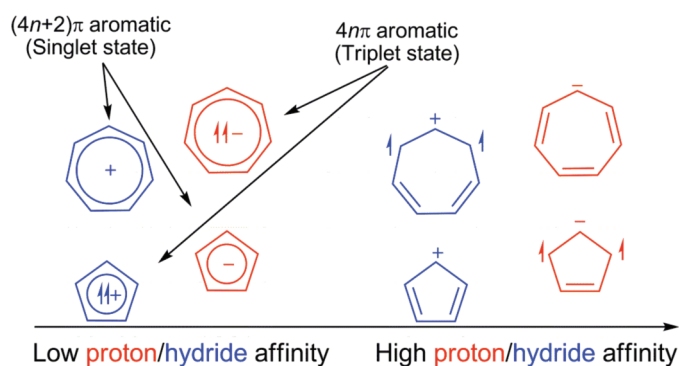# Proton and Hydride Affinities in Excited States: Magnitude Reversals in Proton and Hydride Affinities between the Lowest Singlet and Triplet States of Annulenyl and Benzannulenyl Anions and Cations

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Aromaticity has importance for proton and hydride affinities in the singlet ground state (S_0) of annulenyl anions and cations so that, e.g., cyclopentadiene is an acidic hydrocarbon. For the lowest $\pi\pi*$ excited triplet state (T_1), Baird's rule concludes that annulenes with $4n$ π-electrons are aromatic and those with $4n+2$ π-electrons are antiaromatic, opposite to Hückel's rule for aromaticity in S_0. Our hypothesis is now that the relative magnitudes of proton and hydride affinities of annulenyl anions and cations reverts systematically as one goes from S_0 to T_1 as a result of the opposite electron counting rules for aromaticity in the two states. Using quantum chemical calculations at the G3(MP2)//(U)B3LYP/6-311+G(d,p) level we have examined the validity of this hypothesis for eight proton and eight hydride addition reactions of anions and cations, respectively, of annulenyl and benzannulenyl type. We categorize the $(4n+2)\pi$-electron systems in S_0 and the $4n\pi$-electron systems in T_1 to be of A-character and $4n\pi$-electron systems in S_0 and $(4n+2)\pi$-electron systems in T_1 to be of AA-character (A, aromatic; AA, anti/nonaromatic). The average proton affinities of anions of A- and AA-characters in S_0 are 1447 and 1521 kJ/mol, respectively, and in T_1 they are 1365 and 1493 kJ/mol. The average hydride affinities of A- and AA-character cations in S_0 are 826 and 996 kJ/mol, and in T_1 they are 790 and 879 kJ/mol, respectively. Thus, the calculated proton and hydride affinities are in general lower for anions and cations of A-character than for those of AA-character, in good support of our hypothesis. The findings could likely be applied in synthetic organic photochemistry and other areas where excited state acid—base chemistry plays a role.

Introduction

Aromaticity is one of the core concepts in chemistry, and it impacts a number of different chemical and physical properties.[1,2] For example, the high acidity of cyclopentadiene and the ease by which cycloheptatriene is oxidized to the tropylium cation in the singlet electronic ground state (S_0) are both attributed to the gain of aromaticity upon formation of aromatic 6π-electron rings, referred to as aromatic sextets.[3–5] Whereas aromaticity is an energetically stabilizing feature of annulenes

(1) *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*; Minkin, V. I., Glukhovtsev, M. N., Simkin, B. Y., Eds.; John Wiley and Sons: New York, 1994.

(2) Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*.

(3) Thiele, J. *Ber.* **1900**, *33*, 666.

(4) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203.

(5) Bordwell, F. G.; Drucker, G. E.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 632.

with $4n+2$ π-electrons ($n = 0, 1, 2, ...$), its opposite, antiaromaticity, is an energetically destabilizing feature of annulenes with $4n$ π-electrons.[6−8] However, despite that the concept of aromaticity is old there is no definite method for determining the degree of aromaticity of a particular compound.

In 1972, Baird deduced that in the lowest $\pi\pi^*$ excited triplet state (T_1) annulenes with $4n$ and $4n+2$ π-electrons, respectively, possess aromatic and antiaromatic features, similar as S_0 state annulenes with $4n+2$ and $4n$ π-electrons, respectively.[9] Thus, the electron counting rule for aromaticity in T_1, referred to as Baird's rule, is opposite to Hückel's rule for aromaticity in S_0, and its validity has been proven through quantum chemical calculations of different properties that link to aromaticity and antiaromaticity.[10−12] According to recent calculations, the rule also extends to the lowest singlet excited state (S_1) of cyclobutadiene, benzene, and cyclooctatetraene,[13,14] and this falls in line with the earlier observations by Wan and co-workers that the acidities of 9*H*-fluorene and 5*H*-suberene in the S_1 state and the photosolvolytic reactivities of 9-fluorenol and 5-suberenol indicate favorable formation of cyclic $4n$ π-electron systems in this state.[15−18]

Even though nearly four decades have passed, Baird's rule has not been extensively applied to rationalize excited-state properties and photochemical reactivities. We have previously used the rule to explain the polarity reversal of fulvenes in their T_1 states and to tune their S_0-T_1 energy differences through rationally placed substituents.[19,20] Moreover, we have shown that aromaticity changes link to the profiles of T_1 potential energy surfaces (PES) of annulenylsubstituted olefins.[21−23]

Another important concept in chemistry is the acid−base concept, and its applications to a broad range of different areas are inexhaustible. Excited state acid−base chemistry has emerged and shown wide usage in recent years,[24,25] although competing photoreactions can complicate the picture, as found for cycloheptatriene singlet-state photochemistry when compared to that of suberene.[26] Yet, the scopes and limitations of excited state acid−base chemistry in organic chemistry need to be further explored and expanded.

Herein, we report on a computational study of the gas-phase proton and hydride affinities (PA and HA, respectively) in the T_1 states of five- and seven-membered anionic and
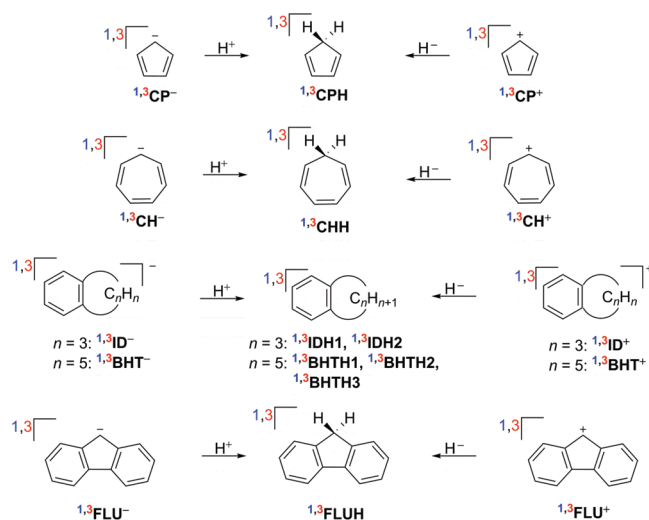
(6) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.
(7) Wiberg, K. B. *Chem. Rev.* **2001**, *101*, 1317.
(8) Allen, A. D.; Tidwell, T. T. *Chem. Rev.* **2001**, *101*, 1333.
(9) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941.
(10) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1945.
(11) Stanger, A. *J. Org. Chem.* **2006**, *71*, 883.
(12) Villaume, S.; Fogarty, H. A.; Ottosson, H. *ChemPhysChem* **2008**, *9*, 257.
(13) Karadakov, P. B. *J. Phys. Chem. A* **2008**, *112*, 7303.
(14) Karadakov, P. B. *J. Phys. Chem. A* **2008**, *112*, 12707.
(15) Wan, P.; Krogh, E. *J. Chem. Soc., Chem. Commun.* **1985**, 1207.
(16) Wan, P.; Krogh, E.; Chak, B. *J. Am. Chem. Soc.* **1988**, *110*, 4073.
(17) Wan, P.; Krogh, E. *J. Am. Chem. Soc.* **1989**, *111*, 4887.
(18) Budac, D.; Wan, P. *J. Org. Chem.* **1992**, *57*, 887.
(19) Möllerstedt, H.; Piqueras, M. C.; Crespo, R.; Ottosson, H. *J. Am. Chem. Soc.* **2004**, *126*, 13938.
(20) Ottosson, H.; Kilså, K.; Chajera, K.; Piqueras, M. C.; Crespo, R.; Kato, H.; Muthas, D. *Chem.—Eur. J.* **2007**, *13*, 6998.
(21) Brink, M.; Möllerstedt, H.; Ottosson, C.-H. *J. Phys. Chem. A* **2001**, *105*, 4071.
(22) Kato, H.; Brink, M.; Möllerstedt, H.; Piqueras, M. C.; Crespo, R.; Ottosson, H. *J. Org. Chem.* **2005**, *70*, 9495.
(23) Villaume, S.; Ottosson, H. *J. Phys. Chem. A* **2009**, *113*, 12304.
(24) Wan, P.; Shukla, D. *Chem. Rev.* **1993**, *93*, 571.
(25) Tolbert, L. M.; Solntsev, K. M. *Acc. Chem. Res.* **2002**, *35*, 19.
(26) Steuhl, H.-M.; Klessinger, M. *Angew. Chem., Int. Ed.* **1994**, *33*, 2431.

FIGURE 1. Investigated compounds together with the abbreviations used herein and the proton and hydride addition reactions. The superscript numbers 1 and 3 preceding the compound abbreviation refer to the compound in the lowest singlet and triplet state, respectively.

FIGURE 2. Proposed relationship between the relative magnitudes of the proton and hydride affinities (PA and HA, respectively) of (benz)annulenyl anions and cations and the electronic state as well as the number of π-electrons.

cationic π-conjugated rings, as well as the benzannulated analogues (Figure 1). We compare these energies against those of the same species in their closed-shell ground states, and in our analysis we exploit the Baird's and Hückel's rules for T_1 and S_0 aromaticity, respectively. Our hypothesis is that the T_1 state $4n$ ($4n+2$) π-electron aromaticity (antiaromaticity) influences the proton and hydride affinities of these species similarly as ground state $4n+2$ ($4n$) π-electron aromaticity (antiaromaticity) influences these properties in S_0. The hypothesis implies a reversal in the relative magnitudes of the proton or hydride affinities of an annulenyl anion or cation, respectively, as one goes from its S_0 to T_1 state and as one goes from a $4n$ to a $(4n+2)\pi$-electron species in either of the two states (Figure 2). We focus exclusively on the triplet-state PA's and HA's as Baird's rule is derived and unambiguously verified for this state, and we do not analyze potentially competing photochemical processes as this dramatically would expand the investigation.

The anions/cations that have been studied are the cyclopentadienyl anion/cation (**CP**$^{-/+}$), the cycloheptatrienyl anion/cation (**CH**$^{-/+}$), the indenyl anion/cation (**ID**$^{-/+}$), the benzoheptatrienyl anion/cation (**BHT**$^{-/+}$), and the fluorenyl anion/cation (**FLU**$^{-/+}$), and the neutral hydrocarbons that have been studied are 1,3-cyclopentadiene (**CPH**), 1,3,5-cycloheptatriene

(CHH), indene (IDH1), isoindene (IDH2), (6Z,8Z)-5H-benzo-cycloheptatriene (BHTH1), (4aZ,7Z,9Z)-6H-benzocyclohep-tatriene (BHTH2), (5Z,8Z)-7H-benzocycloheptatriene (BHT-H3), and 9H-fluorene (FLUH).

Although the influence of aromaticity/antiaromaticity of a compound cannot be determined in a definite manner through one single measure, we use the concepts as guiding tools for analysis, whereby stabilization indicates some influence of aromaticity and a destabilization indicates some influence of antiaromaticity. Support for our hypothesis on reversal of the magnitudes of the PA's and HA's as one goes from S_0 to T_1 should point to novel applications of Baird's rule in for example synthetic organic photochemistry, and it should allow for a rationalization of acid−base chemistry of cyclic π-conjugated molecules in their lowest excited states (T_1/S_1).

Computational Methods

All calculations were performed with the Gaussian 03 suite of programs,[27] and all structures were geometry optimized at the (U)B3LYP/6-311+G(d,p) level.[28,29] All compounds were optimized to minima on the potential energy surfaces, which was verified through frequency calculations revealing no imaginary frequencies. The stabilities of the Kohn−Sham solutions were analyzed with regard to potential RKS/UKS instabilities. From the calculated structures the total energies were calculated using the G3(MP2) composite ab initio method,[30] where the geometry optimizations and frequency calculations were carried out at (U)B3-LYP/6-311+G(d,p) level (G3(MP2)//(U)B3LYP/6-311+G(d,p)). The scaling factor for the frequencies at the (U)B3LYP/6-311+G-(d,p) level was set to be equal to the scaling factor used for (U)B3LYP/6-31G(d).[31] The 298 K heats of formation (ΔH_f) were calculated as described by Nicolaides et al.[32]

Potential multireference (MR) character of the singlet state AA-character compounds $^1CP^+$, $^1CH^-$, $^1ID^+$, $^1BHT^-$, and $^1FLU^+$ was examined through T_1 diagnostics[33] of the CCSD wave function at the (U)CCSD(T)/6-31G(d)//(U)B3LYP/6-311+G(d,p) level, i.e., the same geometry used for the G3(MP2)//(U)B3LYP/6-311+G(d,p) composite calculation. Only one of the species ($^1CP^+$) had a T_1 diagnostics value above 0.02 (see Table S2 in the Supporting Information); i.e., the threshold for MR character of a CCSD wave function.[33] To obtain an improved PA of $^1CP^+$ which is adjusted for MR character we

replaced the UQCISD(T)/6-31G(d) calculation in the G3(MP2)//(U)B3LYP/6-311+G(d,p) with a UBD(T)/6-31G(d) calculation, where the latter method properly handles MR character. The HA value obtained with the UBD(T) included G3(MP2)//(U)B3LYP/6-311+G(d,p) is 1118 kJ/mol, to be compared with 1117 kJ/mol obtained when including the UQCISD(T) computation.

The results of the ΔH_f were used to derive gas phase PAs and HAs according to the equations

$$PA = \Delta H_f(M^-) + \Delta H_f(H^+) - \Delta H_f(MH)$$

$$HA = \Delta H_f(M^+) + \Delta H_f(H^-) - \Delta H_f(MH)$$

Here, $M^{+/-}$ refers to a (benz)annulenyl anion/cation in either the lowest singlet or triplet state and MH is the reduced/oxidized neutral counterpart in either the S_0 or the T_1 state, respectively. The heats of formation of the proton and the hydride ions were set to the values 1530 and 145 kJ/mol, respectively.[34,35] The equation for PA is the IUPAC definition of PA, and herein, we use the analogous equation to define HA. Note also that we use HA as abbreviation for hydride affinity rather than for hydrogen atom affinity as used in ref 34.

In order to estimate the degree of aromaticity/antiaromaticity we used the harmonic oscillator model of aromaticity (HOMA) of Krygowski.[36] HOMA is a quantitative measure of aromaticity based on bond lengths, and it is defined according to the formula

$$HOMA = 1 - \frac{\alpha}{n}\sum_i (R_{opt} - R_i)^2$$

where n is the number of bonds in consideration, α is a normalization constant (257.7 for CC bonds), and R_{opt} is the optimal value of the bond lengths in an ideal aromatic system (1.388 Å for CC bonds). The R_i are the values of the individual bond lengths in the system under consideration. The values of α and R_{opt} are derived for an aromatic singlet ground state system, and application to determine T_1 state aromaticity should therefore be done with some care, remembering that the CC bonds of a T_1 state aromatic compound are slightly longer than in a singlet ground state aromatic compound. For example, the CC bond lengths of D_{8h} symmetric cyclooctatetraene in T_1 are 1.403 Å at (U)B3LYP/6-311+G(d,p) level whereas the CC bonds of D_{6h} symmetric benzene in S_0 at this level are 1.394 Å.

Results and Discussion

Herein, planar ionic compounds which are S_0 state $(4n+2)$ π-electron or T_1 state $4n\pi$-electron species will be referred to as being of A-character, and compounds which are S_0 state $4n\pi$-electron or T_1 state $(4n+2)\pi$-electron species will be referred to as being of AA-character. Following the qualitative Hückel's and Baird's rules, the A-character state corresponds to the state (closed-shell singlet or open-shell triplet) which should be the most aromatic, and the AA-character state corresponds to the state which should be the antiaromatic/nonaromatic state of the two states considered. In order to assess if triplet state aromaticity affects the proton/hydride affinity of a particular anion/cation in its T_1 state, we compare with the proton/hydride affinity in the S_0 state leading to the same isomer of the hydrocarbon. Although the formation of two different hydrocarbon isomers in the S_0 and T_1 states may be preferred energetically for the larger benzannulated anions and cations,

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cui, J. V. O. Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Revision E. 01 ed.; Gaussian Inc.: Wallingford CT, 2004.
(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.
(29) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
(30) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.
(31) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(32) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460.
(33) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem.* **1989**, *S23*, 199.

(34) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
(35) Goebbert, D. J.; Wenthold, P. G. *Int. J. Mass. Spectrom.* **2006** *257*, 1.
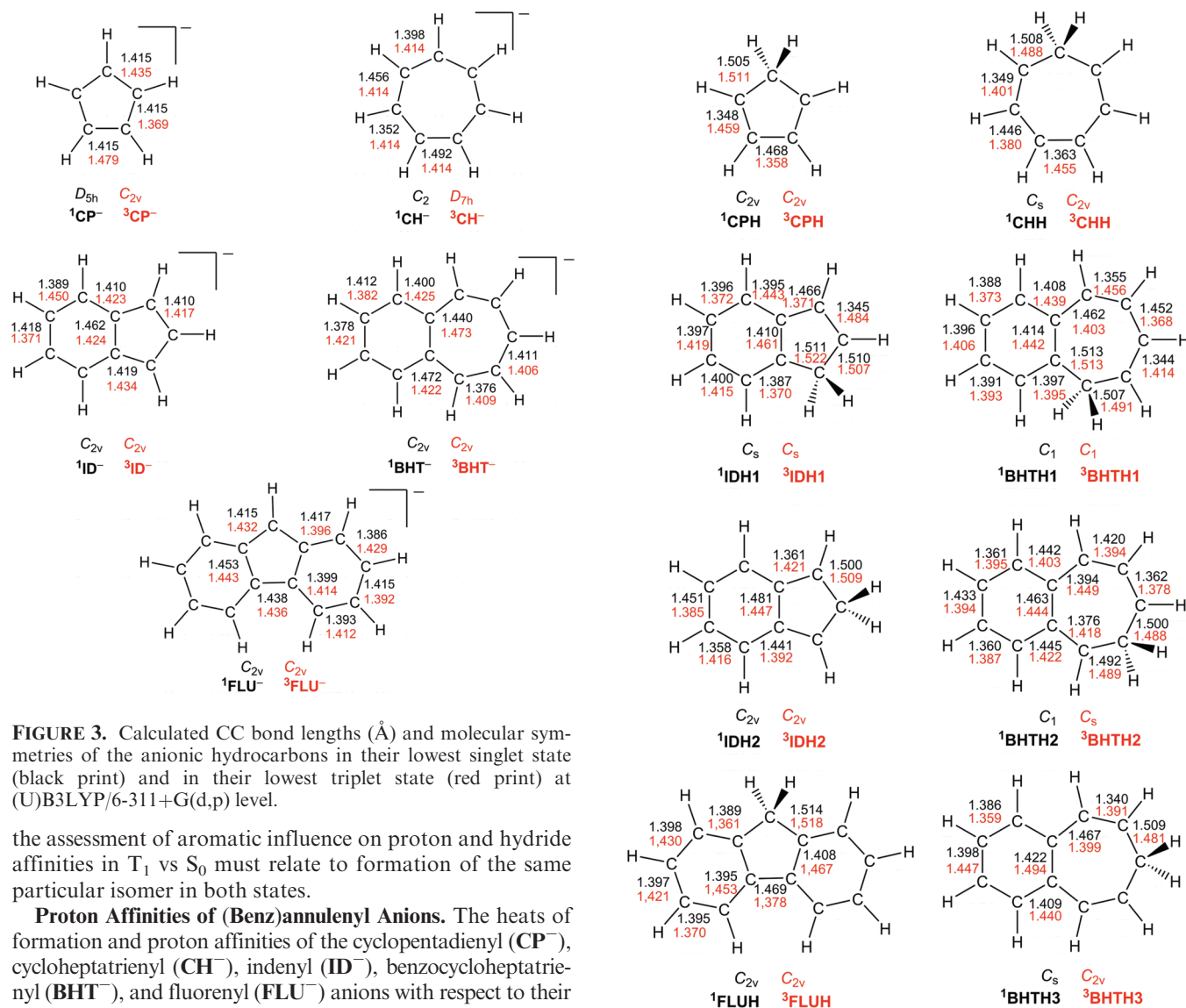(36) Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70.

FIGURE 3. Calculated CC bond lengths (Å) and molecular symmetries of the anionic hydrocarbons in their lowest singlet state (black print) and in their lowest triplet state (red print) at (U)B3LYP/6-311+G(d,p) level.

the assessment of aromatic influence on proton and hydride affinities in T_1 vs S_0 must relate to formation of the same particular isomer in both states.

Proton Affinities of (Benz)annulenyl Anions. The heats of formation and proton affinities of the cyclopentadienyl (**CP⁻**), cycloheptatrienyl (**CH⁻**), indenyl (**ID⁻**), benzocycloheptatrienyl (**BHT⁻**), and fluorenyl (**FLU⁻**) anions with respect to their different protonated isomers were calculated in the S_0 and T_1 states. For **FLU⁻**, only the proton affinity with respect to 9*H*-fluorene was calculated. The calculated CC bond lengths, and molecular symmetries of the anionic and the neutral compounds, are presented in Figures 3 and 4, respectively. The structures of **¹CP⁻**, **¹CH⁻**, **³CH⁻**, **¹ID⁻**, and **¹FLU⁻** have previously been calculated at B3LYP and MP2 levels,[37,38] and the calculated structures in Figure 3 agree with these earlier studies. All the calculated anionic structures, except **¹CH⁻**, are planar, and in order to estimate the degree of aromaticity based on the geometry, the HOMA values were calculated (Table 1).

The HOMA(total) values for the compounds in their A-character states are larger than 0.8, and for the compounds in their AA-character states the values are smaller than 0.8. It is noteworthy that the HOMA(total) values of the benzannulated AA-character compounds increase as the system size increases, while the values for the A-character systems are constant. This indicates that the distinction between A- and AA-character states becomes gradually less apparent with

FIGURE 4. Calculated CC bond lengths (Å) and molecular symmetries of the neutral hydrocarbons in their singlet ground states (black print) and in their lowest triplet states (red print) at (U)B3LYP/6-311+G(d,p) level.

increasing system size which agrees with findings from earlier studies.[39,40] Still, the selection of (benz)annulenyl anions and cations examined herein are suitable for probing the dependence of T_1 state proton affinities on the aromaticity/antiaromaticity of this state.

The results of the calculated heats of formation and HOMA(6) values of the neutral compounds are listed in Table 2, and calculated heats of formation and proton affinities (PA's) of the anionic compounds are shown in Table 3. In Table 3, we have also tabulated the difference in PA of a particular anion in its state of AA-character relative to that in its state of A-character (ΔPA(AA−A)). The values in parentheses are experimentally determined

(37) Jian, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075.
(38) Trietel, N.; Shenhar, R.; Aprahamian, I.; Sheradsky, T.; Rabinovitz, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1113.

(39) Wannare, C. S.; Moran, D.; Allinger, N. L.; Hess, B. A., Jr.; Schaad, L. J.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 2983.
(40) Miao, S.; Schleyer, P. v. R.; Wu, J. I.; Hardcastle, K. I.; Bunz, U. H. F. *Org. Lett.* **2007**, *9*, 1073.

TABLE 1. HOMA Values at (U)B3LYP/6-311+G(d,p) Level for the Anions of Figure 3

compd	character	HOMA-(total)[a]	HOMA(5)[a]	HOMA(6)[a]	HOMA(7)[a]
1CP−	A	0.812			
3CP−	AA	0.308			
1CH−	AA	0.159			
3CH−	A	0.826			
1ID−	A	0.864	0.569	0.684	
3ID−	AA	0.532	0.628	0.496	
1BHT−	AA	0.602		0.818	0.331
3BHT−	A	0.819		0.522	0.593
1FLU−	A	0.853	0.356	0.712	
3FLU−	AA	0.758	0.370	0.658	

[a] HOMA(total) refers to the value calculated for the peripheral CC bonds, HOMA(5), HOMA(6) and HOMA(7) refer to the values of the five-, six-, and seven-membered rings of the benzannulated compounds.

TABLE 2. Calculated Heats of Formation at 298 K (ΔH_f) and HOMA Values of the Six-Membered Rings HOMA(6) of the Neutral Hydrocarbons (Numbers in Parentheses are Experimentally Determined Values)

	S_0 state			T_1 state		
compd	ΔH_f[a] (kJ/mol)	HOMA(6)[b]	compd	ΔH_f[a] (kJ/mol)	HOMA(6)[b]	
1CPH	128 (133)[43]		**3CPH**	379		
1CHH	175 (187)[44]		**3CHH**	366		
1IDH1	148 (161)[45]	0.965	**3IDH1**	433	0.544	
1IDH2	233	0.139	**3IDH2**	367	0.781	
1BHTH1	197	0.947	**3BHTH1**	427	0.736	
1BHTH2	274	0.342	**3BHTH2**	400	0.802	
1BHTH3	208	0.908	**3BHTH3**	456	0.063	
1FLUH	168 (175)[46]	0.971	**3FLUH**	472	0.383	

[a] G3(MP2)//(U)B3LYP/6-311+G(d,p), 298 K; numbers in parentheses are experimentally determined values. [b] (U)B3LYP/6-311+G(d,p).

heats of formation and PA's, and these values are in reasonable agreement with the calculated ones. All the anionic compounds are singlet ground state molecules, but the ΔE_{ST} are significantly larger for the S_0 A-character compounds than for the S_0 AA-character compounds (see Table S1 of the Supporting Information), reflecting the low HOMO−LUMO gaps of $4n\pi$-electron compounds.[41,42]

Before an analysis of the proton affinities of the anions in T_1 vs those in S_0 is given it should be remarked that the average proton affinity corresponding to the eight protonation reactions in T_1 (1429 kJ/mol) is lower than the average proton affinity corresponding to these eight reactions in S_0 (1484 kJ/mol). The lower proton affinities of the anions in their T_1 states than in their S_0 states should stem from the fact that the T_1 state is an electronically excited state, in which an orbital with more antibonding character is occupied. A proton added to an anion in this state will therefore in general be less strongly bound than when added to an anion in its electronic ground state.

With regard to the proton affinities in S_0, the anions which have S_0 states of A-character have lower average PA (1447 kJ/mol) than the anions which have S_0 states of AA-character (1521 kJ/mol), a result of aromatic stabilization in the ground state A-character anions. In support of our hypothesis (Figure 2), the same relationship between the magnitudes of the average PA's is now found in the T_1 states because the

(41) Dietz, F.; Tyutyulkov, N.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 157.
(42) Dietz, F.; Rabinovitz, M.; Tadjer, A.; Tyutyulkov, N. *J. Chem. Soc., Perkin Trans. 2* **1995**, 735.

anions with T_1 states of A-character have significantly lower average PA (1365 kJ/mol) than those with T_1 states of AA-character (1493 kJ/mol). In further support of our hypothesis, the results of the calculated PA's show that all except two of the protonation reactions yield higher PA's in their AA-character state than in their A-character state with ΔPA-(AA − A) values ranging from 11 to 193 kJ/mol (Table 3). More specifically, five of the eight investigated protonation reactions compared in the S_0 and T_1 states have $\Delta PA(AA − A)$ values in the range 81−193 kJ/mol, that of **CP−** has a small value, whereas one protonation reaction of **ID−** and the protonation at the 9-position of **FLU−** give values of opposite sign to that expected from our hypothesis. Another aspect to note is that for three of the four protonation reactions of anions with S_0 states of AA-character, the $\Delta PA(AA − A)$ values are particularly large (175−193 kJ/mol).

With regard to both the small and the negative $\Delta PA(AA − A)$ values these can in part be explained by the fact that the PA's of the T_1 states are generally lower than those of the S_0 states, as observed above. A second contributing factor to the negative $\Delta PA(AA − A)$ values is the ability of the larger anions to avoid the destabilizing antiaromaticity of the AA-character state. For **ID−**, and similarly for **FLU−**, the finding of the negative $\Delta PA(AA − A)$ can be rationalized by comparing the geometries and HOMA values of **1ID−** and **3ID−** with those of **1IDH1** and **3IDH1** (Figures 3 and 4 and Table 1) so as to obtain estimates of the most important resonance structure contributions. With regard to **1ID−** it is best described by a 10π-electron aromatic ring involving the peripheral CC bonds, supported by the high HOMA(total) value of 0.864 and a maximal bond length variation of merely 0.030 Å. On the other hand, in the T_1 state **3ID−** has a large maximal bond length variation in the peripheral bonds of 0.079 Å. Yet, the variation within the five-membered ring is only 0.017 Å, and the average CC bond length of this ring (1.425 Å) is just slightly longer than the CC bond length of the D_{5h} symmetric cyclopentadienyl anion in S_0 (1.415 Å). The HOMA(5) and HOMA(6) values further indicate that the five-membered ring is the most aromatic ring (Table 1). Based on the geometry, anion **3ID−** should therefore to a substantial degree be represented by a resonance structure with a 6π-electron closed-shell aromatic five-membered ring (Figure 5), a conclusion which is also supported by the spin density distribution (see Figures S1−S3 and Tables S4−S6 in the Supporting Information). Consequently, **ID−** is influenced by closed-shell $4n+2$ π-electron aromaticity both in S_0 and T_1.

As it is the protonation of **ID−** leading to isomer **IDH1** which has a negative $\Delta PA(AA − A)$, one needs to regard also the geometries of this neutral hydrocarbon in the S_0 and T_1 states. The CC bond lengths together with HOMA(6) values of 0.965 and 0.544, respectively (Table 2), suggest that **1IDH1** and **3IDH1** are represented by the resonance structures shown in Figure 5. Consequently, protonation of **ID−** in its S_0 A-character state to give **1IDH1** leads from one aromatic compound to another aromatic compound. However, in the T_1 state, **3ID−** is stabilized by some 6π-electron closed-shell aromaticity, but the aromaticity is clearly lost upon protonation to yield **3IDH1**. As a result, the PA of **ID−** will be low in the T_1 state which is of AA-character, and the $\Delta PA(AA − A)$ becomes negative. Indeed, this reveals the limitations of our hypothesis as polycyclic anionic compounds can adjust their

TABLE 3. Calculated Heats of Formation (ΔH_f), Proton Affinities (PA), and Differences in Proton Affinities between AA- and A-Character States ($\Delta PA(AA - A)$)

|		S$_0$ state				T$_1$ state			
compd[a]	character	ΔH_f^b (kJ/mol)	PA (kJ/mol)	compd[a]	character	ΔH_f^b (kJ/mol)	PA (kJ/mol)	$\Delta PA(AA - A)$ (kJ/mol)
^{1}CP$^-$	A	75	1477 (1481)[47]	**^{3}CP$^-$**	AA	337	1488	11
^{1}CH$^-$	AA	224	1579 (1570)[47]	**^{3}CH$^-$**	A	231	1395	184
^{1}ID$^-$ (1)	A	84	1466 (1472)[48]	**^{3}ID$^-$ (1)**	AA	333	1430	−36
^{1}ID$^-$ (2)	A	84	1381	**^{3}ID$^-$ (2)**	AA	333	1496	115
^{1}BHT$^-$ (1)	AA	198	1531	**^{3}BHT$^-$ (1)**	A	253	1356	175
^{1}BHT$^-$ (2)	AA	198	1454	**^{3}BHT$^-$ (2)**	A	253	1383	81
^{1}BHT$^-$ (3)	AA	198	1520	**^{3}BHT$^-$ (3)**	A	253	1327	193
^{1}FLU$^-$	A	103	1466 (1466)[48]	**^{3}FLU$^-$**	AA	313	1372	−94

[a]Numbers in parentheses indicate which isomer of the neutral hydrocarbon is formed upon protonation. [b]G3(MP2)//(U)B3LYP/6-311+G(d,p), 298 K; numbers in parentheses are experimentally determined values.
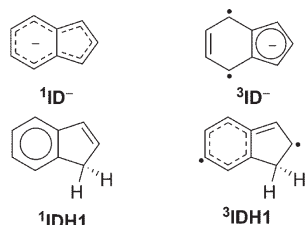
FIGURE 5. Important resonance structure representations of **^{1}ID$^-$**, **^{3}ID$^-$**, **^{1}IDH1**, and **^{3}IDH1** based on the calculated bond lengths, HOMA values, and spin densities.

geometries in both states so as to adopt high aromaticity in one or several of their rings, depending on what is optimal for each particular state.

One should also note the differences between the PA in the T$_1$ and S$_0$ states for protonation at the various sites of the anions (Tables 2 and 3). For example, protonation of **ID$^-$** in S$_0$ will preferentially give **IDH1** because this **IDH*n*** isomer (n = 1 or 2) has lowest ΔH_f and the protonation reaction also corresponds to the highest PA. In the T$_1$ state, on the other hand, the **IDH2** isomer has lowest ΔH_f and its formation goes with the highest PA. Whereas **IDH1** based on HOMA-(6) is more aromatic than **IDH2** in the S$_0$ state, the opposite applies for the two isomers in the T$_1$ state (Table 2). To significant extent, **^{3}IDH2** is well described by a resonance structure composed of a closed-shell singlet aromatic benzene sextet, as indicated by a HOMA(6) value in T$_1$ of 0.781, and due to its aromatic influence, the PA for going to this species should be high. The **^{3}IDH1** is, as concluded above, not represented by an aromatic resonance structure (Figure 5). Similar differences are found for the three possible protonation reactions of **BHT$^-$** in S$_0$ vs T$_1$. Indeed, these variations point to potential synthetic applications as protonation under photochemical conditions could lead to a different hydrocarbon isomer as compared to when the protonation is carried out in the ground state.

Hydride Affinities of (Benz)annulenyl Cations. With regard to the hydride affinities, it should first be remarked that several aspects resemble those of the PAs, and therefore, this
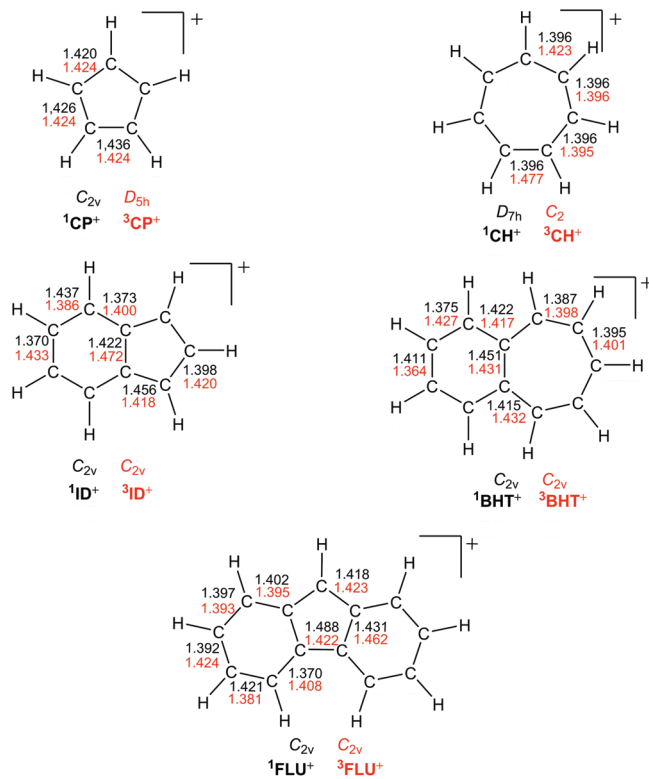
FIGURE 6. Calculated CC bond lengths (Å) and molecular symmetries of the cationic compounds in their lowest singlet states (black print) and their lowest triplet states (red print) at (U)B3LYP/6-311+G(d,p) level.

section is more brief. The calculated ΔH_f, hydride affinities (HA), and differences in hydride affinities between AA- and A-character states ($\Delta HA(AA - A)$) are tabulated in Table 4, and the HOMA values of the cationic compounds are presented in Table 5. The singlet−triplet energy gaps (ΔE_{ST}) are given in Table S1 in the Supporting Information. The annulenyl cations which are of AA-character in their S$_0$ states may have multireference character, and to check for this possibility the T$_1$ diagnostics[33] of the CCSD/6-31G(d) wave functions were analyzed. In one case, **^{1}CP$^+$**, we found a T$_1$ diagnostics value above the threshold for multireference character of 0.02 (see Table S2 in the Supporting Information). For this cation, a G3(MP2)//(U)B3LYP/6-311+G(d,p) composite calculation

(43) Furuyama, S.; Golden, D. M.; Benson, S. W. *J. Chem. Thermodyn.* **1970**, *2*, 161.

(44) Roth, W. R.; Bohm, M.; Lenhartz, H.-W.; Vogel, E. *Angew. Chem.* **1983**, *95*, 1011.

(45) Roux, M. V.; Temprado, M.; Chickos, J. S.; Nagano, Y. *J. Phys. Chem. Ref. Data* **2008**, *37*, 1855.

(46) Rakus, K.; Verevkin, S. P.; Schätzer, J.; Beskhaus, H.-D; Rüchardt, C. *Chem. Ber.* **1994**, *127*, 1095.

TABLE 4. Calculated Heats of Formation (ΔH_f), Hydride Affinities (HA), and Differences in Hydride Affinities between AA- and A-Character States ($\Delta HA(AA - A)$)

	lowest singlet state				lowest triplet state			
compd[a]	character	ΔH_f (kJ/mol) [b]	HA (kJ/mol)	compd[a]	character	ΔH_f (kJ/mol) [b]	HA (kJ/mol)	$\Delta HA(AA - A)$ (kJ/mol)
$^1CP^+$	AA	1102	1117 (1118)[c]	$^3CP^+$	A	1076	843	274
$^1CH^+$	A	876	846	$^3CH^+$	AA	1206	985	139
$^1ID^+$ (1)	AA	1002	999	$^3ID^+$ (1)	A	1058	770	229
$^1ID^+$ (2)	AA	1002	913	$^3ID^+$ (2)	A	1058	837	76
$^1BHT^+$ (1)	A	900	849	$^3BHT^+$ (1)	AA	1125	843	−6
$^1BHT^+$ (2)	A	900	771	$^3BHT^+$ (2)	AA	1125	870	99
$^1BHT^+$ (3)	A	900	838	$^3BHT^+$ (3)	AA	1125	814	−24
$^1FLU^+$	AA	979	956	$^3FLU^+$	A	1037	710	246

[a]Numbers in parentheses indicate which isomer of the neutral hydrocarbon is formed in the reaction. [b]G3(MP2)//(U)B3LYP/6-311+G(d,p), 298 K. [c]HA obtained with a modified G3(MP2)//(U)B3LYP/6-311+G(d,p) composite scheme which included a (U)BD(T)/6-31G(d) calculation instead of a (U)QCISD(T)/6-31G(d) calculation.

TABLE 5. HOMA Values at the (U)B3LYP/6-311+G(d,p) Level of the Cations of Figure 6

compd	character	HOMA-(total)[a]	HOMA(5)[a]	HOMA(6)[a]	HOMA(7)[a]
$^1CP^+$	AA	0.627			
$^3CP^+$	A	0.666			
$^1CH^+$	A	0.984			
$^3CH^+$	AA	0.610			
$^1ID^+$	AA	0.570	0.453	0.711	
$^3ID^+$	A	0.823	0.438	0.597	
$^1BHT^+$	A	0.889		0.695	0.797
$^3BHT^+$	AA	0.773		0.693	0.770
$^1FLU^+$	AA	0.698	0.201	0.847	
$^3FLU^+$	A	0.856	0.250	0.687	

[a]HOMA(total) refers to the value calculated for the peripheral CC bonds; HOMA(5), HOMA(6), and HOMA(7) refer to the values in the five-, six-, and seven-membered rings of the benzannulated compounds.

FIGURE 7. Important resonance structure of $^3BHT^+$.

was run with the UQCISD(T)/6-31G(d) calculation replaced by a UBD(T)/6-31G(d) calculation giving a HA of 1118 kJ/mol instead of 1117 kJ/mol.

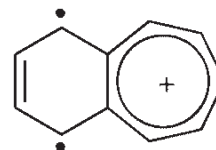All the calculated structures except $^1BHT^+$ and $^3BHT^+$, which to our knowledge have not been reported elsewhere, are in agreement with the results of earlier studies.[37] The cations have singlet ground states apart from the cyclopentadienyl cation, $^3CP^+$, which has a triplet multiplicity ground state in line with the experimental findings by Saunders et al.[49] Similar as for the anionic compounds, the HOMA-(total) values are higher than 0.8 for A-character states except for $^3CP^+$ and lower than 0.8 for AA-character states. The lower HOMA(total) value of $^3CP^+$ (0.666) is explained by the fact that this T_1 aromatic species has slightly longer CC bond lengths (1.424 Å) than is the HOMA reference CC bond length of an aromatic compound (R_{opt} = 1.388 Å). This exemplifies that HOMA should be used with care in the analysis of triplet state aromaticity.

Similar as for the proton affinities, the hydride affinities of the cations are in general higher in the S_0 state than in the T_1 state (average HA are 911 and 834 kJ/mol for the S_0 and T_1 states, respectively), a fact that needs to be taken into consideration when regarding the $\Delta HA(AA - A)$ values, in particular when the AA-character state is a T_1 state. The lower average HA in T_1 than in S_0 should stem from weakened bonding character in T_1 as an electronically excited state.

In the S_0 state the cations of A-character have lower average HA than the ones of AA-character (826 vs 996 kJ/mol, respectively), and the same relationship is found in the T_1 state because the HA of the A-character compounds in T_1 are on average lower (790 kJ/mol) than those of the AA-character compounds (879 kJ/mol).

With regard to the $\Delta HA(AA - A)$ values only two of the eight protonation reactions considered have negative values, these being the protonations of BHT^+ leading to **BHT1** and **BHT3**, respectively. However, similar as for $^3ID^-$ it can be concluded that $^3BHT^+$ to a significant extent is represented by a resonance structure with a closed-shell aromatic seven-membered ring (Figure 7), and that $^3BHTH1$ and $^3BHTH3$ are not favorable T_1 state structures while $^3BHTH2$ is. For the other cations, the $\Delta HA(AA - A)$ range 76 − 274 kJ/mol, with the highest values for cations for which the S_0 state is of AA-character and the T_1 state is of A-character. This is similar to the trend observed in the $\Delta PA(AA - A)$ and reflects the fact that T_1 state compounds possess lower average HA's for both the A- and AA-character systems as well as the fact that larger polycyclic cations are able to redistribute their electron density in the unfavorable AA-character state so as to avoid antiaromaticity. This underlines the scope of our hypothesis that aromatic stabilization indeed influences HA, but that the possibility to generate a (local) closed-shell A-character loop in cations which are in their open-shell AA-character states limits the principle.

Finally, it could be argued that **IDH1**, **BHTH3**, and **FLUH** can be used as hydride transfer reagents in their T_1 states, particularly as these three cations have significantly lower HA than ^1CHH which has a known function as a hydride transfer reagent in S_0.[50] Although such applications are speculative it would serve as a direct application of excited state aromaticity.

(47) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

(48) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463.

(49) Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M., Jr.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017.

(50) Kimura, T.; Takahashi, T.; Nishiura, M.; Yamamura, K. *Org. Lett.* **2006**, *8*, 3137.

Conclusions

Baird's rule on $\pi\pi^*$ triplet state (T_1) aromaticity, i.e., that $4n\pi$-electron annulenes display aromatic character and $(4n+2)\pi$-electron annulenes display antiaromatic character, can be used to rationalize the acid−base chemistry involving annulenyl anions and cations in their T_1 states, in similar way as Hückel's rule can be used to explain acid−base chemistry involving annulenyl anions and cations in S_0. We put forward the hypothesis that annulenyl anions/cations with high proton/hydride affinity in S_0 will have low proton/hydride affinity in T_1, and vice versa. We have validated the hypothesis through G3(MP2) calculations, and found that it is in general correct. However, the effects are greatest in monocyclic annulenyl species rather than in the analogous benzannulated species where the possibility for formation of closed-shell aromatic sextets is possible. The reversal of the electron counting rules for aromaticity, and as a result the acid−base properties of cyclic π-conjugated hydrocarbons, in the lowest triplet state could potentially be exploited in synthetic organic photochemistry, as well as in other areas, and its scopes and limitations deserve further investigations.

Supporting Information Available: Table of the energy differences between lowest singlet and lowest triplet state (ΔE_{ST}) for compounds presented in Figures 3 and 6, table of the calculated electronic energies of the AA-character singlet state compounds $^1CP^+$, $^1CH^-$, $^1ID^+$, $^1-$, and $^1FLU^+$, respectively, and their respective T_1-diagnostics of the (U)CCSD/6-31G(d) wave functions. Table of calculated heats of formation at 298 K (ΔH_f) for $^1CP^+$ and ^1CPH and hydride affinity for $^1CP^+$. SCF spin density isosurfaces and Mulliken spin densities of $^3ID^-$, ^3IDH, and $^3BHT^+$. Cartesian coordinates, G3(MP2)//(U)B3LYP/6-311+G(d,p) total energies, and (U)B3LYP/6-311+G(d,p) electronic energies of the compounds presented in Figures 3, 4, and 6. This material is available free of charge via the Internet at http://pubs.acs.org.