AB INITIO STRUCTURES FOR 90°-TWISTED *s-trans*-1,3-BUTADIENE AND FOR CYCLOOCTATETRENE; THE NAKED sp^2-sp^2 BOND AND OTHER DISCLOSURES ABOUT EQUILBRIUM STRUCTURES OF BUTADIENE

DAVID FELLER, *Department of Chemistry, Washington State University, Pullman, WA 99164-4630*; NORMAN C. CRAIG and ALBERT R. MATLIN, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*.

The bond length of a carbon-carbon sp^2-sp^2 σ-bond without the perturbing effects of π-electron interactions has been estimated by high-level ab initio calculations [CCSD(T)/cc-pVNQ with CBS extrapolation] on two prototypical systems: a 90°-twisted form of butadiene and the tub conformer of cyclooctatetraene. The butadiene system yields a value of 1.4818 Å, considerably longer than previous estimates. The corresponding bond length in cyclooctatetraene is slightly shorter due to some π-electron delocalization. Ab initio results for related equilibrium structures of other rotamers/transition states of butadiene along the internal rotation coordinate (C-C bond) will be reported and compared with an experimental potential function.[a]

[a] R. Engeln, D. Consalvo, J. Reuss, Chem. Phys. 160, 427 (1992).