# Analysis of Permanent Electric Dipole Moments of Aliphatic Hydrocarbon Molecules. 2. DFT Results

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The B3LYP hybrid DFT method was applied to calculate the permanent electric dipole moments of aliphatic hydrocarbon molecules. For most of the molecules, it was found that the B3LYP results are in good agreement with the calculated data published previously and with the experimental values. For molecules that contain conjugate C=C and C≡C bonds, the DFT calculated values are closer to the experimental ones. The situation is the reverse for molecules containing conjugate C=C bonds. The experimental predictions of the dipole moment for 1-buten-3-yne range from 0.22 to 0.44 D, whereas DFT supports a value of ∼0.39 D.

## INTRODUCTION

The permanent electric dipole moment is an important physical vector quantity. By definition, the dipole moment vector points from the center of the positive charge distribution to the center of the negative charge distribution. It provides valuable information on the structure and polarity of the molecule under consideration. In the parametrization of the most widely used semiempirical quantum chemical methods, experimental dipole moments have been taken into account. The necessary condition of the goodness of a classical molecular point charge system is the reproducibility of the experimental or calculated quantum mechanical dipole moment.[1]

Microwave spectroscopy is the best tool for determining gas-phase experimental values.[2] Generally, the components of the dipole moment vector are also available. In several cases, in addition to data referring to the ground vibrational state, information can be found for the excited states too.

Recently, we studied the permanent electric dipole moments of aliphatic hydrocarbon molecules.[3] We found that the RHF/6-311G**//MP2(FC)/6-311G** ab initio quantum chemistry model (Model I) affords reliable results. FC (frozen core) in parentheses means that the inner shell electrons were excluded from the electron correlation (post-HF) calculations.

For the 1-buten-3-yne molecule, several "experimental dipole moments" can be found in the literature: 0.22,[4,5] 0.4[6] and 0.44 D.[7] According to Model I, the first value is too small.[3]

Particularly for aliphatic alkanes, the RHF/6-311++G** wave function at the MP2(FC)/6-311G** geometry is even better for calculating the electric dipole moment vector than the RHF/6-311G** one.[3] For propane, isobutane, and *gauche*-butane, the calculated scalar magnitudes are 0.0853, 0.1269, and 0.0907 D, respectively. These values are in good

accordance with the experimental results of 0.084,[8] 0.132,[9] and 0.090 D,[10] respectively. Using the calculation results obtained on aliphatic alkane molecules as reference data, we performed the parametrization of an effective one-electron method.[11]

The present paper reports the results obtained on aliphatic hydrocarbons with the B3LYP[12,13] hybrid DFT method,[14] which has been proven in several areas[13,15−18] to be one of the best DFT methods. For comparison, we also report the Model I[3] and AM1[19] results.

## EXPERIMENTAL DIPOLE MOMENTS

Most of the experimentally determined gas-phase dipole moments referring to the ground vibrational state of the ground electronic state of molecules were taken from a reference book.[5] In most cases, the values were verified from the original publications. The first column in Table 1 gives the experimental scalar values, $\mu$(exp), together with the literature reference. In the reference book,[5] the following notation is used to designate the quality of the experimental values: for **A**, **B**, **C**, and **D**, the absolute values of the estimated experimental uncertainties are <0.01, <0.02, <0.05, and <0.1 D, respectively, provided that the experimental values are <1 D. Ambiguous results are indicated by the letter **Q**. The letter **i** denotes the presence of rotational isomers. The same quality indicators are used in Table 1.

## THEORETICAL RESULTS

The ab initio and B3LYP calculations were performed on a CRAY C90 computer with the Gaussian 94 package.[22] We used the B3LYP functional form implemented in the Gaussian program.[23] The inputs for the GAUSSIAN program were prepared and the results were evaluated with the PcMol package[24] on a PC. For AM1 calculations, the MOPAC 6.0[25] and the PcMol programs were used.

For the B3LYP calculations, the 6-311G** basis set was used. Through calculation of the eigenvalues of the Hessian, the stationary point was checked in every case. The second

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**Table 1.** Experimental and Calculated Electric Dipole Moments (in Debye) of Aliphatic Hydrocarbon Molecules[a]

| molecule | experimental value | model II value | model I value | AM1 value |
|---|---|---|---|---|
| propane | 0.084 (A)[8] | 0.0768 (*) | 0.0742 (*) | 0.0043 (!) |
| *gauche*-butane | 0.090 (A)[10] | 0.0834 (*) | 0.0732 (*) | 0.0118 (!) |
| isobutane | 0.132 (A)[9] | 0.1192 (*) | 0.1148 (*) | 0.0095 (!) |
| isopentane | 0.13 (C)[5] | 0.0856 (+) | 0.0826 (+) | 0.0095 (!) |
| propene | 0.366 (A)[5] | 0.3802 (*) | 0.3711 (*) | 0.2296 (!) |
| *cis*-1-butene | 0.438 (A)[5] | 0.4459 (*) | 0.4227 (*) | 0.2392 (!) |
| *skew*-1-butene | 0.359 (A)[5] | 0.3548 (*) | 0.3543 (*) | 0.2187 (!) |
| *cis*-2-butene | 0.253 (A)[5] | 0.2778 (−) | 0.2536 (*) | 0.2694 (*) |
| isobutene | 0.503 (A)[5] | 0.5304 (−) | 0.5540 (−) | 0.3559 (!) |
| 1-pentene | 0.5 (Q)[5] | 0.3731(!) | 0.3682 (!) | 0.2269 (!) |
| *trans*-3-methyl-1-butene | 0.320 (A)[5] | 0.3026 (*) | 0.3112 (*) | 0.1945 (!) |
| *gauche*-3-methyl-1-butene | 0.398 (A)[5] | 0.3925 (*) | 0.3822 (*) | 0.2234 (!) |
| 1,2-butadiene | 0.403 (A)[5] | 0.4050 (*) | 0.4179 (*) | 0.2058 (!) |
| *trans*-1,3-pentadiene | 0.585 (A)[5] | 0.6297 (−) | 0.6015 (*) | 0.3254 (!) |
| *cis*-1,3-pentadiene | 0.500 (B)[5] | 0.5528 (−) | 0.5111 (*) | 0.3094 (!) |
| isoprene | 0.25 (A)[5] | 0.2488 (*) | 0.2407 (*) | 0.1805 (−) |
| propyne | 0.784 (A)[5] | 0.7844 (*) | 0.7715 (*) | 0.3974 (!) |
| 1-butyne | 0.782 (A)[20] | 0.7646 (*) | 0.7730 (*) | 0.3943 (!) |
| *trans*-1-pentyne | 0.842 (A)[5] | 0.8204 (*) | 0.8219 (*) | 0.4238 (!) |
| *gauche*-1-pentyne | 0.77 (C)[5] | 0.7431 (+) | 0.7398 (+) | 0.3756 (!) |
| 3-methyl-1-butyne | 0.721 (A)[21] | 0.7085 (*) | 0.7269 (*) | 0.3944 (!) |
| 1-hexyne | 0.83 (Ci)[5] | 0.8858 (+) | 0.8812 (+) | 0.4310 (!) |
| 3,3-dimethyl-1-butyne | 0.661 (A)[5] | 0.6531 (*) | 0.6775 (*) | 0.3998 (!) |
| 1-buten-3-yne | 0.22 (B)[4,5] | 0.3940 (*) | 0.5556 (!) | 0.2307 (!) |
|  | 0.4,[6] 0.44[7] |  |  |  |
| 1-penten-3-yne | 0.66 (B)[5] | 0.6562 (*) | 0.4663 (!) | 0.2891 (!) |
| *cis*-3-penten-1-yne | 0.78 (B)[5] | 0.8171 (−) | 0.9581 (!) | 0.5054 (!) |
| *trans*-3-penten-1-yne | 1.06 (C)[5] | 1.0570 (*) | 1.2027 (!) | 0.5958 (!) |
| 2-methyl-1-buten-3-yne | 0.513 (B)[5] | 0.4985 (*) | 0.5284 (*) | 0.2509 (!) |

[a] See text for meanings of symbols in parentheses.

column in Table 1 gives the scalar magnitudes of the B3LYP/6-311G**//B3LYP/6-311G** (Model II) calculated dipole moments. The additional columns show the Model I[3] and AM1 results.

## DISCUSSION

The density functional methods[14] fill in the gap between the more sophisticated and time-consuming ab initio and conventional semiempirical quantum chemical methods. In certain cases, the exchange-correlation functional $E_{xc}$ contains some semiempirical parameters that were determined by fitting to experimental data. For the parametrization of the B3LYP functional,[12,13] the original G2 test set of molecules[26] was used. It has been found that the B3LYP DFT method can be successfully applied to calculate standard heats of formation,[15] vibrational spectra,[13,16,17] and gas-phase proton affinities.[18] As far as we know, the performance of this method for calculating permanent electric dipole moments has not yet been considered.

According to Table 1, the Model I and Model II dipole moments are close to each other and to the experimental values. The close matching (often within the experimental accuracy) is indicated by an asterisk in Table 1. For both Model I and Model II, 19 out of 28 cases belong to this category. In addition to these cases, for three molecules (isopentane, *gauche*-1-pentyne, and 1-hexyne) the differences are within the reported experimental accuracy. In Table 1, the symbol + denotes these data, but they belong to class C. It is noteworthy that the calculated Model I and Model II values are very close to each other in these cases too.

For the 1-pentene molecule, the discrepancies between calculated and experimental values are serious (symbol !), but the experimental value falls in class **Q**. Model I and Model II afford the same value in this case too. All of the models (including AM1) predict that the dipole moment of 1-pentene molecule is close to that of propene.

For the *cis*-2-butene molecule, Model I affords a result which is closer to the experimental value than that of Model II. (If the discrepancy from the experimental result is not so serious, the symbol − denotes the calculated dipole moment.) For the isobutene molecule, the situation is the reverse.

For the *trans*-1,3,-pentadiene and *cis*-1,3-pentadiene molecules, the Model I dipole moments are better than those provided by Model II. These molecules contain two conjugate C=C bonds.

For molecules containing conjugate C=C and C≡C bonds (1-buten-3-yne, 1-penten-3-yne, *cis*-3-penten-1-yne, *trans*-3-penten-1-yne, and 2-methyl-1-buten-3-yne), the performance of Model II is much better than that of Model I. For 1-buten-3-yne, the Model II results suggest that the most reliable experimental value is 0.4 D.[6] It is worth noting that the AM1 method affords a good qualitative trend for these molecules, in contrast to Model I.

To evaluate the overall goodness of various quantum chemistry models, linear regression analyses were performed for the molecules in Table 1, using the following expression (eq 1):

$$\mu(\exp) = \beta\mu(calculated) \qquad (1)$$

1-Pentene was excluded from the set of molecules because of the ambiguity of the measurement. Figures 1−3 show the relations between the experimental and calculated scalar magnitudes. The statistical data obtained ($\beta$, regression
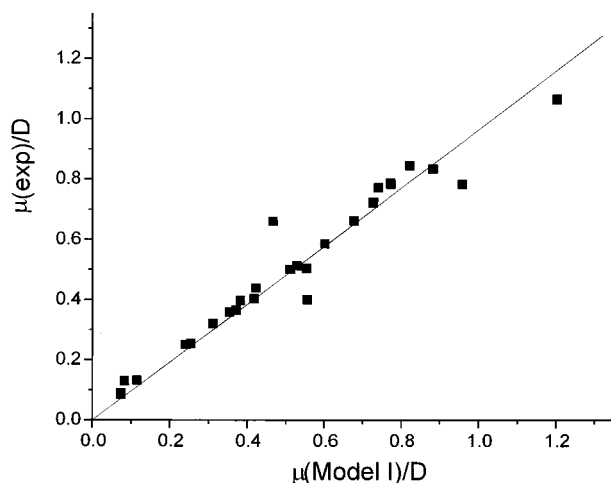
ANALYSIS OF ELECTRIC DIPOLE MOMENTS BY DFT METHOD

*J. Chem. Inf. Comput. Sci., Vol. 38, No. 2, 1998* **315**



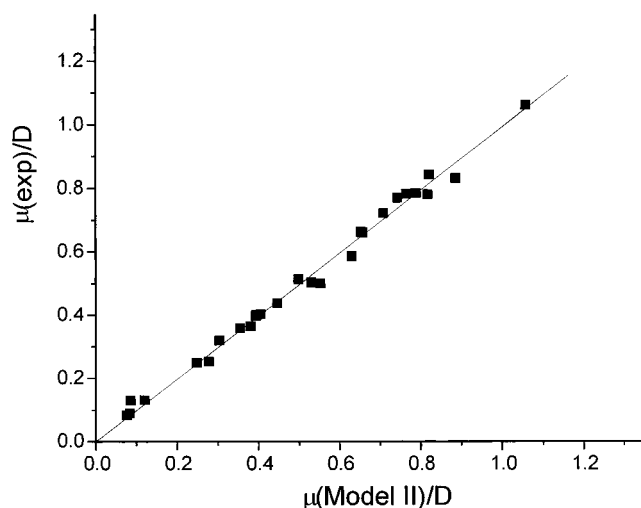**Figure 1.** Graphical representation of the relation $\mu$(exp) versus $\mu$(Model I) for aliphatic hydrocarbons.



**Figure 2.** Graphical representation of the relation $\mu$(exp) versus $\mu$(Model II) for aliphatic hydrocarbons.
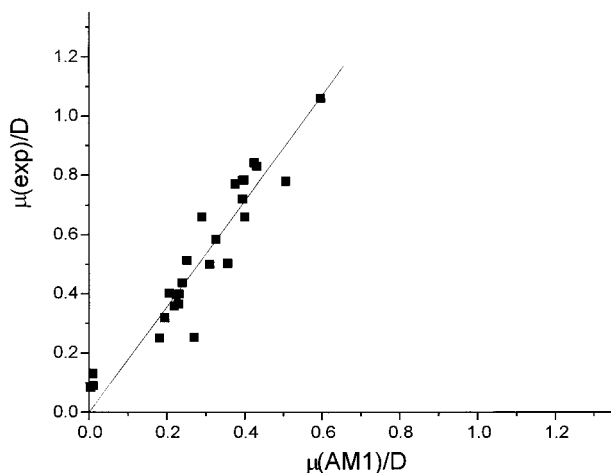


**Figure 3.** Graphical representation of the relation $\mu$(exp) versus $\mu$(AM1) for aliphatic hydrocarbons.

coefficient; SE($\beta$), estimated standard error of $\beta$; $\rho$, linear correlation coefficient; and $\sigma$, root-mean-square deviation) are found in Table 2. It can be seen that the fitting is very good for Model I and Model II: $\beta$ and $\rho$ are both close to 1, and the estimated standard errors of the regression coefficients are small enough. The statistical data also

**Table 2.** Statistical Data Obtained by Linear Regression Analysis

| model | $\beta$ | SE($\beta$) | $\rho$ | $\sigma$ |
|---|---|---|---|---|
| model I | 0.9595 | 0.0214 | 0.9936 | 0.0639 |
| model II | 0.9914 | 0.0081 | 0.9991 | 0.0234 |
| AM1 | 1.7820 | 0.0530 | 0.9887 | 0.0865 |

demonstrate that Model II is better than Model I at predicting experimental dipole moments for these molecules.

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