

Short communication

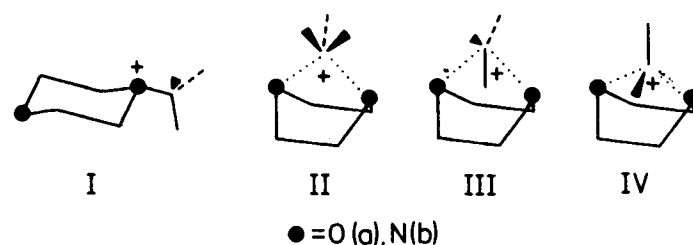
SOLVATION OF CARBOCATIONS BY 1,4-HETEROSUBSTITUTED
CYCLOHEXANES. A PENTACOORDINATED CARBON ATOM?

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Compounds containing pentacoordinated carbon have received much attention from both experimental [1] and theoretical [2] points of view. A possibility for their formation would be a simultaneous coordination (chelation) of two suitable electronegative groups to a carbocation. This situation could arise in 1-alkyl-1,4-heterosubstituted cyclohexanium salts, where isomerism II–IV is in principle possible. It would be of interest to establish the relative stabilities of structures II–IV and to compare them with that of the most stable non-chelated species I.



A molecular orbital study of these systems has been carried out employing the CNDO/2 method with geometry optimization [3]. The applicability of the method to the problem in hand was tested in three ways: (i) a plot of calculated binding energies vs. experimental heats of atomization, which includes open chain, cyclic and O-, N- and F-stabilized carbocations gives a linear relationship with a correlation coefficient of 0.995; (ii) CNDO/2 results [2] parallel sophisticated ab initio results [4] for the methonium ion, CH_5^+ , a species with bonding characteristics similar to the systems studied; and (iii) the calculated boat–chair energy difference for cyclohexane ($4.9 \text{ kcal mol}^{-1}$) agrees well with experimental estimates ($5.3 \text{ kcal mol}^{-1}$) [5], with results from ab initio molecular orbital calculations ($7.2 \text{ kcal mol}^{-1}$) [6] and with results from molecular mechanics calculations ($5.3\text{--}8.5 \text{ kcal mol}^{-1}$) [7].

The results show that II is more stable than either III or IV in analogy with the methonium ion, where a species containing only reflection planes of point group C_s is favoured [2, 4]. Ion IIa is less stable than Ia by $8.2 \text{ kcal mol}^{-1}$, suggesting the possibility of fluxional behaviour of Ia.

The energy difference IIb—Ib is 2.2 kcal mol⁻¹ smaller than IIa—Ia. This may be interpreted as the results of the increased ring puckering of the nitrogen heterocycle [8], which will favour preferentially the species with small bonding angles around the carbon atom.

Fluorine and methyl substituents are known to stabilize free carbocations relative to hydrogen by conjugation with the empty *p*-orbital on the carbon atom. In the system studied these substituents destabilize II with respect to I, undoubtedly reflecting the predominance of inductive over conjugative effects and the shorter distance between positive charge and substituent in II than in I.

Ab initio calculations have been carried out with STO-3G basis set [9] on model systems, where the parent heterocycle has been replaced by HO(CH₂)₂OH or H₂N(CH₂)₂NH₂. The results show qualitative trends similar to those presented above.

The association of triphenylmethyl cation with several linear and cyclic ethers and acetals has recently been studied [10]. Linear correlations were reported between the equilibrium constants and the basicities of the ethers on the one hand and between ΔH^0 and ΔS^0 on the other. 1,4-Dioxane was found to fit into these correlations thus suggesting a behaviour towards coordination to the cation similar to that of the other ethers studied. This undoubtedly reflects the bulkiness of the phenyl groups which makes arrangements such as II—IV improbable.

Part of the energy difference between II and I arises from the chair-to-boat isomerisation of the cycle. Higher rings are easier to deform and consequently may provide systems where species such as II are favoured over I. The calculations are being extended to assess the generality of the chelation process*.

REFERENCES

- 1 H. Hogeveen and P. W. Kwant, *Accounts Chem. Res.*, 8 (1975) 413 and refs. therein.
- 2 P. Cremaschi and M. Simonetta, *Theor. Chim. Acta*, 37 (1975) 341 and refs. therein.
- 3 J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
- 4 J. B. Collins, P. v. R. Schleyer, J. S. Binkley, J. A. Pople and L. Radom, *J. Am. Chem. Soc.*, 98 (1976) 3436.
- 5 W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *J. Am. Chem. Soc.*, 82 (1960) 1255.
- 6 J. R. Hoyland, *J. Chem. Phys.*, 50 (1969) 2775.
- 7 G. M. Kellie and F. G. Riddell, *Top. Stereochem.*, 8 (1973) 225.
- 8 C. Romers, C. Altona, H. R. Buys and E. Havinga, *Top. Stereochem.*, 4 (1970) 57.
- 9 W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, 51 (1969) 2657; R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 54 (1971) 724.
- 10 S. Slomkowski and S. Penczek, *J. Chem. Soc. Perkin Trans. 2*, (1974) 1718.
- 11 J.-M. Lehn, *Struct. Bonding (Berlin)*, 16 (1973) 1.

*This chelation process is in principle similar to the saturation of the coordination sites of metal cations by polyethers and related compounds [11].