Introduction

The concept of aromaticity of monocyclic planar conjugated \((4n + 2)\) \(\pi\)-electron systems and of anti-aromaticity of the corresponding \(4n\) \(\pi\)-electron systems has so far been restricted to the ground state [1]. From this arises the question: is it possible to extend (generalize) the terms aromaticity and anti-aromaticity to electronic excited states? The aim of the present study is to answer this question.

Recently, it was shown [2] that the antiaromatic cyclobutadiene and cyclopentadienylium cation, respectively, show aromatic character in some low-lying excited singlet and triplet states. The aromatic “benzene either loses or reduces the aromatic character upon electronic excitation” [2].

The transition states of pericyclic reactions in ground and excited states were termed to be aromatic or anti-aromatic [3 - 7]. Special rules for the characterization of the transition state of pericyclic thermal and photochemical reactions as aromatic or anti-aromatic depending on the number of atoms and on the charge of even- and odd-membered cyclic conjugated ring systems have been proposed [5, 6].

There are some indications that the aromatic character of some compounds in the ground state is changed to a more or less anti-aromatic character upon electronic excitation of the molecules. Results of quantum-chemical calculations have shown [8] that the excitation of molecules which are built up from odd-membered cyclic conjugated ring systems by annelation or by connection through double bonds results in a charge transfer from the formal negatively charged \((4n + 2)\) \(\pi\)-electron fragment to the formal positively charged \((4n + 2)\) \(\pi\)-fragment. This electron transfer upon excitation creates species in the excited state whose electronic structure can be described by anti-aromatic \(4n\) \(\pi\)-fragments, e.g.

Another example is the s-indacene which shows all the features of an anti-aromatic compound (small excitation energy, bond alternation) [9]. Relatively large excitation energies for the \(S_1 \rightarrow S_2\) and \(S_2 \rightarrow S_3\) transitions and a (quantum-chemically calculated) maximum equalization of the bond lengths in the excited singlet states are typical criteria for aromatic properties [10].

Various criteria have been used to characterize the term aromaticity (and anti-aromaticity). Generally, these criteria are connected with typical physical and chemical properties:

(i) geometrical structure,
(ii) molecular spectra
   (NMR spectra, energy spectra),
(iii) magnetic properties,
(iv) chemical reactivity.

Recently, Schleyer [11] has proposed the following definition: “Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic delocalization may also result in equalization of the bond length, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilization”. The opposite features should be valid for anti-aromatic character.

Besides these criteria other typical features can be used to distinguish between aromatic and anti-aromatic character. In an earlier paper [10] we have proposed criteria to characterize the anti-aromatic character of molecules:

1. Geometry criterion. While aromatic monocycles (e.g. benzene, cyclopropenide anion, tropylium cation) show a maximum bond length equalization, the geometric configurations of anti-aromatic structures are characterized by an alternation of the bond distances and anomalously long bond distances $R$ (in typical cases $R > 1.5 \text{ Å}$).

2. Energy criterion. Aromatic (4$n$ +2) $\pi$-electron systems are characterized by a high excitation energy and a red shift of the longest-wavelength absorption if the conjugated $\pi$-electron system is extended. Contrary to this behaviour, the relatively stable Jahn-Teller forms of anti-aromatic species have small excitation energies (wide infra). If the anti-aromatic 4$n$ $\pi$-electron system is perturbed (extended), the HOMO-LUMO gap is increased and a blue shift of the longest-wavelength absorption results.

3. Charge distribution criterion. For more complex compounds with an odd-membered antiaromatic structural element (e.g. a cyclopentadienyl cation fragment), the sum of the $\pi$-net charges ($Q$) of the atoms of the anti-aromatic monocyclic fragment can be compared with $Q$ of the unsubstituted anti-aromatic monocycle.

An additional criterion is the validity of Breslow’s stability criterion [12]. Breslow [12] has defined an anti-aromatic compound as “a cyclic conjugated system ... if its $\pi$-electron energy is higher than that of a suitable (iso-$\pi$-electronic) reference compound which is not cyclically delocalized”.

The aim of this paper is to characterize the first excited singlet state of azulene 1 and naphthalene 2 as aromatic or anti-aromatic using these criteria.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{azulene_naphthalene.png}
\caption{Azulene and naphthalene structures.}
\end{figure}

Results and Discussion

Geometry criterion. Azulene is a typical nonbenzoide aromatic compound which can be thought to be built up from an aromatic cyclopentadienide anion and an aromatic cycloheptatrienyl cation.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{azulene_structures.png}
\caption{Structures of azulene: 1a, 1b, 1c, 1d.}
\end{figure}

The molecular structure of azulene was discussed controversially in the literature [13]. All the observed properties of the molecule correspond to the structure $1c$ ($1d$) of $C_{2v}$ symmetry with equalized C-C bonds, and not to the valence-tautomeric structures $1a$, $1b$ of $C_3$ symmetry with alternation of the bond lengths. The structure $1c$ ($1d$) was recently confirmed by high-level ab initio calculations (with basis sets up to TZP+f quality) [13]. The results (see Fig. 1) are in good agreement with the experimentally determined (X-ray analysis assuming $C_{2v}$ symmetry) structure [14]. The structure shows a maximum equalization of the C-C bond lengths typical for molecules with aromatic character.

Upon excitation of azulene to the first excited singlet state it can be expected that the structure is distorted. One criterion of the anti-aromaticity of the 4$n$ ($\pi$-electron containing) annulenes is the unusually strong alternation of the bond lengths [10] as a result of a second order Jahn-Teller effect [16]. From the energy spectra of the aromatic molecules (e.g. naphthalene or azulene) it follows that for these molecules a Jahn-Teller effect can also be expected in their first excited singlet state. The energy of the electron-vibronic interaction of a molecule in an electronic state $p$ (second order perturbation theory) is given by the expression [17]
\[
\Delta E^{(2)} = \sum_{q \neq p} \frac{\langle \psi^*_p | \frac{\partial U}{\partial Q_q} | \psi_q \rangle}{E_q - E_p} \langle \psi^*_p | \frac{\partial U}{\partial Q_q} | \psi_q \rangle
\]

where \( E_q \) and \( \psi_q \) are the energy and the wave function of the electronic state \( q \), respectively, and \( \frac{\partial U}{\partial Q_q} \) are the coupling operators. From eq. (1) it can be seen that the energy of the electron-vibronic coupling \( \Delta E^{(2)} \) and therefore also the geometry in the electronic state \( p \) are strongly influenced by the energy difference between the states \( p \) and \( q \), i.e. the excitation energy (denominator in eq. (1)). The relatively small value of the energy difference \( E_1 - E_2 \) (we consider the \( S_1 \) state of the molecules) of aromatic compounds (e.g. azulene and naphthalene) determines a large value of \( \Delta E^{(2)} \). This means that a strong electron-vibronic coupling in the first excited singlet state leads to a significant change of the geometric configuration with an alternation of the bond lengths of the molecule as in the case of the anti-aromatic \( \pi \)-systems in their ground state.

The geometry of azulene in the first excited singlet state (\( S_1 \)) was optimized using the QCFF/PI (CISD) and the CASSCF (3-21G basis set) procedures [15], respectively. The bond lengths obtained by Negri and Zgierski [15] are within 0.01 Å to those of Bearpark et al. [18] optimized at CAS10 level. An “experimental” \( S_1 \) geometry of azulene [15] was evaluated by a correction of the \( ab \) \initio \ HF (6-31G basis set) ground state geometry using CIS/6-31G calculated normal coordinates and experimentally estimated displacement parameters of the C-C stretch vibration frequencies. Both of these \( S_1 \) geometries (see Fig. 1) are characterized by a significant alternation of the C-C bond lengths.

![Fig. 1. Bond lengths (in Å) of azulene in the singlet ground state: \( ab \) \initio \ SCF optimized values [13] (outside the rings), and experimental data [14] (inside the rings), and in the first excited singlet state: \( ab \) \initio-CASSCF (3-21G basis set) optimized [15] (outside the rings), and “experimentally” determined [15] (see text, inside the rings).](image)

Considering the \( S_0 \) and \( S_1 \) geometries and the sums of the \( \pi \)-net charges in the five- and seven-membered rings the structures of azulene in the ground and first excited singlet states can be represented by the schematic formulae given in Fig. 2.

Naphthalene is iso-\( \pi \)-electronic with azulene. The \( ab \) \initio optimized (GAMESS-UK, 6-31G* basis set) geometry is in good agreement with the experimentally determined geometry [19] (Fig. 3). Bond lengths of the \( S_1 \) state were taken from the literature (\( ab \) \initio MCSCF geometry optimization) [20]. The bond distances in the excited state are better equalized in relation to those in the ground state. Only the 9-10 bond distance is strongly enlarged so that the structure corresponds to the perimeter of the [10] annulene.

**Energy criterion.** The experimental excitation energies [21] \( S_0 \rightarrow S_1 \) and \( S_1 \rightarrow S_2 \) of azulene are 1.79 eV and 1.31 eV, respectively. In this case the aromatic character of the ground state is indicated by a relatively high \( S_0 \rightarrow S_1 \) energy difference in comparison with the lower \( S_1 \rightarrow S_2 \) energy difference which could be a feature of the anti-aromatic character of \( S_1 \).
At extension of the conjugated π-electron system, a red shift of the experimental $S_0 \rightarrow S_1$ excitation energies can be seen (Fig. 4a) for azulene and 2-phenylazulene [22] and azulene and 1,2-benzazulene [22], respectively. For the corresponding $S_1 \rightarrow S_2$ excitation energies a blue shift is observed at extension of the conjugated π-system.

Conclusions as to the anti-aromatic character of the excited state of naphthalene can be drawn from the $S_1 \rightarrow S_2$ excitation energy in relation to the $S_0 \rightarrow S_1$ energy difference. The large experimental value $\Delta E(S_0 \rightarrow S_1) = 3.97$ eV [22] and the very small $\Delta E(S_1 \rightarrow S_2) = 0.32$ eV [22] are an indication that the aromatic molecule in the ground state has a more or less anti-aromatic character in the first excited singlet state.

As in the case of azulene, the longest-wavelength transition $S_0 \rightarrow S_1$ shows a red shift if the π-system is extended (Fig. 4b), and a blue shift for the $S_1 \rightarrow S_2$ transition.

Charge distribution criterion. An additional indication for this is the distribution of the π-net charges within the five- ($\sum O^5$) and seven-membered ($\sum Q^7$) rings in $S_0$ and $S_1$ of azulene. While the five-membered ring is partially negatively charged and the seven-membered ring is partially positively charged in the ground state, in the first excited state the partial charges of the rings are exchanged. This can also be expressed by the magnitude and direction of the calculated dipole moment in ground and first excited singlet states (Fig. 2): in the ground state the dipole moment is directed from the seven- to the five-membered ring (experimental value $\mu = 1.7$ D [24]), upon excitation the direction is reversed. The dipole moment of the first excited singlet state $S_1$ of azulene was experimentally estimated to be $\mu(S_1) = 0.42$ D [25, 26].

Acknowledgements

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