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Short Communication

Perpendicular Component of Dipole Moment in Methyl Groups

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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 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 (σ) 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.

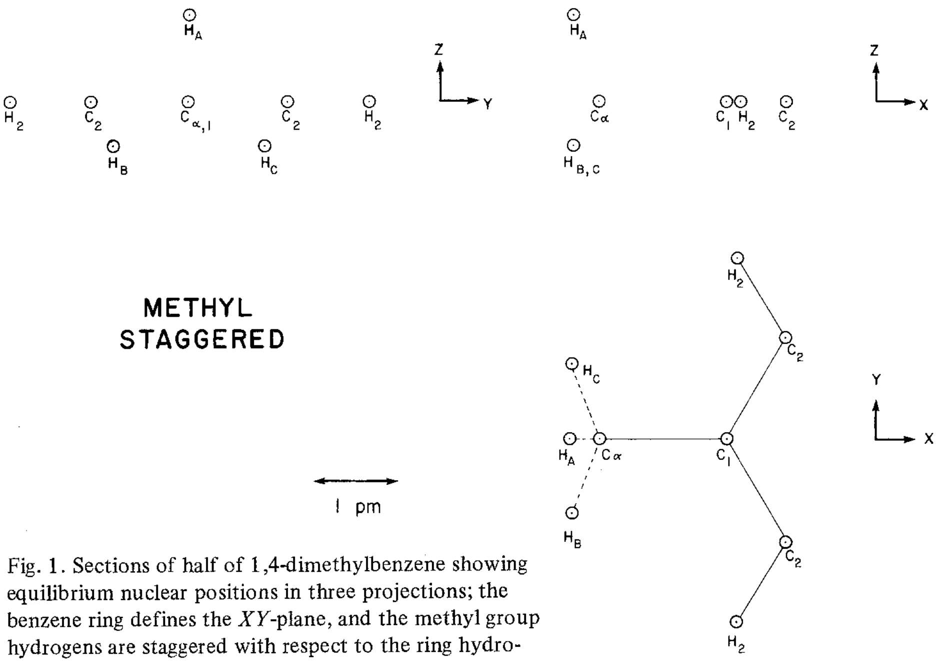

Fig. 1. Sections of half of 1,4-dimethylbenzene showing equilibrium nuclear positions in three projections; the benzene ring defines the *XY*-plane, and the methyl group hydrogens are staggered with respect to the ring hydrogens at carbon-2

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 *ab initio* methods impracticable. How dipole moments are derived by the CNDO/2 and INDO procedures [2] and their success are well documented [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 3×10^{-35} Cm. The difference in energies between the staggered and eclipsed conformers was 1.53×10^{-20} J (2.08×10^{-20} J experimentally [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-typal 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

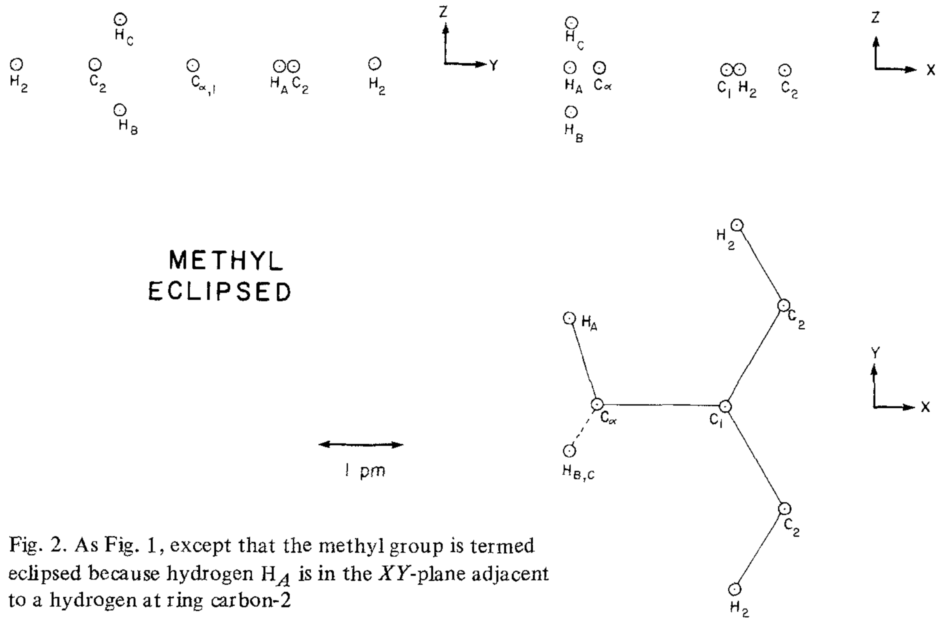

Fig. 2. As Fig. 1, except that the methyl group is termed eclipsed because hydrogen H_A is in the XY-plane adjacent to a hydrogen at ring carbon-2

case, the six-fold barrier to rotation, 9.5×10^{-23} J (CNDO/2) and 1.01×10^{-22} J (INDO) compared with 9.65×10^{-23} J experimentally [6], is much smaller that the three-fold barrier of ethane. For toluene the eclipsed conformer, depicted in Fig. 2, is found to be the more stable. The smallest distances between hydrogen atoms at the methyl group to those at 2-positions on the phenyl ring are two at 273.6 pm, and one at 229.17 pm in the eclipsed conformer, and two at 241.9 pm, and one at 311.8 pm in the staggered conformer. For comparison, the corresponding separations are 226.7 pm and 248.9 pm for ethane in eclipsed and staggered conformers respectively.

The total dipole moment of toluene is estimated to be 7.1×10^{-31} Cm (CNDO/2) or 5.1×10^{-31} Cm (INDO), to be compared with the experimental value of 1.25×10^{-30} Cm [6]. But of greater interest is the prediction of a component of dipole moment perpendicular to the axis of the methyl group, of a magnitude about one-third the dominant component. The perpendicular component varies from 2.1×10^{-31} Cm for the staggered form to 1.9×10^{-31} Cm in the eclipsed form according to CNDO/2, and 1.8×10^{-31} and 1.7×10^{-31} Cm correspondingly from INDO.

What are the possibilities of observing such effects? Direct measurements in condensed phases are impracticable because intermolecular effects, even of non-polar molecules, would mask the observation or hinder its interpretation. Only in the gas or vapour phase at small densities could measurements be expected to be definitive, and microwave absorption spectrometry or molecular beam electric resonance experiments may then be sufficiently sensitive. The observation of such a small effect is perhaps least hindered if there be no other mechanisms for producing allowed spectroscopic transitions [7], so a molecule without any other component of electric moment would be preferable. These considerations lead to the conclusion that 1,4-dimethylbenzene (*p*-xylene) would be a suitable test species. In this case the total dipole moment for the centrosymmetric conformation would still be zero; but if the two methyl groups were aligned parallel so as to leave a plane of symmetry passing the 1- and 4-carbon positions of the ring, a maximum dipole moment is predicted to be 3.9×10^{-31} Cm, entirely comparable with the electric moment of carbon monoxide, which is 3.74×10^{-31} Cm [8] in the ground electronic state ($v = 0$). As an aid to searching for microwave transitions of this, 1,4-dimethylbenzene, principal moments of inertia are estimated to be 1.5797×10^{-45}, 5.7608×10^{-44} and 7.2327×10^{-45} kg m^2, leading to rotational parameters $A = 5.312$, $B = 1.457$ and $C = 1.1604$ GHz. Replacement of the hydrogen atoms of the methyl groups by fluorine atoms, to yield 1,4-bistrifluoromethylbenzene, produces a somewhat smaller perpendicular component of dipole moment, 2.5×10^{-31} Cm. In this case the staggered conformer is predicted to be more stable than the eclipsed form by 2.85×10^{-22} J; thus the effective barrier to internal rotation may be almost three times as large as that of *p*-xylene. The moments of inertia and rotational parameters are estimated to be 4.266×10^{-45}, 2.749×10^{-44}, 2.883×10^{-44} kg m^2, and $A = 1.967$, $B = 0.3053$, $C = 0.2911$ GHz respectively. As for the 1,4-dimethylbenzene conformers, the barriers to internal rotation were estimated from the mono-substituted benzene; in this case trifluoromethylbenzene is predicted to have a dipole moment of 9.37×10^{-30} Cm, apparently without experimental check at this time.

In conclusion, the evidence from our semi-empirical molecular-orbital computations seems to indicate that a significant component of dipole moment exists in a direction perpendicular to the local C_3 axis of a methyl group attached to a planar moiety. Both CNDO/2 and INDO procedures agree in the order of magnitude of the effect, and also predict small but finite barriers to rotation which may make these dipole moments measureable. We suggest that the observation and interpretation of such a phenomenon may be achieved with the use of 1,4-dimethylbenzene or its bistrifluoromethyl counterpart. Less massive molecules, such as trans butene-2, would likely be unsuitable because the structure and symmetry give rise to no metastable rotamers with net dipole moments. Finally these polarities, of greater extension than individual bond moments, may play an important role in intermolecular interactions, such as secondary structure in solid phases.

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