Cycloproparenyl anions: From models to real systems*

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Abstract: An overview of our recent work on cycloproparenyl anions is given. Preparation, the electronic structure, and the properties of the progenitor of the series, cyclopropabenzenyl anion, are discussed. It is shown that the cyclopropabenzenyl anion is by ca. 145 kJ mol^{-1} more stable than the parent cyclopropenyl anion according to results of the MP2/6-31+G(d) calculations. This finding was attributed to a delicate balance of two opposing effects: (a) propensity of the aromatic ring to alleviate unfavorable 4π electron interaction within the three-membered ring by the anionic resonance effect and (b) a pyramidalization of the anionic center, which tends to maximize the s-character of the lone pair. We have also shown that stability of the cyclopropabenzenyl anion could be considerably enhanced by substitution of the aromatic ring with fluorine and cyano groups, as well as by a linear extension of the aromatic backbone. Finally, the impact of the fusion of additional cyclopropenyl ring to the benzene moiety to acidity of the benzylic position in cyclopropabenzene is discussed.

Keywords: Cycloproparenes; gas-phase acidity; solvent effects; substituent effects; strain.

INTRODUCTION

Fusion of a cyclopropene ring to an aromatic moiety generates a family of experimentally and theoretically interesting compounds known as cycloproparenes [1]. Their chemistry is characterized by an interplay of two antagonistic effects: aromaticity, which is generally known to stabilize compounds, and angular strain, which destabilizes them. Their juxtaposition leads to some new and sometimes unexpected novel features, leading to a plethora of fascinating compounds [1]. It is interesting to mention for historical reasons that the parent member of these compounds—cyclopropabenzene—was first reported by Perkin in his seminal paper entitled "Synthetical formation of closed-chains in the aromatic series. Part I. On some derivatives of hydrindonaphthene and tetrahydronaphthalene" more than a century ago [2].

In the same paper, Perkin described synthesis of less strained representatives of cycloalkarenes—indene and tetralin—while synthesis of more strained representatives—cyclobutabenzene and cyclopropabenzene—was achieved more than 60 years later, apparently because of their lesser stability due to the angular strain. Thus, cyclobutabenzene was prepared by Cava and Napier in 1958 [3], and the first synthesis of unsubstituted cyclopropabenzene was published by Vogel and coworkers [4]. These discoveries initiated tremendous interest from both experimental and theoretical chemists in their physicochemical properties [1]. Most of the theoretical work in this area has been focused on the struc-

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tural perturbations imposed upon the aromatic ring as a result of annelation by the highly strained three-membered ring [1,5–7] and changes in their chemical reactivity. Our contributions to this topic are summarized in ref. [5].

In the present paper, we shall focus on acid/base chemistry of selected classes of cyclopropsarenes with emphasis on analysis of intrinsic properties of their anions derived by deprotonation within the small ring. This is of considerable importance from a synthetic point of view, since some of these carbanions are involved in a variety of synthetically important processes, to mention only recently developed syntheses of alkylidenecycloproparenes, some of which exhibit exceptional fluorescent characteristics [8]. Surprisingly, theoretical studies of the respective carbanions are scarce and limited mostly to the cyclopropabenzenyl anion (**1**) [9,10]. Moreover, most of the previous calculations [9] were carried out at a low level of theory, which was not suitable for studying carbanions derived from strained molecules by the current standards.

In collaboration with S. R. Kass's group, we have recently reported on the first preparation of the cyclopropabenzenyl anion in the gas phase and explored its electronic structure using MP2/6-31+G(d) method [10]. Here, we shall give a brief summary of the most important results of this study and then continue by considering effect of solvation on stability of **1** and compare it with that of the closely related benzyl anion (**2**).

Then, we shall switch to some model molecules and explore possibilities of amplifying stability of the parent cyclopropabenzenyl anion ion by putting fluorine or cyano substituents at the aromatic ring or by extension of the aromatic framework.

Finally, we shall briefly discuss the effect of strain on stability of the cyclopropabenzenyl anion imposed by attachment of an additional three-membered ring to the benzene moiety.

We will refrain from presenting any experimental and computational details; they can be found in the references [10,11].

CYCLOPROPABENZENYL ANION

Gas-phase acidity of cyclopropabenzene

Deprotonation of the cyclopropabenzene (**1H**) can take place, in principle, at three different sites—two of them within the aromatic ring and the third one at the benzylic position belonging to the small ring. All three modes of deprotonation have been observed in solution and extensively exploited in preparative chemistry. According to the MP2/6-31+G(d) calculations, the most acidic site is associated with the small ring, as intuitively expected [10].
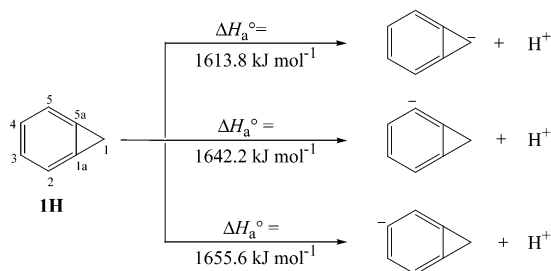

The corresponding anion is also the most interesting one from the theoretical point of view. It is an 8π electron species and can be viewed as a combination of an aromatic (i.e., benzene moiety) and an antiaromatic subunit, the latter being highly strained cyclopropenyl anion moiety. This raises the question "Do the aromatic or antiaromatic component prevail, or do they 'cancel' each other, resulting in a nonaromatic, but highly strained species?"

Early experimental work, mostly from Eaborn's group [12], provided firm evidence that a cyclo-propabenzenyl anion is a remarkably stable species in solution in comparison to the parent cyclopropenyl anion, which escaped all attempts of preparation so far [13]. Moreover, by comparing the relative rates of base-induced decomposition of 7-trimethylsilylcyclopropabenzene and trimethylsilylbenzene, Eaborn and coworkers found that cyclopropabenzene is by 5 pK_a units more acidic than toluene. This, in turn, indicates that cyclopropabenzenyl anion should be somewhat more stable than the benzyl anion. They also corroborated their conclusion by the Hartree–Fock STO-3G calculations [9c] of pK_a of the parent molecule and toluene (**2**), which predicted that cyclopropabenzene was by 8 pK_a units more acidic than toluene. More recently, the existence of **1** in solution was also confirmed by spectroscopic investigations [14].

We have prepared the anion **1** in the gas phase by deprotonating cyclopropabenzene with hydroxyl ion, and its basicity was measured by variable temperature-flowing afterglow technique [10]. Evidence that the generated carbanion has a cyclopropabenzenyl structure has been obtained from the observations that (i) the ion undergoes 1 hydrogen/deuterium exchange upon reaction with deuterium oxide; (ii) 7-deuteriocyclopropabenzene (**1D**) reacts with hydroxide to give both (**1D** - H) and (**1D** - D) ions; and (iii) that the deuterium label in the former ion can be washed out by reacting it with water (i.e., 1 H/D exchange occurs) [10].

By employing bracketing technique using a set of standard acids and bases, we found that acidity of cyclopropabenzene lies between that of fluorobenzene and piperidine, resulting in a ΔH_a value of 1615 ± 13 kJ mol^{-1}. The measured acidity was in a very good agreement with the calculated value of 1613.8 kJ mol^{-1} obtained employing the MP2/6-31+G(d) method. Within the same study, we have also shown that, according to the MP2/6-31+G(d) calculations, cyclopropabenzenyl anion was by 144.3 kJ mol^{-1} more stable than the cyclopropenyl anion (**3**) [10].

$$\text{(1)}$$

3 **1H** **3H** **1**
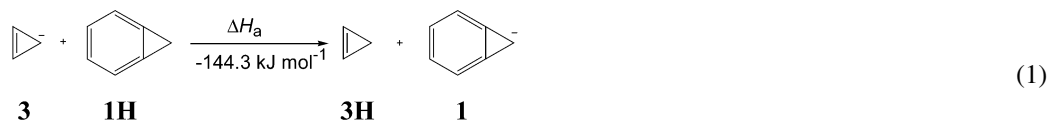
Based on analysis of calculated molecular and electronic structure of the cyclopropabenzenyl anion (Fig. 1), its remarkable stability relative to the unsubstituted cyclopropenyl carbanion **3**, was accounted for by a balance of two counter effects: (i) propensity of the aromatic ring to alleviate unfavorable 4π electron interaction within the three-membered ring by the anionic resonance effect and (ii) by a pyramidalization of the anionic center, which tends to maximize the s-character of the lone pair.
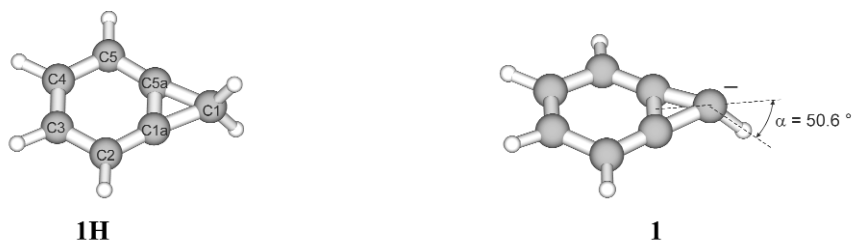
1H	**1**

Bond lengths/pm	Bond angles/°	Bond lengths/pm	Bond angles/°
C1–C1a: 150.7	C1–C5a–C1a: 63.3	C1–C1a: 146.7	C1–C5a–C1a: 61.7
C1a–C2: 138.5	C1a–C2–C3: 113.0	C1a–C2: 137.9	C1a–C2–C3: 114.5
C1a–C5a: 135.4	C1a–C5a–C5: 124.5	C1a–C5a: 139.0	C1a–C5a–C5: 123.5
C2–C3: 141.1	C2–C3–C4: 122.5	C2–C3: 144.6	C2–C3–C4: 121.8
C3–C4: 141.0		C3–C4: 138.9	

Fig. 1 MP2/6-31+G(d) optimized structures for cyclopropabenzene (**1H**) and cylopropabenzenyl anion (**1**) [10]. Numbering of atoms is given in structure **1H**.

The second important finding of this study is given by a reversal in the relative basicities of the cyclopropabenzenyl anions and benzyl anion upon going from the liquid phase to the gas phase. This is not surprising in view of difference in the electronic structure of these two anions, in particular due to the s-character of the lone pair at the deprotonation site in the anion **1**. In order to gain more quantitative insight into the effect of solvation on the relative acidities of these two molecules, we have calculated their pK_a values in water. It should be stressed that the calculated pK_a values cannot be directly compared with the experimentally available pK_a values, since they refer to mixed solvents systems (H$_2$O/DMSO and H$_2$O/MeOH for **1H** and **2H**, respectively). Since we are interested in relative changes in acidities, any error introduced by this difference will cancel out.

Effect of solvation on relative acidities of cyclopropabenzene and toluene

For an acid species AH, the pK_a value is defined as minus logarithm of the dissociation constant of the reaction.

$$AH_{aq} \rightleftharpoons A^-{}_{aq} + H^+{}_{aq} \tag{2}$$

It is given by the well-known thermodynamic relation

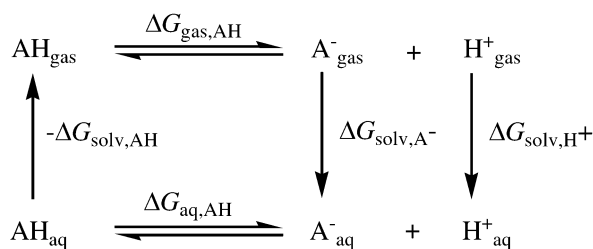$$pK_a = \Delta G_{aq,AH}/2.303RT \tag{3}$$

The Gibbs free energy variation of deprotonation reaction in aqueous solution is calculated by adding a solvation contribution to the gas-phase value as follows:

$$\Delta G_{aq,AH} = \Delta G_{gas,AH} + \Delta\Delta G_{solv,AH} \tag{4}$$

$$\Delta G_{gas,AH} = G_{gas,A^-} + G_{gas,H^+} - G_{gas,AH} \tag{5}$$

$$\Delta\Delta G_{solv,AH} = \Delta G_{solv,A^-} + \Delta G_{solv,H^+} - \Delta G_{solv,AH} \tag{6}$$

according to the thermodynamic cycle reported in Scheme 1.

Scheme 1 Thermodynamic cycle used for calculation of solvation energies.

where $\Delta G_{gas,AH}$ and $\Delta G_{aq,AH}$ are the free energies for the proton abstraction in the gas phase and in water, respectively, and $\Delta G_{solv,AH}$, $\Delta G_{solv,A^-}$, and $\Delta G_{solv,H^+}$ correspond to the energy change associated with the transfer of AH, A^-, and H^+ from the gas phase to the water.

For G_{gas,H^+}, we used a value of -26.3 kJ mol^{-1} [15,16] and the value for $\Delta G_{solv,H^+}$ -1107.1 kJ mol^{-1}, was derived from experimental thermodynamic cycle for acetic acid [17]. It should be noted that this value is slightly lower than the earlier estimate of -1104.5 kJ mol^{-1} obtained by Tissandier and coworkers [18] using the cluster-pair-base approximation. Free energies of solvation are calculated using Barone and Cossi's [19] implementation of the polarizible conductor model, which is based on the polarized continuum model (PCM) of Tomasi and coworkers [20] in conjunction with the dielectric constant of 78.39 corresponding to water at 298.15 K. In the continuum model calculations on neutral systems, the isolated molecule optimal geometries were used, while for anions, calculations were performed both at the gaseous phase geometries (hereafter denoted as model M1), and by reoptimizing gas-phase spatial structure in aqueous solution, taking into account the influence of the solvent (hereafter denoted as model M2). The gas free energies of the considered anions and their conjugate acids were calculated using the Peterson's CBS-QB3 method [21]. Finally, as the calculation of $\Delta G_{gas,AH}$ uses a reference state of 101325 Pa and the ΔG_{solv} and ΔG_{aq} use 1 M reference state, the $\Delta G_{gas,AH}$ was converted to 1 M state by using eq. 7

$$\Delta G_{gas,AH}(1\ M) = \Delta G_{gas,AH}(101325\ Pa) + RT\ln(24.46) \tag{7}$$

Taking all these steps into account, the pK_a values are calculated using eq. 8

$$pK_a = \{G_{gas,A^-} - G_{gas,AH} + \Delta G_{solv,A^-} - \Delta G_{solv,AH} - 269.0\}/1.3644 \tag{8}$$

The results are summarized in Table 1, while the superimposition of geometries of the anions optimized in the gas phase and in a bulk of water are shown in Fig. 2.

Table 1 Effect of solvation on acidities of **1H** and **2H**.

	1H		2H	
	M1[a]	M2[b]	M1[a]	M2[b]
ΔG_{gas}[c]/kJ mol^{-1}	1582.8	1582.8	1578.2	1578.2 (1568.6)[d]
$\Delta G_{solv,A^-}$/kJ mol^{-1}	-230.1	-240.2	-207.9	-208.4
$\Delta G_{solv,AH}$/kJ mol^{-1}	-12.6	-12.6	-6.3	-6.3
pK_a	46.6	44.8	48.6	48.5
pK_a (exp.)	36 [12]		41 [23]	

[a]$\Delta G_{solv,A^-}$ and $\Delta G_{solv,AH}$ were calculated using CPCM/HF/6-31+G(d)//B3LYP/CBSB7 level of theory.
[b]$\Delta G_{solv,A^-}$ was calculated using CPCM/HF/6-31+G(d) level of theory for geometry optimized in water.
[c]Calculated using CBS-QB3 approach.
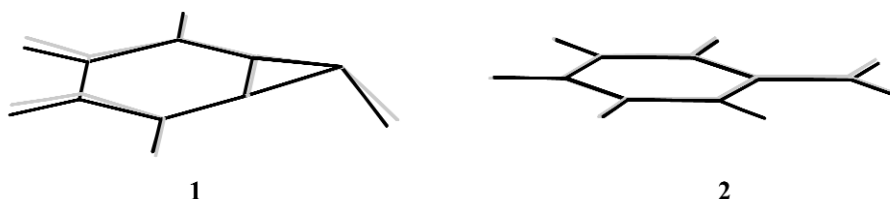[d]Experimental value, see ref. [22].

Fig. 2 Superimposition of gas-phase and solution-phase geometries of **1** and **2** calculated using CPCM/HF/6-31+G(d)//B3LYP/CBSB7 and CPCM/HF/6-31+G(d) methods. The gas-phase optimized geometries are shown in gray and the geometries optimized in water in black.

It appears that solvation free energies for both neutral molecules are small and close to each other. On the other hand, solvation free energies of the anions are large and differ considerably. The cyclo-propabenzenyl anion gets more stabilized by solvation than the benzyl anion, leading ultimately to the acidity ordering of cyclopropabenzene and toluene encountered experimentally in a condensed phase. It is also noteworthy that separate geometry optimization of anions in the gas phase and in aqueous so-lution improves the agreement between the calculated and experimental difference in pK_as of **1** and **2**.

EFFECT OF SUBSTITUENTS WITHIN AROMATIC RING ON STABILITY OF CYCLOPROPABENZENYL ANION

In the course of our studies on the cycloproparenyl carbanions, we have explored the possibility of tun-ing stability of **1** by introducing substituents attached to the carbanionic center [24], as well as by sub-stituents within the aromatic ring. Only the latter topic will be discussed here. For this purpose, we shall consider two examples—the effect of multiple substitution by fluorine atoms and with cyano groups. They are deliberately selected for this purpose since they have small steric demands, being at the same time powerful electron-withdrawing atoms/groups. Particularly interesting is the effect of cyano groups that are well documented to lead to a pronounced enhancement of acidity of several classes of organic acids owing to a very strong anionic resonance stabilization in their conjugate bases [25]. On the other hand, fluorine is considered as a representative of substituents operating primarily via inductive/field mechanisms and by enhancing the polarizability of the benzene ring. The calculated proton affinities of the studied carbanions **4–9** (see eqs. 9–11) are summarized in Table 2, along with the total energies and ZPVE corrections.

Table 2 Calculated electronic energies, zero-point vibration energies, and proton affinities for **1** and **4–9** at the MP2/6-31+G(d) level of theory.

| Molecule	E /a.u.	ZPVE[a] /a.u.	PA[b] /kJ mol^{-1}
1H	–269.36 856	0.10 127	
1	–268.74 029	0.08 502	1614.2
4H	–467.42 354	0.08 603	
4	–466.81 119	0.06 911	1571.1
5H	–467.41 689	0.08 574	
5	–466.80 563	0.06 979	1570.3
6H	–665.45 694	0.07 036	
6	–664.86 085	0.05 448	1530.5
7H	–453.40 120	0.09 683	
7	–452.83 573	0.08 275	1453.9
8H	–453.39 977	0.09 693	
8	–452.82 366	0.08 229	1480.7
9H	–637.41 666	0.09 260	
9	–636.89 441	0.07 930	1342.2

[a]ZPVE values scaled by 0.9670 [26].
[b]PA values are corrected to 298 K and include RT work term. For temperature corrections (0 → 298 K), vibrational frequencies were scaled by 0.9434 [26].

Comparison of the calculated PA values of anions **4–9** with that of anion **1** clearly show that both substituents exhibit pronounced effect on acidity. For instance, substitution of the aromatic ring in **1H** by fluorine at 2,5-positions increases acidity by 43.1 kJ mol^{-1} relative to the parent hydrocarbon. Similarly, substitution by fluorines in the 3,4-positions causes a decrease of PA by 43.9 kJ mol^{-1}, whereas replacement of all aromatic protons with fluorine, leading to 2,3,4,5-tetrafluoro derivative **6**, lowers acidity by 83.7 kJ mol^{-1}. It is interesting to note in this regard that the effect of fluorine atoms on proton affinity of cyclopropabenzenyl anion is roughly additive.

Analysis of the efficacy of stabilization of the neutral molecule **1H** and the anion **1** with multiple fluorine substitution by employing isodesmic reactions is given by eqs. 9a–c and 10a–c, respectively, clearly showing that the observed increase in acidities on passing from **4H** to **6H** is due to the increase in stability of the corresponding anions. It should be noted in this regard that the fluorine atoms are considerably more negative in anions than in their neutral counterparts. However, only a small fraction of negative charge comes from the anionic center, which becomes only slightly less negative than in **1** (–0.41 vs –0.50 e) (see, e.g., 9 in Fig. 3).

(9)
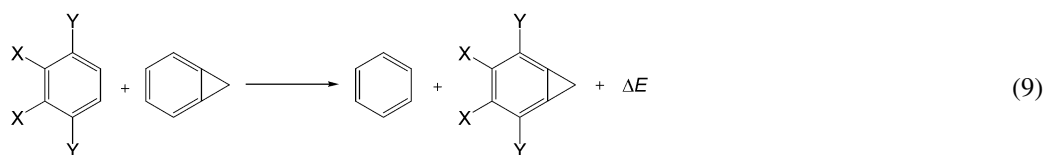
(a) **4H**: X = H; Y = F $\Delta E =$ 2.1 kJ mol^{-1}
(b) **5H**: X = F; Y = H $\Delta E =$ 3.8 kJ mol^{-1}
(c) **6H**: X = Y = F $\Delta E =$ −1.7 kJ mol^{-1}


(10)
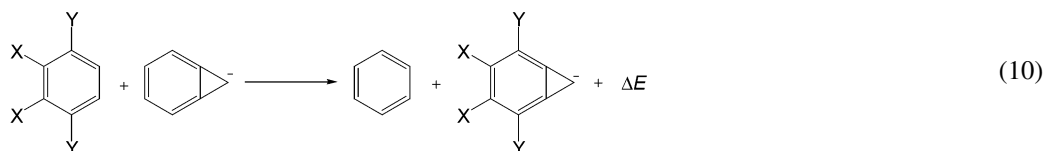
(a) **4**:   X = H; Y = F $\Delta E =$ −38.5 kJ mol^{-1}
(b) **5**:   X = F; Y = H $\Delta E =$ −9.1 kJ mol^{-1}
(c) **6**:   X = Y = F $\Delta E =$ −19.8 kJ mol^{-1}

(11)
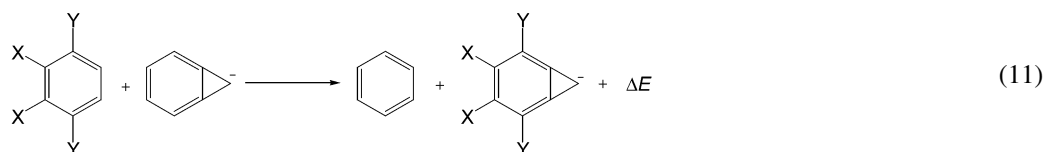
(a) **7**:   X = H; Y = CN $\Delta E =$ −159.0 kJ mol^{-1}
(b) **8**:   X = CN; Y = H $\Delta E =$ −134.3 kJ mol^{-1}
(c) **9**:   X = Y = CN $\Delta E =$ −272.6 kJ mol^{-1}

Substitution by the cyano groups exerts considerably stronger effect on stability of the cyclo-propabenzenyl anion, as illustrated by the isodesmic reaction shown in eqs. 11a–c. The marked increase in acidity due to cyano substitution could be qualitatively understood in terms of enhanced anionic resonance effect, since CN groups extend the conjugation between carbanionic site and the aromatic ring that already exists in **1** via resonance forms shown below:
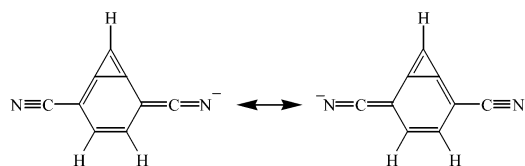
Moreover, in contrast to fluorinated anions, stabilization of the parent anion by the cyano groups strongly depends on proximity of the site of substitution to the anionic center. Thus, substitution of the benzene ring by the cyano groups in the 2,5-positions lowers PA of the anion **1** by 160.2 kJ mol^{-1}, which is by 26.8 kJ mol^{-1} larger than by substitution in the 3,4-positions (133.5 kJ mol^{-1}). This can be linked to more efficient charge transfer from the anionic center to the CN groups in the 2,5-positions, as evidenced by calculated distribution of atomic charges in **9** in Fig. 3. Consistent with this conclusion is also observation that the C_{Ar}–CN bonds in the 2,5-positions of **9** undergo more pronounced shortening (by 0.6 pm) owing to deprotonation than the corresponding bonds in the 3,4-positions (Fig. 3).

Finally, we note that PA of **9** is by 272.6 kJ mol^{-1} lower than that of **1**, implying that some resonance saturation is taking place [27].

6H
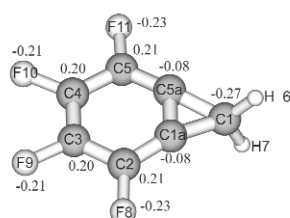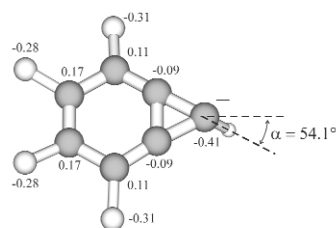
Bond lengths/pm		Bond angles/°	
C1–C1a:	150.1	C1–C5a–C1a:	62.9
C1a–C2:	137.0	C1a–C2–C3:	114.8
C1a–C5a:	136.7	C1a–C2–F8:	125.7
C2–C3:	140.4	C1a–C5a–C5:	123.4
C2–F8:	135.1	C2–C3–C4:	121.6
C3–C4:	140.5	C4–C3–F9:	118.3
C3–F9:	134.8		

6

Bond lengths/pm		Bond angles/°	
C1–C1a:	146.7	C1–C5a–C1a:	61.5
C1a–C2:	135.6	C1a–C2–C3:	116.9
C1a–C5a:	140.1	C1a–C2–F8:	124.9
C2–C3:	142.8	C1a–C5a–C5:	121.9
C2–F8:	139.3	C2–C3–C4:	120.7
C3–C4:	138.0	C4–C3–F9:	119.0
C3–F9:	137.7		

9H
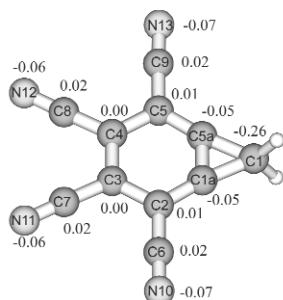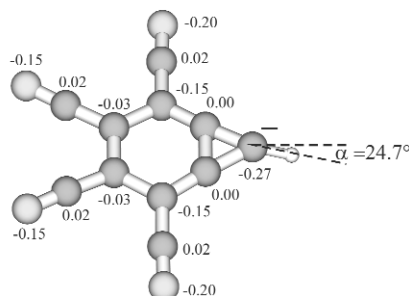
Bond lengths/pm		Bond angles/°	
C1–C1a:	150.5	C1–C1a–C5a:	63.3
C1a–C2:	138.4	C1a–C2–C3:	113.3
C1a–C5a:	135.2	C1a–C2–C6:	124.8
C2–C3:	142.7	C1a–C5a–C5:	124.7
C2–C6:	143.2	C2–C3–C4:	121.8
C3–C4:	142.3	C4–C3–C7:	118.8
C3–C7:	143.2		
C6–N10:	118.6		
C7–N11:	118.7		

9

Bond lengths/pm		Bond angles/°	
C1–C1a:	140.8	C1–C1a–C5a:	60.2
C1–C5a:	141.0	C1–C5a–C1a:	60.1
C1a–C2:	137.9	C1a–C2–C3:	113.1
C1a–C5a:	140.1	C1a–C5a–C5:	124.4
C2–C3:	146.8	C1a–C2–C6:	124.1
C2–C6:	142.1	C2–C1a–C5a:	124.2
C3–C4:	139.8	C2–C3–C4:	121.9
C3–C7:	142.7	C3–C4–C5:	122.0
C6–N10:	118.9	C4–C3–C7:	118.9
C7–N11:	118.9	C4–C5–C5a:	113.4

Fig. 3 MP2 optimized structures of 1,2,3,4-tetrafluoro- (**6**) and 1,2,3,4-tetracyanobenzocyclopropenyl (**9**) anions and their conjugate acids **6H** and **9H**, respectively. Atomic charges derived by symmetric Löwdin orthogonalization of the corresponding MP2/6-31+G(d) wave functions are shown too. Numbering of atoms are given in structures **6H** and **9H**.

Comparison of the optimized geometries of anions **4–9** with those of their conjugated acids (not shown here) [28] indicates that deprotonation leads to more pronounced alternation of bond lengths within the six-membered ring than in **1**. This is illustrated by comparing geometries of acid/base pairs **6H/6** and **9H/9**, which are shown in Fig. 3 as characteristic examples. As for the three-membered ring,

there is also a striking difference in the geometry of the three-membered rings in carbanions **6** and **9**. Specifically, distribution of the bond lengths within the small ring changes from fully asymmetric to an almost equilateral in passing from the former to the later carbanion. Furthermore, the length of the bonds emanating from the anionic center clearly suggests more efficient delocalization of the negative charge from the anionic center into aromatic ring in the tetracyano-substituted anion **9**. This is accompanied by a marked difference in the pyramidalization angle α at the anionic center, which is by 29.4° larger in the tetrafluoro anion **6** than in **9** as a consequence of less efficient delocalization of the negative charge from the anionic center into aromatic moiety.

   We have previously shown that the distortion of the aromatic ring in cycloalkarenes can be conveniently described by the bond localization index $L(d_{CC})$

$$L(d_{CC}) = \Sigma \left| d_{CC}^{(n)} - \bar{d}_{CC} \right| / pm \tag{12}$$

where $\bar{d}_{CC}$ is the average bond length and $d_{CC}^{(n)}$ refers to the n-th bond of the benzene moiety. Values for $L(d_{CC})$ of zero and 0.36 are obtained for the perfectly symmetric D_{6h} benzene structure and a completely localized cyclohexatriene ring, respectively [29]. Another useful criteria is provided by $L(\pi)$ defined by eq. 13, where $\bar{\pi}_{CC}$ and $\pi_{CC}^{(n)}$ refer to the average π-bond order and to the π-bond order of the n-th bond, in the ring under scrutiny, respectively.

$$L(\pi) = \Sigma \left| \pi_{CC}^{(n)} - \bar{\pi}_{CC} \right| \tag{13}$$

   In analogy to $L(d_{CC})$, $L(\pi)$ is zero in the free benzene and as its value increases aromatic defect is higher. The calculated $L(d_{CC})$ and $L(\pi)$ indices for the carbanions **4–9** and their conjugate acids **4H–9H** are summarized in Table 3, along with the NICS(1) values for the benzene moieties.

Table 3 Comparison of the localization indices $L(d_{CC})$ and $L(\pi)$ with the NICS(1) values for the aromatic ring in carbanions **1** and **4–9** and their conjugate acids **1H** and **4H–9H**, respectively.

Molecule	NICS(1)[a]/ppm	$L(d_{CC})$	$L(\pi)$
benzene	−10.2	0.00	0.00
1H	−10.2	0.11	0.03
1	0.3	0.16	0.57
4H	−10.4	0.11	0.07
4	−2.9	0.14	0.50
5H	−10.0	0.09	0.05
5	−1.4	0.16	0.66
6H	−10.5	0.11	0.05
6	−4.4	0.17	0.52
7H	−10.0	0.11	0.15
7	1.8	0.24	0.81
8H	−10.2	0.15	0.09
8	4.4	0.16	0.42
9H	−10.0	0.16	0.11
9	4.4	0.21	0.61

[a]NICS(1) values are calculated 100 pm above the geometrical center of the considered ring by the gauge invariant atomic orbital (GIAO) approach [30] at the B3LYP/6-311+G(d,p) level of theory for the MP2/6-31+G(d) optimized geometries.

Perusal of the data displayed in Table 3 clearly shows that all three indices of each of the neutral molecule are close to each other and very close to that in free benzene. It is also evident that all of the investigated species experience a drastic reduction of aromaticity upon deprotonation. For instance, the $L(d_{CC})$ indices of the fluorinated carbanions assume values from 0.14–0.17 on passing from **4** to **6**, whereas the $L(\pi)$ values lie between 0.50 and 0.66. For the anions **7–9**, the trend of changes in aromatic defect predicted by $L(d_{CC})$s is identical to that in the $L(\pi)$ values. Most importantly, both approaches predict the largest aromatic defect for the 2,5-dicyano- derivative **7**. Concerning the NICS(1) values, all fluorinated carbanions have slightly negative NICS(1) values (–1 to –4.4 ppm), whereas the NICS(1) values of the species **7–9** fall in the range of 1.8–4.4 ppm. This in turn suggests that the benzene ring in at least **8** and **9** should be considered to be magnetically antiaromatic! This shows that the usage of the NICS(1) values in discussing aromaticity of the benzene ring in the substituted cyclopropabenzenyl anions should be taken with a due care.

EFFECT OF EXTENDING AROMATIC BACKBONE ON THE STABILITY OF THE CYCLOPROPARENYL ANIONS

In view of the relatively large size of the higher analogs of **1** included in this study and those to be studied in the future, we selected the DFT BVWN5/6-31+G(d) method for the geometry optimizations, as well as for the calculations of their proton affinities. The selection of the anions studied so far is shown in Fig. 4, along with the PA values calculated at the B3LYP/6-311+G(3df,2p) level of theory at the geometries optimized with the BVWN5/6-31+G(d) method. Before discussing the results, we note in passing that the calculated PA of **10** (1535.5 kJ mol^{-1}) is in very good agreement with experimentally determined acidity of **10H** (1527.6 ± 8.8 kJ mol^{-1}) [11].

	1	**10**	**11**
PA:	1609.6	1535.5	1607.5

	12	**13**	**14**
PA:	1483.6	1611.7	1531.3
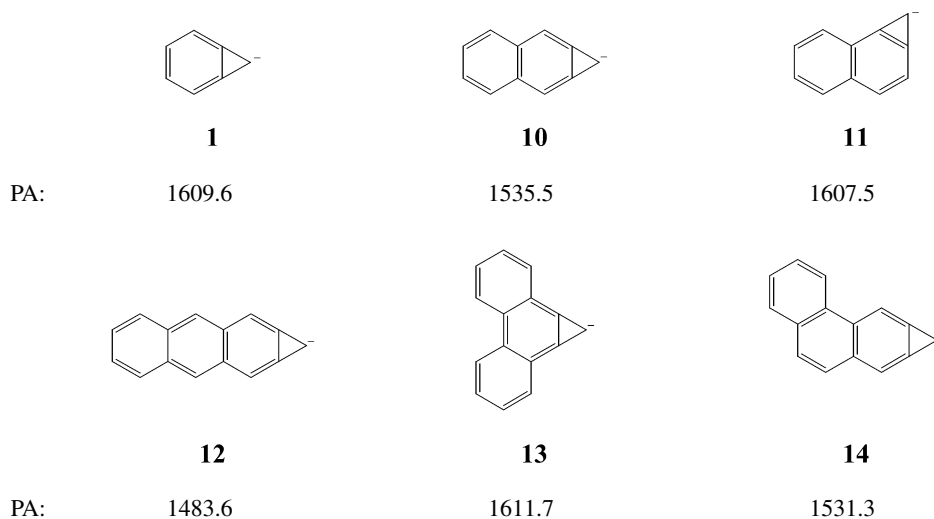
Fig. 4 Schematic representation of the cycloproparenyl anions **10–14**. The PA values at 298 K are given in kJ mol^{-1}.

Perusal of the calculated proton affinities reveals that PA depends strongly on the size of the aromatic backbone, as well as on the site of annelation. Let us take cyclopropa[*a*]- (**10**) and cyclopropa[*b*]naphthalenyl (**11**) anions as examples.

Analysis of the calculated PAs (Fig. 4) shows that acidity of the angular cyclopropanaphthalene is by 72.0 kJ mol^{-1} lower than acidity of the linear isomer. Given that the size of the aromatic subunit in the two ions is the same, it is clear that a decrease in acidity is a consequence of the π-bond local-

ization pattern inherent to the naphthalene ring. This is qualitatively understood by considering the res-
onance structures of the anions **10** and **11**, as discussed in more detail earlier in ref. [11].

Comparison of the optimized geometries of the two anions is also instructive in this regard. Thus,
by comparing the BVWN5/6-31+G(d) optimized structures of the two anions (Fig. 5), we observe a
pronounced difference in the pattern of bond distances within the peripheral aromatic ring, which
changes from 1,3-butadiene like in the angular anion **11** to the practically even distribution of bond dis-
tances (with exception of the central bond) in the linear isomer **10**. This is in contrast with geometries
of the central ring, which exhibit stronger alternation of the bonds in the linear isomer. We also observe
that the difference between the length of the vicinal and the distal bonds within the small ring, as well
as the pyramidalization angle α at the anionic center, in carbanion **10** are smaller than in **11.**

10   **11**

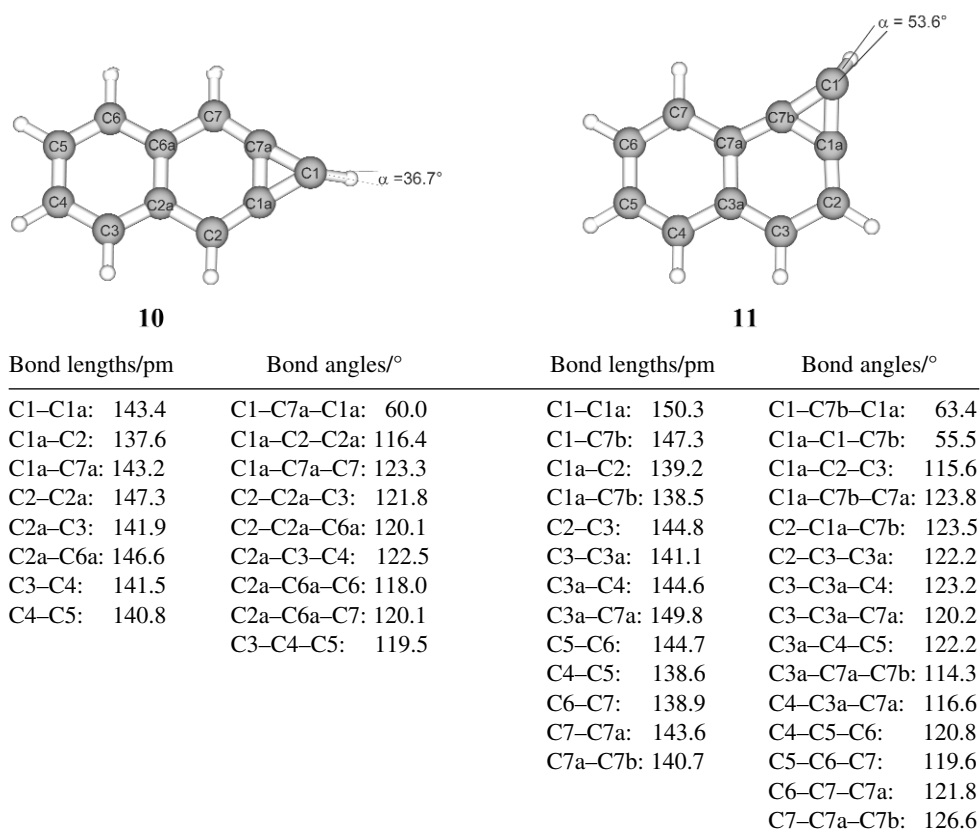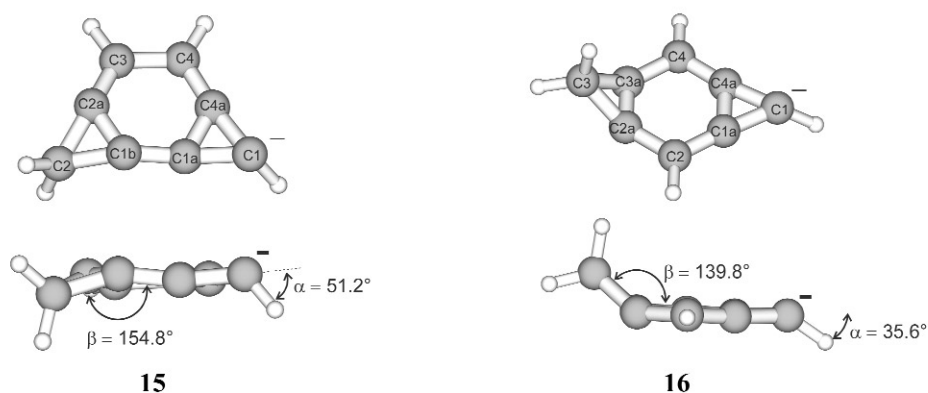| Bond lengths/pm		Bond angles/°		Bond lengths/pm		Bond angles/°	
C1–C1a:	143.4	C1–C7a–C1a:	60.0	C1–C1a:	150.3	C1–C7b–C1a:	63.4
C1a–C2:	137.6	C1a–C2–C2a:	116.4	C1–C7b:	147.3	C1a–C1–C7b:	55.5
C1a–C7a:	143.2	C1a–C7a–C7:	123.3	C1a–C2:	139.2	C1a–C2–C3:	115.6
C2–C2a:	147.3	C2–C2a–C3:	121.8	C1a–C7b:	138.5	C1a–C7b–C7a:	123.8
C2a–C3:	141.9	C2–C2a–C6a:	120.1	C2–C3:	144.8	C2–C1a–C7b:	123.5
C2a–C6a:	146.6	C2a–C3–C4:	122.5	C3–C3a:	141.1	C2–C3–C3a:	122.2
C3–C4:	141.5	C2a–C6a–C6:	118.0	C3a–C4:	144.6	C3–C3a–C4:	123.2
C4–C5:	140.8	C2a–C6a–C7:	120.1	C3a–C7a:	149.8	C3–C3a–C7a:	120.2
		C3–C4–C5:	119.5	C5–C6:	144.7	C3a–C4–C5:	122.2
				C4–C5:	138.6	C3a–C7a–C7b:	114.3
				C6–C7:	138.9	C4–C3a–C7a:	116.6
				C7–C7a:	143.6	C4–C5–C6:	120.8
				C7a–C7b:	140.7	C5–C6–C7:	119.6
						C6–C7–C7a:	121.8
						C7–C7a–C7b:	126.6

Fig. 5 Calculated BVWN5/6-31+G(d) geometries of cyclopropa[*a*]- (**10**) and cyclopropa[*b*]naphthalenyl (**11**)
anions.

What would happen if one would extend the aromatic framework even more? For instance, if we
replace naphthalene ring in the linear anion with anthracene framework the resulting anion (**12**) be-
comes less basic by ca. 51.9 kJ mol^{-1} (Fig. 4). This is only slightly less than observed in passing from
cyclopropabenzenyl anion to the cyclopropa[*b*]-naphthalenyl anion. However, moving to the anions
13H and **14H** derived from cyclopropaphenanthrenes, we observe that their PAs do not differ consid-
erably from the PA values of the corresponding cyclopropanaphthalenyl anions, in spite of the same size
of the aromatic backbone as in anthracene. Thus, PA of the carbanion **13** is very close to that of cyclo-
propa[*b*]naphthalenyl anion, while PA of the carbanion **14** is practically identical to that of cyclo-
propa[*a*]naphthalenyl anion. This strongly suggests that the angular extension of the aromatic backbone
of cycloproparenes does not affect proton affinity.

DEPROTONATION OF DICYCLOPROPABENZENES

Dicyclopropabenzenes **15H** and **16H** have been subject of interest of several recent theoretical studies, with emphasis on their molecular and electronic structure [1,5–7]. Furthermore, computational results of the strain energies for both molecules have been reported [31] according to which attachment of the three-membered ring to **1H** was proposed to lead to doubling of the strain energy relative to **1H**, with the angular isomer being by ca. 30 kJ mol^{-1} more strained. This poses an interesting question to what extent such an increase in strain energy influences acidity of the benzylic positions within the three-membered ring in **15H** and **16H**, respectively. As none of these species are known experimentally, we thought it of interest to tackle this problem computationally. The optimized geometries of the anions **15** and **16** derived from the linear and angular isomers, respectively, are shown schematically in Fig. 6, along with their key-geometrical parameters. The calculated proton affinities are summarized in Table 4, which also includes the relevant results for deprotonation of 2,3- (**17H**) and 3,4-dimethylcyclopropabenzene (**18H**) for the sake of comparison.

Bond lengths/pm		Bond angles/°		Bond lengths/pm		Bond angles/°	
C1–C1a:	145.7	C1–C4a–C1a:	60.8	C1–C1a:	143.4	C1–C4a–C1a:	60.5
C1–C4a:	148.1	C1a–C1–C4a:	56.7	C1a–C2:	138.5	C1a–C1–C4a:	59.0
C1a–C1b:	138.0	C1a–C1b–C2a:	119.6	C1a–C4a:	141.3	C1a–C2–C2a:	109.7
C1a–C4a:	139.6	C1a–C4a–C4:	124.6	C2–C2a:	145.1	C2–C1a–C4a:	125.4
C1b–C2:	150.6	C1b–C1a–C4a:	116.8	C2a–C3:	151.9	C2a–C3a–C4:	125.0
C1b–C2a:	139.3	C1b–C2a–C3:	124.5	C2a–C3a:	135.2	C3a–C2a–C3:	63.6
C2–C2a:	151.5	C1b–C2a–C2:	62.2				
C2a–C3:	137.6	C2a–C1b–C2:	62.8				
C3–C4:	146.3	C2a–C3–C4:	115.9				
C4–C4a:	138.4	C3–C4–C4a:	117.4				

Fig. 6 Calculated MP2/6-31+G(d) geometries of dicyclopropa[*a,c*]- (**15**) and dicyclopropa[*a,d*]- (**16**) benzenyl anion and their conjugate acids **15H** and **16H**, respectively. Also shown are out-of-plane angles at the anionic centers.

Table 4 Calculated electronic energies, zero-point vibration energies and proton affinities for anions **15**–**18** at the MP2/6-31+G(d) level of theory.

	E_{MP2} /a.u.	ZPVE[a] /a.u.	PA (298 K)[b] /kJ mol^{-1}
15H	−307.25 801	0.10 932	
15	−306.63 354	0.09 331	1605.4
16H	−307.26 970	0.10 958	
16	−306.65 542	0.09 385	1579.0
17H	−347.71 368	0.16 155	
17	−347.08 256	0.14 446	1620.9
18H	−347.71 183	0.16 202	
18	−347.08 110	0.14 480	1619.2

[a]Scaled using 0.9670 scaling factor [26].
[b]PA values are corrected to 298 K and include RT work term. For temperature corrections (0 → 298 K), vibrational frequencies were scaled by 0.9434 [26].

The results indicate that substitution of **1** with the methyl groups slightly decreases acidity. On the other hand, substitution by the three-membered ring enhances acidity, with the effect being more pronounced in the case of the linear isomer. Specifically, its PA decreases by 35.1 kJ mol^{-1} relative to that of the cyclopropabenzenyl anion. Another interesting finding concerns the out-of-plane bending of the neutral three-membered ring in the anions, as exemplified by their MP2/6-31+G(d) optimized structure. It is also interesting to note that this phenomenon is more pronounced in the linear isomer **16**, presumably due to the higher π-character of the corresponding annelated bond.

FINAL REMARKS

Based on the results of the MP2/6-31+G(d) calculations, the remarkable stability of the cyclopropabenzenyl anion is ascribed to a delicate balance between two opposing effects: (a) propensity of the aromatic ring to alleviate unfavorable 4π electron interaction within the three-membered ring by the anionic resonance effect and (b) by a pyramidalization of the anionic center, which tends to maximize the s-character of the lone pair. We have also shown that stability of the cyclopropabenzenyl anion can be considerably enhanced by substitution of the aromatic ring with fluorine and cyano groups as well as by linear extension of the aromatic backbone. On the other hand, angular extension of the aromatic framework influences stability of the considered anions only slightly. Finally, fusion of the second cyclopropenyl ring to the benzene moiety was found to increase acidity of benzylic position in cyclopropabenzene, with the effect being more pronounced in the linear isomer.

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REFERENCES

1. For a recent review articles, see e.g. (a) B. Halton. *Chem. Rev*. **103**, 1327–1369 (2003); P. Müller. In *Advances in Theoretically Interesting Molecules*, Vol. 3, R. P. Thummel (Ed.), pp. 37–107, JAI Press, Greenwich, CT (1995); (c) P. Müller. "Carbocyclic ring compounds", in Houben-Weyl *Methoden Organischen Chemie*, Vol. E/17d, A. de Meijere (Ed.), pp. 2866–2948, Thieme, Stuttgart (1997); (c) B. Halton. In *The Chemistry of the Cyclopropyl Group*, Vol. 2, Z. Rappoport (Ed.), 707–772, John Wiley, New York (1995).
2. W. H. Perkin. *J. Chem. Soc.* 1 (1888).
3. M. P. Cava and D. R. Napier. *J. Am. Chem. Soc.* **80**, 2255–2257 (1958).
4. E. Vogel, W. Grimme, S. Korte. *Tetrahedron Lett.* 3625–3631 (1965).
5. Z. B. Maksic and M. Eckert-Maksic. *Theoretical Organic Chemistry*, C. Parkanyi (Ed.), in *Theoretical and Computational Chemistry*, Vol. 5, P. Politzer and Z. B. Maksic (Ser. Eds.), pp. 203–231, Elsevier, Amsterdam (1998).
6. Y. Apeloig, R. Boese, D. Blaser, B. Halton, A. H. Maulitz. *J. Am. Chem. Soc*. **120**, 10147–10153 (1998); S. Grimme. *J. Am. Chem. Soc*. **118**, 1529–1534 (1996); S. Shaik, A. Shukri, D. Danovich, P. C. Hiberty. *Chem. Rev*. **101**, 1501–1540 (2001).
7. A. Stanger. *J. Am. Chem. Soc*. **120**, 12034–12040 (1998); K. Baldridge and J. S. Siegel. *J. Am. Chem. Soc*. **114**, 9583–9587 (1992).
8. B. Halton and P. J. Stang. *Synlett* 145–158 (1997).
9. (a) O. Sinanoglu. *Tetrahedron Lett.* **29**, 889–892 (1988); (b) B. Halton and M. P. Halton. *Tetrahedron* **29**, 1717–1720 (1973); (c) C. Eaborn and J. G. Stamper. *J. Organomet. Chem.* **192**, 155–161 (1980).
10. L. Moore, R. Lubinski, M. C. Baschky, G. D. Dahlke, M. Hare, T. Arrowood, Z. Glasovac, M. Eckert-Maksic, S. R. Kass, *J. Org. Chem.* **62**, 7390–7396 (1997).
11. I. Antol, Z. Glasovac, M. C. Hare, M. Eckert-Maksic, S. R. Kass. *Int. J. Mass Spectrom.* **222**, 11–26 (2003).
12. C. Eaborn, R. Eidenschink, S. J. Harris, D. R. M. Walton. *J. Organomet. Chem*. **124**, C27–C29 (1977).
13. For synthesis of the substituted cyclopropenyl ions, see: R. K. Sachs and S. R. Kass. *J. Am. Chem. Soc*. **116**, 783–784 (1994).
14. G. Szeimies and P. Wimmer. Unpublished observations (1985); P. Wimmer. Diplomarbeit, University of Munich (1985).
15. D. M. McQuarrie. *Statistical Mechanics*, Harper and Row, New York (1970).
16. I. A. Topol, G. J. Tawa, S. K. Burt, A. A. Rashin. *J. Chem. Phys*. **111**, 10998–11014 (1999).
17. $\Delta G_{solv,H}+ = -1107.1$ kJ mol^{-1}, see: M. D. Liptak and G. C. Shields. *J. Am. Chem. Soc*. **123**, 7314–7319 (2001).
18. M. D. Tissandier, K. A. Cowen, W. Y. Feng, E. Gundlach, M. H. Cohen, A. D. Earhart, J. V. Coe, T. R. Tuttle. *J. Phys. Chem. A* **102**, 7787–7794 (1998).
19. V. Barone and M. Cossi. *J. Phys. Chem. A* **102**, 1995–2001 (1998).
20. S. Miertus, E. Scrocco, J. Tomasi. *Chem. Phys.* **55**, 117–129 (1981).
21. J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson. *J. Chem. Phys*. **110**, 2822–2827 (1999).
22. G. B. Ellison, G. E. Davico, V. Bierbaum, Ch. DePuy. *Int. J. Mass. Spectrom. Ion Process.* **156**, 109–131 (1996).
23. C. Eaborn and D. R. M. Walton. *J. Chem. Soc., Chem. Commun*. 937–939 (1975).
24. M. Eckert-Maksic and Z. Glasovac. *J. Phys. Org. Chem*. **18**, 763–772 (2005).
25. Z. B. Maksic and R. Vianello. *New J. Chem.* **28**, 843–846 (2004); Z. B. Maksic and R. Vianello. *Eur. J. Org. Chem.* 1940–1945 (2004).
26. A. P. Scott and L. Radom. *J. Phys. Chem.* **100**, 16502–16513 (1996).

27. F. G. Bordwell, M. v. Der Puy, N. R. Vanier. *J. Org. Chem*. **41**, 1885–1886 (1976).
28. The optimized geometries can be obtained on request from authors.
29. Z. B. Maksic, D. Kovacek, M. Eckert-Maksic, M. Böckmann, M. Klessinger. *J. Phys. Chem.* **99**, 6410–6416 (1995).
30. R. Ditchfield. *Mol. Phys*. **27**, 789–807 (1974); J. R. Cheesman, G. W. Trucks, T. A. Keith, M. J. Frisch. *J. Chem. Phys*. **104**, 5497–5509 (1996).
31. Y. Apeloig, M. Karni, D. Arad. In *Strain and Its Implications in Organic Chemistry*, A. de Meijere and S. Blechert (Eds.), pp. 457–462, Kluwer Academic Press, Dordrecht (1989).