PAPER

NJC
www.rsc.org/njc

Tailoring of strong neutral organic superacids: DFT-B3LYP calculations on some fulvene derivatives

Zvonimir B. Maksić*[ab] **and Robert Vianello**[a]

[a] *Quantum Organic Chemistry Group, Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, POB 180, 10 002, Zagreb, Croatia. E-mail: zmaksic@spider.irb.hr; Fax: +385 1 4561118; Tel: +385 1 4561117*

[b] *Faculty of Natural Science and Mathematics, The University of Zagreb, Marulićev trg 19, 10 000, Zagreb, Croatia*

Received (in Montpellier, France) 12th December 2003, Accepted 8th March 2004
First published as an Advance Article on the web 10th June 2004

The design of new powerful neutral superacids is of great importance in organic chemistry. It is shown by using a reliable theoretical model that cyano derivatives of fulvene provide very good candidates for potent organic superacids. The origin of the high acidity is identified as the aromatization of the five-membered ring upon deprotonation. Their acidity is enhanced by the Lewis acid-base interaction between a –CH_2–CH_2–CH_2–BX_2 chain and the anionic O^- center in the corresponding conjugate bases. X stands here for F, Cl and Br atoms. There are good reasons to believe that the proposed neutral organic superacids are amenable to laboratory preparation.

Introduction

The generation of anions under mild reaction conditions is of great importance, because they can participate in a number of interesting and useful chemical transformations. Consequently, the design of neutral organic superacids, which easily give up a proton, is vital from both scientific and practical points-of-view. For instance, weakly coordinating anions are important in olefin polymerization[1] and seem to be an essential ingredient in new lithium battery technology.[2] Important contributions to tailoring new superacids were made by Koppel *et al.*[3] by using two scenarios. In the first, they exploited the intrinsic acidity of characteristic sites (CH, NH, OH, SH) and its amplification by some carefully chosen substituents leading to favorable field/inductive and π-electron resonance effects, which is combined with a high polarizability of the substituents applied. The second strategy is based on the Yagupolskii concept of electronic superacceptor substituent(s)[4] exemplified, for instance, by $=NSO_2CF_3$, which by replacing an oxygen doubly bonded to S, P and I atoms gives very strong superacids in the gas phase[3–5] and acetonitrile.[6] The reason behind this is that one or more highly dipolar superacceptor groups and some strongly polarizable substituents form an extended conjugated system in the corresponding conjugate bases.

Our point of departure is similar and yet distinctly different. It is given by triadic formula analysis,[7] which has shown that the higher ionization potential of an anionic conjugate base, calculated in Koopmans' frozen electron density + clamped nuclei approximation, results in stronger acidity. Obviously, very large IP^{Koop} ionization potentials are found in systems that undergo strong anionic resonance or aromatic stabilization upon deprotonation in accordance with chemical intuition. Therefore, a potentially useful strategy in constructing strong neutral organic superacids is to find systems that would exhibit pronounced anionic aromatization in the corresponding conjugate base forms. The second condition to be fulfilled is that they are prone to chemical synthesis. We feel that both prerequisites are satisfied by some judiciously selected fulvenes discussed here.

DOI: 10.1039/b316290g

Theoretical procedures

A theoretical model offering a very good compromise between accuracy and practicality (feasibility) is B3LYP/6-311+G**//B3LYP/6-31G*, which provides acidity values in good agreement with experiment and more accurate G2 [or G2(MP2)] methods.[8–10] The gas phase acidity, defined as the deprotonation enthalpy (ΔH_{acid}) of the reaction

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

is calculated as:

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

where ΔE_{acid} is the change in the total energy, which includes the zero point energy and the finite temperature (298.15 K) corrections, whilst $\Delta(pV)$ stands for the pressure–volume work term. All calculations were performed by the GAUSSIAN 98 suite of programs.[11]

Results and discussion

Acidity

The chemistry of fulvenes is well-known.[12,13] The systems explored are depicted in Fig. 1, which illustrates a very large number of possible prototropic tautomers. Their relative total enthalpies obtained at the B3LYP/6-31G* level are given in Table 1. The most stable tautomer for compounds $n = 1$–4 is $O(n)_{t6}$, where the hydrogen atom is shifted from the hydroxy group to the five-membered ring, thus forming a C(sp^3) center at the *ortho* position. For systems $n = 5$, 6 and 7 the most stable tautomer involves the OH group, which at the same time is the most acidic site (*vide infra*). Finally, the molecule including the BBr_2 group yields $O(8)_{t10}$ as the most stable structure. It is important to realize that the differences in total molecular enthalpies between the most stable and other tautomers for each family of compounds are large with one notable exception: the difference between $O(7)_{t1}$ and $O(7)_{t10}$ is only 0.8 kcal mol^{-1}. This implies that we have to consider only

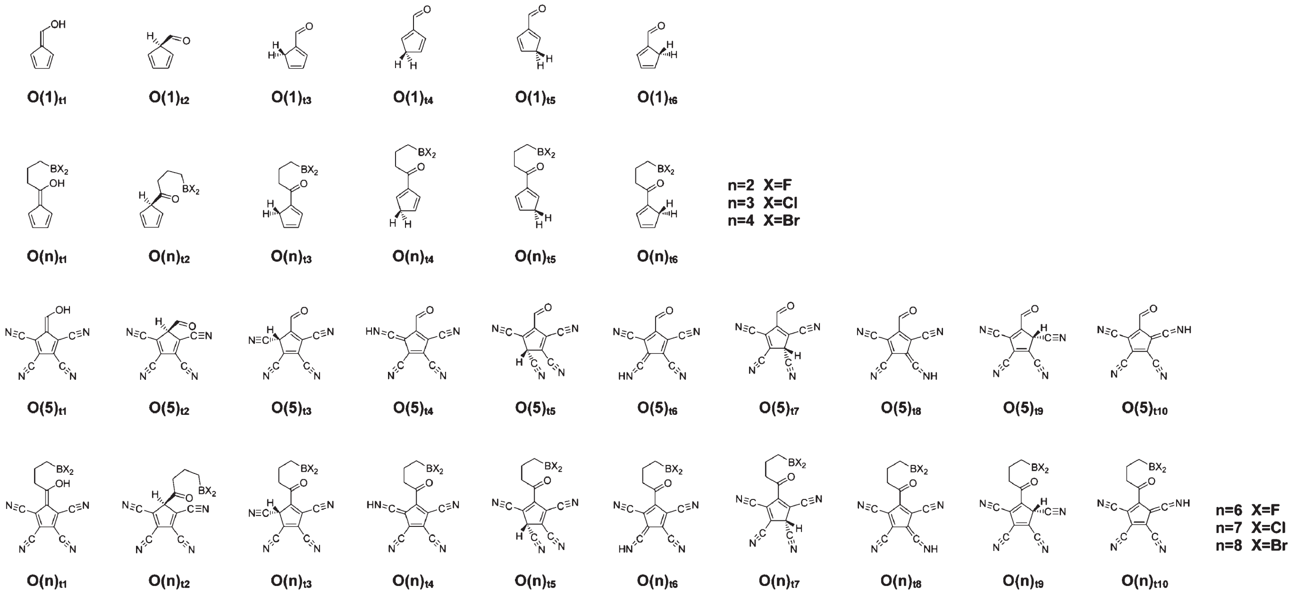


Fig. 1 Proton tautomerism in substituted fulvenes.

the deprotonation of the most stable tautomers and treat O(7)$_{t1}$ and O(7)$_{t10}$ as a special case. It is important to point out that the substituents R_1 and R_2 were chosen as the most favourable ones after extensive calculations on other fulvenes involving a large variety of substituent groups. Molecules involving the hydrogen atom (R_1, R_2 = H) serve as a reference.

Let us discuss the results obtained for acids O(n)$_{tm}$ for $n = 1$–4 and $m = 1$–6 first. It is interesting to observe that the proton that jumps from the hydroxy group to the C(2) position of the five-membered ring is the most acidic one. The reason is that the corresponding anions are the same, regardless of whether the cleaved proton comes from the hydroxy group or the C(sp^3) center at position 2 within the ring. It follows as a corollary that the difference in acidity between O(n)$_{t1}$ and O(n)$_{t6}$ ($n = 1$–4) is given by the difference in the total energies of the initial acids (Table 1). It is also remarkable that all prototropic tautomers involving the ring C(sp^3) centers are less acidic than the parent molecules containing the OH group. Hence prototropic tautomerism diminishes acidity, but some of the examined systems still exhibit highly pronounced acidity as the forthcoming considerations will conclusively show.

The parent fulvene O(1)$_{t1}$ is not a very acidic compound (ΔH_{acid} = 326.3 kcal mol^{-1}). Its acidity is enhanced by the anionic corona effect in full analogy with the corresponding phenomenon observed earlier in some superbases upon protonation.[14] Whereas in the protonated forms of superbases the aminopropyl chain forms a pseudo-aromatic six-membered ring moiety with the protonated atom by formation of a relatively strong intramolecular hydrogen bond, anions of compounds O(2)$_{t1}$, O(3)$_{t1}$ and O(4)$_{t1}$ form a pseudo-six-membered ring with the propyl–BX_2 (X = F, Cl, Br) chain *via* interaction between the Lewis acid fragment (BX_2) and the Lewis base center (O^- anion). This kind of stabilization of the resulting conjugate bases increases acidity by some 32 kcal mol^{-1} along the series. It should be mentioned that these gas phase results might be somewhat modified in highly polar solvents like water. For example, a small H_2O molecule could be interpolated between the BX_2 group and OH (or O^-) center. However, a relatively small influence is expected in aprotic solvents of moderate polarity like DMSO. Hence, all conclusions should hold in principle for solutions such as DMSO and acetonitrile.

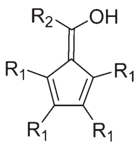
Similar behavior is found in the corresponding most stable tautomers O(n)$_{t6}$ (n = 1, 2, 3, 4), which are more stable in their neutral forms than the parent compounds (Table 1) and consequently are less acidic. The four-fold substitution of the parent fulvene five-membered ring by the CN group has a dramatic influence on the acidity (Table 2), which is substantially increased in systems O(n)$_{t1}$ (n = 5, 6, 7). Apparently, the electron-withdrawing CN groups, in combination with the anionic

Table 1 Relative total molecular enthalpies of fulvene tautomers obtained at the B3LYP/6-31G* level of theory (in kcal mol^{-1}). Negative values indicate more stable tautomers. Relative enthalpies of the most stable tautomers are denoted with boldface numbers.[a]

Tautomer	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
O(n)$_{t1}$	0.0	0.0	0.0	0.0	**0.0**	**0.0**	**0.0**	0.0
O(n)$_{t2}$	−2.0	−4.0	−9.7	−10.7	13.2	10.6	10.3	11.6
O(n)$_{t3}$	−9.2	−14.1	−21.3	−22.7	16.5	14.3	12.3	11.9
O(n)$_{t4}$	−8.6	−11.7	−18.0	−19.3	13.1	12.5	8.9	8.7
O(n)$_{t5}$	−6.9	−10.4	−17.1	−18.4	15.1	13.9	13.2	13.0
O(n)$_{t6}$	**−11.2**	**−15.5**	**−22.7**	**−24.0**	11.4	10.4	6.9	6.7
O(n)$_{t7}$	—	—	—	—	16.0	14.6	13.5	13.4
O(n)$_{t8}$	—	—	—	—	11.4	9.8	5.7	5.6
O(n)$_{t9}$	—	—	—	—	14.3	12.2	10.2	9.8
O(n)$_{t10}$	—	—	—	—	7.5	6.5	0.8	**−5.3**

[a] Total molecular enthalpies of compounds O(n)$_{t1}$ for n = 1–8 are −307.30368, −649.22461, −1369.89750, 5592.90918, −676.27396, −1018.19463, −1738.86698, −5961.87974, respectively (in au).

Table 2 Acidity of fulvene derivatives calculated at the B3LYP/6-311+G**//B3LYP/6-31G* level. All values are in kcal mol^{-1}.

System	R_1	R_2	Most stable tautomer	Acidity
	H	H	O(1)$_{t6}$	333.6
	H	C_3H_6–BF_2	O(2)$_{t6}$	312.4
	H	C_3H_6–BCl_2	O(3)$_{t6}$	306.6
	H	C_3H_6–BBr_2	O(4)$_{t6}$	304.6
	CN	H	O(5)$_{t1}$	277.4
	CN	C_3H_6–BF_2	O(6)$_{t1}$	271.4
	CN	C_3H_6–BCl_2	O(7)$_{t1}$	266.1
	CN	C_3H_6–BCl_2	O(7)$_{t10}$	264.1
	CN	C_3H_6–BBr_2	O(8)$_{t1}$	263.1
	CN	C_3H_6–BBr_2	O(8)$_{t10}$	265.2

corona effect, lead to neutral organic superacids exhibiting unprecedented strengths as evidenced by the very low deprotonation enthalpies of 277.4 and 265.2 kcal mol^{-1} for $O(5)_{t1}$ and $O(8)_{t1}$, respectively. It is noteworthy that in compounds $O(n)_{t1}$ (n = 5, 6, 7) the hydroxy proton is the most acidic one. This is not the case for the propyldibromoborane chain compound, for which two tautomers $O(8)_{t1}$ and $O(8)_{t10}$ show similar acidities. The former possesses a hydroxy group, whereas the latter involves a carbonyl group and an imino group attached to the five-membered ring. The corresponding ΔH_{acid} values for $O(8)_{t1}$ and $O(8)_{t10}$are 263.1 and 265.2 kcal mol^{-1}, respectively. Since the difference is only 2.1 kcal mol^{-1}, which is slightly below the estimated error of our theoretical procedure, it is justified to ignore this distinction. Similarly, the propyldichloroborane side chain leads also to two tautomers, $O(7)_{t1}$ and $O(7)_{t10}$, with corresponding acidities of 266.1 and 264.1 kcal mol^{-1}, respectively. It follows as a corollary that $O(5)_{t1}$, $O(6)_{t1}$, $O(7)_{t1}$, $O(7)_{t10}$, $O(8)_{t1}$ and $O(8)_{t10}$ represent powerful neutral organic superacids.

Structural parameters

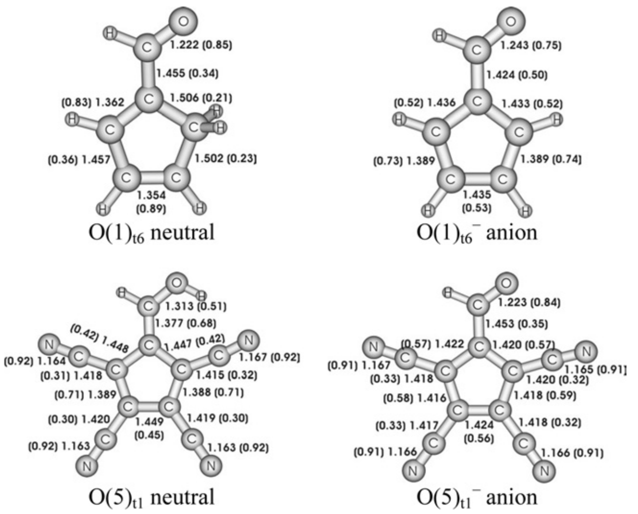
The question arises why the cyano derivatives of fulvene are so strongly acidic? The answer is given by the fact that the five-membered ring is aromatized upon deprotonation, which is assisted by CN groups. This is illustrated by comparison of the bond distances and Löwdin π-bond orders,[15] as calculated by the HF/6-31G*//B3LYP/6-31G* method, in $O(1)_{t6}$ and $O(5)_{t1}$and their conjugate bases $O(1)_{t6}^{-}$ and $O(5)_{t1}^{-}$, which are selected as paradigmatic cases (Fig. 2). Inspection of the data displayed in Fig. 2 shows that the cyclopentadiene ring in $O(1)_{t6}$ is transformed into a delocalized cyclopentadienyl anion moiety. However, there is a significant asymmetry in the C–C bonds, two of them being more localized than the remaining three C–C bonds. This is reflected in their bond distances and the corresponding Löwdin π-bond orders. The latter assume two characteristic values, 0.74 and 0.52, in the five-membered ring of the anion. It is also noteworthy that the exo-C–C bond carrying the carbonyl group is shorter in the $O(1)_{t6}^{-}$ anion, possessing an increased π-bond order relative to the neutral parent compound (0.50 *vs.* 0.34). Undoubtedly, there is an appreciable amount of anionic resonance effect triggered by deprotonation. The resonance effect is increased to a large extent in the $O(5)_{t1}$ anion, where it is evident that deprotonation leads to almost perfect equalization of the bond lengths in the five-membered ring accompanied by very similar π-bond orders, which vary between 0.56 and 0.59.

It is interesting to observe that the change in the π-bond orders in $O(5)_{t1}^{-}$ along the C–C≡N fragments are very small and yet they have far-reaching consequences in enhancing acidity. The π-bond order of the π-bond perpendicular to the molecular plane of the cyano group is diminished by 0.01, whilst that in the C–C single bond emanating from the five-membered ring and carrying the cyano group has π-bond orders increased on average by 0.02 upon deprotonation. This is indicative of the anionic resonance effect, which places some π-electron density on the peripheral nitrogen atoms, thus distributing the negative charge over the whole molecule. The equality of the π-bond orders over the five-membered ring shows that the resonance structure involving the C–O^{-} single bond is just as important. The charge redistribution in the initial acids and their conjugate bases is illustrated by Fig. 3, where selected Löwdin atomic charges are given. In the $O(1)_{t6}$ anion the carbon atoms of the ring increase their electron density, assuming an almost even distribution of charge. It is remarkable that the deprotonated carbon atom has a lesser electron density than at the C(sp^{3}) center in $O(1)_{t6}$. In addition, the charge density on the oxygen atom of the carbonyl group increases by −0.15 e. A somewhat different situation occurs upon deprotonation of $O(5)_{t1}$. The carbonyl oxygen retains its electron density upon proton release. It turns out that the largest portion of the electron density in anion $O(5)_{t1}^{-}$ is distributed over the nitrogen atoms in the cyano groups, whereas the negative charge of the carbons in the five-membered ring increases in the absolute sense, albeit to a very small extent. It follows that there is not a single anionic center but rather a distribution of the density of the unpaired electron over the peripheral parts of the $O(5)_{t1}$ anion.

As a final point we would like to discuss the pyramidalization of the BX_2 group. For this purpose a suitable definition of the pyramidalization is necessary. It is given by:[16]

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

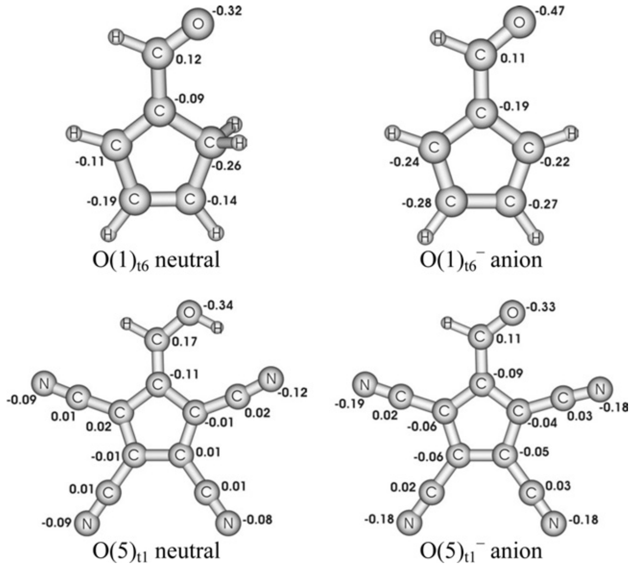
where DP stands for the degree of pyramidalization and the summation is over the bond angles α_i of the pyramidal boron atom. The calculated degree of pyramidalization is given in Table 3. Perusal of the data reveals that, as a rule, pyramidalization is considerably increased in anions. Simultaneously



$O(1)_{t6}$ neutral $O(1)_{t6}^{-}$ anion

$O(5)_{t1}$ neutral $O(5)_{t1}^{-}$ anion

Fig. 2 Selected bond distances (in Å) and Löwdin πp bond orders (given within parentheses) calculated by the B3LYP/6-31G* and HF/6-31G*//B3LYP/6-31G* methods, respectively, in the characteristic compounds $O(1)_{t6}$ and $O(5)_{t1}$ (neutral and anionic forms).



$O(1)_{t6}$ neutral $O(1)_{t6}^{-}$ anion

$O(5)_{t1}$ neutral $O(5)_{t1}^{-}$ anion

Fig. 3 Selected Löwdin atomic charges in the characteristic compounds $O(1)_{t6}$ and $O(5)_{t1}$ (neutral and anionic forms).

Table 3 Interatomic B···O distances and DPs in neutral acids and their conjugate bases.

	B···O bond length/Å		Degree of pyramidalization of BX_2 group (%)	
	Neutral	Anion	Neutral	Anion
$O(2)_{t6}$	1.669	1.542	16.7	27.3
$O(3)_{t6}$	1.566	1.476	22.7	33.1
$O(4)_{t6}$	1.546	1.462	24.4	35.0
$O(6)_{t1}$	2.906	1.667	0.0	18.0
$O(7)_{t1}$	2.993	1.543	0.2	25.9
$O(8)_{t10}$	1.519	1.524	24.4	27.6

the B···O distances are decreased in the anionic species in an apparent tendancy to increase the Lewis acid-base interaction. The decrease in the B···O distance is particularly dramatic in the $O(6)_{t1}$ and $O(7)_{t1}$ systems, being 1.24 and 1.45 Å, respectively. Pyramidalization of the B atom in the $O(2)_{t6}^-$ and $O(6)_{t1}^-$ anions taken as illustrative examples (Fig. 4) is a consequence of a transfer of electron density from the oxygen lone pair to the boron sp^3 hybrid orbital. It is clear that the sp^3 hybrid orbital is not only energetically more favourable in accommodating the electron density than a pure p-orbital, but it increases in addition the overlap between the $B(sp^3)$ and $O(sp^3)_{lp}$ hybrids (the subscript lp denotes a lone pair).

Concluding remarks

To summarize, the cyano derivatives of fulvene are excellent candidates for potent organic superacids, which might play an important role in acid-base chemistry. Their acidity is further amplified by the propyldihalideborane side chain, which forms a pseudo-six-membered ring with the oxygen anion *via* a Lewis acid-base interaction. It is noteworthy that the length of the propyl group is optimal. The ethyl and buthyl fragments substituted by BF_2, BCl_2 and BBr_2 groups lead to compounds exhibiting weaker acidity. In spite of this, they can be useful too in providing rungs on the acidity ladder once they are prepared. We believe that the compounds discussed here are amenable to laboratory preparations, since some similar systems have already been synthesized.[17]

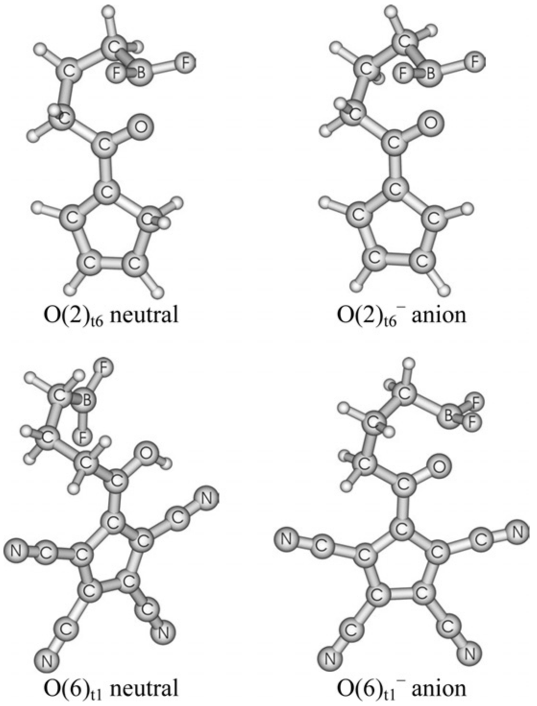

$O(2)_{t6}$ neutral
$O(2)_{t6}^-$ anion
$O(6)_{t1}$ neutral
$O(6)_{t1}^-$ anion

Fig. 4 Orientation of the BF_2 group in some characteristic fulvene superacids and their conjugate bases.

Acknowledgements

We thank the John von Neumann Institut für Computing des Forschungszentrums Jülich for allocation of computer time within the project "The Hydrogen Bond and a Spontaneous Proton Transfer Between Superacids and Superbases".

References

1 A. M. Thayer, *Chem. Eng. News.*, 1995, **73**, 15.
2 K. Sappelt, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1025.
3 I. A. Koppel, R. W. Taft, F. Anvia, S.-Z. Zhu, L.-Q. Hu, K.-S. Sung, D. D. DesMarteau, L. M. Yagupolskii, Y. L. Yagupolskii, N. V. Ignat'ev, N. V. Kondratenko, A. Y. Volkovskii, V. M. Vlasov, R. Notario and P.-C. Maria, *J. Am. Chem. Soc.*, 1994, **116**, 3047.
4 L. M. Yagupolskii, V. I. Popov, N. V. Pavlenko, R. Y. Gavrilova and V. V. Orda, *Zh. Org. Khim.*, 1986, **22**, 2169.
5 I. A. Koppel, P. Burk, I. Koppel and I. Leito, *J. Am. Chem. Soc.*, 2002, **124**, 5594.
6 L. M. Yagupolskii, V. N. Petrik, N. V. Koudratenko, L. Suoväli, I. Kaljurand, I. Leito and I. A. Koppel, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1950.
7 Z. B. Maksić and R. Vianello, *Chem. Phys. Chem.*, 2002, **3**, 696.
8 B. J. Smith and L. Radom, *Chem. Phys. Lett.*, 1995, **245**, 123.
9 G. N. Merrill and S. R. Kass, *J. Phys. Chem.*, 1996, **100**, 17 465.
10 I. A. Koppel, P. Burk, I. Koppel, I. Leito, T. Sonoda and M. Mishima, *J. Am. Chem. Soc.*, 2000, **122**, 5114.
11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUSSIAN 98 (Revision A.10)*, Gaussian, Inc., Pittsburgh, PA, 2001.
12 J. H. Day, *Chem. Rev.*, 1953, **53**, 167.
13 G. H. McCain, *J. Org. Chem.*, 1958, **23**, 632.
14 B. Kovačević, Z. Glasovac and Z. B. Maksić, *J. Phys. Org. Chem.*, 2002, **15**, 765 and references cited therein.
15 P. O. Löwdin, *J. Chem. Phys.*, 1950, **18**, 365.
16 Z. B. Maksić and B. Kovačević, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2623.
17 M. Kotora, H. Matsumura, G. Gao and T. Takahashi, *Org. Lett.*, 2001, **3**, 3467.