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Scope and Limitations of Baird's Theory on Triplet State Aromaticity: Application to the Tuning of Singlet–Triplet Energy Gaps in Fulvenes

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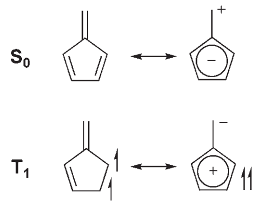
Abstract: Utilizing Baird's theory on triplet state aromaticity, we show that the singlet–triplet energy gaps (ΔE_{ST}) of pentafulvenes are easily varied through substitution by as much as 36 kcal mol^{-1}. This exploits the fact that fulvenes act as aromatic chameleons in which the dipoles reverse on going from the singlet ground state (S_0) to the lowest ππ* triplet state (T_1); thus, their electron distributions are adapted so as to achieve some aromaticity in both states. The results are based on quantum chemical calculations with the OLYP density functional theory method and the CASPT2 ab initio method, as well as spectroscopic determination of ΔE_{ST} by triplet sensitization. The findings can also be generalized to fulvenes other than the pentafulvenes, even though the effect is attenuated as the size of the fulvene increases. Our studies thus reveal that triplet-state aromaticity can greatly influence the properties of conjugated compounds in the T_1 state.

Keywords: ab initio calculations · aromaticity · density functional calculations · fulvenes · triplet sensitization

Introduction

Pentafulvenes are dipolar hydrocarbons since they involve zwitterionic resonance structures with a positively charged exocyclic C atom and a negatively charged, aromatic cyclopentadienyl ring (Scheme 1).[1,2] This is the situation in the electronic ground state (S_0), and we recently showed theoretically that pentafulvenes also are dipolar in the lowest ππ* triplet excited state (T_1), but in the opposite direction to the S_0 state.[3] This reversed polarity is rationalized by Baird's theory of triplet-state aromaticity,[4] which states that [n]annulenes with $4n$ π electrons are aromatic in the T_1 state, whereas those with $4n+2$ π electrons are antiaromatic in T_1, that is, reversal of Hückel's rule for aromaticity in the S_0 state. Schleyer and co-workers verified Baird's theory through quantum chemical calculations of aromatic stabilization energies and nucleus-independent chemical shifts of a series of $4n$-π-electron annulenes in S_0 and T_1.[5] We used the theory to explain how different fulvenes adapt their electron density distribution such that they are influenced by aromaticity in both S_0 and T_1 (Scheme 1), and we therefore tentatively called them aromatic chameleons.[3]



Scheme 1.

From experimental studies it is known that substitution influences the polarity of fulvenes in S_0, since the parent pentafulvene has a dipole moment of 0.42 D, whereas the dipole moment of 6-dimethylaminopentafulvene is 4.5 D.[1,6] This finding is supported by results from quantum-chemical calculations.[7–10] The aromaticity of the ring, which serves as a measure of the importance of zwitterionic resonance struc-

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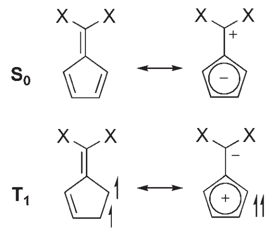
tures in exocyclically substituted pentafulvenes and heptafulvenes, also correlates strongly with the σ^+ and σ^- constants of the substituents.[7] In addition, there are excellent correlations between various energetic, geometric, and magnetic measures of the aromaticity of substituted pentafulvenes and heptafulvenes.

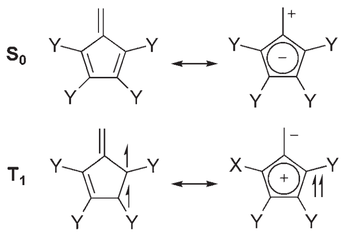
Based on the aromatic-chameleon property of pentafulvenes[3] and the possibility to vary their ground-state aromaticity through substitution,[7–10] we now predict that their singlet–triplet energy gaps (ΔE_{ST}) can be tuned. Stabilization of the T_1 state and simultaneous destabilization of the S_0 state, or vice versa, could possibly be achieved through substitution (Schemes 2 and 3). Electron-withdrawing groups (EWG) at the exocyclic C atom should help delocalize the partial negative charge at this position in the T_1 state, and thus stabilize T_1 relative to S_0. Electron-donating groups (EDG) at the same position should have the opposite effect. The energy gap could presumably also be tuned through substitution at the C atoms of the ring, and now an electron-donor group should stabilize T_1 relative to S_0, whereas an electron-withdrawing group will destabilize T_1. Thus, variation in ΔE_{ST} can be postulated, but the hypothesis must be verified, and the magnitude of the variation determined.



ΔE_{ST}(X=EWG) < ΔE_{ST}(X=H) < ΔE_{ST}(X=EDG)

X = H (**1a**), CH_3 (**1b**), F (**1c**), OH (**1d**), NH_2 (**1e**), CN(**1f**), NO_2 (**1g**), BH_2 (**1h**)

Scheme 2.



ΔE_{ST}(Y=EDG) < ΔE_{ST}(X=H) < ΔE_{ST}(Y=EWG)

X = Cl (**1i**), CN (**1j**)

Scheme 3.

The ability to tune ΔE_{ST} in various classes of fulvenes (pentafulvenes, heptafulvenes, benzofulvenes, and dibenzofulvenes) was investigated computationally. The purpose is twofold: first, the principle of excited-state tuning is demonstrated for pentafulvenes both computationally and experimentally, and thereafter its generality for other fulvene systems is probed. For a selected series of pentafulvenes, the compounds were synthesized and ΔE_{ST} measured to experimentally prove the validity of our hypothesis. The fulvenes subjected to computational investigations were chosen both to probe how the concept extends to larger fulvene systems, and to relate our findings to compounds that have found usage in materials chemistry. For example, derivatives of dibenzofulvene have recently been shown to be key compounds in the development of solid-state emissive dyes.[11] These are based on aggregation-induced emission, and thus are very sensitive to even subtle changes in substitution patterns. Heterofulvenes and heterofulvalenes also have properties of interest for materials applications. For example, dithiafulvenes are attracting much attention in charge-transfer systems, either as redox partners by themselves,[12] or in large conjugated systems in which two dithiafulvene units form an extended tetrathiafulvalene.[13] Many such systems are prepared as novel compounds for nonlinear optical materials. Especially in donor–π-acceptor systems, in which the aromaticity varies upon excitation, peripheral sulfur atoms have proved important in affecting the hyperpolarizability of such chromophores.[14] Even though this present investigation is fundamental in character, we thus hope that the results presented here can also initiate further investigations in more applied research areas.

Results and Discussion

Computed S_0 and T_1 properties of substituted pentafulvenes: The ΔE_{ST} of pentafulvenes **1a**–**1h** were calculated at the (U)OLYP/TZ2P and CASPT2/[4s3p2d/3s1p]//(U)OLYP/TZ2P levels. Agreement between the inexpensive OLYP and the more computationally demanding CASPT2 calculations is good (Table 1), and the maximum deviation is 4.5 kcal mol^{-1} for pentafulvene **1d** (X = OH). Previously, triplet and singlet excited states of the parent pentafulvene and 6,6-dimethylpentafulvene (**1b**) were studied in the gas phase by electron energy loss spectroscopy (EELS), and two valence triplet states were observed.[15] The vertical transitions to these states were found at 54.2 and 71.5 kcal mol^{-1} (2.35 and 3.10 eV) for **1a**, and 54.2 and 69.2 kcal mol^{-1} (2.35 and 3.00 eV) for **1b**. These measured energies agreed well with calculated CASPT2 energies (52.3 and 68.5 kcal mol^{-1} for **1a** and 54.0 and 67.6 kcal mol^{-1} for **1b**), and OLYP/TZ2P vertical excitation energies to T_1 are very similar (52.3 kcal mol^{-1} in **1a** and 54.3 kcal mol^{-1} in **1b**).

When compared to **1a**, two π-electron-donating groups at the exocyclic position raise ΔE_{ST} by up to 15 kcal mol^{-1} at the OLYP level and 12 kcal mol^{-1} at the CASPT2 level (Table 1). On the other hand, two π-electron-withdrawing groups lower the gap by maximally 14 kcal mol^{-1} at the OLYP and 15 kcal mol^{-1} at the CASPT2 level. Thus, a variation in ΔE_{ST} of 27–29 kcal mol^{-1} is achieved through simple substitution at the exocyclic C atom, that is, one can selectively stabilize the S_0 state or the T_1 state by substitution at C6, which increases the importance of either the 6π-electron

Table 1. Computed data of fulvenes **1a**–**1m**.[a]

Fulvene	X, Y	Symmetry		Active space	No of electrons	ΔE_{ST} (OLYP)	ΔE_{ST} (CASSCF)	ΔE_{ST} (CASPT2)	$\mu(S_0)$ (OLYP)	$\mu(S_0)$ (CASSCF)	$\mu(T_1)$ (OLYP)	$\mu(T_1)$ (CASSCF)
		S_0	T_1									
1a	H, H	C_{2v}	C_{2v}	(2,2,2,4)	10	36.78	42.98	36.35	0.59	0.32	−0.87	−0.50
1b	Me, H	C_{2v}	C_2	S_0: (2,2,2,4) T_1: (4,6)	10	39.87	41.61	39.49	1.99	1.16	−0.02	0.05
1c	F, H	C_{2v}	C_{2v}	(2,2,4,6)	14	43.30	43.20	41.60	−0.12	−1.54	−1.89	−2.54
1d	OH, H	C_2	C_2	(4,6)	10	44.73	54.53	40.27	4.20	2.66	1.31	0.87
1e	NH_2,H	C_2	C_2	(4,6)	10	51.70	56.23	48.75	4.47	2.67	0.55	−0.56
1f	CN, H	C_{2v}	C_{2v}	(2,2,4,6)	14	23.48	33.68	24.70	−5.02	−5.26	−6.85	−5.61
1g	NO_2,H	C_2	C_s	S_0: (7,9) T_1: (6,10)	14	23.65	52.13	21.64	−4.43	−4.79	−7.18	−7.17
1h	BH_2,H	C_s	C_s	(5,5)	10	22.62	30.48	22.97	−1.15	−1.27	−4.57	−3.05
1i	H, Cl	C_{2v}	C_{2v}			29.65			1.61		0.44	
1j	H, CN	C_{2v}	C_{2v}			30.77			4.86		3.90	
1k	Me,Cl	C_2	C_2			31.71			3.60		1.57	
1l	CN,Cl	C_{2v}	C_{2v}			15.98			−4.33		−6.08	
1m	$N(C_4H_8)$, Cl	C_2	C_2			42.63			8.92		3.82	

[a] Energies in kcal mol^{-1} and dipole moments in debye. We define the dipole moment as going from a negative to a positive charge distribution. A positive dipole moment implies a dipole directed from the ring system to the exocyclic position, and vice versa for a negative dipole moment.

S_0-aromatic or the 4π-electron T_1-aromatic zwitterionic resonance structure shown in Scheme 1.

The dipole moments display interesting patterns. For the electron-donor-substituted fulvenes **1b**, **1d**, and **1e**, the dipole moments decrease considerably on going from S_0 to T_1 at both OLYP and CASSCF levels (Table 1). Interestingly, the dipole moment of **1c** is already negative in the S_0 state and becomes even more negative in the T_1 state. On the other hand, fulvenes **1f**–**1h** with π-electron-acceptor substituents exhibit an increase in dipole moment on going from S_0 to T_1. Thus, the zwitterionic resonance structure with T_1-aromatic 4π-electron cyclopentadienyl cation increases in importance in the T_1 states of acceptor-substituted fulvenes compared to the parent fulvene **1a**. The opposite is true for donor-substituted fulvenes, where this resonance structure should play a smaller role than in **1a** because of charge repulsion between the negative charge that forms at the exocyclic C atom in T_1 and the electron-rich donor substituents.

Since the triplet aromatic resonance structure shown in Scheme 1 differs in importance in the T_1 states of the various fulvenes **1a**–**1h**, the geometries of these fulvenes are interesting (Figure 1). The fulvenes in T_1 are in all but two cases C_2- or C_{2v}-symmetric, as in their S_0 states (Table 1). Only **1g** and **1h** are nonplanar with twisted NO_2 and BH_2 groups leading to C_s-symmetric structures.

The exocyclic C=C bond length varies notably in the T_1 state (Figure 1), similar to what was observed by Krygowsky

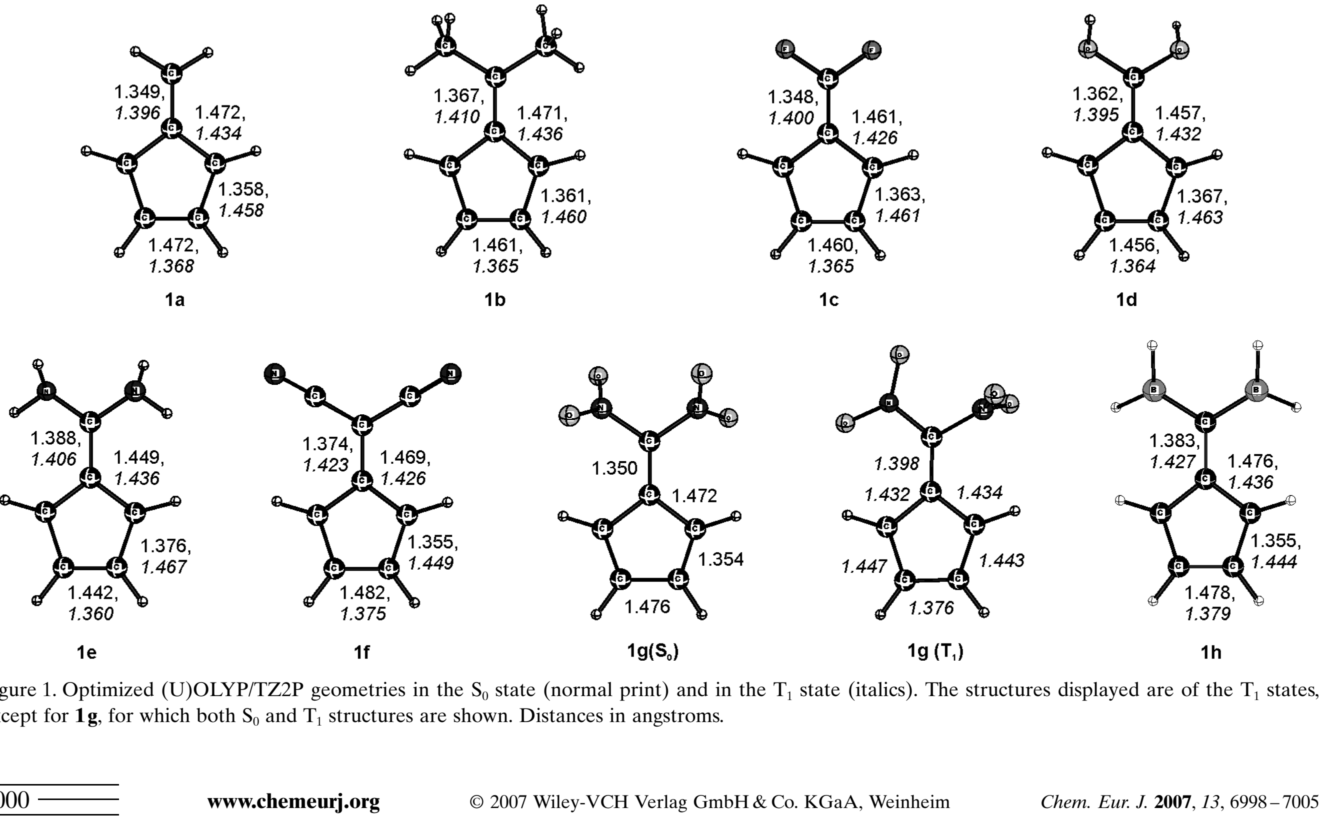
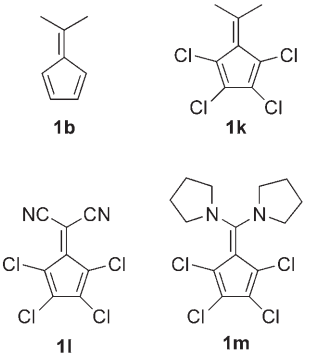


Figure 1. Optimized (U)OLYP/TZ2P geometries in the S_0 state (normal print) and in the T_1 state (italics). The structures displayed are of the T_1 states, except for **1g**, for which both S_0 and T_1 structures are shown. Distances in angstroms.

and co-workers for neutral substituted fulvenes in S_0, for which a variation in r_{CC} of 0.037 Å was calculated for this bond at the B3LYP/6-311+G(d,p) level.[10] In our smaller set of disubstituted fulvenes we find that the variation in the exocyclic C=C bond length is 0.040 Å in S_0 and 0.032 Å in T_1 at the (U)OLYP/TZ2P level. Variations in T_1 are also observed for the C–C bonds of the cyclopentadienyl ring. For **1e** in the T_1 state, the difference between the longest and shortest bond [Δr_{CC}(cp)] is 0.107 Å, indicative of substantial bond-length alternation and a nonaromatic species. However, for **1f** and **1h** in T_1 Δr_{CC}(cp) is reduced to 0.074 and 0.065 Å, respectively. The corresponding HOMA values for these fulvenes of 0.08 (**1e**), 0.26 (**1a**), 0.49 (**1f**), and 0.43 (**1h**) suggest no T_1-state aromaticity in the first fulvene and some influence of aromaticity in the last two. However, these HOMA values should be taken with care because only HOMA parameters derived for the S_0 state are available,[16] and these parameters will not be optimal for evaluating T_1-state aromatic compounds. If the optimal C–C bond length of cyclooctatetraene in the T_1 state ($r_{CC}=1.407$ Å at the UOLYP/TZ2P level), that is, a T_1-state aromatic compound, is used as R_{opt} for the HOMA calculation, then HOMA values of 0.43 (**1e**), 0.58 (**1a**), 0.73 (**1f**), and 0.73 (**1h**) are obtained. These geometric findings match the earlier conclusion of Krygowsky et al. that an increased exocyclic C=C bond length in S_0 correlates with an increased degree of aromaticity of the cyclopentadienyl ring, as measured by HOMA,[10] and extends their conclusion to the lowest triplet state.

Substituents at the ring C atoms could also influence ΔE_{ST} (Scheme 3), and thus ΔE_{ST} of **1i** and **1j** (Scheme 3) were compared to that of **1a**. Fulvene **1i** should have a smaller ΔE_{ST} and **1j** a larger ΔE_{ST} than **1a**. Indeed, **1i** has a ΔE_{ST} of 29.7 kcal mol^{-1} at the OLYP/cc-pVTZ level, which is 7.1 kcal mol^{-1} smaller than that of **1a**. Thus, it can be anticipated that fulvenes with particularly small ΔE_{ST} can be designed by combining electron-donor groups at the ring positions with electron-acceptor groups at the exocyclic positions. Interestingly, the electron-withdrawing cyano groups at the ring positions do not have the expected reversed effect on ΔE_{ST}, because ΔE_{ST} of **1j** is 30.8 kcal mol^{-1}, that is, similar to that of **1i**. However, the lowering effect of the cyano groups of **1j** can be understood in terms of a longer π-conjugated system. For comparison, ΔE_{ST} of cyclopentadiene and 1,2,3,4-tetracyanocyclopentadiene are 57.6 and 40.7 kcal mol^{-1}, respectively, at the (U)OLYP/cc-pVTZ level.

Thus, the π-donor/acceptor ability of a fulvene substituent clearly influences ΔE_{ST}, as postulated in the introduction. Indeed, it is possible to tune ΔE_{ST} beyond the 27–29 kcal mol^{-1} calculated for **1a**–**1h** by combining appropriate substitution at the exocyclic C atom with suitable substituents at the ring C atoms (vide infra). To verify our hypothesis on tunable ΔE_{ST} in fulvenes we synthesized pentafulvenes **1k**, **1l**, and **1m** (Scheme 4), which together with commercially available **1b** provide an experimental test of the validity of our hypothesis. If the hypothesis is correct, pentafulvene **1m** should have the largest ΔE_{ST} among **1k**–**1m**, and **1l** the smallest. Moreover, **1k** should have a smaller ΔE_{ST} than **1b**.



Scheme 4.

Experimental studies on singlet excited states: Before determining ΔE_{ST} of **1b** and **1k**–**1m**, we compared their UV/Vis spectra. Clearly, variation in the energy of the lowest singlet excited state among the pentafulvenes is large (Figure 2), as previously observed.[17] All of the experimentally investigated pentafulvenes show two distinct, but broad, absorption features in the region 250–800 nm. These two bands are of similar intensity only for **1m**, whereas the low-energy band

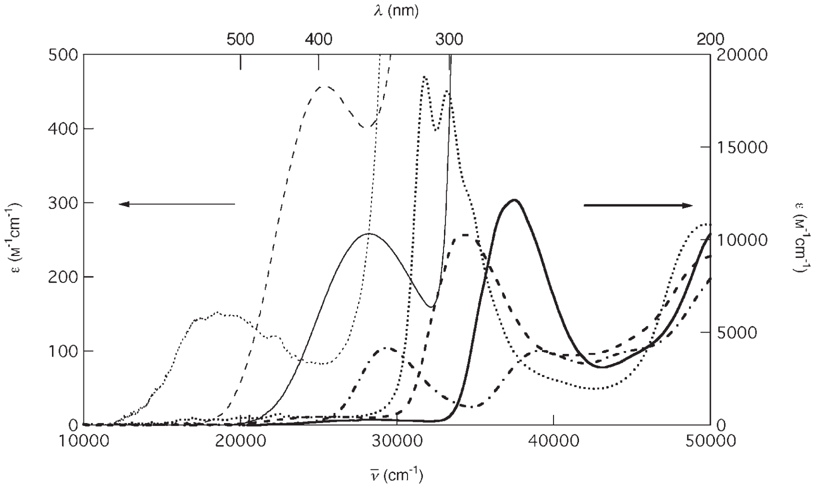


Figure 2. Absorption spectra of pentafulvenes in acetonitrile (–•–• **1m**, —— **1b**, ----- **1k**, ••••• **1l**). Thick lines refer to the right-hand axis, and thin lines to the left-hand axis.

Table 2. Experimental and computed excited-state energy levels.

	1b	**1k**	**1l**	**1m**
$\tilde{\nu}_{max}(S_0–S_1)$ [cm^{-1} (kcal mol^{-1})]	28250 (80.7)	25300 (72.3)	18700 (53.4)	29250 (83.6)
ε [M^{-1} cm^{-1}]	260	460	150	4160
$\tilde{\nu}_{max}(S_0\text{-}S_2)$ [cm^{-1} (kcal mol^{-1})]	37450 (107.0)	34250 (97.9)	31750 (90.7)	39050 (111.6)
ε [M^{-1} cm^{-1}]	12150	10270	18820	4000
$\Delta E_{ST(exptl)}$ [cm^{-1} (kcal mol^{-1})]	16000 (45.7)	12100 (34.6)	$<$9500 ($<$27.1)	17500 (50.0)
$\Delta E_{ST(calcd, vert)}$ [cm^{-1} (kcal mol^{-1})][a]	18900 (54.0)	15700 (45.0)	9800 (28.1)	19100 (54.5)
$\Delta E_{ST(calcd, adiab)}$ [cm^{-1} (kcal mol^{-1})][b]	13700 (39.3)	11100 (31.7)	5600 (16.0)	14900 (42.7)

[a] Vertical singlet–triplet energy splittings calculated at the (U)OLYP/cc-pVTZ level. [b] Adiabatic singlet–triplet energy splittings calculated at the (U)OLYP/cc-pVTZ level.

has significantly lower oscillator strength than the high-energy band for the other three pentafulvenes. The energies of the lowest bands, as determined from the maximum, are listed in Table 2. Among **1k**–**1m**, the S_1 state of **1l** is 7000 cm^{-1} (20.0 kcal mol^{-1}) lower than that of **1k**, which in turn lies 4000 cm^{-1} (11.4 kcal mol^{-1}) below that of **1m**. Furthermore, the energy of this state in nonchlorinated **1b** is higher than that of chlorinated **1k** by 3000 cm^{-1} (8.6 kcal mol^{-1}). It thus seems possible to rationalize the energies of the S_1 state in similar terms as for the T_1 state. On the other hand, the S_2 states of the four pentafulvenes are more similar in energy, but still show the trend **1l**<**1k**<**1m** and **1k**<**1b**. Thus, the energy difference between the S_1 and S_2 states is smallest for **1m** and largest for **1l**. These observations for the S_1 state are in line with our hypothesis for the T_1 state, and should open up future computational investigations of the transferability of the aromatic-chameleon property to singlet excited states of fulvenes.

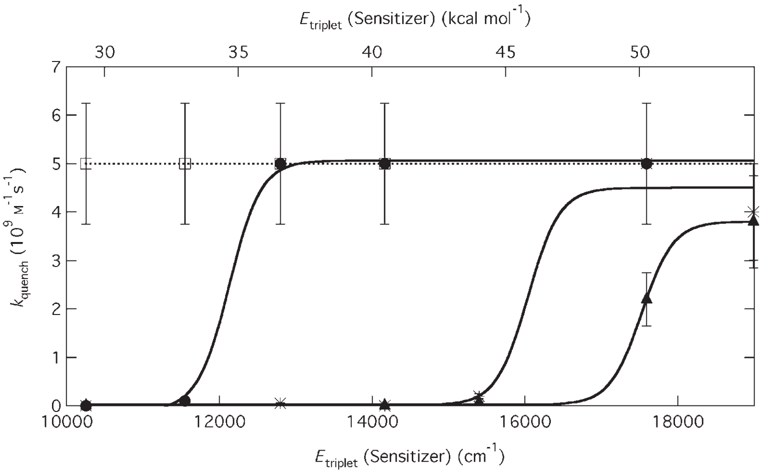


Figure 3. Quenching rate constants of the sensitizer by the pentafulvenes (▲ **1m**, * **1b**, ● **1k**, □ **1l**), measured from transient absorption. Solid lines are best fits to the Sandros equation [Eq. (1)].

Experimental studies on the lowest triplet states: As none of the pentafulvenes are phosphorescent, an indirect approach must be taken to determine the energy level of the T_1 state. Therefore, the lowest triplet energy of the pentafulvenes was estimated by triplet sensitization, whereby the lifetime of the T_1 state of a sensitizer with known T_1 energy is measured by nanosecond transient absorption in the absence of a fulvene and with an excess of fulvene. If the triplet energy of the sensitizer is much higher than that of the pentafulvene, triplet energy transfer and diffusion-controlled quenching of the triplet lifetime of the sensitizer take place. In contrast, neither energy transfer nor quenching of the triplet lifetime occurs if the T_1 energy of the sensitizer is much below that of the pentafulvene. By using a range of sensitizers with known T_1 energies and suitable photophysics, the T_1 energy of the pentafulvene is estimated by analyzing the quenching rate constants with the Sandros equation [Eq. (1)][18]

$$k_{quench} = k_{diffusion}/[1+\exp(-\Delta E_T/RT)] \quad (1)$$

where ΔE_T is the difference in T_1 energy of sensitizer and fulvene. A fairly steep transition between diffusion-controlled energy transfer and no energy transfer occurs (Figure 3). In a plot of quenching rate constants versus T_1 energy of the sensitizer, and the T_1 energy of the pentafulvene is given by the midpoint of the reflection curve.

As for the S_1 energies, the order of the T_1 energies of the four pentafulvenes is **1l**<**1k**<**1b**≈**1m** (Table 2), and this fully supports our hypothesis on tunability of ΔE_{ST}. Noteworthily, even the sensitizer with the lowest triplet energy, tetracene (29.3 kcal mol^{-1}), is fully quenched by **1l**. Thus, an upper limit of its T_1 energy can be determined as approximately 1000 cm^{-1} (2.9 kcal mol^{-1}) lower than the T_1 energy of tetracene, that is, **1l** should have a T_1 energy of less than 9250 cm^{-1} (26.4 kcal mol^{-1}).[19] For the other three pentafulvenes the range of the sensitizers used covers both higher and lower energies than their T_1 energies, which therefore are determined more accurately.

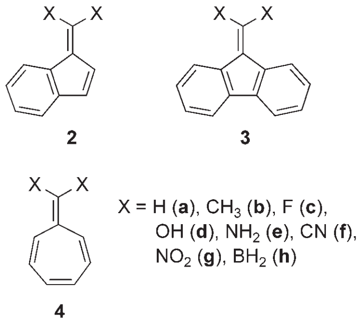
Comparison of measured and computed ΔE_{ST}: The trend in measured triplet energies for the four pentafulvenes is the same as in the calculations, but in all cases the measured energy of a particular fulvene lies between its calculated vertical and adiabatic T_1 energies (Table 2). The vertical T_1 energy of **1b** (54.2 kcal mol^{-1} by EELS)[15] is higher than the energy determined by triplet sensitization (46 kcal mol^{-1}). According to OLYP and CASPT2 calculations the vertical T_1 energy is 54.2 and 53.9 kcal mol^{-1}, whereas the corresponding adiabatic T_1 energy is 39.5 and 39.9 kcal mol^{-1}. The calculated (U)OLYP/TZ2P differences in enthalpy and Gibbs free energies between the two states at 298 K are 38.0 and 35.6 kcal mol^{-1},[20] respectively. Using the IEF-SCRF method, which takes nonspecific interaction of the acetonitrile solution into account, the Gibbs free-energy difference between the S_0 and T_1 states of **1b** becomes 36.0 kcal mol^{-1}, which is 10 kcal mol^{-1} below the experimental value. The corresponding energies calculated for **1k**, **1l**, and **1m** are 31.7, 16.0, and 42.7 kcal mol^{-1}, respectively, which also differ from the experimentally determined energies. However, it was previously found that a discrepancy between T_1 energy from experiments employing the Sandros equation (or extensions thereof) and the calculated adiabatic triplet energy can be as much as 25 %, depending on the structural flexibility of the triplet donor and acceptor.[21] In our studies no special care was taken to use only nonflexible sensitizers, so a measured T_1 energy 15 % higher than the calculated value is reasonable.

The series of tetrachloro-substituted pentafulvenes **1k**–**1m**, convincingly demonstrates and proves the concept of ΔE_{ST} tuning, whereby the dicyano-substituted pentafulvene has the lowest ΔE_{ST} and the dipyrrolidinyl-substituted pentafulvene the highest (Table 2). In calculations of the vertical excited triplet state as well as the relaxed (adiabatic) triplet state, the difference achieved is more than 25 kcal mol^{-1}, which agrees well with our experimental data, where the difference in ΔE_{ST} is larger than 23 kcal mol^{-1}.

Consequently, both experiments and calculations reveal that two π-electron-withdrawing groups at the exocyclic position of a pentafulvene lower ΔE_{ST} and that two donor groups increase the gap (Table 1). Chloro substituents at the ring also lower the gap compared to the unsubstituted species, and singlet–triplet energy gaps that range between 16 and 52 kcal mol^{-1} can be achieved according to calculations, that is, a variation of 36 kcal mol^{-1}. An interesting observation can be made with regard to the magnitudes of the dipole moments of **1k**–**1m**. For **1l**, which has the smallest ΔE_{ST}, the difference between $\mu(S_0)$ and $\mu(T_1)$ is merely 1.75 D, whereas for **1m** this difference is 5.10 D.

Generalization of ΔE_{ST} tuning for other classes of fulvenes: It would be desirable if the tunability of ΔE_{ST} in pentafulvenes could be generalized for other classes of fulvenes with larger conjugated systems. It could then provide a tool to predictably tune the band gap of organic materials for semiconducting or conducting purposes. Hence, we computed ΔE_{ST} of fulvenes **2**–**4** (Scheme 5) with the same set of exocyclic substituents as for **1** (Table 3). The computations were performed at the (U)OLYP/6-311G(d) level only.

For benzofulvene derivatives **2** ΔE_{ST} can also be varied by substitution at the exocyclic C atom, but the variation of 21.2 kcal mol^{-1} is slightly smaller than that of pentafulvene (29.1 kcal mol^{-1}). The effect of the substituents are the same, that is, boryl, cyano, and nitro substituents decrease the gap to a similar extent, whereas the hydroxyl group causes the largest increase, as opposed to the amino group in the case of pentafulvene. Substitution also affects the variation in ΔE_{ST} for the dibenzofulvene derivatives, but now the hydroxyl substituent gives the largest effect and the amino group has no effect on ΔE_{ST} compared to the unsubstituted dibenzofulvene. Interestingly, the abilities of the hydroxyl and amino groups to shift ΔE_{ST} switch as one goes from **1** to **2** to **3**. The extent of the variation in **3** (17.8 kcal mol^{-1}) is also smaller than for the benzofulvenes, that is, the substituent effects on ΔE_{ST} are gradually attenuated as the fulvene system becomes larger.



Scheme 5.

Table 3. Symmetries, singlet–triplet energy gaps (ΔE_{ST}) and dipole moments of fulvenes **2**–**4**[a].

Molecule	Symmetry S_0	Symmetry T_1	ΔE_{ST}	$\mu(S_0)$	$\mu(T_1)$
2a	C_s	C_s	45.9	0.44	0.91
2b	C_1	C_1	42.7	1.72	0.61
2c	C_s	C_1	48.6	0.32	2.39
2d	C_1	C_1	53.9	2.87	1.51
2e	C_1	C_1	53.0	4.47	0.61
2f	C_1	C_1	33.0	6.08	7.48
2g	C_1	C_1	33.6	5.82	8.23
2h	C_1	C_1	32.7	1.94	4.82
3a	C_{2v}	C_{2v}	48.7	0.18	0.26
3b	C_2	C_1	38.7	1.40	0.64
3c	C_{2v}	C_1	48.5	0.54	2.35
3d	C_2	C_1	50.6	0.20	1.42
3e	C_2	C_2	48.7	4.94	0.46
3f	C_{2v}	C_1	37.3	6.64	4.66
3g	C_1	C_2	32.8	5.70	5.24
3h	C_2	C_1	36.8	2.19	0.90
4a	C_{2v}	C_{2v}	28.9	−0.81	0.58
4b	C_1	C_2	26.8	−0.18	1.86
4c	C_{2v}	C_{2v}	25.4	−1.45	0.01
4d	C_2	C_2	23.8	2.16	4.27
4e	C_2	C_2	18.8	1.98	5.42
4f	C_{2v}	C_{2v}	33.8	−8.46	−5.30
4g	C_1	C_1	34.8	−8.30	5.53
4h	C_2	C_1	30.4	−6.76	−1.81

[a] Energies in kcal mol^{-1} and dipole moments in debye.

The heptafulvene derivatives **4** are particularly useful for testing the concept of triplet-state aromaticity, because the effect on the ΔE_{ST} of π-donor and π-acceptor substituents at the exocyclic position should be opposite to what is observed for the analogous pentafulvenes, benzofulvenes, and dibenzofulvenes. Indeed, π-electron-donor groups at the exocyclic positions of **4** lower ΔE_{ST}, and π-electron-acceptor groups raise it, an effect of the opposite polarity of heptafulvene versus pentafulvene in both the S_0 and T_1 states.[2,3] However, the extent of the variation at the OLYP level (16.0 kcal mol^{-1}) is substantially smaller than that of pentafulvene (29.1 kcal mol^{-1}). The amino and nitro groups give the smallest and largest gap, respectively.

Tuning of singlet–triplet gaps in heterofulvenes such as dithiafulvenes should also be attractive, particularly because these compounds already have found applications. However, initial calculations indicate that the situation is more complex and difficult to rationalize, presumably due to possible nπ* character of the T_1 states of such systems. The discussion of the tunability of the ΔE_{ST} of these systems thus requires further analysis and will be reported elsewhere.

Conclusion

By making use of the aromatic-chameleon property of pentafulvenes on going from the singlet ground state (S_0) to the lowest ππ* triplet state (T_1), we have shown both computationally and spectroscopically that the singlet–triplet energy gaps of these species are easily tuned. Electron-withdrawing groups at the exocyclic position and electron-donor substituents at the ring C atoms reduce ΔE_{ST} compared to the parent pentafulvene. Electron-donating groups at the exocyclic position have the opposite effect. The reversal of the substituent effects in the T_1 state compared to the S_0 state is explained by Baird's theory on triplet-state aromaticity and the fact that pentafulvenes have reversed polarities in T_1 and S_0 due to their behavior as aromatic chameleons. Thereby, ΔE_{ST} can be effectively tuned through substitution by as much as 36 kcal mol^{-1}. Solely through exocyclic substitution, it can be varied by 29 kcal mol^{-1}.

The qualitative arguments on how to tune ΔE_{ST} can also be applied to other classes of fulvenes, such as substituted heptafulvenes, benzofulvenes, and dibenzofulvenes. In heptafulvenes a particular substituent has the opposite effect on ΔE_{ST} to that in pentafulvenes, and this supports the fact that triplet-state aromaticity can be varied by substitution in a similar manner as for the singlet ground state. However, the extent to which the ΔE_{ST} can be varied decreases as the size of the fulvene increases; for example, with the same set of exocyclic substituents as for the pentafulvenes, ΔE_{ST} in dibenzofulvene can only be varied by 18 kcal mol^{-1}, that is, about 10 kcal mol^{-1} less.

Our investigation shows the importance of triplet-state aromaticity for the properties of fulvenes in their lowest triplet state. Presumably, fulvenes are influenced by substituents because of a similar aromaticity in the lowest excited singlet state, since the S_1 state, except for the multiplicity, most likely has a similar electron configuration to the T_1 state. The influence of substituents on the energy of the S_1 state indicates that this is indeed the case.

Clearly, qualitative arguments can be used to rationalize the singlet–triplet energy gaps of substituted fulvene derivatives. This knowledge should be useful, for example, for tuning the band gaps of novel materials. Previously, Pranata, Grubbs, and Dougherty estimated through valence effective Hamiltonian calculations that polyfulvene should have properties comparable to polythiophene and polypyrrole.[22] From our findings, it can be postulated that the band gaps of polyfulvenes can be varied rather extensively, and this possibly would enable design of novel zero-band-gap polymers.

Experimental Section

Computational methods: Density functional theory (DFT) calculations were carried out using the gradient-corrected OPTX exchange functional of Handy and Cohen,[23] together with the gradient-corrected correlation functional of Lee, Yang, and Parr (LYP),[24] that is, the OLYP method. The OLYP method has been shown to give better descriptions of olefins and radical compounds than the BLYP method.[25] For compounds without chlorine atoms, Dunning's TZ2P triplet-ζ basis set was used.[26] For the compounds with chlorine atoms Dunning's cc-pVTZ basis set,[27] was used instead, as the TZ2P triplet-ζ basis set is not available for the chlorine atom. Frequencies were calculated to confirm that all optimized structures correspond to minima on the potential-energy surfaces, and stabilities of the Kohn–Sham solutions were also checked.[28] The nonspecific action of a surrounding acetonitrile solution was simulated using the polarizable continuum model in the integral-equation formalism (IEF-PCM) of Tomasi and co-workers.[29] Atomic charges were calculated with natural population analysis as implemented by Weinhold.[30] All DFT calculations were carried out with the Gaussian 03 program package.[31]

Calculations were also performed at the level of complete active space self-consistent field (CASSCF) and at that of second-order perturbation theory (CASPT2)[32,33] with the (B,C,N,O/4s3p2d, H/3s1p) atomic natural orbital (ANO) basis set.[34] The active space (Table 1) includes the valence π orbitals, the two highest occupied σ orbitals, and two σ* orbitals. The calculations were performed with Molcas 6 program.[35]

Synthesis: 1,2,3,4-Tetrachloro-6,6-dicyanopentafulvene (**1l**) and 1,2,3,4-tetrachloro-6,6-dipyrrolidinopentafulvene (**1m**) were synthesized according to the literature.[17] 1,2,3,4-Tetrachloro-6,6-dimethylpentafulvene (**1k**) was synthesized by reaction of *N*-propyl-2-propanimine with 1,2,3,4-tetrachlorocyclopentadiene at −78 °C according to the procedure described in the literature.[36,37] The compounds were identified by UV/Vis, IR, and melting point, which agreed with literature data. 6,6-Dimethylpentafulvene (**1b**) was purchased from Aldrich and used without any further purification.

Spectroscopic measurements: Acetonitrile (HPLC grade, LabScan) and toluene (HPLC grade, LabScan) were used as received. All experiments were performed at ambient temperature. All sensitizers (dibenzoyl, 9-fluorenone, 2′,4′,5′,7′-tetraiodofluorescein, 9,10-dichloroanthracene, 5,10,15,20-tetraphenylporphyrins (zinc and free-base), and tetracene were commercially available and used as received.

Steady-state absorption spectra were recorded on a HP Aglient 8253 spectrophotometer. Transient absorption was measured by using a nanosecond flash photolysis system from Applied Photophysics. Monochromatic pump light was generated from a frequency-tripled Q-switched Nd:YAG laser (Quantel) pumping a optical parametric oscillator, delivering flashes of about 10 ns and about 15 mJ. The probe light came from a pulsed 100 W xenon lamp and was filtered through a monochromator before analysis.

The sensitizers were excited at their 0–0 transition, and their most characteristic feature was used as detection wavelength.[38] Acetonitrile was used as the solvent, except for sensitization with free-base tetraphenylporphyrin, for which toluene was used. Concentration of the sensitizer was determined by requiring an absorbance of <0.1 (1 cm path length) at the excitation wavelength, and the fulvene concentration was 10 times higher to ensure pseudo-first-order conditions of sensitizer quenching. In all cases the fulvene concentration was in the range 0.1–10 mM. All sensitizer samples were subjected to three freeze–pump–thaw cycles (<0.1 mbar). In general, the triplet lifetime of the sensitizer was determined first, after which the fulvene was added under air-free conditions (under argon), and the resulting triplet lifetime of the sensitizer was measured. However, in a few experiments involving **1m**, the fulvene was mixed with the sensitizer before the freeze–pump–thaw cycles due to the low solubility of this fulvene, and the sensitizer lifetime measured separately. Absorption spectra were measured before and after flash photolysis. In cases of very short sensitizer lifetimes in the presence of small concentrations of fulvene, the resulting very large quenching rate constants ($>5\times10^9\,\mathrm{M}^{-1}\mathrm{s}^{-1}$) are likely to be somewhat uncertain. Thus, these diffusion-controlled quenching rate constants were fixed at $5\times10^9\,\mathrm{M}^{-1}\mathrm{s}^{-1}$ in the analysis. This had no significant influence on the resulting ΔE_{ST} ($<100\,\mathrm{cm}^{-1}$).

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