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On the stability of methyl cations with aromatic substituents. Theoretical approach

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Abstract

The extreme stability of methyl cations surrounded by certain aromatic fragments was studied using density functional theory methods. The pK_{R+}, aromaticity, ionization potential and dipole moment of tris[6-(dimethylamino)-1-azulenyl]methyl [**1**] and 2,6,10-tris(dimethylamino)trioxatriangulenium [**2**], as well as the corresponding for crystal violet [**3**] and *tert*-butanol [**4**], these last as the reference precursors of stable carbenium, were calculated and the results were found to be in agreement with experimental results previously reported. Furthermore, the calculations suggest that the large stability is a direct consequence of inductive effects as well as the intrinsic aromaticity of the branches as measured by the HOMA (harmonic oscillator model of aromaticity) method.
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Keywords: Methyl cations; Stability; Aromaticity; Inductive effect; Theoretical calculations

1. Introduction

The great stability of carbenium ions has been an important theme of study for several years [1], the main feature to consider for this phenomenon is the capability of the substituents to disperse the positive charge. A simple CH_3 group substituted to the central methyl increases to an important degree the stability of the cation. The presence of directional orbitals can account for this stability; therefore, a carbon atom with available atomic p orbitals is an adequate option for charge delocalization.

The existence of different kinds of bonds in organic fragments implies different hybridization and in a concomitant way different delocalization pathways, since the electronic flow can be improved in addition to σ framework with the inclusion of π bonds. Therefore, the nature of the substituent is crucial for the stability of a particular carbenium ion.

The π framework of an aromatic ring can be an excellent candidate to produce the suggested charge delocalization.

However, Larsen and his co-workers [2] indicated on the base of experimental results, that the stability of a tertiary cation in an acid solution, in some cases decreases from alkyl substituted species to the aryl ones. They suggested that this phenomenon can be best explained by a careful study of the solvation influence and the inductive effect associated with both kinds of structures. Arnett [3] suggested that the behaviour is predicted by classical theory, i.e. aryl substituted ion is more stable than the alkyl substituted one in the gas phase.

All these features have been matter of discussion for several years, however, there are certain kinds of molecules that have been experimentally studied, in particular tris[6-(dimethylamino)-1-azulenyl]methyl [4] [**1**], 2,6,10-tris(di-methylamino)trioxatriangulenium [5] [**2**], crystal violet [6] [**3**], and *tert*-butanol [**4**] [3] (see Fig. 1) have shown large pK_{R+} values in solution during the process of the formation of the corresponding carbenium ions [3–6]. In all cases, the substituents to the central carbon atom that bear the positive charge, are aromatic with the exception of the case [**4**].

The aim of this work is to study by theoretical methods the nature of the molecules that show the behaviour described above looking for the reasons that cause the exceptional stability of the corresponding cations. In this sense, the geometry of the carbinols of the molecules cited

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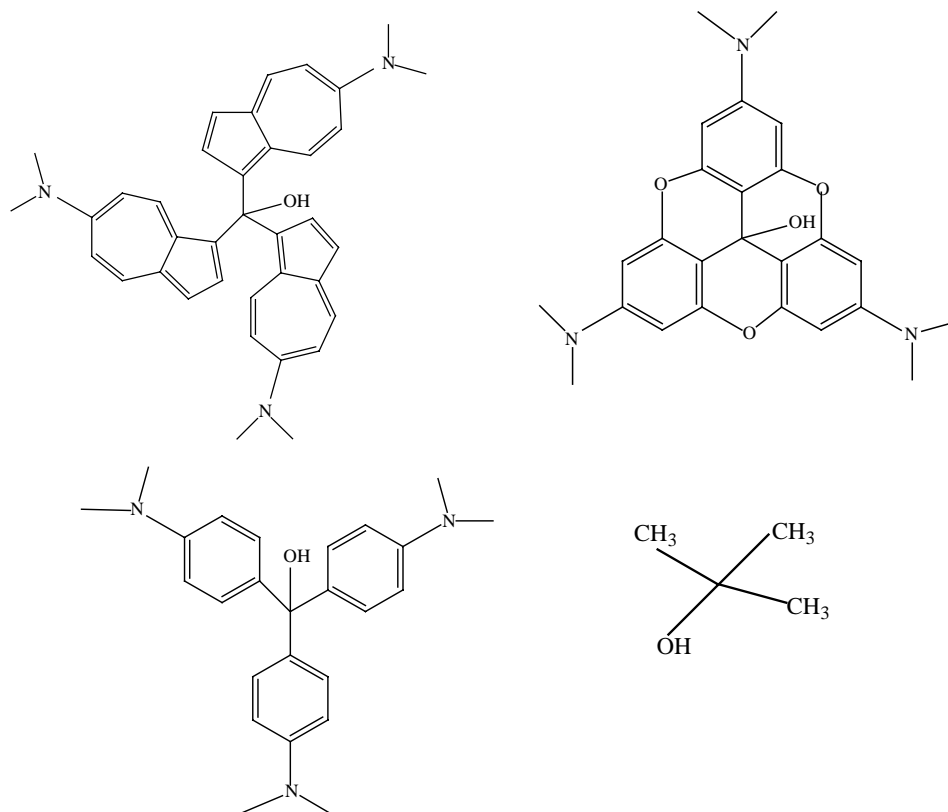*E-mail address:* salcedo@servidor.unam.mx (R. Salcedo).

Fig. 1. Molecules under study.

above was fully optimized, their thermodynamic values were determined and with this information the pK_{R+} values were calculated in all the cases and compared with those obtained by experimental methods previously cited. Several properties as delocalization, aromaticity, inductive effects and ionization potentials were investigated to establish the source about the stability of the named intermediated.

2. Methods

All structures, the neutral species as well as the corresponding cations, were optimized in the gas phase using the Jaguar 4.0 package [7a]. A pure DFT method containing the Becke's gradient corrections [8] for exchange and Perdew–Wang's for correlation [9] were used for the optimization of all of the geometries and the energy evaluation, all calculations were performed using the 6-31G** basis set. Frequencies calculations were done at the same level of theory to confirm that the optimized structures were at minima of the potential surfaces. These frequencies were then used to evaluate the zero-point vibrational energy, the thermal vibrational corrections to the enthalpy and Gibbs free energy. The bond lengths of the optimized structures were used for the harmonic oscillator model of aromaticity (HOMA) method [10] used for the study of aromaticity. The natural bond orbital (NBO) method for atomic charge calculations was chosen

considering its correspondence with the chemist's Lewis structure representation, describing appropriately the molecular environment and consequently the electron density. The polarizability, α, was calculated according to the equation shown below, as the arithmetic average of the three diagonal elements of the polarizability tensor

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

where α_{xx}, α_{yy}, and α_{zz} values are obtained through the same frequencies calculations performed by means of Jaguar 4.0.

The solvation thermodynamic properties were obtained at the same level of theory by the Poisson–Boltzmann method [7b,c] included in the same Jaguar 4.0 software package. In these cases, it was considered a dielectric constant of 63.27 D that corresponds to the 50% aqueous acetonitrile solution was used by Laursen in his experimental probes [5]. The zero-point vibrational energy corrections and entropic contributions calculated for the solvation-phase geometries were used throughout.

The pK_{R+} is defined by

$$pK_{R+} = -\log K_{R+} = \Delta G^0_{R+}/2.303RT$$

where G^0_{R+} are the free energies in solution of the neutral and the cationic species in each case, considering the equilibrium between the species R^+/ROH as was suggested early [11a]. Therefore, a large pK_{R+} index indicates a small K_{R+} value and, in turn, a higher stability of the carbocation.

3. Results and discussion

The molecules under study are shown in Fig. 1. The tris[6-(dimethylamino)-1-azulenyl]methyl [**1**] was synthesized by Asao and co-workers [4] whilst they were looking for a substance that could provide stable carbocations. On the other hand, 2,6,10-tris(dimethylamino)-trioxatriangulenium [**2**], is the perdiethylamino derivative of the popular molecule known as trioxotriangulenium (TOTA) [12] and was first prepared by Laursen and co-workers [5]. Crystal violet [**3**] is a more popular compound classified as a dye. It has found wide application in analytical chemistry and it plays an important role in textile and laser technology. It has been included in this study because it has the possibility to generate a very stable carbocation. Similarly, calculations of *tert*-butanol [**4**] and the *tert*-butyl cation are included for reasons of comparison of the stability of this tertiary cation with the others included in this analysis.

It has been suggested [2] that the main differences among all the molecules that can yield a stable carbocation are the size, the resonance interactions, inductive effects, and the polarizabilities. Some of these effects are analyzed in this study in an attempt to find an explanation of the large stability, as well as, the differences in stability among these molecules.

We can expect that the effect of size is not of great importance in the present study since the original suggestion [2] was made with respect to the comparison between phenyl and methyl substituents where the difference in size is large, but in the present case this difference is not so marked; therefore, this aspect is not considered. On the other hand, the present study considers mainly aromatic substituents and hence this feature is added to the group of factors mentioned above.

Each of these molecules has different characteristics, which result in each specific behaviour, for this reason they are studied and described separately with a final global analysis. The results concerning molecules [**3**] and [**4**] are intercalated among the others, and in all cases a comparison is made.

3.1. Compound [*1*]

The group of Asao has produced several reports in which the synthesis and characteristics of (1-azulenyl)methyl cations are described [11]. Nitta and Naya [13] have worked on doubly charged cations in similar compounds. In general, all structures investigated by these groups have shown the particular characteristic of being capable of generating very stable carbocations. Compound [**1**] gives the species with the highest value of pK_{R+}, and for this reason it is included in the present study.

First, the pK_{R+} value for the ionization reaction of the corresponding carbinol was estimated using the reaction shown in Scheme 1. The products are the carbocation under

$$ROH + H^+ \rightarrow R^+ + H_2O$$
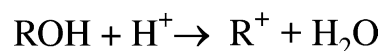
Scheme 1. Dissociation reaction of the molecules under study.

study and the H_2O molecule. (These values and others of interest are shown in Table 1 for all considered compounds).

The pK_{R+} of carbocation from **1** was obtained following the procedure described in Section 2. The value obtained was 21.9 which is comparable with the 24.3 value obtained by Asao [4]. Some differences could be expected between experimental value and the theoretical one because the original determination by Asao was performed spectrophotometrically in DMSO/water whereas the solvent acetonitrile/water was simulated in the present case. However, the result is close to that reported by Asao, to validate the other determinations. The same procedure was applied to the case of *tert*-butyl cation from [**4**] which shows a value of 12.8 in comparison to 14.7 reported by Arnett [3].

The values of aromaticity of the neutral and ionic forms were obtained by means of the HOMA method [10]. This method was chosen because it is expected that the main differences in aromaticity could be due to geometrical factors, and in this case HOMA is the best method for such an analysis. The results are shown in Fig. 2, the optimized geometries in all cases were sufficient to reach a high degree of local symmetry for the azulenyl fragments. Therefore, in neutral and the charged species, the bond lengths for each of the corresponding substituents was practically the same in each individual molecule, but there were significant differences between the neutral and ionized forms and it is exactly this difference which we attempt to evaluate.

The aromaticity value was estimated for both the seven and five membered rings. The result (Fig. 2) for one azulenyl substituent in the molecule is the same for every other azulenyl fragment, as was explained in the last paragraph in terms of bond lengths. It is interesting to note that the aromaticity of the seven membered ring is slightly large than that of the five membered ring, and it should be noted that this order is contrary to that found for free azulene [14]. This phenomenon can be explained by the fact that the seven membered ring has a strong electronic donor substituent. Furthermore, the five membered ring is bond to the atom, which generates the carbocation in the neutral species or bonded to the carbocation itself in the ionic case.

Table 1
Calculated values of some interesting variables

Compound	ΔG_{reac} (cal/mol)	pK_{R+}	μ (Debyes)	α (Å³)
1	−29,825.4	21.9	5.94[a], 7.10[b]	67.9[b]
2	−23,833.01	17.5	1.43[a], 0.2[b]	45.1[b]
3	−10,622.7	7.8		
4	−17,432.2	12.8		
TOTA	−11,140.3	8.18	0.05[a], 0.002[b]	28.3[b]

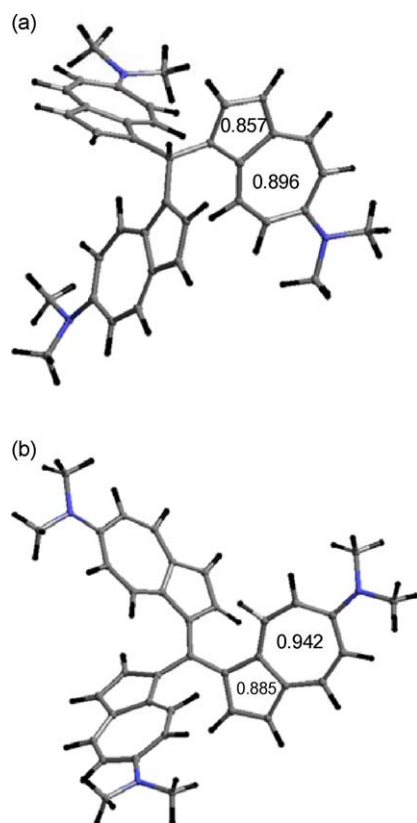[a] Neutral species.
[b] Ionized species.

Fig. 2. HOMA results for: (a) molecule [1] and; (b) the corresponding cation.

These two factors explain why there is a change in the polarization and therefore in the aromaticity.

The aromaticity is slightly increased in the case of the ionic form in a similar way in which the free azulene has a tendency to form a zwitterion that favours the more aromatic configuration. Azulene has been theoretically investigated at many computational levels [15] and it has been established that in the ground state a zwitterionic structure is favoured with a negative charge density on the five membered ring and a positive charge density on the seven membered ring. This behaviour comes from the tendency of both rings to attempt to reach an aromatic configuration. Thus, the result is the formation of a cyclopentadienyl anion from the five membered ring and a tropyllium cation from the seven membered ring. Therefore, the formation of the carbenium ion favours the dispersion of the positive charge in the seven membered ring as was suggested by Asao [4] giving a more stable configuration.

This phenomenon helps in the explanation of the stabilization of the carbenium ion but this is not enough to explain why the same molecule without -N(CH$_3$)$_2$ substituents does not show the same strong effect. For this reason, the unsubstituted molecule was calculated at the same theoretical level and the corresponding pK_{R+} was obtained. The value was 9.58 and this compares well with 11.3 reported by Asao [4]. With this result it is possible to confirm that the aromaticity is a phenomenon that

collaborates to give stabilization due to the contribution of the delocalized π framework. This is a special case because the particular polarization in this molecule helps to improve the stability, however, this result is not enough to completely clarify the situation, and for this reason other factors will be considered.

Another phenomenon to evaluate is the polarizability. This effect is particularly notorious in the case of aromatic fragments because the framework of double bonds can be rearranged yielding a polarized structure that can be thought of as a quinoidal ring in the case of a single six member aromatic ring or as a species as such that shown in Fig. 3 for carbocation from [1]. In this case, the NBO population analysis given by the DFT calculation shows a strong negative charge density (-0.88) on the nitrogen atoms and a positive charge density (1.1) on carbon atoms bond to the amino substituent in the carbenium structure. These results contrast with those of the neutral structure in which the charge density values are near zero. Therefore, the phenomenon of polarizability accounts in an important way for the dispersion of the charge.

Larsen [2] suggested that one of the important effect in dispersion of the charge should be the inductive effect. The evaluation of this feature is not direct. By definition, the inductive effect is the polarization of one bond caused by the polarization of an adjacent bond due to the intrinsic electronegativity of the involved particles [1]. This polarization is difficult to estimate in complicated molecules such as those considered here, therefore, the evaluation was made in two parts, one that consider the whole effect indirectly by the study of the molecular dipole moment and other one in which the influence of the -N(CH$_3$)$_2$ group is analyzed.

The dipole moments of the neutral molecule with -N(CH$_3$)$_2$ substituents and the molecule unsubstituted are 5.94 and 2.34 D, respectively. Considering that the dipole moment is the vector sum of the individual bond moments, which are estimated as the product of the distance and charge, this sum can indirectly quantify the change in the inductive effect. The result shows that this effect is greater
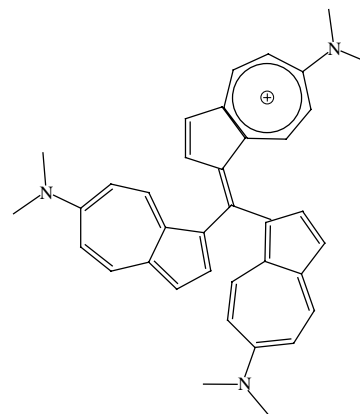

Fig. 3. The resonance structure of carbocation from [1] with the formation of a tropyllium ring.

for the substituted molecule. However, the same analysis for the corresponding carbenium ions is dramatic, the values are 7.10 D for the substituted species and 2.8 D for the unsubstituted one. This suggests that high electronic density is concentrated on the more electronegative nitrogen atom, making available its non-bonding electrons. We can note that the inductive effect is very important as suggested by Larsen. This last result cannot be conclusive because dipole moments strongly depend on the particular coordinates. The best procedure for checking these trends is to calculate the intrinsic polarizability. The results keep the same tendency, the polarizability values for the charged species are 67.9 Å^3 for the substituted ion and 51.5 Å^3 for the unsubstituted one.

Additionally, the influence of the $-N(CH_3)_2$ substituents is important in other contexts. The vertical ionization potential values of both the substituted and unsubstituted species were evaluated (Koopmans theorem) and we found that there is a significant difference, the values are 4.96 eV for the substituted molecule and 5.1 eV for the unsubstituted; therefore, again the inductive effect has a collateral consequence since these values suggest that the presence of the $-N(CH_3)_2$ fragments make the species from [1] more reactive.

Other feature that accounts on the evaluation of the global effect is the position of the substituent, in this sense a new calculation (in which the $-N(CH_3)_2$ fragments were changed of position) was performed. The result
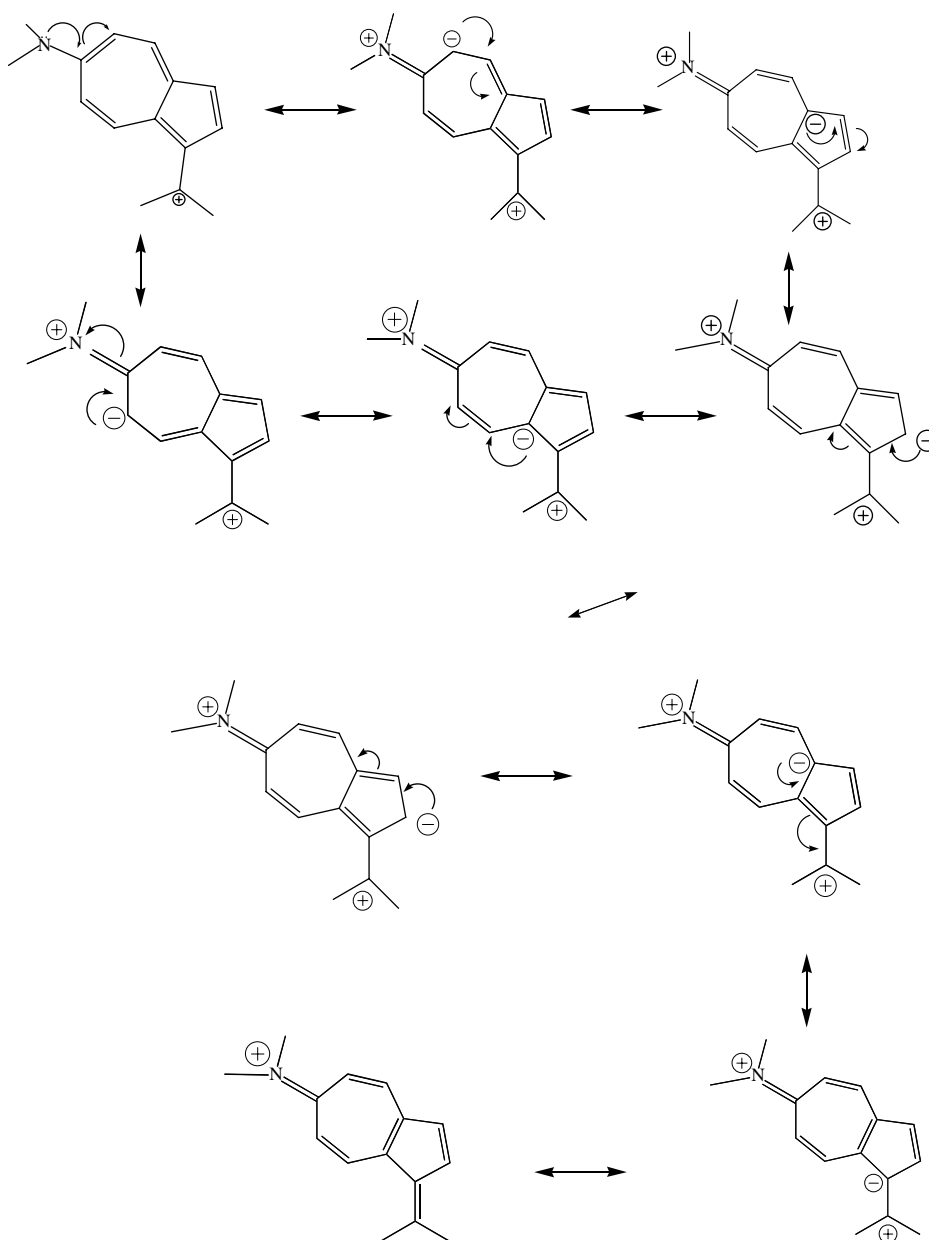

Fig. 4. Resonance forms in carbenium from **1**.

of this calculation, shows that the intermediate from **1** (**1a** with the substituent in C-5) is less stable with an energy difference of 0.95 eV and this result helps to evaluate the importance of the electronic delocalization. The phenomenon can be explained by the visualization of the canonical forms of both isomers (that is shown in Figs. 4 and 5), there are more resonance structures for **1** (Fig. 4) than from **1a** (Fig. 5) this last suggests more stability, besides in Fig. 4 is appreciated that the resonant forms of carbenium from **1** gives place to a case in which electronic density is placed in the five membered ring of the azulenyl fragment, whereas in the case of carbenium from **1a**, the electronic density trends to situate in the seven membered ring, it is expected this last situation causes higher energy species with low contribution to hybrid's stabilization.

The last argument is also useful to note that the stabilization effect is the result of 27 canonical structures, which can be achieved due to the fluxionality of the carbenium structure.

3.2. Compound [2]

Laursen and his co-workers [5,16] experimentally investigated the triangulenium molecules and there are some theoretical studies in which this kind of molecule has been the subject of analysis [17]. Furthermore, the ability of the unsubstituted derivative (TOTA) as acceptor in electron transfer reactions is under study [18].

Laursen and his group [5] established the large stability of the trioxotriangulenium dimethyl-amino derivative by

the determination of the pK_{R+} value using absorption spectroscopy in a DMSO/water/Bu$_4$NOH solvent system, and found a value of 19.7. The lower values of pK_{R+} found in TOTA and crystal violet [3] (9.05 and 9.36, respectively [19]) suggest less stability according to previous reports [5,19]. In our case, the theoretical values (considering acetonitrile/water media) are 17.5 for the species from [2], 7.8 for carbocation from crystal violet and 8.18 for the species from TOTA.

This study reveals some interesting features that account for the large stability of this ion. First, the HOMA method yields the following results for the aromaticity of carbenium from [2] considering all aromatic rings as equivalents, 0.993 for the neutral form and 0.955 for the cation (Fig. 6), i.e. in this case the aromaticity of the ionic form is slightly smaller than that of the neutral case in contrast to that found for the ion from [1], the explanation is that the behaviour of the aromatic fragments in both molecules is different because in the case of [1], the formation of the zwitterionic form improves the stabilization, whereas in the case of [2], the presence of the positive charge induces the formation of a quinoidal structure (Fig. 6) with the concomitant localization of the π bonds. This effects is partially diluted by the intrinsic delocalization of the charge among the three aromatic systems, but the bond lengths of the molecule compared with the ion are slightly different (Fig. 6) and this is precisely the parameter measured by the HOMA method. Therefore, the consideration of aromaticity alone is not enough to explain the change in stability in this case.
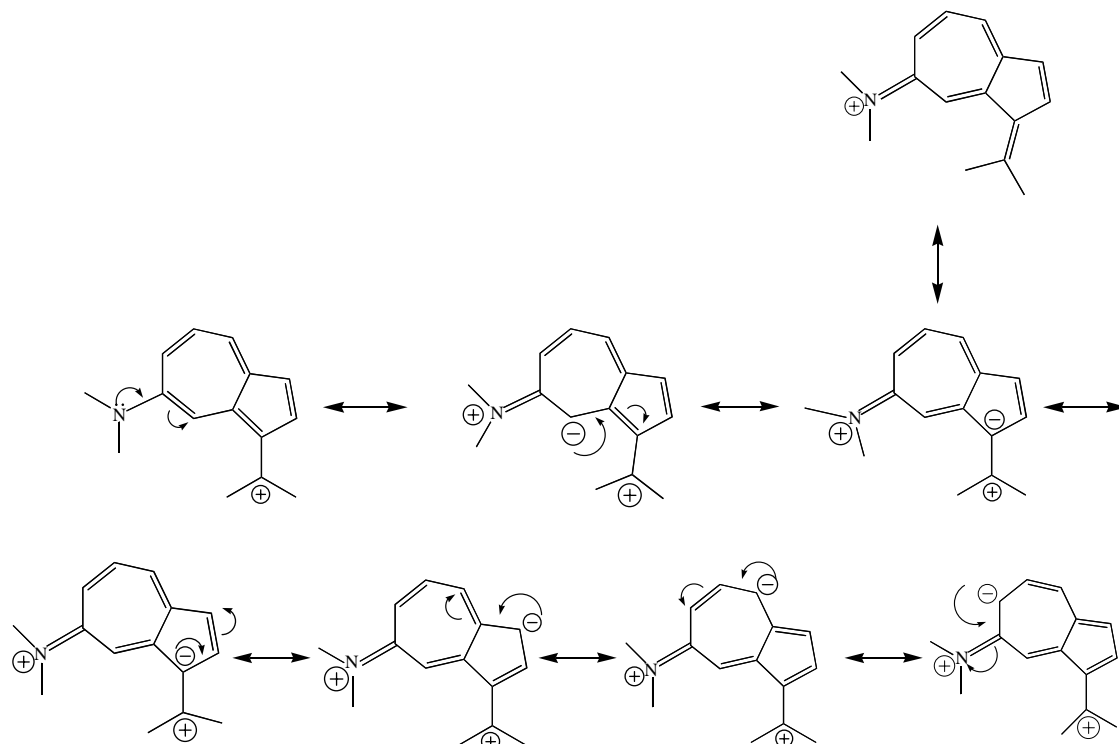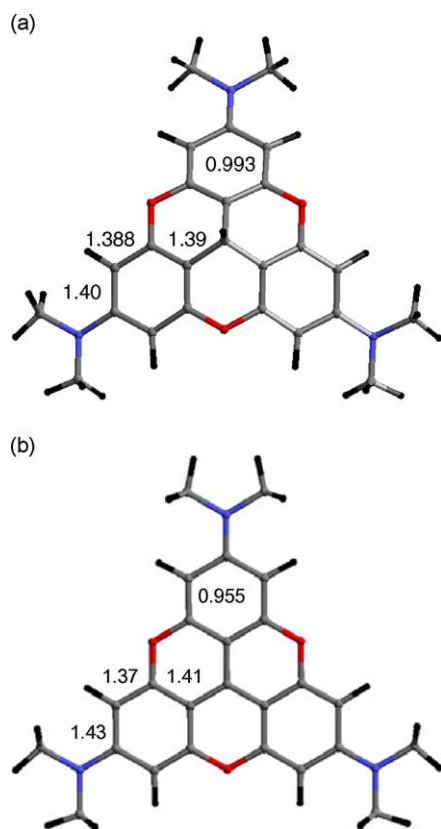

Fig. 5. Resonance forms in carbenium from **1a**.

Fig. 6. HOMA and bond length values for (a) molecule [2] and (b) the corresponding ion. Note that the value in the upper ring corresponds to the HOMA and the three values in the lower ring corresponds to the bond lengths.

The polarizability is not of great importance in this case because the presence of quinoidal forms contributes to localize rather than delocalize the positive charge. Thus, the most important phenomenon is the inductive effect and the possibility of electronic delocalization as in the case of [1]. Therefore, a similar analysis was performed for the compound [2].

The TOTA belongs to the D_3h point group, and this high symmetry for the precursor of [2] suggests that the dipole moment should be low, and this is correct, the value found is 0.05 D. In the case of [2], the presence of the dimethylamine groups cause a loss of symmetry and a dipole moment of 1.43 D, the corresponding carbenium ions have very small values, the cation of TOTA remains in the D_3h point group but additionally it is planar, and therefore the dipole moment is even smaller (0.002) than those of the neutral TOTA. A similar effect occurs in the species from [2], the planar geometry of the cation gives rise to a low value at the dipole moment of 0.2 D but the presence of the dimethylamine groups and quinoidal structures means that it is greater than in the TOTA case. Again, the dipole moment results are assured with the calculation of the corresponding polarizabilty values, they are 45.1 Å^3 for the carbocation from [2] and 28.3 Å^3 for the ion from TOTA.

The important fact is that the dipole moment and the polarizability are larger in [2] than in TOTA and therefore the inductive effect is more important in the former case. Following our model, this situation yields a more stable carbocation, therefore, the situation is similar than in the case of [1] supporting the empirical proposition of Larsen.

Finally, compound [2] shows a value (Koopman's theorem) of 5.93 eV whereas the same for TOTA is 6.21. The substituted molecule has a smaller value, this last suggests a low ionization energy to generate the carbenium species.

4. Conclusions

Stable carbocations generation was theoretically analyzed on the base of different intrinsic characteristics of aromatic compounds. The pK_{R+} values of the more stable compounds cited in the literature were calculated with a good qualitative and acceptable quantitative agreements, furthermore some known stable species were also calculated in order to establish comparisons. Factors such as aromaticity, measured by the HOMA method, polarizability and inductive effect (indirectly estimated by the analysis of the dipole moment) were obtained from the results of the calculations. The inductive and electronic delocalization effects proved to be the most important factors, showing that the introduction of -N(CH$_3$)$_2$ groups on the aromatic rings collaborates in important manner to the increase in the pK_{R+} value.

Acknowledgements

References

[1] (a) S. Naya, M. Warita, Y. Mitsumot, M. Nitta, J. Org. Chem. 69 (2004) 9184;
   (b) G.A. Olah, G.K.S. Prakash, Carbocation Chemistry, Wiley, New York, 2004;
   (c) J. March, Advanced Organic Chemistry, fourth ed., Wiley, New York, 1992.
[2] J.W. Larsen, P.A. Bouis, C.A. Riddle, J. Org. Chem. 45 (1980) 4969.
[3] E.M. Arnett, T.C. Hofelich, J. Am. Chem. Soc. 105 (1983) 2889.
[4] S. Ito, S. Kikuchi, N. Morita, T. Asao, J. Org. Chem. 64 (1999) 5815.
[5] B.W. Laursen, F.C. Krebs, M.F. Nielsen, K. Bechgaard, J.B. Christensen, N. Harrit, J. Am. Chem. Soc. 120 (1998) 12255.
[6] (a) N.C. Deno, W.L. Evans, J. Am. Chem. Soc. 79 (1957) 5804;
   (b) C.D. Ritchie, W.F. Sager, E.S. Lewis, J. Am. Chem. Soc. 84 (1962) 2349;
   (c) S.V. Kulkarni, R. Schure, R. Filler, J. Am. Chem. Soc. 95 (1973) 1859.

[7] (a) Jaguar 4.0, Schrödinger Inc., Portland, OR, 1991–2000.

    (b) D.J. Tannor, B. Marten, R. Murphy, R.A. Friesner, D. Sitkoff, A. Nicholls, M. Ringnalda, W.A. Goddard III, B. Honig, J. Am. Chem. Soc. 116 (1994) 11875;

    (c) D. Chasman, M.D. Beachy, L. Wang, R.A. Friesner, J. Comput. Chem. 19 (1998) 1017.

[8] A.D. Becke, Phys. Rev. A 38 (1988) 3098.

[9] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.

[10] (a) T.M. Krygowski, J. Chem. Inf. Comput. Sci. 33 (1993) 70;

    (b) J. Kruszewski, T.M. Krygowski, Tetrahedron Lett. (1972) 3839;

    (c) T.M. Krygowski, R. Anulewicz, J. Kruszewski, J. Acta Crystallogr. B 39 (1983) 732;

    (d) T.M. Krygowski, M.K. Cyranski, Tetrahedron 52 (1996) 10255;

    (e) T.M. Krygowski, M.K. Cyranski, Chem. Rev. 101 (2001) 1385.

[11] (a) S. Ito, S. Kikuchi, T. Okujima, N. Morita, T. Asao, J. Org. Chem. 66 (2001) 2470(and references therein);

    (b) S. Ito, T. Kubo, N. Morita, T. Ikoma, S. Tero-Kubota, A. Tajiri, J. Org. Chem. 68 (2003) 9753.

[12] E. Clar, D.G. Stewart, J. Am. Chem. Soc. 75 (1953) 2667.

[13] S. Naya, M. Nitta, Tetrahedron 59 (2003) 4157 (and references therein).

[14] P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.R. van Eikema Hommes, J. Am. Chem. Soc. 118 (1996) 6317.

[15] (a) R.C. Haddon, K. Raghavachari, J. Am. Chem. Soc. 104 (1982) 3516;

    (b) R.C. Haddon, K. Raghavachari, J. Chem. Phys. 79 (1983) 1093;

    (c) F. Negri, M.Z. Zgierski, J. Chem. Phys. 99 (1993) 4318;

    (d) R.C. Peck, J.M. Schulman, R.L. Disch, J. Phys. Chem. 94 (1990) 6637;

    (e) J.O. Morley, J. Chem. Soc. Perkin Trans. 2 (1989) 103;

    (f) M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc. 107 (1985) 3902;

    (g) M.J.S. Dewar, E.G. Zoebisch, J. Mol. Struct. THEOCHEM 180 (1988) 1.

[16] (a) C. Herse, D. Bas, F.C. Krebs, T. Bürgi, J. Weber, T. Wesolowski, B.W. Laursen, J. Lacour, Angew. Chem. Int. Ed. Engl. 42 (2003) 3162;

    (b) B.W. Laursen, D. Krebs, Angew. Chem. Int. Ed. Engl. 39 (2000) 3432.

[17] (a) J. Reynisson, R. Wilbrandt, V. Brinck, B.W. Laursen, K. Norgaard, N. Harrit, A.M. Brouwer, Photochem. Photobiol. Sci. 1 (2002) 763;

    (b) J. Reynisson, G. Balakrishnan, R. Wilbrandt, N. Harrit, J. Mol. Struct. 520 (2000) 63.

[18] S. Dileesh, K.R. Gopidas, Chem. Phys. Lett. 330 (2000) 397.

[19] (a) J.C. Martin, R.G. Smith, J. Am. Chem. Soc. 86 (1964) 2252;

    (b) R.J. Goldacre, J.N. Phillips, J. Chem. Soc. (1949) 1724.