Tetrahedron Letters,Vol.23,No.42,pp 4379-4380,1982   0040-4039/82/424379-02$03.00/0
Printed in Great Britain

BOND ORDERS IN 1,5-BENZODIAZEPINIUM CATIONS COMPARED TO THOSE IN BIPHENYLENES. ANOTHER EXAMPLE OF BONDS OF LOW BOND ORDER WHICH ISOLATE π-ELECTRON SYSTEMS.

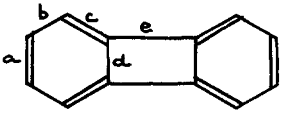
Christopher Glidewell and Douglas Lloyd*
Department of Chemistry, Purdie Building, University of St. Andrews
St. Andrews, Fife, Scotland, KY16 9ST

The bonds which link separate stabilising π-electron systems in 1,5-benzodiazepinium cations are shown from X-ray analysis and MNDO calculations to be of very low bond order, like the bridging bonds in biphenylenes, thereby inhibiting destabilising interaction between the π-electron systems.

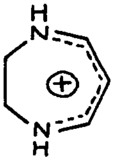
A major point of interest in the chemistry of biphenylene (I) has been concerned with bond fixation in the molecule and the very long bonds which form the links between the two six-membered rings. Results obtained from an electron-diffraction study[1] are included in Table 1. They are in good agreement with X-ray crystallographic results.[2] Also listed in this table are calculated values of the bond orders based on the experimental geometry and obtained using the MNDO method.[3] These values accord with the structure implied by formula (I) and emphasise the low bond orders of the bridging bonds. This structure has been considered to be a consequence of the attempted minimising both of cyclobutadienoid structure in the central ring and of electronic interaction between the two stabilising 6-π-electron systems of the outer rings which could lead to a destabilising peripheral 12-π-electron system.

Table 1. Bond Lengths and Bond Orders in Biphenylene (I)

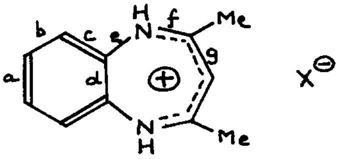
Bonds	Bond Lengths[1] (Å)	Bond Orders
a	1.370	1.578
b	1.428	1.248
c	1.372	1.569
d	1.432	1.218
e	1.534	0.968



(I)



(II)



(III)

We describe now another example in which two stabilising π-electron systems, which might interact with one another to produce destabilising π-electron systems, either peripheral or in one ring, are in fact kept at arms' length, in that they are connected by bonds of very low order.

Dihydrodiazepinium cations (II) include a delocalised vinamidinium system[4] which imparts a stabilisation energy of ~20 k cal mole^{-1}.[5] In the 1,5-benzodiazepinium cations, *e.g.* (III), electronic interaction between the vinamidinium system and the benzene ring would provide a peripheral destabilising 12-π-electron system. An X-ray crystallographic study[6] of (III, X = Cl) shows the cation to be nearly planar. MNDO calculations, using the experimental geometry of the heavy-atom framework and optimised positions for the hydrogen atoms, show that bonds *e* are of very low bond order (see Table 2). The vinamidinium system is largely delocalised as in the dihydrodiazepinium cation.[7] The benzene ring shows less bond fixation than is evident in biphenylene but bond *d* has by far the lowest bond order. Aside from destabilising peripheral conjugation, interaction between the vinamidinium system and π-electrons in this bond would provide a destabilising 8-π-electron system in the seven-membered ring.

Table 2. Bond Lengths and Bond Orders in the 1,5-Benzodiazepinium Cation (III)

Bonds	Bond Lengths[6] (Å)	Bond Orders
a	1.357	1.433
b	1.371	1.391
c	1.385	1.407
d	1.389	1.331
e	1.427	0.941
f	1.326	1.329
g	1.375	1.331

1,5-Benzodiazepinium salts thus resemble biphenylenes in that in both cases stabilising electronic systems are separated by long bonds of low bond order, thereby minimising realisation of an overall destabilising electronic interaction.

1. A. Yokozeki, C.F. Wilcox and S.H. Bauer, *J. Am. Chem. Soc.*, 96, 1026 (1974).
2. J.K. Fawcett and J. Trotter, *Acta Cryst.*, 20, 87 (1966).
3. M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 99, 4899 (1977); W. Thiel, P. Weiner, J. Stewart and M.J.S. Dewar, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Program 428.
4. D. Lloyd and H. McNab, *Angew. Chem.*, 88, 496 (1976); *Angrew. Chem. Internat. Edn.*, 15, 459 (1976).
5. D. Lloyd and D. R. Marshall, *Chem. Ind.*, 335 (1972); D. Lloyd, C. Nyns, C.A. Vincent and D.J. Walton, *J. Chem. Soc. Perkin II*, 1441 (1980).
6. J.C. Speakman and F.B. Wilson, *Acta Cryst.*, B32, 622 (1976).
7. G. Ferguson, W.C. Marsh, D. Lloyd and D.R. Marshall, *J. Chem. Soc. Perkin II*, 74 (1980).

(Received in UK 14 July 1982)