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Ab initio study of the effect of α-substituents on the acidity of cyclopropabenzene[†]

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ABSTRACT: The effect of substituents directly bound to the deprotonation site (C-7) on the acidity of cyclopropabenzene was studied using the MP2/6–31+G* method. The studied substituents encompass a variety of π- and σ-accepting groups including the highly electronegative fluorine atom. It is shown that all substituents enhance the acidity of cyclopropabenzene with the effect being the smallest (0.02 kcal mol^{-1}) for the methyl group and the largest (33.7 kcal mol^{-1}) for the hydrosulfonyl group. It is further shown that the α-subsituents employed stabilize the cyclopropabenzenyl anion less efficiently than the cyclopropenyl anion, with the effect being more pronounced for the substituents acting via inductive/field effects. This is attributed to the fact that attachment of inductively/field acting substituents to the carbanionic site predominantly stabilize the cyclopropenyl anion by increasing the s character of the lone pair, diminishing the antiaromatic character of the three-membered ring at the same time. Hence these two effects are operative in concert. The opposite occurs in related cyclopropabenzenyl anions. Here, the rehybridization at the carbanionic center does stabilize the lone pair, but decreases the anionic resonance of the whole system, because of a decrease in overlap between the lone pair and the π-AO of the annelated bond. The reverse picture holds for the conjugatively acting substituents.

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KEYWORDS: *ab initio* calculations; basicity; cyclopropenyl anions; cyclopropabenzenyl anions; substituent effects

INTRODUCTION

Among many aspects of the acid–base chemistry of strained hydrocarbons, the basicity of geometrically restricted α-substituted carbanions has attracted special attention.[1] In particular, the intrinsic gas-phase basicity of a variety of α-substituted cyclopropyl[2,3] and cyclopropenyl[2,4] anions has been probed by numerous theoretical and experimental studies.

As a part of our interest in the properties of cycloproparenyl anions, we have recently reported on the preparation of and MO calculations on cyclopropabenzenyl[5] and cyclopropa[*b*]naphthalenyl[6] anions. In addition, the effect of cyano, fluorine and methyl substituents on the aromatic ring on the acidity of cyclopropabenzene was considered.[7] This work was extended here to cyclopropabenzenes substituted at the deprotonation site. The substituents studied encompass widely different groups including CH_3, F, NH_2, OH, $CH{=}CH_2$, SiH_3, CF_3, NC, CN, CHO, NO_2 and hydrosulfonyl (SO_2H), which exhibit large differences in acidifying effects. Apart of being interesting from the theoretical point of view[5,8] *per se*, the resulting anions are of considerable importance as prototypes of α-substituted cycloproparenyl anions, which play a pivotal role as intermediates in the preparation of a variety of synthetically useful molecules,[9] to mention only the synthesis of highly strained alkylidenecycloproparenes.[9,10] The second motivation for the present investigation was a comparison of stabilizing ability of the σ- and π-electron-withdrawing substituents attached directly to the carbanionic center in the cyclopropabenzenyl moiety with that in the parent cyclopropenyl anion. Given the substantial difference in the electronic structures of the two anions, a profound difference can be expected in the extent of their stabilization due to the substituents, both acting predominantly via the inductive/field or through the resonance effect.

COMPUTATIONAL METHODS

The geometries of all species considered were optimized with the second-order Møller–Plesset perturbation theory employing the 6–31+G* basis set. This model will henceforth be denoted MP2.[11] The nature of the stationary points was characterized by vibrational frequency

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calculations, which were also used to obtain zero-point vibrational energies (ZPVEs). A scaling factor of 0.9670 was employed[12] to correct ZPVEs. The computed structures are interpreted by making use of simple qualitative bond indices such as hybridization parameters[13] and Coulson's π-bond orders.[14] For this purpose, the amount of s character was calculated by natural bond orbital (NBO) analysis.[15] Bader's topological parameters[16] were employed in describing the bond critical points and atomic charges, π-electron densities and π-bond orders were deduced by using density partitioning based on symmetric Löwdin's orthogonalization.[17] NICS values[18] were calculated at 1 Å above the geometric center of the considered ring by the gauge invariant atomic orbital (GIAO) approach[19] using the B3LYP/6–311+G** method for the MP2/6–31+G* optimized geometries.

All calculations were carried out with Gaussian 98[20] or GAMESS-US[21] programs implemented on Linux-based dual AthlonMP PCs and a cluster of dual AthlonMP PCs at the Ruđer Bošković Institute in Zagreb and a cluster of dual Xeon Pentium IV PCs at the University Computing Center in Zagreb (SRCE).

RESULTS AND DISCUSSION

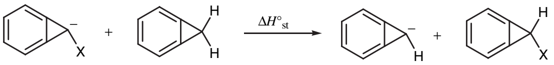
The cyclopropabenzenyl (**1**–**13**) and cyclopropenyl (**14**–**26**) carbanions studied are summarized in Scheme 1.

We shall first consider the energetic properties of cyclopropabenzenyl carbanions (**1**–**13**) and their conjugate acids (**1H**–**13H**), focusing on the changes in the proton affinity (*PA*) values of the anions upon substitution. The latter are equal to the gas-phase acidity of the corresponding conjugate acid (ΔH°_{acid}), which are defined as the enthalpy change for the reaction

$$AH \rightarrow A^- + H^+ \tag{1}$$

The ΔH°_{acid} values are calculated as the difference between the computed total electronic energies of A^- and AH, corrected for the changes in the ZPVEs. The total electronic energies of the fully optimized geometries of the considered cyclopropabenzenes and their deprotonated forms, along with the corresponding ZPVEs used in estimating ΔH°_{acid} values, are summarized in Table 1.

Also included in Table 1 are substituent stabilization energies, ΔH°_{st}, which are calculated according to isodesmic reaction (2). They can be taken as a measure of (de)stabilization of the anions due to substitution relative to the initial acids. Specifically, positive values of ΔH°_{st} imply an increase in the stabilization of the anion upon substitution relative to the stabilization in the parent benzocyclopropenyl anion.



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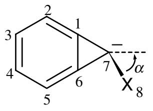
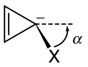
X	 	
H	**1**	**14**
CH_3	**2**	**15**
NH_2	**3**	**16**
OH	**4**	**17**
F	**5**	**18**
$CH{=}CH_2$	**6**	**19**
SiH_3	**7**	**20**
CF_3	**8**	**21**
NC	**9**	**22**
CN	**10**	**23**
CHO	**11**	**24**
NO_2	**12**	**25**
SO_2H	**13**	**26**

Scheme 1

Table 1. Calculated electronic energies, zero-point vibrational energies, acidities and substituent stabilization energies for cyclopropabenzene (**1H**) and its derivatives **2H**–**13H**

Molecule	E (a.u.)	$ZPVE_{sc}$[a] (a.u.)	ΔH°_{acid} (kcal mol^{-1})	ΔH°_{st}[b] (kcal mol^{-1})
1H	−269.36856	0.10102	384.1	—
1	−268.74029	0.08481		
2H	−308.54243	0.12891	383.9	0.2
2	−307.91439	0.11267		
3H	−324.56289	0.11787	382.4	1.7
3	−323.93783	0.10213		
4H	−344.40791	0.10521	381.1	3.0
4	−343.78507	0.08971		
5H	−368.40276	0.09398	378.3	5.7
5	−367.78370	0.07785		
6H	−346.50952	0.13320	369.6	14.5
6	−345.90426	0.11690		
7H	−559.52940	0.11605	367.9	16.1
7	−558.92748	0.10049		
8H	−605.65500	0.10611	363.9	20.1
8	−605.05960	0.09069		
9H	−361.34578	0.09935	361.5	22.6
9	−360.75471	0.08431		
10H	−361.38333	0.09929	357.1	27.0
10	−360.79978	0.08483		
11H	−382.40294	0.10994	353.7	30.4
11	−381.82485	0.09546		
12H	−473.39779	0.10399	351.1	32.9
12	−472.82401	0.08976		
13H	−817.03103	0.11081	350.4	33.7
13	−816.45774	0.09590		

[a] ZPVEs are scaled using a 0.9670 scaling factor.
[b] Calculated using Eqn (2).

The data in Table 1 reveal that all of the substituents examined significantly enhance the acidity of the parent hydrocarbon, with the exception of the methyl group, which has a negligible acidifying effect (0.2 kcal mol^{-1}; 1 kcal = 4.184 kJ). The latter indicates that the electron-donating ability of the methyl group is overwhelmed by its polarizability.[22] Turning to the other substituents, it is evident that the substituents acting by inductive/field effects are far less efficient in increasing acidity than the substituents acting predominantly by the resonance effect. For instance, a rather weak enhancement of acidity (1.7–5.7 kcal mol^{-1}) is observed on substitution by the strong σ-electron accepting groups F, OH and NH_2. The increase in acidity follows their electronegativity order[23] ($F > OH > NH_2$), suggesting that the influence of their π-donor abilities, acting in the opposite direction, is smaller than the prevailing σ-effect. This finding is in accord with previously published experimental and computational studies of acidity in the closely related cyclopropyl anions.[24,25] The stronger stabilization of the anion by the CF_3 group relative to that calculated for fluorine can be traced back to the reduction in electron-pair repulsion of its fluorine atoms and the carbanionic center, and to the involvement of anionic hyperconjugation. It is also interesting that the CF_3 substituent exhibits a similar effect on the stability of the anion as the SiH_3 group (20.1 vs 16.1 kcal mol^{-1}), in spite of the large difference in their electronic properties. The former is expected to exert a stabilizing effect through simultaneous action of the inductive/field effect and negative hyperconjugation,[26] whereas the SiH_3 group acts through a polarization mechanism and by negative hyperconjugation.[27] Most of the remaining substituents (CHO, $CH_2{=}CH$, NO_2 and CN) are strong π-acceptors and consequently stabilize the anions by delocalizing the negative charge from the carbon lone pair into a low-lying vacant orbital of π-symmetry of the substituents, thus offering additional resonance forms for carbanions (anionic conjugation). The effect ranges from ca 14.5 kcal mol^{-1} for **6** to ca 30 kcal mol^{-1} for **10**, **11** and **12**. Another point worth mentioning is that the effect of the isocyano group on stability of the anion is found to be slightly lower (by 4.3 kcal mol^{-1}) than that of the CN group. This is in accord with the theoretical study of Wiberg and Castejon, who found that in the gas phase cyclopropyl and alkyl isonitriles were 6–10 kcal mol^{-1} less acidic than the corresponding nitriles.[3b] We note in passing that the latter values are in fair agreement with the experimentally determined difference in acidities of acetonitrile and methyl isocyanide in the gas phase of 8 kcal mol^{-1}.[28] Finally, the largest acidifying effect is observed for the highly polar hydrosulfonyl group (33.7 kcal mol^{-1}), which is generally accepted to act via inductive and through-space field effects, the latter being due to its large internal group dipole moment.[29] The stabilization due to conjugation seems to be of less importance, as indicated by the large pyramidalization and considerable inversion barrier of anion **13**.

Having established general trends of the electronic effects of the considered substituents on the acidity of cyclopropabenzene, it would be of interest to separate individual effects in terms of Taft's parametrization[22] of Hammett's σ-constants encompassing polarizability (P), field/inductive (F) and resonance (R) effects by using the equation

$$\Delta H_{st} = -\rho_P\sigma_P + \rho_F\sigma_F + \rho_R\sigma_R \tag{3}$$

where ρ_P, ρ_F and ρ_R denote the reaction constants and σ_P, σ_F and σ_R are the substituent parameters, corresponding to the P, F and R effects, respectively. Before continuing further discussion, we should emphasize that the reliability of this approach for α-substituted carbanions has been questioned because some of them undergo large changes in geometry upon substitution.[30] If these perturbations become too large, the required non-collinearity between the independent substituent parameters σ_P, σ_F and σ_R might be lost. The matter is even more complicated owing to the limited availability of reliable gas-phase experimental data for this type of anion. Surprisingly, Peerboom *et al.*[3c] found that linear regression analysis utilizing Eqn (3) gives satisfactory results for a series of cycloalkyl carbanions $[X{-}c\text{-}C_nH_{2n-2}]^-$ ($n = 3$, 4, 5, 7), albeit with π-accepting substituents with a limited range of σ_R^- from 0.1 to 0.19 (X = Ph, CN, COOMe, NO_2).[3c] Prompted by this finding, we applied the same approach to the cyclopropabenzenyl anions considered in this work. Values of the substituent parameters σ_P, σ_F and σ_R^- were taken from Ref. 22. The data for the anions **2**, **7**, **8**, **10**, **11**, **12** and **13** (X = CH_3, SiH_3, CF_3, CN, CHO, NO_2, SO_2H) and for the anions **3–5** (X = F, NH_2 and OH) were treated separately in order to allow for a more reliable treatment of the repulsive lone pair–lone pair interactions (which exert an acid weakening effect) in the latter. Compound **9** was not included in the analysis because of a lack of the σ constants for the NC group, and the vinyl group was excluded from correlation owing to the uncertainty of the reported σ_R^- constant. In view of the small number of points involved in the second correlation, we shall restrict our discussion to the correlation obtained for the first set of anions, which is given by

$$\Delta H^\circ_{st} = -17.01\sigma_P + 21.29\sigma_F + 81.28\sigma_R \tag{4}$$

The quality of the correlation (4) is high, as evidenced by $r^2 = 0.996$ and the standard deviaton of 0.89. An attempt to employ slightly modified σ_P or σ_F constants suggested by Exner[31] and Marriot *et al.*[32] did not have a significant impact on the quality of the correlation.

The estimated values of the three kinds of substituent effects ($P = \rho_P\sigma_P$, $F = \rho_F\sigma_F$ and $R = \rho_R\sigma_R$) obtained for individual substituents are given in Table 2.

Table 2. Analysis of carbanion stabilization energies by Eqn (4)

Anion	σ_R^-	σ_F	σ_P	R^-	F	P	ΔH°_{st} (kcal mol^{-1})	ΔH°_{st} (corr.)[a] (kcal mol^{-1})
1	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0
2	−0.08	0.00	−0.35	−6.50	0.00	5.95	0.2	−0.5
7	0.06	−0.02	−0.72	4.88	−0.43	12.25	16.1	16.7
8	0.07	0.44	−0.25	5.69	9.37	4.25	20.1	19.3
10	0.10	0.60	−0.46	8.13	12.78	7.82	27.0	28.7
11	0.19	0.31	−0.46	15.44	6.60	7.82	30.4	29.9
12	0.18	0.65	−0.26	14.63	13.84	4.42	33.0	32.9
13	0.12	0.59	−0.62	9.75	12.56	10.54	33.7	32.9

[a] Calculated sign using Eqn (4).

The following points should be noted. The *P*, *R* and *F* values for various substituents span a range of 17, 22, and 15 kcal mol^{-1}, respectively, within the total range of the ΔH°_{st} values of 37 kcal mol^{-1}. Depending on the substituent, any of the three kinds of the stabilization effects may be predominant. For example, the results clearly demonstrate that the difference in the intramolecular mechanism leading to stabilization by the CH_3 and SiH_3 groups is mainly due to a difference in their electron-donating abilities. Furthermore, comparison of the data for the SiH_3 and CF_3 groups shows that in anion **7** the polarization term plays a decisive role, whereas in anion **8** a clear predominance of the inductive/field effect is observed. The results also underline the importance of the inductive/field effect in the stabilizing ability for the CN group, as mentioned above. Finally, it is interesting to note that the contribution of the resonance and field effects to the stability of anion **12** is predicted to be approximately the same, whereas for anion **13** all three effects are of the same order of magnitude. Although these results should be treated with caution, because of the small number of substituents considered, it appears that their analysis provides a useful insight into the mechanism of interaction between the individual substituents and the anionic center.

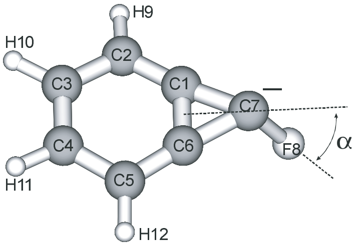
Effect of α-substituents on molecular and electronic structure of the cyclopropabenzenyl anion

In previous work we showed that deprotonation of cyclopropabenzene has a pronounced effect on the geometry of both the aromatic and the three-membered ring.[5] Similar trends are observed on deprotonation of the species **2H–13H**, as exemplified by the summary of the optimized structural parameters given in Table S1 in the Supplementary material. Briefly, the changes in the aromatic ring on deprotonation involve pronounced lengthening of the annelated bond (C1—C6) and the C2—C3/C4—C5 bonds with respect to the corresponding neutral molecule. In contrast, the bonds *ortho* to the coalesced (annelated) bond (C1—C2 and C5—C6) and the distal bond placed vis-à-vis to the three-membered ring (C3—C4) become shorter. This is in accordance with the Mills–Nixon effect, which despite some disputes takes place in many systems.[33,34] Accordingly, all anions investigated exhibit a stronger bond alternation pattern in the aromatic ring than in the corresponding conjugate acids, as illustrated by the optimized geometries of carbanions **5**, **7** and **11** shown in Fig. 1.

The reason for these structural changes has been analyzed previously for the cyclopropabenzenyl anion[5] and therefore will not be discussed here in detail. Enhancement of the bond localization pattern within the aromatic ring in all anions considered is substantiated by the calculated π-bond orders, and also by results of the topological analysis of the electron density distribution which are summarized in Table S2 in the Supplementary material. Additional evidence is provided by calculating the NICS(1) values of the aromatic ring in the neutral molecules and their deprotonated forms (Table 3). Their analysis clearly shows that deprotonation causes a strong decrease in diatropicity of the NICS(1) values, with the lowering of its absolute value being less pronounced for the substituents acting via the inductive/field effect mechanism. In other words, the aromatic character of the benzene ring decreases in general. We shall return to this point in the next section.

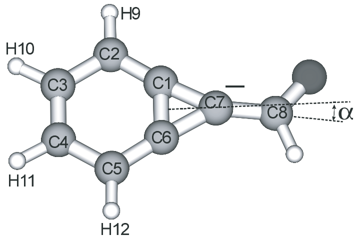
Turning to the three-membered ring, the most salient feature common to all considered anions is pyramidalization of the carbanionic center. The results in Table 4 show that the extent of the pyramidalization angle α (for definition see Scheme 1) varies from 14.4° (**11**) to 64.7° (**5**). It is noteworthy that these angles are considerably smaller than in substituted cyclopropenyl anions, where α assumes values in the range 35.0–76.6° (Table 4). This is obviously a consequence of partial delocalization of the lone pair into the aromatic ring in the cyclopropabenzenyl anions, which contributes to alleviation of antiaromaticity within the three-membered ring.[5,35] It is also interesting to mention in this regard that the NICS(1) values of the three-membered ring are of the same order of magnitude as in the six-membered ring in all considered anions (Table 3).

As expected, the pyramidalization increases upon substitution with atoms or groups with a lone pair of electrons adjacent to the negative charge (e.g. NH_2,



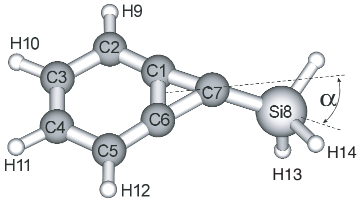
5

bond length /Å		bond angle / °	
C1-C2	1.386	C1-C2-C3	114.5
C1-C6	1.379	C1-C6-C5	123.2
C1-C7	1.490	C2-C3-C4	121.6
C2-C3	1.423	C3-C4-C5	121.6
C3-C4	1.404	C1-C6-C7	62.4
C2-H9	1.093	C1-C7-C6	55.2
C3-H10	1.092	α	64.7
C7-F8	1.493		
		dihedral angle / °	
		C7-C1-C6-C5	176.2
		C1-C2-C5-C4	169.8
		C2-C3-C4-H11	-178.3



11

bond length /Å		bond angle / °	
C1-C2	1.378	C1-C2-C3	114.3
C1-C6	1.398	C1-C6-C5	123.4
C1-C7	1.437	C2-C3-C4	122.1
C2-C3	1.438	C3-C4-C5	122.2
C3-C4	1.393	C4-C5-C6	114.3
C4-C5	1.437	C6-C1-C2	123.8
C5-C6	1.380	C1-C6-C7	60.9
C6-C7	1.439	C1-C7-C6	58.2
C2-H9	1.090	α	14.4
C3-H10	1.091	**dihedral angle / °**	
C7-C8	1.396	C7-C1-C6-C5	178.1
		C1-C2-C5-C4	179.7
		C2-C3-C4-H11	180.0



7

bond length /Å		bond angle / °	
C1-C2	1.377	C1-C2-C3	114.2
C1-C6	1.385	C1-C6-C5	123.8
C1-C7	1.465	C2-C3-C4	121.9
C2-C3	1.446	C3-C4-C5	121.9
C3-C4	1.389	C4-C5-C6	114.2
C4-C5	1.446	C6-C1-C2	123.8
C5-C6	1.377	C1-C6-C7	61.8
C6-C7	1.465	C1-C7-C6	56.4
C2-H9	1.091	α	39.1
C3-H10	1.092	**dihedral angle / °**	
C7-Si8	1.817	C7-C1-C6-C5	176.9
Si8-H13	1.522	C1-C2-C5-C4	177.1
Si8-H14	1.499	C2-C3-C4-H11	-179.8

Figure 1. Key structural parameters of anions **5**, **7** and **11**

Table 3. NICS(1) values of the aromatic and the three-membered rings in anions **1**–**13** and their conjugate acids **1H**–**13H**

Anion	NICS(1)		Conjugate acid	NICS(1)	
	6-membered	3-membered		6-membered	3-membered
1	0.30	1.83	**1H**	−10.33	−6.70
2	−0.05	−0.65	**2H**	−10.39	−6.61
3	−2.78	−4.49	**3H**	−10.17	−8.81
4	−5.27	−8.06	**4H**	−10.21	−9.76
5	−7.00	−10.65	**5H**	−10.48	−11.17
6	1.09	1.70	**6H**	−10.47	−7.85
7	0.07	3.07	**7H**	−10.69	−6.57
8	−4.06	−2.36	**8H**	−10.92	−8.90
9	−5.35	−5.45	**9H**	−10.53	−9.49
10	−3.42	−1.24	**10H**	−10.95	−8.55
11	−1.88	0.54	**11H**	−10.64	−8.33
12	−4.69	−3.39	**12H**	−10.90	−11.27
13	−5.43	−4.29	**13H**	−11.05	−10.89

OH, F). The latter is in line with Bent rule,[36] which states that an electronegative atom attached to carbon prefers increased p character in the hybrid atomic orbital of the bonded carbon atom. The enhanced p character leads to bond lengthening and ultimately to a decrease in electron–electron repulsion. Naturally, as the electronegativity and the number of lone pairs of the substituent ($N < O < F$) increase, the pyramidalization becomes larger. Concomitantly, the corresponding inversion barriers in anions **3**, **4** and **5** increase in the same direction (Table 4). The characteristic bond lengthening by the σ-accepting substituents involves also the C1—C7 and C6—C7 bonds relative to those in the neutral molecule. For instance, in **5** (Fig. 1) the C7—F bond lengthens by 0.088 Å, whereas the C1—C7 and C6—C7 bonds are elongated by 0.015 Å. It is also interesting that the C1—C7/C6—C7 bonds in **5** are considerably longer than those in the unsubstituted carbanion **1**. The latter is consistent with increased s character of the lone pair and the accompanying decrease in the average s content of the respective C—C bonds (28.1 vs 26.9%, Table S2 of Supplementary material). Analysis of the Laplacian and ellipticity values derived from topological analysis of the electron density distribution in **1** and **5** provides further support for this observation. For example, there is a slight decrease in Laplacians, $\nabla^2\rho_c$, (−0.358 vs −0.368) on going from **1** to **5**. A shift in the electron density ρ_c is also observed, although to a smaller extent (0.241 vs 0.236). Similarly, the ellipticity, ε, (a measure of the anisotropy of the charge distribution) increases from 0.386 to 0.556, as expected owing to substitution by highly electronegative fluorine atom (Table S1 in the Supplementary material). It should be recalled in this regard that contrary to the anisotropy of an alkene double bond, the major axis of ε for the bonds forming the three-membered ring is not perpendicular but parallel to the plane of the carbon nuclei.[37] It is also noteworthy that the aromatic ring in anion **5** is puckered in such a way that the overlapping between the lone pair orbital and π-atomic orbitals of the aromatic moiety is enhanced as if their interaction were increased.

Table 4. Pyramidalization angles α[a] in carbanions **1**–**26** and inversion barriers (IB)[b] for anions **1**–**13**

Anion	α(°)	IB (kcal mol^{-1}	Anion	α(°)
1	50.7	6.51	**14**	69.2
2	48.0	8.82	**15**	63.3
3	51.9	12.62	**16**	66.8
4	59.3	18.55	**17**	72.9
5	64.7	23.88	**18**	76.6
6	22.8	0.91	**19**	48.5
7	39.1	2.26	**20**[c]	—
8	55.1	8.30	**21**	65.7
9	55.5	9.43	**22**	69.0
10	44.1	3.17	**23**	63.9
11	14.4	0.23	**24**	35.0
12	38.8	2.18	**25**	55.4
13	57.9	8.73	**26**	68.4

[a] For the definition of α see Scheme 1.

[b] IB is defined as the difference in the total energies of the pyramidal and the planar forms of the considered anions. The planar structures of the anions **14**–**19** and **21**–**26** were found to be saddle points of the second or higher order at the MP2/6–31 + G* level. Therefore, their inversion barriers were not calculated and are not discussed here.

[c] The miniumum energy structure of deprotonated **20H** at the MP2/6–31 + G* level corresponds to the 2-silylcyclopropen-1-yl anion.

On the other hand, rehybridization at the anionic center upon substitution with CN, NO_2, $CH{=}CH_2$ or CHO groups leads to a more planar sp^2 canonical state. This is accompanied by a considerable decrease in the carbanion inversion barrier, suggesting that resonance stabilization gains importance across the series of these substituents. The most pronounced flattening is found in anion **11** (Fig. 1), the structure of which will be discussed in some detail next. First, it is important to note that the CHO group (and also other π-accepting substituents) in the anion **11** assumes an orientation opposite to that in its conjugate acid. More specifically, the CHO group in the neutral molecule is oriented in such a way relative to the three-membered ring that good overlapping between the C=O π-bond and the Walsh orbital of the three-membered ring of appropriate symmetry can take place.

In other words, the CHO group is coplanar with the symmetry plane of the molecule. In contrast, the CHO group in the preferred conformation of the anion is perpendicular to the former symmetry plane in order to achieve efficient transfer of charge from the anionic center to the empty π*-MO orbital of the C=O double bond. This leads to a decrease in the C7—CH(O) bond length by 0.098 Å, whereas the C=O bond is lengthened by 0.047 Å relative to the neutral molecule. This is also reflected in the π-bond orders of the respective bonds, which assume values of 0.71 and 0.45, respectively. We note in passing that similar structural changes take place upon deprotonation of acids **10H** and **12H**, but are less pronounced. For instance, in the case of cyanide (**10H**), formation of the anion leads to a decrease in the C7—CN bond length by 0.047 Å and an increase in the N≡C bond length by 0.013 Å. The observed trend is indicative of less efficient charge transfer from the carbanionic site to the substituent via the π-interaction relative to that in anion **11** (Table S2 in the Supplementary material).

Comparison of the structural parameters of the three-membered rings in **1** and **11** is also revealing. For example, the bonds emanating from the anionic center become 0.028 (0.030) Å shorter on passing from **1** to **11**, whereas the annelated bond (C1—C6) elongates by 0.008 Å. The shortening of the vicinal bonds (C1—C7 and C6—C7) in **11** can be understood as a consequence of planarization of the anionic center, which leads to an increase in the average s character of the respective bonds and a stronger interaction of the lone pair with the aromatic ring in carbanion **11**. This is indeed the case, as evidenced by the results of the NBO analysis and the Löwdin π-bond orders in Table S2 in the Supplementary material. Hence there is a substantial increase in the s character upon deprotonation (22.3 vs 27.4%) of the hybrid AOs emanating from C7 and directed to the junction atoms C1 and C6, respectively. The π-bond orders of the respective bonds increase from 0.32 in **1** to 0.50 in anion **11**. The pronounced difference in the electronic structure of the three-membered ring in **1** and **11** is corroborated by Bader's topological analysis (Table S2 in the Supplementary material).

Finally, the effect of the SiH_3 group on the geometry of the anion **7**, which can be considered as the prototype of the key intermediates involved in the synthetically important preparation of alkylidenecyclopropanes, deserves comment.[10] As mentioned above, the SiH_3 group owes its stabilizing ability to the large polarizability and the possibility of anionic hyperconjugation with the anionic center. The latter is reflected in considerable shortening of the exocyclic C—Si bond (0.080 Å) relative to the neutral molecule **7H**. Significant also is the considerable lengthening of the Si—H bond (Si—H13), which is coplanar to the lone pair orbital (by 0.068 Å), whereas the remaining two Si—H bonds are only slightly stretched (by 0.012 Å) relative to the neutral molecule (Table S1 in the Supplementary material). These geometric changes are accompanied by reduction of charge on the hydrogen atoms within the SiH_3 group, as compared with those in the neutral molecule (Table S2 in the Supplementary material). All these features can be attributed to the tendency of maximizing interaction of the lone pair with one of the low-lying σ_{SiH}* orbitals of the SiH_3 group, which is coplanar with the lone pair AO. The presence of the SiH_3 group is also manifested by considerable shrinkage of the C1—C7 and C6—C7 carbon–carbon bonds (by 0.054 Å) within the three-membered ring with respect to the neutral molecule. The latter is likewise in the acid–base pair **11H–11** a consequence of an increase in the average s character in the respective bonds on deprotonation and partial delocalization of the charge from the anionic site to the π-manifold of the aromatic ring. This is substantiated by the NBO and Bader's topological analysis (Table S2 in the Supplementary material). Finally, it is interesting that replacement of the hydrogen atom at the anionic center in **1** with an SiH_3 group has only a marginal effect on the geometry of the aromatic moiety (Fig. 1 and Table S1 in the Supplementary material).

The changes induced by the substituents described above are also reflected in the geometries of the three-membered ring in the planar forms of the anions considered (Table S1 in the Supplementary material). Concomitantly, there is a fair linear relationship between the difference in the bond lengths of the CC bonds of the three-membered ring in the anion and the related bonds in its planar transition state form and the inversion barrier (IB) (Fig. 2).

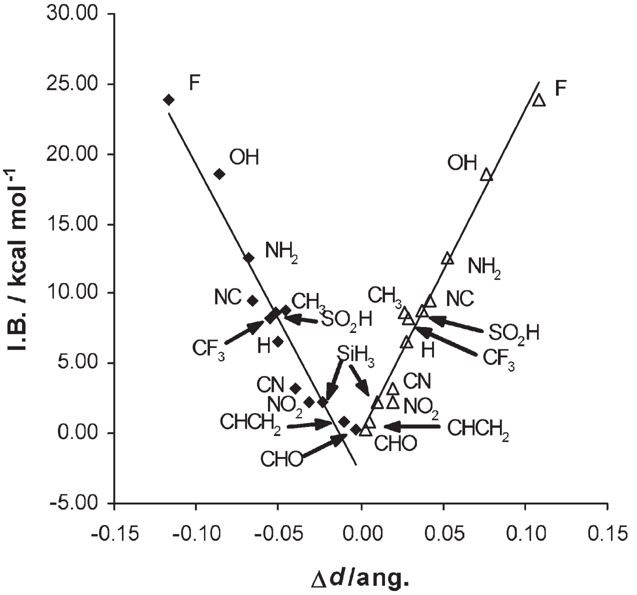
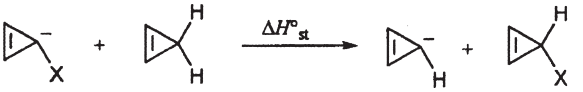


Figure 2. Correlation between inversion barrier (IB) and the difference between the C1—C7 and C1—C6 bond lengths (Δd) in anions **1–13** and their planar forms. The left line relates to the C1—C7 bond ($y = -220.17x - 2.84$; $r^2 = 0.936$; SD = 1.85; $n = 13$) and the right line to the annelated (C1—C6) bond ($y = 230.21x - 0.01$; $r^2 = 0.969$; SD = 1.30; n = 13)

Comparison of α-substituent effects on stabilities of cyclopropabenzenyl and cylopropenyl anions

Based on analysis of the calculated molecular and electronic structures of cyclopropabenzenyl anions, its remarkable thermodynamic stability relative to the parent cyclopropenyl anion was accounted for by a delicate balance of two counteracting effects: (i) the propensity of the aromatic ring to alleviate unfavourable 4π-electron interaction within the antiaromatic three-membered ring via the anionic resonance effect and (ii) pyramidalization of the anionic center, which tends to maximize the s character of the lone pair, thus contributing to its stabilization.[5] The latter is antagonistic, since it diminishes the anionic resonance effect at the same time owing to a decrease in overlap between the hybrid AO occupied by a lone pair and the π-AO of the annelated CC bond. Their interplay can be tuned by the choice of substituent at the carbanionic site. Given that the first mode of stabilization is not present in the cyclopropenyl anions, we deemed it worthwhile to explore the extent to which α-substituents influence the relative stabilities of the two carbanions. For this purpose we calculated *PA* values and substituent stabilization energies of the cyclopropenyl anions **14**–**26**. The latter were calculated using the equation



(5)

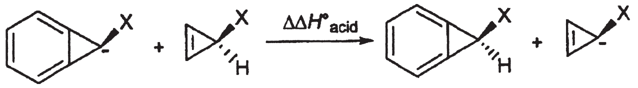
The results are given in Table 5, along with the corresponding ZPV energies and deprotonation energies (ΔH°_{acid}) (calculated at 0 K). The geometries of some of these anions (**14**, **15**, **23**, **24**) and their conjugate acids (**14H**, **15H**, **23H**, **24H**) have been studied previously by Kass and co-workers,[4a,35] using various DFT and MP2 methods in combination with the 6–31+G* basis set. [For the unsubstituted cyclopropenyl anion (**14**), MCSCF calculations have also been performed.[35]] Our calculated geometries (Table S2 in the Supplementary material) are in overall good agreement with those data and will not be discussed here. Analysis of the data in Table 5 reveals that the relative ordering of ΔH°_{acid} values differs from that found for cyclopropabenzenyl anions (Table 1). For example, the vinyl group exerts a less pronounced effect on acidity than the hydroxyl group and fluorine and the effect of the NC, CN and CHO groups (NC > CN > CHO) is opposite to that in the cyclopropabenzenyl series.

Table 5. Calculated electronic energies, zero-point vibrational energies, acidities and substituent stabilization energies for cyclopropene (**14H**) and its derivatives **15H**–**26H**

Molecule	E (a.u.)	ZPVE$_{sc}$[a] (a.u.)	ΔH°_{acid} (kcal mol^{-1})	ΔH°_{st}[b] (kcal mol^{-1})
14H	−116.21187	0.05488	418.4	0.0
14	−115.52927	0.03907		
15H	−155.38348	0.08256	412.2	6.3
15	−154.71077	0.06667		
16H	−171.40868	0.07178	407.0	11.5
16	−170.74421	0.05584		
17H	−191.25501	0.05885	400.1	18.4
17	−190.60208	0.04350		
18H	−215.25341	0.04766	393.4	24.9
18	−214.61070	0.03191		
19H	−193.35220	0.08690	401.5	16.8
19	−192.69644	0.07105		
20H	−406.36849	0.06967	397.5	—[c]
20[c]	−405.72062	0.05529		
21H	−452.50188	0.05997	388.5	29.9
21	−451.86731	0.04455		
22H	−208.19513	0.05309	382.6	35.9
22	−207.57032	0.03800		
23H	−208.23111	0.05311	383.8	34.6
23	−207.60462	0.03832		
24H	−229.24942	0.06379	384.9	33.6
24	−228.62159	0.04936		
25H	−320.24867	0.05786	374.2	44.4
25	−319.63807	0.04359		
26H	−663.87823	0.06492	369.8	48.7
26	−663.27347	0.04947		

[a] ZPVEs are scaled using a 0.9670 scaling factor.
[b] Calculated using Eqn (5).
[c] α-Silyl-substituted cyclopropenyl anion is not a minimum on the PES imaginary frequencies (NImag 2). The global energy minimum structure corresponds to the 2-silyl-cyclopropen-1-yl anion.

Another point of interest is to compare the influence of the same substituents on the stability of the cyclopropabenzenyl and cyclopropenyl anions. For this purpose we shall make use of the differences in calculated ΔH°_{acid} values, hereafter denoted $\Delta\Delta H^\circ_{acid}$, between the substituted cyclopropabenzenyl anions and their substituted cyclopropenyl counterparts as defined by Eqn (6):



(6)

Table 6. Comparison of substituent effects on relative stabilities of cyclopropabenzenyl and cylopropenyl anions

X	$\Delta\Delta H^\circ_{acid}$[a] (kcal mol^{-1})	δ (kcal mol^{-1})
H	34.4	—
NH_2	24.6	9.8
OH	19.0	15.4
F	15.1	19.3
$CH{=}CH_2$	32.0	2.4
CF_3	24.6	9.8
NC	21.2	13.2
CN	26.7	7.7
CHO	31.3	3.1
NO_2	23.1	11.3
SO_2H	19.4	15.0

[a] $\Delta\Delta H^\circ_{acid}$ calculated according to Eqn (6).

These differences are in all cases smaller than for the unsubstituted anions. In other words, all of the α-substituents considered stabilize the cyclopropenyl anion more efficiently than the cyclopropabenzenyl anion. The $\Delta\Delta H^\circ_{\text{acid}}$ values are summarized in Table 6. For the purpose of discussion it is convenient to normalize $\Delta\Delta H^\circ_{\text{acid}}$ values relative to $X = H$. The values so obtained, hereafter denoted as δ are also included in Table 6.

It appears that the largest δ is encountered for the strong σ-accepting substituents (F, OH, NC) and for the SO_2H group. This is not surprising in view of rehybridization at the anionic center occurring upon deprotonation, which is particularly strong for the electronegative substituents in accordance with Bent's rule.[37] As a consequence, pyramidalization increases, implying that the s character of the lone pair also increases (see above). This in turn increases the stability of the anionic center in the cyclopropenyl anion. To illustrate this point, NBO analysis from MP2 calculations indicates that the lone pair of the cyclopropenyl carbanion has s character of 42.4%, as opposed to 59.2% in, e.g., carbanion **18**. It should be stressed that the increased s character of the lone pair decreases the antiaromaticity of the three-membered ring, because the π-component of the lone pair orbital hybrid atomic orbital is diminished, thus leading to less efficient overlapping with the π-bond in the cyclopropenyl carbanion. A different situation occurs in structurally related cyclopropabenzenyl anions **1** and **5,** where the corresponding s characters are 30.19 and 48.20%, respectively. They are smaller than in the cyclopropenyl carbanion, since their increase leads to a decrease in anionic resonance in the extended benzocyclopropenyl π-system resulting in less efficient stabilization. This antagonism is the main reason behind the more pronounced stabilization effect in cyclopropenyl carbanions by the σ-electron withdrawing substituents.

In contrast, in the cyclopropabenzenyl and cyclopropenyl carbanions substituted by groups acting predominantly through the resonance effect (e.g. vinyl or CHO group), a large fraction of the negative charge of the carbanionic center becomes delocalized into the substituted group (Table S2 in the Supplementary material). Consequently, the angle between the lone pair and the p atomic orbitals of the π-manifold in both types of carbanions decreases owing to planarization, which amplifies the overlapping and ultimately the delocalization effect. In the cyclopropabenzenyl anions both of these factors contribute to stabilization of the anion because the antiaromaticity of the three-membered ring is remedied by the annelated aromatic ring. In contrast, in cyclopropenyl anions these two factors act against each other. Consequently, the difference in stabilization energy of the benzocyclopropenyl and cyclopropenyl anions substituted by π-withdrawing groups becomes smaller than for the σ-accepting substituents, but the latter anions are still more stabilized. It is noteworthy that the difference in the aromatic character of the benzene rings in cyclopropabenzenyl anions substituted with σ-accepting and strong π-accepting groups is qualitatively reflected in the NICS(1) values of the aromatic ring. Specifically, the former substituents lead to NICS(1) values ranging from -5.4 to -7 ppm. On the other hand, the NICS(1) values of the anions belonging to the second group of substituents fall in the range between -4 and 1.08 ppm (Table 3), suggesting that the aromatic stabilization of the benzene fragment in these species is either very small or negligible.

CONCLUSIONS

The results of MP2/6–31+G* calculations for the series of α-substituted cyclopropabenzenyl anions presented here indicate that all of the investigated substituents increase the stability of the parent anion, thus amplifying the acidity of its conjugate acid. The smallest enhancement of acidity is observed for the methyl-substituted cyclopropabenzene (0.2 kcal mol^{-1}) and the largest for the cyclopropabenzene carrying a hydrosulfonyl group (33.7 kcal mol^{-1}). The observed trends are rationalized as a trade-off balance between resonance, inductive/field and polarizability effects.

Further, it appears that all of the α-substituents employed stabilize the cyclopropenyl anion more efficiently than the cyclopropabenzenyl anion, with the effect being more pronounced for substituents acting via inductive/field effects. This is attributed to the fact that substituents acting predominantly via an inductive/field mechanism on the carbanionic site (e.g. F, OH and NH_2) stabilize the cyclopropenyl anion by increasing the s character of the lone pair, thus diminishing the antiaromatic character of the three-membered ring at the same time. Hence these two effects operate in concert. The opposite occurs in related cyclopropabenzenyl anions. Here, the rehybridization at the carbanionic center does stabilize the lone pair, but decreases the anionic resonance of the whole system, because of a decrease in overlapping between the lone pair and the π-AO of the annelated bond. The reverse picture holds for the π-accepting substituents, but the stabilization of the cyclopropenyl anions is still somewhat larger.

Supplementary material

The structural parameters, charge distribution, π-bond orders, NBO s characters and Bader bond critical point indices for substituted cyclopropabenzenes and their anions are given in Tables S1 and S2 available in Wiley Interscience.

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