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ON THE VALIDITY OF EXTENDED HUCKEL CALCULATIONS IN THE STUDY OF CARBONIUM ION REACTIONS

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Abstract—The increasing use of Extended Huckel Theory in the study of reactions which involve some cyclic carbonium ions is noted and questioned.

An Extended Huckel calculation is performed upon the ring closure reactions of 3-exomethylene bicyclo [3.3.1]nonan-7-yl carbonium ion yielding the adamantyl cation and of the corresponding 3-spirocyclopropyl bicyclo [3.3.1] ion which produces the homoadamantyl cation. The results do not permit any valid inferences to be made concerning the relative abilities of a cyclopropyl group and a double bond to participate in the reaction and do not conform with chemical experience.

The anomalous NMR spectrum of the adamantyl cation presents a static and more propitious problem. A fresh interpretation is given.

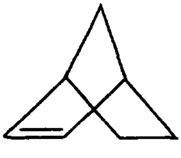
It is suggested that the application of Extended Huckel Theory to the chemistry of carbonium ions be discontinued.

Some introductory remarks

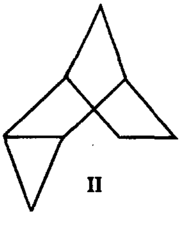
The degree of anchimeric assistance afforded by a cyclopropyl group or a double bond in the solvolysis of certain bridged ring compounds is quite astounding. Table 1 lists the relative rates of solvolysis at 25° for a number of molecules which are apposite. They have been arranged in three classes according as to whether the participating group is one, two or more than two carbon atoms distant from the reaction centre.

In class one and class two the cyclopropyl group is seen to exert a greater influence than the double bond, with a rate increase being effected by either group in class two greater than 10.^{10} This behaviour is reversed in class three where the double bond is now the more dominant. The enhancement in rate is again high but is only near to half that found in class two: for comparison the appropriate rate factor of *endo-anti*-tricyclo[3.2.1.0^{2,4}]octan-8-yl *p*-nitrobenzoate is 10.^{7}

What is the origin of these large increases in rate and what factors determine the relative abilities of a cyclopropyl group and a double bond to participate in the reaction? Articles by Fort and Schleyer,[1] and by Sargent[2] present a panoramic background to this absorbing question. A satisfying answer has yet to be given.

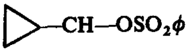
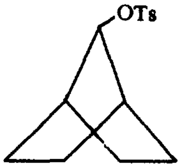
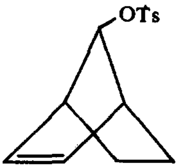
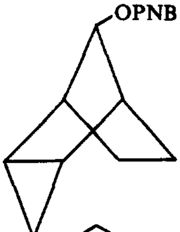
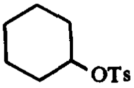
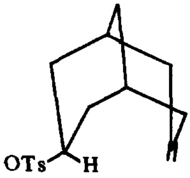
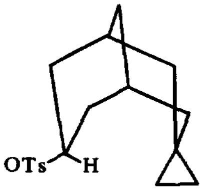


I



II

TABLE 1. RELATIVE RATES OF SOLVOLYSIS AT 25°

Class I	$CH_3—CH_2—OSO_2\phi$	1
	$CH_2{=}CH—CH_2—OSO_2\phi$	36
		500
Class II		1
		10^{11}
		10^{14}
Class III		1
		13,500
		4,375

It might be thought that a possible avenue to an understanding of reactions involving charged species lay through Huckel MO theory. Indeed some have already started upon such a course.[3] In particular, Extended Huckel calculations upon the norbornenyl cation (I) and the corresponding *endo*-bicyclo[3.2.1.0^{2,4}]octan-8-yl cation (II) show that the cyclopropyl group produces a greater stabilisation than does the double bond.[4] The result is quite convincing, yet needs to be looked at with much circumspection. Application of Huckel theory, in the simple or extended forms, to the problem of assessing the relative stabilities of carbonium ions is unfounded in principle. It may be that in rare cases by a fortuitous cancellation of terms a meaningful result is obtained, but this is not the norm.

The theory underlying this matter has been delineated by Coulson and Dewar who in 1947 considered the "Difficulties in the Application of Molecular Orbital Theory to Mesomeric Ions".[5] More recently Dewar has reiterated quite succinctly some pertinent objections.[6] Slater also discusses the problem.[7] The question is whether the variation in the sum of the one electron energies as a molecule alters shape, faithfully mirrors the change in the total energy of the molecule. Within the Hartree-Fock approximation, the sum of the one electron energies is equal to the total energy plus a term which allows for the overcounting of electron-electron interactions, minus a term representing the repulsion between the nuclei. For a neutral molecule, the last two terms tend to counterbalance each other as the internuclear distance changes, and the sum of the one electron energies follows the total energy. This is not the case for a charged species such as a carbonium ion, where the deficit of an electron leads to an imbalance between the terms.

Rather than repeat the analysis, perhaps a telling example from an atomic Hartree-Fock calculation may serve as an illustration. The energy of $S(1s^2 2s^2 2p^6 3s^2 3p^4)\ ^3P$ obtained by simply allocating the sixteen electrons in pairs of opposite spin amongst the one electron energy levels, and summing the orbital energies, is —492 Rydbergs. Similarly, the energy of the excited state $S(1s^2 2s^2 2p^6 3s^1 3p^3 3d^2)\ ^7F$ may be evaluated to be —498 Rydbergs. That is the excited state lies below the ground state! When electron interactions are properly accounted, chemical sense is restored and the excited state is found to lie 1·8 Rydbergs above the ground state. If this situation can be found for atoms, clearly one must tread with care in like realms for molecules.

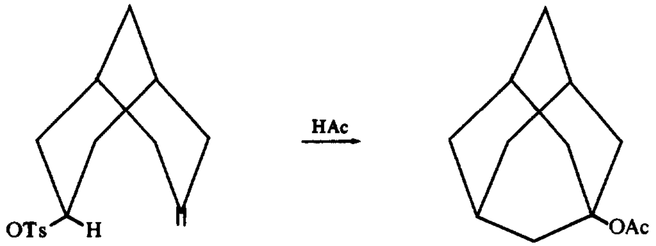
With this said, let us return to the result on the norbornane system. Instead of rejecting it as worthless out of hand, it might be wiser to see if the bridged ring systems have been found to offer an example where Extended Huckel Theory is reflecting correctly behaviour at a deeper level. The reactions of class three in Table 1 are calling out to be studied. This seems a good opportunity to look at them a little more closely.

The closure reaction

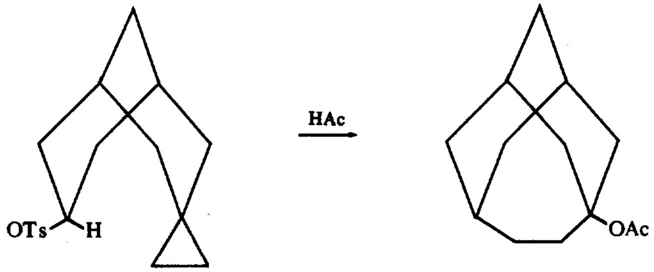
On solvolysis in buffered acetic acid, 3-exo-methylene bicyclo[3.3.1]nonan-7-yl yields adamantyl acetate, 3-spirocyclopropyl bicyclo[3.3.1]nonan-7-yl tosylate yields homoadamantyl acetate, reactions labelled III and IV respectively.

A possible pathway (V) for these reactions involves the intermediate formation of the adamantyl or homoadamantyl cation in the closure step A to B.

It is proposed to perform an Extended Huckel calculation to simulate the step A to B in reactions III and IV, and examine the variation in the sum of the one electron

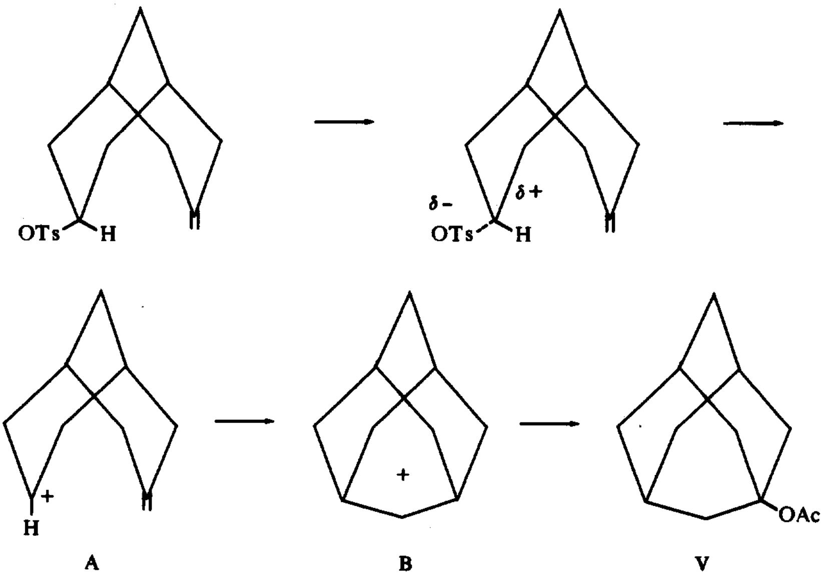


...III



...IV

energies during the closure, together with the changing pattern of the charge distribution, to see if they conform with chemical experience. Naturally, this will require a choice to be made for the changes in bond length and bond angle which occur during the reaction. These are shown in Fig. 1. Bond lengths and angles have been taken to



vary linearly with the angles θ or λ respectively, which define the extent of closure in each case; θ ranges from 0° to 54° 44′, λ from 73° 56′ to 7° 48′.

The bicyclo skeleton is assumed to remain unaltered during the course of reaction III. In the homoadamantyl case the initial bicyclic sketeton has been opened out slightly to permit a smooth transition to take place between the opened and closed structures. The reaction may so be envisaged, in either case, as involving the motion of the participating group towards the carbonium ion centre with a resultant dispersal of the positive charge and the formation of the cyclic cation.

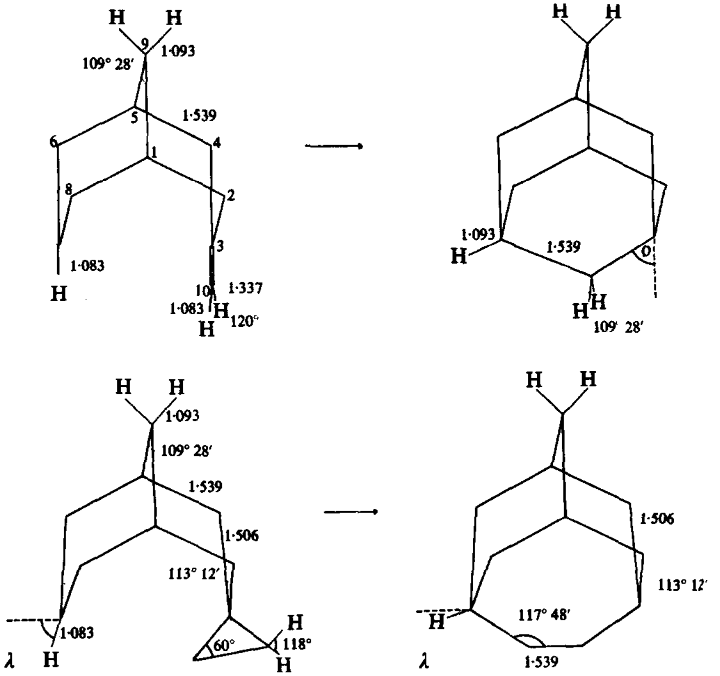


Fig. 1 The changes of geometry in the closure reactions.

The method of calculation

The extended form of Huckel MO theory has been formulated many times elsewhere[8] and need not be expressed again here. It is sufficient to note that the closure reaction (III) involves the solution of a secular determinant $|H_{ij} - e_i S_{ij}|$ with elements involving the 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals upon each of ten carbon atoms together with the 1s orbitals of fifteen H atoms.

The diagonal elements H_{ii} and the orbital exponents of the participating orbitals have been placed equal to the one electron orbital energies for carbon calculated by Clementi[9] and the Slater exponents respectively, a choice for which there is little

TABLE 2. DIAGONAL ELEMENTS H_{ii} (ev) AND ORBITAL EXPONENTS k

	H_{ii}	k
C (2s)	−19·32	1·625
C (2p)	−11·70	1·625
H (1s)	−13·60	1·0

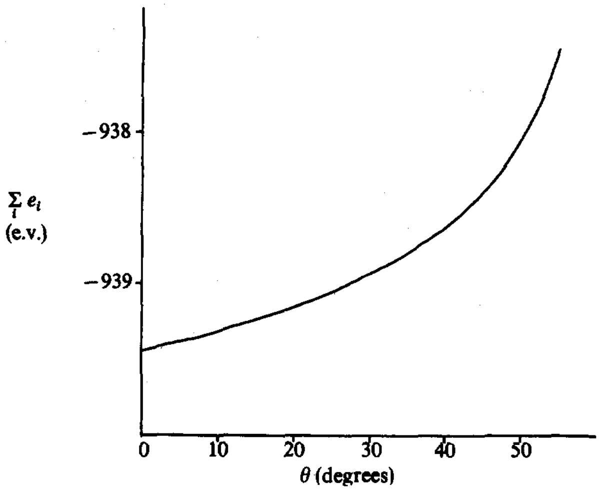


Fig. 2 The variation in the sum of the one electron orbital energies (e.v.) during the adamantyl closure reaction.

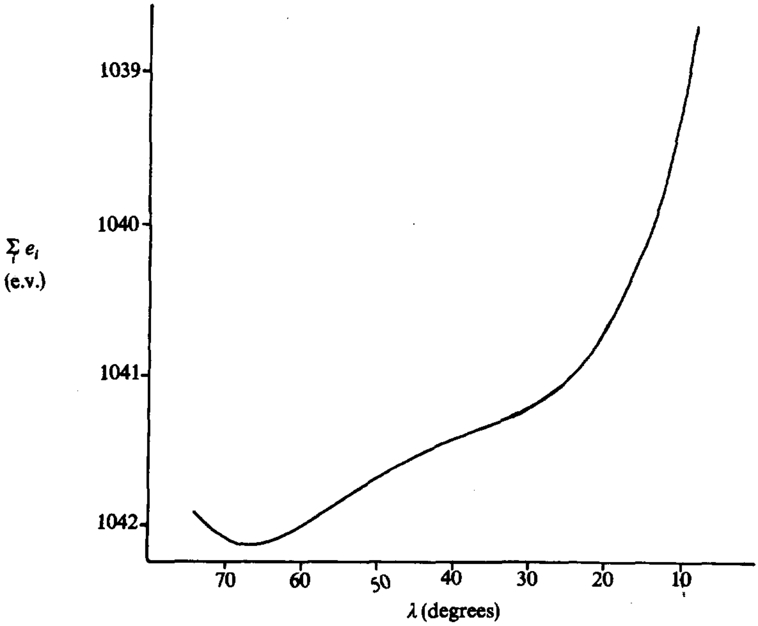


Fig. 3 The variation in the sum of the one electron orbital energies (e.v.) during the homoadamantyl closure reaction.

justification other than that it is the simplest in a field rank with speculation. The parameters for hydrogen are likewise equated with the free atom orbital energy and exponent. These values are collated in Table 2. The off-diagonal elements H_{ij} have been approximated in a conventional manner using the expression $H_{ij} = K S_{ij}[H_{ii} + H_{jj}]/2$ with K equal to 1·80.

On solution of the secular equation the fifty four electrons are distributed in pairs amongst the orbitals of lowest energy e_i and the corresponding distribution of charge evaluated by a Mulliken population analysis.

A discussion of the results

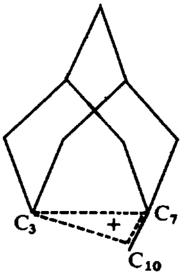
Depicted in Figs 2 and 3 is the variation in the sum of the one electron energies $\sum_{\text{occ. orbitals}} e_i$ with the angles θ and λ respectively. Fig. 2 pertains to reaction (III), Fig. 3 to reaction (IV). A sharp contrast may be seen between the two profiles. The curve for the homoadamantyl closure exhibits a shallow minimum. There is no minimum in the curve for adamantyl. This might be interpreted as indicating a preferential stabilisation by the cyclopropyl group over the double bond in such reactions. Such an inference is in complete discord with the experimental evidence cited earlier.

More disturbing is that in both reactions the open structure is favoured over the closed structure. One would therefore expect to find products resulting from ring opening in those reactions in which bridgehead carbonium ions are generated. Such products are not observed. On the contrary, there is a pronounced tendency for a wide variety of hydrocarbons to yield adamantanes on treatment with Lewis acids.[10]

Our conclusion is that the curves of Figs 2 and 3 in no way reflect observed chemical behaviour.

Whilst deductions based upon one electron energy summations would be in the present context erroneous, it is sometimes claimed that the Extended Huckel Method yields a distribution of charge comparable with that obtained from more sophisticated methods of calculation. Indeed this has been given as a justification for the use of the extended method on carbonium ions.[3]

Fig. 4 shows the change in electron density at the C atoms C_3, C_7, and C_{10} involved in the closure to the adamantyl cation, as the reaction proceeds. A smooth transfer of charge directly across from atom 3 to atom 7 is seen to occur, with very little alteration in charge at the terminal C atom C_{10}. If this result is at all meaningful it would imply that a non-classical carbonium ion of type VI is not formed during the course of the reaction. Similar behaviour, displayed in Fig. 5, is found for the homoadamantyl closure.



VI

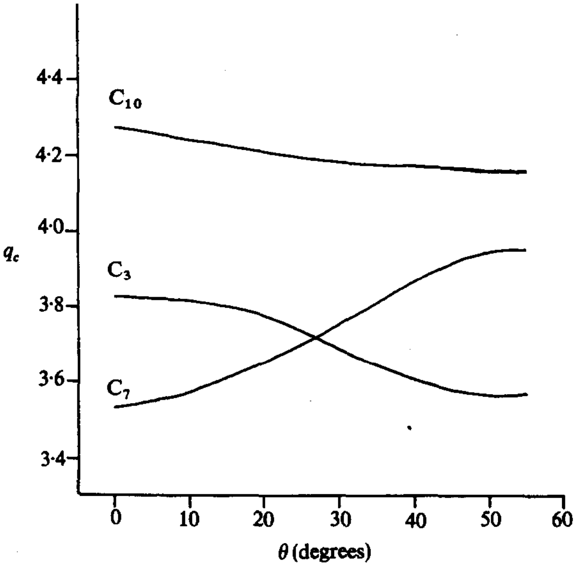


Fig. 4 The variation in charge density during the reaction at the C atoms directly involved in the adamantyl closure.

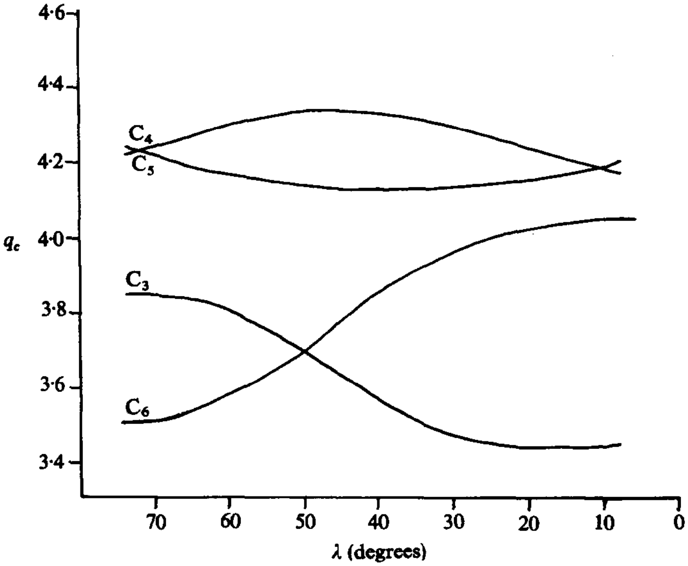
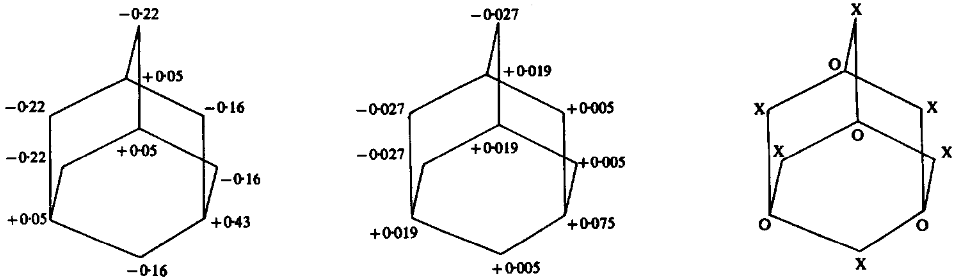


Fig. 5 The variation in charge density during the reaction at the C atoms directly involved in the homoadamantyl closure.

One engaging feature in the chemistry of the adamantyl cation is its NMR spectrum.[11] As is usual with carbonium ions the proton signals are all shifted downfield with respect to the parent hydrocarbon. What is unusual is that in the adamantyl cation the three bridgehead protons exhibit a greater shift than those adjacent to the formal carbonium ion centre.

When one looks at the charge distribution for the adamantyl cation in Fig. 6, this behaviour is not perhaps so strange. The bridgehead carbon atoms are distinguished by the fact that they appear to bear a small net positive charge. In consequence the bridgehead protons will be in a different environment to the β or δ protons. One might except this alteration in charge between the three types of site to be reflected in an alternating pattern of proton signals, as is observed.



Initial Distribution Self-Consistent Distribution Alternant Character

FIG. 6 The initial and self-consistent charge distribution in the adamantyl cation and an illustration of the ions alternant character.

On iteration of the charge to self-consistency the magnitude of the charge differences is dampened considerably as may be seen, but the alternating character of the charge distribution is still in evidence. Such an alternation in the charge distribution is not totally unexpected, for as is illustrated in Fig. 6, the adamantyl cation is an alternant species.* In contrast, the homoadamantyl cation is a non-alternant and likely to exhibit quite different properties.

CONCLUSION

The Extended Huckel Method, when applied to the dynamical problem of determining the relative abilities of a cyclopropyl group and a double bond to participate in a carbonium ion closure reaction, yields results which are completely out of key with observed chemical behaviour. For a static problem, relating to the distribution of charge in the adamantyl cation, the results are more harmonious.

Is this distinction between dynamic and static the essential factor? Even if it is, one is reluctant to place much credibility upon inferences drawn from the charge distribution when the reactions have been so grossly misrepresented by the theory.

The interpretation of the NMR spectrum in terms of the alternant character of the

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* The use of the word "alternant" here is in the sense that the 3^y carbon atoms are symmetry equivalent and distinguished from the 2^y carbon atoms by the starring process employed to define an alternant aromatic system. The Coulson Rushbrooke theorem and other properties of aromatic alternants are not implied.

adamantyl cation is independent of the calculation. That the calculated charge distribution supports this simple explanation is interesting, but a better founded study is required if it is to be substantiated.

Here lies the crucial objection. The application of Extended Huckel Theory in the elucidation of the chemistry of carbonium ions is so unfounded that one has no right to suggest that the results obtained have any chemical significance at all, no matter how appealing they may appear.

If calculations upon the relative stabilities of carbonium ions are to be performed then either a more refined approximation of MO theory needs to be adopted, or the classical methods of conformational analysis employed. The use of Extended Huckel Theory should be discontinued.

Acknowledgements—We should like to thank Dr. W. Parker for many illuminating discussions and for his continual interest in this work. We are indebted also to J. Danielsen (Aarhus) for the use of an Algol Huckel programme. One of us (T. F. W. McK.) also wishes to thank the Trustees of the Ramsay Memorial Fellowship Trust for the award of a Fellowship.

REFERENCES

[1] R. C. Fort and P. von R. Schleyer, *Adv. in Alicyclic Chem.* **1**, 283 (1966)

[2] G. D. Sargent, *Quart Revs* **20**, 301 (1966)

[3] R. E. Davis and A. Ohno, *Tetrahedron* **24**, 2063 (1968); J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.* **90**, 4311 (1968); A. C. Hopkinson, R. A. McClelland, K. Yates and I. G. Csizmadia, *Theoret Chim Acta* **13**, 65 (1969)

[4] R. Hoffmann, *J. Am. Chem. Soc.* **86**, 1259 (1964); *Tetrahedron Letters* No. 43, 3819 (1965)

[5] C. A. Coulson and M. J. S. Dewar, *Discussions of Far. Soc.* **2**, 54 (1947)

[6] M. J. S. Dewar, *Chem. Soc. Spec. Pub. 'Aromaticity'* **21**, 177 (1967)

[7] J. C. Slater, *Quantum Theory of Molecules and Solids* Vol. 1, p. 108, McGraw Hill, New York (1963)

[8] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963); **40**, 2480 (1964)

[9] E. Clementi, *Supp. to I.B.M. Journal of Research & Development* **9**, 2 (1965)

[10] M. Nomura, P. von R. Schleyer and A. A. Arz, *J. Am. Chem. Soc.* **89**, 3657 (1967)

[11] P. von R. Schleyer, R. C. Fort, W. E. Watts, M. B. Comisarow and G. A. Olah, *Ibid.* **86**, 4195 (1964)