Theor Chem Acc (2000) 104:455–460
DOI 10.1007/s002140000167

Theoretical
Chemistry Accounts

Regular article

Overestimation of the stability of the π-delocalized versus the σ-localized configuration in radicals by current density functionals: the case of vinylacyl radicals

Maurizio Guerra

I.Co.C.E.A. Consiglio Nazionale delle Ricerche, Via Gobetti 101, 40129 Bologna, Italy

Received: 13 January 2000 / Accepted: 16 March 2000 /

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 π-delocalized configuration of the vinylacyl radical, $CH_2{=}CH{-}C(\bullet){=}O$, to be more stable than the σ-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, $Y\text{-}C(\bullet){=}CH_2$, bearing π-type α 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 π-delocalized versus σ-localized configurations in radicals since they favor the π configuration for the γ-methylvinylacyl radical, $CH_3{-}CH{=}CH{-}C(\bullet){=}O$, 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 π-type α substituents provided contrasting results. Calculations performed on $Y\text{-}C(\bullet){=}CH_2$ radicals [Y = C≡CH, C(=O)OH, C≡N] with the QCISD method predicted the σ-localized bent configuration (Fig. 1A) to be more stable than the π-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≡N, phenyl) [2]. It should be noted that the α-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 π-type α substituents [Y = C≡CH, C(=O)OH, C≡N, phenyl] should be linear at the radical center (π-type radical). This conclusion was questioned for the α-acryl [Y=C(=O)OCH$_3$] and α-cyanovinyl radicals [8]. In fact, the large ^{13}C hyperfine coupling (hfs) constant observed for these radicals is consistent with a bent structure (σ-type radical). The equivalence of the vinylic β 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, $Y\text{-}C(\bullet){=}O$, experimental results indicate unequivocally that radicals bearing π-type α substituents such as γ-substituted vinylacyls, $X\text{-}CH{=}CH{-}C(\bullet){=}O$, are localized σ radicals. Thus, this class of radicals has been studied to establish which method (DFT, QCISD) is more reliable for describing the relative stability of σ-localized and π-delocalized configurations in radicals.

2 Computational details

Unrestricted DFT calculations were carried out on the σ- and π-type configurations of vinylacyl 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-ζ 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-ζ quality in the p space but

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e-mail: guerra@area.bo.cnr.it

Fig. 1. Structures for α-substituted vinyl radicals: **A** bent σ radical, **B** linear π radical

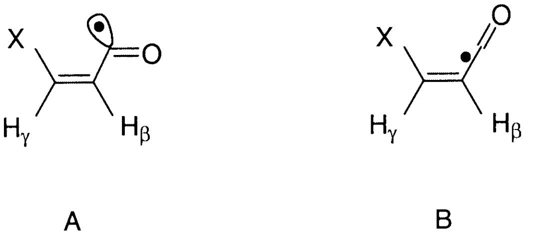

Fig. 2. Structures of the vinylacyl radicals: **A** bent σ radical, **B** linear π radical

Table 1. Relative energy, E_{rel} (kcal mol^{-1}), and ^{1}H hyperfine coupling constants (*hfs*) constants (gauss) for the σ- and π-type configurations of the vinylacyl radical, $CH_2{=}CH{-}C(\bullet){=}O$, computed with different methods employing the 6-311G** basis set

Method	Configuration	E_{rel}[a]	$^{1}H_\beta$	$^{1}H_\gamma$[b]	S^2
UQCISD	σ	0.0	18.1	−2.6, −2.9	0.7617
	π	0.9	1.8	−20.9, −21.6	0.7643
UCCSD	σ	0.0	17.3	−1.8, −2.1	0.7648
	π	0.9	2.1	−21.2, −21.8	0.7674
UCCSD(T)[c]	σ	0.0	18.0	−2.6, −2.9	
	π	1.2	0.6	−20.0, −20.6	
UB3LYP	σ	2.9	17.5	0.6, 0.1	0.7532
	π	0.0	1.1	−17.0, −17.5	0.7636

[a] Values corrected for the difference in the zero-point vibrational energies computed at the UB3LYP/6-311G** level

[b] H_{cis} and H_{trans} values are reported in order

[c] UCCSD geometry

actually of full double-ζ quality in the s space [13]. The local spin density (LSD) functionals include the Slater exchange functional along with the correlation functional fitting the random phase approximation (RPA) and the Ceperley-Alder solution to the uniform electron gas in SVWN and SVWN5, respectively [14]. The nonlocal or gradient-corrected functionals include the Becke 1988 [15] exchange functional along with the correlation functional of Lee, Yang, and Parr [16] in BLYP and that of Perdew and Wang [17] in BPW91. The modified Perdew–Wang 1991 exchange functional [18] was also used in MPWPW91. The hybrid functionals include a mixture of Hartree–Fock (HF) exchange with gradient-corrected exchange-correlation functionals. The B3LYP and B3PW1 functionals use Becke's three-parameter hybrid functional with 20% HF exchange [19] and the half-and-half hybrid functional BH&HLYP [20] includes 50% HF exchange.

Geometries and hfs constants were also determined using ab initio correlated methods. Electron correlation was estimated with perturbation theory up to fourth order, unrestricted second-order Møller–Plesset (UMP2), unrestricted third-order Møller–Plesset (UMP3), unrestricted fourth-order Møller–Plesset with single, double and quadruple excitations [UMP4(SDQ)], with the UQCISD method and with coupled-cluster methods, unrestricted coupled-cluster with double excitations (UCCD) ≡ unrestricted quadratic configuration interaction with double excitations (UQCID), unrestricted coupled-cluster with single and double excitations (UCCSD). Single-point calculations were performed including triple excitations [UCCSD(T)]. QCI and coupled-cluster calculations were carried out using the ACES II program [21].

In the correlated calculations the core electrons were held frozen. Their inclusion is not expected to significantly influence the optimum geometries and was found to give a small contribution to the hfs constants for second- [22] and third-row atoms [23] using an unrestricted HF (UHF) reference determinant since spin-polarization effects are included explicitly.

Selected single-point calculations were carried out by adding a tight *s* orbital to the hydrogen 6-311G** basis set to test the reliability of the computed ^{1}H hfs constants. Its exponent was determined by geometric continuation as suggested by Chipman [24].

Computed total energies were corrected for the zero-point vibrational energies (ZPVE) that were scaled to eliminate systematic errors in computed frequencies. Unfortunately, the scale factor for valence triple-ζ basis sets is available only at the B3LYP level. Hence, the relative energies (E_{rel}) of the σ- and π-type configurations were corrected for the difference in the ZPVE values computed with the UB3LYP method using a scale factor for frequencies of 0.989 [25].

3 Results and discussion

The relative stability E_{rel} of the bent and linear forms of the unsubstituted vinylacyl radical $CH_2{=}CH{-}C(\bullet){=}O$ were computed both with the UQCISD and UB3LYP methods, employing the moderate-sized 6-311G** basis set.

In the bent σ radical the unpaired electron is localized in an sp^2 hybrid carbon orbital in the molecular plane (Fig. 2A), while in the linear π radical the unpaired electron is delocalized over the allylic-type π system that 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, $a(^{1}H_\beta)$, 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 vinylacyl radicals, which are in the range 18–20 G [27]. By contrast, the UB3LYP method favors the linear form by 2.9 kcal mol^{-1} and the computed $a(^1H_\beta)$ value (1.1 G) is in complete disaccord with the experimental values observed in γ-substituted vinylacyl radicals. The E_{rel} value computed at the UB3LYP level should not be significantly influenced by contamination of the doublet states by higher spin multiplets since spin contamination is negligible for both configurations as usually found with many DFT methods. It should be noted, however, that the π configuration is slightly more contaminated than the σ configuration, so the energy of the π configuration could be slightly underestimated favoring, in turn, the σ configuration.

Figure 3 shows that the structural parameters do not change significantly on going from UB3LYP to UQCISD calculations, so the discrepancy between the DFT and ab initio methods cannot be due to differences in the structural parameters. Indeed, E_{rel} computed with the UB3LYP method changes by only 0.03 kcal mol^{-1} using the UCCSD geometries (UB3LYP//UCCSD) instead of the UB3LYP geometries.

Table 1 shows that the $a(^1H_\beta)$ and $a(^1H_\gamma)$ constants computed with the UB3LYP method are, however, close to those computed with the UQCISD and UCCSD methods for each electronic configuration.

These findings cannot prove with absolute certainty that the UB3LYP method overestimates the stability of the π-delocalized versus the σ-localized configuration since there is no experimental evidence that the unsubstituted vinylacyl radical has a bent σ configuration. Hence, the UB3LYP calculations were carried out on γ-substituted vinylacyl radicals, *X*-CH=CH—C(•)=O (*X* = CH_3, OCH_3, $OCOCH_3$), to compare directly the computed hfs constants with the experimentally available values.

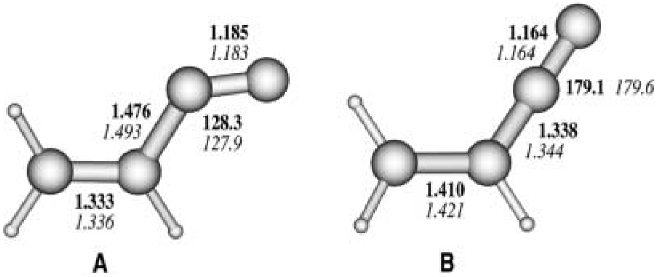

Fig. 3. Selected structural data for **A** the bent σ configuration and **B** the linear π configuration of the vinylacyl radical at the UB3LYP/6-311G** (*bold*) and UCCSD/6-311G** (*italic*) levels of theory. Bond lengths are in angstroms and bond angles in degree

Table 2 shows that the hfs constants computed with the UB3LYP approach for the σ configuration of these radicals are in excellent accord with experiment.

A large hfs constant (about 19 G) is predicted for the β hydrogen, the deviation from the experimental value being about 1 G. On the other hand, the hfs constants computed for the π configuration are in complete disaccord with experiment for $X = CH_3$ since the calculations predict a large coupling constant for the methyl hydrogens in addition to a large coupling constant for the γ-hydrogen. This finding indicates that the γ-methylvinylacyl radical has a σ-type electronic configuration. For $X = OCH_3$ and $OCOCH_3$ calculations predict only one large hfs constant for the γ hydrogen, the agreement with experiment being excellent for the former and poor for the latter. However, ESR spectra of vinylacyl radicals where the β hydrogen is substituted with a methyl group indicate that the large hfs constant observed in γ-substituted vinylacyl radicals is due to coupling with the β hydrogen rather than with the γ hydrogen [27, 28], so all these radicals should have a σ-type configuration.

The excellent agreement between the $a(^1H_\beta)$ constants computed for the σ configuration and those observed experimentally confirms that the B3LYP functional provides good hfs constants for doublet states [29–31].

On the other hand, the values of the relative stability (E_{rel}) reported in Table 2 indicate that the UB3LYP approach underestimates the stability of the σ-localized versus the π-delocalized configuration since the bent structure (σ radical) is computed to be less stable than the linear form (π radical) at the UB3LYP/6-311G** level, except for $X = OCH_3$. In this latter case, the oxygen lone pair of the methoxy group should destabilize the π configuration, preventing delocalization of the allylic-type unpaired electron and should stabilize the σ configuration, increasing the delocalization of the paired electrons of the π system. Consequently, the stability of

Table 2. Relative energy, E_{rel} (kcal mol^{-1}), for the σ- and π-type configurations of γ-substituted vinylacyl radicals, *X*-CH=CH—C(•)=O, at the UB3LYP/6-311G** level. Theoretical ^1H hfs constants (gauss) are compared with the experimental values reported in *italics*

X	Configuration	E_{rel}[a]	$^1H_\beta$	$^1H_\gamma$	$^1H\ (CH_3)$[b]	S^2
CH_3[c]	σ	1.2	18.5 (19.7)	2.2 (2.3)	−0.6 (−0.2)	0.7532
	π	0.0	1.5 (1.6)	−17.5 (−18.6)	17.1 (18.3)	0.7640
			19.5[d]	–	–	
OCH_3	σ	0.0	18.6	1.1	0.1	0.7534
	π	0.9	1.7	−13.9	1.1	0.7632
			19.63[e]	–	–	
$OCOCH_3$	σ	1.7	18.0	1.4	0.0	0.7533
	π	0.0	1.3	−18.6	1.5	0.7630
			19.5[e]	–	–	

[a] Values corrected for the zero-point vibrational energies

[b] Average value of the three ^1H hfs constants of the methyl group

[c] ^1H hfs constants computed by adding a tight s orbital to the hydrogen basis set are reported in *parentheses*

[d] From Ref. [28]

[e] From Ref. [27]

Table 3. Relative energy, E_{rel} (kcal mol^{-1}), and ^1H hfs constants (gauss) of the σ- and π-type configurations for the γ-methylvinylacyl radical, CH_3-—CH=CH—C(•)=O, computed with different correlated methods employing the 6-311G** basis set

Method	Configuration	E_{rel}[a]	$^1H_\beta$	$^1H_\gamma$	^1H (CH_3)[b]	S^2
UHF	σ	0.2	10.2	9.6	−5.0	0.8040
	π	0.0	13.5	−39.2	19.7	0.8479
UHF + LYP	σ	0.3	17.7	2.7	−1.2	0.7620
	π	0.0	8.1	−28.7	19.6	0.8181
UMP2	σ	0.0	53.6	−37.0	20.7	0.7710
	π	3.0	−9.5	−19.5	16.2	0.8117
UMP3	σ	0.0	44.8	−27.1	15.0	
	π	2.3	−4.8	−19.7	15.5	
UMP4(SDQ)	σ	0.0	39.9	−22.4	12.5	
	π	2.0	−3.2	−20.2	15.6	
UCCD[c]	σ	0.0	43.1 (45.7)	−25.7 (−27.1)	14.2 (15.0)	0.7805
	π	2.3	−4.0 (−4.4)	−19.6 (−20.6)	15.4 (16.3)	0.8220
UQCISD	σ	0.0	18.6	−0.6	1.0	0.7590
	π	2.0	2.2	−21.2	15.3	0.7655
UCCSD(T)[c,d]	σ	0.0	19.0 (19.9)	−0.9 (−1.0)	1.4 (1.5)	0.7615[e]
	π	2.5	0.9 (1.0)	−20.0 (−21.1)	15.2 (16.1)	0.7692[e]
Expt.[f]			19.5	–	–	

[a] Values corrected for the difference in the zero-point vibrational energies computed at the B3LYP/6-311G** level

[b] Average value of the three ^1H hfs constants of the methyl group

[c] ^1H hfs constants computed by adding a tight s orbital to the hydrogen basis set are reported in *parentheses*

[d] UQCISD geometry

[e] UCCSD values

[f] From Ref. [28]

the bent structure with respect to the linear form should sizably increase for this radical, so the UB3LYP method gives the correct global minimum for the methoxy derivative even if this approach underestimates the stability of the σ configuration.

Hereafter we focus our attention on the γ-methyl derivative that surely has a σ configuration and can be studied with highly correlated methods at moderate cost. Table 3 shows that the UQCISD calculations performed on this radical favor the localized σ configuration by 2.0 kcal mol^{-1} and provide hfs constants in good accord with experiment.

The hfs values computed for the less stable linear π configuration are in evident contrast with experiment, as previously found for UB3LYP calculations.

The σ configuration is favored with respect to the π configuration also including only double excitations in estimating correlation energy (UQCID≡UCCD) or using perturbation theory (UMPn, $n = 2$–4), the relative stability being of the order of 2–3 kcal mol^{-1}. However, the hfs constants computed with these methods are largely in error as found previously for the isoelectronic imidoyl radicals [Y–C(•)=N-R] [32]. Comparison of the hfs values computed including only double excitations in perturbation theory (MP3) and in the coupled-cluster approach (UCCD), which takes account of the effect of double excitations through all orders of perturbation, indicates that only a minor part of this discrepancy is due to a slow convergence of double amplitudes. The improvement due to contributions from single excitations estimated perturbatively [MP4(SDQ)] is small. Indeed, it was shown that single excitations should be included iteratively in post-HF calculations to obtain a correct spin density distribution when a localized unpaired σ electron can interact with a lone pair in the presence of a polarizable π system [32].

Chipman [24] showed that in restricted multiconfiguration self-consistent-field calculations addition of a tight s orbital to the basis set provides a significant improvement in the spin density especially at the hydrogens. Then, single-point calculations were carried out by adding a tight s orbital to the 6-311G** hydrogen basis set at the UB3LYP, UCCD and UCCSD(T)//UQCISD levels to test the reliability of the computed ^1H hfs constants. Tables 2 and 3 show that the ^1H hfs constants do not change significantly, the agreement with experiment improving slightly as was previously found in unrestricted QCI calculations on alkylsilyl radicals [33].

Hence, these calculations show that the UQCISD method correctly predicts both the relative state ordering and magnetic properties of vinylacyl radicals and demonstrate that the UB3LYP approach overestimates the stability of the π-delocalized versus the σ-localized configuration but provides good hfs constants for each doublet state. In contrast, correlated methods that do not estimate iteratively the effect of single excitations provide correct relative energies but poor hfs constants. The effect of the type of density functional (local, gradient-corrected, hybrid) on the relative stability of the σ and π radicals was then examined for the γ-methylvinylacyl radical. Table 4 shows that all density functionals give incorrectly the linear structure to be more stable than the bent one.

The LSD approximation provides the worst performance, the error being larger than 3–4 kcal mol^{-1}. The relative stability of the linear form sizably decreases using gradient-corrected functionals. The Becke and modified Perdew–Wang 1991 exchange functionals provide the same result. As far as correlation functionals are concerned the LYP functional performs better than the PW91 functional, the error decreasing by about 1 kcal mol^{-1}. The use of hybrid functionals produces a further

Table 4. Relative energy, E_{rel} (kcal mol^{-1}), and ^{1}H hfs constants (gauss) of the σ- and π-type configurations for the γ-methylvinylacyl radical, CH_3-—CH=CH—C(•)=O, computed with various types of density functional theory functionals employing the 6-311G** basis set

Functional	Configuration	E_{rel}[a]	$^{1}H_{\beta}$	$^{1}H_{\gamma}$	^{1}H (CH_3)[b]	S^2
Local spin density						
SVWN	σ	4.1	16.2	−0.3	−0.3	0.7516
	π	0.0	−0.9	−10.7	17.7	0.7527
SVWN5	σ	3.7	16.1	−0.3	−0.3	0.7518
	π	0.0	−0.9	−11.5	17.8	0.7530
Gradient-corrected						
BPW91	σ	2.7	17.7	0.1	−0.3	0.7523
	π	0.0	0.4	−15.7	18.0	0.7570
MPWPW91	σ	2.7	19.0	2.1	−0.3	0.7523
	π	0.0	0.5	−16.2	16.6	0.7569
BLYP	σ	1.6	17.8	0.2	−0.2	0.7522
	π	0.0	0.3	−14.6	18.3	0.7562
Hybrid						
B3PW91	σ	2.2	17.2	0.1	−0.4	0.7534
	π	0.0	1.6	−18.0	18.3	0.7650
B3LYP	σ	1.2	18.5	2.2	−0.6	0.7532
	π	0.0	1.5	−17.5	17.1	0.7640
BH&HLYP	σ	0.4	17.2	0.3	−0.5	0.7557
	π	0.0	3.9	−21.2	19.7	0.7823
Expt.[c]			19.5	–	–	

[a] Values corrected for the difference in the zero-point vibrational energies computed at the B3LYP level
[b] Average value of the three ^{1}H hfs constants of the methyl group
[c] From Ref. [28]

slight improvement, the error being larger than 1.2 kcal mol^{-1} for the three-parameter B3LYP functional that includes 20% HF exchange. However, the smallest error was obtained using the simple half-and-half hybrid functional BH&HLYP, which includes 50% HF exchange. The same trend was previously found in other cases where currently available density functionals were found to fail [34, 35]. This finding might indicate that the results improve by increasing the amount of the admixture of HF exchange density. Then, calculations were carried out at the HF level by estimating electron correlation with the LYP functional. Table 3 shows that the π configuration remains favored, its relative stability (0.4 kcal mol^{-1}) is comparable to that estimated with the BH&HLYP functional. Interestingly, the error slightly decreases at the simple UHF level, the σ configuration lying only 0.2 kcal mol^{-1} higher in energy than the π configuration. That is, the best DFT correlation functional (LYP) provides comparable correlation energy for the σ- and π-type configurations. On the other hand, UMP2 calculations, which take into account the effect of a limited number of double excitations, correctly predict the bent σ configuration to be more stable than the linear π configuration by 3.0 kcal mol^{-1}. The relative stability decreases slightly considering all double excitations in perturbation theory ($E_{\mathrm{rel}} = 2.3$ kcal mol^{-1} at the UMP3 level) and should not change at higher orders in the perturbation expansion since E_{rel} does not change at the UCCD (≡UQCID) level. The introduction of single excitations both at perturbation level [UMP4(SDQ)] and iteratively (UQCISD) reduces the stability of the σ configuration by only 0.3 kcal mol^{-1}. This means that the main contribution (2-3 kcal mol^{-1}) to the stability of the σ configuration versus the π configuration derives from dynamic correlation. Indeed, the dynamic correlation energy is expected to decrease with electron delocalization. By contrast, in the DFT approach the correlation energy computed with the LYP functional is similar for the σ- and π-type configurations, favoring slightly the latter. Thus, in hybrid functionals, which perform better than the other functionals, the discrepancy due to the best and most popular correlation functional (about 2.5 kcal mol^{-1}) is larger than that due to either the best, BH&H (about 0.2 kcal mol^{-1}), or the most popular, B3 (about 0.8 kcal mol^{-1}), exchange functionals. Very recently, Cramer [36] concluded that the DFT method cannot properly handle the electronic states of 2,3-didehydro-1,4-benzoquinone when the a_2 π^* orbital is singly occupied. In particular, the DFT method overestimates its electron affinity. The 2,3-didehydro-1,4-benzoquinone anion π state is similar to the vinylacyl radical π state studied in the present work. This suggests that the overestimation of the relative stability of the π-delocalized versus the σ-localized configuration by DFT methods is likely to be due to the overstabilization of the π state.

4 Conclusions

In the present study the effect of currently available density functionals on the relative stability of the σ- and π-type configurations of vinylacyl radicals was investigated.

It was found that the current density functionals overestimate the stability of the π configuration versus the σ configuration, so they predict incorrectly the γ-methylvinylacyl radical to be a linear π radical in evident contrast with information obtained with ESR spectroscopy. On the other hand, UQCISD calculations favor the bent σ radical in accord with experimental evidence. Care should be then exercised in comparing the total energy of the σ- and π-type configurations of radicals using the current DFT functionals. In the present case the most popular DFT functional, B3LYP, overestimates the stability of the π-delocalized versus the σ-localized configuration by about 4 kcal mol^{-1} with respect to that computed with the UQCISD method. This difference is mainly due to an incorrect estimate of dynamic correlation with the DFT approach.

Acknowledgement. This research was supported by the Progetto Strategico Modellistica Computazionale di Sistemi Molecolari Complessi of the Italian Research Council (CNR).

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