Design of Strong, Neutral Organic Superacids: DFT-B3LYP Calculations on Some Isobenzofulvene Derivatives

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Isobenzofulvenes heavily substituted by cyano groups provide very good candidates for neutral organic superacids of unprecedented strength. The latter can be additionally enhanced by the anionic corona effect realized by interaction between the propyl–BX_2 chain, where X = F, Cl and Br, and the O^- atom in the corresponding conjugate bases. The main reason for the highly pronounced acidity is found, however, in the aromatization of the isobenzofulvene moiety upon deprotonation, which, in turn, is assisted by the electron-withdrawing CN groups.

Introduction

The notion of acidity is one of the most important pillars of chemistry. In the Brønsted sense acidity is the ability of a substance to lose a proton and to accept negative charge. Its equally important counterpart is basicity, which reflects the ability to accept a proton and accommodate a positive charge. They are both pivotal ingredients of acid/base chemistry, which in the gas phase has contributed immensely to the understanding of the structure/reactivity relationship as it can be directly related to intrinsic reactivity not "contaminated" by the environment.[1−7] Consequently, many experimental and theoretical efforts have been devoted to the elucidation of acidity in widely different compounds.[8−11] Work on the interpretation of the underlying principles determining acidity is particularly important, since it provides a useful insight into the relative contributions to the deprotonation process, which enables the design of compounds exhibiting enhanced proton-releasing ability.[12,13] This is both of scientific and practical value, since the generation of anions under mild reaction conditions is useful in, for example, olefin polymerization[14] and new lithium battery technology.[15]

It is important to emphasize that superacids are essential in so-called general acid catalysis, where the rate is amplified not only by an increase in solvent H^+ ion concentration, but also by an increase in the concentration of other acids exerting a catalytic activity. In this type of catalysis the strongest acids are the best catalysts.[16] Interestingly, Brønsted acids are sometimes complementary to Lewis acids in this respect. For example, the reaction of 3,4-disubstituted piperidines with methylaluminium dichloride yields *trans*-piperidines possessing diastereomeric ratios of up to 93:7. On the contrary, the Prins cyclization, catalyzed by hydrochloric acid, gives *cis*-piperidines with diastereomeric ratios of up to 98:2.[17] In some cases strong Brønsted acids are better catalysts than comparable Lewis acids, as in the case of the hetero-Michael addition of carbamates, alcohols and thiols to α,β-unsaturated ketones, alkylidenemalonates and acrylimides.[18] It therefore comes as no surprise that considerable attention has been focused on the design of new superacids[19] by using two scenarios. In the first, the intrinsic acidity of characteristic groups (CH, NH, OH, SH) was examined and subsequently amplified by some carefully chosen substituents possessing high polarizability, which, in turn, has led to favorable field/inductive and π-resonance effects. The second strategy was based on Yagupolskii's concept of electronic superacceptor substituents[20] exemplified by $=NSO_2CF_3$, which, by replacing an oxygen atom doubly bonded to S, P or I, yields very strong superacids in the gas phase[19,20,21] and acetonitrile.[22] The reason behind these pronounced acidities is that one or more highly dipolar superacceptor groups and some judiciously selected strongly polarizable substituents form an extended conjugate system in the corresponding conjugate bases. Our starting point is different, yet related. It is embodied in the triadic formula analysis, which shows that the higher ionization potential of the anionic conjugate base, calculated in Koopmans' approximation, leads to higher acidity.[12] Obviously, very large Koopmans ionization potentials (IP^{Koop}) are found as a rule in systems that undergo strong anionic resonance or aromatic stabilization upon deprotonation, in accordance with chemical intuition and the results of Koppel, Yagupolskii et al.[20−22] Therefore, a profitable strategy in tailoring strong neutral organic superacids would be to find molecules that would exhibit

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pronounced anionic aromatization in the corresponding conjugate base forms. It is the aim of this paper to show that deliberately substituted isobenzofulvenes provide superacids of unprecedented strength. This computational study is prompted by the fact that successful synthetic routes to isobenzofulvenes and their derivatives are well established.[23,24]

Computational Procedure

According to Brønsted, acidity is the capability of a molecule to give up a proton. Concomitantly, acidity is given by the enthalpy change $\Delta_r H$ for the reaction:

$$AH(g) \rightarrow A^-(g) + H^+(g) \quad (1)$$

which is calculated as:

$$\Delta H_{acid} = \Delta E_{acid} + \Delta(pV) \quad (2)$$

Here, ΔE_{acid} represents the change in the total energy, which includes the zero-point energy and the finite temperature (298.15 K) correction, whereas $\Delta(pV)$ denotes the pressure-work term. A theoretical model representing a very good compromise between reliability (accuracy) and practicality (feasibility) is the B3LYP/6-311+G**//B3LYP/6-31G* approach. It provides acidities that are in good agreement with experiment and with more accurate G2 [or G2(MP2)] methods.[25−27] All calculations are performed with the GAUSSIAN 98 suite of programs.[28]

Results and Discussion

Acidity

The systems explored are shown in Figure 1, which illustrates the fact that a very large number of prototropic tautomers are possible. Their total and relative molecular enthalpies obtained by the B3LYP/6-31G* method are summarized in Table 1. It should be mentioned that the enthalpies of the tautomers are calculated at the B3LYP/6-31G* level since their relative stabilities were desired. Some pilot calculations have shown that the relative stabilities of tautomers estimated by B3LYP/6-311+G**//B3LYP/6-31G* and B3LYP/6-31G* are similar. Hence, the latter method was employed in view of the large number of tautomers, since it is more economical.

Let us consider compounds **O(*n*)**, n = 1, 2, 3 and 4, first. The reference level for each group of ten tautomers **O(*n*)t$_m$**

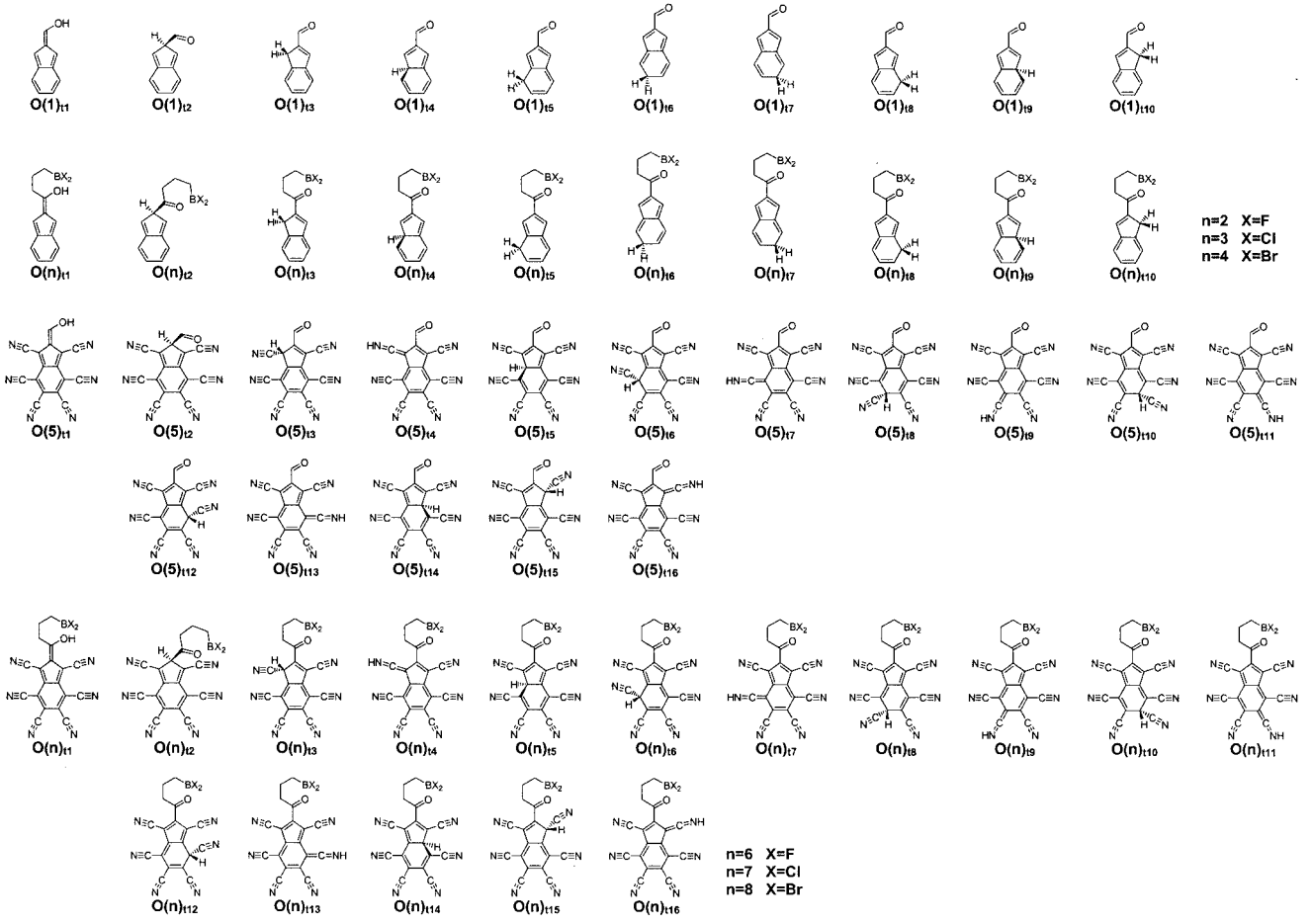


Figure 1. Proton tautomerism in substituted isobenzofulvenes

Table 1. Relative total molecular enthalpies of isobenzofulvene tautomers obtained at the B3LYP/6-31G* level of theory (in kcal/mol); relative enthalpies of the most stable tautomers are denoted in boldface

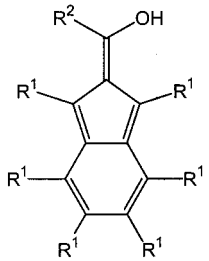
System[a]	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
$\mathbf{O(}n\mathbf{)_{t1}}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\mathbf{O(}n\mathbf{)_{t2}}$	0.5	−1.2	−7.1	−8.0	17.9	16.6	17.9	17.9
$\mathbf{O(}n\mathbf{)_{t3}}$	−26.8	−31.4	−38.7	−40.0	4.4	4.4	2.3	1.3
$\mathbf{O(}n\mathbf{)_{t4}}$	8.9	6.0	−0.5	−1.7	3.1	5.7	2.3	1.4
$\mathbf{O(}n\mathbf{)_{t5}}$	1.5	−3.4	−10.9	−12.3	28.2	29.7	28.5	27.7
$\mathbf{O(}n\mathbf{)_{t6}}$	−2.2	−5.9	−12.8	−14.1	29.1	31.0	27.8	26.4
$\mathbf{O(}n\mathbf{)_{t7}}$	−0.9	−5.1	−12.2	−13.6	17.2	19.4	14.6	13.6
$\mathbf{O(}n\mathbf{)_{t8}}$	0.0	−4.6	−11.9	−13.2	25.4	27.0	25.3	24.3
$\mathbf{O(}n\mathbf{)_{t9}}$	−10.3	6.9	0.2	−1.1	15.7	17.9	13.9	13.0
$\mathbf{O(}n\mathbf{)_{t10}}$	**−28.9**	**−32.8**	**−39.9**	**−41.2**	25.9	28.0	25.6	24.5
$\mathbf{O(}n\mathbf{)_{t11}}$	–	–	–	–	15.7	18.1	13.6	12.7
$\mathbf{O(}n\mathbf{)_{t12}}$	–	–	–	–	27.7	29.3	26.7	25.4
$\mathbf{O(}n\mathbf{)_{t13}}$	–	–	–	–	15.2	16.8	11.9	11.1
$\mathbf{O(}n\mathbf{)_{t14}}$	–	–	–	–	28.8	30.9	29.0	28.3
$\mathbf{O(}n\mathbf{)_{t15}}$	–	–	–	–	1.8	2.5	0.4	−0.3
$\mathbf{O(}n\mathbf{)_{t16}}$	–	–	–	–	**−2.4**	**−1.5**	**−7.7**	**−10.5**

[a] Total molecular enthalpies of compounds $\mathbf{O(}n\mathbf{)_{t1}}$ for $n = 1-8$ are −460.88578, −802.80670, −1523.47956, −5746.49132, −1014.32217, −1356.24335, −2076.91555 and −6299.92863, respectively (in au).

($m = 1-10$) is given by $\mathbf{O(}n\mathbf{)_{t1}}$ ($n = 1-4$) meaning that they all involve a hydroxy group, which provides the most acidic proton. Interestingly, they do not make the most stable tautomers. The latter are obtained by the hydrogen shift to the 2-position of the five-membered ring, thus forming a C(sp^3) center in $\mathbf{O(}n\mathbf{)t_{10}}$ ($n = 1-4$). An alternative route for the hydrogen shift to position C(6) in $\mathbf{O(}n\mathbf{)t_3}$ ($n = 1-4$) is only 1−2 kcal/mol less stable. It is important to note that the most acidic proton belongs either to the hydroxy group or to the C(sp^3) center, implying that the resulting conjugate base is always the same within each family of tautomers $\mathbf{O(}n\mathbf{)_{t1-t10}}$ for $n = 1-4$. In other words, their relative acidities are determined by differences in the stability of the initial acids. We would like to point out that only the most stable tautomer determines the acidity of a particular system. Nevertheless, we shall discuss the acidity of some interesting, but less stable, tautomers too, because this will shed more light on the dependence of acidity on the electronic structure of the initial acids and final conjugate bases. Sextuple substitution by the cyano group increases the number of tautomers to sixteen in families $\mathbf{O(}n\mathbf{)}$ ($n = 5$, 6, 7 and 8). A salient feature of these acids is that the most stable tautomers are formed by a hydrogen shift from the hydroxy group to the nitrogen atom thus forming a carbonyl and an imino group in tautomers $\mathbf{O(}n\mathbf{)_{t16}}$ ($n = 5-8$). Deprotonation of the imino group leads to the highest acidity. Perusal of the data presented in Table 1 reveals that positions t1, t15, t4 and t3 in families $\mathbf{O(}n\mathbf{)_{tm}}$, where $n = 5-8$ and $m = 1-16$, are quite acidic too. Another outstanding feature of the systems $\mathbf{O(}n\mathbf{)}$ for $n = 2-4$ and $n = 6-8$ is the presence of a characteristic corona ring formed by a propyl−BX_2 chain (X = F, Cl and Br) and the oxygen atom of a hydroxy or oxo group. This is a consequence of a Lewis acid (BX_2) and Lewis base (OH or =O) interaction, which is enhanced upon deprotonation (vide infra).

The deprotonation enthalpies ΔH_{acid} for characteristic systems are given in Table 2. The parent compound $\mathbf{O(1)_{t1}}$ forms a family of compounds $\mathbf{O(1)_{tm}}$ ($m = 1-10$) that are not very acidic. Tautomers $\mathbf{O(1)_{t3}}$ and $\mathbf{O(1)_{t10}}$ are considerably more stable than the others. The enthalpies of the proton abstraction from their C(sp^3) centers are 336.1 and 338.6 kcal/mol, respectively. Previous studies of basicity of neutral organic compounds have led to an interesting structural and electronic motif named the cationic corona effect. It turned out that an aminopropyl chain attached to an imino nitrogen atom N(sp^2) forms a pseudo-six-membered ring with a protonated N(sp^2) atom in the conjugate acid through an intramolecular H-bond.[29] A similar idea leads to the anionic corona effect formed by the propyl−BX_2 chain (X = F, Cl, Br) and the anionic oxygen center, which decreases the enthalpy of deprotonation for the $\mathbf{O(}n\mathbf{)_{t3}}$ position ($n = 2$, 3, 4) yielding values of 321.0, 316.9 and 315.2 kcal/mol for X = F, Cl and Br, respectively. The corresponding data for the t10 position are 322.8, 318.3 and 316.8 kcal/mol. Obviously, the Lewis acid/base interaction between BX_2 and the oxygen atom increases in the conjugate bases along the series fluorine, chlorine and bromine atoms. However, it is very important to stress that sixfold CN substitution dramatically increases the acidity of isobenzofulvenes, as evidenced by the deprotonation enthalpies for $\mathbf{O(5)_{t1}}$ and $\mathbf{O(5)_{t16}}$, which become as low as 264.5 and 268.6 kcal/mol, respectively. The corona effect further contributes to a decrease in ΔH_{acid} as illustrated by the values presented in Table 2. The most acidic compound is $\mathbf{O(6)_{t1}}$, with ΔH_{acid} equal to 260 kcal/mol, which is remarkable indeed. It is interesting to put these numbers into perspective by comparison with some well-known very strong neutral acids. For example, the experimental ΔH_{acid} values for HNO_3, H_2SO_4 and $HClO_4$ are 317.8, 299.0 and 288.0 kcal/mol, respectively. Hence, $\mathbf{O(5)_{t1}}$ and $\mathbf{O(5)_{t16}}$ surpass their acidities considerably. It is therefore fair to conclude that compounds $\mathbf{O(5)_{t1}}$, $\mathbf{O(5)_{t16}}$, $\mathbf{O(6)_{t1}}$, $\mathbf{O(6)_{t16}}$, $\mathbf{O(7)_{t16}}$ and $\mathbf{O(8)_{t16}}$ are very good candidates for highly potent neutral organic superacids.

Table 2. Acidity of isobenzofulvene derivatives calculated at the B3LYP/6-311+G**//B3LYP/6-31G* level; all values are in kcal/mol

System	R^1	R^2	Tautomer	Acidity
	H	H	$\mathbf{O(1)_{t3}}$	336.1
	H	H	$\mathbf{O(1)_{t10}}$	338.6
	H	C_3H_6–BF_2	$\mathbf{O(2)_{t3}}$	321.0
	H	C_3H_6–BF_2	$\mathbf{O(2)_{t10}}$	322.8
	H	C_3H_6–BCl_2	$\mathbf{O(3)_{t3}}$	316.9
	H	C_3H_6–BCl_2	$\mathbf{O(3)_{t10}}$	318.3
	H	C_3H_6–BBr_2	$\mathbf{O(4)_{t3}}$	315.2
	H	C_3H_6–BBr_2	$\mathbf{O(4)_{t10}}$	316.8
	CN	H	$\mathbf{O(5)_{t1}}$	264.5
	CN	H	$\mathbf{O(5)_{t16}}$	268.6
	CN	C_3H_6–BF_2	$\mathbf{O(6)_{t1}}$	259.8
	CN	C_3H_6–BF_2	$\mathbf{O(6)_{t16}}$	265.4
	CN	C_3H_6–BCl_2	$\mathbf{O(7)_{t16}}$	265.2
	CN	C_3H_6–BBr_2	$\mathbf{O(8)_{t16}}$	264.4

Structural Parameters and Electron-Density Distribution

The origin of the highly pronounced acidity of the cyano derivatives of isobenzofulvenes is interesting. It appears that it is determined by aromatization of the planar bicyclic framework by formal formation of a 10π-electron pattern in the conjugate-base anion, at least in the simplified picture. The aromatic effect is enhanced by the CN substituents as the following analysis shows. Let us consider for this purpose the structural characteristics of the parent system $\mathbf{O(1)_{t1}}$ and its sixfold substituted derivative $\mathbf{O(5)_{t1}}$. It is illustrative to compare their bond lengths with the corresponding anions $\mathbf{O(1)}_{t1}{}^{-}$ and $\mathbf{O(5)}_{t1}{}^{-}$ (Figure 2).

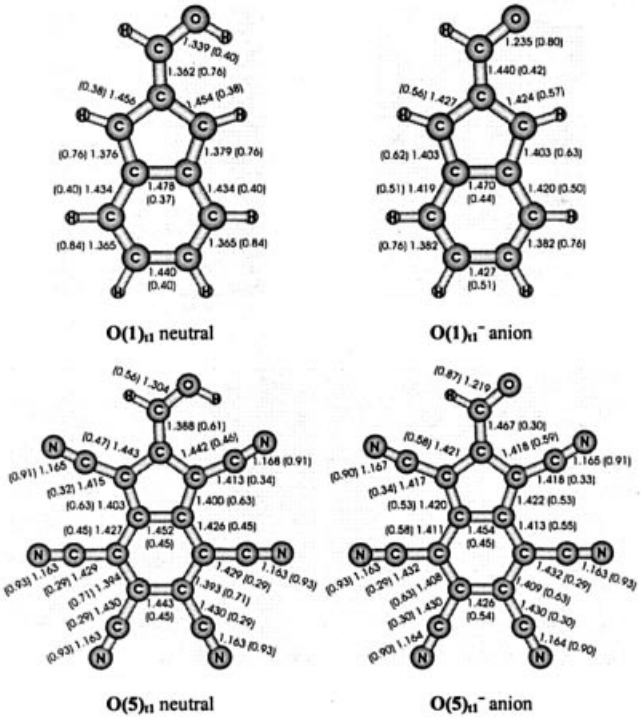


Figure 2. Selected bond lengths [Å] and Löwdin π-bond orders (in parentheses) in the characteristic compounds $\mathbf{O(1)_{t1}}$ and $\mathbf{O(5)_{t1}}$ and their anionic forms, calculated by the B3LYP/6-31G* and HF/6-31G*//B3LYP/6-31G* methods, respectively.

Deprotonation of $\mathbf{O(1)_{t1}}$ introduces the largest changes in the molecular fragment involving the cleavage center and its immediate neighborhood. Thus, the former C−O single bond attains a strong double-bond character, whereas just the contrary holds for the C=C *exo*-double bond. These structural changes are reflected also in the corresponding π-electron bond orders calculated by the Löwdin formula.[30] Hence, it turns out that the C=C *exo*-bond in $\mathbf{O(1)_{t1}}$ retains a partial double-bond character, as evidenced by the π-bond order of 0.4, and it thus forms a part of the delocalized π-electron network. Another obvious and significant feature of the $\mathbf{O(1)_{t1}}^{-}$ anion is the redistribution of the π-electron density in both coalesced rings with an apparent equalization tendency. As a consequence, the π-bond orders within the five-membered ring vary in a close range between 0.56 and 0.63, with one notable exception: the annelated C−C bond has the smallest value (0.44). The six-membered ring exhibits a much larger disparity in the π-bond orders, possessing two distal, clearly recognizable C−C bonds with pronounced localized character. Variation in the C−C bond lengths is compatible with changes in the π-electron distribution.

A sextuple CN substitution in $\mathbf{O(5)_{t1}}$ leads to an increased π-electron delocalization from the outset as compared with the parent compound $\mathbf{O(1)_{t1}}$. This is reflected both in the bond lengths and π-bond orders. The π-electron delocalization is further enhanced by deprotonation. Leaving the annelated C−C bond apart, one observes an almost perfect equalization of the C−C distances of the five-membered ring and a nearly even distribution of the π-bond orders. The same holds for the six-membered ring. Since the fused C−C bond is left practically unchanged, one is tempted to conclude that deprotonation triggers aromatization of the π-electron framework of the isobenzofulvene moiety extended on the perimeter C−C bonds. Comparison of the $\mathbf{O(1)_{t1}}^{-}$ and $\mathbf{O(5)_{t1}}^{-}$ anions indicates that such aromatization is stimulated by the electron-withdrawing CN substituents. Needless to say, the bond lengths follow the same pattern as the π-bond orders. Compound $\mathbf{O(5)_{t1}}$ is paradigmatic of other systems exhibiting high acidity studied here. Therefore, one can safely conclude that the acidity of isobenzofulvenes is a consequence of the aromaticity of the resulting conjugate bases. It is additionally amplified by a special effect embodied in the anionic corona structural and electronic motif.

The distribution of atomic charges, as retrieved by a Löwdin symmetrical orthogonalization procedure,[29] is also very instructive (Figure 3). It should be kept in mind that the distribution of the electron density in the vicinity of the atomic nuclei has profound consequences on the molecular energies.[31] It appears that even a very modest redistribution of the electron density can produce large effects. For example, consider the atomic charges in $\mathbf{O(1)_{t1}}$. It turns out that −1.55 |e| charge is partitioned over the heavy atoms at the expense of the hydrogen atoms. The lowest electron charge is placed at the H atom attached to oxygen (−0.39 |e|). This electron charge is additionally distributed over the $\mathbf{O(1)_{t1}}^{-}$ anion upon proton cleavage. The total electron charge of the ring carbon atoms is increased by only 0.33 |e| in the absolute sense, yet this small amount is scattered in a way that increases the aromatic character of isobenzofulvene, thus influencing its stability. One should resist, however, the temptation to assign a negative −1.0 |e| charge to, for example, the five-membered ring and its π-network in $\mathbf{O(1)_{t1}}^{-}$, since the actual change in the electron density is small (−0.23 |e|). Although the aromatic $(4n+2)$π-electron count is attractive and intuitively appealing, the changes, in reality, are subtler. In fact, the "number" of π-electrons distributed over the carbon atoms of the isobenzofulvene skeleton is 9.59 |e|, which is very close to the magic aromatic value of 10π-electrons and yet it is distinctly different. Similarly, redistribution of the electron density in $\mathbf{O(5)}_{t1}{}^{-}$ leads to a tiny increase in the negative charge (in an absolute sense) of the ring carbon atoms and the peripheral nitrogen

atoms. The total π-electron density placed on the carbon atoms in the isobenzofulvene moiety is 9.32 |e|. It seems that a way of spin coupling leading to equalization of the π-bond orders is more important than the formal $4n+2$ number of π-electrons.

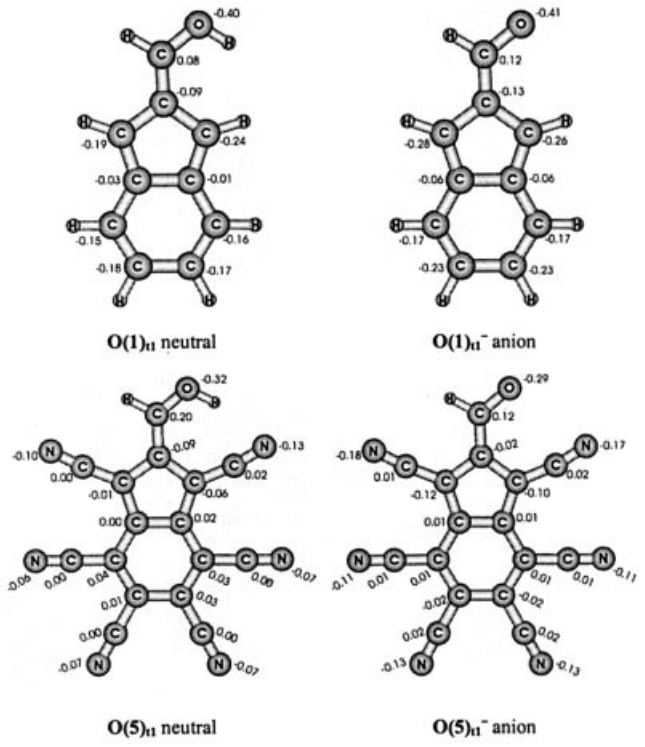


Figure 3. Selected Löwdin atomic charges in the characteristic compounds **O(1)$_{t1}$** and **O(5)$_{t1}$** and their anionic forms

Finally, we would like to comment briefly on the structural features related to the corona ring formation in some selected acids and their anions. In particular, we shall focus on the nonbonding B···O distances and changes in the pyramidalization of the BX_2 groups (X = F, Cl, Br) upon deprotonation. For this purpose a convenient definition of pyramidalization will be used:[32]

$$DP(\%) = \left[360 - \sum_{i=1}^{3} \alpha_i \right] / 0.9 \qquad (3)$$

where *DP* denotes the degree of pyramidalization and the summation goes over bond angles α_i of the pyramidal boron atom (in degrees). The calculated *DP* values are presented in Table 3. It appears that pyramidalization is increased after deprotonation in systems **O(n)$_{t10}$** (n = 2, 3, 4) and **O(n)$_{t16}$** (n = 6, 7, 8). Simultaneously, the nonbonding B···O distances are decreased, with one notable exception for **O(8)$_{t16}$**, where it remains constant. Both findings are indicative of a strengthened interaction between the BX_2 group (X = F, Cl, Br) and the oxygen atom in anions, for obvious reasons. Increased pyramidalization of the B atom implies that the "empty" hybrid orbital (HO) oriented towards the oxygen atom has higher s-content. This is energetically favorable because the "empty" HO accommodates the lone-pair electrons of the oxygen atom. It should be recalled that higher s-character implies a lower energy of

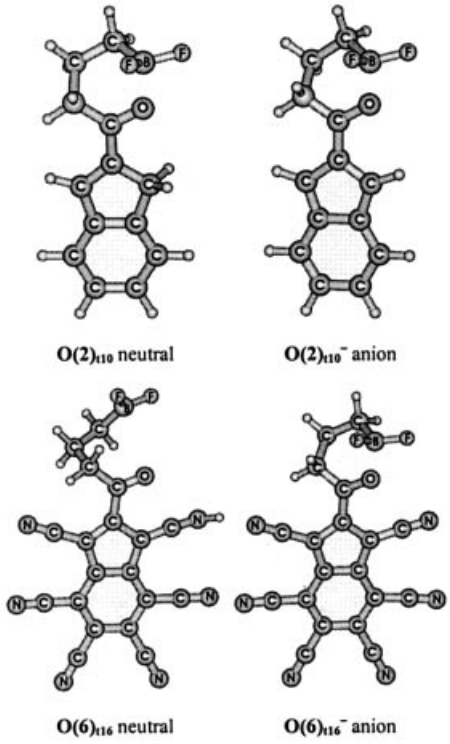


Figure 4. Orientation of the BF_2 group in some characteristic isobenzofulvene superacids and their conjugate bases

Table 3. Interatomic B···O distances and degrees of pyramidalization of BX_2 groups (X = F, Cl, Br) in some neutral isobenzofulvenes and their conjugate bases

Compound[a]	B···O bond length [Å]		Degree of pyramidalization of BX_2	
	neutral	anion	neutral	anion
O(2)$_{t10}$	1.671	1.562	16.6	25.4
O(3)$_{t10}$	1.566	1.491	22.8	31.4
O(4)$_{t10}$	1.545	1.478	24.4	33.1
O(6)$_{t16}$	3.108	1.661	0.1	17.8
O(7)$_{t16}$	1.578	1.563	19.9	24.0
O(8)$_{t16}$	1.537	1.538	21.9	25.6

[a] B3LYP/6-31G* values.

the hybrid orbital. A shortened B···O distance leads to a more intense interaction between the boron and oxygen atoms as well. The constant B···O distance in $\mathbf{O(8)_{t16}}$ and $\mathbf{O(8)_{t16}}^-$ is probably a consequence of the size of the Br atoms. The orientation of the BF_2 group in $\mathbf{O(2)_{t10}}$ and $\mathbf{O(6)_{t16}}$ as well as in their anions is shown in Figure 4.

Conclusion

It has been shown that a sextuple substitution by CN groups makes isobenzofulvene an extremely potent superacidic system. This is reflected in a very low ΔH_{acid} value of $\mathbf{O(5)_{t1}}$ of 264.5 kcal/mol. A more stable prototropic tautomer $\mathbf{O(5)_{t16}}$ is somewhat less acidic, with ΔH_{acid} equal to 268.6 kcal/mol. The anionic corona effect slightly increases acidity, which is evident if the ΔH_{acid} value of $\mathbf{O(5)_{t16}}$ is compared with the corresponding data obtained for $\mathbf{O(}n\mathbf{)_{t16}}$, where n = 6, 7 and 8. It follows that judiciously substituted isobenzofulvenes are very good candidates for neutral organic superacids. The origin of the highly pronounced acidity is identified as aromatization of the isobenzofulvene carbon framework reflected in a substantial π-electron delocalization over the C−C perimeter. This effect is dramatically amplified by the strongly electron-withdrawing CN substituents.

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