

Geometry-based analysis of Azulene and Azulene-like systems with H- or Li-bonding[†]

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ABSTRACT: B3LYP/6–311+G** optimization was carried out for azulene and its analogs, in which CH—CH—CH fragment was replaced with O··X··O (X = H or Li). π -electron delocalization in four possible derivatives with H-bonding and three possible derivatives with Li-bonding was described by the use of HOMA index. All derivatives with Li-bonding exhibit high π -electron delocalization similar to that found for azulene. Among four H-bonded systems, two exhibit lower π -electron delocalization (HOMA < 0.39) and higher total electron energy than the other two derivatives. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: azulene; π -electron delocalization; aromaticity; H-bonding; Li-bonding

INTRODUCTION

For a long time aromaticity of azulene has been considered as something mysterious.¹ Usually non-alternant hydrocarbons are not stable and hence considered as non- or even anti-aromatic.² Five-membered π -electron rings, for example, fulvene derivatives,³ are stabilized by electron donating substituents, whereas in the case of seven-membered π -electron rings, for example, heptafulvene, they are stabilized by electron accepting ones. Indeed, an increase of electron donating power of substituent linked to the exo-cyclic carbon atom of fulvene increases its stability.⁴ In a similar manner electron accepting substituents increase stability of seven-membered ring.⁵ In both cases the odd-membered rings tend to possess six π -electrons, and intramolecular charge transfer (mesomeric effect) allows fulfilling the Hückel's $4N + 2$ rule.⁶

Azulene is the case where five- and seven-membered rings are fused, and the above-mentioned intramolecular charge transfer from the seven-membered ring to the five-membered one occurs leading to appearance of electrical dipole moment (1.08 D).⁷ This transfer increases both π -electron delocalization and stability of the system. Resonance energy of azulene⁸ estimated from the heat of hydrogenation is $28.3 \text{ kcal mol}^{-1}$ and may be compared with $36.0 \text{ kcal mol}^{-1}$ for benzene estimated by the same method.⁹

Azulene is the valence isomer of naphthalene, and it is worth comparing them. Azulene is less stable than naphthalene – thermochemical estimation of resonance energy gives $81.8 \text{ kcal mol}^{-1}$ for naphthalene and $49.2 \text{ kcal mol}^{-1}$ for azulene.¹ The same method applied to benzene gives $42.4 \text{ kcal mol}^{-1}$.¹ Topological resonance energy (TRE) gives for azulene and naphthalene 0.151 and 0.389, in $|\beta|$ units, respectively¹⁰ similarly as the Hess–Schaad estimations: 0.231 and 0.550 in $|\beta|$, respectively.¹¹ The direct comparison of electron energies for these two isomers computed at B3LYP/6-31G(d) level of theory shows that naphthalene is more stable than azulene by $34.23 \text{ kcal mol}^{-1}$,¹² which is qualitatively in line with thermochemical and theoretical results presented above. Obviously, the strain present in azulene decreases its stability by $\sim 16 \text{ kcal mol}^{-1}$,¹³ still indicating that naphthalene is a more stable system. Undoubtedly, different methods of estimation of aromatic stabilization energy (ASE)¹⁴ lead to different absolute values but still indicate lower stability of azulene.

Magnetic studies of π -electron delocalization in azulene and naphthalene show less differentiated picture.¹⁵ Diamagnetic susceptibility exaltation values, Λ , (defined as a difference of the experimental value of diamagnetic susceptibility between the system in question and the reference cyclopolyene) for azulene and naphthalene are 29.6 and $30.5 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, respectively. New estimations of magnetic susceptibility of naphthalene¹⁶ and azulene¹⁷ are -123.6 and -88.3 ppm cgs, respectively, showing greater difference between those two systems than the older data. Another magnetism-based quantitative measure of π -electron delocalization, the Schleyer's NICS, gives for five- and

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[†]Dedicated to Professor Marek K. Kalinowski on the occasion of his 70th birthday.

seven-membered rings of azulene the values of -19.7 and -7.0 , respectively, (calculated at B3LYP/6-31+G* using GIAO method) whereas for a ring in naphthalene NICS is -9.9 .¹⁸ However, it has been previously reported that NICS approach¹⁹ overestimates the aromaticity for the five-membered rings and underestimates for the seven-membered rings (in comparison with the NICS value for benzene).¹⁸ On the other hand, π -electron currents induced in polycyclic benzenoid and non-benzenoid hydrocarbons gives values 1.093 for each ring in naphthalene and 1.069 and 1.150 for seven- and five-membered rings of azulene, respectively (in units of the value for benzene).²⁰ However, the ring currents in individual rings in non-alternant hydrocarbons are less reliable than those for alternant systems since in the non-benzenoid ones the current is present almost only in the perimeter.²¹

Comparison of the above data leads to a conclusion that aromatic stability of azulene is definitely lower than that of naphthalene even if the correction for strain energy is taken into account. However, magnetic susceptibility values suggest, in some way, a similar π -electron delocalization in both azulene and naphthalene. This finding is not surprising since aromaticity as a notion is a collective phenomenon²² and energetic,^{14,23} magnetic,²⁴ and geometric²⁵ criteria are not always uniquely defined and equivalent.²⁶ It is also well known that different aromaticity indices may show similar picture when applied for π -electron systems belonging to structurally closely related families.^{4d,5b} Naphthalene and azulene belong to two topologically different classes of π -electron compounds, so-called alternant and non-alternant hydrocarbons,²⁷ respectively, and hence equivalency of different aromaticity indices is not expected.^{26e}

Recently, the systems topologically analogous to naphthalene where CH—CH—CH fragment in one of the rings was replaced with O...X...N^{28a} or O...X...O,^{28b,c} where X = H or Li, have been studied. It was found that the Li-bonded derivatives exhibit relatively high π -electron delocalization in both carbocyclic and quasi-ring resembling the situation in naphthalene. In the case of H-bonded systems π -electron delocalization observed in the benzenoid ring is high whereas in the quasi-ring is definitely smaller, but still significant. Similarly higher π -electron delocalization in the quasi-ring of Li-bonded derivative than H-bonded one is observed when the benzene analog, malonaldehyde, has been investigated.²⁹

The aim of this report is to answer the following question: what happens if we replace CH—CH—CH fragment in azulene with O...X...O, where X is H or Li? Will we observe similar situation as that found in naphthalene analogs?^{28c}

METHODOLOGY

Ab initio optimizations at B3LYP/6-311+G**³⁰ level were carried out in Gaussian03³¹ for molecules presented

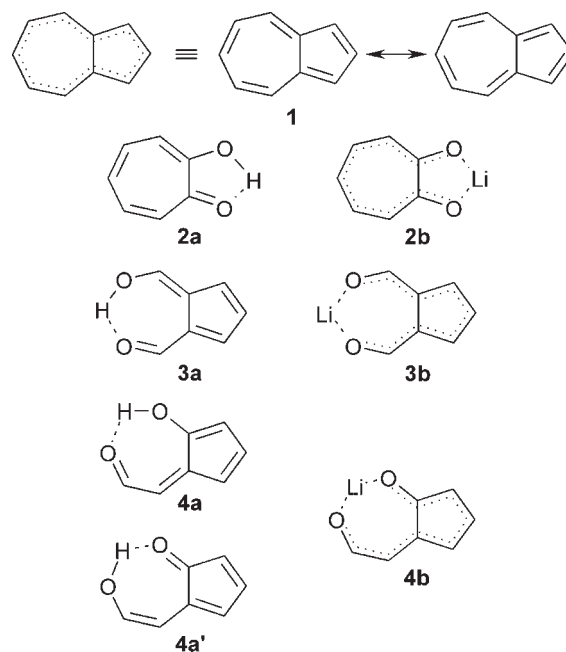


Figure 1. Labeling of the studied systems

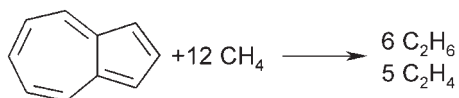
in Fig. 1. For **1**, **2b**, and **3b** the C_{2v} symmetry of the molecules has been assumed (the energy differences between the molecules with and without constrained symmetry were insignificant).

Geometry parameters of the ring (C—C and C—O bond lengths) were used to calculate aromaticity index HOMA³² according to the following equation:

$$\text{HOMA} = 1 - \frac{1}{n} \sum_{j=1}^n \alpha_i (R_{\text{opt},i} - R_j)^2 \quad (1)$$

where n represents the total number of bonds taken into summation; α_i is a normalization constant (for C—C bonds $\alpha_{\text{C—C}} = 257.7$ and for C—O bonds $\alpha_{\text{C—O}} = 157.38$) fixed to give HOMA = 0 for a model non-aromatic system, for example, Kekulé structure of benzene³³ and HOMA = 1 for the system with all bonds equal to the optimal value $R_{\text{opt},i}$ assumed to be realized for fully aromatic systems ($R_{\text{opt,C—C}} = 1.388 \text{ \AA}$, $R_{\text{opt,C—O}} = 1.265 \text{ \AA}$).

We have also applied the Bond Separation Reaction approach, which allows to study, for example, bond separation reaction energy (E_{BSR})³⁴ describing energetics of the systems in question. E_{BSR} is the energy difference between the reference systems with localized single and double bonds and the system in question, provided that the number of all atoms at both sides of the bond separation reaction is the same. It means that E_{BSR} estimates the energy of stabilization of the studied system in comparison with the reference systems without any kind of delocalization. Scheme 1 illustrates this concept for azulene as an example.



Scheme 1. Example Bond Separation Reaction (BSR) for azulene

The BSRs are a subgroup of isodesmic reactions serving as the basis for estimation of non-additivity of energy due to some particular kind of interaction(s).^{14,34,35}

Estimation of the approximate value of H-bonding energy is carried out following the procedure suggested by Grabowski.³⁶ This approximate energy is calculated as a difference between the energy of the closed (H-bonded) and open conformation of the studied system (see Fig. 2). In this procedure apart from the energy of H-bonding formation, the energy resulting from π -electron reorganization in the molecule is also included.

RESULTS AND DISCUSSION

At the beginning, we stress once again that a fundamental difference between naphthalene and azulene is in the alternant and non-alternant character of these molecules. This results in a substantial difference in the calculated length of the central bond: 1.432 Å for naphthalene (C4a–C8a) and 1.498 Å for azulene (C3a–C8a). In the case of naphthalene both rings are fused through the bond participating in π -electron delocalization, which is not the case for azulene. This difference is manifested in a different bond length alternation in the perimeter. HOMA for naphthalene perimeter is 0.84 whereas for azulene is 0.97. This may be interpreted in terms of so-called bond number conservation rule³⁷ applied to C–C bonds in π -electron hydrocarbons. Qualitatively, $2p_z$ orbital at each of the fusion carbon atoms in both naphthalene and azulene overlap with three neighboring carbon $2p_z$ orbitals. This leads to a possibility of π -electron conjugation in all three directions. Such situation occurs in the case of naphthalene. Bond lengths linking atoms C4a and C8a with adjacent carbon atoms are of a similar magnitude (1.420, 1.420, and 1.432 Å) being at the same time similar to the bond lengths in graphite 1.422(1) Å.³⁸ In the case of azulene the situation is different. One of

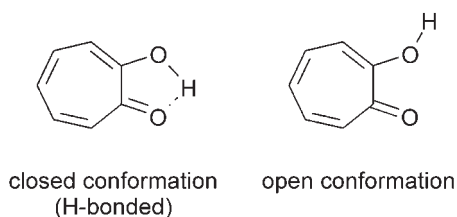


Figure 2. Scheme of closed and open conformation

those three bonds is definitely longer (1.498 Å) from the others (1.390 and 1.405 Å) and the $2p_z$ orbital at fusion atom overlaps mostly with $2p_z$ orbitals of two neighboring peripheral carbon atoms. Therefore the conjugation in the perimeter may be much stronger exhibiting a greater π -electron delocalization than in the individual rings. The $2p_z$ orbitals at C3a and C8a carbon atoms overlap only slightly.

The situation presented above is also observed in the cases where CH–CH–CH fragment in one ring is replaced with O···X···O (X = H or Li), that is, the system being a subject of this study. Figure 3 presents all molecules considered in this work along with selected bond lengths. HOMA values for fragments of perimeter consisting of heavy atoms (all CC and CO bonds except C3a–C8a bond) are presented in Table 1. Comparison between HOMA values for H-bonded systems (**2a**, **3a**, **4a**, and **4a'**) in closed and open conformations (see Fig. 2) shows that forming of intramolecular H-bonding is associated with an increase of HOMA values by 0.2–0.6 indicating increase of π -electron delocalization. This effect may be explained in terms of modified substituent properties due to H-bonding interaction in comparison with non-interacting substituent.³⁹ H-bonding increases electron donating properties of the –OH group toward the aromatic moiety since proton moving away increases the negative charge at the oxygen atom. Simultaneously proton interacting with the oxygen atom of the carbonyl group causes an increase of electron attracting ability of the carbonyl group. In consequence a stronger substituent effect occurs leading to a stronger bond length equalization, that is, stronger π -electron delocalization in comparison with the open conformation. This effect is associated with an increase of stability by 11.3–18.2 kcal mol⁻¹ (Table 1).

It may be concluded that H-bonding formation increases π -electron delocalization in the heavy atom part of the perimeter more than it would be expected from the sole substituent effect between π -electron donating –OH group and π -electron accepting –C=O group without H-bonding.

When HOMA values for H-bonded conformations of **2a**, **3a**, **4a**, and **4a'** are compared, an interesting rule is found. For cases where heavy atom skeleton has an approximate symmetry plane of the heavy atom skeleton (**2a**, **3a**) the HOMA values are higher than 0.77, whereas for cases without this kind of symmetry (**4a**, **4a'**) HOMA is lower than 0.39.

Molecules **3a**, **4a**, and **4a'** are the isomers in which the CH–CH–CH fragment from the seven-membered ring is replaced with O···H···O. The Grabowski³⁶ approximate estimation of H-bond strength shows that **3a** system forms a substantially stronger H-bonding (18.2 kcal mol⁻¹) than **4a** (11.3 kcal mol⁻¹) and **4a'** (12.6 kcal mol⁻¹). Additionally, in **3a**, differences in C–O bonds length between the closed and open conformation are 0.028 Å and 0.031 Å, whereas for **4a** and **4a'** the greatest differences are

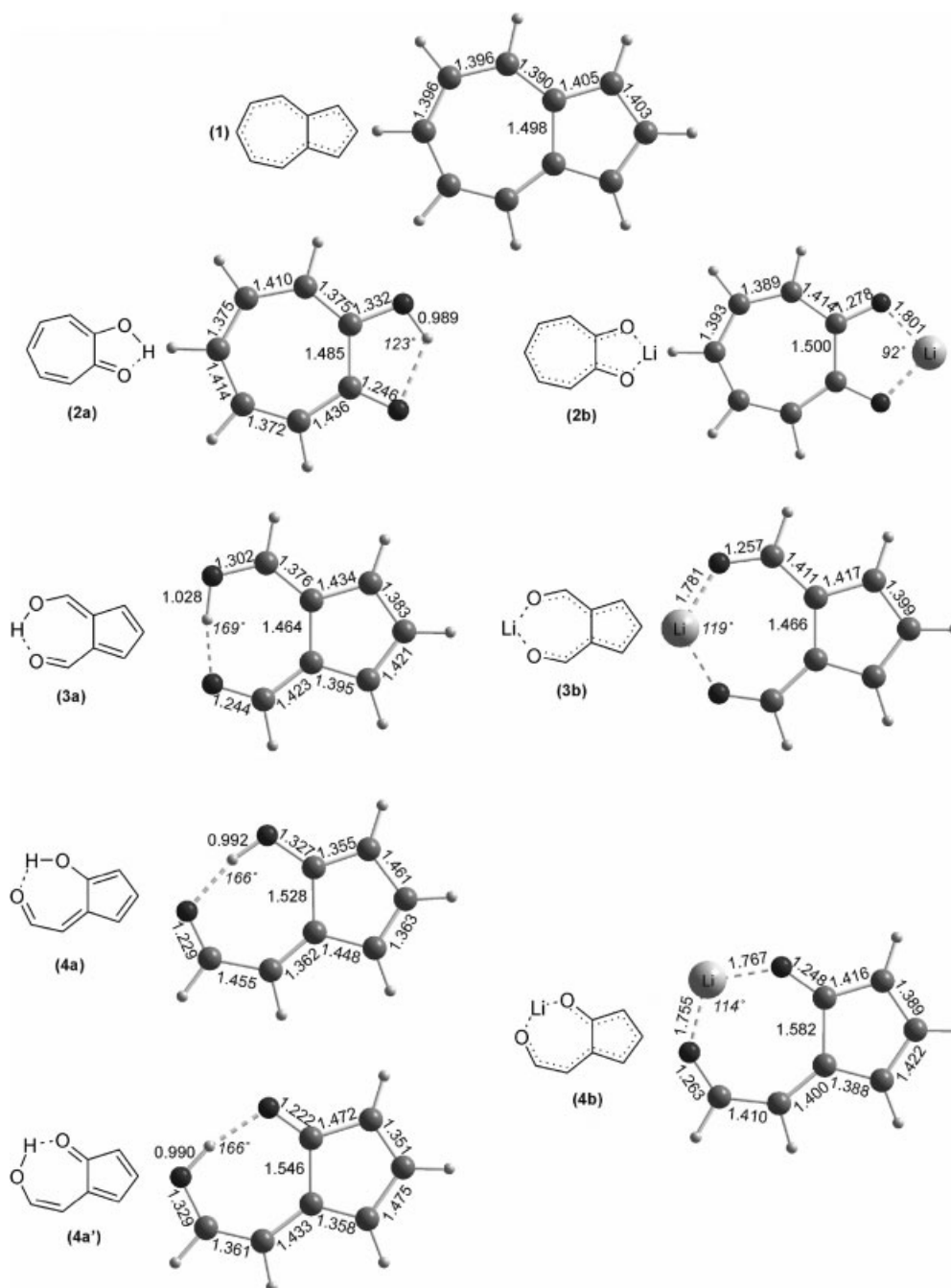


Figure 3. Structures of the studied systems along with selected bond lengths and O...X...O angles

$\Delta = 0.020$ and 0.023 \AA . This indicates again that the strongest H-bonding is in the case **3a**.

Comparison of HOMA values across H- and Li-bonded systems shows that the H-bonded ones exhibit always lower π -electron delocalization. It may be stated that Li-bonded systems resemble azulene itself. This may be due to possible participation of unoccupied 2p lithium orbital in delocalization since the energy of this orbital is significantly lower than that for hydrogen.^{28a} Thus in the cases of Li-bonded systems the lithium atom may play a

similar role in π -electron delocalization as sp^2 hybridized carbon atom.

CONCLUSIONS

π -Electron delocalization in azulene analogs in which various CH—CH—CH fragments were replaced with O...X...O (X = H or Li) resembles that observed in azulene itself. The similarity is much stronger in the case

Table 1. HOMA values calculated for the heavy atom part of the perimeter, total energy, E , and BSR energy, E_{BSR} , for studied systems; (open) indicates the form without intramolecular H-bonding (see Fig. 2)

Molecule	HOMA perimeter	$E/\text{hartree}$	$E_{\text{BSR}}/\text{kcal mol}^{-1}$
1	0.97	-385.790	88.5
2a	0.77	-420.786	84.7
2a (open)	0.56	-420.767	72.8
2b	0.95	-427.808	118.0
3a	0.82	-420.782	82.2
3a (open)	0.42	-420.753	64.0
3b	0.90	-427.809	118.6
4a	0.39	-420.751	62.8
4a (open)	-0.21	-420.733	51.5
4a'	0.25	-420.756	65.9
4a' (open)	-0.23	-420.736	53.3
4b	0.91	-427.772	95.4

when $X=\text{Li}$ than in the $X=\text{H}$ case (π -electron delocalization was calculated only for the heavy atom fragment of the perimeter excluding the central C—C bond).

H-bonded systems with heavy atom skeleton having an approximate symmetry plane exhibit higher π -electron delocalization expressed by HOMA and greater values of E_{BSR} . The Li-bonded analogs exhibit high π -electron delocalization independently of the above-mentioned symmetry and similar to that observed in azulene. However, those having symmetry plane exhibit higher E_{BSR} .

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