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Journal of Molecular Structure (Theochem) 362 (1996) 163–173

THEO  
CHEM

# An assessment of density functional theory on evaluating activation barriers for small organic gas-phase rearrangement reactions

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Received 22 July 1995; accepted 18 September 1995

## Abstract

Several gas-phase isomerization reactions have been studied with density functional theory (DFT) using both the local density approximation (LDA) and non-local (NL) gradient-corrected methods. Besides the validity of each of these pure density functional procedures, the relative accuracy of the hybrid B3LYP model (Becke's 3 parameter-functional with the NL correlation of Lee, Yang and Parr) has also been tested. The predicted geometries and relative energetics for the reactions have been examined and compared with those of Hartree–Fock (HF), MP2 and QCISD (quadratic configuration interaction with single and double excitations) calculations. Our results indicate that the NL level of DFT is reliable at estimating reaction barriers and transition state structures, especially when using the B3LYP functional, which outperforms or at least equals MP2 calculations. This theoretical investigation demonstrates that DFT methods can be used to obtain thermochemical information as accurate as that provided by means of some ab initio post-HF methods.

*Keywords:* Activation barrier; Density functional theory; Gas-phase rearrangement; Reaction energy; Thermochemistry; Transition-state structure

## 1. Introduction

In the search for accurate energies, Hartree–Fock (HF) theory is the procedure followed most often as a first approximation. This method generally yields more than 99% of the true (Born–Oppenheimer) energy, but the method of recovering the remaining 1%, i.e. correlation energy, is much more tough. Although a wide variety of techniques (including both perturbational and variational procedures) are available for predicting

correlation energy, most methods are computationally expensive compared with HF. Moreover, since most of these methodologies take the HF wavefunction as reference, when the system is not well described at this level of theory, post-HF results are likely to be inaccurate.

Density functional theory (DFT) [1–6] is an alternative approach which uses functionals of the electron density to compute exchange and correlation energies. DFT is an exception to most correlated methods in that it provides an estimate of the correlation energy relatively cheaply. Such modest computational cost is, of course, a necessary prerequisite for correlated studies of large systems; hence, investigation of

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the quality of density functional methods deserves attention.

There is a growing literature [7–14] on systematic comparisons of DFT theories with HF and post-HF treatments and also with experiment. Preliminary results suggest that DFT, whose origin arises from solid-state physics, is a cost-effective general procedure for studying physical properties of molecules, structures, vibrational frequencies or dipole moments, among others. However, from a thermochemical point of view, few studies have dealt so far on whether DFT is also adequate for describing transition-state structures and reaction profiles.

The complete characterization of a chemical reaction requires the full determination of the potential energy surface for the reaction system, where the energy is a function of the nuclear coordinates. In classical and variational transition-state theories this requirement may be reduced to determining the surface around the reactant(s), the product(s), the transition state (saddle point), and the lowest energy pathway connecting them.

The first determination of a transition-state structure based on approximate DFT appeared recently. Fan and Ziegler [15] studied the isomerization reaction  $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ . While the energy barrier for the process was determined experimentally [16] with high accuracy to be  $38.4 \text{ kcal mol}^{-1}$ , the barrier calculated by the Hartree–Fock–Slater (HFS) (or  $X\alpha$  method) [3–6] is  $40.8 \text{ kcal mol}^{-1}$ . In turn, the best ab initio calculation [17] based on SDQ-MBPT(4) with  $10^7$  configurations gave a higher barrier of  $41 \text{ kcal mol}^{-1}$ . It is worth mentioning that although Fan and Ziegler [18] demonstrated that the local density approximation (LDA) and non-local (NL) energies are similar to the values obtained from post-HF calculations, these authors found the LDA method to predict energy barriers which were much too low for some hydrogen abstraction reactions involving  $\text{CH}_4$  and  $\text{CH}_3\text{Cl}$ , while the NL method successfully corrected the errors.

Other examples were reported by Stanton and Merz [19], where LDA and NL methods were used and compared. These authors concluded that NL corrections were necessary when calculating barrier heights in some organic and

organometallic systems like the reaction of zinc hydroxide with carbon dioxide or the pericyclic Diels–Alder reaction and a (1,5)-sigmatropic shift in 1,3-pentadiene. However, in other cases, as in the formaldehyde formation reaction, both LDA and NL methods were found to predict structures and energies similar to those obtained at the MP2 level of theory. More calculations are still needed to provide an assessment of how DFT methods will represent transition-state structures and activation barriers. Such calculations should probably involve more accurate approximate DFT methods than the simple HFS scheme.

Moreover, there has been long interest in the problem of coupling HF theory with local density-functional approximations for the calculation of dynamic correlation energy [20,21]. In doing so, one attempts to exploit the obvious strengths of each partner. The first one provides an exact treatment of exchange and is a practical tool even for large chemical systems. Unfortunately, it suffers from well-known, severe deficiencies in describing chemical bonding and cannot be used without further corrections in thermochemical applications, excepting isodesmic reactions. On the contrary, density-functional approximations can be evaluated extremely easily and quickly and appear to offer a convenient alternative to conventional post-HF technology, which does not scale efficiently with molecular size and is impractical in a great number of large systems, at least at present. As a result, a mixed approach has been proposed (the so-called hybrid models), in which the exchange functional is a linear combination of the HF exchange and a functional integral of the density and, in some cases, the density gradient as well.

Very promising results of earlier tests [9,22,23] have encouraged us to investigate the potential power of DFT in reactivity studies. Therefore, the aim of this paper is to test a related set of pure functionals and also to assess the accuracy of a hybrid functional on evaluating energy barriers. Emphasis will be laid on a comparison with the relative energies obtained by HF and post-HF methods. Three simple chemical gas-phase rearrangement reactions ( $\text{H}_2\text{SO} \rightarrow \text{HSOH}$ ,  $\text{F}_2\text{SS} \rightarrow \text{FSSF}$  and  $\text{HNC} \rightarrow \text{HCN}$ ) have been chosen.

## 2. Methodology

Both DFT and conventional *ab initio* SCF calculations have been performed using the GAUSSIAN 92 program [24]. Intermediates were located through full geometry optimization. Further, transition states were located in the full potential energy hypersurface and characterized by the existence of a single negative eigenvalue of the Hessian matrix.

The basis set employed has been the 6-31G\* of Pople and co-workers [25], usually used in studies of moderately large organic molecules. This polarization function-augmented basis set has been shown to be necessary to describe polar molecules [26] with electronegative atoms like F, O or N. Moreover, *d* orbitals are essential for a proper description of hypervalent sulfur in H<sub>2</sub>SO [27] and F<sub>2</sub>SS [28], yet they are much less important in the normal valent HSOH and FSSF. Although larger basis sets including diffuse functions would improve the results (especially for compounds containing third-row elements), the use of this basis set allows us to keep the amount of computing time within reasonable limits.

### 2.1. Conventional *ab initio* computations

Full geometry optimizations were done for all systems at the MP2 level. Moreover, both the isomerization of H<sub>2</sub>SO and the HCN hydrogen migration were also investigated by means of quadratic configuration interaction including single and double excitations (QCISD). HF results are extracted from Ref. [29].

### 2.2. Density functional calculations

The pure functionals used in this paper are separated into exchange and correlation parts. The exchange part is either Slater [30] (S), corresponding to the free-electron gas, or Becke [31] (B), which includes a gradient correction. The correlation part is either treated by LDA theory using the Vosko, Wilk and Nusair (VWN) parameterization [32] of exact uniform gas results [33], or treated using the gradient corrections of Perdew, along with his 1986 local correlation functional [34] (P86). As far as the

hybrid model is concerned, the B3LYP method is chosen here; this is the Becke's 3 parameter functional [35] with the NL correlation provided by the gradient-corrected functional of Lee, Yang and Parr [36] (LYP), as transformed by Miehlich et al. [37].

A sufficiently large integration grid was used so that sensitivity to grid size was minimized. Coarser grids can be required for larger molecules. Our emphasis in this study is laid on testing the functionals without the complication of numerical quadrature errors.

## 3. Results and discussion

In this section we present the results obtained for the H<sub>2</sub>SO → HSOH, F<sub>2</sub>SS → FSSF and HNC → HCN gas-phase rearrangement reactions. First, geometrical parameters are examined and discussed; and second, a comparison of relative energetics for the reactions is made. The second part is actually the main objective of this paper.

### 3.1. Molecular structures

Tables 1, 2 and 3 gather the geometrical parameters (equilibrium distances and bond angles) of reactants, products and transition states (TSs) of the three rearrangement reactions studied. For the sake of clarity, all first-order saddle points have been drawn in Fig. 1.

Recently Iraqi and Schwarz [38] reported experimental evidence for the gas-phase existence of hydrogen thioperoxide (HSOH) and thiooxonium ylide (H<sub>2</sub>SO). However, no structural data are available for any isomers. Nevertheless, we can start from our QCISD values as a reference.

Table 1 shows that HF bond lengths are systematically shorter than both MP2 and QCISD for reactant and product. This is not at all surprising if one takes into account the deficiency in correlation energy corrections. Bond lengths at saddle points are less affected than at minima with respect to HF underestimation.

Regarding the DFT-optimized parameters, there is a fairly good agreement with those obtained at post-HF levels. When using the Becke–Perdew

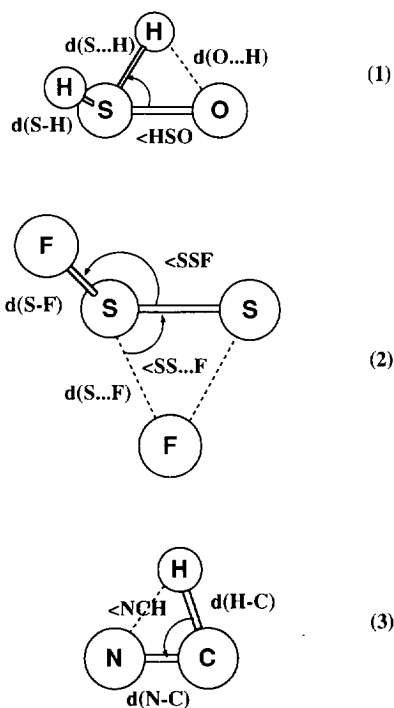


Fig. 1. First order saddle points for the reactions  $\text{H}_2\text{SO} \rightarrow \text{HSOH}$  (1),  $\text{F}_2\text{SS} \rightarrow \text{FSSF}$  (2) and  $\text{HNC} \rightarrow \text{HCN}$  (3).

(BP86) functional, distances for reactant and product become longer than the reference due to the inclusion of NL corrections, which are probably unnecessary here to describe such molecular structures. In fact, the SVWN results show that LDA is reliable enough to obtain accurate bond distances. This fact has previously been remarked by Becke [39]. Further, recent calculations by Andzelm and Labanowski [5] and Pederson and Jackson [40] indicate that geometrical parameters optimized by LDA are of the same quality as those optimized by the MP2 ab initio method [41] for organic molecules.

Table 1 shows that the B3LYP hybrid model is even closer to post-HF results. The differences between B3LYP and QCISD distances are smaller than 0.025 Å. Recently, Murray et al. [14] have reported calculations on several diatomic molecules and have found that, on average, bond lengths from a hybrid method are much better than HF bond lengths (although, from a practical point of view, adding HF density to density functional energy expressions can be less preferable than using pure DFT [14]).

Conclusions similar to those that arise above are drawn for the  $\text{F}_2\text{SS} \rightarrow \text{FSSF}$  rearrangement

Table 1

Calculated structural parameters of  $\text{H}_2\text{SO}$  and  $\text{HSOH}$  together with those of the transition state (TS) of the  $\text{H}_2\text{SO} \rightarrow \text{HSOH}$  isomerization reaction (distances in Å and angles in deg)

|                        | HF <sup>a</sup> | MP2   | QCISD | SVWN  | BP86  | B3LYP |
|------------------------|-----------------|-------|-------|-------|-------|-------|
| <i>H<sub>2</sub>SO</i> |                 |       |       |       |       |       |
| <i>d</i> (S–O)         | 1.479           | 1.505 | 1.511 | 1.499 | 1.517 | 1.506 |
| <i>d</i> (S–H)         | 1.343           | 1.375 | 1.382 | 1.413 | 1.415 | 1.391 |
| ∠HSO                   | 109.0           | 110.3 | 109.8 | 110.7 | 110.6 | 110.2 |
| ∠HSH                   | 89.7            | 87.0  | 87.3  | 84.9  | 85.2  | 86.4  |
| <i>TS</i>              |                 |       |       |       |       |       |
| <i>d</i> (S–O)         | 1.691           | 1.655 | 1.706 | 1.642 | 1.681 | 1.683 |
| <i>d</i> (S–H)         | 1.329           | 1.362 | 1.365 | 1.402 | 1.400 | 1.375 |
| <i>d</i> (S···H)       | 1.381           | 1.379 | 1.395 | 1.388 | 1.392 | 1.389 |
| <i>d</i> (O···H)       | 1.445           | 1.527 | 1.512 | 1.566 | 1.573 | 1.534 |
| ∠HSO                   | 55.0            | 59.6  | 57.3  | 61.6  | 60.7  | 59.0  |
| <i>HSOH</i>            |                 |       |       |       |       |       |
| <i>d</i> (S–O)         | 1.655           | 1.693 | 1.696 | 1.673 | 1.708 | 1.694 |
| <i>d</i> (O–H)         | 0.949           | 0.975 | 0.974 | 0.980 | 0.983 | 0.972 |
| <i>d</i> (S–H)         | 1.328           | 1.345 | 1.352 | 1.371 | 1.372 | 1.358 |
| ∠HOS                   | 108.8           | 106.1 | 106.5 | 106.1 | 105.2 | 106.2 |

<sup>a</sup> From Ref. [29].

Table 2  
Calculated and experimental structural parameters (in Å and deg) of F<sub>2</sub>SS and FSSF isomers, and the TS structure

|                        | HF <sup>a</sup> | MP2   | QCISD | SVWN  | BP86  | B3LYP | Exp. <sup>b</sup> |
|------------------------|-----------------|-------|-------|-------|-------|-------|-------------------|
| <i>F<sub>2</sub>SS</i> |                 |       |       |       |       |       |                   |
| <i>d</i> (S–S)         | 1.879           | 1.865 | 1.884 | 1.883 | 1.903 | 1.893 | 1.860             |
| <i>d</i> (F–S)         | 1.579           | 1.647 | 1.636 | 1.634 | 1.669 | 1.644 | 1.598             |
| ∠SSF                   | 107.9           | 108.3 | 108.1 | 108.1 | 108.4 | 108.2 | 107.5             |
| ∠FSF                   | 92.0            | 90.6  | 90.9  | 91.7  | 92.4  | 91.8  | 92.5              |
| <i>TS</i>              |                 |       |       |       |       |       |                   |
| <i>d</i> (S–S)         | 1.825           | 1.850 | 1.865 | 1.861 | 1.881 | 1.870 | –                 |
| <i>d</i> (S–F)         | 1.575           | 1.633 | 1.633 | 1.623 | 1.659 | 1.634 | –                 |
| <i>d</i> (S⋯F)         | 2.165           | 2.190 | 2.260 | 2.193 | 2.278 | 2.264 | –                 |
| ∠SSF                   | 107.9           | 109.8 | 108.1 | 109.8 | 110.5 | 109.4 | –                 |
| ∠SS⋯F                  | 67.7            | 63.7  | 67.0  | 65.0  | 65.9  | 66.3  | –                 |
| <i>FSSF</i>            |                 |       |       |       |       |       |                   |
| <i>d</i> (S–S)         | 1.953           | 1.925 | 1.944 | 1.910 | 1.937 | 1.942 | 1.888             |
| <i>d</i> (F–S)         | 1.611           | 1.659 | 1.658 | 1.653 | 1.687 | 1.663 | 1.635             |
| ∠SSF                   | 104.3           | 106.6 | 105.6 | 110.5 | 110.6 | 108.4 | 108.3             |
| ∠FSSF                  | 88.6            | 88.9  | 88.9  | 89.3  | 89.4  | 89.1  | 87.9              |

<sup>a</sup> From Ref. [29].

<sup>b</sup> From Ref. [44].

reaction (Table 2). In this case, the thermochemical study at the most expensive QCISD level has been omitted due to the presence of a third-row atom. However, both QCISD and experimental data are available for geometries.

The isolation and identification of the two isomers of disulfur difluoride was first accomplished by Kuczowski and co-worker [42–44] and was confirmed by other groups [45–48]. The S–S and S–F bond lengths in the F<sub>2</sub>SS isomers are 1.860 and 1.589 Å, respectively, and 1.888 and 1.635 Å, respectively, in FSSF according to microwave spectroscopic studies [44]. Angles ∠SSF and ∠FSF in F<sub>2</sub>SS are 107.5 and 92.5°, respectively, whereas in FSSF the angle ∠SSF and the dihedral angle ∠FSSF amount to 108.3 and 87.9° respectively [44].

From Table 2 and experimental data, it is shown that HF yields geometric parameters quite accurate for F<sub>2</sub>SS, although for the FSSF isomer the HF methodology yields the largest errors. Furthermore, bond lengths are slightly yet systematically overestimated at the MP2 level; this is caused by the excessive covalent character induced by this perturbational method on the S–F bonds. Among all three DFT functionals tested, SVWN appears to be the most successful one in predicting molecular

structures for F<sub>2</sub>SS and FSSF, since the two functionals including gradient corrections give even longer distances than the MP2 procedure.

Table 3 displays the last set of geometric parameters. A direct assessment of the quality of the theoretical results for the HNC → HCN species is again possible because available experimental data allow for a complete structure determination of both isomers [49,50]. Judging from the experimental N–C and C–H distances, the most accurate values are those obtained with B3LYP, outperforming the QCISD bond lengths.

### 3.2. Activation energy barriers and thermochemistry

We now turn our attention to the determination of barrier heights for the reactions under investigation. The computational results are summarized in Tables 4–9, where reactants have been selected to be the energy minimum closest to the transition states.

Very recent ab initio calculations on HOS<sup>−</sup>, HSO<sup>−</sup>, HOSH and H<sub>2</sub>SO demonstrated that HOS<sup>−</sup> and HOSH are more stable than the HSO<sup>−</sup> and H<sub>2</sub>SO isomers [51], respectively. In particular, the H<sub>2</sub>SO → HSOH reaction had been

Table 3

Calculated and experimental structural parameters (in Å and deg) of HNC and HCN isomers, and the calculated values of the TS structure

|                | HF <sup>a</sup> | MP2   | QCISD | SVWN  | BP86  | B3LYP | Exp.               |
|----------------|-----------------|-------|-------|-------|-------|-------|--------------------|
| <i>HNC</i>     |                 |       |       |       |       |       |                    |
| <i>d</i> (H–N) | 0.985           | 1.002 | 1.002 | 1.010 | 1.010 | 1.000 | 0.994 <sup>b</sup> |
| <i>d</i> (N–C) | 1.154           | 1.187 | 1.182 | 1.180 | 1.189 | 1.177 | 1.165 <sup>b</sup> |
| <i>TS</i>      |                 |       |       |       |       |       |                    |
| <i>d</i> (N–C) | 1.169           | 1.196 | 1.201 | 1.194 | 1.205 | 1.192 | –                  |
| <i>d</i> (H–C) | 1.155           | 1.177 | 1.193 | 1.203 | 1.209 | 1.194 | –                  |
| ∠NCH           | 77.5            | 72.8  | 70.4  | 69.1  | 69.1  | 70.8  | –                  |
| <i>HCN</i>     |                 |       |       |       |       |       |                    |
| <i>d</i> (N–C) | 1.132           | 1.177 | 1.166 | 1.162 | 1.169 | 1.157 | 1.153 <sup>c</sup> |
| <i>d</i> (C–H) | 1.059           | 1.069 | 1.072 | 1.081 | 1.080 | 1.070 | 1.065 <sup>c</sup> |

<sup>a</sup> From Ref. [29].

<sup>b</sup> From Ref. [49].

<sup>c</sup> From Ref. [50].

studied previously at the HF/6-31G\* level [27,29]. In those studies, an activation barrier of 53.76 kcal mol<sup>-1</sup> and a reaction energy of -32.39 kcal mol<sup>-1</sup> were reported (relative to the H<sub>2</sub>SO isomer).

Both DFT and post-HF results from Table 4 confirm the exothermicity of this reaction. With respect to the QCISD result, it is found that all DFT methods underestimate the stability of the HSOH isomer, the B3LYP relative energy being closer to the QCISD value than pure DFT. When comparing the barrier height for the selected methods, remarkably different results are obtained. Taking as a reference our post-HF values of 42.8 kcal mol<sup>-1</sup> (MP2) or 43.5 kcal mol<sup>-1</sup> (QCISD), it can be seen that HF overestimates

Table 4

Relative energies (in kcal mol<sup>-1</sup>) of the TS and HSOH with respect to the H<sub>2</sub>SO isomer calculated at selected levels of conventional ab initio theory as well as DFT. The imaginary frequency (in cm<sup>-1</sup>) of the first order saddle point is included

| Method | Δ <i>E</i> (TS)   | Δ <i>E</i> (HSOH)  | ν <sup>‡</sup> |
|--------|-------------------|--------------------|----------------|
| HF     | 53.8 <sup>a</sup> | -32.4 <sup>a</sup> | 2074.4i        |
| MP2    | 43.5              | -27.6              | 1773.3i        |
| QCISD  | 42.8              | -29.0              | 1550.2i        |
| SVWN   | 38.3              | -21.7              | 1381.8i        |
| BP86   | 38.7              | -21.6              | 1348.2i        |
| B3LYP  | 41.9              | -25.3              | 1503.9i        |

<sup>a</sup> From Ref. [29].

the barrier by more than 10 kcal mol<sup>-1</sup>, while pure DFT models yield a reaction energy slightly smaller with respect to QCISD (4.5 and 4.1 kcal mol<sup>-1</sup> for LDA and NL, respectively). Interestingly the B3LYP barrier becomes closer to that obtained at the highly correlated QCISD level, spending far less computer time.

A brief mention must be made here of a parameter often overlooked in theoretical analyses: the imaginary frequency associated with the transition state, which measures the curvature of the intrinsic reaction path at the saddle point. This parameter can give a general idea of the accuracy reached by a given method in relation to vibrational frequencies. Thus, as shown in Table 4, the HF frequency clearly overestimates the QCISD value of 1550.2i cm<sup>-1</sup>. MP2 deviates from this reference by more than a 14% error. On the contrary, both pure and hybrid DFT frequencies underestimate the QCISD result, but while the former moves away from it by about 11%, the latter has an error of less than 3%, thus being the best approximation.

Similar trends to those discussed before are observed when the reaction enthalpy (Δ*H*<sup>0</sup>) and the Gibbs energy (Δ*G*<sup>0</sup>) are evaluated, as shown in Table 5. Taking QCISD values as reference, HF overestimates both Δ*H*<sup>0</sup> and Δ*G*<sup>0</sup>, especially when the TS is involved. Conversely, MP2 energies lie very close to QCISD energies, which can be seen

Table 5  
Contributions to  $\Delta G^\circ$  at 298.15 K relative to the reactant for different species involved in the  $\text{H}_2\text{SO} \rightarrow \text{HSOH}$  gas-phase reaction

| Method | Species | ZPE <sup>a</sup> | $\Delta H^{\circ a}$ | $\Delta S^{\circ b}$ | $\Delta G^{\circ a}$ |
|--------|---------|------------------|----------------------|----------------------|----------------------|
| RHF    | A       | 14.83            | 0                    | 0                    | 0                    |
|        | TS      | 11.76            | 50.96                | 0.804                | 50.72                |
|        | B       | 15.50            | -31.31               | 0.847                | -31.57               |
| MP2    | A       | 13.67            | 0                    | 0                    | 0                    |
|        | TS      | 11.62            | 41.53                | 0.321                | 41.43                |
|        | B       | 14.40            | -26.43               | 0.956                | -26.71               |
| QCISD  | A       | 13.26            | 0                    | 0                    | 0                    |
|        | TS      | 10.98            | 40.66                | 0.563                | 40.49                |
|        | B       | 14.26            | -27.63               | 0.927                | -27.90               |
| BP86   | A       | 12.19            | 0                    | 0                    | 0                    |
|        | TS      | 10.53            | 37.16                | 0.382                | 37.05                |
|        | B       | 13.56            | -19.79               | 0.922                | -20.07               |
| SVWN   | A       | 12.38            | 0                    | 0                    | 0                    |
|        | TS      | 10.78            | 36.73                | 0.289                | 36.64                |
|        | B       | 13.79            | -19.96               | 0.801                | -20.20               |
| B3LYP  | A       | 13.01            | 0                    | 0                    | 0                    |
|        | TS      | 10.94            | 39.93                | 0.476                | 39.79                |
|        | B       | 14.10            | -23.86               | 0.924                | -24.13               |

<sup>a</sup> In kcal mol<sup>-1</sup>.

<sup>b</sup> In e.u.

as an improvement due to the inclusion of correlation. As far as DFT results are concerned, none of the functionals studied manage to outperform MP2 here. Thus, pure functionals underestimate  $\Delta G^\circ$  by about 7 kcal mol<sup>-1</sup> (with respect to the QCISD value of -27.9 kcal mol<sup>-1</sup>). The hybrid B3LYP approximation becomes slightly less deviated, with a difference of 3 kcal mol<sup>-1</sup>. In fact, results from Table 5 reflect those already displayed in Table 4. Analyzing the contributions to  $\Delta G^\circ$ , it is clear from Table 5 that the entropy factor does not contribute significantly (less than 1%), as expected for a gas-phase rearrangement reaction (stoichiometry 1:1). Zero point energies (ZPEs) and thermal corrections cause only very slight modifications to the global  $\Delta H^\circ$ , representing less than 10% and 1%, respectively. What really makes all the difference are the relative internal energies (shown in Table 4), which on average provide about the 90% of the weight of contributions to enthalpy.

Even more interesting conclusions are drawn

Table 6  
Relative energies (in kcal mol<sup>-1</sup>) of the TS and FSSF with respect to the F<sub>2</sub>SS isomer calculated at selected levels of conventional ab initio theory as well as DFT. The imaginary frequency (in cm<sup>-1</sup>) of the first order saddle point is included

| Method | $\Delta E(\text{TS})$ | $\Delta E(\text{FSSF})$ | $\nu^\ddagger$ |
|--------|-----------------------|-------------------------|----------------|
| HF     | 72.5 <sup>a</sup>     | -6.3 <sup>a</sup>       | 658.2i         |
| MP2    | 45.9                  | 0.8                     | 571.9i         |
| QCISD  | 51.4                  | 3.8                     | -              |
| SVWN   | 50.5                  | 4.2                     | 498.3i         |
| BP86   | 46.3                  | 2.0                     | 469.2i         |
| B3LYP  | 50.6                  | 0.3                     | 505.1i         |

<sup>a</sup> From Ref. [29].

from the results displayed in Tables 6 and 7, where the thermochemistry of the  $\text{F}_2\text{SS} \rightarrow \text{FSSF}$  reaction is reported. According to Seel and Budenz [45],  $\text{F}_2\text{SS}(\text{g})$  is transformed into the molecular complex  $[\text{FSSF}, \text{F}_2\text{SS}](\text{g})$  upon cooling the sample down to -80°C, indicating that FSSF is the most stable isomer at low temperatures. From another experimental work [46], the  $\text{F}_2\text{SS}$  isomer is also regarded to be less stable than the FSSF species as it slowly isomerizes to the FSSF structure at temperatures below approximately -100°C. These results [45,46] demonstrate that the two disulfur difluoride isomers have similar energies, the FSSF being more stable at low temperatures.

Thus, careful attention has to be paid to theoretical energies from Table 6. Since no thermal corrections have been taken into consideration, they are not directly comparable to experimental data. When including ZPE and thermal corrections at 298.15 K as in Table 7, both enthalpies close to zero or favoring the  $\text{F}_2\text{SS}$  isomer are expected to be found, whereas at low temperatures (Table 6) both null enthalpies or favoring the FSSF isomer are more likely to be expected. Therefore, the value of Table 6 corresponding to the  $\text{F}_2\text{SS} \rightarrow \text{FSSF}$  reaction energy predicted by the QCISD method seems a good prediction both in sign and magnitude. Among the remaining methods, only HF happens to give a correct negative sign, but the amount of 6.3 kcal mol<sup>-1</sup> seems somewhat too large. In this sense the prediction of 0.3 kcal mol<sup>-1</sup> is preferable, becomes more accurate than pure functionals and outperforms MP2 result.

Slightly different conclusions are drawn as

Table 7

Contributions to  $\Delta G^\circ$  at 298.15 K relative to the reactant for different species involved in the  $F_2S_2 \rightarrow FSSF$  gas-phase reaction

| Method | Species | ZPE <sup>a</sup> | $\Delta H^\circ$ <sup>a</sup> | $\Delta S^\circ$ <sup>b</sup> | $\Delta G^\circ$ <sup>a</sup> |
|--------|---------|------------------|-------------------------------|-------------------------------|-------------------------------|
| RHF    | A       | 5.19             | 0                             | 0                             | 0                             |
|        | TS      | 3.86             | 71.05                         | 0.877                         | 70.79                         |
|        | B       | 4.55             | -6.71                         | 0.636                         | -6.89                         |
| MP2    | A       | 4.64             | 0                             | 0                             | 0                             |
|        | TS      | 3.49             | 50.04                         | 0.837                         | 49.79                         |
|        | B       | 4.14             | 3.45                          | 0.216                         | 3.38                          |
| BP86   | A       | 4.20             | 0                             | 0                             | 0                             |
|        | TS      | 3.12             | 45.06                         | 1.082                         | 44.73                         |
|        | B       | 3.82             | 1.76                          | -0.060                        | 1.77                          |
| SVWN   | A       | 4.49             | 0                             | 0                             | 0                             |
|        | TS      | 3.34             | 49.19                         | 1.038                         | 48.88                         |
|        | B       | 4.09             | 3.92                          | -0.016                        | 3.93                          |
| B3LYP  | A       | 4.45             | 0                             | 0                             | 0                             |
|        | TS      | 3.29             | 49.23                         | 1.110                         | 48.90                         |
|        | B       | 3.96             | -0.07                         | 0.330                         | -0.17                         |

<sup>a</sup> In kcal mol<sup>-1</sup>.

<sup>b</sup> In e.u.

regards the barrier height. With the basis set considered here, MP2 gives an activation energy only 1 kcal mol<sup>-1</sup> below the QCISD reference, while DFT energies are smaller, ranging from 46.3 to 50.6 kcal mol<sup>-1</sup>. Bickelhaupt et al. [28] reported for the same reaction a value of 45.9 kcal mol<sup>-1</sup> corresponding to an MP4/6-31G\*/6-31G\* calculation. Their value lies 0.4 kcal mol<sup>-1</sup> below our NL BP86 energy. A noticeable remark is that the hybrid approximation obtains again a better description than non-mixed DFT methods. In turn, HF overestimates the barrier by more than 20 kcal mol<sup>-1</sup>.

From the point of view of relative stabilities of the  $F_2SS$  and  $FSSF$  species, going from low temperatures (Table 6) to high temperatures (Table 7) means that  $FSSF$  structure is no longer the predominant isomer and therefore, a change in sign of energy differences (always relative to  $F_2SS$ ) should be expected. Nevertheless, contributions added to  $\Delta E$  in order to give  $\Delta H^\circ$  are so small that only in the case of the already close to zero B3LYP energies does the sign actually change, although in the incorrect direction. In the remaining levels and methodologies just a slight reduction

Table 8

Relative energies (in kcal mol<sup>-1</sup>) of the TS and HCN with respect to the HNC isomer calculated at selected levels of conventional ab initio theory as well as DFT. The imaginary frequency (in cm<sup>-1</sup>) of the first order saddle point is included

| Method     | $\Delta E(\text{TS})$ | $\Delta E(\text{HCN})$ | $\nu^\ddagger$ |
|------------|-----------------------|------------------------|----------------|
| HF         | 39.8 <sup>a</sup>     | -12.5 <sup>a</sup>     | 1227.6i        |
| MP2        | 36.4                  | -21.0                  | 1310.1i        |
| QCISD      | 34.7                  | -17.2                  | 1203.9i        |
| SVWN       | 31.5                  | -16.9                  | 1088.5i        |
| BP86       | 31.2                  | -17.2                  | 1100.5i        |
| B3LYP      | 33.4                  | -16.6                  | 1148.4i        |
| BP86/SVWN  | 31.2                  | -17.2                  | -              |
| B3LYP/SVWN | 33.3                  | -16.6                  | -              |

<sup>a</sup> From Ref. [29].

(on average 0.3 kcal mol<sup>-1</sup>) of  $\Delta H^\circ$  in favor of the reactant is attained. However, since a nearly null but positive enthalpy is expected at high temperatures this invariability in the sign benefits now all methods excepting HF.

Earlier studies pointed out the need to employ an exchange-correlation functional which allows for NL corrections in order to obtain a reasonable description of bonding energies [9]. Although this is true for a wide range of systems, sometimes LDA does not need to be improved by means of gradient corrections, e.g., in the formaldehyde formation reaction [19]. Another example where NL gradient corrections are not needed is that illustrated in Table 8 for the  $\text{HNC} \rightarrow \text{HCN}$  rearrangement reaction. Here both local and NL functionals predict very similar heights for the activation barrier (31.5 and 31.2 kcal mol<sup>-1</sup>, respectively). In fact, our conclusions follow those observed by Fan and Ziegler [18], who examined several small systems (e.g., the photodissociation of  $\text{CH}_2\text{O}$ , the isomerization of  $\text{CH}_3\text{CN}$  and also HCN hydrogen migration) using DFT in conjunction with the frozen core approximation. They found that for these reactions there was an agreement between the LDA and NL density functional methods when predicting reaction barriers.

However, if one takes the QCISD value of 34.7 kcal mol<sup>-1</sup> as the reference for this isomerization reaction (Table 8), the closest value from all the remaining ones is that provided by the B3LYP model; its prediction of 33.4 kcal mol<sup>-1</sup> equals



Table 9  
Contributions to  $\Delta G^\circ$  at 298.15 K relative to the reactant for different species involved in the HNC  $\rightarrow$  NCH gas-phase reaction

| Method | Species | ZPE <sup>a</sup> | $\Delta H^{\circ a}$ | $\Delta S^{\circ a}$ | $\Delta G^{\circ a}$ |
|--------|---------|------------------|----------------------|----------------------|----------------------|
| RHF    | A       | 10.70            | 0                    | 0                    | 0                    |
|        | TS      | 7.29             | 35.96                | 3.444                | 34.94                |
|        | B       | 11.29            | -12.26               | -0.806               | -12.02               |
| MP2    | A       | 9.86             | 0                    | 0                    | 0                    |
|        | TS      | 6.90             | 33.03                | 3.243                | 32.07                |
|        | B       | 10.00            | -21.10               | -0.671               | -20.90               |
| QCISD  | A       | 9.87             | 0                    | 0                    | 0                    |
|        | TS      | 6.65             | 30.97                | 3.166                | 30.02                |
|        | B       | 10.16            | -17.20               | -0.807               | -16.96               |
| BP86   | A       | 9.44             | 0                    | 0                    | 0                    |
|        | TS      | 6.43             | 27.65                | 2.915                | 26.78                |
|        | B       | 9.97             | -17.06               | -1.073               | -16.74               |
| SVWN   | A       | 9.65             | 0                    | 0                    | 0                    |
|        | TS      | 6.60             | 27.94                | 3.105                | 27.02                |
|        | B       | 10.06            | -16.84               | -0.869               | -16.58               |
| B3LYP  | A       | 9.81             | 0                    | 0                    | 0                    |
|        | TS      | 6.66             | 29.75                | 3.042                | 28.84                |
|        | B       | 10.34            | -16.48               | -1.015               | -16.18               |

<sup>a</sup> In kcal mol<sup>-1</sup>.

<sup>b</sup> In e.u.

that obtained at the MP2 level. The difference between B3LYP and QCISD is 1.3 kcal mol<sup>-1</sup>, whereas the MP2 energy lies 1.7 kcal mol<sup>-1</sup> above the reference.

Apart from the activation barriers, this accuracy is also noticeable when reaction energies are compared. The three DFT methods become better at reproducing the QCISD value of -17.2 kcal mol<sup>-1</sup> than the MP2 method.

The addition of ZPE, thermal energies and the entropic factor to reaction energies does not affect a great deal the results from Table 8. In fact it reduces the differences in energy by only about 0.1–0.5 kcal mol<sup>-1</sup>. Thus, for the three reactions studied, one can state that if a method properly describes the relative internal energies (shown in Table 8, and also in Tables 4 and 6) it will present a quite correct behavior in the evaluation of  $\Delta H^\circ$  and  $\Delta G^\circ$  (see Table 9, and also Tables 5 and 7).

In order to complete this theoretical investigation, a last detail will be discussed concerning the advantage of performing a single point

calculation by means of a gradient-corrected method, using the geometry optimized by means of a cheaper LDA technique. As can be seen in Table 8, when following such a strategy the calculated energies remain almost unaffected, yet less computational effort is required. Although this strategy has been tested on a simple gas-phase rearrangement reaction, it reveals a potential advantage which can be extremely useful for the study of many larger systems.

#### 4. Conclusions

We have examined in this work the geometries and relative energetics for three gas-phase rearrangement reactions. Comparison has been made with the results of HF and post-HF calculations.

In general, it is assumed that HF deficiencies do not begin to be important until specially troublesome or considerably large chemical systems are treated. However, our investigation on a series of simple reactions has demonstrated that even for small molecules containing C, N, O, F, H and S atoms, equilibrium geometries are better described when correlation is taken into account. In particular, DFT methods manage to give a geometrical description which is more accurate than that provided by HF methods, while reaching a quality similar to that obtained by post-HF methods. With regard to pure functionals, no significant improvement has been observed due to the inclusion of NL gradient corrections. On the contrary, LDA seems to be good enough for searching reasonable molecular structures for the isomers investigated here. The hybrid B3LYP model deserves particular attention, especially when performing the geometrical characterization for the last and simplest rearrangement reaction (i.e., the HCN hydrogen migration). It is interesting to see that its prediction for the bond lengths of HNC and HCN fit experimental values quite well.

As far as activation barriers and reaction energies are concerned, the DFT methods selected predict barrier heights as accurately as those evaluated by the MP2 procedure. Moreover, by means of taking into account HF exchange, hybrid

B3LYP calculations are able to improve the already correct pure DFT results for both the barrier height and the reaction energy, yielding values in fair agreement with those obtained at the computationally more expensive QCISD level. These conclusions confirm earlier calculations reported by Stanton and Merz [19] and Andzelm and Wimmer [9]. However, in their calculations only a comparison between DFT and MP2 energies was made, whereas in this paper pure/hybrid DFT and QCISD methods are also compared. To the best of our knowledge, no previous studies on reactivity have compared this number of electronic structure methods. Taking QCISD as the reference to evaluate  $\Delta G^\circ$  for these isomerization reactions, one can conclude that: (a) HF is unable to describe energy differences properly, errors being both by excess or by defect; (b) MP2 and DFT calculations are of similar quality; (c) however, while the MP2 result can be found indistinctly above or below the QCISD reference, DFT systematically underestimates the reference and, finally, (d) this DFT underestimation is less pronounced (or nearly zero) when short-distance reactions like HCN hydrogen migration are studied.

To sum up, it is apparent from the results discussed above that DFT can be judged as an efficient way of determining activation barriers. Our results also indicate that the B3LYP procedure provides a better description of the geometry of the stationary points studied and particularly the shape of their potential energy surface around minima as compared with other procedures. This notwithstanding, careful attention must be paid to calculations of relative internal energies since they are mainly responsible for the accuracy in evaluating  $\Delta H^\circ$  and  $\Delta G^\circ$  afterwards.

Here we have only provided a hint of the potential usefulness of DFT for studying chemical reactivity. Given the general interest in the subject as shown by the recent literature, further research is under way.

### Acknowledgments

One of us (M.T.) gratefully acknowledges the

financial support provided by the Comissionat per a Universitats i Recerca de la Generalitat de Catalunya through a Graduate Fellowship.

This work has been funded through DGICYT Project No. PB92-0333.

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