

## Description of C(sp<sup>2</sup>)–C(sp<sup>2</sup>) Rotation in Butadiene by Density Functionals

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Received: May 31, 2001; In Final Form: August 16, 2001

The torsional potential of 1,3-butadiene has been calculated using several ab initio methodologies. For each value of the C=C–C=C torsional angle, the fully relaxed geometry and energy have been determined using the Hartree–Fock (HF) method, Möeller–Plesset perturbation theory up to the second order (MP2), and the coupled-cluster method with single, doubles, and parenthetical triples (CCSD(T)), as well as using several exchange–correlation combinations of functionals in density functional theory (DFT) calculations. From the results obtained, the achievements and drawbacks of current density functionals in the description of torsional profiles have been rationalized, and some possible breakthroughs have been proposed to improve their performance.

### 1. Introduction

Nowadays, conformational analysis<sup>1</sup> plays a central role in the field of chemical applications. It is not until recently that quantum chemical methods have been applied successfully to the understanding of conformational concepts (see, for instance refs 2–7 for the present state-of-the-art strategies). Indispensable for such pursuit is the existence of highly accurate theoretical methodologies, embedding the most important correlation effects, such as coupled-cluster theory<sup>8–10</sup> or composite methods based on it,<sup>11</sup> and one-particle basis sets providing a systematic asymptotic behavior toward the basis set limit, namely, the cc-pVnZ sequence (see ref 12 for a recent review). This double convergence is possible to be achieved, with the present available computational resources, in molecules of only moderate size,<sup>13–18</sup> but to obtain results for larger molecules, it is necessary to roughly truncate the space expanded by the basis set as well as the level of correlation energy treatment. Hence, density functional theory (DFT),<sup>19–24</sup> demanding less computation effort, could be an alternative for the study of conformational properties if the major part of the effects covered by ab initio methods were also included through its Kohn–Sham implementation.<sup>25</sup> On the other hand, DFT is not plagued by the basis set convergence slowness showed by the ab initio methods since the asymptotic regime of the basis set is reached earlier.<sup>26,27</sup> By all these reasons, DFT has emerged as a promising tool for many chemical applications, including the field of conformational analysis. Whereas DFT has been applied extensively to compute the torsional potential of a variety of systems,<sup>28–41</sup> the quantitative evaluation of torsional profiles of conjugated molecules remains unsolved. Even for the simplest conjugated hydrocarbon, 1,3-butadiene, it is not well understood why DFT common functionals failed to calculate, as accurate as desired, the torsional curves. Closely related systems such as styrene, biphenyl, or stybene are also affected by a similar error,<sup>34,35</sup> so a detailed study deserves to be done. Moreover, application of DFT to butane,<sup>28,34,35,37</sup> 1-butene,<sup>34,36</sup> or related systems,<sup>31</sup> which involves C(sp<sup>3</sup>)–C(sp<sup>3</sup>) or C(sp<sup>2</sup>)–C(sp<sup>3</sup>) rotation, respectively, has provided a good overall quality.<sup>42,43</sup>

compared to the more costly G2 method.<sup>44</sup> The torsional potential of 1,3-butadiene is mainly controlled by two kind of interactions. The electronic  $\pi$ -conjugation tends to stabilize the coplanar conformers, and the unfavorable steric, nonbonding, effects are largely the responsible of the appearance of a second stable conformer, commonly called gauche. If DFT is able to describe accurately the torsional potential of butane and 1-butene, the discrepancies are probably not due to the possible errors in the description of nonbonding interactions but to the description of the partial  $\pi$ -bond breaking. Taking into account the previous points, the analysis carried out along this work will shed light on the applicability, and predictive usefulness, of DFT methods in the calculation of the torsional potential of conjugated molecules, choosing the 1,3-butadiene as the most representative prototype.

### 2. Computational Methods

The program package GAUSSIAN98<sup>45</sup> was used for all the electronic structure calculations. Fully relaxed torsional potentials were imposed for the C–C single bond rotation, which means that for each fixed value of the C=C–C=C dihedral angle, all the other geometrical parameters were optimized. The internal angle was regularly changed by increments of 10°, which leads to a regular and tight grid of rotational angles. As our intention is to test the reasons of the previously reported failures, we have splitted the exchange–correlation functional into its constituent parts. Accordingly, the following expression serves us to define the chosen composition for the functionals employed along this work:

$$E_{xc}[\rho] = A_{\text{HF}} E_{\text{x}}^{\text{HF}} + A_{\text{x}}^{\text{LDA}} E_{\text{x}}^{\text{LDA}} + A_{\text{x}}^{\text{non-LDA}} \Delta E_{\text{x}}^{\text{B}} + A_{\text{c}}^{\text{LDA}} E_{\text{c}}^{\text{LDA}} + A_{\text{c}}^{\text{non-LDA}} E_{\text{c}}^{\text{LYP}} \quad (1)$$

From a pure DFT point of view it should be noted that, historically, exchange and correlation functionals are designed and optimized by fitting against accurate reference values, in such a way that they altogether provide a reasonable description of the exchange and dynamical correlation effects. Despite this practical aspect, we are trying to isolate if the detected anomalies are due to an incomplete treatment provided either by the

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**TABLE 1: Summary of the Composition of the Functionals Used in This Work According to Formula 1 of the Text**

abbrev.	$A_{\text{HF}}$	$A_{\text{x}}^{\text{LDA}}$	$A_{\text{x}}^{\text{non-LDA}}$	$A_{\text{c}}^{\text{LDA}}$	$A_{\text{c}}^{\text{non-LDA}}$	ref
(A) Exchange Only						
$X_{\alpha}$	—	1.00	—	—	—	46
B	—	1.00	1.00	—	—	47
B3	0.20	0.80	0.72	—	—	48
BHandH	0.50	0.50	0.50	—	—	50
(B) Exchange-Correlation						
SVWN	—	1.00	—	1.00	—	51, 52
BLYP	—	1.00	1.00	—	1.00	47, 53
B3LYP	0.20	0.80	0.72	0.19	0.81	48, 53
BH and HLYP	0.50	0.50	0.50	—	1.00	50, 53

exchange or correlation or by both functionals simultaneously. By this reason, Table 1 presents the composition of the exchange-only and exchange-correlation functionals, including allowed mixing with exact Hartree–Fock (HF) exchange that will be used along the rest of the work. For the exchange part, we have selected the local  $X_{\alpha}$  functional,<sup>46</sup> recommended when the LDA exchange is used without a correlation functional, as well as the well-known functional developed by Becke (B)<sup>47</sup> because of its prolific and extended use. Guided by the amount of exact exchange in the B3PW91 original 3-parameter hybrid functional,<sup>48,49</sup> we define in a similar fashion the B3 exchange functional simply by neglecting the correlation term of the original expression ( $A_{\text{c}}^{\text{LDA}} = A_{\text{c}}^{\text{non-LDA}} = 0$ ). This B3 ad hoc functional has a 20% of HF exchange, lying between the pure B and the equally mixed BHandH functional. For BHandH and BHandHLYP, neither of these is actually the formulation proposed by Becke in his paper,<sup>50</sup> but our intention is to establish an equal mixing of HF and B exchange in order to test the influence of the portion of the HF exchange introduced. Although the above-mentioned paper reveals a second formulation involving slightly different coefficients, we restricted ourselves to a maximum weight of 50% for the HF contribution of the exchange hybrid functional selected. For composing the exchange-correlation functional, we add the local VWN to the  $X_{\alpha}$  functional, resulting the SVWN<sup>51,52</sup> entry of Table 1. LYP correlation functional<sup>53</sup> completes the B, B3, and BHandH exchange to give the labeled BLYP, B3LYP, and BHandHLYP. Other tested correlation functionals, P86<sup>54</sup> and PW91,<sup>49</sup> did not bring any additional information so that they are excluded from the results presented here.

Zero-point vibrational energy corrections to the energetics of the system were not considered because our purpose is to emphasize the relative performance of DFT functionals, with respect to ab initio methods, more than to compute thermal corrections to the torsional potentials. Residual scalar relativistic, core correlation, and other secondary contributions were not quantified because of their expected minuscule influence. To explore the dependence of the results with the basis set and, consequently, to show the invariance of the conclusions reached under changes in the one-particle expanded space, the calculations were performed with the standard correlation-consistent polarized  $n$ -tuple basis set<sup>55,56</sup> cc-pVnZ. Specifically, the cc-pVDZ and cc-pVTZ basis set were utilized, whose schemes are [3s2p1d/2s1p] and [4s3p2d1f/3s2p1d] for the [C/H] atoms. There is a general agreement in the fact that for computing DFT molecular relative energies, a basis set of spdf quality is usually sufficient to get the asymptotic regime.<sup>57</sup> Of course, the same is not true for ab initio methods without assistance of extrapolation techniques.<sup>58</sup> Finally, calculated DFT torsional potentials can be compared with available experimental results,<sup>59</sup> but in order to get a proper understanding of the performance of exchange-correlation functionals, ab initio calculations should

**TABLE 2: Relative Stability of the Stationary Points (in kcal/mol) with Respect to the Global s-trans Minimum<sup>a</sup>**

method	s-cis	gauche	TS
cc-pVDZ			
HF	4.08	3.37 (39.3°)	6.25 (101.4°)
MP2	3.64	3.07 (35.7°)	6.44 (101.0°)
CCSD	3.45	2.95 (36.0°)	5.74 (101.0°)
CCSD(T)	3.43	3.05 (33.6°)	6.06 (100.5°)
$X_{\alpha}$	4.15	3.92 (28.4°)	8.36 (99.6°)
B	3.92	3.88 (20.6°)	7.64 (97.9°)
B3	3.92	3.75 (33.7°)	7.20 (99.9°)
BHandH	3.94	3.58 (28.1°)	6.68 (98.9°)
HF-LYP	4.08	3.35 (38.2°)	6.60 (101.9°)
SVWN	3.99	3.80 (27.1°)	8.36 (99.6°)
BLYP	3.98	3.92 (20.0°)	8.10 (98.3°)
B3LYP	3.92	3.77 (32.6°)	7.61 (100.3°)
BHandHLYP	3.94	3.58 (27.0°)	7.09 (99.2°)
cc-pVTZ			
HF	4.31	3.50 (40.3°)	6.23 (101.4°)
MP2	3.70	3.07 (35.9°)	6.50 (101.3°)
CCSD <sup>b</sup>	3.67	3.16 (34.9°)	5.98 (101.1°)
CCSD(T) <sup>b</sup>	3.60	3.18 (35.5°)	6.30 (100.7°)
$X_{\alpha}$	4.24	3.84 (31.9°)	7.89 (99.7°)
B	3.98	3.85 (26.7°)	7.11 (97.8°)
B3	4.01	3.74 (31.8°)	6.82 (98.8°)
BHandH	4.07	3.63 (35.7°)	6.47 (99.8°)
HF-LYP	4.30	3.49 (39.1°)	6.63 (101.7°)
SVWN	4.08	3.71 (30.7°)	7.96 (99.7°)
BLYP	4.07	3.90 (26.3°)	7.53 (97.4°)
B3LYP	4.04	3.75 (30.8°)	7.24 (99.1°)
BHandHLYP	4.10	3.65 (34.7°)	6.89 (100.1°)
exp. <sup>c</sup>	4.00	2.84	5.93

<sup>a</sup> Optimal angle (in deg) in parentheses. <sup>b</sup> cc-pVDZ for hydrogen atoms. <sup>c</sup> Taken from ref 59.

be included for completeness. Among them, the very costly CCSD/cc-pVTZ and CCSD(T)/cc-pVTZ calculations, keeping fixed the cc-pVDZ on the hydrogen atoms and with the frozen core approximation, were performed specifically for this work, while the remaining ab initio results were taken from the extensive recent study carried out by the authors.<sup>7</sup>

### 3. Results and Discussion

The viability of density functional methodologies to the description of the problem of the partial double bond breaking is shown in Table 2 for all the basis sets and the combinations of exchange and correlation functionals used in this work. The experimental gas-phase barriers comes from ref 59. These are based in the assignments of the observed Raman transitions and their fitting to a one-dimensional potential. For both basis sets, cc-pVDZ and cc-pVTZ, the first group of entries summarizes the ab initio energies (in kcal/mol) of the different stationary points relative to the energy of the global s-trans minimum using HF, MP2, CCSD, and CCSD(T) methodologies. The second block of values shows the results of exchange-only calculations, named  $X_{\alpha}$ , B, B3, and BHandH, respectively, whereas the third one presents the effect of the correlation functional added to the HF,  $X_{\alpha}$ , B, B3, or BHandH exchange. All these calculations were run in the specific DFT routine of the GAUSSIAN98 package.

An examination of the DFT results listed in Table 2 indicates that there is a clear separation between the accuracy of the s-trans/s-cis energy difference on one side and the s-trans/gauche and s-trans/TS one on the other. Amazingly, all the DFT results met the stringent “calibration accuracy” energetic criteria ( $\pm 0.24$  kcal/mol of error<sup>11</sup>) for the s-trans/s-cis difference, but the same cannot be said for the entire torsional potential when rotation is investigated. It has been shown that to describe

correctly the loss of the partial double-bond character of the central C-C bond upon rotation, the inclusion of electron correlation at high level is necessary.<sup>7</sup> The nonplanarity introduced by the rotation breaks the electronic delocalization and only a sophisticated treatment of the electron correlation effects is able to include properly the consequences for the energetic profile.<sup>7</sup> Systematic application of the CC/cc-pVnZ methods would lead to the dual convergence of the correlation corrections to the HF energy and of the completeness of the basis set. But DFT—and this is one of its major inabilities—cannot be interpreted under the same reasoning. Although each functional should converge to a particular value regarding the completeness of the basis set, there is no possibility to judge if there would be a systematic improvement toward the exact values. Rather than test the convergence of exchange-correlation functionals, we aim for an interpretation of the wrong computed results for the *s*-trans/*gauche* and *s*-trans/TS energy differences.

The DFT errors for the *s*-trans/*s*-cis energy difference are in the region of 0.1–0.2 kcal/mol, with independence of the basis set or exchange-correlation functional employed. Moreover, the portion of HF exchange on the exchange functional does not alter significantly the results (the maximum difference being 0.1 kcal/mol between B/cc-pVnZ and BHandH/cc-pVnZ), and even the inclusion of the LYP correlation functional also does not modify the corresponding HF or DFT results (the maximum difference being less than 0.1 kcal/mol between B/cc-pVnZ and BLYP/cc-pVnZ, for example).

The situation markedly changes when the *s*-trans/*gauche* energy differences are examined. The DFT exchange-only results range from 3.6 to 3.9 kcal/mol, which is roughly 1 kcal/mol above the exact value and ~0.5 kcal/mol above the other *ab initio* results, and the inclusion of the LYP correlation functional gave newly almost similar results. The point to note in this case is the influence of the HF exchange as a part of the hybrid functionals. The energy difference  $\Delta E_{s\text{-trans}/\text{gauche}}$  decreases systematically following the sequence B → B3 → BHandH, irrespective of the basis set used, and, as a consequence of the previously commented negligible importance of the correlation functional, also for the related BLYP → B3LYP → BHandHLYP results. It is worth to mention that neither DFT nor coupled-cluster methods are able to reach the “calibration accuracy” for the *s*-trans/*gauche* energy difference. Regarding the localization of the second minimum, the DFT optimal torsional angles for the existence of the *gauche* conformer are generally smaller than those of the correlated *ab initio* methods. Once again, the wrong trend is corrected with the successive increment of the HF exchange in the composition of the exchange-only or exchange-correlation functional (the BHandH/cc-pVTZ and BHandHLYP/cc-pVTZ values are very close to their CCSD or CCSD(T) counterparts). The definitive role of the HF exchange is evidenced through the inspection of the last column of Table 2.

It is assumed that the X<sub>α</sub> or the SVWN functionals, based on the description of the homogeneous electron gas, are a deficient starting point to compute the *s*-trans/TS energy difference and then the errors of more than 2 kcal/mol may be attributable to this fact. The reasons why density-gradient corrections improve atomization energies or barrier heights has been recently rationalized.<sup>60</sup> It was shown that whenever a bond is stretched and/or partially broken, the contribution of the gradient corrections in the exchange-correlation functional increases, thus improving the description of, for example, torsional potentials. In fact, the use of the Becke functional corrects the local exchange results toward the experimental

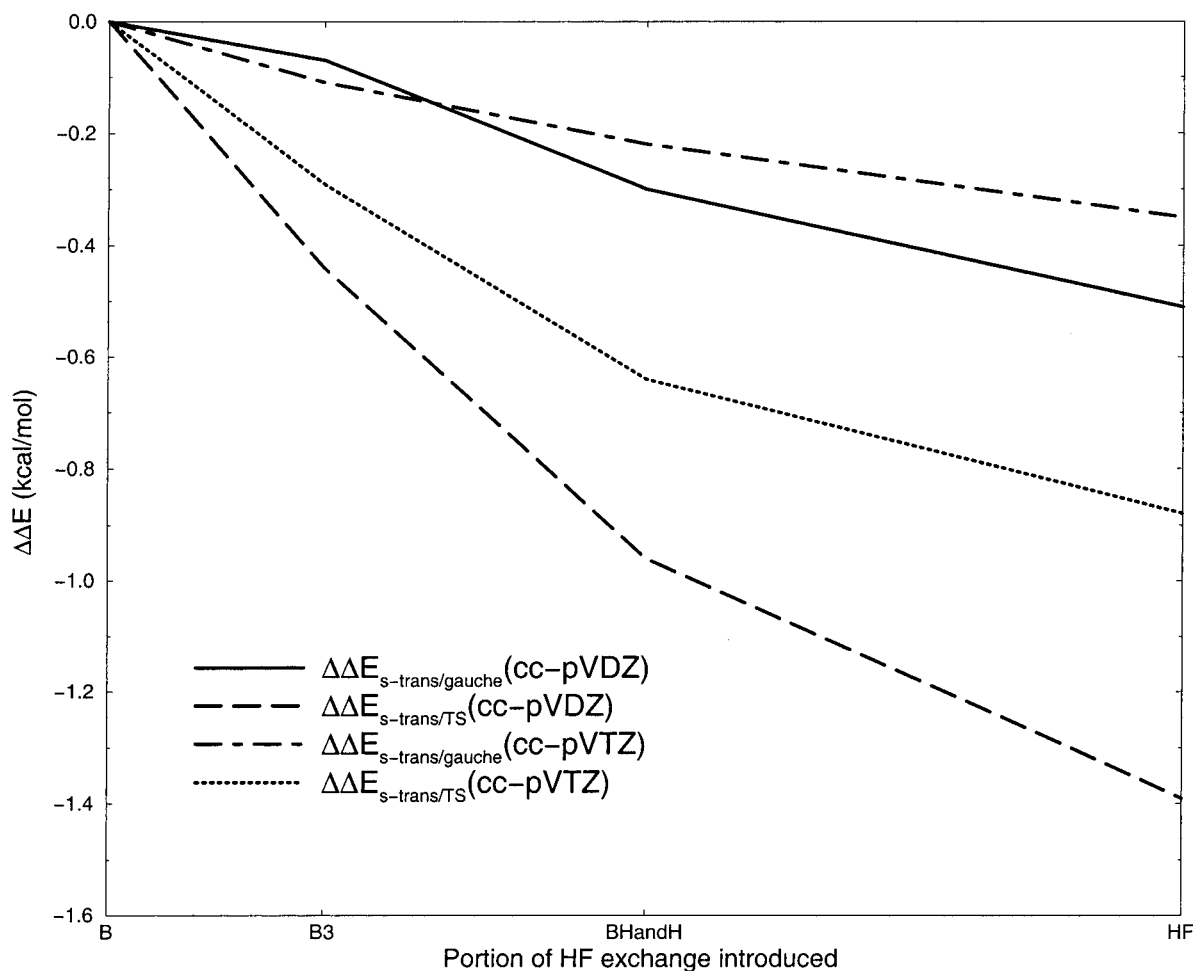
values, but it is also true that an additional lowering of the relative energies occurs when HF exchange is incorporated into the functionals. From B to BHandH, the improvement of the  $\Delta E_{s\text{-trans}/\text{TS}}$  barrier height is found to be 0.96 and 0.64 kcal/mol for the cc-pVDZ and cc-pVTZ basis sets, respectively. Astonishingly, the incorporation of electron correlation, either in the HF or in the exchange-only schemes, produces an increment of ~0.4 kcal/mol for the barrier height and, hence, a worsening of the final results. The BLYP/cc-pVDZ and BLYP/cc-pVTZ errors of 2.2 and 1.6 kcal/mol are few times larger than the magnitude of any conceivable uncertainty for the theoretical predictions. On the other hand, the “calibration accuracy” for the *s*-trans/TS energy difference seems to be reached in conjugated molecules only with *ab initio* methods. These facts preclude the indiscriminate use of common DFT functionals when an accurate description on the whole range of torsional angles is needed.

Finally, with the above points in mind, we represent graphically in Figure 1 the effect of the HF exchange on the *s*-trans/*gauche* and *s*-trans/TS energy differences. Along the horizontal axis, we list the portion of HF exchange introduced, in exchange-only calculations, in order of increasing approachness toward a pure 100% HF exchange. Along the other, we list the decrease in the mentioned energy differences, with respect to the Becke values, caused by the amount of HF exchange. Figures 2 and 3 are still more illustrative in the sense that they provide a clear visual picture of the noticed effects. Figure 2 compares the DFT exchange-only torsional potential with the HF curve for the cc-pVTZ basis sets. On the other hand, the effect of adding the LYP correlation functional can be inspected from Figure 3.

#### 4. On the Performance of DFT

To analyze the previous findings, the physical description of involved electronic effects will be considered in the following through changes in some selected geometrical parameters. The dependence of the central bond length on the torsion is usually chosen as indicative of the conjugative effects. These effects are maximum in the coplanar forms (for a torsion angle of 0° or 180°), having at these geometries the central bond length its minimum value due to the partial double bond character. On the other hand, in the *s*-cis conformation the C=C-C angle should be larger than in the *s*-trans isomer because of the needed opening to avoid as much as possible the steric interactions between nonbonded hydrogens. Deviations of the DFT computed geometrical parameters with respect to *ab initio* results will give us information about why the DFT methods differ in the treatment of steric and conjugative effects.

To understand the effects due to conjugative interactions, we have compared in Table 3 the calculated cc-pVTZ DFT exchange-only C-C bond lengths and C=C-C angles for a few selected intermediate geometries with HF, CCSD(T), and HF-LYP values. It has been found previously<sup>61</sup> that all gradient-corrected exchange functionals lead to bond lengths which are too long. The lengthening of the DFT exchange-only bond distances is related to the fact that Becke's functional produces a charge displacement toward antibonding regions.<sup>62–64</sup> If the density decreases in the bonding region, the obvious consequence is the increment of the internuclear C-C distance. Consistently, the progressive incorporation of the HF exchange compensates this effect for all conformeric structures. The LYP functional shortens systematically the HF internuclear distances so that the use of the HF-LYP scheme is a backward step for the calculation of equilibrium distances, as can be seen in Table



**Figure 1.** Influence of the HF exchange in the decrease of the s-trans/skew and s-trans/TS energy differences.

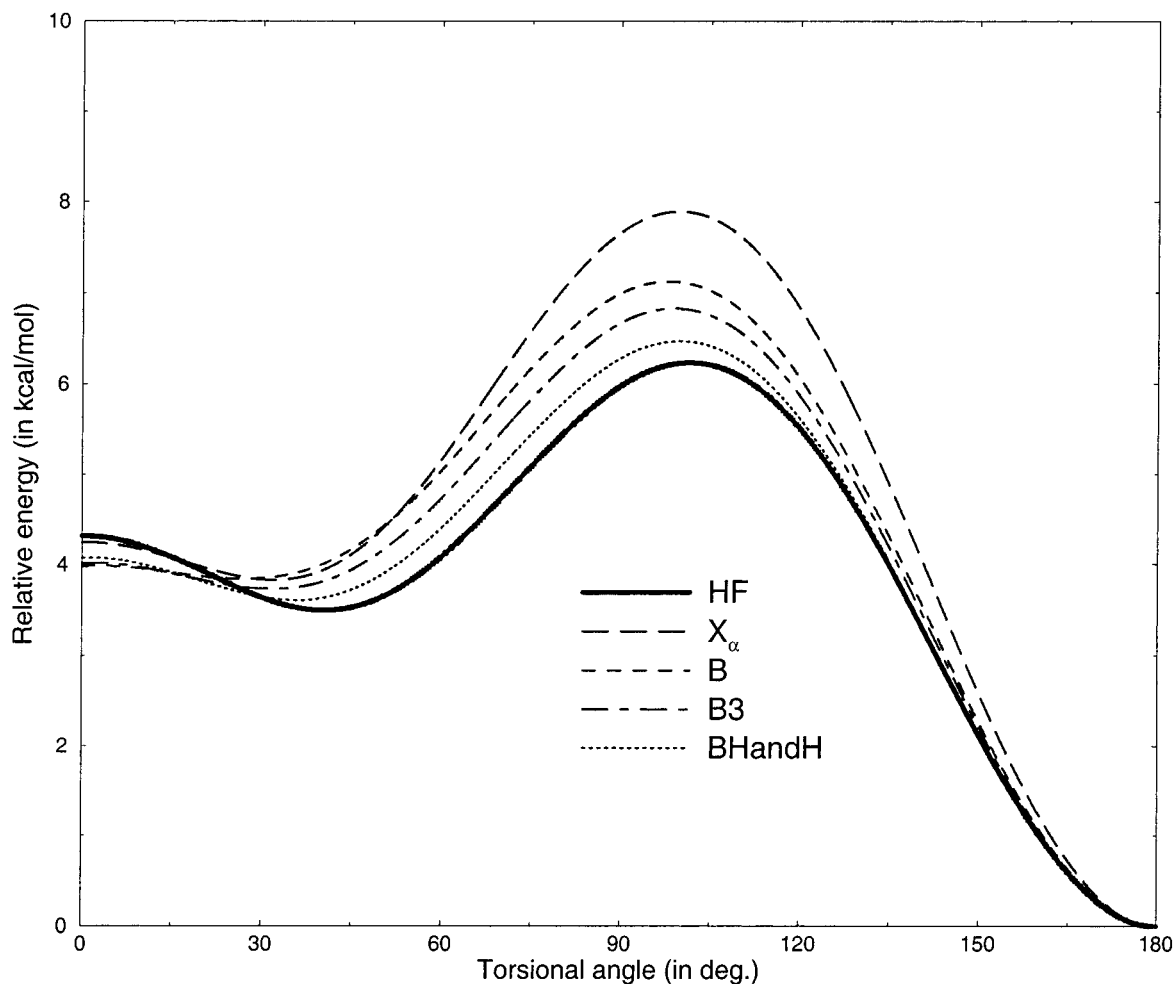
3 and as have been noted previously.<sup>63–65</sup> Normally, when the bonds become larger, the angles are closed because the hybrid orbitals get less s-character,<sup>66</sup> but this is not the case for the s-cis conformation. Becke exchange slightly overestimates steric effects and it might be expected that these unfavorable interactions to drop off rapidly as the torsional angle moves away from 0°, explaining the lower angle of the Becke value for the gauche conformer.

With respect to steric effects, Table 4 presents the differences between s-cis and s-trans C–C distance for the cc-pVTZ basis set. The  $r_{\text{C-C}}^{\text{s-cis}} - r_{\text{C-C}}^{\text{s-trans}}$  values corroborate the conclusion about the treatment of steric effects by Becke exchange functional because the larger difference is found to be 0.0153 (Å) whereas greater HF exchange percentage of the hybrid functional brings the values to their correct CCSD(T) result.

We will now focus our attention on the reasons why DFT calculations of the s-trans/TS barrier height do not agree significantly with experimental or ab initio references. The differences between the calculated bond lengths in the top of the curve and in the s-trans conformation ( $r_{\text{C-C}}^{\text{TS}} - r_{\text{C-C}}^{\text{s-trans}}$ ) are also given in Table 4. The inclusion of the MP2 results fills the gap between uncorrelated HF and CCSD(T) methods. The predictions of all the ab initio methods are sensibly different to that of the Becke functional since, in an exchange-only scheme, the use of this functional provided the largest difference (0.0357 Å represents a relative error of 32.2% with respect to the CCSD(T) value). If we center our attention in the difference between B (0% of HF exchange) and BHandH (50% of HF exchange)

results and in the well-predicted BHandH value for the s-trans/TS barrier height (the BHandH barrier is the closest to the CCSD(T) one), we can definitely correlate the larger  $r_{\text{C-C}}^{\text{TS}} - r_{\text{C-C}}^{\text{s-trans}}$  difference with the overestimation of the s-trans/TS energy difference. The overestimation of the Becke exchange contribution to the atomization energy has been shown to be especially significant for multiple-bonded diatomic molecules,<sup>64</sup> and it was argued that the reason was the extra Fermi correlation, between like-spins electrons belonging to different molecular orbitals, introduced by Becke's functional. This general overbinding is related, as it has been recently illustrated,<sup>67</sup> to the delocalized character over several atomic centers of the exchange hole in molecular systems, which cannot be mimicked by an exchange functional sampling density information only at the reference point  $\mathbf{r}$  (the exchange hole might have different structure for points  $\mathbf{r}'$  on other centers). The delocalized nature of  $\pi$ -bonds in the coplanar conformers reflects also in a delocalization of the exchange hole that, as explained in ref 67, is poorly described by Becke's functional. This is the ultimate reason DFT calculations employing Becke's exchange functional overestimate the energies of the coplanar forms with respect to the noncoplanar structures and, hence, produces an artificial larger value for the s-trans/TS barrier height. The previous conclusions can be visualized in Table 5, which presents the magnitude of the HF and Becke exchange energies, the later calculated at the HF optimized geometry, as well as the corresponding absolute error. As it can be observed, the exchange energy provided by the Becke functional is always greater than the exact values with a maximum deviation for





**Figure 2.** Torsional potential of 1,3-butadiene using exchange-only functionals. Employed basis set: cc-pVTZ.

the *s*-cis and *s*-trans isomers. The work carried out here allows clarifying the performance of the Becke functional and serves to enhance the level of knowledge about this effect reached since now. From the calculations, the reasons of the failures are examined, using exchange-only and exchange-correlation schemes, and the errors due to the use of the Becke exchange are rigorously quantified.

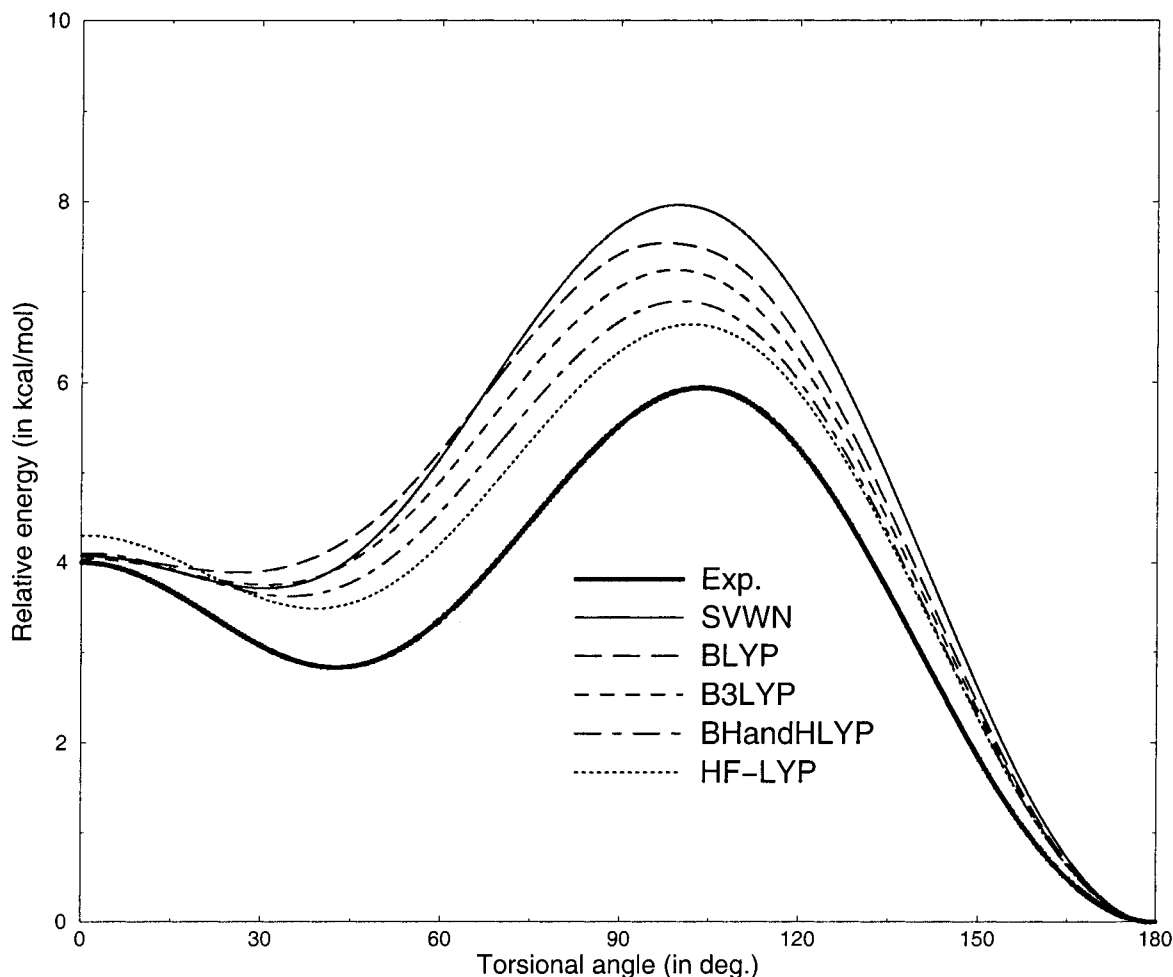
There exists, in our opinion, few possibilities to overcome the deficiencies encountered in the application of DFT to torsional profiles of conjugated systems. Systematic optimization of the majority of the gradient-corrected exchange or correlation functionals, regardless of how they are determined, is defined by fitting the involved parameters on a atomic and/or molecular calibration data.<sup>68,69</sup> This is the usual procedure employed last by several of the developer groups of exchange-correlation functionals (Becke et al.,<sup>48,50,67,70-74</sup> Scuseria et al.,<sup>75</sup> Filatov and Thiel,<sup>76,77</sup> Perdew et al.,<sup>78-80</sup> Handy and Tozer et al.,<sup>81-85</sup> and Salahub et al.,<sup>86</sup> among others). The most used calibration set is based in the G2 thermochemical data,<sup>44,87,88</sup> which consists of a relative large number of heats of formation, ionization potentials, electron affinities, proton affinities, and total atomic energies. In addition to energetic data, gradient and exchange-correlation potential data have been recently added in the optimization procedure. We propose to include in the reference data of choice the accurate reproduction of the entire torsional profile of 1,3-butadiene, as a first step. Another heterobutadiene rotamers,<sup>89</sup> accurately studied (as glyoxal,<sup>90</sup> nitrosoformaldehyde or *N*-nitrosomethanimine<sup>91</sup>), could also be included for completeness although their conjugation is smaller and, therefore,

the delocalization energy would not be so influenced by the use of Becke's exchange functional. Second, the application of exchange-correlation functionals that goes beyond the conventional gradient approximation by including contributions from the laplacian of the density or from the kinetic energy density ("meta-GGA" in the usual nomenclature) should help in the assessment of the performance of the functionals for the treatment of stabilizing conjugative effects. It has been suggested that the reliability of DFT methods for computing activation barriers strongly depends on the exchange functional,<sup>92-94</sup> being usually the hybrid methods the preferred election. Recent and pioneering studies on several activation barriers with the newer exchange-correlation functionals<sup>95-97</sup> showed the same quality than the hybrid functional employed. Encouraged by these results, we are mainly interested in two directions for a proper understanding of the performance of DFT to difficult cases as the description of the torsional potential of conjugated molecules: extension of the present work to closely related molecules and application of "meta-GGA" functionals to the problem of torsional potentials.

## 5. Conclusions

From the results of the previous sections, several conclusions can be drawn regarding the performance of DFT calculations on torsional profiles in conjugated dienes:

1. There is a general trend in the exchange-only and exchange-correlation calculations of better torsional profiles as the percentage of the HF exchange is increased from 0%



**Figure 3.** Torsional potential of 1,3-butadiene using exchange-correlation functionals. Employed basis set: cc-pVTZ.

**TABLE 3: Dependence of Some Selected Geometrical Parameters on the Torsion (Bond Lengths in Å, Angles in deg)<sup>a</sup>**

	method	$r_{C-C}$	C=C-C	method	$r_{C-C}$	C=C-C
0°	HF	1.4780	127.20	B	1.4965	128.33
	CCSD(T)	1.4733	126.35	B3	1.4904	127.94
	HF-LYP	1.4565	126.54	BHandH	1.4869	127.21
30°	HF	1.4763	126.12	B	1.4974	127.16
	CCSD(T)	1.4724	125.11	B3	1.4909	126.79
	HF-LYP	1.4548	125.43	BHandH	1.4864	126.58
60°	HF	1.4778	124.92	B	1.5040	125.73
	CCSD(T)	1.4788	123.83	B3	1.4960	125.43
	HF-LYP	1.4570	124.38	BHandH	1.4908	125.27
90°	HF	1.4869	124.59	B	1.5157	125.25
	CCSD(T)	1.4853	123.74	B3	1.5067	125.04
	HF-LYP	1.4649	124.29	BHandH	1.4977	124.55
120°	HF	1.4856	124.26	B	1.5115	124.93
	CCSD(T)	1.4838	123.67	B3	1.5034	124.72
	HF-LYP	1.4636	124.02	BHandH	1.4977	124.55
150°	HF	1.4724	124.06	B	1.4920	124.85
	CCSD(T)	1.4687	123.60	B3	1.4860	124.61
	HF-LYP	1.4509	123.75	BHandH	1.4821	124.41
180°	HF	1.4645	124.02	B	1.4812	124.87
	CCSD(T)	1.4595	123.62	B3	1.4761	124.62
	HF-LYP	1.4432	123.73	BHandH	1.4732	124.40

<sup>a</sup> Basis set employed: cc-pVTZ.

(Becke), to 20% (B3), to 50% (BHandH), up to 100% (HF). This behavior is attributable to the overestimation of Fermi correlation characteristic of Becke's exchange functional whenever the delocalization of the exchange hole is important, as with coplanar 1,3- $\pi$ diene bonds. This explains why the s-trans/

**TABLE 4: Differences between the Calculated s-cis and TS Central Bond Length (in Å), with Respect to that of the s-trans Isomer, and Relative Error (in %) Referring to the CCSD(T) Values<sup>a</sup>**

method	$r_{C-C}^{s-cis} - r_{C-C}^{s-trans}$	$\epsilon_r$	$r_{C-C}^{TS} - r_{C-C}^{s-trans}$	$\epsilon_r$
HF	0.0135	-2.2	0.0236	-12.6
MP2	0.0140	+1.4	0.0264	-2.2
CCSD(T)	0.0138		0.0270	
HF-LYP	0.0133	-3.6	0.0229	-15.2
B	0.0153	+10.9	0.0357	+32.2
B3	0.0143	+3.6	0.0318	+17.8
BHandH	0.0137	-0.7	0.0280	+3.7

<sup>a</sup> Basis set employed: cc-pVTZ.

s-cis energy difference of 1,3-butadiene is accurately predicted by B, B3, or BHandH mixings, since this overestimation occurs almost in the same amount for both conformers. In contrast, the s-trans/gauche and the s-trans/TS energy differences are severely overestimated when Becke exchange is used because of, in this case, the overestimation mainly affects the s-trans conformer.

2. For apparent reasons, the torsional profiles of  $sp^3-sp^3$  or  $sp^3-sp^2$  C-C bond rotation will not suffer from the above problems, and previous works have confirmed the good overall quality of DFT calculations on these systems, including Becke exchange.

3. As it has been reported in previous studies, a side effect of the above-mentioned fact is that Becke exchange tends to enlarge the bond distance. Again, this effect is more important for either the s-trans or s-cis conformers than for the transition

**TABLE 5: Exchange Energies (in au) Calculated Using HF or Becke Functional at Few Selected Intermediate Geometries and Absolute Errors (in kcal/mol) for Becke's Functional<sup>a</sup>**

	$E_x^{\text{HF}}$	$E_x^{\text{B}}$	$\epsilon_a$
0°	-22.87077	-22.88250	7.36
30°	-22.86995	-22.88109	6.99
60°	-22.86835	-22.87821	6.19
90°	-22.86713	-22.87644	5.84
100°	-22.86713	-22.87647	5.86
120°	-22.86784	-22.87762	6.14
150°	-22.87017	-22.88099	6.79
180°	-22.87125	-22.88274	7.21

<sup>a</sup> Basis set employed: cc-pVTZ.

state and explains the results of Tables 3 and 4 for the C-C bond length.

4. The effect of the LYP correlation functional is somewhat independent of the exchange, since the weight of the correlation potential to the effective KS potential is quite small, with an overall worsening with respect to the exchange-only results for the s-trans/TS energy difference.

5. One possible solution for the poor torsional profiles computed with Becke exchange could be to reparametrize hybrid schemes including the transient-state barriers for several 1,3-dienes in the optimization set. Recent developments in the description of the exchange hole increasing the nonlocality of exchange density functionals are very promising in remedy this problem of current exchange-correlation functionals.<sup>67</sup>

**Acknowledgment.** This work has been supported by the DGICYT of Spain under Projects PB97-0122 and 1FD1997-1358 and by the Generalitat Valenciana (GV00-095-2). Computing time in the CPD of the University of Alicante is also acknowledged. We thank Prof. Alfred Karpfen for providing us with some useful references.

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