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Substituent Effects on the Electron Affinities and Ionization Energies of Tria-, Penta-, and Heptafulvenes: A Computational Investigation

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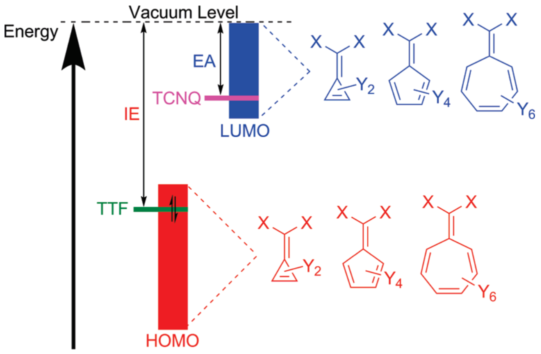

The extent of substituent influence on the vertical electron affinities (EAs) and ionization energies (IEs) of 43 substituted tria-, penta-, and heptafulvenes was examined computationally at the OVGF/6-311G(d)//B3LYP/6-311G(d) level of theory and compared with those of tetracyanoquinodimethane (TCNQ) and tetrathiafulvalene (TTF) as representing strong electron-acceptor and -donor compounds, respectively. The substituents X at the exocyclic positions of the fulvenes were either NH_2, H, or CN, while the substituents Y at the ring positions were H, Cl, F, CN, or NH_2. The variations of the EAs and IEs were rationalized by qualitative arguments based on frontier orbital symmetries for the different fulvene classes with either X or Y being constant. The minimum and maximum values found for the calculated EAs of the tria-, penta-, and heptafulvenes were 0.51−2.05, 0.24−3.63, and 0.53−3.14 eV, respectively, and for the IEs 5.27−9.96, 7.07−10.31, and 6.35−10.59 eV, respectively. Two of the investigated fulvenes outperform TCNQ (calcd EA = 2.63 eV) and one outperforms TTF (calcd IE = 6.25 eV) with regard to acceptor and donor abilities, respectively. We also evaluated the properties of bis(fulvene)s, i.e., compounds composed of a donor-type heptafulvene fused with an acceptor-type pentafulvene, and it was revealed that these bis(fulvene)s can be designed so that the IE and EA of the two separate fulvene segments are retained, potentially allowing for the design of compact donor−acceptor dyads.

Introduction

Fulvenes are compounds whose lowest electronic excitation energies can be varied widely by choice of substituents.[1] Using Baird's rule on aromaticity of $4n$ π-electron annulenes in their lowest $\pi\pi^*$ excited triplet state it is easy to rationalize the opposite polarity in the lowest excited triplet state (T_1) as compared to the polarity in the electronic ground state (S_0).[1−3] Because of this opposite polarity, a particular substituent will have opposite electronic influence on the fulvene in T_1 vs in S_0. As a result, substituents which influence the

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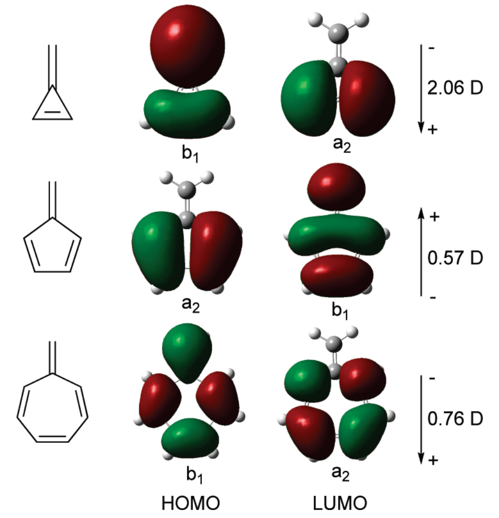


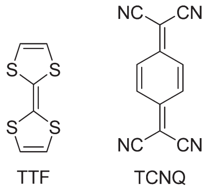
FIGURE 1. HOMOs and LUMOs of the parent tria-, penta-, and heptafulvenes, their orbital symmetries, and the dipole moments in the S_0 state at B3LYP/6-311G(d) level.

electronic structure will either increase or decrease the singlet–triplet energy splitting (ΔE_{ST}) as compared to the unsubstituted species, and the substituent effect alternates successively between increasing and decreasing the ΔE_{ST} as one goes from tria- to penta-, to heptafulvenes. For example, the pentafulvene with dicyano substituents at the exocyclic C atom has a smaller ΔE_{ST} than the parent pentafulvene, but the same substitution pattern generates a heptafulvene with a larger ΔE_{ST} than found for the parent heptafulvene.[1]

The symmetries of the frontier orbitals also alternate as one goes from tria- to penta- to heptafulvenes (Figure 1). Whereas the HOMOs of tria-, penta-, and heptafulvenes are of b_1, a_2, and b_1 symmetries, respectively, the LUMOs of the three successive compounds are of a_2, b_1, and a_2 symmetries. The b_1 symmetric orbitals have large lobes at the exocyclic C atom, but the a_2 symmetric orbitals have a nodal plane involving the exocyclic C=C double bond. On the basis of the frontier orbital symmetries, exocyclic substituents should therefore primarily influence the ionization energies (IEs) of tria- and heptafulvenes while they should influence the electron affinities (EAs) of pentafulvenes. On the other hand, substituents at the exocyclic positions should have smaller effects on the EAs of tria- and heptafulvenes as well as on the IEs of the pentafulvenes. A similar approach has previously been exploited by Houk and co-workers for the rationalization of IEs of pentafulvenes obtained from photoelectron spectroscopy and quantum chemical calculations.[4] The effects of the substituents at the ring positions on the IEs and EAs are, on the other hand, less clear-cut for qualitative estimations, but a computational study should reveal possible trends.

Herein, we examine the extent of the substituent effects on the IEs and EAs by computational means and analyze the results in terms of qualitative orbital arguments, a study which should be useful for the design of new functional materials. In particular, how widely can one tune the fulvene EAs and IEs through substitution? Can one lower the IE to reach values similar to that of the good electron donor tetrathiafulvalene (TTF, IE = 6.70–6.72 eV,[5,6] Scheme 1) or raise the EA to that of the widely used electron acceptor tetracyanoquinodimethane (TCNQ, EA = 2.8 eV,[7–9] Scheme 1)? Can one even identify fulvenes that are stronger donors and acceptors than TTF and TCNQ? If so, these findings could potentially be very useful for the design of new redox active materials.

SCHEME 1. Tetrathiafulvalene and Tetracyanoquinodimethane



The IEs and EAs of 43 differently substituted tria-, penta-, and heptafulvenes (Figure 2), as well as TCNQ and TTF, were calculated using the outer valence Green's function approximation (OVGF).[10] We investigated the IEs and EAs of tria-, penta-, and heptafulvenes with the exocyclic substituents X being CN, H, or NH_2 (from electron-withdrawing to electron-donating character) and with the ring substituents Y chosen as Cl, H, F, or CN (from weakly electron-donating to electron-withdrawing character). For the triafulvene we also examined species with Y = NH_2. The analysis of each fulvene category is primarily performed in classes defined by the endocyclic Y substituents so as to allow for probing the extent to which qualitative theory is valid. With regard to the analysis of the properties in terms of constant X substituents, we perform this for all IEs but limit the analysis of EAs to pentafulvenes with X = CN as only for this class were positive EAs found for each Y. Concerning the endocyclic substituents, we analyze fulvenes having Y at all endocyclic positions, and at present we refrain from an in-depth analysis of the effect of Y at each particular position. At this point, it should also be noted that some of our fulvenes are not directly suitable from an applications point of view because of stability reasons; however, our study aims at clarifying to what extent the redox properties of fulvenes can be tuned.

The fulvenes in their neutral ground states are influenced by zwitterionic aromatic resonance structures, and the extent by which these resonance structures contribute to the electronic structure is determined by the substitution pattern.[11,12] In the parent compounds, the contributions were previously found by Radom and co-workers to be 19, 7, and 5% for the tria-, penta-, and heptafulvenes, respectively, based on Mulliken π-electron populations and calculated dipole moments.[13] As shown in Figure 2, the possibility for contribution from an aromatic

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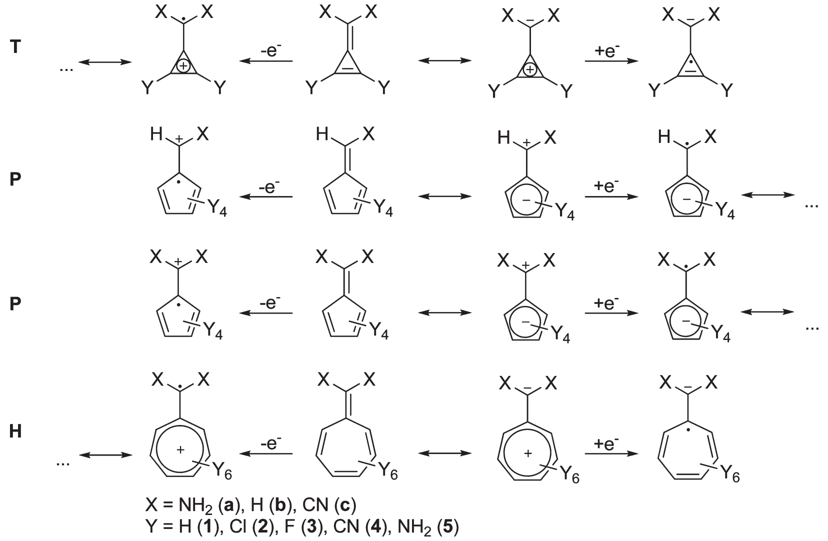

FIGURE 2. Resonance structures of tria- (**T**), penta- (**P**), and heptafulvenes (**H**) and the corresponding oxidized and reduced forms. Circles inscribed in the radical cations and anions indicated which species can be influenced by aromaticity. The substituted fulvenes are named according to their parent species, followed by letter and number corresponding to substituents Y and X; e.g., **P1b** designates the unsubstituted pentafulvene. For pentafulvenes, suffixes **D** or **M** denote di- or monosubstituted exocyclic carbon, respectively.

resonance structure in the radical anion/cation which forms upon electron attachment/detachment will also affect the EAs and IEs as these are influenced by both the initial and final states. For example, reduction of the triafulvene will add one electron to LUMO which is of a_2 symmetry having a node at the exocyclic C atom. The added electron will thus be confined to the three-membered ring leading to a situation with no influence of an aromatic cyclopropenium cationic ring. This should lead to overall low EAs of triafulvenes. In contrast, upon reduction of a pentafulvene the new electron is added to a b_1-symmetric LUMO, which to some extent allows the pentafulvene to keep its aromatic influence. Thus, pentafulvenes should in general have higher EAs than triafulvenes. A similar, but reversed, argumentation can be used for the oxidation processes, i.e., a low IE indicate aromatic influence in the radical cation, whereas a high IE indicate no aromatic gain upon oxidation.

The study described herein is fundamental in character, although there should be areas of applications, e.g., to form new redox-active materials.[14] Moreover, it is known that fulvenes can dimerize and/or coordinate metals upon reduction,[15,16] a feature that has been utilized for the formation of sandwich-type transition-metal complexes.[17] The investigated fulvenes could therefore potentially function as ligands with tunable properties in metallocene complexes giving different coordination modes.[18] Furthermore, a properly substituted bis(fulvene) could display the fundamental characteristics found in donor−acceptor (D−A) compounds, a current area of many research groups. In broad terms, the interest in D−A compounds stems from their potential usage in organic electronics and optoelectronics; e.g., because of large hyperpolarizabilities they can be of interest for nonlinear optics (NLO) applications.[19] Lately, particular focus has also been given to D−A compounds in which the D and A moieties are connected via a short π-conjugated unit or even directly connected into compactly fused D−A dyads.[20−27] With proper substituent pattern, various bis(fulvene)s, i.e., compounds composed of a donor-fulvene fused with an acceptor fulvene, could potentially also be designed as compact D−A dyads.

Computational Methods

All computations were performed with the Gaussian 03 program package.[28] All structures were optimized at the B3LYP/6-311G(d) hybrid density functional theory level,[29,30] and frequency calculations were performed at the same level to verify that stationary points correspond to minima. Stability analyses were also performed for the bis(fulvene)s to ensure

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that there were no RKS−UKS instabilities of the restricted Kohn−Sham solutions.

The aromaticity of the compounds was evaluated utilizing the harmonic oscillator model of aromaticity (HOMA) by Krygowski.[31] The vertical IEs and EAs were calculated with a semidirect algorithm for the outer valence Green's function (OVGF) approximation[10] using the 6-311G(d) split-valence triple-ζ basis set of Pople and co-workers.[32] The 6-311G(d) basis set was chosen as it allows for OVGF computations of all species investigated herein, including the large bis(fulvene) dyads. The EAs and IEs of five fulvenes, TCNQ, and TTF were also calculated with the aug-cc-pVDZ and cc-pVTZ basis sets and showed strong linear correlation ($r^2 > 0.99$) with the values obtained employing the smaller 6-311G(d) basis set. This reveals that the trends discussed herein are the same as when larger and better basis set are used (see the Supporting Information).

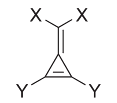
Results and Discussion

We discuss the three fulvene categories separately while continuously comparing their IEs and EAs with those calculated for TTF and TCNQ, respectively. As for the mono- and disubstituted pentafulvenes, the aromaticity has previously been evaluated using the different aromaticity indices of aromatic stabilization energies (ASE), nucleus independent chemical shifts (NICSs), magnetic susceptibility exaltations (Λ), and values from the harmonic oscillator model of aromaticity (HOMA).[11,12] It was shown that the monosubstituted species exhibited excellent correlations between the different indices while the correlations between the indices for the disubstituted pentafulvenes were worse. This was partially attributed to the steric effect which changes the torsion angle between the ring plane and the plane formed by the bonds at the exocyclic carbon so that the interaction with the substituents changes. In this work, we only use the HOMA value as a measure for aromaticity (positive HOMA) or antiaromaticity (negative HOMA).

The tria-, penta-, and heptafulvenes are labeled with prefixes **T**, **P**, and **H**, and in addition, for the pentafulvenes which are mono- and disubstituted at the exocyclic C atom we use the suffices **M** and **D**, respectively. The substitution pattern is shown in Figure 2. We also explore the possibility of designing fused bis(fulvene)s which potentially can be described as dual electron acceptors and donors. The small and symmetric character of fulvenes allows for design of compounds for which the HOMO and LUMO are predominantly localized on two different molecular segments, potentially enabling the design of compact compounds with low-lying charge-transfer states.

Tetracyanoquinodimethane (TCNQ). The vertical EA of TCNQ at OVGF/6-311G(d)//B3LYP/6-311G(d) level is 2.63 eV, in good agreement with the experimental values (2.8 ± 0.1 and 2.84 ± 0.05 eV)[7−9] and with the value previously calculated at OVGF/augsp-cc-pVDZ//HF/cc-pVDZ level (2.74 eV).[33] As the EA of TCNQ will be compared to the EAs of the differently substituted fulvenes (Figure 2), and these in turn to the much larger bis(fulvene)s (Figure 6), we are restricted to a moderately sized basis set.

SCHEME 2. Triafulvenes (T) Investigated Herein



T1a - T5c

X = NH_2 (**a**), H (**b**), CN (**c**)
Y = H (**1**), Cl (**2**), F (**3**), CN (**4**), NH_2 (**5**)

TABLE 1. Calculated Electron Affinities (EA) and Ionization Energies (IE) of Triafulvenes, TCNQ, and TTF, as well as the HOMA Values of the Triafulvenes

compd	X	Y	HOMA	EA[a]/eV	IE/eV
TTF					6.25
TCNQ				2.63	9.11
T1a	NH_2	H	0.137		7.39
T1b	H	H	0.048		7.94
T1c	CN	H	0.536		9.05
T2a	NH_2	Cl	−0.080		7.45
T2b	H	Cl	−0.174		8.18
T2c	CN	Cl	0.485		8.81
T3a	NH_2	F	−0.971		6.71
T3b	H	F	−0.336		8.41
T3c	CN	F	0.324		9.37
T4a	NH_2	CN	−0.317	0.51	7.29
T4b	H	CN	0.058	0.75	9.22
T4c	CN	CN	0.538	2.05	9.96
T5a	NH_2	NH_2	−0.069		5.27
T5b	H	NH_2	0.412		6.33
T5c	CN	NH_2	0.912		7.20

[a]Calculated EAs with negative values are not given.

Tetrathiafulvalene (TTF). Our calculated IE for TTF is 6.25 eV, i.e., an underestimation by 0.45−0.47 eV when compared to the experimental values (6.70−6.72 eV).[5,6] Still, our OVGF value is closer to the experimental result than the IE obtained from an MS-CASPT2/ANO-L calculation (6.07 eV).[34]

Triafulvenes. Triafulvenes are usually found as segments in larger conjugated compounds, e.g., calicene derivatives.[35] Among the triafulvenes investigated in this paper (Scheme 2), the parent triafulvene **T1b** and several derivatives of **T5** have previously been generated.[36−40] Fulvene **T1b** was estimated to have a half-life of 20 h in pentane at −78 °C,[36] while on the other hand, the **T5** derivatives are relatively stable at ambient conditions.[39,40]

As seen in Table 1, the degree of aromaticity according to HOMA varies widely among the selected triafulvenes; **T3a** is antiaromatic (a markedly negative HOMA), whereas **T1c**, **T4c**, and especially **T5c** have some aromatic character (positive HOMA). For **T3** and **T4** series where the ring substituent Y is an EWG and for **T5** where the ring-substituent is an EDG, the aromaticity is significantly and steadily

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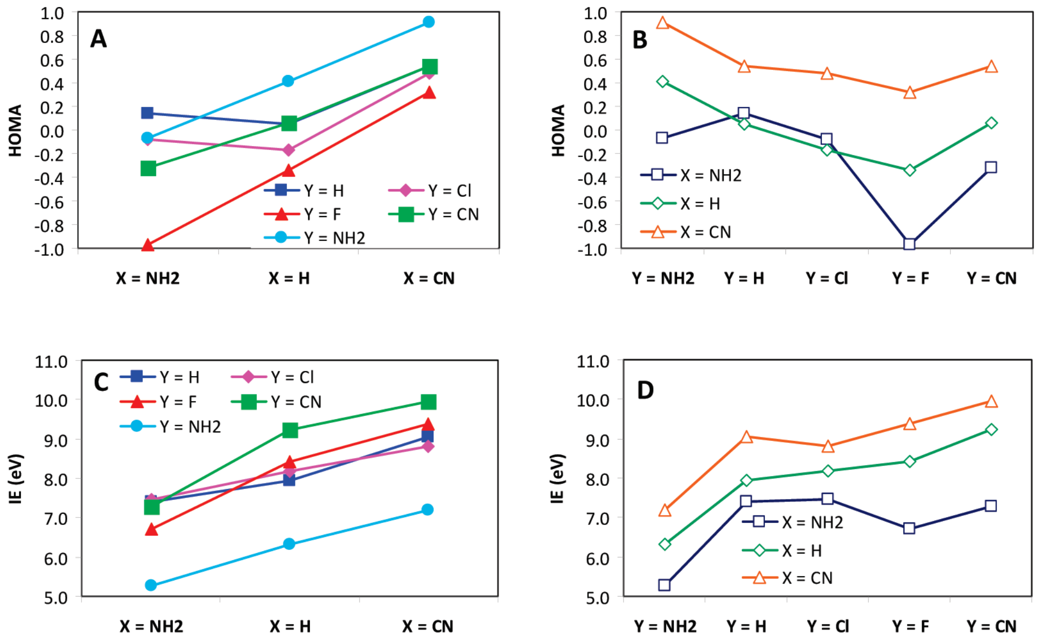

FIGURE 3. Variation in HOMA values and IEs for triafulvenes. Variation in HOMA as a function of (A) the exocyclic substituents X and (B) the ring substituents Y. Variation in IE as a function of (C) the exocyclic substituents and (D) the ring substituents Y.

enhanced as the exocyclic substituent X increases in EWG character (Figure 3A). However, for the two series **T1** and **T2** the HOMA values for the triafulvenes with X = H do not fall in between those of triafulvenes having X as EDG or EWG, even though X = CN leads to more aromatic character than X = NH_2. Still, the general degree of aromaticity for these two series increases as one goes from X = NH_2 (**a**) to X = CN (**c**), in line with the finding that triafulvenes with electron-withdrawing X are reasonably stable.[39,41,42] When X is kept constant and Y is varied, the Y = F always leads to the least aromatic triafulvene regardless of X (Figure 3B), whereas the most aromatic triafulvene is found for Y = NH_2 when X = H or CN but for Y = H when X = NH_2.

The HOMO of the parent triafulvene has a large lobe at the exocyclic carbon, and substituents at this position should therefore have a particularly large influence on the IEs. With regard to the IEs, the variations with substituent X are 1.66 (**T1a**–**c**), 1.36 (**T2a**–**c**), 2.66 (**T3a**–**c**), 2.67 (**T4a**–**c**), and 1.93 (**T5a**–**c**) eV, respectively, so that the largest variations are found for the triafulvene class with Y = CN and F, and this is also seen in Figure 3C. Upon oxidation an electron is taken from the b_1-symmetric HOMO, and the radical cation formed will to some extent be described by a resonance structure with an aromatic cyclopropenium cationic segment (Figure 2). Thus, triafulvenes should in general have low IEs, and interestingly, one of the substituted triafulvenes (**T5a**) has an IE of 5.27 eV (Table 1), about one eV lower than our calculated values for TTF. It is rewarding that the HOMA value of this triafulvene when in the neutral state reveals a nonaromatic rather than antiaromatic character, suggesting that it could be reasonably stable, and thus, a potential synthetic target.

With regard to the effect of the Y substituents on the IEs with X being constant, the variations in IE within the three series are 2.18 eV (X = NH_2), 2.89 eV (X = H), and 2.76 eV (X = CN), respectively, which reveals that a slightly larger variation may be achieved through change of the Y substituents than of the X substituents, although the triafulvenes with X = NH_2 do not follow the exact trend of triafulvenes with X = H and CN (Figure 3D). The highest IEs in the three series are obtained for Y = Cl with constant X = NH_2 and for Y = CN with constant X = H and CN. The lowest values are found for Y = NH_2 for each constant X substituent. It can also be noted that Y = NH_2 always gives the lowest IEs (Figure 3D), which is appealing as this is possibly also the class which is most synthetically accessible.

Concerning the EAs, only one triafulvene class has positive EAs for all substituents X, this being the **T4** class. As stated in the Introduction, triafulvenes should have low EAs as they lose aromaticity in the radical anionic state, and indeed, the average EA for the **T4** class is 1.10 eV, which is significantly lower than for the **P4** class (vide infra). The fact that only 3 out of 15 triafulvenes have positive EAs is also in line with the qualitative explanation of Figure 2 on low EAs as the aromatic influence of **T4** will be annihilated upon reduction. Interestingly, the EA of **T4c** approaches that of TCNQ, while its HOMA retains a reasonably high value, suggesting some degree of aromatic character and stability.

Finally, it should be noted that the variation in EAs for the Y = CN series (1.51 eV), the only series with all positive EAs, is smaller than the variation in IEs for the same triafulvene series (2.67 eV). This verifies that the substituents at the exocyclic position of triafulvenes have their largest effect on the IEs rather than on the EAs, in line with our qualitative arguments in the introduction exploiting the frontier orbital symmetries.

Pentafulvenes. In contrast to the triafulvenes, the HOMA values for the pentafulvenes within each class **P1**–**P4** become more negative when going from X = NH_2 over X = H

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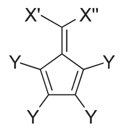
(42) Ammon, H. L. *J. Am. Chem. Soc.* **1973**, *95*, 7093–7101.

SCHEME 3. Pentafulvenes (P) Investigated Herein



P1aM - P4cD

X = NH_2 (**a**), H (**b**), CN (**c**)
Y = H (**1**), Cl (**2**), F (**3**), CN (**4**)
M: X' = H , X'' = X
D: X' = X'' = X

TABLE 2. Calculated Electron Affinities (EA) and Ionization Energies (IE) of Pentafulvenes Monosubstituted at the Exocyclic Position, TCNQ, and TTF, as well as the HOMA Values of These Pentafulvenes

compd	X	Y	HOMA	EA[a]/eV	IE/eV
TTF					6.25
TCNQ				2.63	9.11
P1aM	NH_2	H	0.237		7.41
P1b	H	H	−0.295		8.22
P1cM	CN	H	−0.338	0.24	8.82
P2aM	NH_2	Cl	0.305		7.51
P2b	H	Cl	−0.319	0.25	8.15
P2cM	CN	Cl	−0.352	1.22	8.48

[a]Calculated EAs with negative values are not given.

TABLE 3. Calculated Electron Affinities (EA) and Ionization Energies (IE) of Pentafulvenes Disubstituted at the Exocyclic Position, TCNQ, and TTF, as well as the HOMA Values of These Pentafulvenes

compd	X	Y	HOMA	EA[a]/eV	IE/eV
TTF					6.25
TCNQ				2.63	9.11
P1aD	NH_2	H	0.406		7.07
P1b	H	H	−0.295		8.22
P1cD	CN	H	−0.382	1.21	9.33
P2aD	NH_2	Cl	0.470		7.54
P2b	H	Cl	−0.319	0.25	8.15
P2cD	CN	Cl	−0.426	1.97	8.71
P3aD	NH_2	F	0.403		7.51
P3bD	H	F	−0.339		8.53
P3cD	CN	F	−0.421	1.72	9.33
P4aD	NH_2	CN	0.729	0.57	8.63
P4bD	H	CN	−0.009	2.32	9.84
P4cD	CN	CN	−0.073	3.63	10.31

[a]Calculated EAs with negative values are not given.

to X = CN (Scheme 3, Tables 2 and 3, Figure 4A). Thus, pentafulvenes behave in the opposite manner to triafulvenes as expected from the different polarities in the contributing aromatic resonance structures (Figure 1). The more negative HOMA values for fulvenes with X = CN suggest some antiaromatic character and lower stabilities of these fulvenes. With regard to the Y substituent, the HOMA is the largest for all X when Y = CN and significantly lower when Y = H, Cl, or F (Figure 4B). For the latter three Y substituents, HOMA attains similar values. Moreover, for each Y the HOMA value is the largest when X = NH_2 and significantly lower when X = H or CN (Figure 4B), although negative HOMA values are not synonymous with unsynthesizable as we previously formed **P2aD**−**P2cD** (HOMA: 0.470, −0.319, −0.426) and found all three to be stable, even though **P2cD** slowly degrades when exposed to ambient atmosphere.[1]

Our calculated IE of the parent pentafulvene (**P1b**) is 8.22 eV, and it agrees well with the peak of HOMO (8.36 eV) in the photoelectron spectrum reported by Heilbronner et al.[43] The variation in the IE among the four pentafulvene classes as a function of the two exocyclic substituents is 1.17−2.26 eV, with the **P2** class (Y = Cl) having the smallest variation and the **P1** class (Y = H) having the largest (Table 3). However, regardless of ring substituent Y the trend for dependence on X is the same for each class (Figure 4C). The 6-amino- and 6,6-diaminopentafulvenes (**P1aM**, **P2aM**, and **P1aD**−**P4aD**) have smaller IEs than the corresponding pentafulvenes where X = H, and with an IE of 7.07 eV, **P1aD** is the strongest electron donor among the pentafulvenes investigated herein. This calculated IE is in reasonable agreement with that of 6,6-dimethylaminopentafulvene recorded with photoelectron spectroscopy (7.43 eV).[43] Overall, our findings agree with those of Houk et al. that EDGs at the exocyclic position decrease the IE of pentafulvenes and EWGs at this position increase the IE.[4]

When X is kept constant and Y is varied, the highest IE is always found for Y = CN, while the lowest is either found for Y = H or Cl (Figure 4D). Here it should, however, be noted that the lowest IE among the pentafulvenes is significantly higher than the lowest IE among the triafulvenes (7.07 vs 5.27 eV for **P1aD** and **T5a**, respectively), in line with the qualitative reasoning above.

However, the more interesting property of the pentafulvenes is the EA because 10 of the 16 investigated pentafulvenes have positive EAs, although it is only the **P4** class which has positive EAs for all fulvenes contained in this class. The finding that a higher ratio of the pentafulvenes than of the triafulvenes has positive EAs supports the qualitative argument that for pentafulvenes an aromatic resonance structure contributes in the radical anion (Figure 2). Consequently, the average EA of the **P4** class (2.17 eV) is higher than that of the **T4** class (1.10 eV), and indeed, one pentafulvene (hexacyanopentafulvene, **P4cD**) has an EA that exceeds our calculated EA of TCNQ by 1.00 eV (Table 3). This pentafulvene has a HOMA value that suggests nonaromatic character, and it should be a worthwhile synthetic target.

Even though a great number of pentafulvenes have positive EAs, it is only with either constant X = CN or Y = CN that all fulvenes in this particular class have positive EAs. With constant Y = CN, the variation among the three fulvenes in this class is 3.06 eV, while with constant X = CN the variation in EA between the four species is 2.42 eV. Finally, in accordance with our qualitative arguments above based on the frontier orbital symmetries, the span in the EAs is larger than in the IEs when regarding classes with either constant Y or constant X. With constant Y the variations in IEs and EAs are 1.68 and 3.06 eV, respectively, while with constant X the variations are 1.60 and 2.42 eV, respectively.

Heptafulvenes. The HOMA values of the heptafulvenes are given in Table 4, but the analysis of these is not straightforward because the heptafulvenes tend to distort from planarity so as to avoid influence of antiaromaticity. The distortions are particularly notable in heptafulvenes with substituents that reinforce the resonance structure with eight π-electrons in the ring, i.e., electron-donating X substituents, as can be seen in the $\omega_{8-1-2-3}$ dihedral angle

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(43) Heilbronner, E.; Gleiter, R.; Hopf, H.; Hornung, V.; De Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 783–794.

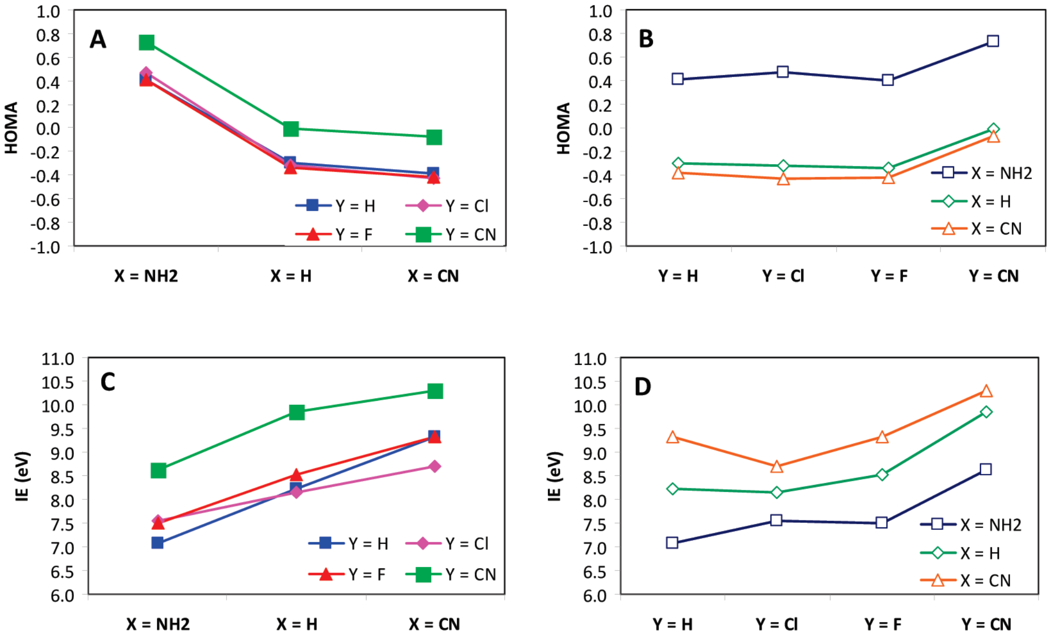


FIGURE 4. Variation in HOMA values and IEs for pentafulvenes. Variation in HOMA as a function of (A) the exocyclic substituents X and (B) the ring substituents Y. Variation in IE as a function of (C) the exocyclic substituents X and (D) the ring substituents Y.

TABLE 4. Calculated Electron Affinities (EA) and Ionization Energies (IE) of Heptafulvenes, TTF and TCNQ, as well as the HOMA Values and Dihedral Angles $\omega_{8-1-2-3}$ between the C8−C1 and C2−C3 Bonds of the Heptafulvenes

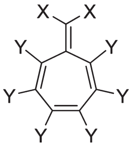
compd	X	Y	HOMA	$\omega_{8-1-2-3}$	EA[a]/eV	IE/eV
TTF						6.25
TCNQ					2.63	9.11
H1a	NH$_2$	H	0.064	145		6.35
H1b	H	H	0.152	180		7.12
H1c	CN	H	0.551	180	0.53	8.00
H2a	NH$_2$	Cl	0.033	124		7.54
H2b	H	Cl	−0.279	124		8.58
H2c	CN	Cl	−0.178	119	1.47	9.10
H3a	NH$_2$	F	0.192	138		7.43
H3b	H	F	0.226	167		8.29
H3c	CN	F	0.491	156	1.38	9.02
H4a	NH$_2$	CN	0.040	137	1.98	8.34
H4b	H	CN	−0.274	133	2.60	10.05
H4c	CN	CN	−0.145	123	3.14	10.59

[a] Calculated EAs with negative values are not given.

(Table 4).[44] Interestingly, for the **H1** and **H3** classes HOMA indicates an increase in aromaticity as one goes from X = NH$_2$ to X = CN, but for the **H2** and **H4** classes a slight decrease is found (Figure 5A). When exocyclic substituent X is kept constant, the variation in HOMA as well as in $\omega_{8-1-2-3}$ is largest for X = CN, whereas a much smaller variation is observed for X = NH$_2$ (Figure 5B), in line with the explanation that this last substituent reinforces the antiaromatic character which is then avoided through ring puckering.

Several of the investigated heptafulvene derivatives have previously been synthesized (Scheme 4), for example, the parent heptafulvene **H1b** and the substituted **H1a**, **H1c**, and **H2c**.[45−48] The reason that a wide range of different heptafulvene derivatives have been synthesized is likely the ability of substituted heptafulvenes to distort to a puckered structure so as to avoid any unfavorable antiaromatic character that they attain at planar conformations.

SCHEME 4. Heptafulvenes (H) Investigated Herein



H1a - H4c

X = NH$_2$ (**a**), H (**b**), CN (**c**)
Y = H (**1**), Cl (**2**), F (**3**), CN (**4**)

The variations in the IEs for different classes of the substituted heptafulvenes are 2−3 eV, with the largest variation for X = H (2.93 eV) and the smallest for X = NH$_2$ (1.99 eV) (Figure 5C). For variations in ring substituents, the **H4** class (Y = CN) shows the largest variation with a value of 2.25 eV (Figure 5D). As with the triafulvenes, the exocyclic substituents should have larger effect on the IEs than on the EAs; however, the maximal variation in IEs among the four different heptafulvene classes is not as large as between the triafulvenes (2.25 vs 2.67 eV), presumably as the triafulvene with the largest IE have significant antiaromatic character.

Although 6 of the 12 investigated heptafulvenes have positive EAs, in particular, all in the **H4** class, the ratio of heptafulvenes with positive EAs is smaller than the corresponding ratio for the pentafulvenes. Moreover, octacyanoheptafulvene

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(44) Stępień, B. T.; Krygowski, T. M.; Cyrański, M. K. *J. Phys. Org. Chem.* **2003**, *16*, 426–430.

(45) Bauer, W.; Daub, J.; Hasenhündl, A.; Rapp, K. M.; Schmidt, P. *Tetrahedron Lett.* **1981**, *22*, 2977–2980.

(46) Bauer, W.; Betz, I.; Daub, J.; Jakob, L.; Pickl, W.; Papp, K. M. *Chem. Ber.* **1983**, *116*, 1154–1173.

(47) Juts, C. *Chem. Ber.* **1964**, *97*, 2050–2065.

(48) Roedig, A.; Försch, M. *Chem. Ber.* **1978**, *111*, 2738–2740.

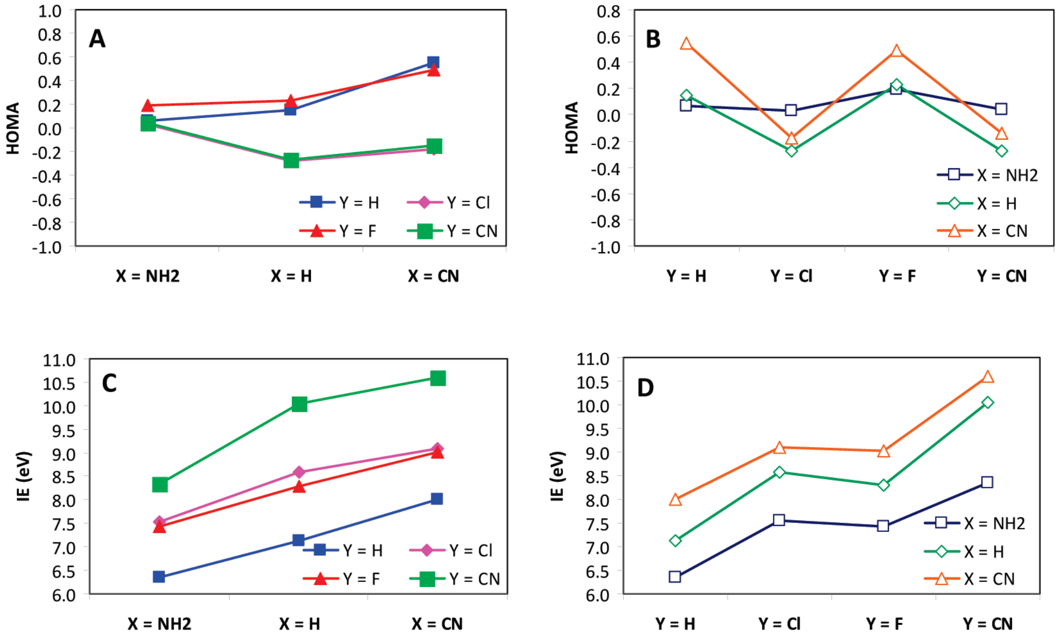

FIGURE 5. Variation in HOMA values and IEs for heptafulvenes. Variation in HOMA as a function of (A) the exocyclic substituents X and (B) the ring substituents Y. Variation in IE in dependence of (C) the exocyclic substituents X, and (D) the ring substituent Y.

has a calculated EA which is higher than that of TCNQ, but despite the eight cyano substituents its EA is lower than that of hexacyanopentafulvene (**P4cD**). This falls in line with the qualitative argument that the hexacyanopentafulvene radical anion to some extent is described by an aromatic resonance structure (Figure 2), but for the octacyanoheptafulvene radical anion no such stabilization is possible.

Finally, it is also noteworthy that the variation of EAs in the **H4** class (1.16 eV) is smaller than the variation of IEs within the same class (2.25 eV), supporting our conclusions that the frontier orbital symmetries dictate the magnitudes by which the redox properties vary.

General Substituent Effects. In general, the tria- and heptafulvenes have lower IEs (on average 0.28 and 0.23 eV, respectively, excluding the **T5** class) than the pentafulvenes due to the possible stabilization of their radical cations by aromatic resonance structures (Figure 2). The variations in IEs among the various classes of tria-, penta-, and heptafulvenes are 5.27−9.96, 7.07−10.31, and 6.35−10.59 eV, respectively. Tetraaminosubstitution as in **T5a**, combined with the aromaticity effect, thus yields a triafulvene that outperforms TTF by 1 eV, and **T5a** should be a suitable synthetic target as it will be a small and easily oxidized compound.

The EAs are more difficult to compare than the IEs as the only comparable values for the tria-, penta-, and heptafulvenes are given by the classes with Y = CN. The problem is that as the ring size increases so does the number of substituents at the ring, i.e., two, four, and six in the tria-, penta-, and heptafulvenes, respectively. Yet, **P4cD** has a higher EA than **H4c**, a fact that can be rationalized by aromaticity arguments. Hexacyanosubstitution combined with the aromatic character of the radical anion thus gives a fulvene (**P4cD**) which has a higher EA than TCNQ.

An interesting feature is the effect that the X substituent has on EA; for the tria- and heptafulvenes the spans are merely 1.54 and 1.16 eV, respectively, while for the pentafulvenes the span is 3.06 eV. The reason for the smaller span in the tria- and heptafulvenes is the symmetry relation between the substituent X and the LUMO, while LUMO of the pentafulvenes has a lobe on the exocyclic carbon which allows for interactions with the substituent.

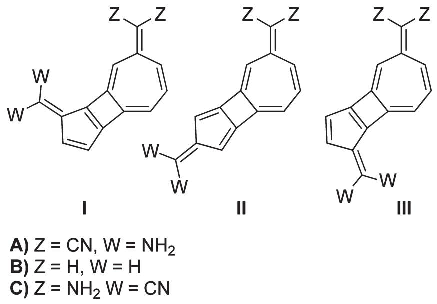

FIGURE 6. Structures of the bis(fulvene)s.

Combination to Donor−Acceptor Dyads. The fusion of a fulvene with a small IE to a fulvene with a large EA can lead to highly polarized molecules (Figure 6), compounds that can be of great interest as they potentially could function as organic conductors.[49] The large dipole moments are a consequence of partial charge transfer, which is a requirement for the molecule to behave as an organic metal.[50] It further suggests that a low-lying intramolecular charge-transfer (CT) state exists which could lead to molecules that show nonlinear optical (NLO) behavior. The fulvene dyads investigated below could also be electrochemically amphoteric compounds, i.e., function as dual electron donors and acceptors.[14] The synthesis of compounds with directly linked donor and acceptor moieties is, however, a challenge, but the synthesis of the bis(fulvene) dyads examined below could be

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(49) Yamashita, Y.; Tomura, M. *J. Mater. Chem.* **1998**, *8*, 1933–1944.
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TABLE 5. Calculated Electron Affinities, Ionization Energies, Dipole Moment, and HOMA for the Two Rings at the OVGF/6-311G(d)//B3LYP/6-311G(d) Level

compd	Z	W	EA	IE	dipole	HOMA 7-ring	HOMA 5-ring
IA	CN	NH_2	0.48	7.00	13.6	0.191	0.656
IB	H	H	0.08	7.06	2.3	−0.328	−0.127
IC	NH_2	CN	1.22	6.04	9.7	0.093	0.279
IIA	CN	NH_2	0.45	6.75	18.1	0.239	0.341
IIB	H	H	0.39	6.86	0.5	−0.195	−0.534
IIC	NH_2	CN	1.45	6.35	13.1	−0.271	−0.147
IIIA	CN	NH_2	0.48	7.03	19.2	0.152	0.624
IIIB	H	H	0.08	6.92	2.5	−0.324	−0.114
IIIC	NH_2	CN	1.22	6.15	14.3	−0.002	0.220

facilitated as they potentially can be generated from a suitable diketone which has the carbon framework of the dyad in place.

A number of dyads with different connectivities can be envisioned on the basis of the fulvenes above. We have screened a set of dyads consisting of one of the better heptafulvene electron donors, diaminoheptafulvene **H1a** (IE = 6.35 eV), and a moderate pentafulvene acceptor, dicyanopentafulvene **P1cD** (EA = 1.21 eV) (Figure 6). The species that exhibited significant steric hindrance between the substituents were excluded, as well as the ones where the HOMO of the donor moiety mixes with the LUMO of the acceptor moiety, i.e., the ones were HOMO and LUMO are not spatially separated on two different molecular segments. Species in which the HOMO and LUMO on the two fulvene segments mix cannot develop equally distinct CT states.[24] Our desired dyads thus have (i) large dipole moments, (ii) spatially separated HOMO and LUMO, and (iii) low IE and high EA.

However, to which degree can the electrochemical properties of fulvene donor−acceptor dyads be tuned? And to which extent do the EAs and IEs of the dyads resemble those of the separate fulvenes? Calculations of the EAs and IEs were made at the OVGF/6-311G(d)//B3LYP/6-311G(d) level, and bis(fulvene)s with Z = CN, W = NH_2 (**A**), Z = W = H (**B**), and Z = NH_2, W = CN (**C**) were examined (Figure 6), where the dyads **B** are the unsubstituted reference systems. In the **B** and **C** systems the heptafulvene segment acts as the donor and the pentafulvene segment as the acceptor, as opposed to case **A** (Table 5). For data on charge distributions and geometries of the bis(fulvene)s, see the Supporting Information.

Indeed, the IEs and EAs of **IA**−**IIIC** are largely characterized by the IEs and EAs of the individual fulvenes, thus revealing the tunability of the individual components and that the bis(fulvene)s should be proper donor/acceptor dyads. The three **C** compounds (Z = NH_2, W = CN) have the largest prospect of behaving as donor/acceptor dyads as these have the lowest IEs and the highest EAs. Their dipole moments (9.7−14.3 D) are intermediate to those of the **A** (13.6−19.2 D) and **B** (0.5−2.5 D) compounds but still large enough to potentially display interesting NLO properties.

To examine if the IEs and EAs can be further tuned, the ring hydrogens on the pentafulvene fragment of **IIIC** were exchanged to chloro substituents. This substitution resulted in an increase of both IE and EA by 0.12 and 0.25 eV to 6.27 and 1.47 eV, respectively, which are in close proximity to the IE of **H1a** (6.35 eV) and intermediate between the EAs of **P1cD** (1.21 eV) and **P2cD** (1.97 eV). The aromaticity of the 5- and 7-rings according to HOMA changed to 0.328 and 0.051, respectively. The dipole moment also showed a small increase to 15.7 D. The above-mentioned values indicate that the IEs and EAs can be further tuned by manipulating the ring positions, but likely not to the same extent as the substitution at the exocyclic positions which bear the largest contribution to the relevant orbitals.

Conclusions

As the IEs and EAs are properties intrinsically connected to the HOMO and LUMO of a compound, the effects of substitution are governed by the shapes and symmetries of these orbitals. For fulvenes, orbitals with large lobes at the exocyclic carbon atom will to a large extent be influenced by substitution at this position, while orbitals that have a nodal plane cutting through this carbon will provide smaller impact. Consequently, the widest range in EAs is found for the pentafulvenes (0.24−3.36 eV), and the widest range in the IEs is found for the triafulvenes (5.27−9.96 eV). As a result of our systematic study, one pentafulvene and one heptafulvene with higher calculated EAs than that of TCNQ (2.63 eV) as well as one triafulvene with lower IE than that of TTF (6.25 eV) have been identified. These compounds are thus small and highly redox active compounds, and they can hopefully be useful in the design of new organic materials for electronics applications.

Moreover, when a pentafulvene with high EA is combined with a heptafulvene with low IE to form fused bis(fulvene) dyads, the original characters of the fulvene fragments can be retained so that the EAs and IEs do not change significantly from those of the two isolated fulvenes. With these properties, the bis(fulvene)s could function as compact electrochemically amphoteric compounds.

Acknowledgment. Drs. Jun Zhu and Sébastien Villaume are acknowledged for discussions and computational assistance. H.O. is grateful for financial support from Uppsala University (the U^{3}MEC Molecular Electronics KoF initiative) and the Swedish Research Council, and K.K. is grateful for financial support from the Torkil Holm Foundation. We also thank the National Supercomputer Center (NSC) in Linköping, Sweden, and the Uppsala Multidisciplinary Center for Advanced Computational Science (UPPMAX) for generous allotment of computer time.

Supporting Information Available: Discussion on basis set dependence of EA and IE calculated with OVGF, data on charge distributions and geometries of the bis(fulvene)s, and listings of Cartesian coordinates and absolute energies of all compounds investigated herein. This material is available free of charge via the Internet at http://pubs.acs.org.