Reassessment of Methyl Rotation Barriers and Conformations by Correlated Quantum Chemistry Methods

ALBERTO DEL RIO,1 ABDOU BOUCEKKINE,1 JEAN MEINNEL2

1LCSIM, UMR 6511 CNRS - Université de Rennes 1, Institut de Chimie de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France
2GMCM, UMR 6626 CNRS - Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

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Abstract: Internal rotations of the methyl group in ortho-substituted and 2,6-disubstituted toluenes in their ground state have been investigated by means of various ab initio quantum chemistry methods. Computed barriers at the Hartree-Fock (HF) level using medium sized basis sets agreed reasonably with experimental results in the case of the studied ortho-substituted toluenes. However, this agreement worsens when using very large basis sets. Furthermore, the determination of the conformation and barriers of more weakly hindered methyl groups, that is, for 2,6-dihalogenotoluenes or toluene itself, necessitates high level correlated computations, because of a possible failure of HF calculations in this case. Density functional theory (DFT) techniques required, in several cases, much more extended basis sets than the post-HF Møller-Plesset perturbation (MP2, MP4) ones, to insure the convergence of the computed barriers. Non-negligible variations of the computed barriers when using different DFT functionals are observed for some systems.


Key words: methyl conformations; rotation barriers; correlation effects

Introduction

The study of the methyl group conformation and rotation barriers is of great interest, especially for understanding the shape and dynamics of complex molecules like proteins and polymers, or proton tunneling in the solid state at low temperatures. It is now clear that steric effects are not the only factors that drive the conformation of this group and that hyperconjugation is often a determining one.1–5 Studies on substituted toluenes (Tol’s) showed that rotation of the methyl group around the single bond is not really free in the general case,6,7 and that this group can exhibit various and unpredictable conformations. Furthermore, the magnitude of the rotation barrier strongly depends on the environment of the methyl group and the electronic state of the molecule. Experimental determinations of barriers in the gas phase are difficult to achieve and only a limited number of results are available, so that quantum chemistry ab initio calculations seem to be the only way to get these properties. To our knowledge, only very few articles8,9 have mentioned basis sets and correlation effects on the computation of methyl rotation barriers for Tol derivatives. Barriers have usually been evaluated at the Hartree-Fock (HF) level. Obviously, correlation effects are supposed to be small for such a property, but because these rotation barriers are low in the case of Tol derivatives—they can be on the order of 100 cm−1 (i.e., 0.2 kcal/mol, or 10−2 eV or 4.10−4 au)—a thorough investigation of this needs to be made. In this article, we evaluate the efficiency of different ab initio methods, including the density functional theory (DFT) techniques, which are nowadays widely used. We start by the study of o-fluorotoluene (oFT), o-xylene (oXl), for which experimental data are available, and a series of halogenotoluenes, then Tol and 2,6-dihalogenotoluenes will be considered, all of these compounds being in their ground states.

Computational Details

For the sake of simplicity, the rotation angle θ of the methyl group of the Tol derivatives under consideration is set equal to zero when one of the three methyl hydrogens lies in the plane of benzene. Figure 1a shows the case of Tol with θ = 0°. For oFT, the θ = 0° reference corresponds to a methyl CH bond in the benzene plane.
and opposite to the fluorine group as shown in Figure 1b. In the same way we define \( \theta = 0^\circ \) for 2,6-difluorotoluene (2,6-diFT) (Fig. 1c). For oXl there are two rotors so we have to define two angles \( \theta \) and \( \varphi \), which are set equal to zero when a CH bond of each methyl group is in the ring plane and they are opposite to each other (Fig. 1d).

Throughout this study, the calculations are carried out fixing \( \theta \) as a dihedral angle for one hydrogen atom of the methyl group and optimizing all the other internal coordinates via the total energy minimization, so that a full relaxation of the molecular geometry accompanying the methyl rotation is allowed.

All calculations are performed using the GAUSSIAN98 software package.\(^{10}\) Five levels of theory are investigated: first, restricted HF for closed-shell (RHF); then, second-order Möller-Plesset perturbation theory applied to RHF wave functions (MP2); and fourth-order Möller-Plesset perturbation theory energy calculation using the MP2 optimized geometry (MP4//MP2). Finally, DFT calculations are carried out with the well-known functional B3LYP\(^{11}\) and with the MPW1PW91 functional.\(^{12}\) The latter functional, which is a modified Perdew-Wang one, is well suited for nonbonded interactions and transition state studies, and usually leads to results that are as reliable as B3LYP’s concerning ground state properties.\(^{13}\)

Several basis sets are used. First, the standard 6-31G double zeta basis set, supplemented by polarization function on heavy atoms, that is, the well-known 6-31G* basis set (and 6-31G**, which includes also hydrogen polarization). Another double zeta basis set is used, the LANL2DZ one, which differs from the 6-31G by the contraction scheme and the Gaussian function exponents (the s and p exponents are different, and the contraction scheme is 2/1 for the s valence orbital and 4/1 for the p one, instead of 3/1 for both). Furthermore, in the LANL2DZ basis set, core electrons are described by means of an effective core potential, and this permits a lower cost and efficient treatment of heavy atoms like iodine. The triple zeta basis sets we use are the 6-311G** with standard polarization and the 6-311++G(2df,pd), which includes diffuse functions on all atoms and more polarization. Finally, the aug-cc-pVQZ quadruple zeta basis set, which includes multiple diffuse functions on all atoms, \( p-, d-, f-\) type polarization for hydrogen and \( p-, d-, f-, g\)-type polarization on the second-row elements, is also used.

**Results and Discussion**

**o-Substituted Tol’s**

The total energy of the molecule is computed as described previously, fixing the dihedral angle \( \theta \) for one C—H bond and optimizing all the other geometrical parameters, and repeating this operation for different values of \( \theta \) varying from 0 to 120° by a step of 15°. According to the Born-Oppenheimer approximation, this energy as a function of \( \theta \) represents the potential \( V(\theta) \) experienced by the nuclei. As usual in this kind of study, we did not include the zero point vibration energy in this potential energy. In fact, in the case of a hindered methyl rotor, the variation of the zero point vibration energy between two conformations should be negligible. Furthermore, some conformations are characterized by an imaginary torsional frequency of the methyl group, so that they are not true minima on the potential energy surface. This may be the case for unstable conformations of the methyl group.

The model function describing this potential as a function of the torsion angle \( \theta \) of the methyl group, taking into account the symmetry of the system, is expressed by the Fourier expansion:

\[
V(\theta) = V_0 + \frac{1}{2} \sum_n V_{3n}(1 - \cos 3n\theta)
\]  

where \( V_{3n} \) is the \( 3n\)-fold contribution to the barrier.

Concerning the experiment, the values \( V_3 = 227 \text{ cm}^{-1} \), \( V_6 = 0 \) are deduced from the analysis of the microwave spectra of oFT,\(^7\) whereas its fluorescence spectra lead to \( V_3 = 228 \text{ cm}^{-1} \) and \( V_6 = 6.6 \text{ cm}^{-1} \).\(^{13,14}\) The experimental model considers the methyl group as a hindered rotor, the potential being described by expansion eq. (1). No standard deviations have been given to the experimental values, but, the good agreement between the two experimental techniques gives us confidence that 227–228 cm\(^{-1}\) is a good estimate for the \( V_3 \) barrier of oFT. Thus, we focus our study on this \( V_3 \) value.

At the HF/6-31G* level, we find, as other authors did,\(^6-9\) that expansion eq. (1) fits exactly the potential \( V(\theta) \). The Fourier expansion up to \( V_6 \) also fits perfectly the \( V(\theta) \) variation in the case of the MP2 and DFT correlated methods. Figure 2 shows the

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**Figure 1.** Definition of the methyl rotation angle and conformations of the studied compounds.
obtained curve in the case of MP2/6-311G** calculations. This result confirms the validity of the model function [eq. (1)] used in this case.

In Table 1, the so-computed \( V_3 \) and \( V_6 \) values are given, with the corresponding correlation coefficient and standard deviation.

As can be seen, the fitting is perfect, when the expansion includes the \( V_6 \) contribution. For instance, the coefficient of correlation equals 0.9999 and the standard error is of an order of 1 cm\(^{-1}\) for the MP2/6-311G** calculations. We observe the highest deviations for MP2/6-311G** when neglecting \( V_6 \); the coefficient of correlation decreases from 0.9999 to 0.9945 and the standard error increases up to 7 cm\(^{-1}\). Nevertheless, the \( V_3 \) value is almost the same, 229 versus 226 cm\(^{-1}\) in both cases. Comparing these values to the experimental ones, perfect agreement is obvious. Furthermore, neglecting the \( V_6 \) term in expansion eq. (1) does not alter significantly the computed \( V_3 \) value. We reached the same conclusions considering the DFT results.

Expansion eq. (1) considering only the threefold potential \( V_3 \), takes the form

\[
V(\theta) = V_0 + (V_3/2)(1 - \cos 3\theta)
\]  

Thus, in such a situation, the value of \( V_3 \) is approximately calculated by the difference between the energies of the two conformers at \( \theta = 0^\circ \) and \( \theta = 60^\circ \) (or \( \theta = 180^\circ \)). For the sake of simplicity, we shall compare the different methods of calculation relative to this estimated value of \( V_3 \). The values for OFT in the ground state are presented in Table 2. In this table the results obtained previously by other authors\(^8,15\) are also given.

For all the methods the most stable conformation is that given by Figure 1b. We observe that extensions of the basis set increase the rotation barriers. We note variations of barriers up to 20% due to basis set effects (max 50 cm\(^{-1}\)) and variations up to 30% due to the method of calculation (and mainly due to correlation effects), the largest ones being between the HF results and the MPW1PW91 ones.

In more detail, firstly, concerning the HF results, it can be seen that the inclusion of hydrogen polarization induces a decrease of the computed barrier when using the double zeta polarized basis sets, namely when passing from 6-31G* to 6-31G** and from LANL2DZ* to LANL2DZ**. Secondly, we observe that the computed barriers are not yet converged even with the most extended basis set, namely the aug-cc-pVQZ, which includes a huge number

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Table 1. \( V_3 \) and \( V_6 \) Barriers (cm\(^{-1}\)) for \( o \)-Fluorotoluene.

<table>
<thead>
<tr>
<th>Method/basis set</th>
<th>( V_3 )</th>
<th>( V_6 )</th>
<th>Correlation coefficient</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G*</td>
<td>212</td>
<td>2</td>
<td>0.9998</td>
<td>1</td>
</tr>
<tr>
<td>HF/6-31G**</td>
<td>212</td>
<td>—</td>
<td>0.9997</td>
<td>1</td>
</tr>
<tr>
<td>HF/6-311G**</td>
<td>214</td>
<td>−5</td>
<td>0.9999</td>
<td>1</td>
</tr>
<tr>
<td>HF/6-311G**</td>
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<td>—</td>
<td>0.9994</td>
<td>2</td>
</tr>
<tr>
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<td>1</td>
</tr>
<tr>
<td>MP2/6-311G**</td>
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<td>—</td>
<td>0.9944</td>
<td>7</td>
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<tr>
<td>B3LYP/6-311G**</td>
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<td>−10</td>
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<td>1</td>
</tr>
<tr>
<td>B3LYP/6-311G**</td>
<td>182</td>
<td>—</td>
<td>0.9970</td>
<td>4</td>
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<tr>
<td>MPW1PW91/6-311G*</td>
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<td>−11</td>
<td>0.9999</td>
<td>1</td>
</tr>
<tr>
<td>MPW1PW91/6-311G*</td>
<td>178</td>
<td>—</td>
<td>0.9964</td>
<td>5</td>
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</table>
of polarization functions (3d 2f 1g for the heavy atoms and 3p 2d 1f for hydrogen) supplemented by diffuse orbitals. This behavior has already been observed by Goodman et al.,\textsuperscript{16} who investigated the methyl rotation barrier of propene. Thirdly, it is worth noting that the geometrical changes that occur after optimization when different basis sets are used do not affect significantly the computed $V_3$. We verified this as follows: we took the optimized MP2/6-311G** geometries of oFT obtained for $\theta = 0^\circ$ and $\theta = 60^\circ$ and used these fixed geometries to compute the energies of the two conformers at different levels of calculation. The HF barrier computed using the 6-31G* basis set and the corresponding optimized geometry is equal to 212 cm$^{-1}$, whereas the $V_3$ estimated, using the fixed MP2/6-311G** geometries, is 213 cm$^{-1}$; the exactly computed barrier is 238 cm$^{-1}$ with the 6-311+G(2df, pd) and using the fixed reference geometries, 241 cm$^{-1}$. Indeed, the latter values remain almost constant when they are estimated using these fixed geometries for the two conformers at $\theta = 0^\circ$ and $\theta = 60^\circ$.

When discussing correlation effects, it must be recalled that pure radial and angular correlation effects are brought to light only when large basis sets are employed. In Table 2, considering the large basis set results, an increase of $V_3$ when passing from HF to MP2 can be seen. This increase is higher for the 6-311G** basis set than for the 6-311+G(2df, pd) one, but in both cases the difference is less than 10%. As said previously, we expected this small influence of electron correlation on the $V_3$ barriers. In the case of the more hindered propene methyl group ($V_3 = 694$ cm$^{-1}$), a barrier variation to the order of 8% was obtained by Goodman et al.,\textsuperscript{16} when passing from an HF to an MP2 calculation using the 6-311G(3df,2p) basis set. We did not carry out an MP2/aug-cc-pVQZ calculation, for computational time reasons, so we are not able to estimate the barrier variation when taking into account electron correlation, in this case. Although of interest, more extended basis sets calculations could not be considered for the same reason. Furthermore, as found before with the HF results, the geometrical changes obtained upon optimization when different basis sets are used have only a slight influence on the computed MP2 barriers.

Calculations performed at the MP4//MP2 level of theory, using the MP2/6-311G** geometry, lead to a slight reduction of the barriers, relative to MP2, and apparently a better agreement with the experiment. The MP4 computations did not include correlation but considered SDTQ excitations. Using the largest basis set, that is, the 6-311+G(2df, pd) one, the $V_3$ value decreases from 243 cm$^{-1}$ (MP2 value) to 235 cm$^{-1}$ (MP4 value), leading to a 3% reduction of the barrier. It is interesting to note that the sign of the MP4 correction is opposite to the MP2 one, so that the MP4 barriers are closer to HF’s. As can be seen, the influence of high order correlation effects is small but not negligible. Unfortunately, for computational time reasons, it has not been possible to check this behavior using the largest aug-cc-pVQZ basis set, but a better agreement with the experiment is expected with a MP4//MP2 calculation. Anyway, MP2 calculations, using large basis sets, permit in the case of oFT a good agreement with the experiment, with less than 5% error. Moreover, it is worth noting that a variation of the same order of magnitude has been obtained by Goodman et al.,\textsuperscript{16}, that is, an increase of 4% of the barrier of the propene methyl group when passing from MP2 to MP4(SDTQ). Incidentally, we notice that in the case of oFT, the MP4 optimized geometries are very close to the MP2 ones, so that our MP4//MP2 result for $V_3$ is as accurate as a full MP4 one.

DFT barriers are systematically lower than the other ones. For instance, the B3LYP/6-311G** computation gives $V_3 = 188$ cm$^{-1}$ versus 230 or 226 cm$^{-1}$ for the Moller-Plesset perturbation techniques. Furthermore, we note that the MPW1PW91 barriers are lower than the B3LYP barriers. It is difficult to analyze these results relative to the HF ones, in particular because the exchange functionals used in the DFT techniques differ from the exact exchange of the HF theory. As can be seen in Table 2, using these B3LYP and MPW1PW91 functionals, much more extended basis sets are needed to reach a good agreement with the experiment, in the case of oFT. However, these DFT computations seem reliable because the computed barriers converge with the experimental value when extending the basis set. Furthermore, it must be remembered that when using the DFT techniques and large basis

<table>
<thead>
<tr>
<th>Basis set</th>
<th>HF</th>
<th>MP2</th>
<th>MP4//MP2</th>
<th>B3LYP</th>
<th>MPW1PW91</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G*</td>
<td>(212)$^a$</td>
<td>237 (237)$^b$</td>
<td>227</td>
<td>192</td>
<td>187</td>
</tr>
<tr>
<td>6-31G**</td>
<td>199 (199)$^a$</td>
<td>212</td>
<td>203</td>
<td>176</td>
<td>169</td>
</tr>
<tr>
<td>LANL2DZ*</td>
<td>211</td>
<td>198</td>
<td>194</td>
<td>173</td>
<td>167</td>
</tr>
<tr>
<td>LANL2DZ**</td>
<td>205</td>
<td>195</td>
<td>192</td>
<td>162</td>
<td>152</td>
</tr>
<tr>
<td>6-311G**</td>
<td>214</td>
<td>230</td>
<td>226</td>
<td>188</td>
<td>183</td>
</tr>
<tr>
<td>6-311+G(2df, pd)</td>
<td>238</td>
<td>243</td>
<td>235</td>
<td>212</td>
<td>202</td>
</tr>
<tr>
<td>6-311+G(2df, pd)</td>
<td>238</td>
<td>211</td>
<td>211</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>248</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>$227^4$-$228^8$</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

$^a$Calculation performed using the 6-311G** basis set for the geometry optimization and 6-311+G(2df, pd) for the evaluation of the energy.

$^b$Ref. 8.

$^c$Ref. 15.

$^d$Ref. 7.

$^e$Ref. 13.

Table 2. Threefold Barriers (cm$^{-1}$) for o-Fluorotoluene.
sets, much less computational time relative to MP2 is needed to achieve accurate results within 5% error.

oXl

oXl is a double rotor case. The model function describing the potential as a function of $\theta$ and $\varphi$ (Fig. 1d) is expressed by the Fourier expansion:

$$V(\theta, \varphi) = \sum_n \frac{1}{2} \left( V_n (2 - \cos n\theta - \cos n\varphi) + V'_n [\cos(n\theta - n\varphi) - 2] \right)$$  (3)

where $\frac{1}{2} V_n' (\cos n\theta \cos n\varphi + \sin n\theta \sin n\varphi - 2)$ is the cross potential term in the expanded form.

We started our study on oXl by a series of HF/6-31G* and MP2/6-311G** calculations. Figure 3 shows the potential energy surface, as a function of $\theta$ and $\varphi$, obtained at the MP2 level of theory. As can be seen, the conformation shown in Figure 1d, corresponding to $\theta = 0^\circ$ and $\varphi = 0^\circ$ is the most stable one. Note that the HF/6-31G* computations that we undertook led us to the same conclusions. Figure 3 indicates also that the least energy way from one minimum to another one can be obtained rotating one methyl group independently of the second one. For instance, passing from the $\theta = 0^\circ$ and $\varphi = 0^\circ$ minimum to another minimum on the potential energy surface can be done fixing $\theta = 0^\circ$ and varying $\varphi$ or vice versa. This result was already obtained on the basis of molecular mechanics calculations. Following Breen et al.\cite{6} and with a view to comparing our computed values to their experimental ones, we assume, likewise, that the approximation of two noninteracting methyl rotors is valid. Thus, eq. (3) can be simplified leading to the single rotor potential model given by eq. (1).

The experimental values of Breen et al.\cite{6} are $V_3 = 425$ cm$^{-1}$ and $V_6 = 18$ cm$^{-1}$. These values have been calculated from dispersed emission and time of flight mass spectra assuming two noninteracting rotors. No error bars are given by these authors. It must be noted that oXl barrier has also been investigated using other experimental techniques. The analysis of the methyl C—H stretching overtone spectra\cite{17} led to a $V_3$ barrier equal to 420 cm$^{-1}$, whereas an earlier microwave study gave $V_3 = 520 \pm 20$ cm$^{-1}$, so that the experimental value for oXl is more questionable than that of oFT. oXl has also been the subject of small basis sets HF calculations.\cite{19,20}

As done previously for oFT, several energy calculations fixing $\varphi = 0^\circ$ and varying $\theta$ were carried out in order to get the hindering potential $V(\theta)$ for oXl. Eq. (1) fits the $V(\theta)$ variation perfectly. HF/6-31G* leads to $V_3 = 462$ cm$^{-1}$, $V_6 = -1$ cm$^{-1}$; MP2/6-311G** gives $V_3 = 428$ cm$^{-1}$, $V_6 = -44$ cm$^{-1}$; and B3LYP/6-311G**, $V_3 = 424$ cm$^{-1}$, $V_6 = -2$ cm$^{-1}$. For both MP2 and B3LYP we obtained a correlation coefficient of 1 and a standard deviation smaller than 2 cm$^{-1}$. Nevertheless, the good agreement between the $V_3$ computed values at the MP2 and B3LYP levels and the experimental one is obvious. We note, on the contrary, the discrepancy for $V_6$ and we have for the moment no explanation for this. The MP2 and B3LYP values for $V_6$ are also very different.

From the result of the fitting, it can be seen that the sixfold potential in eq. (1) for oXl is much smaller than the $V_3$ contribution. HF/6-31G* leads to $V_3 = 462$ cm$^{-1}$, $V_6 = -1$ cm$^{-1}$; MP2/6-311G** gives $V_3 = 428$ cm$^{-1}$, $V_6 = -44$ cm$^{-1}$; and B3LYP/6-311G**, $V_3 = 424$ cm$^{-1}$, $V_6 = -2$ cm$^{-1}$. For both MP2 and B3LYP we obtained a correlation coefficient of 1 and a standard deviation smaller than 2 cm$^{-1}$. Nevertheless, the good agreement between the $V_3$ computed values at the MP2 and B3LYP levels and the experimental one is obvious. We note, on the contrary, the discrepancy for $V_6$ and we have for the moment no explanation for this. The MP2 and B3LYP values for $V_6$ are also very different.

From the result of the fitting, it can be seen that the sixfold potential in eq. (1) for oXl is much smaller than the $V_3$ contribution. Neglecting $V_6$ and fitting the potential with expansion eq. (2) we found almost the same values of $V_3$ at all the levels of calculation. Thus, in the same way as for oFT, and in order to compare the different methods of calculation, we only consider

Figure 3. Potential energy surface (MP2/6-311G**) for o-xylene.
First of all, all the methods of calculation lead to the same most stable conformation of the molecule, namely that shown in Figure 1d. We note the increase of the computed barrier with the extension of the basis set, as already observed in the case of oFT. Considering the correlated methods it should be noted that we only take into account and discuss the extended basis sets results. Contrarily to oFT, MP2 barriers of oXl are not so underestimated relative to the MP2 ones. MP2 and particularly B3LYP lead to the best agreement with the experimental value of Breen et al.\textsuperscript{6} when the largest basis set is used (a polarized triple zeta basis set is needed in order to achieve a good agreement with the experiment within a 2% deviation). Note that the same model of two noninteracting methyl rotors has been applied to the analysis of both the theoretical potential energy surface and the observed spectra, so that the present comparison is relevant, although as said previously, the experimental barrier of oXl must be considered with caution. In the case of oXl we see that the HF/6-31G* barrier is within 10% of this experimental value.

### o-Chlorotoluene and o-Bromotoluene

Conformations and barriers for o-chlorotoluene and o-bromotoluene have also been investigated. We observed similar trends, comparing the different methods, as for oFT and oXl. The following $V_3$ barriers, 403 and 422 cm$^{-1}$ were respectively obtained for o-chlorotoluene and o-bromotoluene at the B3LYP/6-311++G(2df,pd) level.

At the end of this o-substituted Tol study, the following preliminary remarks can be made: first, from a practical point of view, we can say that HF performs rather well, the standard 6-31G* basis set giving $V_3$ barriers with an error of less than 10%. Of course, this agreement with the experiment is probably due to the compensation of the errors due to the basis set limitation and the neglect of electron correlation. It is interesting to note that the two medium sized basis sets used in this work (Tables 2 and 3), namely the polarized double zeta 6-31G and LanL2DZ ones, led to insignificant variations of the barriers at the HF level, but to more important deviations at the post-HF or DFT levels. As a reminder, for these o-substituted Tol’s the conformation of the methyl group and the barrier heights is mainly driven by hyperconjugation.\textsuperscript{1-5} Second, correlation effects are small but non-negligible. The other practical conclusion is that DFT techniques require large basis sets to insure converged results. Nevertheless, it must be noted that, using the latter techniques, much less computational time, relative to MP2, is needed to achieve good accuracy.

#### Tol and 2,6-Disubstituted Tol’s

**Tol**

The total energy of the molecule has been computed as described previously, fixing the dihedral angle $\theta$ for one C—H bond and optimizing all the other geometrical parameters. Repeating this operation for different values of $\theta$ generates the potential $V(\theta)$, which has been fitted using expansion eq. (1). Indeed, the Fourier expansion eq. (1) up to $V_6$ fits perfectly the $V(\theta)$ variation in the case of MP2/6-311G** (the curve has been plotted using seven points between $\theta = 0^\circ$ and $\theta = 30^\circ$, with a $5^\circ$ step). We obtained $V_6 = -17$ cm$^{-1}$, $V_3 = -3$ cm$^{-1}$ with a coefficient of correlation equal to one. The $V_1$ contribution to expansion eq. (1) is found to be very small relative to the $V_6$ one. If the $V_3$ contribution is neglected, eq. (1) takes the simplified form:

$$V(\theta) = V_0 + (V_3/2)(1 - \cos 6\theta)$$

When neglecting the $V_1$ term, $V_6 = -18$ cm$^{-1}$ and the correlation coefficient is 0.99996 whereas the standard error is 0.2 cm$^{-1}$. Under such conditions, $V_6$ can be simply evaluated as the energy difference between the $\theta = 0^\circ$ and $\theta = 30^\circ$ (or $90^\circ$) conformers.

Several experimental estimations of the $V_6$ barrier for Tol are available. The microwave value is 4.8 cm$^{-1}$\textsuperscript{1-2} whereas fluorescence experiments led to $V_6$ having a value equal to 10$^6$ or 12.7 cm$^{-1}$\textsuperscript{22} but in these articles no indication is given about the most stable conformation of Tol in the gas phase.

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<table>
<thead>
<tr>
<th>Basis set</th>
<th>HF</th>
<th>MP2</th>
<th>B3LYP</th>
<th>MPW1PW91</th>
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</tr>
<tr>
<td>LANL2DZ**</td>
<td>431</td>
<td>389</td>
<td>371</td>
<td>368</td>
</tr>
<tr>
<td>6-31G**</td>
<td>444</td>
<td>426</td>
<td>419</td>
<td>414</td>
</tr>
<tr>
<td>6-311++G(2df,pd)/6-31G***</td>
<td>454</td>
<td>432</td>
<td>423</td>
<td>413</td>
</tr>
<tr>
<td>6-311++G(2df,pd)</td>
<td>456</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental value\textsuperscript{b}</td>
<td>425</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{b}See footnote \textsuperscript{a} of Table 2.

\textsuperscript{a}Ref. 6.
The results of our calculations are presented in Table 4. A negative barrier value means that the most stable conformation of the methyl group is for a perpendicular hydrogen \( (\theta = 90^\circ) \).

HF gives almost null barriers, which means that the methyl group is a free rotor. Almost the same result is obtained with B3LYP, although the barriers are slightly negative, which indicates that the \( \theta = 90^\circ \) conformation is the most stable. This result is corroborated by the MP2 calculations, but the computed barriers are higher, in absolute value, than the B3LYP ones. We carried out MP4//MP2 calculations on Tol, but as already observed for substituted Tol’s, this only led to a very slight reduction of an order of 1–2 cm\(^{-1}\) for the MP2 barriers. It is worth noting that such a level of accuracy is likely not easy to achieve (1 cm\(^{-1}\) = 4.10\(^{-6}\) au !) because of the small numerical errors that may occur in standard calculations. In the case of very low hindered rotors, in order to avoid numerical and round-up errors, computations must be carried out at a high level of accuracy. For our part, we used the scf = tight, opt = tight, and int (grid = ultrafine) options of GAUSSIAN98, for tight scf and geometry optimization convergences and very accurate integral evaluation. So, the theoretically computed barriers for Tol are quite different, but it is difficult to say which of the DFT or MP techniques works better, because of the uncertainty about the experimental \( V_6 \) value. It could have been interesting to appeal to more extended post-HF techniques, like G2,\(^{23}\) but because the MP4 correction was found to be negligible in this case, it is likely that such sophisticated calculations would not modify substantially the MP2 result. Basically, the used model, which considers that the variation of the whole potential energy of the molecule when the methyl group rotates corresponds solely to the rotor hindering potential, is questionable. The same argument stands for the interpretation of the experimental data. The rotation axis itself undergoes small oscillations in space during the methyl group rotation. Furthermore, for very low hindered or free rotors, the contribution to the potential energy of other atomic displacements, for instance, those relative to the benzene ring deformation,\(^{24}\) is probably not negligible.

### Table 4. Sixfold Barriers (cm\(^{-1}\)) for Toluene.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>HF</th>
<th>MP2</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G(^*)</td>
<td>-1 (-1(^b))</td>
<td>-18 (-18(^b))</td>
<td>-6</td>
</tr>
<tr>
<td>6-31G(^*)</td>
<td>-2</td>
<td>-21</td>
<td>-7</td>
</tr>
<tr>
<td>LANL2DZ(^*)</td>
<td>1</td>
<td>-11</td>
<td>-4</td>
</tr>
<tr>
<td>LANL2DZ(^*)</td>
<td>0</td>
<td>-8</td>
<td>-5</td>
</tr>
<tr>
<td>6-311G(^*)</td>
<td>-2</td>
<td>-18</td>
<td>-6</td>
</tr>
<tr>
<td>6-311G(^*)</td>
<td>1</td>
<td>-18</td>
<td>-3</td>
</tr>
<tr>
<td>Experimental</td>
<td>10(^b); 4.8(^c); 5(^d); 12.7(^f)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)See footnote a of Table 2.
\(^b\)Ref. 8.
\(^c\)Ref. 7.
\(^d\)Ref. 21.
\(^e\)Ref. 9.
\(^f\)Ref. 22.

2,6-diFT

\( V(\theta) \) has been computed in the same manner as for Tol, and at the same level of accuracy. This hindering potential has been fitted using eq. (1). In Table 5, the obtained \( V_3 \) and \( V_6 \) values are given, with the corresponding correlation coefficient and standard deviation. It is known\(^{4,25,26}\) that barriers for 2,6-dihalogenotoluene are

### Table 5. \( V_3 \) and \( V_6 \) Barriers (cm\(^{-1}\)) for 2,6-Difluorotoluene.

<table>
<thead>
<tr>
<th>Method/basis set</th>
<th>( V_3 )</th>
<th>( V_6 )</th>
<th>Correlation coefficient</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G(^*)</td>
<td>0.2</td>
<td>14</td>
<td>0.9984</td>
<td>0.2</td>
</tr>
<tr>
<td>HF/6-31G(^*)</td>
<td>-</td>
<td>14</td>
<td>0.9981</td>
<td>0.2</td>
</tr>
<tr>
<td>HF/6-311G(^*)</td>
<td>0</td>
<td>-1</td>
<td>0.9976</td>
<td>0</td>
</tr>
<tr>
<td>HF/6-311G(^*)</td>
<td>-</td>
<td>-1</td>
<td>0.9974</td>
<td>0</td>
</tr>
<tr>
<td>MP2/6-311G(^*)</td>
<td>0.3</td>
<td>-2</td>
<td>0.9999</td>
<td>0</td>
</tr>
<tr>
<td>MP2/6-311G(^*)</td>
<td>-</td>
<td>-2</td>
<td>0.9996</td>
<td>0</td>
</tr>
<tr>
<td>B3LYP/6-311G(^*)</td>
<td>0.5</td>
<td>-9</td>
<td>0.9997</td>
<td>0</td>
</tr>
<tr>
<td>B3LYP/6-311G(^*)</td>
<td>-</td>
<td>-9</td>
<td>0.9994</td>
<td>0</td>
</tr>
<tr>
<td>MPW1PW91/6-311G(^*)</td>
<td>0.3</td>
<td>-9</td>
<td>0.9999</td>
<td>0</td>
</tr>
<tr>
<td>MPW1PW91/6-311G(^*)</td>
<td>-</td>
<td>-9</td>
<td>0.9998</td>
<td>0</td>
</tr>
</tbody>
</table>
very much smaller than those of ortho-halogenotoluenes. For 2,6-
diFT, we found, as did other authors,2,5,21,22 that the \( \nu_1 \) term in
equation (1) is negligible [at the HF/6-31G* level, \( \nu_1 = 0 \)
cm\(^{-1} \), and \( \nu_2 \) is low (14 cm\(^{-1} \)), at the B3LYP/6-311G**, \( \nu_3 = 0.5 \)
cm\(^{-1} \) and \( \nu_6 = -9 \) cm\(^{-1} \)].

First of all, considering the computed barriers given in Table 5, we see that the 2,6-diFT methyl group is a very low hindered rotor. The calculated \( \nu_6 \) barriers, for all the methods and basis sets, are much smaller than the \( \nu_3 \) barriers of ortho-substituted Tol’s. Negative values of barriers mean that the most stable conformer is obtained with \( \theta = 90^\circ \), that is, when a methyl hydrogen is placed perpendicularly to the plane of benzene. The \( V_6 \) barrier has also been estimated, as the energy difference between the \( \theta = 0^\circ \) and \( \theta = 90^\circ \) conformers, using the large 6-311+G(2df,pd) basis set. The following results have been obtained, respectively at the HF, MP2, B3LYP, and MPW1PW91 levels: 10, 2, 0, and –1 cm\(^{-1} \). The DFT techniques using large basis sets lead to zero or negative
values of barriers. On the contrary, HF, except for the 6-311G**
result, overestimates the stability of the \( \theta = 0^\circ \) conformer. The
MP2 results, just like the DFT ones, indicate also that the barrier is
very small, on the order of \( \pm 2 \) cm\(^{-1} \), so that the methyl rotor is
nearly free for 2,6-diFT in the gas phase: however, no experimental
data are available for this compound for comparison.

2.6-Dichlorotoluene and 2,6-Dibromotoluene

Conformations and barriers of 2,6-dichlorotoluene and 2,6-dibromo-
toluene were also investigated. Our main result is that these
compounds differ from 2,6-difluorotoluene; they adopt unambigu-
ously the conformation \( \theta = 0^\circ \) shown in Figure 1c, both exhib-
ting a barrier of an order of 35 cm\(^{-1} \) [B3LYP/6-311+G(2df,pd)
calculations]. Concerning the methyl group conformation and the
rotation barriers, and contrarily to \( \sigma \)-substituted Tol’s, hypercon-
jugative effects should be less important in the case of Tol’s and
2,6-disubstituted Tol’s because of the symmetrical environment of
the methyl rotor.

Conclusions

Different \textit{ab initio} techniques have been used to determine the
most stable conformation and the rotation barriers of several Tol
derivatives. Basis set effects can be responsible for non-negligible
variations of the calculated barriers at all the levels of theory
tested. We found that HF could either over- or underestimate the
barriers, relative to the correlated methods depending on the basis
set, deviations being important for weakly hindered rotors. Never-
theless, simple HF calculations using the standard polarized
double zeta basis set (HF/6-31G*) gave a reasonable agreement
with the experiment in the case of \( V_3 \) barriers for ortho-substituted
Tol’s.

A general trend is that for ortho-substituted Tol’s, DFT barriers
are lower than the MP2 ones, but the magnitude of this effect
depends on the compound under investigation. We found also that
MP4/MP2 gave almost the same results as MP2, which indicates
that, as expected, higher order correlation effects are weak regard-
ing this property, even for low hindered rotors.

Ortho-substituted Tol’s exhibit a \( V_3 \) barrier, whereas the 2,6-
disubstituted Tol’s present a \( V_6 \) one, as expected for symmetry
reasons. Contrarily to 2,6-difluorotoluene, for which the calculations
indicate that the methyl group is a nearly free rotor, 2,6-dibromo-
toluene and 2,6-dichlorotoluene present a \( \theta = 0^\circ \) conformation
(in-plane methyl hydrogen) and a significant \( V_6 \) barrier, whereas
the most stable conformation of Tol is obtained with a perpendic-
ular hydrogen (\( \theta = 90^\circ \)). In all cases, B3LYP or MP2, using large
basis sets, agree, except Tol for which the computed \( V_6 \) barriers are
different but very low. For such almost-free rotors we are
practically at the limit of accuracy of our theoretical model and
numerical computations.

References