Fulvenes, Fulvalenes, and Azulene: Are They Aromatic Chameleons?

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In 1972, Baird used perturbational molecular orbital (PMO) theory to show that annulenes which are aromatic in their singlet ground states (S_0) are antiaromatic in their lowest triplet state (T_1), and vice versa for annulenes that are antiaromatic in S_0.[1] The validity of this theory was later probed through quantum chemical calculations by Schleyer and co-workers.[2] Aromatic stabilization energies and nucleus-independent chemical shifts, calculated with CCSD(T) and GIAO-HF, supported Baird's theory on reversal of Hückel's aromaticity rule when going from S_0 to T_1. This theory has so far not been widely applied to rationalize excited-state properties of conjugated hydrocarbons; however, if shown to be generally applicable, it could serve as a handy back-of-an-envelope tool to tailor new compounds for, e.g., functionalized materials.

It is known that fulvenes, [n,m]fulvalenes with $n \neq m$, and azulene in S_0 shift their π-electrons due to influence of dipolar aromatic resonance structures (Scheme 1).[3−5] However, their polarizations differ markedly, e.g., MP2/6-31G(d) calculations showed that the dipolar resonance structures contribute only 5% to the electronic structure of heptafulvene (**3**, Scheme 2), but 31 and 22% to those of calicene (**7**) and pentaheptafulvalene (**8**).[3a]

On the basis of Baird's theory, we propose that similar polarizations, but in opposite directions to those in S_0, occur in the T_1 states of fulvenes (Scheme 1), and in the lowest quintet states (Q_1) of [n,m]fulvalenes and azulene, as these states can be decomposed into two T_1 state aromatic rings. These molecules could thus be influenced by aromaticity in both S_0 and T_1/Q_1, and they would act as "chameleons", as they will adapt to both S_0 and T_1/Q_1 by shifts of their π-electrons so as to adopt some aromaticity. To test this hypothesis, we performed quantum chemical calculations on **1−9** (Scheme 2). Calculated T_1/Q_1 dipole moments and π-electron density distributions were compared to those of S_0. The energies and geometries of the T_1/Q_1 states were also computed.

Geometries were optimized at the (U)OLYP/TZ2P level[6−8] and thereafter used in CASSCF and CASPT2 calculations with an atomic natural orbital (ANO) type basis set of triple-ζ quality [C/4s3p2d, H/3s1p].[9−11] A notable agreement in the $\Delta E_{ST}/\Delta E_{SQ}$ of OLYP and CASPT2 gaps is found (Table 1), although several states have multiconfigurational character.[12,13] Interestingly, if **1−6** are fixed to C_{2v} symmetry, one finds an excellent correlation ($R^2 = 0.972$) between the ΔE_{ST} energies of (U)OLYP/TZ2P and the HOMO−LUMO energy gaps of Hückel MO theory.

According to the (U)OLYP calculations, the compounds with five- and seven-membered rings are planar in both S_0 and T_1/Q_1, but those with three-membered rings pucker in T_1/Q_1. The CC bond lengths of **4** and **5** in T_1 are similar and intermediate between CC single and double bonds, indicating some aromaticity (Figure 1). Moreover, fulvene **4** in T_1 has the exocyclic methylene group

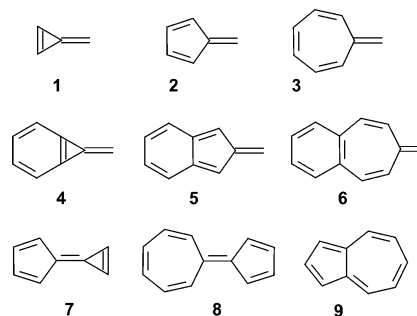† Chalmers University of Technology.
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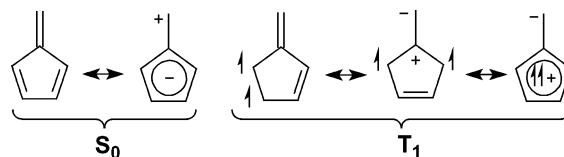
Scheme 1

Scheme 2

Table 1. $S_0−T_1$ (**1−6**) and $S_0−Q_1$ (**7−9**) Energy Splittings[a]

molecule	sym[b]	$\Delta E_{ST}/\Delta E_{SQ}$		
		(U)OLYP	CASSCF	CASPT2
1	C_{2v}; C_2	51.3	53.2	49.2
2	C_{2v}; C_{2v}	36.8	40.6	36.1
3	C_{2v}; C_{2v}	29.8	27.9	28.8
4	C_{2v}; C_{2v}	52.7	57.1	53.0
5	C_{2v}; C_{2v}	11.9	18.1	11.7
6	C_{2v}; C_{2v}	43.9	45.4	42.8
7	C_{2v}; C_1	113.9	105.0	110.7
8	C_{2v}; C_{2v}	87.2	97.6	86.2
9	C_{2v}; C_{2v}	116.0	123.3	113.9

[a] $\Delta E_{ST}/\Delta E_{SQ}$ in kcal/mol. [b] Molecular symmetries for S_0; T_1/Q_1.

perpendicularly twisted with respect to the cyclic part, so that the C=C π-bond is broken. For fulvenes **1−3** and **6−9**, the CC bond lengths alternate with similar magnitudes in S_0 and T_1/Q_1.[14] The S_0 states of these species are considered nonaromatic,[15,16] and these results indicate that the T_1/Q_1 states should be considered likewise.

The CASSCF dipole moments of **1−9** in S_0 and T_1/Q_1 are slightly smaller than those of OLYP (Figure 1). However, with each respective method they are of similar magnitudes in S_0 and T_1/Q_1 and, most importantly, always of opposite directions, supporting our hypothesis on chameleon behavior (Scheme 1). Since the dipole moments are of similar sizes in both states, this suggests that the T_1/Q_1 states are equally influenced by T_1/Q_1 aromatic resonance structures as are the S_0 states by S_0 aromatic resonance structures. Such resonance structures are most important for **1** and the fulvalenes. Natural population analyses at the (U)OLYP/TZ2P level show that they contribute 21, 8, and 8% to the S_0 states of **1−3**,

1.403 (1.445) 1.493 (1.324) 1.381 (1.333)
−2.0, −1.9
1.4, 1.3

1.458 (1.357) 1.434 (1.472) 1.368 (1.472) 1.395 (1.349)
0.6, 0.3
−0.9, −0.5

1.376 (1.445) 1.419 (1.359) 1.436 (1.465) 1.449 (1.360) 1.398 (1.364)
−0.8, −0.2
0.6, 0.3

1.426 (1.408) 1.383 (1.385) 1.428 (1.339) 1.397 (1.408) 1.402 (1.381) 1.414 (1.439)
−1.4, −1.2
0.4, 0.7

1.410 (1.365) 1.434 (1.372) 1.439 (1.466) 1.394 (1.435) 1.440 (1.489) 1.395 (1.448) 1.390 (1.354)
0.8, 0.3
−0.6, −0.1

1.367 (1.392) 1.399 (1.458) 1.404 (1.355) 1.438 (1.459) 1.437 (1.410) 1.489 (1.427) 1.440 (1.395) 1.395 (1.363)
−0.9, −0.4
1.0, 0.4

1.451 (1.370) 1.464 (1.431) 1.393 (1.357) 1.439 (1.456) 1.453 (1.330) 1.377 (1.452) 1.438 (1.456) 1.533 (1.431) 1.448 (1.370)
4.5, 3.7
−3.8, −1.9

1.404 (1.369) 1.397 (1.433) 1.459 (1.451) 1.445 (1.370) 1.445 (1.366) 1.454 (1.459) 1.379 (1.452) 1.412 (1.403)
−3.6, −1.5
4.4, 1.9

1.421 (1.400) 1.416 (1.394) 1.430 (1.399) 1.440 (1.407) 1.421 (1.405) 1.489 (1.500)
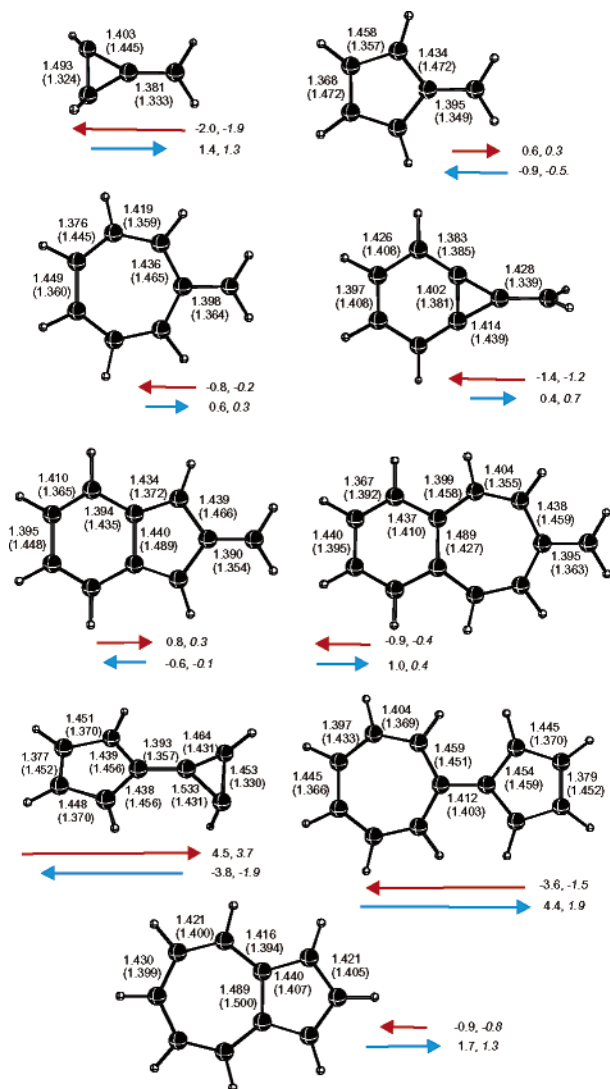−0.9, −0.8
1.7, 1.3

Figure 1. Optimal UOLYP/TZ2P geometries of **1**−**9** in their T_1/Q_1 states. CC bond distances in Å in T_1/Q_1 (normal print) and S_0 (in parentheses), and dipole moments in D in S_0 (red arrow) and T_1/Q_1 (blue arrow) calculated with (U)OLYP (normal print) and CASSCF (italics).

and 19, 8, and 7% to their T_1 states. In **4**−**6**, dipolar resonance structures contribute with 11, 11, and 4% in S_0 and 1, 4, and 9% in T_1. Of the fulvalenes, only the π-population of **8** was examined due to the low symmetry of **7** in Q_1. In **8**, the contributions are 24 and 28% to the S_0 and Q_1 states. Consequently, the population analyses reveal a similar influence of the dipolar resonance structures in T_1/Q_1 as in S_0 states.

Influence of aromaticity should further stabilize the fulvene T_1 states and the fulvalene and azulene Q_1 states so that these are of lower energy than analogous states in isoelectronic molecules that are aromatic in S_0 and antiaromatic in T_1/Q_1. Indeed, this is the case as ΔE_{ST} of benzene (89.8 and 86.3 kcal/mol with (U)OLYP and CASPT2//(U)OLYP) is higher than that of **2** (Table 1), and ΔE_{SQ} of naphthalene (155.3 and 153.7 kcal/mol with (U)OLYP and CASPT2//(U)OLYP) is higher than that of **9**.

The answer to the question of the title is therefore indisputably "yes". The chameleon behavior of fulvenes, fulvalenes, and azulene

is rationalized by use of Baird's theory. As a result, fulvenes are dipolar in T_1, and fulvalenes and azulene are dipolar in Q_1, but in both cases in opposite directions to those in S_0. Our study thus shows that aromaticity also influences excited-state properties, and highlights the importance of Baird's more than 30-year-old contribution to the field of organic photochemistry. It is noteworthy that a polarity in the S_1 and S_2 states of azulene which is opposite to that of S_0 has previously been observed.[17] It might thus be argued that the investigated compounds also in general are able to act as aromatic chameleons so as to adapt to several excited states. Moreover, as fulvenes in S_0 are influenced by their exocyclic substituents,[15] one could predict that several properties are influenced in an opposite manner in T_1 when compared to S_0. We now investigate both computationally and experimentally the possibility to tune their ΔE_{ST} through substitution, which ultimately could lead to design of fulvenes as novel compounds for molecular magnets.

Supporting Information Available: Listing of Cartesian coordinates and absolute energies of **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The active space comprised the valence π orbitals, the two highest occupied σ orbitals, two σ^* orbitals, and two extra π^* orbitals for all systems except molecules **7** and **9**, for which the extra π^* orbitals were not included because of computational limitations.
(12) The dominant configurations in the T_1 and Q_1 states of **6**, **8**, and **9** contribute with 68, 75, and 72%, according to CASSCF//(U)OLYP.
(13) The spin contamination from the UOLYP calculations is also small, as $\langle S^2 \rangle$ before annihilation is less than 2.03 for T_1 and 6.02 for Q_1 states.
(14) The difference between the longest and shortest CC bonds of a compound **1**−**9** is 0.045−0.156 Å in T_1 and 0.093−0.135 Å in S_0. The average CC bond lengths range 1.408−1.444 Å in T_1 and 1.387−1.415 Å in S_0.
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