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Quantification of the (anti)aromaticity of fulvenes subject to ring size

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Abstract

Tria-, penta-, hepta- and nonafulvenes (**1**–**4**) have been studied theoretically at the MP2 ab initio level of theory. For the global minimum structures, the occupation of the bonding $\pi_{C=C}$ orbital of the exocyclic C=C double bond, obtained by NBO analysis, quantitatively proves π-electron delocalization which can reveal partial 2-, 6- and 10-π-electron aromaticity, and 4-, 8- and 12-π-electron antiaromaticity of the ring moieties. Beside the corresponding occupation number, this conjugation was quantified by the length of the exocyclic C=C double bond whilst the (anti)aromaticity of the ring moieties of **1**–**4** was visualized and quantified by through space NMR shielding surfaces (TSNMRS).

Keywords: Fulvenes; Through space NMR shieldings; MP2 ab initio calculations; GIAO, NICS; Aromaticity; Antiaromaticity

Fulvenes, conjugated ring systems with one exocyclic C=C double bond, attract continuous interest due to their unique cross conjugated structure which can generate $(4n+2)$ π-electron aromatic and $4n$ π-electron antiaromatic moieties via bond polarization (cf. Scheme 1). Depending on the number of conjugated π-electrons in fulvenes **1**–**4**, dipolar mesomeric electronic structures **1a**,**b**–**4a**,**b** can be attained resulting in partial (anti)aromatic character of the compounds.

Fulvenes **1**–**4** have previously been synthesized (triafulvene **1**,[1–3] pentafulvene **2**,[4] heptafulvene **3**[5] and nonafulvene **4**),[6] and were studied with respect to their dipole moments[7–9] and NMR spectra.[1,3,10–14] The ^1H and ^{13}C NMR spectra of triafulvene **1** (both protons and carbon atoms of the 3-membered ring moiety display resonances in the region of aromatic compounds) evidence a significant contribution of the resonance form **1b**;[1,3] the corresponding NMR spectra of **2**–**4**, however, display typical olefinic compounds with strongly alternating bond lengths and only a small extent of charge separation[10–14] (corroborated by the relatively small dipole moments).

In addition, extensive theoretical studies of fulvenes **1**–**3** have been reported; concerning (anti)aromaticity, the contributions of dipolar canonical structures to overall structures were calculated[15–17] [**1b** (19–22%), **2a** (7–8%) and **3b** (5–8%)], intensity [**1** (1.90 ± 0.02 D),[7] **2** (0.42 D)[8] and **3** (0.27 D),[9] calc. 0.48 D][18] and direction of the corresponding dipole moments were determined, and several energetic, magnetic and geometric criteria[17,19,20] were employed. Also **1**–**3** were compared with analogues which are differently substituted at the exocyclic C=C double bond or have the terminal CH_2 group replaced by potential hetero atoms.[17,19–23] Dependent on the criterion employed, **1**–**4** were reported as partially aromatic, non- or even antiaromatic. Also, the calculated molecular polarizabilities of **1**–**4** were not helpful in this respect.[24]

The major aim of the present study is to investigate fulvenes **1**–**4** by the application of NBO analysis to the global minimum structures obtained from ab initio calculations at the MP2 level of theory. Examination of the occupation numbers of the bonding $\pi_{C=C}$ orbital of the exocyclic C=C double bond permits quantification of the shift of π electrons from this bond to the fulvene moieties aspiring to (anti)aromaticity. The ratio $\pi_{C=C}/\pi^*_{C=C}$, which appears to be the most general criterion for quantifying the

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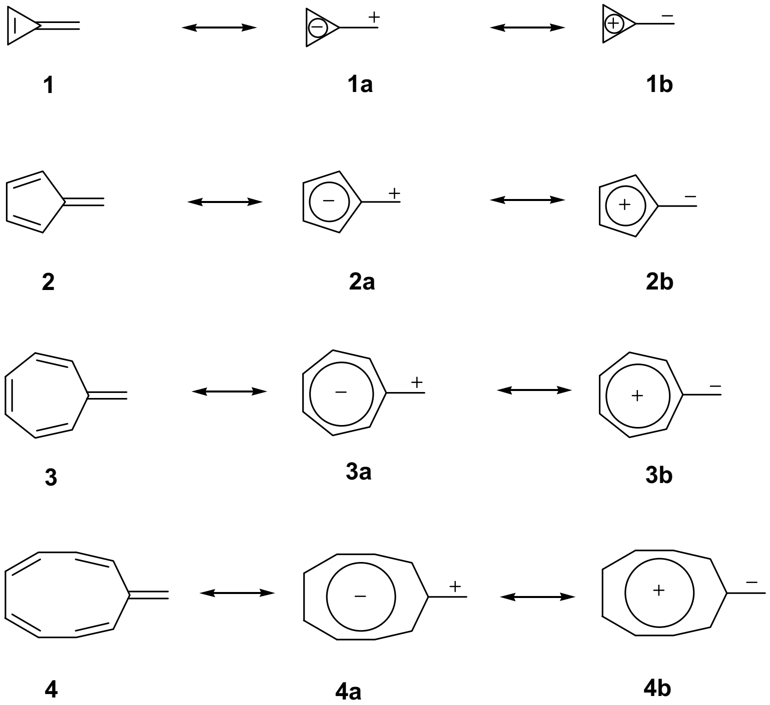

Scheme 1. Canonical structures of the compounds studied.

push–pull effect in push–pull alkenes,[25] was similarly examined but proved not to be sensitive.

In addition, the through space NMR shielding surfaces (TSNMRS) for fulvenes **1**–**4** were calculated employing the NICS concept of Schleyer and co-workers;[26] TSNMRS values can be used to visualize the *anisotropic effect* of functional groups and the *ring current effect* of aromatic moieties by iso-chemical-shielding surfaces (ICSS) of various sizes and signs[27] to quantify the aromaticity or antiaromaticity present.[28] This new approach to quantify and visualize the partial aromaticity/antiaromaticity of **1**–**4** ring moieties is expected to offer a comprehensive picture of this situation and a new successful method to be applied for the study of similar phenomena in physical organic chemistry.

The concept of employing spatial NICS[29] for the quantitative analysis of (anti)aromaticity[28,29] was meanwhile extended to solid state systems[30] and applied to fulvalenes,[31,32] fullerenes[33] and a large variety of aromatic compounds.[28]

Of significant note though, there have been some recent developments of NICS[34] showing that none of the various methods can safely assign aromaticity[35] and these parameters not measurable have proven to be generally unsuitable for the quantitative evaluation of aromaticity.[36] In addition, the conventional interpretation of deshielded ^{1}H chemical shifts for aromatic protons has proven to be due to reasons other than deshielding ring current effects[37] and thus they are not reliable indicators of aromaticity either.[38] For example, NICS analysis was shown to lead to an incorrect prediction of aromaticity for the cyclopropenyl anion.[39]

Ab initio MO calculations were performed using the GAUSSIAN 03 program package.[40] Geometry optimization was performed at the MP2/6-31G** level of theory without restrictions and the resulting geometries are depicted in Figures 1–3. Generally, only the global minimum structures are given and have been employed in the present discussions; in the case of the *twisted* 9-membered ring moiety in **4**, the corresponding *planar* conformer proved to be ca. 30 kcal mol^{-1} less stable than the preferred conformer under discussion.

The chemical shieldings surrounding the molecules were calculated based on the NICS concept of Paul von Rague Schleyer[26] whereby the molecule was placed in the centre of a grid of ghost atoms ranging from -10.0 to $+10.0$ Å in all the three dimensions with a step width of 0.5 Å resulting in a cube of 68,921 ghost atoms. The chemical-shielding calculations were performed using the GIAO[41] method at the HF/6-31G** level of theory.[42] At the same level of theory and on the basis of the MP2/6-31G** structures, both ^{1}H and ^{13}C chemical shifts of fulvenes **1**–**4** were calculated; the corresponding values together with the experimental chemical shifts are given in Table 1. Excellent agreement in the NMR shielding of both nuclei proved the correctness of the present estimations. In addition, the ^{13}C chemical shift of C-2 in **1**, not yet published, was obtained.

Since GIAO is a coupled HF method that uses gauge-independent atomic orbitals for the calculation of shielding values, it can be applied to the calculation of NICS. Starting structures were generated by the SYBYL modelling software.[43] From the GIAO calculations, the coordinates and isotropic shielding values of the ghost atoms were