09.X-04 THEORETICAL STUDIES OF BONDING AND STRUCTURE AT DuPONT. By F. A. Van-Catledge, R. J. McKinney, and D. L. Thorn, Central Research and Development Department, E. I. Du Pont de Nemours and Co., Inc., Wilmington, DE 19898, 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 Huckel 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 naphtalene, anthracene or naphtacene 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.

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09.1-02 HYBRIDIZATION, CONJUGATION AND GEOMETRIC VARIATIONS IN THREE-MEMBERED CARBOCYCLES by Frank H. Allen, Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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

Geometric data for ~400 Δ and Δ̲-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 a 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 (Walsh) model, and the MO model. Four aspects of Δ and Δ̲ bonding have been studied:-

(i) Hybridization in ring and substituent bonds: Δ and C=C are chemically analogous and the C(Δ) hybrid used in substituent bond formation is close to sp^2. Comparative analysis of R-X distances (R= C=C, Δ) indicate ~30.5% s-character in the C(Δ) hybrid ($sp^{2.2}$). The % s-character in ring bent-bonds is thus low (~19%). Such arguments account for the short central-ring bonds of III, made up of $sp^{2.2}$ substituent hybrids. In Δ̲ the C(1) substituent hybrid has ~44% s-character (based on the 1.477Å distance in II) in line with the vinylic nature of C(1) protons. Poor overlap of ring bond hybrids at C(1,3) yields a long (1.509Å) single bond, but pπ overlap in the Δ̲ double bond is very strong.

(ii) Conjugative interaction of Δ with π-acceptor substituents: Electron-density transfer from Δ(3e')-orbitals to π-acceptor orbitals in IV give 1-2 bond shortening by δÅ, and 1-3, 2-3 lengthening by δ/2Å on the MO model (Hoffmann et.al. JACS, 93, 5699 & 6941, 1971); the effect is conformation dependent. Data in IV give $\delta(=D_{12}-\Sigma D/3)=-0.026$ (5)Å for C=O. Other δ-values (Allen, Acta Cryst, B35, 81, 1980) are C=C -0.022(4); C≡N -0.017(2)Å etc.

(iii) π-Donor substitution of Δ and Δ̲ : Experimental trends (V-VIII) indicate a reverse of the acceptor effect. Pure π-donation would lengthen all three ring-bonds (Hoffmann et. al. vide supra), but Deakyne et. al. (JACS, 99, 1342 & 3895, 1977) show that rehybridization and σ-interactions foreshorten 1-3, 2-3. Such π and σ effects are largely responsible for the geometry of VII, VIII, rather than large resonance contributions from the 2π-aromatic cyclopropenium structure IX.

(iv) Effect of small-ring fusion on benzene. The angle α(X) in cyclopropabenzene is 109.2(5), with β=126(1). The analysis was extended from $(CH_2)_1$-$(CH_2)_6$ in X and a linear relationship β=96.3 + 0.20ε was found to hold, in agreement with simple molecular mechanics calculations.