

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

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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

^aR. Engeln, D. Consalvo, J. Reuss, *Chem. Phys.* 160, 427 (1992).