

THEORETICAL JUSTIFICATION OF THE DIFFERENT STAGES OF TRANSFORMATION OF 1(3,6)-PHENANTHRENA-4-(1,4)-BENZENACYCLOHEXAPHANE-2,5-DIENE TO CORONENE

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A theoretical study of the molecule 1(3,6)-phenanthrena-4-(1,4)-benzenacyclohexaphane-2,5-diene and of all intermediates of its transformation to coronene has been performed using the AM1 method. Geometric parameters of the compounds are compared with the goal of confirming the experimental reaction pathway. Possible interconversions of the most probable compounds are also explored.

Keywords: AM1 method; Semiempirical calculations; Reaction mechanism; Annulenes; Coronene; Benzoannulenes; Cyclophanes.

Benzoannulenes like annulenes display a series of steric hindrances as a result of interactions of interior hydrogens of the molecular ring, thus giving rise to their non-planarity^{1,2}. One of the most significant processes in which benzoannulenes are involved is isomerization³, leading to the formation of the corresponding dihydrobenzoannulenes⁴⁻⁶. In a subsequent reaction of them, the hydrogens of the macroring interior are removed to afford a fused polycyclic compound⁷⁻¹⁰. In benzo[10]annulene, two hydrogen atoms of the macroring interior are removed at the same time to afford a polycyclic compound¹¹. In larger annulenes, more hydrogens are present in the ring. In the case of such molecules with a larger number of clustered hydrogen atoms, some experimental works¹² have considered that the reaction first forms the corresponding dihydroannulene with no loss of hydrogen atoms, and then the hydrogen atoms are lost until the fused polycyclic compound is attained¹³. However, other authors have pointed to the possibility that the hydrogen atoms would be removed in successive stages and, at the same time, other metacyclophanes and dihydroannulenes would be formed prior to the appearance of a polycyclic compound⁸.

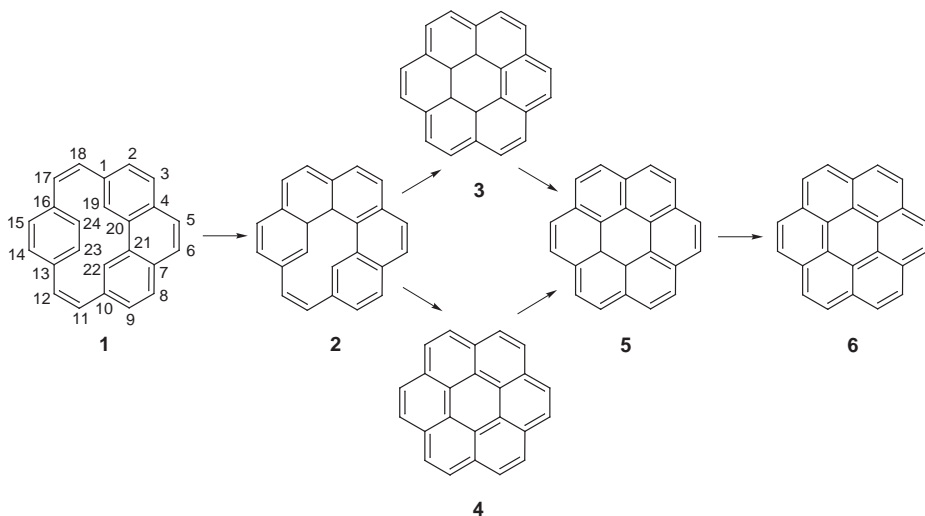
In previous works^{14,15} we studied the isomerization of different metacyclophanes into dihydroannulenes using the AM1 method. In the smallest

molecules of the series, their interconversions exhibit a single chair point. However, the conversion of [2.2.2]paracyclophane-19,17-triene involves the existence of several intermediate compounds¹⁶.

In the present work we offer a theoretical study of possible isomerizations of 1(3,6)-phenanthrena-4-(1,4)-benzenacyclohexane-2,5-diene (**1**), a compound synthesized by Du Vernet *et al.*¹⁷, who also recorded its NMR spectrum. The assignment of those authors made for this compound was macroring interior of four equivalent protons at 2.91(t) ppm. The aim of the present work is to perform a conformational study of the compounds shown in Scheme 1 and to discuss the possibility of studying theoretically formation of different intermediates from compound **1** and the pathway followed until its final transformation into coronene. The numbering used for compound **1** is indicated in Scheme 1. We also study conversions of compound **1** and of its most stable isomer.

COMPUTATIONAL

All calculations were done using the AM1 method¹⁸, which is included in the MOPAC package¹⁹. This permits systematic investigation of the potential energy hypersurface, optimization of geometries, and characterization of stationary points of the hypersurface by diagonalizing its Hessian matri-



SCHEME 1

The molecules studied with the used numbering

ces and analyzing their eigenvalues. Study of these molecules with the AM1 method is suitable, as can be seen in the results obtained using this method for other smaller molecules of the series²⁰, which are comparable with those obtained using *ab initio* methods²¹. A limit value of $1 \cdot 10^{-5}$ eV was used as the convergence criterion for the gradient norm.

RESULTS AND DISCUSSION

The parameters considered to be of interest for the molecules studied in the present work are shown in Tables I–IV, geometrical structures in Fig. 1.

Molecule **1** has four clustered hydrogen atoms inside the macroring, giving rise to strong stretchings. This is the main reason for the observed non planarity. In addition, the interaction of the clustered hydrogen atoms seems to be responsible for the fact that the six-membered rings of the molecule have bond lengths different from 1.39 Å (ranging between 1.361 and 1.435 Å, *cf.* Table I). This situation, which does not occur in small members of the series, has been demonstrated for larger compounds²². Additionally, at the periphery of the [18]annulene ring and the interior 14-membered ring, only atoms 10, 11, 12, 13 and 16, 17, 18, 1 show alternation similar to that of [18]annulene²³ and [14]annulene²⁴ while in the rest of the bonds, the deviations from 1.39 Å are less pronounced than in the [18]annulene and [14]annulene rings. The fused six-membered rings have a very strong effect on the distance at which the carbon atoms bound to the clustered hydrogen atoms are found, which in this case is 3.458 Å. This is considerably higher than the 2.6 Å obtained for other members of the series^{14,15}.

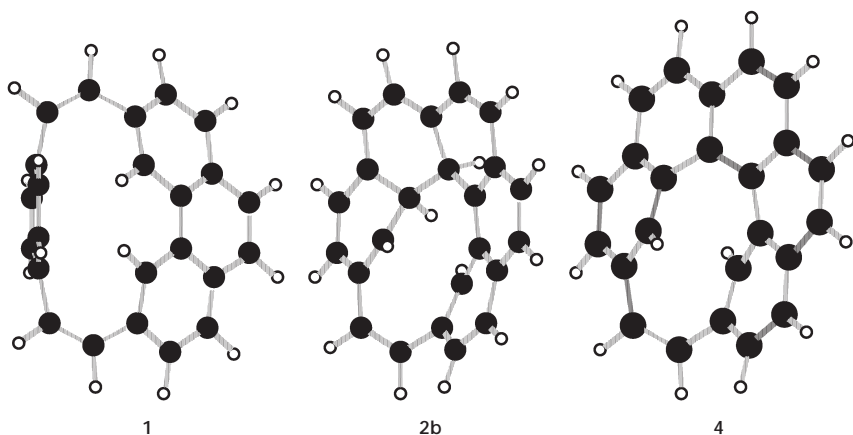


FIG. 1
The geometry of molecules **1**, **2b** and **4** calculated by AM1 method

TABLE I
Bond lengths (Å) of the molecules studied

Bond	1	2a	2b	3a	3b	4	5	6
2-1	1.417	1.448	1.444	1.360	1.447	1.423	1.434	1.425
3-2	1.381	1.345	1.346	1.435	1.350	1.369	1.362	1.369
4-3	1.415	1.450	1.449	1.363	1.450	1.423	1.434	1.425
5-4	1.435	1.422	1.423	1.449	1.404	1.433	1.415	1.425
6-5	1.361	1.368	1.371	1.350	1.389	1.363	1.379	1.369
7-6	1.435	1.419	1.421	1.449	1.404	1.430	1.415	1.425
8-7	1.415	1.424	1.423	1.363	1.450	1.417	1.449	1.425
9-8	1.381	1.373	1.375	1.435	1.350	1.381	1.350	1.369
10-9	1.417	1.423	1.422	1.361	1.446	1.417	1.446	1.425
11-10	1.456	1.462	1.458	1.443	1.357	1.459	1.357	1.425
12-11	1.344	1.350	1.347	1.347	1.446	1.350	1.444	1.369
13-12	1.462	1.454	1.462	1.441	1.356	1.459	1.357	1.425
14-13	1.404	1.459	1.454	1.359	1.447	1.417	1.446	1.425
15-14	1.393	1.356	1.349	1.442	1.350	1.381	1.350	1.369
16-15	1.404	1.459	1.447	1.359	1.447	1.417	1.449	1.425
17-16	1.462	1.347	1.356	1.441	1.356	1.430	1.415	1.425
18-17	1.344	1.442	1.447	1.347	1.447	1.363	1.379	1.369
1-18	1.456	1.356	1.357	1.443	1.357	1.433	1.415	1.425
19-1	1.387	1.503	1.514	1.497	1.496	1.410	1.411	1.409
20-19	1.410	1.512	1.498	1.490	1.493	1.438	1.441	1.429
20-4	1.412	1.395	1.391	1.459	1.407	1.410	1.411	1.409
21-7	1.412	1.422	1.418	1.458	1.407	1.415	1.394	1.409
21-20	1.444	1.437	1.418	1.357	1.404	1.445	1.416	1.429
22-10	1.387	1.385	1.383	1.497	1.496	1.390	1.500	1.409
22-21	1.410	1.428	1.420	1.491	1.493	1.414	1.492	1.429
23-22	3.458	2.416	2.487	1.525	1.529	2.422	1.492	1.429
23-13	1.402	1.364	1.355	1.508	1.494	1.390	1.500	1.409
24-23	1.394	1.494	1.484	1.537	1.525	1.390	1.500	1.409
24-16	1.402	1.498	1.513	1.508	1.494	1.415	1.394	1.409
24-19	3.458	1.528	1.558	1.525	1.530	1.445	1.416	1.429

TABLE II
Bond angles (°) of the molecules studied

Angle	1	2a	2b	3a	3b	4	5	6
3-2-1	120.5	121.1	121.8	121.4	122.1	120.5	121.2	121.0
4-3-2	121.0	121.4	121.3	120.7	122.0	120.5	121.2	121.0
5-4-3	122.2	117.3	119.1	123.1	121.7	120.5	122.3	122.0
6-5-4	121.0	120.6	121.0	121.3	120.5	121.2	120.7	121.0
7-6-5	121.0	119.6	120.0	121.4	120.5	120.3	120.7	121.0
8-7-6	122.2	120.9	122.4	123.1	121.7	122.8	121.5	122.0
9-8-7	121.0	120.5	120.6	120.7	122.0	120.6	121.6	121.0
10-9-8	120.5	119.8	120.1	121.4	122.1	120.2	122.2	121.0
11-10-9	120.7	119.0	120.8	122.0	124.1	120.7	123.5	122.0
12-11-10	126.7	125.4	123.7	122.0	121.2	125.6	120.9	121.0
13-12-11	126.1	124.3	125.6	122.3	121.1	125.6	120.9	121.0
14-13-12	119.7	120.6	117.1	121.8	124.2	120.7	123.5	122.0
15-14-13	120.4	120.7	120.9	120.0	122.8	120.2	122.2	121.0
16-15-14	120.4	120.7	121.6	120.0	122.9	120.6	121.6	121.0
17-16-15	119.7	127.3	123.0	121.8	124.2	122.8	121.5	122.0
18-1-2	120.7	120.6	122.1	122.0	124.1	120.5	122.3	122.0
18-17-16	126.1	119.6	119.3	122.3	124.2	120.3	120.7	121.0
19-1-2	118.3	117.1	119.8	119.5	117.0	119.7	118.8	119.0
20-19-1	121.6	117.1	114.5	112.6	115.6	118.6	119.8	120.0
20-4-3	118.8	121.3	120.6	119.5	119.0	119.7	118.8	119.0
21-7-6	119.0	119.5	118.7	117.2	119.2	118.5	119.3	119.0
21-7-8	118.8	119.4	118.7	119.5	119.0	118.6	119.3	119.0
21-20-4	119.6	117.7	118.2	120.2	120.0	117.3	119.9	120.0
22-21-20	120.9	123.9	121.4	123.1	120.4	122.3	118.3	120.0
22-21-7	118.9	116.1	118.0	116.6	119.5	117.7	121.2	120.0
22-10-9	118.4	118.1	118.6	119.5	117.0	118.0	117.7	119.0
23-13-12	121.5	122.4	123.7	120.2	118.8	120.7	118.7	119.0
24-23-13	120.4	114.9	123.6	107.0	114.4	119.7	114.8	119.0
24-16-15	118.7	111.7	119.1	118.0	116.7	118.6	119.3	119.0

TABLE III
Dihedral angles (°) of the molecules studied

Dihedral angle	1	2a	2b	3a	3b	4	5
4-3-2-1	4.	357.	4.	351.	357.	5.	358.
5-4-3-2	172.	194.	181.	185.	184.	182.	181.
6-5-4-3	191.	170.	179.	170.	178.	177.	178.
7-6-5-4	0.	3.	3.	0.	357.	6.	358.
8-7-6-5	169.	193.	187.	169.	178.	184.	180.
9-8-7-6	188.	169.	171.	185.	184.	175.	184.
10-9-8-7	356.	10.	7.	351.	357.	8.	359.
11-10-9-8	173.	195.	196.	181.	176.	194.	172.
12-11-10-9	207.	132.	137.	188.	179.	137.	181.
13-12-11-10	357.	15.	11.	4.	12.	11.	13.
14-13-12-11	255.	141.	137.	165.	179.	137.	181.
15-14-13-12	168.	186.	191.	185.	176.	194.	172.
16-15-14-13	0.	8.	7.	17.	358.	8.	359.
17-16-15-14	192.	202.	165.	186.	176.	175.	184.
18-17-16-15	105.	174.	189.	165.	179.	184.	180.
18-1-2-3	187.	168.	172.	-179.	176.	182.	181.
19-1-2-3	4.	343.	353.	354.	350.	0.	0.
20-19-1-2	349.	28.	3.	28.	23.	348.	4.
20-4-3-2	356.	10.	2.	359.	2.	0.	0.
21-7-6-5	353.	9.	4.	355.	0.	3.	1.
21-7-8-9	4.	353.	4.	-1.	2.	356.	3.
21-20-4-3	170.	183.	173.	200.	188.	170.	185.
22-10-9-8	356.	6.	7.	354.	350.	5.	349.
22-21-20-4	188.	182.	187.	156.	166.	196.	171.
22-21-7-8	2.	348.	174.	24.	13.	347.	8.
23-13-12-11	71.	329.	320.	346.	4.	326.	4.
24-23-13-12	192.	139.	160.	136.	205.	148.	198.
24-16-15-14	8.	21.	348.	5.	351.	356.	3.

Concerning the bond angles, this molecule shows quite high values of the bond angles in the interior 14-atom ring. Furthermore, the bonds involved in these angles are those exhibiting the largest alternation. Again, the effect of the six-membered rings is observed. Although the interior 14-atom ring does not correspond exactly to the periphery of [14]annulene²⁴, it is possible to establish differences between the values obtained for the two rings. In [14]annulene, the largest deviations from the bond angle of 120° correspond to the angles formed by atoms 19, 20, 21, 22 (125.0°)²⁵ while the angles formed by atoms 1, 18, 17, 16 deviate less. In our case, it is just the latter angle 18, 17, 16 that undergoes the largest deviation (*cf.* Table II). A study of dihedral angles shows that the molecule is not flat. The three-fused six-membered rings lie almost in the same plane whereas the other six-membered ring is in a plane almost perpendicular to the previous ones (*cf.* Table III). This observation is consistent with an experimental NMR study of this molecule carried out by Du Vernet²⁶. The situation is also similar to that observed for [2.2.2.]paracyclophane-1,9,17-triene¹⁶ accounting for the large distance observed between the carbon atoms linked to clustered hydrogens. This is in contrast to other smaller members, in which the carbons linked to clustered hydrogens form parts of the six-membered rings, such as in *anti*-[2.2]metacyclophane-19-diene, where the six-membered rings lie on almost parallel planes²¹.

TABLE IV
Energy of the molecules studied

Compound	Heat of formation kcal/mol	Electronic energy eV	Core-core repulsion eV	μ , D	Ionitiation potential eV	$E(\text{HOMO})$ eV	$E(\text{LUMO})$ eV
1	130.2	-26 049.1	22 758.8	0.47	8.3	-8.3	-0.6
2a	181.5	-26 437.2	23 149.1	0.13	7.8	-7.8	-1.0
2b	161.3	-26 463.2	23 174.2	0.30	7.7	-7.7	-1.0
3a	159.2	-26 513.4	23 224.2	0.15	7.4	-7.4	-1.3
3b	130.5	-26 510.4	23 220.1	0.05	7.9	-7.9	-0.9
4	146.2	-25 571.0	22 308.8	0.04	8.3	-8.3	-0.7
5	120.6	-25 637.4	22 374.0	0.10	8.0	-8.0	-0.9
6	96.2	-24 771.7	21 534.6	0.00	8.2	-8.2	-1.0

The transformation of this molecule to coronene as happens with other benzoannulenes requires a prior step of a hydroannulene, as previously reported in many experimental works^{3,27}. In this transformation, a new bond is formed between atoms 19 and 24, which leads to the formation of two isomers, depending on the position adopted by the hydrogens bound to atoms 23 and 24. If these hydrogen atoms remain on the same side of the plane, they are designated as **2a** whereas if they are on the other side of the plane, they are designated **2b**. The heats of formation of the two possible isomers are 181.5 and 161.3 kcal/mol, respectively. These values are much higher than that obtained for compound **1** (130.2 kcal/mol) suggesting that the isomers are intermediate products which have lost a part of their resonance energy and therefore show a larger energy content and lower stability. The formation of these dihydroannulenes also involves an increase in planarity of the compound, despite the stretching that occurs among the hydrogen atoms bound to the carbon atoms 22 and 23, which show separations of 2.416 and 2.487 Å for compounds **2a** and **2b**, respectively. The bond angles of these molecules are more altered and the 10–11–12 bond angle in **2b** decreases by about 3° with respect to molecule **1** while the 11–12–13 angle decreases only by approximately 1°. Moreover, in this molecule, angles 12–13–14 and 15–16–17 also depart considerably from 120°. The remaining angles of the periphery of the [18]annulene ring of this molecule do not show marked differences compared with molecule of **1**. In molecule **2a**, the angles most departing from 120° are 15–16–17, 10–11–12 and 11–12–13, the first being the one with the most pronounced difference from molecules **1** and **2b**.

From a study of the dihedral angles, it may be inferred that molecule **2** is much flatter than molecule **1**, although, due to the clustering of the hydrogen atoms bound to atoms 22 and 23, they are still far from being flat. This increase in planarity is seen more clearly in the 11–12–13–14 dihedral angle. Likewise, the six-membered ring formed by atoms 13, 14, 15, 16, 24, 23 lies almost in the same plane as that formed by the other six-membered rings, atoms 22 and 23 deviating most from this reference plane. The increase in planarity has also been observed experimentally for this and other molecules analogous to those studied by Otsubo²⁷.

Experimentally, the pathway proposed for the transformation in coronene²⁷ is **3**→**5**→**6**. However, in the present work it was also thought appropriate to study the **4**→**5**→**6** pathway in order to confirm whether the relative stability of these compounds does in fact correspond with the pathway followed by the reaction. In molecule **3**, two isomers may appear, depending on the position occupied by the hydrogen atoms when the

six-membered ring closes. Molecule **3a** refers to molecules whose hydrogens bound to atoms 22 and 23 are on the same side of the plane and whose hydrogens bound to atoms 19 and 24 are on the opposite side. Molecule **3b** refers to molecules whose hydrogens bound to atoms 22 and 24 are on the same side of the plane and whose hydrogens bound to atoms 23 and 19 are on the opposite side.

The alternation in the periphery of [18]annulene shown by compounds **3** is similar to that reported for [18]annulene²³. On studying its bond length, it may be deduced that molecule **3b** is the one whose periphery most resembles that of [18]annulene. The bond between atoms 22 and 23 gives rise to much flatter molecules than the previous **2**. In this case, some of the carbon atoms deviate only slightly from the plane, as can be seen in Table III. These observations are in good agreement with experimental work on analogous molecules containing a sulfur atom¹³. However, a fundamental difference appears in the six-membered ring formed by atoms 4, 5, 6, 7, 20, 21 of compound **3b**: the bond lengths are 1.40 Å. By contrast in molecule **3a**, this ring displays an even more pronounced alternation than in the previous cases. This situation would make molecule **3b** more aromatic and, as a result, more stable. The heats of formation indicate that molecule **3b** is much more stable than **3a**. According to this, molecule **3b**, and not **3a**, is formed. Similarly, the heat of formation of compound **3b** is very similar to that recorded for compound **1**, since the observed differences of 0.5 kcal/mol are not significant. This suggests that a tautomerism must exist between these two compounds unless the activation energy of tautomerization is very high, as has been confirmed for other compounds of the same type¹⁶. To check this point, we studied the interconversion process between compound **1** and **3b**; two saddle points were observed of 208.2 and 257.5 kcal/mol, comparable to those of other previously studied metacyclophanes, found¹⁶.

Studying compound **4**, it can be seen that this molecule has an interior [10]annulene ring. This ring shows a very pronounced alternation for bonds 10–11, 11–12 and 12–13. The other bonds of this ring have lengths above 1.40 Å, by about 0.04 Å. At the periphery of the [18]annulene ring of this molecule there are longer alternating bonds than those exhibited by molecule **1**, of the same order as those shown by molecule **3b**. Both the interior [10]annulene ring and the periphery of the [18]annulene have less alternating bonds than other metacyclophanes²⁰. The largest deviations from the 120° bond angles correspond to angles 10–11–12, followed by 6–7–8 and 9–10–22. The larger deviations of these angles are due to the non-bonding interactions of the hydrogen atoms bound to atoms 22 and 23.

The planarity of this molecule resembles that of molecule **2** to a considerable extent although it is slightly flatter, undoubtedly owing to the loss of two hydrogen atoms. Its heat of formation is higher than that of molecule **1** and hence it is less stable. However, its molecule is more stable than molecules **2** and **3a**, showing the C_{2h} symmetry not observed in the other two ones. This symmetry has also been observed for molecules **1** and **3b**, suggesting that the greater symmetry of these molecules directly affects their stability. On the basis of the stability of these molecules the easiest pathway for this transformation to occur would be through **3b** and not through **4**.

Finally, both compound **3** and compound **4** are transformed into **5** and subsequently into **6**, which shows the C_{2h} symmetry. The periphery of the [18]annulene ring exhibit alternating values, that of compound **5** being most similar to the alternating values obtained for [18]annulene. Molecule **5** is much flatter than the previous ones, only carbon atoms 22 and 23 depart very little from planarity. Molecule **6** is completely flat, as expected for this type of molecule, it shows less alternating bonds than molecule **5**, and its bond angles are closer to 120° . The values obtained for compound **6** are in good agreement with the data obtained in crystallographic studies²⁸. The heats of formation for compounds **5** and **6** are lower than those for all the other compounds in the study, compound **6** being the most stable and having the greatest degree of planarity and symmetry.

At this point, the dipole moments shown by these molecules (**1-6**) should be mentioned. The moment is small, as expected for molecules of this type, which is why they are only sparingly soluble in polar solvents in general, although the easiest molecule to dissolve would be molecule **1**.

CONCLUSIONS

The stability of these compounds (**1-6**) allows the prediction that the pathway followed in the transformation of **1** into coronene would be **1**→**2b**→**3b**→**5**→**6**. The diatropism of this type of molecule is conserved. The tautomerism between compound **1** and compound **3b** is possible, as in other smaller metacyclophanes. In all cases, the molecules are transformed until a flat molecule is attained. Finally, the resonance energy produced in molecule **4** due to the loss of hydrogens in position 19 and 24 does not compensate the lower bond energy observed in molecule **3b**.

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