

Aromatic behavior of three membered rings

Roberto Salcedo*, Carlos Olvera

Instituto de Investigaciones en Materiales, UNAM, Circuito exterior, Ciudad Universitaria, 04510, D.F. Coyoacán, Mexico

Received 3 April 1998; accepted 21 July 1998

Abstract

The aromatic behavior of three membered ring compounds has been analyzed by mean of GAUSSIAN94 theoretical calculations at B3LYP//6-311 + + G(2d,p) level. Diamagnetic exaltation values obtained from magnetic susceptibilities as well as NICS show the expected aromatic character of the cyclopropyl cation, but the correspondent anion also shows aromatic behavior. This unexpected result is analyzed as well as the character of the other three membered ring derivatives. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aromaticity; Cyclopropyl cation; Three membered rings

1. Introduction

Huckel's rule has been the best guide to establish aromaticity or antiaromaticity behavior for many years [1–3] — following this rule the smallest organic compound that can show aromatic behavior is the cyclopropenyl cation.

The cyclopropenyl ion and several of its derivatives have received considerable attention due their presence in oxidative flames [4] or because of their detection in outer space [5–9]. For the same reason there are many theoretical reports in many different contexts [10–15].

The isomeric form of the cyclopropenyl cation, named the propargyl cation, is less stable than the former [10–16] and this is good evidence that there must be some additional stabilization factor that ensures the predominance of the cyclic isomer; this factor is the aromaticity.

The aim of this paper is to establish a relative aromaticity scale of several three membered rings.

The results will be useful in predicting the behavior of each organic species in the context of different reactions. It has been proposed that this type of molecules can not be studied by means of their magnetic properties [17] because of the effects of σ -aromaticity [18]. However, our results indicate that there is a well behaved qualitative trend from species to species, and that this type of study is useful for comparison to experimental studies.

2. Computational methods

The quantum chemical calculations were carried out using the GAUSSIAN94 program [19] at B3LYP/6-311 + + G(2d,p) level with full-geometry optimization without symmetry constrains. The magnetic properties were calculated at this level using the continuous set of gauge transformation method [20, 21]. The corresponding diamagnetic exaltation was calculated following the work of Schleyer [22] by the equation

$$\Lambda = \chi_m - \chi_{m'}$$

* Corresponding author.

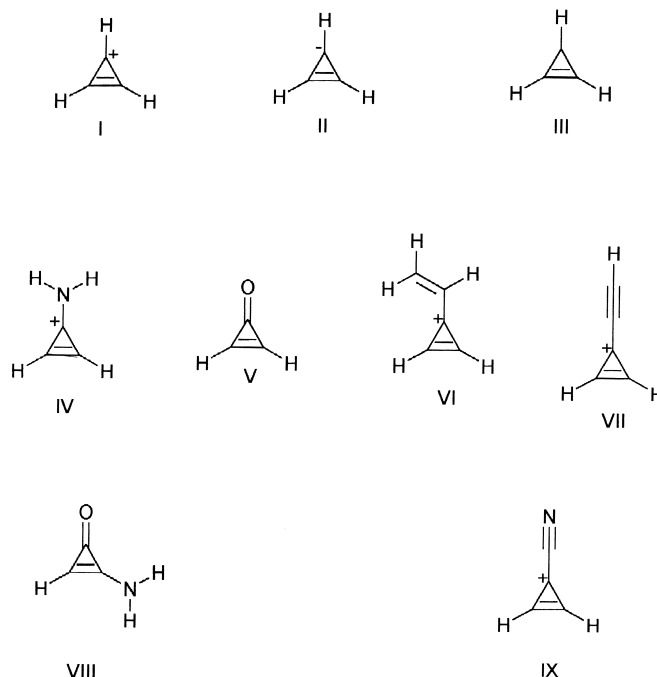


Fig. 1. The molecules studied.

Where χ_m' corresponds to the magnetic susceptibility of a non-aromatic compound in order to have a reference system. The nucleus-independent chemical shifts (NICS [23–25]) were computed at GIAO-HF/6-311G* level with the GAUSSIAN94 program.

3. Results and discussion

In the first approximation GAUSSIAN94 calculations

Table 1
Magnetic susceptibility (χ) and diamagnetic exaltation (Λ)

Compound	χ	Λ	NICS
I	-16.9065	-31.9795	-28.065
II	-16.0152	-31.0882	-17.653
III	15.0730	0.0	-4.034
IV	-27.7184	-42.7914	-27.562
V	-22.4831	-37.5561	-18.303
VI	-30.7388	-45.8118	-28.862
VII	-30.8466	-45.9196	-26.966
VIII	-34.2777	-49.3507	-26.844
IX	-26.0138	-41.0868	-29.159

were carried out for the cyclopropenyl cation (I) and anion (II) (see Fig. 1).

The first task was to find a non-aromatic three membered ring compound and carry out the corresponding calculations in order to have a reference for the appraisal of the magnetic exaltation. The species chosen was the cyclopropenyl free radical (III) that can be considered the 'neutral' item of the series, Table 1 show the magnetic susceptibility, diamagnetic exaltation and NICS obtained for all the molecules analyzed in this study.

Following Scheleyer's work [22] a negative diamagnetic exaltation value indicates an aromatic behavior. Thus in this sense the cyclopropenyl cation shows a normal behavior because we expect an aromatic species. Furthermore the value of the ^1H chemical shift obtained by us is 10.85 ppm, in very good agreement with the experimental value of 11 ppm and is in the known range for aromatic compounds. However in the case of the anion the result was very unexpected since it is almost as aromatic as the cation; this result requires careful consideration.

There has been a great controversy about the

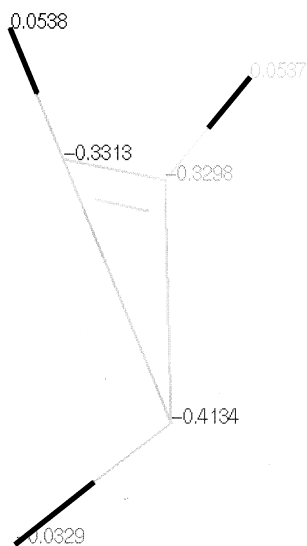


Fig. 2. Charges of the molecule II.

antiaromatic nature of the cyclopropenyl anion as well as cyclobutadiene [26–32]. Indeed the classical textbooks present these cases as the best examples of antiaromaticity [33], with the rectangular shape of cyclobutadiene helping to assure this fact. However in the case of the cyclopropenyl anion this is not completely clear because there are reports that claim there is an absence of conjugation in the three

membered ring for the four π electrons [26, 34]. This implies the localization of both π electron pairs.

Our calculations confirm these propositions. In first place the molecule of cyclopropenyl anion belongs to the C_{2v} point group, whereas the cation belongs to the D_{3h} group because it is a more symmetrical molecule. This distortion for the anion compels the hydrogen atoms to take positions out of the plane, as was suggested by Hess and coworkers [34]. The energetic difference between the non-planar and the planar molecules is 2.046 eV favouring the non-planar isomer.

The shape of the molecule and the Mulliken charges (including the hydrogen atoms) are shown in Fig. 2. The value of the charges confirms that there is no conjugation because there are two partial and different negative localized charges, one on the double bond and other one on the single carbon, it is interesting to compare this feature in the same way as the cyclopropenyl cation where the symmetrical distribution of the positive charge confirms the electronic conjugation (see Fig. 3).

The electronic density analysis shows two main negative zones for the anion, again these are localized on the double bond and on the single carbon atom (see Fig. 4).

The analysis of the frontier orbitals for both species emphasize the great differences between them. The

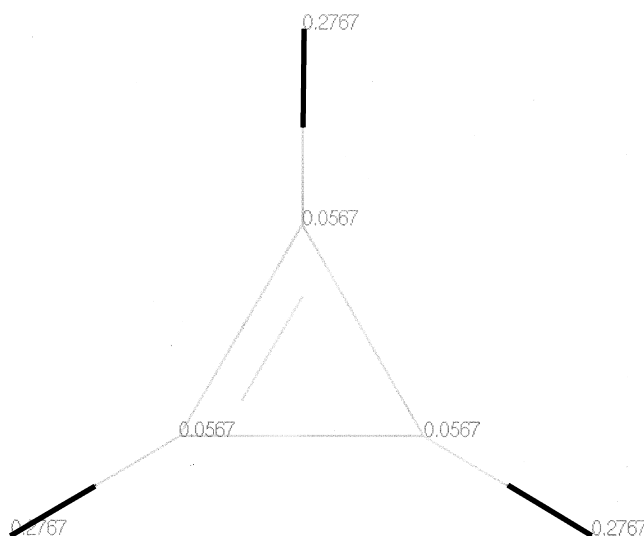


Fig. 3. Charges of molecule I.

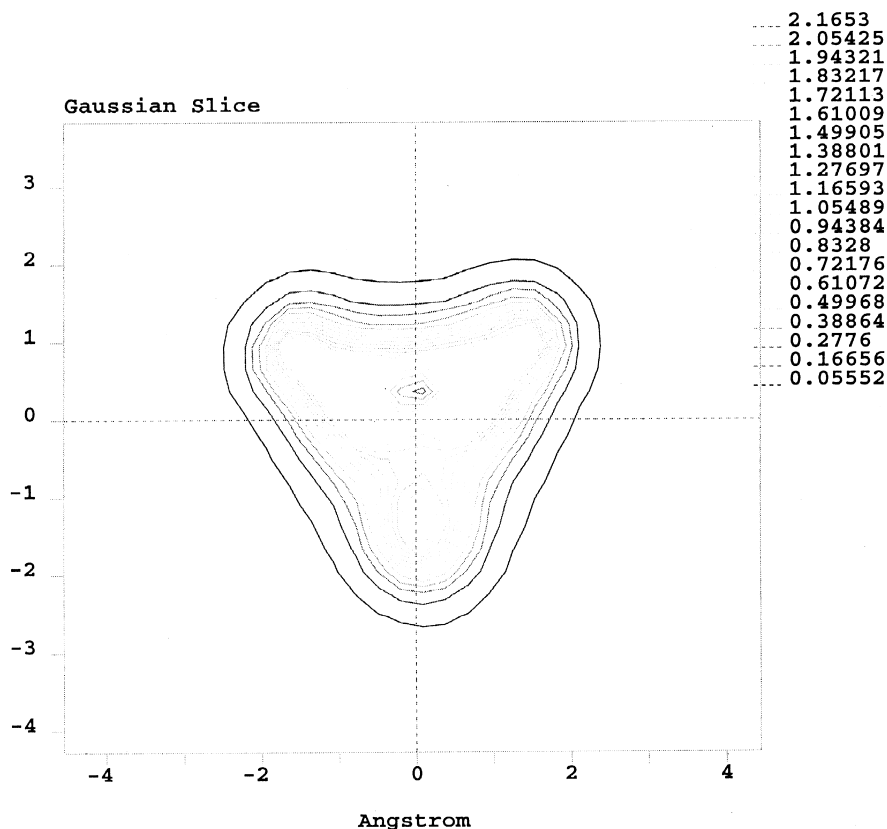


Fig. 4. The contour scheme of electrostatic density of molecule II, the molecule is not presented for clarity, the double bond is horizontal and is localized on the upper side of the triangle formed.

HOMO and LUMO of I are the irreducible representations e' and e'' , respectively, belonging to the D_{3h} point group. The shape of the wave functions are shown in Fig. 5. We see that this is a very symmetrical situation and ensures the conjugation and aromatic character of the molecule. Meanwhile, the anion II shows a system with a very interesting HOMO that corresponds to a b_1 irreducible representation, where there is a large zone near the single carbon atom that can shelter the lone electronic pair; the corresponding shape of this molecular orbital is shown in Fig. 6.

All this evidence indicates that one of the π electron lone pair does not participate in the conjugation of the ring, but the original question remains. Why does the anion have a strong negative value of the diamagnetic exaltation? Why does it exhibit aromatic behavior? The answer is found in the HOMO of the anion, this is a molecular orbital that can allow the

movement of one of the electronic pair, and this pair is the one found on the double bond. This electron pair suffers repulsion from the outer lone pair and moves around the ring. This phenomenon generates diamagnetic anisotropy and thus we have a large negative value of the magnetic susceptibility in the plane formed by the three carbon atoms, and this is the reason for the large value of diamagnetic exaltation. The definition of antiaromaticity by Clark [35] on this same system states that the antiaromaticity is the increase in energy on allowing the delocalization of the lone pair of electrons into the double bond. Therefore, following this point of view, we could consider that the stable situation of lowest energy would be that with the lone pair outside of the ring.

It has been suggested that the cyclopropenyl anion should be represented as a triplet [36]. We have carried out the corresponding calculations in order

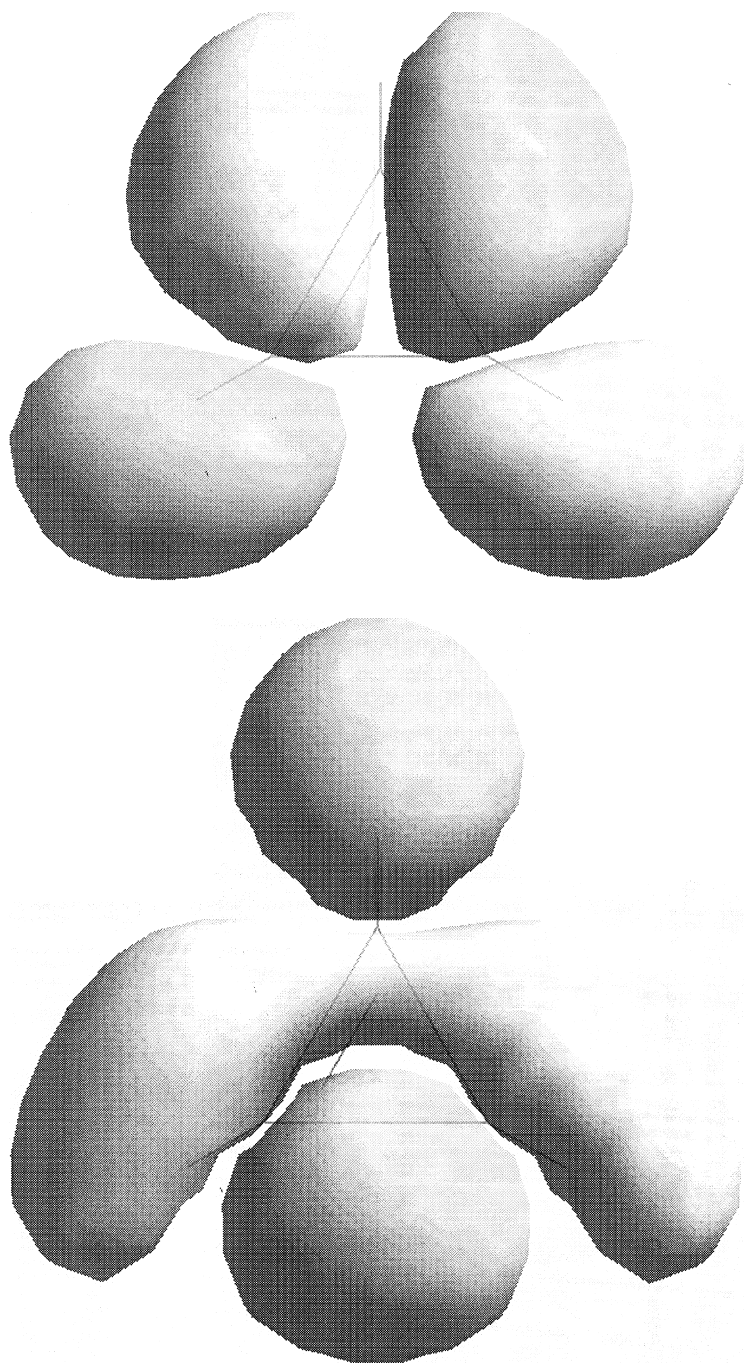


Fig. 5. HOMO and LUMO of molecule I.

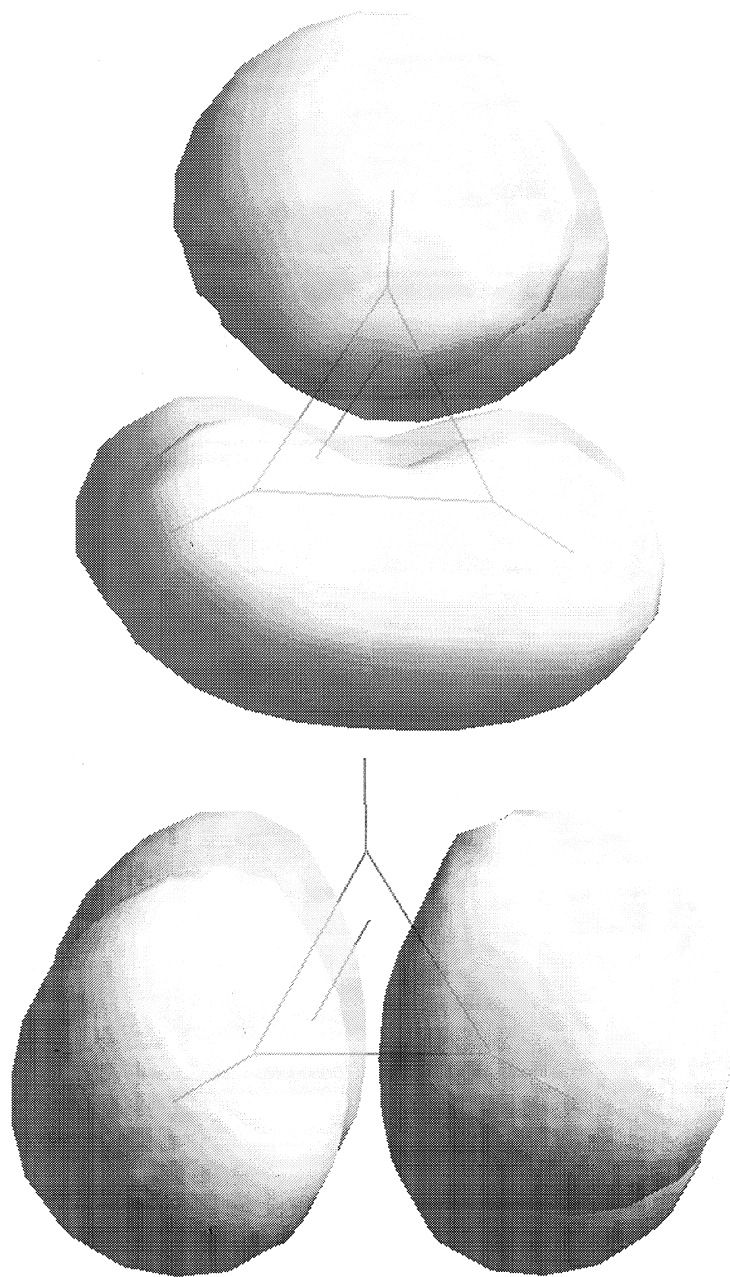


Fig. 5. (continued)

to study this possibility, but we find that the corresponding triplet is more unstable than the singlet (by 8 kcal mol^{-1} approx.) therefore we do not consider it within this study.

We carried out calculations for five more molecules

in order to understand how the aromaticity is affected by the presence of substituents. The molecules involved in this study were cyclopropenone, cyclopropenylacetylene, cyclopropenylethylene, nitrilycyclopropenyl and aminocyclopropenone.

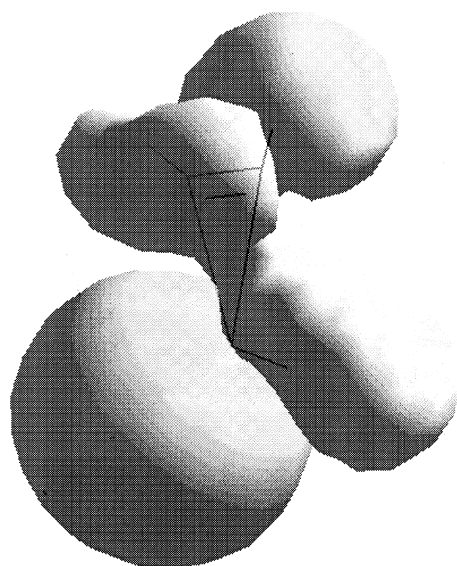


Fig. 6. HOMO of molecule II.

Cyclopropenone (V) is a known and stable species and has been object of several experimental and theoretical studies [37–40]. Its role as an aromatic species is controversial. It has been suggested [37] that the resonant structures of V have a greater aromatic character and can account to improve the stability of the molecule. Staley [41] has suggested that cyclopropenone should be a moderately aromatic compound. Furthermore Dailey [42] and co-workers have carried out calculations on difluorocyclopropenone and cyclopropenone searching for ^{19}F , ^{17}O , ^{13}C and ^1H NMR chemical shifts as a criteria of aromaticity. They found a value of 8.7 ppm for ^1H chemical shift of cyclopropenone, very near to the experimental value of 9.08 ppm and also near to the value of 11.0 ppm corresponding to the aromatic cyclopropenyl cation. However, Breslow [43] carried out measurements of the magnetic susceptibility anisotropy and suggests that the ring current in cyclopropenone is almost equivalent to that of non-aromatic cyclopropene.

In our case the corresponding data of the diamagnetic exaltation for cyclopropenone (see Table 1), suggests it should be aromatic. Furthermore, we obtain a value of 9.28 ppm for the ^1H chemical shift in this compound, in good agreement with the experimental value. Thus we conclude that V is aromatic.

The activation of an aromatic ring with the

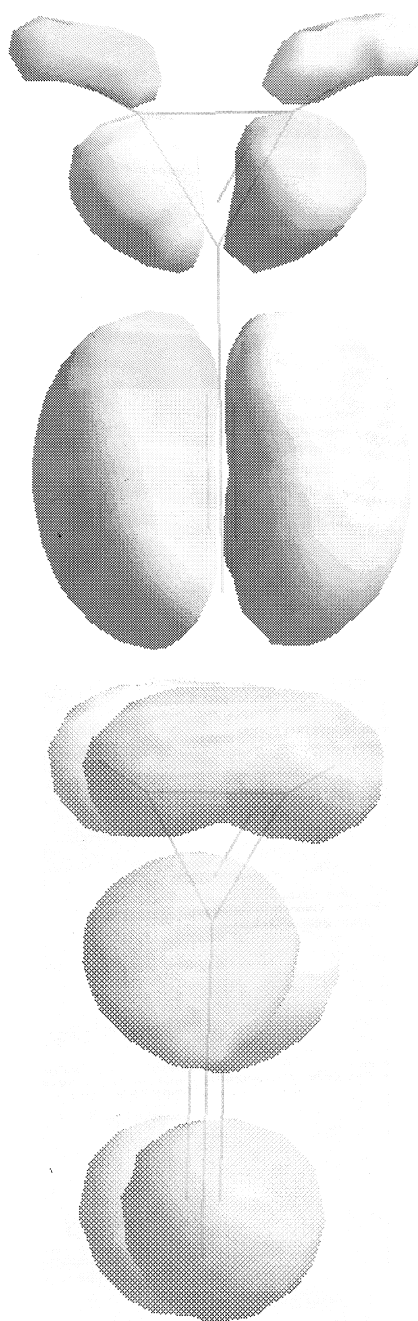


Fig. 7. HOMO and LUMO of molecule VII.

substitution of a group that releases electrons is a well-known fact [44]. For this reason we decided to calculate the amine substituted derivative of cyclopropenone (VIII) in order to establish the magnitude of

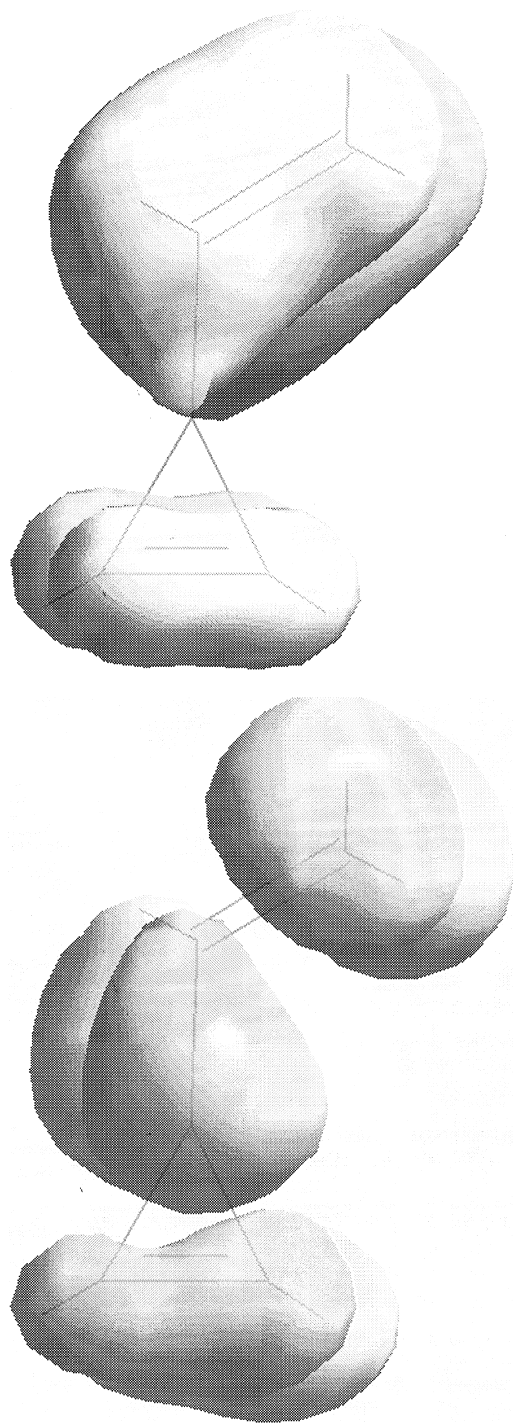


Fig. 8. HOMO and LUMO of molecule VI.

the effect on a tested aromatic species. We can see that the value of the diamagnetic exaltation is the biggest in Table 1. In general a molecule can be moderately aromatic, but this can be increased by mean of an activating substituent.

Vincyclopropenyl (VI) and ethynylcyclopropenyl (VII) ions were studied because of the presence of unsaturated bonds can provide a better electronic delocalization. There are many experimental and theoretical studies on VII [45–49], because it is very stable and a common ion observed in mass spectra [50–53]. The actual structure of the fragment $C_5H_3^+$ is as yet not known but many authors conclude that the more stable form among all those proposed, should be VII. There is a significant energetic difference between VII and a linear diacetylenic isomer and it is $21.5 \text{ kcal mol}^{-1}$ in good agreement with the values obtained by Traeger and coworkers [46], and Weiner [47]. This large difference is a consequence of two phenomena, first the intrinsic resonance energy of the three membered aromatic ring and, second the resonance effect between this ring and the triple bond. Both effects can be appreciated in the frontier orbitals HOMO–LUMO of this molecule shown in Fig. 7, the energetic gap between both orbitals is 5.21 eV . Moreover, this result and that shown in Table 1 demonstrate of the aromatic character of VII and this accounts for the great stability of this ion in mass spectrometry.

The same collection of effects and arguments can be applied to the case of the multicited species VI [17, 47, 54] but in this case, we found slightly lower delocalization between the ring and the lateral chain, as can be seen in Fig. 8 where we show the HOMO and LUMO shapes. This phenomenon seems to be due to the lower symmetry of this molecule compared with VII (C_{2v}). Moreover, the delocalization is present and we calculate the rotational barrier of the bond between the ring and the vinyl group as having a value of $10.7 \text{ kcal mol}^{-1}$ that clearly shows there is a strong electronic flux in this part of the molecule.

Aminecyclopropenyl (IV) [17] and nitrilcyclopropenyl (IX) [55] ions were calculated in order to account for the influence of the two different types of substituents on the inductive effect or the ring. One has an electronic release effect on the ring (IV) and other one with electronic withdrawal effect (IX). The result is very interesting because the diamagnetic

exaltation is almost the same for both molecules (see Table 1), but the value of the ^1H chemical shift are 9.08 ppm for aminocyclopropenyl ion and 10.03 ppm for nitylcyclopropenyl ion. The second molecule shows a greater aromaticity than the former, and the explanation is that in the case of IX we have a molecule that has the possibility of electronic resonance and in IV this can not occur, therefore the effect of the resonance is bigger than the inductive effect.

In all cases, nucleus-independent chemical shifts (NICS) were calculated. NICS is the negative of the absolute magnetic shielding constant computed at the ring center at GIAO-HF/6-311G* level. Negative NICS denote aromaticity and positive NICS antiaromaticity; non-aromatic molecules show negligible NICS. It has been suggested that magnetic exaltation is very dependent of the ring size [23], therefore we carried out the corresponding calculations with NICS in order to compare with our results with magnetic susceptibility exaltation, establishing a good agreement. There are some points to remark: the NICS of III is so poor (-4.034) indicating it is a non-aromatic molecule; it is expected because that is the radical we use as reference in order to calculate Λ . Second, the NICS for II is the lowest value in the table for aromatic compounds (-17.653), but it remains as an aromatic species which is a confirmation of the results discussed with the Λ criterion. Third, cyclopropenone has a low value of NICS but is aromatic in the same argument as II, so this probe assures the aromatic character of this molecule. All other arguments discussed on terms of exaltation remain the same since there are not any drastic changes in the NICS analysis.

4. Conclusions

The aromatic character of a series of three membered ring molecules has been studied from a theoretical point of view at B3LYP/6-311G++(2d,p) level on the basis of diamagnetic exaltations and NICS. We have confirmed the aromatic nature of all of the molecules chosen, but with the surprising result that the cyclopropenyl anion, which we expected would show antiaromatic character, also presents an aromatic behavior. This phenomenon arises because of the localization of an

electronic pair outside of the ring and the resonance of the other electronic pair that results in electronic repulsion. The aromaticity of cyclopropenone that has been a theme of discussion, is confirmed. The influence of conjugated substituents shows that the aromaticity of these small systems can be explained by the extent of the electronic delocalization on lateral chains and the influence of the substituents has been analyzed from a point of view of the resonance and inductive effects and we conclude that the resonance effect is larger than inductive effect.

Acknowledgements

This work was supported by grants from the CONACYT project 3157P-A. The authors thank Dr. Stephen Muhl for valuable discussion and Ms Maria Teresa Vazquez and Ms Sara Jimenez for technical help.

References

- [1] E. Hückel, *Z. Phys.* 70 (1931) 204.
- [2] E. Hückel, *Z. Phys.* 76 (1932) 628.
- [3] E. Hückel, *Z. Elektrochem. Angew. Phys. Chem.* 42 (1937) 752–827.
- [4] R.D. Kern, H.J. Singh, K. Xie, *J. Phys. Chem.* 94 (1990) 3333.
- [5] S.A. Korth, M.L. Marconi, D.A. Mendis, A.K. Krueger, A.K. Richter, R.P. Lin, D.L. Mitchell, K.A. Anderson, C.W. Carlson, H. Rème, J.A. Sauvaud, C. d'Ulston, *Nature* 52 (1989) 337.
- [6] P. Thadeus, J.M. Vrtilik, C.A. Gottlieb, *Astrophys. J.* 299 (1985) L63.
- [7] N. Brouillet, A. Baudry, G. Daigne, *Astron. Astrophys.* 199 (1988) 312.
- [8] P. Cox, R. Güsten, C. Henkel, *Astron. Astrophys.* 206 (1988) 108.
- [9] P. Cox, C.M. Walmsley, R. Güsten, *Astron. Astrophys.* 209 (1989) 382.
- [10] S.A. Maluendes, A.D. McLean, K. Yamashita, E. Herbst, *J. Chem. Phys.* 99 (1993).
- [11] K. Lammertsma, P.v.R. Schleyer, *J. Am. Chem. Soc.* 112 (1990) 7935.
- [12] L. Radom, P.C. Hariharan, J.A. Pople, P.v.R. Schleyer, *J. Am. Chem. Soc.* 98 (1976) 10.
- [13] D. Talbi, F. Pauzat, *Chem. Phys. Lett.* 244 (1995) 269.
- [14] K. Raghavachari, R.A. Whiteside, J.A. Pople, P.v.R. Schleyer, *J. Am. Chem. Soc.* 103 (1981) 5649.
- [15] T.-K. Ha, F. Graf, Hs. H. Gunthard, *J. Mol. Struct.* 15 (1973) 335.
- [16] S.E. Galembeck, R. Fausto, *J. Mol. Struct. (Theochem)* 332 (1995) 105.

- [17] P. Burk, J.L.M. Abboud, I.A. Koppel, *J. Phys. Chem.* 100 (1996) 6992.
- [18] K. Jug, A.M. Köster, *J. Am. Chem. Soc.* 112 (1990) 6772.
- [19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogl, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. People, *Gaussian 94 (Revision B.1)*, Gaussian Inc., Pittsburg, PA, 1995.
- [20] T.A. Keith, R.F.W. Bader, *Chem. Phys. Lett.* 20 (1993) 223.
- [21] T.A. Keith, R.F.W. Bader, *Chem. Phys. Lett.* 194 (1992) 1.
- [22] P.v.R. Schleyer, P.K. Freeman, H. Jiao, B. Goldfuss, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 337.
- [23] P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.v.E. Hommes, *J. Am. Chem. Soc.* 118 (1996) 6317.
- [24] G. Subramanian, P.v.R. Schlayer, H. Jiao, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 2638.
- [25] H. Jiao, P.v.R. Schlayer, Y. Mo, M.A. McAllister, T.T. Tidwell, *J. Am. Chem. Soc.* 119 (1997) 7075.
- [26] R. Breslow, *Angew. Chem. Int. Ed. Engl.* 7 (1968) 565.
- [27] H. Kollmar, V. Staemler, *J. Am. Chem. Soc.* 100 (1978) 4304.
- [28] L.J. Schaad, B.A. Hess Jr, C.S. Ewig, *J. Am. Chem. Soc.* 101 (1979) 2281.
- [29] L.J. Schaad, B.A. Hess Jr, C.S. Ewig, *J. Org. Chem.* 47 (1982) 2904.
- [30] B.A. Hess Jr, P. Cársky, L.J. Schaad, *J. Am. Chem. Soc.* 105 (1983) 695.
- [31] W.T. Borden, E.R. Davidson, R. Hart, *J. Am. Chem. Soc.* 100 (1978) 388.
- [32] J.A. Jafri, M.D. Newton, *J. Am. Chem. Soc.* 100 (1978) 5012.
- [33] J. March, *Advanced Organic Chemistry*, 2nd ed., McGraw-Hill, New York, 1977.
- [34] B.A. Hess, L.J. Schaad, P. Cársky, *Tetrahedron Lett.* 25 (1984) 4721.
- [35] D.T. Clark, *Chem. Comm.* 637 (1969).
- [36] P.J. Garrat, *Aromaticity*, Wiley, New York, 1986.
- [37] B. Halton, M.G. Banwell, In *The Chemistry of the Cyclopropyl Group*. Rappoport Z, Wiley, New York, 1987.
- [38] A.W. Krebs, *Angew. Chem. Int. Ed. Engl.* 4 (1965) 10.
- [39] T. Eicher, J.L. Weber, *Top. Curr. Chem.* 37 (1975) 1.
- [40] K.T. Pots, J.S. Baum, *Chem. Rev.* 74 (1974) 189.
- [41] S.W. Staley, T.D. Norden, W.H. Taylor, M.D. Harmony, *J. Am. Chem. Soc.* 109 (1987) 7641.
- [42] C.A. Jacobs, J.C. Brahms, W.P. Dailey, K. Beran, M.D. Harmony, *J. Am. Chem. Soc.* 114 (1992) 115.
- [43] R. Benson, W.H. Flygare, M. Oda, R. Breslow, *J. Chem. Soc.* 95 (1973) 2772.
- [44] D. Ferguson, *Chem. Rev.* 50 (1952) 47.
- [45] J. Dannacher, E. Heibronner, J.P. Stadelmann, J. Vogt, *Helv. Chim. Acta* 62 (1979) 2186.
- [46] B.M. Kompe, J.B. Peel, J.C. Traeger, *Org. Mass Spectrosc.* 28 (1993) 1253.
- [47] B. Weiner, C.J. Williams, D. Heany, M.C. Zerner, *J. Phys. Chem.* 94 (1990) 7001.
- [48] K. Lammertsma, P.v.R. Schleyer, *J. Chem. Soc.* 105 (1983) 1049.
- [49] F. Östük, M. Moini, F.W. Brill, J.R. Eyler, T.J. Buckley, S.G. Lias, P.J. Ausloos, *J. Phys. Chem.* 93 (1989) 4038.
- [50] J. Momigny, L. Brakier, L. D'Or, *Bull. Cl. Sci. Acad. R. Belg.* 48 (1962) 1002.
- [51] J.L. Franklin, S.R. Carrol, *J. Am. Chem. Soc.* 91 (1969) 6564.
- [52] J.L. Franklin, S.R. Carrol, *J. Am. Chem. Soc.* 91 (1969) 6564.
- [53] E.T.M. Selim, M.A. Rabbih, M.A. Fahmey-Ahmad, A.S. Shalbi, *Arab. Gulf. J. Sci. Res.* 7 (1989) 53.
- [54] M.-D. Su, *Tetrahedron* 51 (1995) 12109.
- [55] M.A. McAllister, T.T. Tidwell, *J. Org. Chem.* 59 (1994) 4506.