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# Stereoelectronic Substituent Effects in Saturated Main Group Molecules: Severe Problems of Current Kohn−Sham Density Functional Theory

S. Grimme,* M. Steinmetz, and M. Korth

*Theoretische Organische Chemie, Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany*

**Abstract:** The Hartree−Fock method, two common density functionals (PBE and B3LYP), and two new functionals (B97-D and B2PLYP) together with very large AO basis sets are used to compute the isomerization energies for substituted (R=H, F, Cl) branched to linear alkanes and silanes. The results of accurate SCS-MP2 computations are taken as reference. These reactions are an important test of how nonlocal electron correlation effects on medium-range lengths scales in saturated molecules are treated by approximate quantum chemical methods. It is found that the unacceptably large errors observed previously for hydrocarbons persist also for the here considered more polar systems. Although the B97-D and B2PLYP functionals provide improved energetics, the problem is not fully solved, and thus these systems are suggested as mandatory benchmarks for future density functionals.
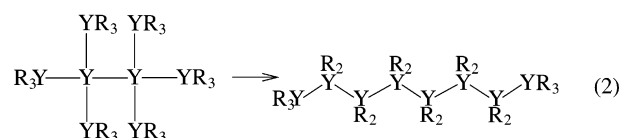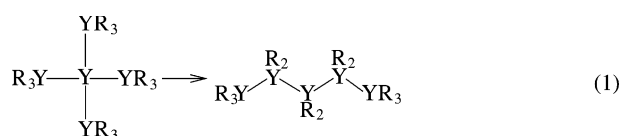
Kohn−Sham density functional theory (KS-DFT) is now the most widely used method for electronic structure calculations in condensed matter physics and quantum chemistry.[1,2] This success mainly results from significant 'robustness', i.e., providing reasonably accurate predictions for many properties of various molecules and solids.[3] However, a general drawback of many common density functionals (DF) is that they cannot be systematically improved, and thus, empirical tests in general chemistry applications are mandatory. Some fundamental failures of common DF are known quite well such as the self-interaction error or that they cannot really describe long-range electron correlations that are responsible for van der Waals (vdW) forces.[4−6] Especially the vdW problem has attracted some attention in the DFT community in recent years (see e.g. refs 7−14) as these interactions play an important role in many chemical systems such as for the structures of DNA and proteins, the packing of crystals, the formation of aggregates, host−guest systems, or the orientation of molecules on surfaces.

In a recent publication[15] it was shown, however, that current DFT also has problems to describe other, seemingly simple electron correlations that are the reason for stereo-

electronic substituent effects.[16] In hydrocarbons, all common DF cannot describe the energetic consequences of medium-range but nonlocal electron correlations originating from different (perfectly) localized σ-orbitals. The effect of such correlations is important when the size or shape of molecules change (for related examples see refs 17−20) although it has nothing to do with 'size-consistency' problem of some approximate quantum chemical methods. Previously,[15] the most simple case, i.e., the isomerizations of branched to linear alkanes (see Scheme 1, Y = C, R = H, denoted as 5CH and 8CH, respectively) has been considered. It was found, that e.g. for the isomerization to *n*-octane (reaction 2), no current DF could provide even the right sign (endergonic) for the isomerization energy ΔE. Similar problems appear in standard semiempirical approaches such as MNDO or AM1 but could be eliminated by pairwise-distance-directed-Gaussian (PDDG) modifications of the interaction potential.[21]

In this study we investigate the obvious question if the problem only appears for hydrocarbons or if it is of more general importance. We extend our computations here to saturated systems of other elements and have chosen as new test molecules halogen-substituted alkanes (Y=C, R=F) and silanes (Y=Si; R=H, F, Cl), respectively. Polychlorinated

* Corresponding author fax: (+49)251-83-36515; e-mail: grimmes@uni-muenster.de.

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**Scheme 1.** Investigated Molecules

$$R_3Y—Y(YR_3)(YR_3)—YR_3 \longrightarrow R_3Y—Y(R_2)—Y(R_2)—YR_3 \quad (1)$$

$$R_3Y—Y(YR_3)(YR_3)—Y(YR_3)(YR_3)—YR_3 \longrightarrow R_3Y—Y(R_2)—Y(R_2)—Y(R_2)—YR_3 \quad (2)$$

Y=C, Si
R=H, F, Cl

**Table 1:** Computed[a] Isomerization (Branched → Linear) Energies $\Delta E$ (in kcal mol$^{-1}$)

| molecule | HF | B3LYP | PBE | B97-D | B2PLYP | SCS-MP2 |
|---|---|---|---|---|---|---|
| 5CH | 0.1 | 1.3 | 1.6 | 3.4 | 2.1 | 3.0 |
| 5CF | 10.4 | 9.8 | 11.5 | 11.5 | 12.5 | 14.1 |
| 8CH | −11.5 | −8.4 | −5.5 | 2.2 | −3.5 | 1.4 |
| 8CF | −5.0 | −5.0 | −1.5 | −0.9 | 2.6 | 7.4 |
| 5SiH | 1.8 | 1.8 | 2.5 | 3.7 | 3.2 | 4.8 |
| 5SiF | 26.7 | 24.7 | 26.5 | 26.7 | 28.1 | 30.9 |
| 5SiCl | 2.0 | 3.3 | 6.0 | 6.2 | 7.9 | 11.0 |
| 8SiH | 2.0 | 2.2 | 4.7 | 8.5 | 6.5 | 11.3 |
| 8SiF | 49.9 | 45.7 | 50.3 | 52.7 | 54.1 | 61.5 |
| 8SiCl | −15.1 | −8.3 | −1.4 | −1.8 | 1.8 | 10.2 |

[a] Single point calculations on MP2/TZVP optimized geometries and employing the cQZV3P AO basis.

alkanes are excluded because repulsive steric interactions between the chlorine atoms are very dominant in these systems. Compared to the previously studied alkanes, the average distance between the $\sigma$-bonds (or substituents) is larger in the silanes, and furthermore, the effect of bond polarity can be investigated quite systematically by comparison of R = H and R = F. We also present first results from a recently developed generalized gradient approximation (GGA) type functional (termed B97-D[22]) that is correct at least in the case of the hydrocarbons. It is based on a reparametrization of Beckes ansatz from 1997[23] but now explicitly includes long-range electron correlations by atom-pair wise dispersion corrections of the form $C_6 \cdot R^{-6}$ as in the DFT-D method.[8] In this new approach double-counting effects of electron correlation are avoided by construction, and the density functional description is restricted to the short-range electron correlations.

Experimental isomerization enthalpies are unfortunately not available for the fluoroalkanes and all silanes. However, recent experience showed that the SCS-MP2 method[24] with large AO basis sets as used here (of polarized quadruple-$\zeta$ quality, see Methods) is accurate to within 0.5 kcal mol$^{-1}$ for the $\Delta E$ values of hydrocarbons. We expect for the bigger systems studied here where also the absolute $\Delta E$ values are generally larger an error of about $\pm(1-2)$kcal mol$^{-1}$. This is in any case accurate enough to judge the quality of approximate functionals that in our case yield large errors of 5−15 kcal mol$^{-1}$.

The results for the linear to branched form isomerization energies are shown in Table 1, and the errors with respect to the SCS-MP2 values taken as reference are shown graphically in Figure 1 (for convenience only errors for reaction

2 are shown). As a quantum chemical method we employ also (uncorrelated) Hartree−Fock (HF) to see how a large fraction of the electron correlation contribution to $\Delta E$ is typically recovered by DFT. As standard functionals we consider the popular B3LYP[25,26] and PBE[27] forms and note in passing that many other functionals (e.g. the meta-GGA TPSS[28]) behave quite similar. Besides the new B97-D GGA, the recently developed 'fifth-rung' virtual-orbital dependent hybrid B2PLYP[14] is used. This functional contains explicitly interpair correlations that seem to be necessary for an accurate description of such isomerization processes.[15]

Before discussing the errors of the investigated methods that is the main point of the present work, a brief look at some general aspects and trends of the $\Delta E$ values in the series of systems seems appropriate. First, for all systems the $\Delta E$ values are positive meaning that the branched form is more stable. Furthermore, the $\Delta E$ values decrease (the branched forms are destabilized) when the core of the molecules is increased from five to eight atoms for Y = C, while they increase for Y = Si (R=H, F) or are almost constant (R=Cl). The different behavior of the alkanes opposed to the silanes can be explained by the much longer Si−Si bonds which lead to much smaller steric interactions than in alkanes, and consequently, the intrinsic effects of electron correlation (that stabilize the branched forms) are more obvious in the silanes. In the chlorosilanes 5SiCl and 8SiCl we once again can observe the steric effects as here the $\Delta E$ values decrease as in the case of Y = C. This is clearly due to the larger size of Cl and the longer Si−Cl bonds that cause more steric interference in the branched forms.

A second point concerns the dependence on the bond polarity. For both, Y = C and Y = Si, the $\Delta E$ values increase for R = Cl, F compared to R = H (with the exception of 8SiCl, see above). When comparing R = H and R = F (where steric effects are of minor importance), the $\Delta E$ values are larger by about a factor of 6 for R = F. From an analyses of the errors of the different methods (see below) and the additive property of the effects, we assign this behavior to an unfavorable arrangement of the bond dipoles in the linear forms compared to the branched ones. This view is corroborated by the energy contribution to $\Delta E$ from the point-charge model in common force-fields.
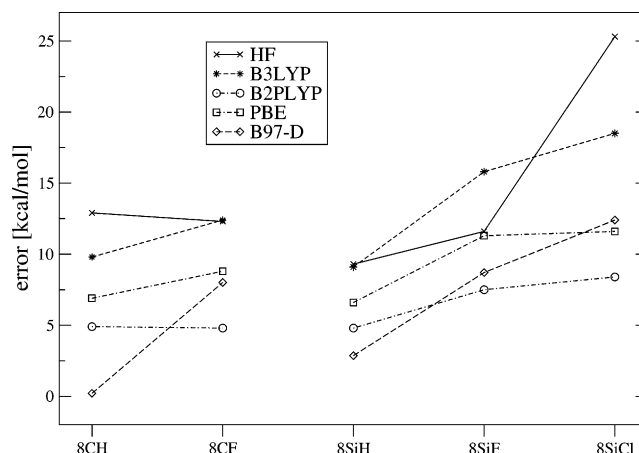


**Figure 1.** Errors with respect to SCS-MP2 as reference for isomerization energies (reaction 2) with different quantum chemical methods.

For the discussion of the errors of the different density functionals considered we restrict ourselves to reaction 2 because the effects are qualitatively the same but more pronounced compared to reaction 1. Inspection of Figure 1 shows clearly that the methods behave quite similar for carbon and silicon, and thus, the problems appear to be of general importance. The errors are huge, i.e., >10 kcal mol$^{-1}$ for HF and B3LYP, between 5 and 10 kcal mol$^{-1}$ for PBE, and between 0 and 10 kcal mol$^{-1}$ for B97-D and B2PLYP. Even more important, for 8CH all methods except B97-D predict the wrong sign for $\Delta E$, and for 8CF and 8SiCl only B2PLYP is right. Errors on the order of 5−15 kcal mol$^{-1}$ are typical for e.g. the atomization energies of medium-sized molecules where the electronic structure changes a lot but are completely unacceptable for a simple isomerization process where the number and type of bonds and the hybridization state of all atoms remains the same.

The much larger errors of the HF and B3LYP methods for 8SiCl can be attributed to missing attractive vdW interactions that are better accounted for by the other methods. This reasoning also applies for the in general larger errors provided by HF and B3LYP. As discussed in ref 15, intra-molecular vdW effects contribute significantly to $\Delta E$, but are not the main reason for the failures. This is also found here for substituents other than hydrogen. In passing we note that also for the halogen substituted systems the amount of nonlocal HF exchange in a density functional has a minor effect on its performance.

The new functionals B97-D and B2PLYP that both try to account for the relevant interactions by empirical and orbital-dependent terms, respectively, perform better than all other functionals. However, there is still room for improvement, i.e., the errors for B97-D increase for R = F, Cl and the B2PLYP errors (although less system-dependent) are still on the order of 4−8 kcal mol$^{-1}$.

The most important finding of the present investigation is that the errors of common density functionals are comparable for a wide range of polar and nonpolar systems. The explanation of the problem[15] due to nonlocal electron correlations between localized $\sigma$-bonds at intermediate distances is fully supported by the present study. It is a very reasonable conjecture that the DFT problems in the description of such isomerization processes, that are *not* element-specific but related to a change in the shape of molecules, indicate only the tip of an iceberg. In many quantum chemical routine studies, these problems may be buried by (counter-effective) basis set incompleteness effects or the fact that only small model systems are studied. For the further systematic development of quantum chemistry and DFT in particular, however, it seems important to solve these problems, and thus, we suggest the here considered systems as mandatory benchmarks for future density functionals.

## Methods

The SCS-MP2 and DFT calculations have been performed with slightly modified versions of the TURBOMOLE suite of programs.[29] As AO basis, triple-$\zeta$ (TZV) or quadruple-$\zeta$ (QZV) sets of Ahlrichs et al.[30] have been employed. In all perturbative treatments (MP2, SCS-MP2, and B2PLYP) the

RI-approximation for the two-electron integrals has been used,[31] and all electrons have been correlated. As RI-auxiliary basis, the sets of Weigend et al.[32] that were optimized for the cc-pVQZ AO basis have been employed. The geometries were fully optimized at the MP2/TZV(d,p) level, and single-point calculations on these structures were performed with a quadruple-$\zeta$ (cQZV3P) AO basis set that includes (3d2f/2pd) polarization functions and (2s2p2d1f) core-polarization/correlation functions taken from ref 33. This basis set provides results to within ±0.1 kcal mol$^{-1}$ of the basis set limit for the (zero-point vibrational energy exclusive) isomerization energies $\Delta E$ in the case of hydrocarbons.[15]

**Note Added in Proof.** At the proof stage of this letter, important related work came to our attention. Schreiner et al. (*Org. Lett.* **2006**, *8*, 3635−3638) and Wodrich et al. (*Org. Lett.* **2006**, *8*, 3631−3634) present other examples of isomerization, where common density functionals fail badly. Zhao et al. propose a new meta-hybrid functional (M05-2X, *J. Chem. Theory Comput.* **2006**, *2*, 364) that seems to solve the here discussed problems at least for medium-sized hydrocarbons.

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(16) We use the term 'stereoelectronic' in a broader sense as e.g. some organic chemists who restrict it to conformational (e.g. gauche or anomeric) effects.

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