Regular article

Overestimation of the stability of the \( \pi \)-delocalized versus the \( \sigma \)-localized configuration in radicals by current density functionals: the case of vinylacyl radicals

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Abstract. Calculations with the density functional theory (DFT) method using the most popular functional, Becke’s three parameter hybrid with the Lee, Yang and Parr correlation functional, predict the \( \pi \)-delocalized configuration of the vinylacyl radical, \( CH_2\equiv CH-C(\bullet)\equiv O \), to be more stable than the \( \sigma \)-localized configuration in contrast with ab initio unrestricted quadratic configuration interaction with single and double excitations calculations as previously found for the isoelectronic vinyl radical, \( Y-C(\bullet)\equiv CH_2 \), bearing \( \pi \)-type \( \pi \) substituents. Experimental evidence on the electronic configuration adopted by vinyl radicals is contrasting. In the present case comparison with experiment indicates firmly that the currently available density functionals overestimate the stability of \( \pi \)-delocalized versus \( \sigma \)-localized configurations in radicals since they favor the \( \pi \) configuration for the \( \gamma \)-methylvinylacyle radical, \( CH_2\equiv CH=CH-C(\bullet)\equiv O \), in contrast with unequivocal electron spin resonance data. This failure is mainly due to an incorrect estimate of dynamic correlation energy with DFT functionals.

Key words: Radicals – Electronic configurations – Energy – Density functional theory – Quadratic configuration interaction with single and double excitations

1 Introduction

Unrestricted quadratic configuration interaction with single and double excitations (UQCISD) and unrestricted Becke’s three parameter hybrid with the Lee, Yang and Parr correlation functional (UB3LYP) calculations performed on vinyl radicals bearing \( \pi \)-type \( \pi \) substituents provided contrasting results. Calculations performed on \( Y-C(\bullet)\equiv CH_2 \) radicals \( [Y = C\equiv CH, C(\equiv O)OH, C\equiv N] \) with the QCISD method predicted the \( \sigma \)-localized bent configuration (Fig. 1A) to be more stable than the \( \pi \)-delocalized linear configuration (Fig. 1B) [1].

The opposite stability was obtained with the density functional theory (DFT) method using the most popular functional B3LYP \((Y = CH=CH_2, CH=O, C\equiv N, \text{phenyl}) \) [2]. It should be noted that the \( \pi \)-cyanovinyl radical was studied employing both methods. Contrasting conclusions were also reached on the basis of experimental evidence. It was concluded from old electron spin resonance (ESR) studies [3–7] that vinyl radicals bearing \( \pi \)-type \( \pi \) substituents \( [Y = C\equiv CH, C(\equiv O)OH, C\equiv N, \text{phenyl}] \) should be linear at the radical center (\( \pi \)-type radical). This conclusion was questioned for the \( \pi \)-acryl \( [Y=C(\equiv O)OCH_3] \) and \( \pi \)-cyanovinyl radicals [8]. In fact, the large \( ^{13}\text{C} \) hyperfine coupling (hfs) constant observed for these radicals is consistent with a bent structure (\( \sigma \)-type radical). The equivalence of the vinylic \( \beta \) protons was explained by a rapid inversion about the radical center on the ESR time scale owing to a small barrier to inversion. Studies of stereoselectivity on these two radicals were in accord with this latter conclusion [9].

In the isoelectronic acyl radicals, \( Y-C(\bullet)\equiv O \), experimental results indicate unequivocally that radicals bearing \( \pi \)-type \( \pi \) substituents such as \( \gamma \)-substituted vinylacyles, \( \chi-CH=CH-C(\bullet)\equiv O \), are localized \( \sigma \) radicals. Thus, this class of radicals has been studied to establish which method (DFT, QCISD) is more reliable for describing the relative stability of \( \sigma \)-localized and \( \pi \)-delocalized configurations in radicals.

2 Computational details

Unrestricted DFT calculations were carried out on the \( \sigma \) and \( \pi \)-type configurations of vinylacyle radicals with the GAUSSIAN 98 system of programs [10] running on a DEC AlphaStation 500 computer. Geometries and hfs constants were determined using various density functionals among the currently available local, nonlocal and hybrid functionals and employing the 6-311G(d,p) basis set [11], i.e. a valence triple-\( \zeta \) basis set supplemented with polarization functions, p functions on hydrogens and five-component d functions on heavy atoms [12]. This basis set was, however, demonstrated to be of valence triple-\( \zeta \) quality in the p space but
Fig. 1. Structures for π-substituted vinyl radicals: A bent σ radical, B linear π radical.

Fig. 2. Structures of the vinylacyl radicals: A bent σ radical, B linear π radical.

Table 1. Relative energy, \( E_{\text{rel}} \) (kcal mol\(^{-1}\)), and \( ^1\)H hyperfine coupling constants (hfs) constants (gauss) for the σ- and π-type configurations of the vinyl radical, CH\(_2\)=CH–C(\(\cdot\))=O, computed with different methods employing the 6-311G** basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>Configuration</th>
<th>( E_{\text{rel}} )</th>
<th>( ^1)H(_\text{cis} )</th>
<th>( ^1)H(_\text{trans} )</th>
<th>( S^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>UQCISD σ</td>
<td>0.0</td>
<td>18.1</td>
<td>−2.6, −2.9</td>
<td>0.7617</td>
<td></td>
</tr>
<tr>
<td>UQCISD π</td>
<td>0.9</td>
<td>1.8</td>
<td>−20.9, −21.6</td>
<td>0.7643</td>
<td></td>
</tr>
<tr>
<td>UCCSD σ</td>
<td>0.0</td>
<td>17.3</td>
<td>−1.8, −2.1</td>
<td>0.7648</td>
<td></td>
</tr>
<tr>
<td>UCCSD((T)) σ</td>
<td>0.0</td>
<td>18.0</td>
<td>−2.6, −2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UCCSD((T)) π</td>
<td>1.2</td>
<td>0.6</td>
<td>−20.0, −20.6</td>
<td>0.7674</td>
<td></td>
</tr>
<tr>
<td>UB3LYP σ</td>
<td>2.9</td>
<td>17.5</td>
<td>0.6, 0.1</td>
<td>0.7532</td>
<td></td>
</tr>
<tr>
<td>UB3LYP π</td>
<td>0.0</td>
<td>1.1</td>
<td>−17.0, −17.5</td>
<td>0.7635</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Values corrected for the difference in the zero-point vibrational energies computed at the UB3LYP/6-311G** level
\(^b\)\( ^1\)H\(_\text{cis} \) and \( ^1\)H\(_\text{trans} \) Values are reported in order
\(^c\)UCCSD geometry

is orthogonal to the π molecular orbital of the carbonyl group (Fig. 2B).

Table 1 shows that the UQCISD method predicts the bent structure to be more stable than the linear one by 0.9 kcal mol\(^{-1}\). The same relative stability was obtained using the strictly related coupled-cluster UCCSD approach. The UHF reference determinants are heavily spin-contaminated not only in the π configuration, as expected, but also in the σ configuration, the expectation value of \( S^2 \) being of the order of 0.86 for both configurations. Calculations including triple excitations should then be used to obtain reliable results. The \( S^2 \) values after annihilation of the quartet contaminant (about 0.751) are only slightly higher than the value expected for a pure doublet state (0.75), so spin contamination is essentially due to the quartet state. Schlegel [26] showed that the UQCISD method removes such contaminants. Indeed, Table 1 shows that this is the case, the spin contamination being small for the UQCISD and UCCSD calculations. Anyway, single-point calculations including triple excitations were carried out to be certain of the reliability of the coupled-cluster results. Inclusion of triple excitations in the UCCSD(\(T\))/UCCSD calculations does not modify the relative state ordering and slightly increases the relative stability of the bent σ configuration up to 1.2 kcal mol\(^{-1}\).

The hfs constant at the β hydrogen, \( a(\text{H}_\beta) \), is computed to be 18.1, 17.3 and 18.0 G at the UQCISD, UCCSD and UCCSD(\(T\))/UCCSD levels, respectively. These computed values are in good accord with the experimental values observed in γ-substituted vinylacetyl radicals, which are in the range 18–20 G [27]. By con-