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Electron Momentum Spectroscopy of the Frontier Electrons of DABCO Does Not Support an sp^3 Hybrid Lone-pair Description

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Abstract

The highest occupied molecular orbital (HOMO) and next-highest occupied molecular orbital (NHOMO) valence orbital electron density distributions of 1,4-diazabicyclo[2.2.2]octane (DABCO) have been investigated by electron momentum spectroscopy, a technique that probes the orbital-like nature of valence (frontier) electron transfer out of a molecule. The experimental results are compared to a range of 6-311++G** calculations to assess the relative merits of three different orbital models that have commonly been used in chemistry. The delocalized (correlated) canonical Kohn–Sham orbitals calculated using the B3LYP or B3PW91 functionals and density functional theory provide near quantitative agreement with the observed valence electron momentum density distributions, and the delocalized canonical molecular orbitals of Hartree–Fock (independent particle) theory are in semiquantitative agreement. In contrast, Pauling's widely used and taught valence bond (hybridization) model, which is equivalent to a localized molecular orbital description, does not correspond at all to the experimental measurements. It follows that, for considerations of electron transfer, the "lone pairs" of DABCO are not localized or hybridized, but rather exist as nondegenerate orbitals that are delocalized differently over the molecular framework. The existence of two different experimental valence orbital electron densities of DABCO provides direct confirmation of the frontier orbital HOMO–NHOMO energy splitting and reordering predicted many years ago by Hoffmann et al. using extended Hückel theory, and interpreted in terms of "through bond" and "through space" interactions.

Key words：Orbitals; Lone pairs; Orbital interaction; Hybridization