Journal of Molecular Structure (Theochem) 678 (2004) 211–215

THEO CHEM

www.elsevier.com/locate/theochem

[8]Circulene. Theoretical approach

Roberto Salcedo[a,*], L. Enrique Sansores[a], Alejandra Picazo[a], Leticia Sansón[b]

[a]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Apartado Postal 70-360, México D.F 04510, Mexico

[b]SVM Formulation Conditionnement Façonnage, BP16-67 138 Muhlbach sur Bruche, France

Received 28 November 2003; revised 28 November 2003; accepted 3 March 2004

Abstract

The electronic characteristics of [8]circulene ($C_{32}H_{16}$) were studied by DFT methods. The neutral form of this molecule has a ruffled structure that shows aromatic behaviour in spite of its non-planar nature. The correspondent dianion has a planar shape but is very unstable. This peculiar behaviour with respect to the expected characteristics due to its structure was analysed on the base of the corresponding MO. The aromaticity of both isomers was estimated by an HOMA study. The results indicate that the planar ionic species is not possible due to the large energy difference relative to the neutral molecule.

Keywords: Circulenes; [8]Circulene; Electronic structure; Aromaticity

1. Introduction

The family of the circulene molecules involves those poliaromatic hydrocarbons that have a central ring with a certain number of carbon atoms and a full saturation of fused benzene rings on all the edges. One of the main members of this set of molecules is the corannulene, a molecule that is well known because it has the same shape as the top fragment of C_{60}. In the last few years all the family has attracted the interest of researchers, since they can lead to the building of polyhedral molecules such as the fullerenes. Furthermore, its large delocalization of charge and its polarizability suggest that they may be interesting candidates as useful optical and electronic materials.

Corannulene ([5]circulene) is an anti-aromatic bowl shaped molecule, it was synthesized some years ago and the conditions under which it is stable were established [1]. This compound is also of interest due to its particular characteristics of a dome shape, the ease to form inversion, etc. It has been theoretically as well as experimentally studied [2], mainly in relation to its ability to form different oxidation states [3], and its peculiar inversion barrier in solution [4]. It is thought that it might be used as an addition to larger molecules to improve their electronic resonance.

Coronene ([6]circulene) is an aromatic planar and very symmetric molecule, it has been studied, synthesized and well characterized [5]. With corannulene, this material has interesting conducting properties due to its large electronic resonance.

Pleiadannulene ([7]circulene) was prepared [6] recently and exhibits a non-planar saddle-shaped structure with obvious low symmetry. Its electronic structure has been the object of various theoretical studies [7].

[8]Circulene (see both structures in Fig. 1), would be the next member of the family, it is conformed by a central cyclooctatetraene fragment fully surrounded by phenyl rings. In spite of the efforts to synthesize it [8], until now this has not been possible. There are a few theoretical studies concerning its structure [9] but no detailed study has been carried out.

In this work we present a theoretical study of the [8]circulene molecule, and its ions, in order to find out which would be the most stable form, the aromatic behaviour of the species and the reason why its synthesis is so difficult. The main part of the study was carried out taking advantage of the HOMA method [10] because the main difference among these species is the geometry.

---

[*] Corresponding author. Address: Department of Polymers, IIM-UNAM, Circuito Exterior, Ciudad Universitaria, Apartado Postal 70-360, México D.FS 04510, Mexico. Tel.: +52-5622-4600; fax: +52-5616-1201.

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

0166-1280/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2004.03.020

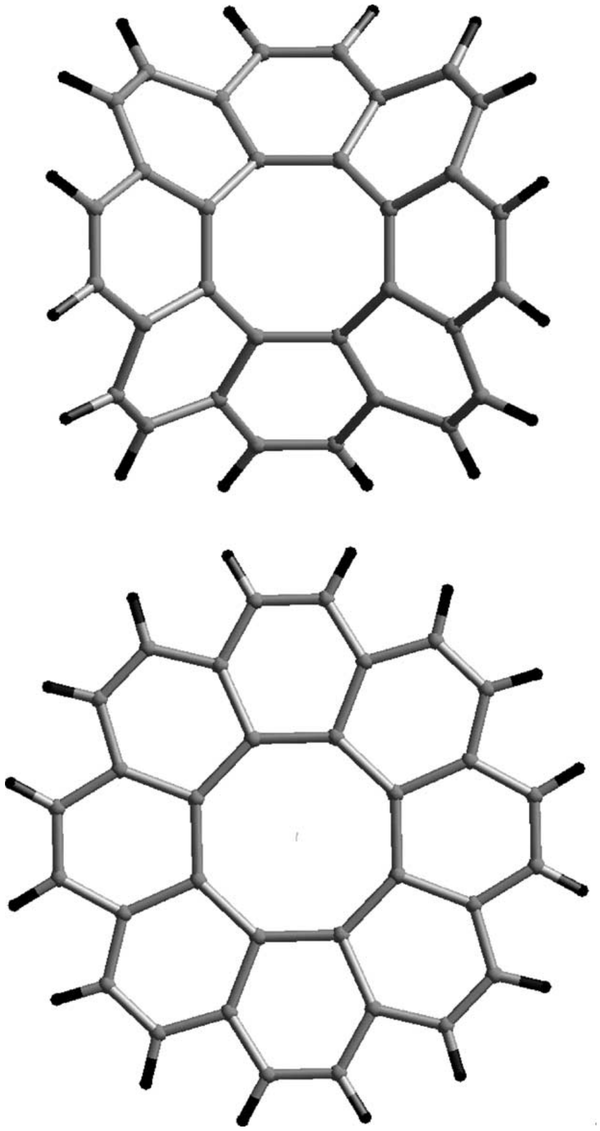

Fig. 1. Structures of [8]circulene, D_{2d} above and D_{8h} below.

2. Methods

The geometry optimisation of both isomers and their corresponding ions was carried out using the Jaguar [11] method with a B3PW91/6-31G** scheme [12a–c]. The molecular orbital analysis and HOMA study were carried out with the B3LYP/6-31G** hybrid method [12a,b,d] included in the GAUSSIAN98 package [13]. The HOMA study was performed following the model developed by Krywoski [14] using his own parameters.

3. Results and discussion

Cyclotetraene has been widely studied because of its very particular chemistry features. The molecule is intrinsically anti-aromatic but can undergo two dynamic process (a) tub inversion and (b) valence-bond shifting [15], a change in the charge gives place to aromatisation and can account for one or both of these process a and b.

It is well known that in certain circumstances a cyclic compound that has anti-aromatic character is able to become an ion and reach an aromatic configuration with the correspondent stabilisation due to this new status. This is a pseudo-aromaticity effect [16]. This may be the situation of the circulenes in general, in fact, there are several studies about how easy it is for corannulene to change its oxidation state [2]. A similar behaviour is expected for the other members of this family, with the exception of the coronene that is initially aromatic. This is the main reason why we have studied the neutral and charged forms of [8]circulene in this work.

The neutral form of the molecule adopts a ruffled shape that belongs to the D_{2d} point group, whereas the initial proposition is that some of the ionic species should be planar (aromatic species) belonging to the D_{8h} point group. Both conformations were designed and submitted to geometry optimisation process.

The HOMO-1, HOMO and LUMO of the neutral [8]circulene are shown in Fig. 2. The molecule adopts the D_{2d} point group conformation after the geometry optimisation. The HOMO belongs to a b_1 irreducible representation, the HOMO-1 is a degenerate set belonging to the e irreducible representation and LUMO is a totally symmetric a_1 representation. These orbitals are important because it is expected that HOMO would change to the HOMO-1 and the LUMO into the HOMO as the molecule is negatively charged during the formation of the dianion. Whereas in the case of the positively charged ion the HOMO and HOMO-1 of the neutral form change to the LUMO and HOMO, respectively, for the dication.

The optimisation process was carried out for both ions, i.e. the positively charged (2 +) and the negatively charged (2 −). In the first case, a completely different scheme from that expected develops and the planar shape is not found. Several calculations were performed in order to find a planar configuration, but in all cases the results were the same, a ruffled geometry.

A more consistent result than that obtained for the positive ion was found with respect to the planar species in the case of the dianion (2 −). The LUMO of the neutral structure changes into the HOMO's ion without changing the symmetry and the same a_1 orbital receives the new electronic pair. The LUMO is placed into a degenerate set with e irreducible representation, This degenerate set is useful to describe the aromaticity of the ion, since it is necessary to have three orbitals for aromaticity, and two of these are in a degenerate state.

Fig. 3 shows the LUMO and the HOMO for the dication, whereas, the HOMO and HOMO-1 for the dianon are shown in Fig. 4. The results of the total energy for the three species are given in Table 1. Obviously the neutral form is the most stable one.

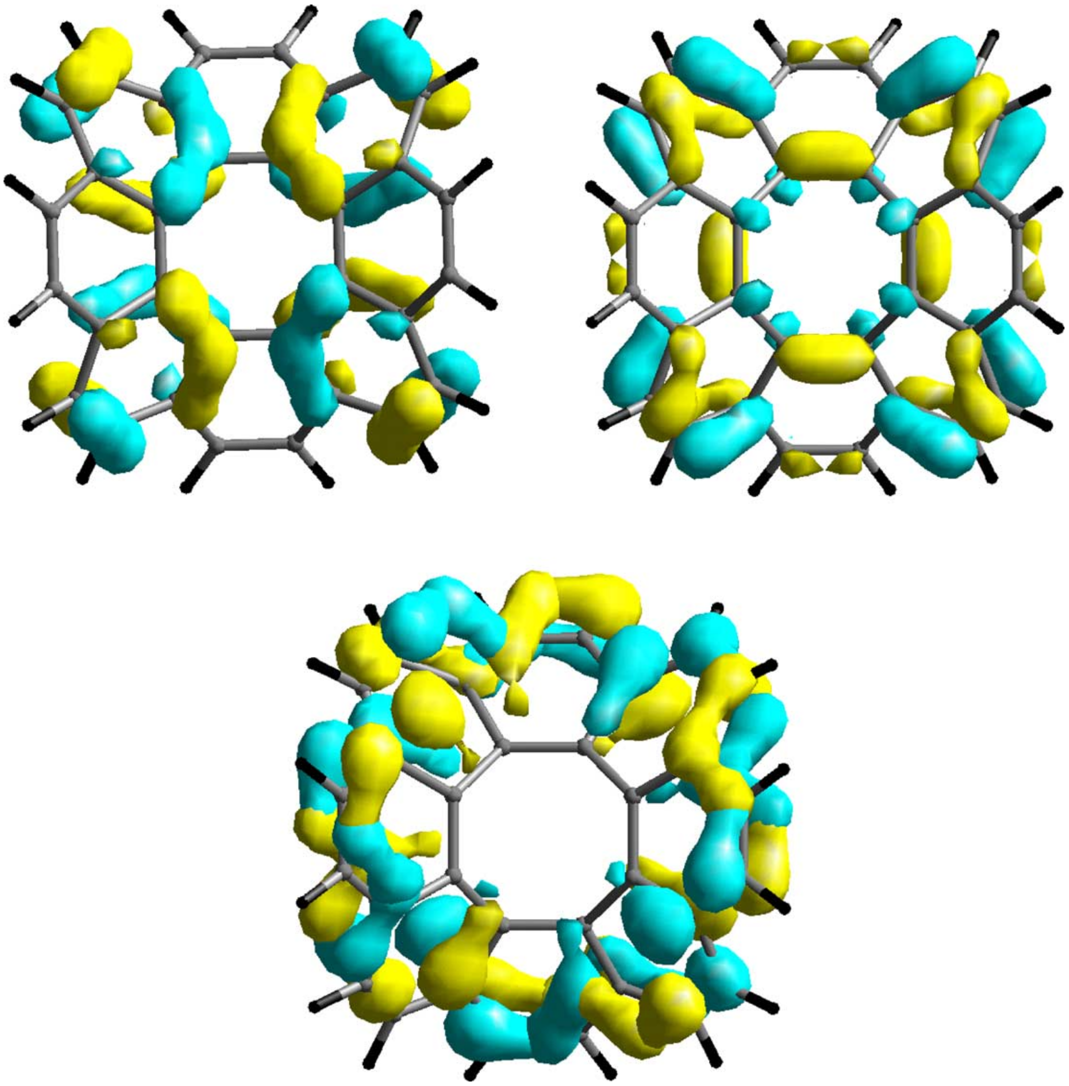

Fig. 2. HOMO, LUMO (above) and HOMO-1 degenerate set (below) of the D_{2d} structure of neutral [8]circulene.

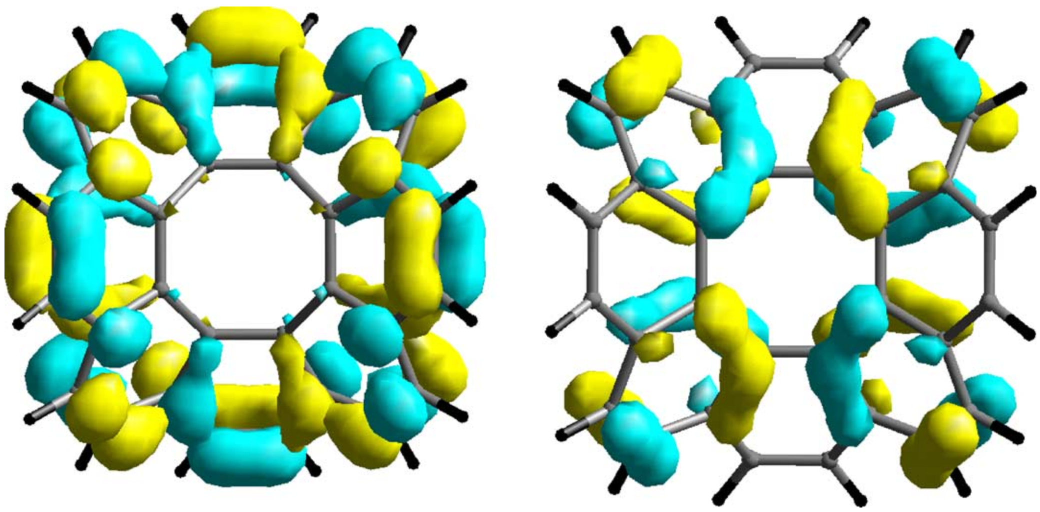

Fig. 3. HOMO and LUMO of the dication of [8]circulene.

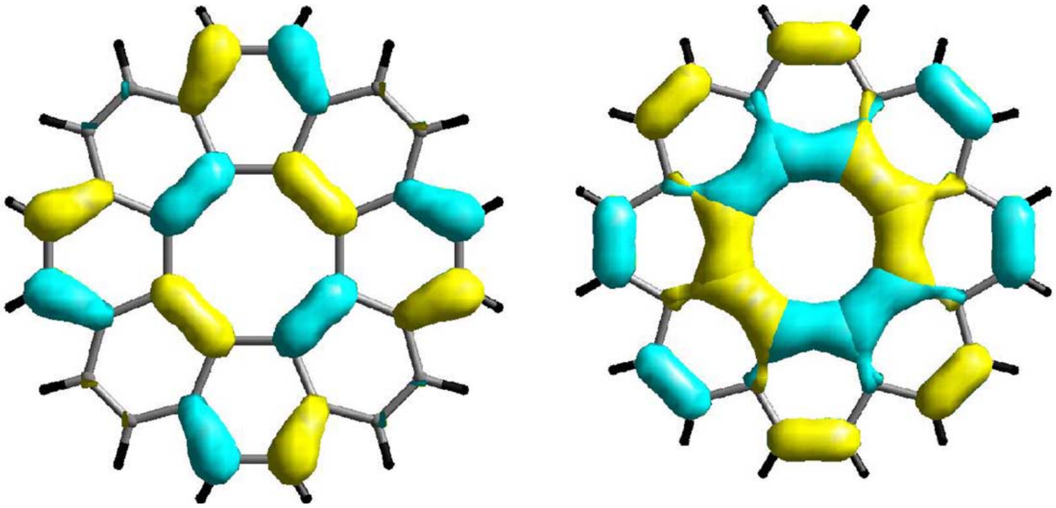

Fig. 4. HOMO and HOMO-1 for the dianion of [8]circulene.

It is well known that corannulene [3] shows an interesting effect of inversion, and that [8]circulene should also have this characteristic. During this inversion the saddle-shape of the molecule pass through planar configuration that suggest that it has an aromatic character.

The HOMA analysis allows to clarify this point, the equation proposed by Krywoski [14] was applied in this case:

$$\mathrm{HOMA} = 1 - \alpha/n\sum(R_{\mathrm{opt}} - R_{ij})^2$$

where α is 98.89, n is the number of the bonds taken into the summation, R_{ij} is the length of the bonds of the molecule under study and R_{opt} is obtained by the equation:

$$R\mathrm{opt} = [R(\mathrm{s}) + 2R(\mathrm{d})]/3$$

where $R(\mathrm{s}) = 1.524$ and $R(\mathrm{d}) = 1.397$ as suggested by Krywoski [14]. A HOMA value near 1 indicates aromaticity and near 0 no-aromaticity.

The results of these calculations are shown in the Table 2 for the eight membered ring and the six membered rings in all cases. The values are surprising, the distorted neutral form shows a more aromatic character with a HOMA index of 0.953 in the eight member ring and an average value of 0.803 for the six member rings. Indeed, the planar dianion is slightly anti-aromatic in the central ring (HOMA index −0.211), whereas the dication is less aromatic than the neutral species. Therefore, the more distorted species show the more aromatic character whereas the planar one is anti-aromatic.

The orbitals HOMO and HOMO-1 on one hand and the e degenerate set on the other are very illustrative of the aromaticity in the distorted species. In the first case, i.e. the neutral form, the π-orbitals around the COT ring that can participate in the aromaticity *are not in the same plane*. Furthermore, the e degenerate set gives rise to an exterior π-crown made up of the electrons delocalized from the six member rings, these rings considerably distorted with respect to the central eight member ring. In both cases the π bonds overlap in spite of the change of the plane maintaining the electronic current and consequently the aromaticity. So, the important feature is that *this molecule has two aromatic systems which surrounds the other being both aromatic*. Therefore, this molecule would have exterior and interior aromaticity.

Double aromaticity has been already suggested [17] in systems such as 3,5-dehydrophenyl cation or cyclo[6]carbon, but in those cases the two aromatic currents are present in the same ring in orthogonal planes. Here, the double aromatic system is on two different but interacting rings that are almost parallel (but in no case are planar) to one another.

This molecular orbital description can be fully assigned to the cation species, but considering a new order, i.e. the HOMO of the neutral form in the case of the cation is the LUMO, whereas the HOMO of the cation is the e degenerate set correspondent to the HOMO-1 of the neutral form, which is the orbital that supports the inner

Table 1
Energy results

	Dication	Neutral	Dianion
Total energy (a.u)	−1228.450	−1229.056	−1228.390
LUMO (a.u)	−0.427	−0.082	0.193
HOMO (a.u)	−0.450 (e)	−0.190	0.170
HOMO-1	−0.454	−0.213 (e)	0.063

Note: e accounts for a double degenerate.

Table 2
HOMA results

Compound	HOMA eight C atoms ring	HOMA six C atoms ring
Neutral	0.953	0.803
Dication	0.566	0.858
Dianion	−0.211	0.275

aromaticity and therefore the cation form also shows aromatic behaviour. The dication has a very large energy difference (Table 1) with respect to the neutral one, and it is probably because of this, that it has not been possible to make it.

The anionic species is also improbable since it involves the existence of several occupied orbitals with positive eigenvalues and a HOMO conformed by a degenerate set that is made up of all the 'exterior aromaticity' without the central counterpart. Furthermore, many of these orbitals have positive eigenvalues as was noted above, and therefore it will be very difficult to synthesize this ion.

It is not easy under these conditions to make propositions about the existence of this molecule and its ions. The best possibility is for the neutral species that can be expected to have extra stability arising from its two own aromatic parts. However, on the other hand [8]circulene should be a very rigid molecule because the planar dianion is very difficult to achieve due to the large energy difference caused by its intrinsic anti-aromaticity. All these propositions are based on the consideration of an isolated molecule in the gas phase since this is the condition used for theoretical calculations, the conditions in the bulk might change this situation and help to some stabilization. Furthermore, the dication is also far in energy from the neutral state although in this case a large aromaticity is expected because the change in geometry should be lower than that of the negative ion. Therefore, processes such as that found in corannulene involving molecular inversion are not expected.

4. Conclusions

From our results we can conclude that [8]circulene is an unstable compound. In the neutral form, its instability is due to the presence of two concentric aromatic currents. The dianion does not reach the aromatic state in spite of its planar conformation, in fact, it is more unstable than the neutral one. Finally, the dication loses the planar symmetry adopting a D_{2d} shape similar to the one without charge and has a higher energy with respect to the neutral form.

Acknowledgements

This research was supported by DGAPA-UNAM (PAPIIT IN100300). The technical assistance of MSc Norma Mireles is gratefully acknowledged.

References

[1] W.E. Barth, R.G. Lawton, J. Am. Chem. Soc. 88 (1996) 381.
[2] (a) M.V. Frash, A.C. Hopkinson, D.K. Bohme, J. Am. Chem. Soc. 123 (2001) 6687.
(b) I. Yavari, E. Taj-Khorshid, D. Nori-Shargh, S. Balalaie, J. Mol. Struct. (THEOCHEM) 393 (1997) 163.
(c) R. Salcedo, J. Mol. Struct. (THEOCHEM) 369 (1996) 189.
[3] J. Janata, J. Gendell, C.-Y. Ling, W. Barth, L. Beckes, H.B. Mark, R.G.J. Lawton, J. Am. Chem. Soc. 89 (1967) 3056.
[4] (a) A. Sygula, P.W. Rabideau, J. Mol. Struct. (THEOCHEM) 333 (1995) 215.
(b) L.T. Scott, M.M. Hashemi, M.S. Bratcher, J. Am. Chem. Soc. 114 (1992) 1920.
[5] (a) J.M. Robertson, J.G. White, J. Chem. Soc. Lond. (1945) 601.
(b) J.C. Hanson, C.E. Nordman, Acta Crystallogr. B 32 (1976) 1141.
[6] K. Yamamoto, T. Harada, M. Nakazaki, T. Nakao, Y. Kay, S. Harada, N. Kasai, J. Am. Chem. Soc. 110 (1988) 3578.
[7] M. Shen, I.S. Ignatyev, Y. Xie, H.F. Schaefer III, J. Phys. Chem. 97 (1993) 3212.
[8] K. Yano, M. Osatani, K. Tani, T. Adachi, K. Yamamoto, H. Matsubara, Bull. Chem. Soc. Jpn 73 (2000) 185.
[9] T. Liljefors, O. Wennerstrom, Tetrahedron 33 (1977) 2999.
[10] T.M. Krygowski, M.K. Cyranski, Chem. Rev. 101 (2001) 1385.
[11] Jaguar 4.0, Schrödinger, Inc., Portland, OR, 1991–2000.
[12] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
(b) A.D. Becke, Phys. Rev. A38 (1988) 3098.
(c) J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
(d) C. Lee, W. Yang, R.G. Parr, Phys. Rev. 37 (1988) 785.
[13] M.J. Frisch, G.W. Trucks, H.P. Schlegel, G.E. Scuseira, 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. Menucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A.Petersson, P.Y. Ayala, K. Morokuma, D.K. Malick, A.D. Rabuck, K.Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, L.R. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN98, Gaussian Inc., Pittsburgh, PA, 1998.
[14] (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.
[15] K.K. Baldridge, J.S. Siegel, J. Am. Chem. Soc. 123 (2001) 1755 and references therein.
[16] (a) K.B. Wiberg, Chem. Rev. 101 (2001) 1317.
(b) R. Vaughan-Williams, Chem. Rev. 101 (2001) 1185.
[17] (a) J. Chandrasekar, D.J. Eluvathingal, P.v.R. Schleye, Tetrahedron Lett. (1979) 3707.
(b) P.v.R. Schleyer, H. Jiao, M.N. Glukhotsev, J. Chandrasekar, E. Kraka, J. Am. Chem. Soc. 116 (1994) 10129.