Short Communication

Perpendicular Component of Dipole Moment in Methyl Groups

John F. Ogilvie

Department of Chemistry, Memorial University of Newfoundland, St. John’s, Newfoundland, Canada A1C 5S7

Consideration of the non equivalence of hydrogen atoms in a methyl group attached to a planar moiety indicates that a component of electric dipole moment should exist in a direction perpendicular to the local \( C_3 \) axis of the \( \text{CH}_3 \) group. Semi-empirical molecular-orbital computations produced estimates of this moment and of the barriers to internal rotation which may make this moment observable.

Key words: Methyl groups, dipole moment in ~

The electric dipole moment of a diatomic molecule depends on the instantaneous internuclear separation. This moment may be estimated theoretically within the Born–Oppenheimer approximation, by calculating the electron distribution as a function of the internuclear separation parameter, but comparison of such an estimate with an observable quantity requires the appropriate averaging over the range of separations accessible during vibrational motion. Because all known homonuclear diatomic molecules in their ground states dissociate into neutral atoms, not ions, for these molecules the electric moment must be zero at all separations. Conversely for heteronuclear diatomic molecules the electric dipole moment is generally finite, but must approach zero toward the limits of the united atom and of the separated atoms (of the neutral dissociation process).

For a polyatomic molecule, symmetry likewise dictates zero magnitude of electric moment in some cases. For a centrosymmetric molecule, the requirement is absolute in the vibrational ground state, but may not be in non-totally symmetric vibrationally excited states. For a tetrahedral molecule such as methane, not centrosymmetric, even rotational motion in the vibrational ground state suffices to permit a small electric moment [1]. Discounting such dynamic (i.e. vibrational and rotational) effects, we can also accept that there will be zero component of dipole moment in a direction perpendicular to either a molecular symmetry plane (\( \sigma \)) or an axis of symmetry (\( C_n, n > 2 \)), although there may be non-zero components in other directions in actual (static) molecules possessing, in part, such symmetry elements.
Fig. 1. Sections of half of 1,4-dimethylbenzene showing equilibrium nuclear positions in three projections; the benzene ring defines the XY-plane, and the methyl group hydrogens are staggered with respect to the ring hydrogens at carbon-2.

The question arises whether a molecular fragment possessing such elements of local symmetry, not pertinent to the entire molecule, necessarily retains a zero component of electric moment in particular energy states. Fig. 1 demonstrates that a combination of a three-fold rotor (such as a methyl group) with a planar group (such as a phenyl moiety) can generate a finite dipole moment in the z-direction (in one or other sense) because the interactions of hydrogen A, and of hydrogen B and C together, with the electron density on either side of carbon-1 of the phenyl ring, are inequivalent.

To investigate the implications of this physical situation and to estimate the magnitude of the effect, we have conducted all-valence-electron semi-empirical molecular-orbital computations because the size of the molecules makes \textit{ab initio} methods impracticable. How dipole moments are derived by the CNDO/2 and INDO procedures \cite{2} and their success are well documented \cite{3, 4}. As a further test of these formulations, the dipole moment of ethane in either staggered or eclipsed conformation was calculated; in neither case was there a component of electric moment in any direction greater than $3 \times 10^{-35}$ Cm. The difference in energies between the staggered and eclipsed conformers was $1.53 \times 10^{-20}$ J ($2.08 \times 10^{-20}$ J experimentally \cite{5}); this magnitude is a measure of the barrier to rotation about the $C_3$ symmetry axis, in the absence of cooperative motion involving methyl rocking modes in addition to torsion. These results are an indication of the precision of these computational procedures, using geometrical parameters fixed at experimental values.

The arch-typical case of the three-fold rotor connected to a planar fragment is probably nitromethane, but because the semi-empirical procedures work best with slightly polar molecules or with hydrocarbons the major computations were done on toluene. In this