Tetrahedron Letters No. 49-50, pp 4303 - 4304, 1974. Pergamon Press. Printed in Great Britain.

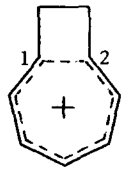
THE INVOLVEMENT OF THE CYCLOBUTANE RING IN HOMOAROMATIC CONJUGATION

Robert C. Haddon*

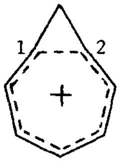
Research School of Chemistry, Australian National University
P.O. Box 4, Canberra, ACT 2600, Australia

(Received in UK 14 October 1974; accepted for publication 24 October 1974)

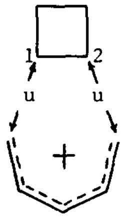
In a previous publication[1] we have shown how a consideration of the Walsh orbitals of cyclopropane and the HMO orbitals of polyenic ions can provide an insight into the mechanism of homoaromaticity, which leads quite naturally to the Winstein[2] picture of an "open" cyclopropane unit. In this study we use a similar approach, to consider whether a cyclobutane ring might be able to replace the traditional cyclopropane ring as a homoaromatic linkage (*cf* 1 and 2).



1



2



3

For simplicity we take as the polyenic system the pentadienyl cation (4)(similar arguments may be applied to the other systems considered in ref 1), and consider its union[1,3] with the cyclobutane ring (3). It will be appropriate to consider the donation of electron density from the cyclobutane ring into χ_3 (4) which is the lowest vacant orbital of the pentadienyl cation[1]. For the valence orbitals of cyclobutane we make use of the Walsh picture (5) which has been fully discussed by Salem and Wright[4], and Hoffmann and Davidson[5]. For the degenerate e_u pairs (ψ_3, ψ_4 and ψ_5, ψ_6) we have adopted the linear combination given by Salem and Wright[4], but the level ordering follows Hoffmann and Davidson[5]. Clearly the bonding situation contrasts markedly with the cyclopropane case[1], for the highest occupied orbitals of cyclobutane, specifically ψ_3 is of the wrong symmetry to interact with χ_3 in the pentadienyl cation (4) (although ψ_5 is of the right symmetry to *accept* electron density from χ_3). Furthermore, while ψ_2 (which is of the correct symmetry to overlap with χ_3), lies fairly high in the occupied manifold[5] it is very different in character from the corresponding orbital in cyclopropane (6). In the case of cyclobutane, ψ_2 has equal coefficients at all carbon atoms, and hence electron density will not be preferentially removed from the 1-2 bond (cf ϕ_2 in 6), and conjugation with this orbital therefore seems unlikely to lead to an "open" cyclobutane unit. Furthermore, due

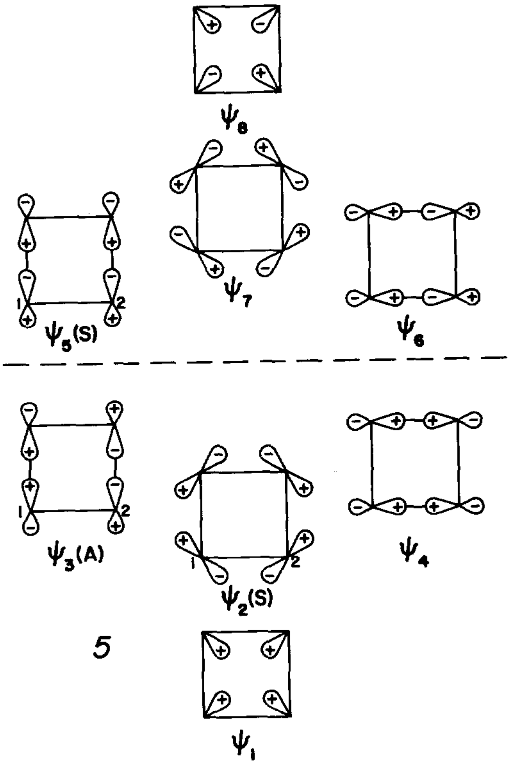
---

* Queen Elizabeth II Fellow, 1973-75

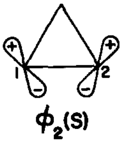
to the angle of the "peripheral" π orbitals in cyclobutane (formally at 45° to the normal as compared to 30° in cyclopropane), overlap of ψ_2 with the $p\pi$ orbitals of a polyene such as 4, may be difficult (and would require a large "opening" of the ring to be improved).

While these considerations certainly do not rule out the participation of the cyclobutane ring in homoaromatic conjugation, it does appear that particularly severe conditions will have to be employed in order to force the cyclobutane ring to approach the ability of the cyclopropane ring to act as a homoconjugate linkage. This may indicate that the cyclopropane ring occupies an exclusive position in homoaromaticity, and may be an essential ingredient for its occurrence. The small amount of available experimental evidence[6] seems to support the arguments presented above, as no great propensity has yet been shown for cyclobutane to enter into homoaromatic conjugation.

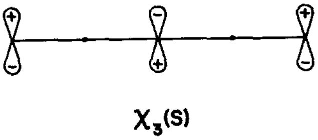
Acknowledgement. The author is grateful to Professor D.P. Craig (ANU) and Professor R. Hoffmann (Cornell) for their comments on the manuscript.



5



6



4

References

1. R.C. Haddon, *Tetrahedron Lett.*, 2797 (1974).
2. S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969).
3. See M.J.S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, and references therein.
4. L. Salem and J.S. Wright, *J.Amer.Chem.Soc.*, 91, 5947 (1969); L. Salem, *Chem.Brit.*, 5, 449 (1969).
5. R. Hoffmann and R.B. Davidson, *J.Amer.Chem.Soc.*, 93, 5699 (1971).
6. (a) E. Vogel, W. Maier and J. Eimer, *Tetrahedron Lett.*, 655, (1966); J.J. Bloomfield and J.R.S. Irelan, *Tetrahedron Lett.*, 2971 (1966).
   (b) L.B. Anderson, M.J. Broadhurst and L.A. Paquette, *J.Amer.Chem.Soc.*, 95, 2198 (1973).