Effect of benzannelation on the conformational flexibility of the rings in oxo, imino, and methylene derivatives of cyclohexa-1,4-diene

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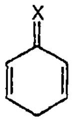
The effect of benzannelation on the equilibrium conformation and flexibility of the dihydrocycle in cyclohexa-1,4-dienone, *para*-quinone, and their imino and methylene analogs was studied by the semiempirical quantum-chemical AM1 method. The equilibrium conformations of the carbonyl derivatives are planar. In the imino- and methylene-substituted analogs, the dihydrocycle adopts a boat conformation due to repulsions between the hydrogen atoms at the exocyclic double bond and in the *peri* positions of the benzene rings. Annelation of cyclohexa-2,5-dien-1-one and *para*-quinone with benzene rings at the C=C double bonds causes an increase in the conformational flexibility of the partially hydrogenated ring owing to an increase in the bending strain in the first compound and a decrease in the conjugation between the carbonyl groups and the remaining part of the molecule in the second compound.

Keywords: cyclohexa-1,4-diene, conformational flexibility, benzannelation, AM1 method.

Previously,[1,2] it has been demonstrated that annelation of cyclohexa-1,4-diene with benzene rings at the C=C double bonds leads to a substantial increase in the conformational flexibility of the dihydrocycle. This effect is attributable to an increase in the bending strain in the benzene analogs of cyclohexa-1,4-diene as a result of replacement of the C(sp^3)—C(sp^2)—H bond angles, which can be rather readily deformed, by the C(sp^3)—C(Ar)—C(Ar) angles in going to the structures that contain rigid aromatic rings. According to *ab initio* calculations,[3] the conformational flexibility of the partially hydrogenated ring decreases somewhat when the methylene groups in cyclohexa-1,4-diene are replaced by the exocyclic double bonds. However, on the whole, this characteristic feature is retained.



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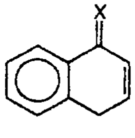

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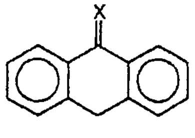

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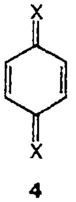

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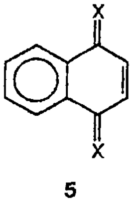

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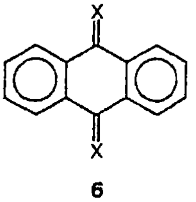

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1—6: X = O (**a**), NH (**b**), CH$_2$ (**c**)

The conformational flexibility of the dihydrocycle in the benzannelated derivatives of these compounds is still poorly studied. Only the contradictory data of ^{1}H NMR spectroscopy of substituted 9-methylene-9,10-dihydroanthracenes are available.[4,5] For this reason, in this work we carried out a theoretical study of the effect of benzannelation on the conformational flexibility of the dihydrocycles in molecules **1**—**6**.

Calculation procedure

The spatial structures of compounds **1**—**6** were calculated by the semiempirical quantum-chemical AM1 method.[6] The conformational flexibility of the dihydrocycles was studied by scanning the C=C—C(sp^3)—C= (molecules **1**—**3**) or C=C—C(=X)—C= (molecules **4**—**6**) torsion angle in the range of ±30° with optimization of the other geometric parameters in each point. The results of calculations are given in Tables 1 and 2.

Results and Discussion

The equilibrium conformations of cyclohexa-2,5-dien-1-one and its imino and methylene analogs (**1a**—**c**) are governed by two groups of opposite factors

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Table 1. Torsion angles (τ) and puckering parameters of the dihydrocycle in molecules **2b**,**c**, **3b**,**c**, **5b**,**c**, and **6b**,**c***

Compound	φ/deg		Puckering parameters		
	C_{ar}—C_{sp^3}—C=C**	C_{ar}—C(=X)—C=C	S	Θ	Ψ
2b	17.3	−19.5	0.3	85.3	0.9
2c	11.3	−12.3	0.2	86.6	1.1
3b	28.3	−29.8	0.5	89.2	1.1
3c	26.9	−27.3	0.5	89.8	0.1
5b	22.7	−22.6	0.4	89.9	0.1
5c	15.5	−15.4	0.3	89.9	0.2
6b	31.6	−31.5	0.5	89.9	0.1
6c	27.8	−27.7	0.5	89.9	0.0

* Equilibrium conformations of the other molecules are planar. ** The values of the second C_{ar}—C(=X)—C=C torsion angle are given for structures **5b**,**c** and **6b**,**c**.

that affect the geometry of the ring.[1,3] The first group involves the bending strain occurring owing to the deformation of the endocyclic bond angles at the saturated C atom; this strain is maximum in the planar conformation. The second group of the factors involves the conjugation between the π systems of the double bonds, which stabilize the planar conformation of the ring, and the 1,2-allylic strain occurring through nonbonded interactions between the methylene hydrogen atoms and the double bonds.

The calculated equilibrium conformations of the rings in molecules **1a**—**c** are planar, which agrees with the theoretical[3,7] and experimental[8,9] data. Annelation of the dihydrocycle with benzene rings at the C=C double bonds leads to an increase in the bending strain in the molecule owing to the higher rigidity of the bond angles of the rigid aromatic rings compared to the $C(sp^3)$—$C(sp^2)$—H and $C(sp^3)$—$C(sp^2)$—$C(sp^2)$ angles in nonannelated form **1**. However, the equilibrium structures of carbonyl derivatives **2a** and **3a** are planar, which is also suggested by the theoretical[10] and experimental[11] data.

In imino and methylene derivatives **2b**,**c** and **3b**,**c**, an additional factor affects the geometry of the dihydrocycle, namely, repulsions between the H atoms at the exocyclic double bond and in the *peri* positions of the benzene rings. The strength of these unfavorable nonbonded interactions is governed by the C=X bond length. The shortening of the exocyclic C=N double bond (compared to C=C) leads to a shortening of the H...H distance and, as a consequence, to an increase in repulsion. As a result, the dihydrocycle in compounds **2b**,**c** and **3b**,**c** adopts a boat conformation. The degree of puckering of the ring in the imino derivatives is larger than that in the methylene-substituted derivatives (see Table 1). It should be noted that an increase in the bending strain in the series **1**—**2**—**3** causes an even more substantial distortion of the equilibrium conformation of the dihydrocycle from planarity.

Table 2. Changes in the energy (kcal mol^{-1}) upon bending of the dihydrocycle in molecules **1**—**6**

Compound	Torsion angle/deg			
	0	10	20	30
1a	0	0.2	0.9	2.1
1b	0	0.2	0.7	1.7
1c	0	0.2	0.9	2.0
2a	0	0.1	0.6	1.5
2b	0.3	0.1	0	0.4
2c	0.1	0	0.1	0.7
3a	0	0	0.1	0.4
3b	1.5	0.8	0.2	0
3c	1.4	0.6	0.1	0
4a	0	0.2	0.7	1.8
4b	0	0.1	0.5	1.4
4c	0	0.3	1.2	2.8
5a	0	0.2	0.6	1.7
5b	0.5	0.3	0	0.2
5c	0.3	0.1	0.1	0.3
6a	0	0	0.3	0.9
6b	3.6	2.0	0.7	0
6c	3.2	1.5	0.3	0

The high conformational flexibility of the dihydrocycle in compounds **1**—**3** is attributable to the presence of two opposite factors that determine the geometry of the ring.[1,3,12] Thus, a transition from a planar equilibrium conformation of the dihydrocycle in cyclohexa-2,5-dien-1-one to a boat conformation with the C=C—$C(sp^3)$—C torsion angle of ±20° leads to an increase in the energy of the molecules by no more than 1 kcal mol^{-1} (see Table 2).

The conformational flexibility of the ring increases somewhat as the polarity of the exocyclic double bond in compounds **1a**—**c** changes. The energy of deformation of the ring in imino derivative **1b** is lower than that in methyl-substituted compound **1c**. As demonstrated previously,[3,13] this is because of the fact that the conformational flexibility of the ring in molecule **1b** calculated by the AM1 method is overestimated.

An increase in the bending strain in the series **1a**—**2a**—**3a** leads to an increase in the flexibility of the dihydrocycle (see Table 2) owing to destabilization of the planar conformation. An increase in repulsion between H atoms in derivatives of 1,4-dihydronaphthalene **2a**—**c** also exerts an analogous effect. The inversion barriers of the rings in these compounds are insignificant (see Table 2). In going to derivatives of 9,10-dihydroanthracene **3b**,**c**, the planar geometry is severely destabilized, which is caused by an increase in the number of unfavorable nonbonded H...H interactions. As a consequence, the conformational flexibility of the partially dihydrogenated ring is substantially decreased.

The replacement of the methylene group in cyclohexa-2,5-dien-1-one by the exocyclic double bond results in the disappearance of the bending strain that destabilizes the planar conformation. However, as demonstrated previously,[3,13] the dihydrocycle in the quinone molecule remains conformationally flexible. In this case, destabilization of the planar structure of the ring is determined by a partial disruption of aromaticity of the cyclic conjugated system.

According to the results of calculations, the equilibrium conformations of the partially hydrogenated rings in molecules **4a—c** are planar, which agrees well with the results of theoretical[14,15] and experimental[16,17] studies. Annelation with benzene rings at the C=C bonds and the change in the nature of the exocyclic double bonds exert an effect on the equilibrium structure of the dihydrocycle analogous to that considered above for compounds **1—3**. The molecules of naphthoquinone **5a** and anthraquinone **6a** remain planar, which is in agreement with the experimental[18,19] and theoretical[20] data. In quinoneimines and quinonemethides **5b,c** and **6b,c**, the dihydrocycle adopts a boat conformation owing to repulsions between H atoms. The degree of puckering in the imino derivatives is higher than that in the methylene-substituted analogs (see Table 1).

As demonstrated previously,[3] the dihydrocycle in compounds **4a—c** remains conformationally flexible. According to the results of AM1 calculations (see Table 2), in the case of *para*-quinone **4a**, a transition from a planar equilibrium conformation to a boat conformation with the C=C—C(=O)—C torsion angle of 20° requires 0.7 kcal mol^{-1}. A decrease in the polarity of the exocyclic double bond leads to an increase in the degree of aromaticity of the cyclic π system and, as a consequence, to a decrease in the flexibility of the dihydrocycle.

The bending strain in molecules **4—6** is absent. Therefore, benzannelation would be expected to have no effect on the flexibility of the ring. However, calculations of compounds **4a**, **5a**, and **6a** demonstrated that in this series, the conformational flexibility of the partially hydrogenated ring also increases. These compounds do not contain a saturated C atom, and therefore this behavior is, apparently, determined by electronic effects.

A detailed analysis of the vibrational characteristics and the geometries of benzoquinone and naphthoquinone, which was carried out in Ref. 20 with the use of *ab initio* quantum-chemical methods, suggested that benzannelation leads to a decrease in the conjugation between the carbonyl groups and the π system of the remaining part of the molecule. This agrees also with the change in the reactivity of the C=O group in the series **4a—5a—6a**. In anthraquinone and benzophenone, the reactivities differ only slightly.[21] Therefore, it can be suggested that it is a decrease in conjugation interactions between these fragments that is responsible for an increase in the conformational flexibility of the dihydrocycle upon successive benzannelation of *para*-quinone.

A comparison of the inversion barriers of the rings in molecules **2b,c**, **3b,c**, **5b,c**, and **6b,c** demonstrated that when the methylene group is replaced by the second exocyclic double bond, these values are doubled. This confirms the suggestion made previously that repulsions between the H atoms at the exocyclic double bond and in the *peri* positions of the benzene rings is the major factor that destabilizes the planar conformation of the dihydrocycle in these compounds. Therefore, according to calculations, annelation of the dihydrocycle with the benzene rings at the C=C double bonds in ylidene derivatives of cyclohexa-1,4-diene results in an increase in its conformational flexibility. In the imino- and methylene-substituted derivatives, the dihydrocycle adopts a nonplanar conformation.

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