-16	1.444	1.444	1.444
18-17	1.348	1.351	1.350
18-8	1.466	1.451	1.454
19-10	1.484	1.539	1.503
10-5	2.782	1.553	2.010
Bond angles (°)			
3-2-1	118.2	119.7	119.2
9-8-7	128.1	119.6	122.1
10-1-2	125.1	119.7	122.4
10-9-8	126.7	119.7	122.7
11-2-1	122.1	122.7	122.2
12-11-2	120.2	121.2	120.9
13-12-11	120.2	120.8	120.4
18-17-16	119.9	120.8	120.5
17-18-8	122.1	121.2	121.3
18-8-9	116.5	122.7	120.9
19-10-9	115.7	106.7	112.9
Dihedral angles (°)			
4-3-2-1	8	14	3
5-4-3-2	-53	5	24
9-8-7-6	31	-15	337
10-1-2-3	-54	5	26
10-9-8-7	1	-5	357
12-11-2-1	176	170	178
13-12-11-2	0	1	1
14-13-12-11	0	3	359
18-17-16-15	8	-3	354
17-18-8-9	158	190	196
19-10-9-8	69	281	284
Heat of formation (kcal mol <sup>-1</sup> )			
	121.569	120.413	170.261
Relative energy (kcal mol <sup>-1</sup> )			
	1.156	0.000	49.174
Dipole moment ( <i>D</i> )			
	0.157	0.004	0.308

ring joined to the 7–8 bond is the one corresponding to the alternating bonds. With respect to the dihedral angles, the type **b** and type **d** molecules are flatter whereas the type **a** and type **c** molecules are less flat. Additionally, the type **a** molecules have the two six-membered rings on almost parallel planes. Furthermore, these rings are on perpendicular planes to the plane containing the C<sub>2</sub>–C<sub>3</sub> and C<sub>7</sub>–C<sub>8</sub> bonds. In the type **c** molecules, the six-membered rings form a dihedral angle of about 9° between each other. Due to steric reasons, the ten-membered rings undergo a process of greater deformation in the methylated compounds. A generalized aperture in the angle 2–3–4–5 can be observed in these molecules. The aperture must be partly brought about by the non-bonded interactions between the methyl groups fused with these carbon atoms, leading to a greater distortion in the molecule. This distortion can be seen in the data on dihedral angles shown in Tables I–IV. Compound **IIc** is less flat, with deviations in the bond angle 2–3–4–5 of 53°. Thus, these molecules display a greater degree of bending than those of type **a**. Although type **a** and type **c** molecules were expected to exhibit the same symmetry, the geometries calculated by AM1 show that whereas the type **a** exhibits C<sub>2h</sub> symmetry, molecules of type **c** have C<sub>2</sub> symmetry (see Figure 2). Transition states of **Ia** and **Ic** compounds are included in Figure 3.

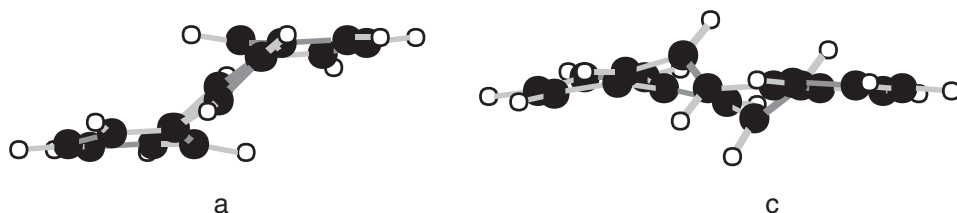


Figure 2. The geometries calculated by AM1 for compounds **Ia** and **Ic**.

By comparing the values obtained for bond angles for the ten-membered ring of type **a** and type **c** with those obtained for [10]-annulene,<sup>4,14</sup> the same tendency to bending is seen although it is remarkable that the more restrictions are imposed on the hydrogen atoms the less is the deformation. Thus, angle 7–8–9 goes from 129.6° in [10]-annulene<sup>14</sup> to 127.1° or 128.1° in compounds **Ic** and **IIc**, respectively, and 125.4° or 124.8° in compounds **Ia** and **IIa**, respectively.

The stability calculated for the bridged valence isomers is in all cases greater than that of their cyclophane isomers. The difference between the energy of the cyclophane and its bridged valence isomer, when both are methylated, is in both cases lower than that shown by the unmethylated com-



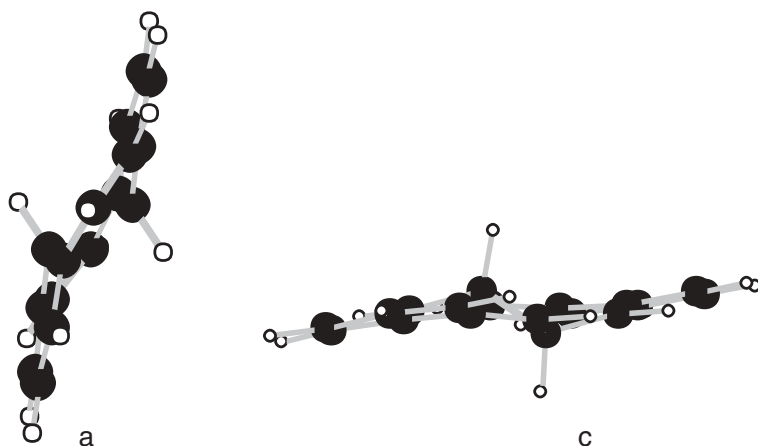


Figure 3. The geometries calculated by AM1 for transition states of **IaIb** and **IcId**.

pounds. These results concur with the observations of Mitchell and Boekelheide.<sup>7,15,16</sup> According to these authors, conversion of these compounds is easier when they are methylated. The heats of formation obtained for these molecules are shown in Tables I–IV. The difference in energy calculated for compounds **Ia-Ib** and that obtained for **Ic-Id**, greater than 7 kcal/mol, suggests that these molecules are not readily converted. The energy difference between the **IIc-IIId** compounds is relatively small: 1.2 kcal/mol and smaller than that shown by **IIa-IIb**. Experimentally, Mitchell and Boekelheide observed that the **IIa-IIb** molecules are interconverted.<sup>8,17</sup> This shows that if conversion occurs, it will be very favourable between the **IIc-IIId** molecules. The polycyclic benzenoid hydrocarbons into which these compounds are presumably transformed have also been studied. In both cases, the structure proves to be flat. The bonds between its atoms can be considered quasi-delocalized. By comparing these bonds with the experimental crystallographic data known in the case of pyrene,<sup>17</sup> good agreement is observed. Both molecules have a lower energy content. In this sense, in the case of naphthacene (**n**), a heat formation of 86.4 kcal/mol is obtained as compared with the 67.3 kcal/mol obtained for pyrene. The difference between compound **Ib** and pyrene is 33.0 kcal/mol and between compound **Id** and naphthacene is slightly lower than 30.8 kcal/mol. This difference is large enough in both cases to take that compounds **Id** and **IIId** are readily transformed into naphthacene, as already observed for pyrene. Moreover, this difference is similar to that calculated between trans-12c,12d-dehydrobenzo[e]pyreno and benzo[e]pyrene, 30.675 kcal/mol and higher than for benzo[a]pyrene and its valence isomers, (25.3 kcal/mol) also calculated using the AM1 method by Rioseras *et al.*,<sup>18,19</sup> this transformation is also known experimentally.<sup>18</sup>

Finally, it was thought of interest to study the transition states for conversions between **Ia-Ib**, **IIa-IIb**, **Ic-Id** and **IId-IIc**. A transition state was found for each of these possible transformations. The bond lengths, bond angles, and the dihedral angles have intermediate values between each of the starting minimum energy geometries. The energies of these transition states are related to the C<sub>5</sub>-C<sub>10</sub> distance. For the methylated compound this distance is in both cases larger, being greater in the case of type **c** and type **d** compounds. Both the heats of formation of these transition states and their relative energies are shown in Tables 1-4. The difference in activation energy between **c** → **d** and **d** → **c** processes for the processes studied indicates that they are similar in compounds of **Ic-Id** and **IId-IIc**, which would more readily produce conversion. The conversion of compounds type **c-d** will occur with ease. These, apart from having a similar activation energy to that of products **IIa-IIb**, have a smaller difference in energy between the two isomers. It has been demonstrated experimentally that the conversion **IIa-IIb** does occur.<sup>8</sup> The activation energy difference of the direct and indirect processes between **Ia** ⇌ **Ib** compounds is higher than for **IIa** ⇌ **IIb** compounds. This result is consistent with the known values experimental.<sup>8</sup>

## CONCLUSIONS

The diatropism of these type of compounds is maintained. The high energy both the cyclophane and the valence isomers, compared with the corresponding polycyclic benzenoid hydrocarbons, indicates that the former will finally be transformed into the latter because they are more stable. The benzenoid rings condensed to the 2-3 and 7-8 bonds give rise to compounds with lower aromaticity; they are less symmetric and hence display greater molecular deformation. Valence isomerization is easier to produce in the methylated compounds. The separation between the C<sub>5</sub>-C<sub>10</sub> atoms is more pronounced when the benzenoid rings are more distant from the non-bonded hydrogen atom repulsions. The periphery of the [10]-annulene ring does not undergo substantial modifications in the type **c** compounds, while in the case of the type **a** compounds the C<sub>1</sub>-C<sub>10</sub>, C<sub>4</sub>-C<sub>5</sub>, C<sub>5</sub>-C<sub>6</sub>, C<sub>9</sub>-C<sub>10</sub> bonds are less localized.

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## SAŽETAK

### Teorijski studij utjecaja dvaju benzenoidnih prstenova na [10]-anulenski rub

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Semiempirijskom metodom AM1 provedena je konformacijska analiza energija i geometrija dvaju dibenzo[10]anulena, njihovih metiliranih derivata i odgovarajućih premošćenih valencijskih izomera. Nađeno je da relativne energije tih spojeva jako ovise o relativnom položaju dvaju benzenoidnih prstenova. Proučena je i interkonverzija u odgovarajuće dehidroanulene. Također su analizirane transformacije u odgovarajuće policikličke benzenoidne ugljikovodike.