Tetrahedron Letters,Vol.24,No.11,pp 1139-1142,1983 0040-4039/83/111139-04$03.00/0
Printed in Great Britain

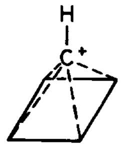
CLUSTER CARBODICATIONS.

THE STABILITY OF A *bis*-PYRAMIDAL D_{4h} STRUCTURE FOR THE FULVALENE DICATION*

Robert M. Moriarty, Lian S. John and Bruce A. Luxon
Department of Chemistry
University of Illinois at Chicago Circle
Chicago, Illinois 60680

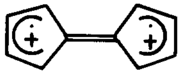
Summary - STO-3G calculations show that the D_{4h} structure of the fulvalene dication 4 is an energy minimum with respect to this constraint lying some 21 kcal/mole above the singlet D_{2h} (3) structure with both being less stable than triplet D_{2h} (3). Analogies are drawn with organometallics.

The pyramidal C_{4v} structure (1) for $C_5H_5^+$ has been the subject of CNDO/2[1a], extended Hückel[1b], CNDO modified[1c], MINDO/3[1d,f] and *ab initio* at the STO-3G level[1e,g] calculations. Extended basis set calculations[2] indicate that the square-based pyramidal structure for 1 is a stable entity; 4-31G calculations place 1 50kcal/mole above the singlet D_{5h} structure.[3]

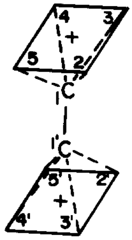


1 C_4v

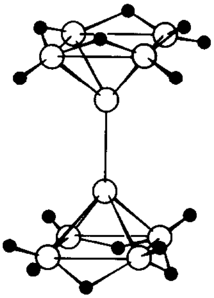
2 triplet D_{5h}



3 triplet D_{2h}



4 D_{4h}



5 $B_{10}H_{16}$

Planar classical D_{5h} (2) is antiaromatic while the pyramidal(1)C_{4v} structure is aromatic because it contains six interstitial electrons in three low energy bonding molecular orbitals. The concept of aromaticity is thus extended to ring-cap three-dimensional structures (*nido* as in 1 or *closo* as in a trigonal bipyramid for $C_5H_5^{+}$[3]) based upon a 4n + 2 array of interstitial electrons using p-orbitals of the $(CH)_n$ annulene and s and p-orbitals of the capping group[3]. This analogy applies to other three dimensional 4n + 2 systems such as isolobal metallocenes[4] and carboranes.[5] Furthermore, analogy exists in the isoelectronicity among +C-H, $Fe(CO)_3$ and B-H for such nido cluster structures which consist of a capping group or an atom attached to a $(CH)_n$ annulene to yield 4n + 2 interstitial electrons.

One may extend this formal relationship between a planar antiaromatic structure and the related cluster type aromatic one to the hypothetical fulvalene dication.[6] The D_{2h} planar structure (3) is antiaromatic in the same sense as 2, and the D_{4h} bis-pyramidal cluster structure (4) is aromatic in that it contains $2(4n + 2) = 12$ interstitial electrons. In 4 the capping group C_1-C_1' is better described as a connecting group and might, a priori, be $+\bar{C}-\bar{C}+$, $+\dot{C}=\dot{C}+$ or $+C\equiv C+$.

Just as 1 is derived formally from 2 by cheletropic shift of of the endo-cyclic $\bar{C}H^+$ unit to an apical position, 3 → 4 involves extrusion of the $+\bar{C}-\bar{C}+$ unit from its bis endocyclic location to a bis apical position relative to the two basal rings. A further relationship between 1 and 4 is found in transition metal cluster chemistry. The $C_4H_4Fe(CO)_3$ molecule is well known;[8] recently a cluster complex $C_4H_4Fe{\equiv}FeC_4H_4(CO)_3$ μ-carbonyl bis (cyclobutadiene carbonyl iron) has been described.[9] Thus the isolobal connection between $Fe(CO)_3$ and $+\bar{C}-H$ is extended to $Fe_2(CO)_3$ and $+\bar{C}-\bar{C}+$. The structure of $B_{10}H_{14}$, 5, completes the analogy in the borane series.[10]

We report now computational validation for this analogy from Gaussian 70[11] with minimal STO-3G basis set[12] calculations on 3 and 4 using the symmetry constraints D_2h and D_4h respectively.

The STO-3G description of singlet D_{4h} (4) is quite satisfactory (Fig 1). It is an energy minimum within the imposed symmetry constraint lying some 21 kcal/mole above the singlet D_{2h} (3) system (Fig. 2). The C_1-C_2 bond length of 1.605 Å compares with the analogous distance calculated for 1 of 1.356 Å (CNDO) 1.583 A (MINDO[1d], 1.589 Å STO-3G[1c] and

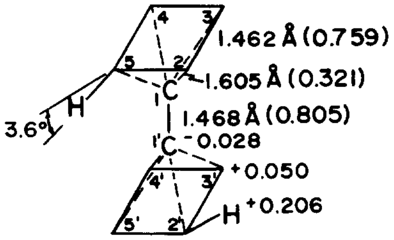


FIG. 1

STO-3G Optimized Geometry
Calculation on D_{4h} (4)
Energy (hartrees)
Singlet=-377.843
Triplet=-377.476

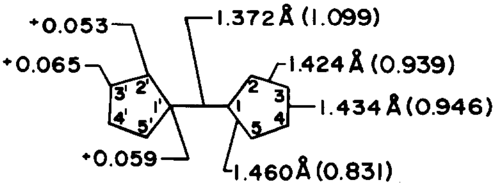


FIG. 2

STO-3G Optimized Geometry
Calculation on D_{2h}
Energy (hartrees)
Triplet=-378.038
Singlet=-377.878

1.613 Å 21G[12]. The basal bond distance of 1.462 Å is similar to 1.477 Å[1c] and 1.472 Å 21G[12] for 1 by the above methods. The C_1-C_1' bond distance 1.468 Å is what one would expect for a single bond[13]. The Mulliken overlap populations reveal reasonably strong cap-ring bonding at 0.321. The C_2-C_3 value of 0.758 and C-H value of 0.766 are very close to the calculated values.[2] The large value of 0.805 for the C_1-$C_{1'}$ bond agrees with concentration of electron density between these two carbon atoms. These may be compared with HC≡CH (0.98) and $H_2C{=}CH_2$ (0.40).[14] The formal charges on the basal carbon atoms are small while those on hydrogen are relatively large. The negative charge at C_1 and C_1' (-0.028) agrees in sign but not magnitude with a value of -0.061 for the apical carbon atom is the C_{5v} structure for $C_6H_5^+$[15]. The out of plane bending of the ring hydrogen atoms by 3° degrees towards the cap carbons suggests the presence of less diffuse bonding orbitals on these carbons[3].

The STO-3G calculations on singlet and triplet D_{2h} (3) are given in Fig. 2. The triplet is 101 kcal/mole more stable than the singlet. Reference to the atomic charges shows that positive charge is fairly equally distributed over the rings with a rather large concentration occurring on hydrogen in both the singlet and triplet states. Both models are characterized by relatively large overlap populations between the rings.

The difference in energy between the triplet D_{2h} (3) (-378.038) and singlet D_{4h} (-377.842) is 122 kcal/mole. We do not place strict quantitative significance upon these numbers other than to note that they are in the same direction as 1 (C_4v) *vs* 2(D_5h). Finally it must be recognized that the STO-3G energy differences are likely to change with the theoretical level employed.

In summary this work is a kind of "reverse isolobal analogy". The hallmark of organometallic cluster compounds is the occurrence of extensive bridging. Dication 4 is unusual from the viewpoint of organic structural theory but routine from the viewpoint of inorganic cluster ions. The propensity for bridging in transition metal clusters ultimately depends upon the availability of d-orbitals of appropriate symmetry and energy for bonding. These are normally not available in simple carbocations. It is interesting to note that in the case of μ-carbonyl *bis* cyclobutadienyl carbonyl iron, $C_4H_4Fe{\equiv}FeC_4H_4(CO)_3$ a structure involving two ferracyclopentadiene rings was considered as a possible molecular formulation.[9]

The relationship between the two structures is analogous to that between 3 and 4. The non-bridged structure was excluded rigorously on the basis of n.m.r evidence[9]. In the case of $B_{10}H_{14}$ (5) the D_{4h} is unique in the utilization of 2s and 2p for maximum bonding of 32 electrons in 40 orbitals[16]. It is of interest to search for other analogies on going from cluster systems to carbocyclic ones and *vice versa*.

References

1) (a) S. Yoneda and Z. Yoshida, Chemistry Letters, 607 (1972), (b) W. D. Stohrer and R. Hoffman, J. Am. Chem. Soc., 94, 1661 (1972), (c) H. Kollmar, H. O. Smith, and P. V. R. Schleyer, J. Am. Chem. Soc., 95, 5834 (1973), (d) M. J. S. Dewar, and R. C. Haddon, J. Am. Chem. Soc., 95, 5836 (1973), (e) W. J. Hehre and P. V. R. Schleyer, J. Am. Chem. Soc., 95, 5837 (1973), (f) M. J. S. Dewar and R. C. Haddon, J. Am. Chem. Soc., 96, 255 (1974) (g) H-J Kohler and H. Lischka, J. Am. Chem. Soc., 101, 3479 (1979).

2) W. J. Hehre, in "Modern Theoretical Chemistry", Plenum Press, New York, N. Y. 1977, Vol. 4, Ch. 7.

3) E. D. Jemmis and P. V. R. Schleyer, J. Am. Chem. Soc., 104, 4781 (1982).

4) M. Elian and R. Hoffman, Inorg. Chem., 14, 1058 (1975), J. K. Burdett, J. Chem. Soc., Faraday Trans, 70, 1599 (1974); D. M. P. Mingos, J. Chem. Soc., Dalton Trans., 602 (1977) M. Elian, M. M. L. Chen, D. M. P. Mingos, R. Hoffman, Inorg. Chem., 15, 1148 (1976); K. Wade, in 'Transition Metal Clusters", B. F. G. Johnson, Ed., John Wiley and Sons, Chichester, 1980, page 193-264.

5) K. Wade, Advan. Inorg. Chem. Radiochem., 18, 67 (1976); Inorg. Chem., 10, 210 (1971).

6) The term hypothetical refers to the fact that this dication has not been detected. The fulvalene anion radical has been studied by e.p.r. A. G. Davies, J. R. M. Giles, J. Lusztzk, J.C.S. Perkin II, 747 (1981).

7) The energy difference, D_{4h}-D_{4d}, for bis(cyclobutadienyl) nickel was calculated to be 1.3 kcal (R. M. Pitzer, J. D. Goddard, and H. F. Schaeffer III, J. Am. Chem. Soc., 103, 5681 (1981).

8) R. Pettit and J. Henery, J. Org. Syn., 21, 50 (1971).

9) I. Fischler, K. Hildenbrand and Koerner von Gustorf, Angew. Chem. Internat. Edit 13, 47 (1974).

10) R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, Proc. Nat. Acad. Science 47, 996 (1961).

11) W. J. Hehre, W. A. Lanthan, R. Ditchfield, M. D. Newton and J. A. Pople, Quantum Chemistry Exchange Program, No. 236. Bond lengths (except C-H) and bond angles under the symmetry constraints D_{2h} for 3 and D_{4h} for 4 have been optimized. The following conformational and configurational changes have been studied for 4: rotation to D_{4d} leads to a barrier of 2 kcal/mole.[7] Movement of the C_4 rings to cisoid or transoid configurations lead to sharp energy increases. Introduction of a dihedral angle of 1 to 5 degrees in the case of 3 leads to small (3-5 kcal/mole) increase in energy. Energy sharply ascends above 10° Ring puckering leads to higher energy forms.

12) W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys., 51, 2657 (1969).

13) P. J. Wheatly, J. Chem. Soc., 4936 (1961).

14) R. S. Mulliken, J. Chem. Phys., 23, 1833, 1841, 2338, 2343 (1955).

15) K. Krogh-Jespersen, J. Chandrasekhar, P. V. R. Schleyer, J. Org. Chem., 45, 1608 (1980).

16) E. B. Moore, Jr, J. Am. Chem. Soc., 85, 676 (1963).

Acknowledgement. R.M.M. thanks Paul von Rague Schleyer, University of Erlangen, for stimulating his interest in this problem. The authors thank Nora Sabelli of this Dept. and Computer Center for guidance. Support under NATO grant 1351 and the hospitality of many at the Institute for Chemistry, Erlangen, deserves our gratitude. We also thank the computer center, UICC for generous allocation of computer time and John A. Morrison of this department for discussions.

*This scientific contribution is dedicated to Ulrich Weiss in honor of his 75th birthday.

(Received in USA 16 November 1982)