THEORETICAL STUDIES OF BONDING AND STRUCTURE. 09.X-04 09.X-02

By E. A. Van-Cleef and D. L. Thorn, Central Research and Development Department, E. I. Du Pont de Nemours and Co., Inc., Wilmington, DE 19888, U.S.A.

The TRIBBLE system, developed by Dr. D. A. Pensak of Du Pont Central Research and Development Department, provides convenient access to a wide variety of computational techniques for the experimental chemist. The design philosophy of the system will be discussed. Interfacing of the INDO/S program of Prof. M. S. Zerner will be briefly described. A discussion will be given of how selected Du Pont chemists, facilitated by the TRIBBLE system, have addressed problems of structure, bonding, and catalytic activity using the extended Hückel method.

09.1-01 LONG C-C SINGLE BONDS.

By A. Dunand, Research School of Chemistry, Australian National University, Canberra, ACT, 2600, Australia.*

This paper treats the molecular structure of twelve photoisomers, resulting from the dimerisation of naphthalene, anthracene or naphthacene derivatives. All these compounds share in common with the well known dianthracene molecule, the characteristic structural feature of elongated central C-C bonds. These C-C single bonds, 1.60 to 1.68 Å are systematically longer than normal C-C single bonds, about 1.54 Å. A strained eclipsed or nearly eclipsed, conformation is achieved around these bonds which hold the aromatic rings in a face-to-face configuration.

The C...C non-bonded contacts, of 1.4 type with respect to the central bonds, are shorter, 2.7 to 2.8 Å, than the usual spacing between aromatic rings, 3.54 Å. Moreover, a geometry favourable for through bond interactions is created.

It is shown that a combination of steric and electronic effects contributes to an apparent 0.06 - 0.07 Å elongation of the central C-C bonds in the basic dianthracene framework. While a further 0.05 - 0.07 Å elongation is brought about by the fusion of a saturated cyclic system onto the central bond. The magnitude of the latter elongation indicates that the central bonds behave like weaker than normal C-C single bonds.

* Present address: Laboratoire de Cristallographie aux Rayons X, Université de Genève, CH-1211 Geneva 4, Switzerland.

HYBRIDIZATION, CONJUGATION AND GEOMETRIC VARIATIONS IN THREE-MEMBERED CARBOCYCLES. 09.1-02

By Frank H. Allen, Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

The physical and chemical characteristics of cyclopropane (A), cyclopropene (A) and their derivatives are typical of normal cycloalkanes and cycloalkenes. Their high strain energy and synthatic utility has prompted many theoretical and structural studies in recent years. Ring geometry (I-X) shows wide variations with 'single' bonds in the range 1.45-1.75Å, depending on the nature and pattern of substitution. Accepted acyclic and alicyclic bonding and hybridization schemes provide an inappropriate comparison criteria.

Geometric data for 440 A and A-containing organic compounds have been assembled and analysed using the Cambridge Structural Database and associated software. X-ray data are augmented with pertinent vapour-phase results. Individual and mean geometries in I-X show wide and unusual range of bond lengths, with large substituent-induced changes. Three related bonding models are available for the interpretation of such effects: the bent-bond model, the trigonal hybrid (Welsh) model, and the MO model. Four aspects of A and A bonding have been studied:

(i) Hybridization in ring and substituent bonds: A and C=C are chemically analogous and the C(A) hybrid used in substituent bond formation is close to sp2. Comparative analysis of R-X distances (R= C=C, A) indicate 30.5% s-character in the C(A) hybrid (sp2-2). The 3% s-character in ring bent-bonds is thus low (19%). Such arguments account for the short central-ring bonds, made up of sp2-2 substituent hybrids. In A the C(1) substituent hybrid has ~44% s-character (based on the 1.47Å distance in II) in line with the vinylic nature of C(1) protons. Poor overlap of ring bond hybrid at C(1) yields a long (1.50Å) single bond, but pm overlap in the A double bond is very strong.

(ii) Conjugative interaction of A with π-acceptor substituents: Electron density transfer from σ*π* orbitals to σ-acceptor orbitals in IV give 1-2 bond shortening by 0.04Å, and 1-3, 2-3 lengthening by 0.02Å on the MO model (Hoffmann et al. JACS, 93, 5695 & 6941, 1971); the effect is conformation dependent. For example in IV, give O(0)=2.02Å, 0.02Å for C=O. Other O-values (Allen, Acta Cryst, 95, B1, 1980) are C=C -0.022Å; C=N -0.017Å etc.

(iii) X-Donor substitution of A and A: Experimental trends (0-VIII) indicate a reverse of the acceptor effect. Pure μ-donation would lengthen all three ring-bonds (Hoffmann et. al. vide supra), but Deskyne et. al. (JACS, 93, 1342 & 3895, 1977) show that rehybridization and O-interactions forshorten 1-3, 2-3. Such μ and π effects are largely responsible for the geometry of VII, VIII, rather than large resonance contributions from the 2π- aromatic cyclopropanem-structure IX.

(iv) Effect of small-ring fusion on benzene. The angle α(A) in cyclopropabenzene is 102.2(15), with μ=128(1). The analysis was extended from (061)-(-100) in X and a linear relationship μ=0.75 + 0.02 was found to hold, in agreement with simple molecular mechanics calculations.