

Topographical Analysis of Electron Density and Molecular Electrostatic Potential for Cyclopropa- and Cyclobutabenzenes

Shridhar R. Gadre*[†] and Savita S. Pundlik

Contribution from the Department of Chemistry, University of Pune, Pune 411007, India

Received March 23, 1995[⊗]

Abstract: The electron density (ED)- and molecular electrostatic potential (MESP)-based topographical studies are carried out for investigating the bonding and charge localization features, respectively, of cyclopropa- and cyclobutabenzenes. The ED topography brings out an increase in the double-bond character of the annulated bond. This analysis also shows that it is not possible to assign alternate single and double bonds for benzene in these compounds, as is conventionally done. The ellipticity data are used for obtaining information regarding the π character of the bonds and anisotropy of charge distribution. The results of MESP topography indicate that the four- and three-membered rings have a “push” and “pull” effect, respectively, on the aromatic nucleus. The ring-opening type of reactions in systems containing cyclopropane and the electrophilic attack at the β position for annulated benzenes are also explained by the MESP analysis.

I. Introduction

The title compounds have attracted a lot of attention after the findings of Mills and Nixon¹ (MN), who showed about 60 years ago that the imposed strain on benzene by the annulating five-membered ring changes its reactivity pattern. Thus, there is a preference for an electrophilic attack at the β position in indan and tetralin. The strain is believed to result in some benzene bonds being longer than the others. Such bond alternation is now commonly referred to as the MN effect. There have been opposing views regarding the presence of such an effect. According to the VB calculations by Hiberty et al.,² geometric distortions and π -orbital interactions are both responsible for the MN effect in benzocyclopropene, whereas in benzocyclobutene, geometric distortions alone are operative. Using ab initio SCF (3-21G) procedures, together with natural bond orbital (NBO) analysis, Faust et al.³ have demonstrated that the main cause of bond alternation in cyclobuta-fused benzenes is hyperconjugation whereas this is attributed to the conjugation effects in the case of benzenes annulated to cyclobutadiene and 3,4-dimethylenecyclobutane. Maksić and co-workers⁴ have found that X-ray analysis data, in general, do not show significant bond alternation: the latter effect is sometimes overestimated by the theory. The bond fixation has been mainly attributed to rehybridization and π -electron redistribution by them.^{4b} There are also contrasting reports by other research workers. Recently, Stanger⁵ compared the bond alternation in the structures of benzene annulated with four-membered rings optimized at the 3-21G level and those of benzene with bent hydrogens (simulating small rings). He suggested that the strain imposed by the small rings in the real systems is compensated by the formation of “banana” bonds

and therefore the MN effect is not observed. Compounds such as tricyclohexabenzene⁶ could, however, resist bent bonding and exhibit this effect. Apart from such geometrical effects, the aromatic character of the annulated system has also been found to dictate the structural characteristics of the overall system.⁶

In an excellent recent review by Siegel,⁷ it has been concluded that there are no appreciable MN-type distortions in simple annulated systems studied by them. The experimental methodologies developed by Boese and co-workers⁸ and the 6-31G** level of theory for calculations, in general, give results that are in agreement. It is also felt that structures similar to tricyclohexabenzene, the compound which had earlier been shown to possess bond alternation at the theoretical level,⁶ need to be studied experimentally for uncovering the presence of this effect. In Siegel's own words, “Mills–Nixon effect is a progeny of the empirical successes of van't Hoff and Kekule”.

Apart from the MN effect, another interesting aspect about the structures of annulated benzenes is the presence of a large C–C–C angle at a formal sp²-hybridized C atom. This angle is as large as 176.9° in benzene angularly annulated with cyclopropane and cyclobutane.^{8d}

Various types of reactions of benzocycloalkanes have been studied by Billups et al.⁹ According to their findings, generally, benzenes annulated with a cyclopropane ring undergo reactions involving cleavage of the three-membered ring. This is supported by the earlier results of Bee et al.,¹⁰ who also showed that the reactivity of the cyclopropane ring is increased upon angular annulation of another four-membered ring to benzene. Cyclobutabenzene is not attacked by (η^4 -1,5-cyclooctadiene)-[bis(trimethylphosphane)]nickel. This compound, however,

[†] Also at the Jawaharlal Nehru Center For Advanced Scientific Research, Jakkur Campus, Bangalore-560064, India.

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1995.

(1) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.

(2) Hiberty, P. C.; Ohanessian, G.; Delbecq, F. *J. Am. Chem. Soc.* **1985**, *107*, 3095.

(3) Faust, R.; Glendening, E. D.; Streitwieser, A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 8263.

(4) (a) Kovaček, D.; Margetić, D.; Maksić, Z. B. *J. Mol. Struct. (THEOCHEM)* **1993**, *285*, 195. (b) Eckert-Maksić, M.; Maksić, Z. B.; Hodoscek, M.; Mitic, D.; Poljanec, K. *J. Mol. Struct. (THEOCHEM)* **1993**, *285*, 187.

(5) Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277.

(6) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.

(7) Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1721.

(8) (a) Neidlein, R.; Christen, D.; Poignee, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruiz-Perez, C.; Hubner, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 294. (b) Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304. (c) Bläser, D.; Boese, R.; Brett, W. A.; Rademacher, P.; Schweger, H.; Stanger, A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 206. (d) Boese, R.; Bläser, D.; Billups, W. E.; Haley, M. H.; Maulitz, A. H.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313.

(9) Billups, W. E.; Rodin, W. A.; Haley, M. M. *Tetrahedron* **1988**, *44*, 1305.

(10) Bee, L. K.; Garrat, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 7076.

reacts with cyclopropabenzene and 3,4-dihydro-1*H*-cyclobuta-[a]cyclopropa[d]benzene to give a product in which Ni binds to the cyclopropane moiety.^{8c} The electrophilic attack on aromatic compounds with annulated strained rings is seen to be at the β position relative to the small ring,^{1,9,11} which has been explained in terms of rehybridization of the σ framework and stress effects.

Although the chapter on the MN effect seems to be closed now, various other interesting aspects like charge localization and bonding features in such annulated systems still remain to be investigated. In this paper, an attempt is made to throw light on the bonding features in aromatic compounds singly or multiply annulated to three- and four-membered rings employing the electron density (ED) topography as a tool. The electron deformation densities have been used previously to examine bending of the bonds in some of these systems.^{8d} Further, an explanation of the observed reactivities in terms of rigorous topographical analysis of molecular electrostatic potential (MESP) is attempted.

II. Electron Density and Molecular Electrostatic Potential

The ED, $\rho(\mathbf{r})$, a fundamental quantity in theoretical calculations, is also determinable experimentally using X-ray scattering.¹² It has been used for defining molecular shapes by Bader et al.,¹³ who have pioneered the use of derivatives of $\rho(\mathbf{r})$ for obtaining an "atoms in molecules" picture. The trajectories of its gradient field, viz. $\nabla\rho(\mathbf{r})$, help define boundaries of atoms in molecules and the Laplacian $\nabla^2\rho$ for the characterization of charge concentration and depletion.

The MESP, $V(\mathbf{r})$, is another related quantity which has emerged as a very powerful tool¹⁴ for probing the charge concentrations in molecules.^{15,16} It is defined as

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}' \quad (1)$$

The first term on the right hand side of (1) results from the contribution of the nuclei and hence is positive. The overall second term due to the continuous electronic charge density is negative. Thus $V(\mathbf{r})$ is positive if nuclear effects dominate, negative if electronic ones take over, and zero if both these effects are in balance.

The topographical analysis of any scalar field $S(\mathbf{r})$ involves locating the critical points (CP's) and characterizing them.¹³ A CP is a point where all the partial derivatives of $S(\mathbf{r})$ vanish, or $\nabla S = 0$. The matrix

$$A = \frac{\partial^2 S}{\partial x_i \partial x_j}$$

of all the second derivatives of S at CP, called a Hessian matrix, is employed for characterizing a CP. The number of non-zero eigenvalues of A constitutes the rank " r " of a CP, and the sum of signs of its eigenvalues, the signature " s ". A CP is then designated as (r, s) . S being a three-dimensional scalar field, only four types of nondegenerate CP's are possible, viz. (3, +3), (3, +1), (3, -1), and (3, -3). A (3, +3) CP represents a minimum, (3, -3) a maximum, and (3, +1) and (3, -1) CP's represent saddle points in $S(\mathbf{r})$.

In the following section, the findings of such topographical studies of ED and MESP are discussed for systems 1–12.

III. Results and Discussion

Experimental geometries⁸ have been available for 1–7. Geometries of 5–8 optimized at the 6-31G(D) level and those of 9–12 optimized at the MP2/6-31G* level have been obtained from Professor Boese. INDMOL package¹⁷ on a 16-node parallel machine PARAM is used for generating SCF wave functions for all the molecules with the 6-31G** basis set. The choice of this basis set is based on the experience that the MESP distribution is quite reliable at this level.¹⁸ For locating and characterizing the CP's in ED and MESP, an efficient parallel program, INDPROP, is used.¹⁹

The ED-topographical analysis²⁰ is carried out for isolating the (3, -1) bond CP's for various C–C bonds in these systems. Using the ED values ρ at bond critical points, the Bader bond orders ($n = \exp[A(\rho - B)]$) are calculated. The parameters A and B are determined by fitting the bond orders of ethane (1), ethylene (2), and acetylene (3). The negative eigenvalues λ_1 and λ_2 ($|\lambda_1| > |\lambda_2|$), at the bond CP, are employed for calculating the bond ellipticities ($\epsilon = (|\lambda_1|/|\lambda_2|) - 1$). These quantities are used in assessing the bond characteristics for various bonds. All the nonannulated benzene bonds are seen to possess a partial double-bond character with $n \approx 1.6$. The bridge bonds tend to be true double bonds: more so when the bridging is with the three-membered ring. This is evident from the bond orders depicted in the figures. For 5, 6, and 7, topographical studies have been carried out with the experimental geometries as well. In 5, the bond orders for annulated bonds of cyclopropane and cyclobutane are respectively 1.95 and 1.81 at the experimental geometry. The corresponding values obtained at the theoretical level are 2.08 and 1.83. In 6, the bond order for the cyclobutane annulated bond is 1.72 with experimental geometry and 1.84 for the theoretically optimized structure. For compound 7, the three- and four-membered rings give bond orders of 1.85 and 1.67, respectively, at the experimental geometry and 2.0 and 1.75, respectively, at the theoretical one. Thus, there is no qualitative difference between the bond orders calculated at theoretical and experimental geometries. The increase in the extent of double-bond character of the bond of annulation could be attributed to an increase in the charge concentration at this bond arising from rehybridization as has been discussed earlier.^{4b}

(11) (a) Streitwieser, A.; Ziegler, G. R.; Mowery, P. C.; Lewis, A.; Lawler, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 1357. (b) Finnegan, R. A. *J. Org. Chem.* **1965**, *30*, 1333. (c) Lloyd, J. B. F.; Ongeley, P. A. *Tetrahedron* **1965**, *21*, 245.

(12) Kappkhan, M.; Tsirel'son, V. G.; Ozerov, R. P. *Dokl. Phys. Chem.* **1989**, *303*, 1025.

(13) For a comprehensive account on ED topography, see: Bader, R. F. W. In *Atoms and Molecules—A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990; especially pp 4, 31, 330, 75–79. (b) Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389. (c) Bader, R. F. W.; Tang, T.; Tal, Y.; Biegler-König, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 940.

(14) For an earlier account of applications of MESP in chemistry, see: (a) Politzer, P. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981; p 7. (b) Bonaccorsi, R.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1970**, *52*, 5270.

(15) Gadre, S. R.; Kulkarni, S. A.; Shrivastava, I. H. *J. Chem. Phys.* **1992**, *96*, 5253.

(16) (a) Claxton, T. A.; Shirsat, R. N.; Gadre, S. R. *J. Chem. Soc., Chem. Commun.* **1994**, 731. (b) Mehta, G.; Khan, F. A.; Gadre, S. R.; Shirsat, R. N.; Ganguly, B.; Chandrasekhar, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1390.

(17) Shirsat, R. N.; Limaye, A. C.; Gadre, S. R. *J. Comput. Chem.* **1993**, *14*, 445.

(18) Gadre, S. R.; Kulkarni, S. A.; Suresh, C. H.; Shrivastava, I. H. *Chem. Phys. Lett.* **1995**, *239*, 273.

(19) Shirsat, R. N.; Bapat, S. V.; Gadre, S. R. *Chem. Phys. Lett.* **1992**, *200*, 373.

(20) A somewhat related, recent publication has come to our notice after submitting the first version of the manuscript: Yanez, O. M. M.; Eckert-Maksić, M.; Maksić, Z. B. *J. Org. Chem.* **1995**, *60*, 1638. This describes bent bonds in benzocyclopropenes and the effect of substituents on them on the basis of ED topography.

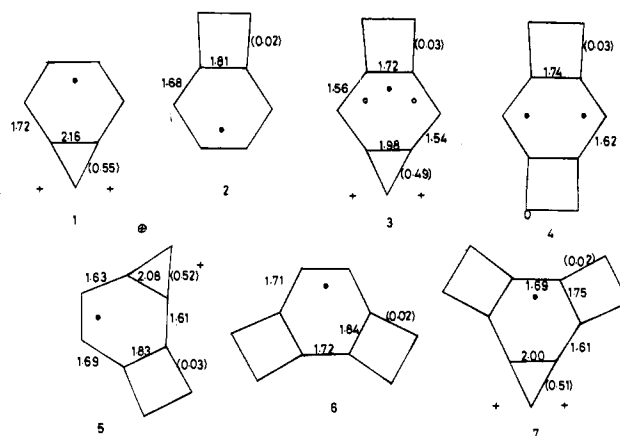


Figure 1. Structures of 1–7 (see text for details). Filled and empty circles represent locations of MESP minima above and below the aromatic nucleus mapped onto the molecular plane; “+” and circled “+” represent locations of MESP minima accompanying cyclopropane in the molecular plane. The numbers marked are Bader bond orders, and those within parentheses are the bond ellipticities for the corresponding bonds. The symmetry-related values are not shown.

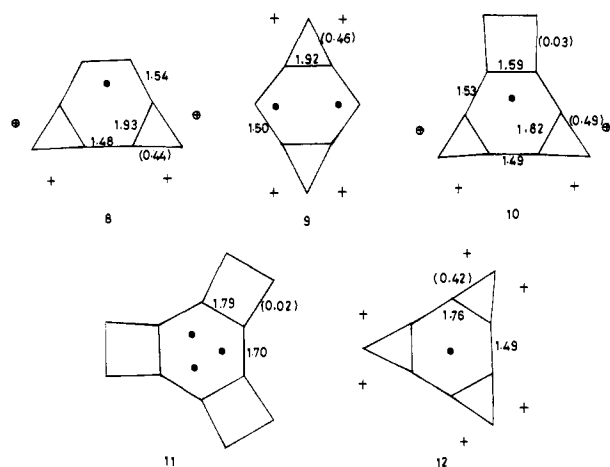


Figure 2. Structures of 8–12. Notations are as in Figure 1.

This effect is further extended in the highly symmetric systems **11** and **12**, and therefore the bond orders show only a limited variation. After this analysis, assignment of double-bond character to benzene bonds in these systems is found to be questionable. It is therefore advisable to avoid drawing them in the sketches. The external (i.e., nonannulated) bonds of both cyclopropane and cyclobutane are seen to be typical single bonds.

The ellipticities of all the bonds in benzene structure are around 0.2, a characteristic value for a delocalized π system, the major axis (direction of eigenvalue λ_2) being perpendicular to the benzene plane. The external bonds of cyclopropane in these systems show high ϵ values ≈ 0.5 , as has been observed for an isolated three-membered ring.^{13,21} In this case, there is a concentration of q along an axis lying in the molecular plane as reflected by the directions of the eigenvalue λ_2 . The bonds of annulation of cyclopropane possess a small ϵ value, and the direction of maximum charge concentration is still perpendicular to the molecular plane. In other words, the annulated bond of cyclopropane adopts the characteristics of a benzene bond. The external bonds in four-membered rings, on the other hand, have negligible ellipticity (≈ 0.02 or less). The angles subtended by the bond critical points with the atom positions constituting the bonds, α , are measured. The bonds in three- as well as four-

Table 1. The Number and MESP Values at Minima for 1–12^a

molecule	type of minimum	number of minima	ESP at minimum
benzene	●	12	−0.0322
1	●	2	−0.0322
	+	2	−0.0179
2	●	2	−0.0390
	○	2	−0.0351
3	●	2	−0.0351
	○	4	−0.035
4	+	2	−0.0191
	●	4	−0.0406
5	●	2	−0.0336 (−0.037)
	+	1	−0.0186 (−0.018)
6	⊕	1	−0.0184 (−0.022)
	●	2	−0.0371 (−0.043)
7	●	2	−0.0331 (−0.040)
	+	2	−0.0212 (−0.023)
8	●	2	−0.0306
	+	2	−0.0171
9	⊕	2	−0.0152
	●	4	−0.0279
10	+	4	−0.0151
	●	2	−0.0309
11	+	2	−0.0189
	⊕	2	−0.0191
12	●	6	−0.0363
	●	2	−0.0262
	+	6	−0.0174

^a The values in parentheses under the last column indicate the MESP values obtained with experimental geometries.

membered rings show bending outside the ring. The α values for the former are ≈ 5.5 , and those for the latter are ≈ 3.5 . The geometric distortions are thus exhibited by both types of annulated rings: the higher the extent, the smaller the ring.²⁰

The sites of charge concentration in a given molecule correspond to minima in MESP. For benzene, there are six (3, +3) CP's (with an MESP value of -0.032 au) each above and below (in all 12 of them) the molecular plane about 3 au away. These are signatures of double bonds, all the benzene bonds thus reflecting a double-bond character. In between two (3, +3) CP's, uninterfered by the molecular framework, there is always a (3, +1) CP which indicates conjugation. On each side of benzene ring, the six minima together with six intervening saddle points (with MESP only slightly higher than that at the minima) in benzene represent a delocalized π -charge cloud. For cyclopropane, three (3, +3) CP's (with an MESP value of -0.028 au) are observed in the molecular plane, external to each C–C bond, about 2.8 au away. These negative MESP sites are interconnected via three (3, +1) saddle points (MESP = -0.008 au) situated on the bisector of each H–C–H angle about 4.3 au away from C. Cyclobutane (with D_{4h} symmetry) too is surrounded by a negative MESP region, the minima being comparatively weak (MESP = -0.005 au) that are present along side each C–C bond, about 3 au away. Three- and four-membered rings thus are surrounded by a delocalized charge cloud, though only the former has been designated as a σ aromatic system.²¹

It is interesting to see how these individual features are reflected in annulated systems 1–12. The MESP values corresponding to all the (3, +3) CP's are listed in Table 1. For compounds 1–4, which have experimental geometries, the symmetrically placed minima do not always have identical MESP values, so the average values are reported in such cases. For systems 5, 6, and 7, the values in parentheses under the last column denote MESP values obtained with experimental geometries. (The (3, +1) saddle points in the π region observed for 3, 4, 9, and 11 with MESP values comparable to the corresponding minima are not shown in order to maintain clarity.) It is clear that the benzene minima reduce in number

(21) Kraka, E.; Cremer, D. In *Theoretical Methods in Chemical Bonding*; Maksić, Z. B., Ed.; Springer-Verlag, 1990; Vol. 2, p 495.

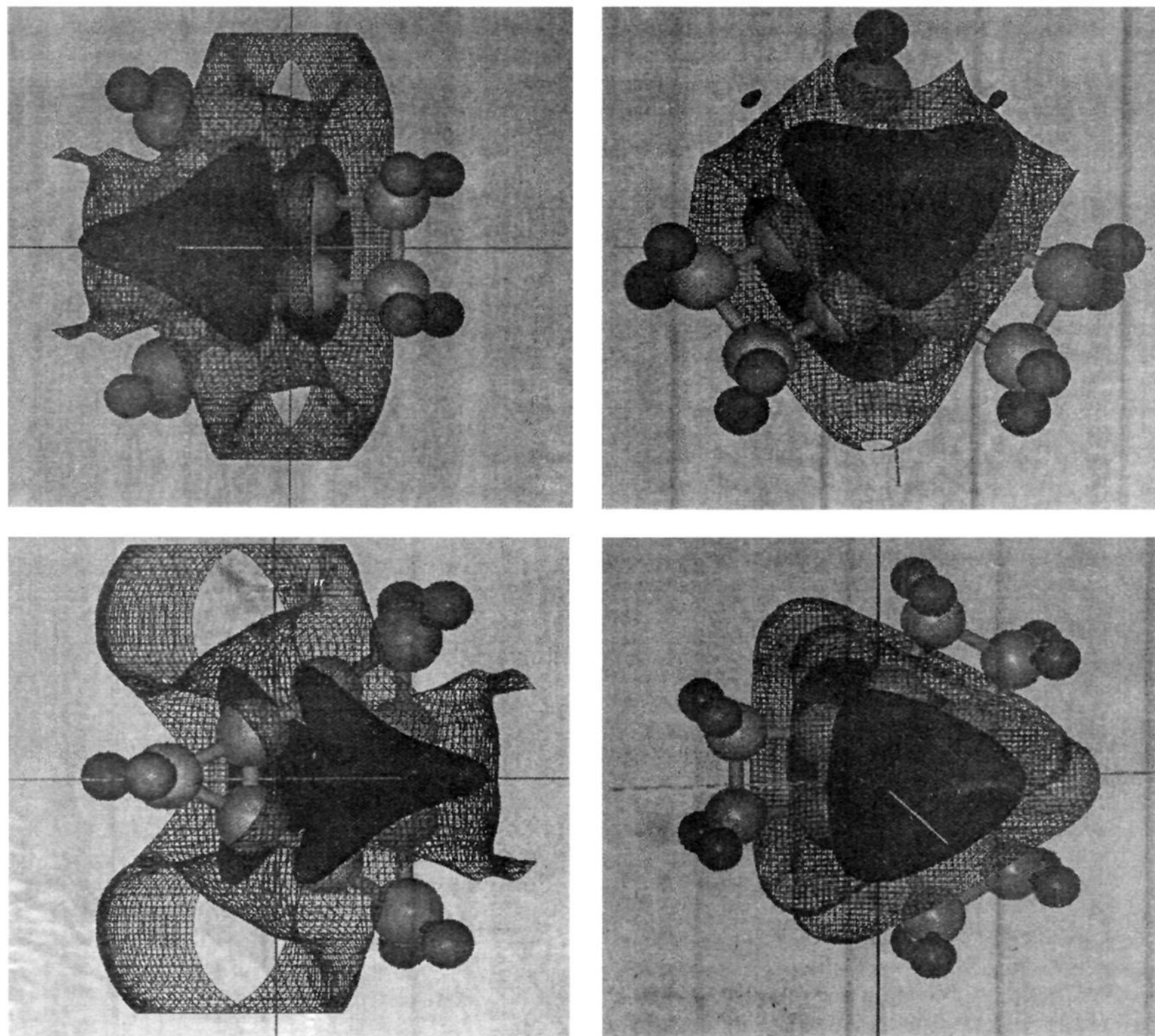


Figure 3. Iso-MESP surfaces for **10**, **7**, **12**, and **11**. The surfaces with dark and light shades correspond to MESP values of -0.02 and -0.005 au, respectively.

because of loss of symmetry. Also, most of these minima are situated near the β position relative to the annulated small ring. Thus, whenever an electrophile is attracted by the π electrons, the attack is expected to be at the β position in accordance with the experimental observation. The origin of such regioselective substitution which was believed to be due to rehybridization and stress effects^{9,11} is now explicable in terms of the MESP results which are more quantitative in nature.

Attaching a single cyclopropane ring (in **1**) does not seem to affect the π -charge concentration since the benzene MESP minimum value remains almost unaltered. However, this could be an artefact of using the experimental geometry. Whenever there are two (**8** and **9**) or three (**12**) such rings, however, the benzene ring is seen to be deactivated as reflected in the raised MESP's (cf. Table 1). The deactivation in the linearly annulated system **9** is more than that in **8**, wherein the small rings are attached angularly, and it is maximum for the triannulated system **12**. On the other hand, annulation with the cyclobutane structures causes activation of the aromatic nucleus. The activation increases in the order **4** and **6** > **2** > **11**. Again, MESP minima in **4** have a lower value than that in **6**. However, comparison would be more meaningful on molecules for which geometries are obtained in a consistent manner (such as theory/basis experiment, etc.). Thus the systems with both types of

small rings should result into "push-pull" systems and one may predict that there is activation of benzene in **7** and deactivation in **10**, which is indeed observed (cf. Table 1). The benzene activation (the push effect) is dominant in diannulated systems **3** and **5** with one ring each of cyclopropane and cyclobutane. The values of MESP at minima in **5**, **6**, and **7** with experimental geometries are somewhat lower. However, the trend observed for theoretically obtained structures is maintained.

The most interesting feature here is that, after annulation, two of the cyclopropane minima are retained, irrespective of whether benzene is already annulated or not. This is best brought out by the plots of iso-valued surfaces (Figure 3) obtained by employing a program UNIVIS.²² Here, the iso-MESP surface corresponding to a value of -0.005 au (with a higher transparency) always extends on the two sides of the cyclopropane ring (Figure 3a-c). In fact, the negative MESP regions above and below the aromatic ring join here. Such a feature is conspicuous by its absence for cyclobutane, e.g. in Figure 3d; for tricyclobutabenzene, the two negative regions remain isolated. In fact, the charge pushing effect of cyclobutane moiety is clearly discernible from Figure 3a. The values

(22) The program UNIVIS on a PC-486 with SVGA color monitor developed by A. C. Limaye, P. V. Inamdar, S. M. Dattawadkar, and S. R. Gadre (unpublished work).

of MESP minima accompanying annulated cyclopropane are raised (-0.015 to -0.021 au) compared to the isolated system. Since both, benzene and cyclopropane get deactivated on annulation, it is clear that the resultant system is a highly delocalized one. The locations of the CP's accompanying cyclopropane are more or less the same in all the systems. Thus, in annulated systems containing three-membered rings since there are sites of charge localization in the molecular plane, one can suspect the possibility of an electrophilic attack. Reactions of cyclopropabenzene with Ag^+ and Ni^+ , in fact, involve breaking of the three-membered ring,^{9,10} such reactions being scarcely observed for cyclobutabenzene.

IV. Summary

In this work, the molecules containing benzene annulated to one or more of three- and/or four-membered rings are studied, the most spectacular feature being the charge concentrations revealed by MESP topographical studies. This aspect has escaped attention in the earlier literature. These charge localization patterns support electrophilic attack at the β position relative to the small annulated ring and ring cleavage type of reactions in compounds containing cyclopropane. There is a "push-pull" effect of charge in systems with both types of rings which is quantified in terms of MESP values. Thus, there is activation

of aromatic nucleus on annulation to cyclobutane and deactivation when cyclopropane is annulated. ED topography is used for investigating the nature of bonding. The distinct features thereby obtained are an increased double-bond character of all the annulated bonds, high ellipticity for the external bonds of cyclopropane, and bending of bonds in both types of annulated rings. The bond order analysis further indicates that the conventional pictures of these compounds found in literature showing alternate single and double bonds are not always correct. The MESP- and ED-topography-based studies thus seem to be extremely useful for unraveling structural features of molecules in general. Further, they offer an effective way for investigating systematic variation in molecules (that belong to a given class) as illustrated by the present work.

Acknowledgment. The authors are grateful to Prof. R. Boese for providing the geometries of all the compounds studied in this work. The financial support from the Council of Scientific and Industrial Research, India (CSIR) [Grant No. 80(0003)/93-EMR-II], and that from the Department of Science and Technology (DST), New Delhi, India [Grant No. SP/S1/H-01/91], is gratefully acknowledged.

JA950953A