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Internal Methyl Rotation and Molecular Structure of Trifluorotoluenes: Microwave Rotational Spectra of 2,3,4- and 2,4,5-trifluorotoluene

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Abstract

The microwave rotational spectra of 2,3,4- and 2,4,5-trifluorotoluenes, along with all ^{13}C isotopic species in natural abundance, have been recorded in the frequency range 8-27 GHz employing pulsed jet Fourier transform microwave spectroscopy. The analysis of the spectra in the lowest torsional state has yielded the rotational constants, centrifugal distortion constants, three fold barrier to methyl rotation and the direction of the internal rotation axis in the moment of inertia principal axes systems of these trifluorotoluenes. For both molecules, the molecular constants of their eight isotopologues have been used to obtain the substitution r_s structures of the ring and the methyl-carbon. The potential barriers hindering the internal rotation of the methyl top in 2,3,4- and 2,4,5-trifluorotluene are 2.5878(80) kJ/mol and 2.2809(23) kJ/mol, respectively.

Keywords: trifluorotoluenes, Internal rotation, Microwave spectroscopy, Molecular structure

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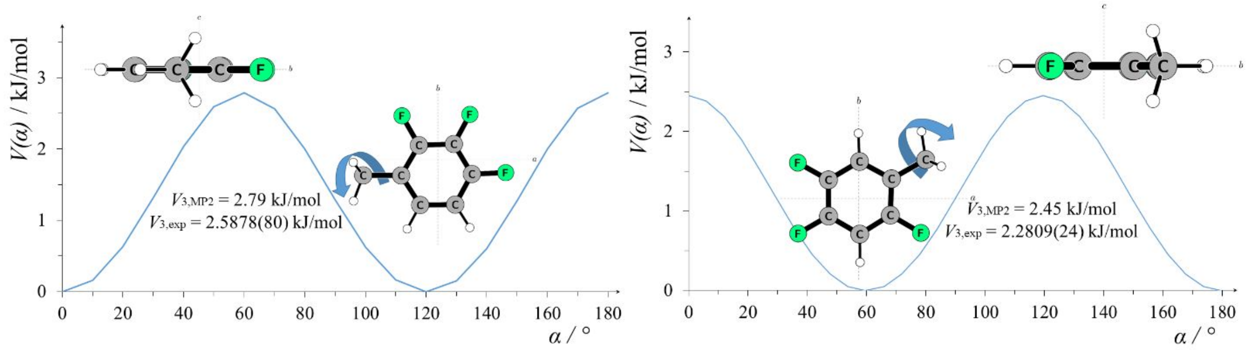
Graphical Abstract

Molecular properties and internal rotation barriers of 2,3,4-trifluorotoluene and 2,4,5-trifluorotoluene were determined from the jet-cooled rotational spectrum.



1. Introduction

The determination of molecular structure from the rotational spectra was a major application of microwave spectroscopy since its introduction in 1934. Beyond the molecular structure, microwave spectroscopic studies exploited their inherent resolution for the determination of nuclear quadrupole hyperfine structures when they are present, molecular electric dipole moment components and large amplitude motions (LAM) in flexible molecules [1-5]. However, in only a few molecular species have simultaneous determination of all these parameters been carried out. Historically, this might be due to the fact that the presence of the minor interactions like nuclear spin rotation interaction, internal rotation, and the presence of many isomers and isotopologues in natural abundance make the spectra congested and/or weak and therefore difficult to analyze. With higher quality *ab initio* calculations becoming increasingly affordable during recent decades, the more reliable prediction of spectra now allows for expedited identification of species and the assignment of quantum numbers to their signals. Even more important are the recent developments of new narrow-band experimental techniques employing FTMW on molecular jets, which have led to significant improvements in resolution and sensitivity while broad-band FTMW spectrometers have made data collection easier and, in certain cases, faster. Recently, we carried out microwave spectroscopic work on a number of di-halogenated toluenes [6-10] where both internal rotation and molecular structures have been derived. In the present investigation we have carried out microwave spectroscopic studies on 2,3,4-trifluorotoluene and 2,4,5-trifluorotoluene and the potential barriers due to internal methyl rotation and ring substitution structures have been accurately determined for both these molecules. Trifluorotoluenes are important organic compounds in industry and are used as solvents in organic reactions in the production of pepsticides and pharmaceuticals. More over monofluroro-, difluoro- and trifluorotoluenes may be possible candidates for astrophysical observations in the coming decade as many ring compounds are expected to be found in interstellar space. To our knowledge there are currently no microwave spectroscopic studies on trifluorotoluenes and the work is in continuation of our earlier studies on diflurorotoluenes to determine potential barriers and also structures in these molecules which may provide a basis for a theoretical interpretation of the change in potential barriers in this kind of molecule. The chemical structures of 2,3,4-trifluorotoluene and 2,4,5-trifluorotoluene in their moment of inertia principal axes systems are shown in Figures 1 and 2.

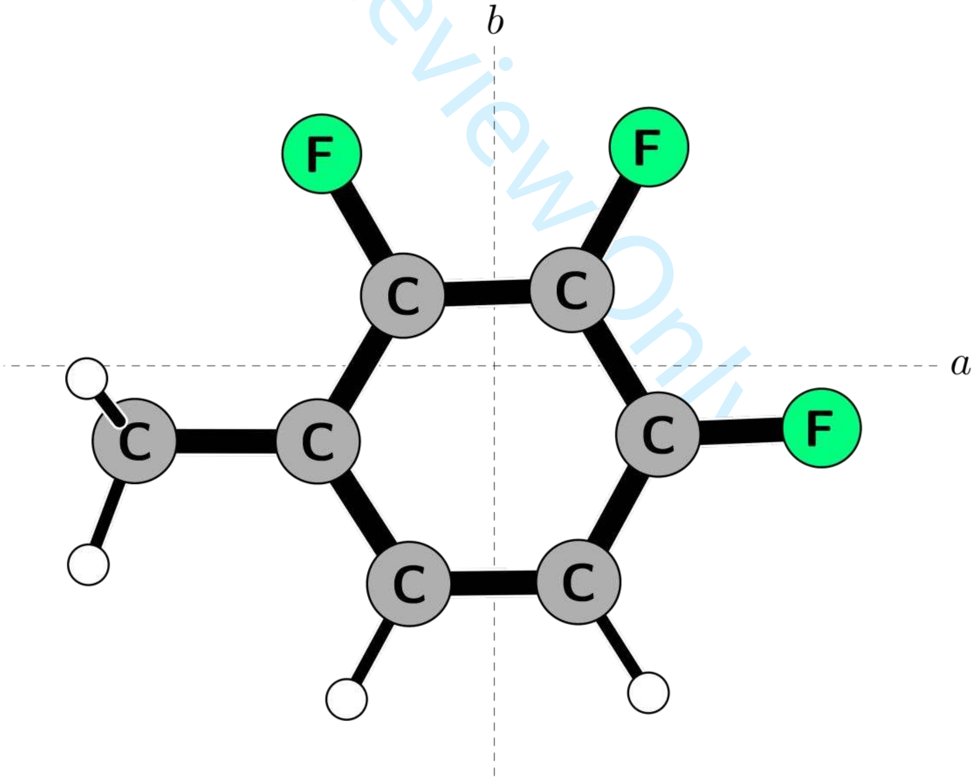


Figure 1: 2,3,4-trifluorotoluene with its heavy atom skeleton lying in the *ab*-plane of its moment of inertia principal axes system.

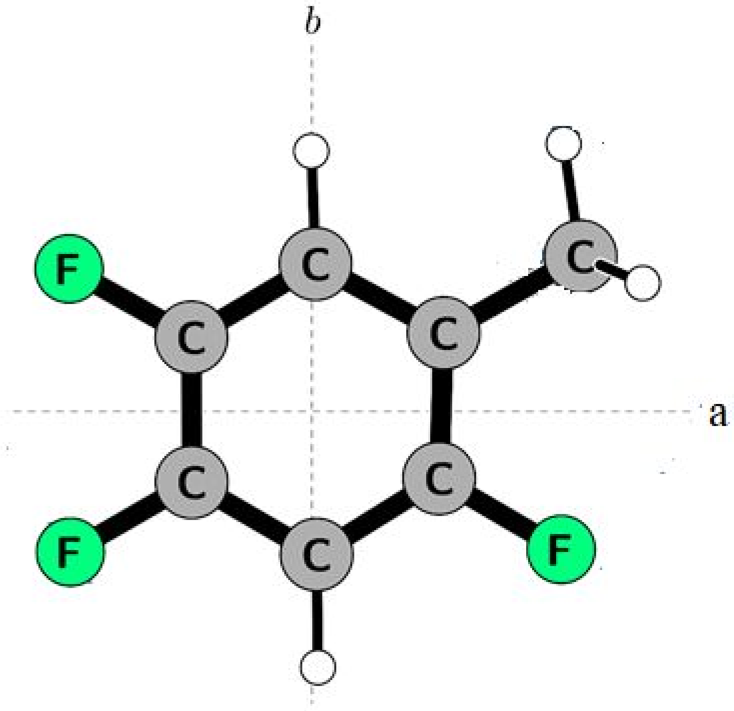


Figure 2: 2,4,5-trifluorotoluene with its heavy atom skeleton lying inthe *ab*-plane of its moment of inertia principal axes system.

2. Experimental

Commercial samples of 2,3,4-trifluorotoluene (Sigma Aldrich, 1g, 99%)and 2,4,5-trifluorotoluene (Alfa Aesar, 5g, 98%) were used without further purification. Two pulsed jet Fourier transform microwave spectrometers were used for the measurements. The more recently designed broad-band FT-MW microwave spectrometer with In-phase/quadrature–phase Modulation Passage-Acquired-Coherence Technique (IMPACT) has been used for the parent molecule and a Coaxially Arranged Molecular Beam with Respect to the Resonator Axis (COBRA) has been used for the measurement of ^{13}C isotopic species. Details of the spectrometers have been given earlier [11-15]. Sample mixtures of about 10 millibar partial pressure of 2,3,4-trifluotoluene or 2,4,5-trifluorotoluene in 4 bar neon at room temperature and a stagnation pressure of 2 bar were used for the measurement. The spectra were taken in the frequency range 8 to 27 GHz. The rotational constants of the molecules were first predicted using the B3LYP DFT-method using Pople's6-311++g(2d,2p) basis set [16] as implemented in Gaussian09. The chosen basis set was found to give reasonably good predictions of the constants in our earlier work on difluorotoluenes. The lines were first searched for in the frequency region 8 to 27GHz employing the broad-band FTMW spectrometer and sufficient numbers of lines could be measured and analyzed for the most abundant isotopologues of 2,3,4- as well as 2,4,5-trifluorotoluene. Both a- and b-dipole moment selection rule transitions could be observed. Only the two lowest states of the methyl internal rotation, namely the v=0, A and E torsional symmetry species of the rotational transitions, could be observed for both molecules. Because of the collisional cooling during the supersonic expansion, higher vibrational or torsional states are depopulated and could not be observed. All frequency measurements were referenced to a rubidium frequency standard and unblended lines have an estimated uncertainty of <1 kHz, with a resolution of about 5 kHz.

The analysis of the observed spectra was based on a model Hamiltonian for an asymmetric rotor with centrifugal distortion terms and internal rotation part. The Hamiltonian employed for the asymmetric rotor in presence of a symmetric internal rotor can be written as

$$H = H_{\mathrm{rr}} + H_{\mathrm{cd}} + H_{\mathrm{ir}} + H_{\mathrm{ird}} \qquad (1)$$

where the standard rigid frame-rigid top Hamiltonian is given by [1, 17-19]. H_{ir} is the rigid-top internal rotation operator and H_{rr} is the rigid top operator

$$H_{\mathrm{rr}} + H_{\mathrm{ir}} = AP_a^2 + BP_b^2 + CP_c^2 + F\pi_\alpha^2 + V(\alpha) \qquad (2)$$

Besides the rotational constants of the molecule (A, B, C) the expression contains the reduced rotational constant F of the methyl top. The components of the total angular momentum are denoted as P_g and refer to the principal inertia axes $g = a,b,c$. Specifically, $\pi_\alpha = P_\alpha - \rho_a P_a - \rho_b P_b$ contains the angular momentum P_α of the methyl top with $\rho_g = \lambda_g I_\alpha / I_g$ ($g = a,b$), the moment of inertia I_α of the methyl top, the structural moments of inertia I_g components of the molecule, and the direction cosines λ_g between the internal rotation axis i and the respective inertial axes ($\lambda_a = \cos\delta$, $\lambda_b = \sin\delta$, $\delta = \angle$ (a,i); $\lambda_c = 0$ by symmetry). With a three-fold symmetry of the torsional problem, the leading term of the hindering potential $V(\alpha)$ is written as

$$V(\alpha) = \frac{V_3}{2}[1 - \cos(3\alpha)] \tag{3}$$

Where α is the internal rotation angle of the methyl group relative to the frame. Higher order potential terms (V_6, V_9 etc.) have been neglected. The centrifugal distortion term H_{cd} in the Hamiltonian comprises standard fourth order terms for a semi-rigid rotor according to Watson's S-reduction (1,20):

$$H_{\mathrm{cd}} = -D_{\mathrm{J}}P^4 - D_{\mathrm{JK}}P^2P_a^2 - D_{\mathrm{K}}P_a^4 + d_1P^2\left(P_+^2 + P_-^2\right) + d_2\left(P_+^4 + P_-^4\right) \tag{4}$$

P_+ and P_- are ladder operators. H_{ird} gives the empirical internal rotation - overall rotation distortion operator in the principle axis system [17-19]

$$\begin{aligned} H_{\mathrm{ird}} &= 2D_{\pi 2\mathrm{J}}(p_\alpha - \rho P_r)^2P^2 + D_{\pi 2\mathrm{K}}\left[(p_\alpha - \rho P_r)^2P_a^2 + P_a^2(P_\alpha - \rho P_r)^2\right] + D_{\pi 2 -} \\ &\left[(P_\alpha - \rho P_r)^2\left(P_b^2 - P_c^2\right) + \left(P_b^2 - P_c^2\right)(p_\alpha - \rho P_r)^2\right] + D_{\mathrm{c3J}}\cos(3\alpha)P^2 \end{aligned} \tag{5}$$

as used in the XIAM code with P_r being the angular momentum vector along the rho axis.

The spectral analyses were performed within the "Combined Axis Method" implemented in XIAM, as described in detail by Hartwig and Dreizler [17-18]. The fit by XIAM yields the rotational and internal rotation parameters. The results for the parent molecule in case of 2,3,4- and 2,4,5-trifluorotoluene are given in Table 1 and 2 respectively. The V_3 potential barrier in the case of 2,3,4-trifluorotoluene was determined to be 2.5878(80) kJ mol^{-1}, which is equivalent to 216.32(66) cm^{-1} and in 2,4,5-triflurotoluene it is 2.2809 (23) kJ/mol equivalent to 190.67(20) cm^{-1}. Transitions originating from ^{13}C isotopologues of all seven in-equivalent substitution positions of the carbon skeleton have also been observed in natural abundance (1%) with the COBRA spectrometer for both molecules. A total of 26 to 48 individual transitions have been measured for each mono-substituted ^{13}C isotopologue, while 627 transitions were obtained for the parent molecule in 2,3,4-trifluorotoluene. A total of 14 to 23 individual transitions for each of the ^{13}C isotopologues and 386 transitions for the parent molecule in the case of 2,4,5-trifluorotolue were used in the analysis. The complete list of rotational transitions is available as supplementary material [Tables S1-S8 for 2,3,4-trifluorotoluene and S9-S16 for 2,4,5-triflurotoluene]. The experimental rotational constants of the ^{13}C species are collected in Tables 3 and 4 along with the parent molecule for both molecules. In the analysis of the isotopologues, only the rotational constants *A*, *B*, *C* are optimized while keeping all other parameters at the respective values of the parent species, except for the angle "δ" between internal rotation *α* axis and principal *a*-axis, which were fixed at the parent's values scaled by the isotopic shift predicted from the B3LYP/6-311++g(2d,2p)geometry. A typical spectrum of 2,3,4-trifluorotoluene ^{13}C-isotopologue substituted at position 1 is shown in Figure 3.

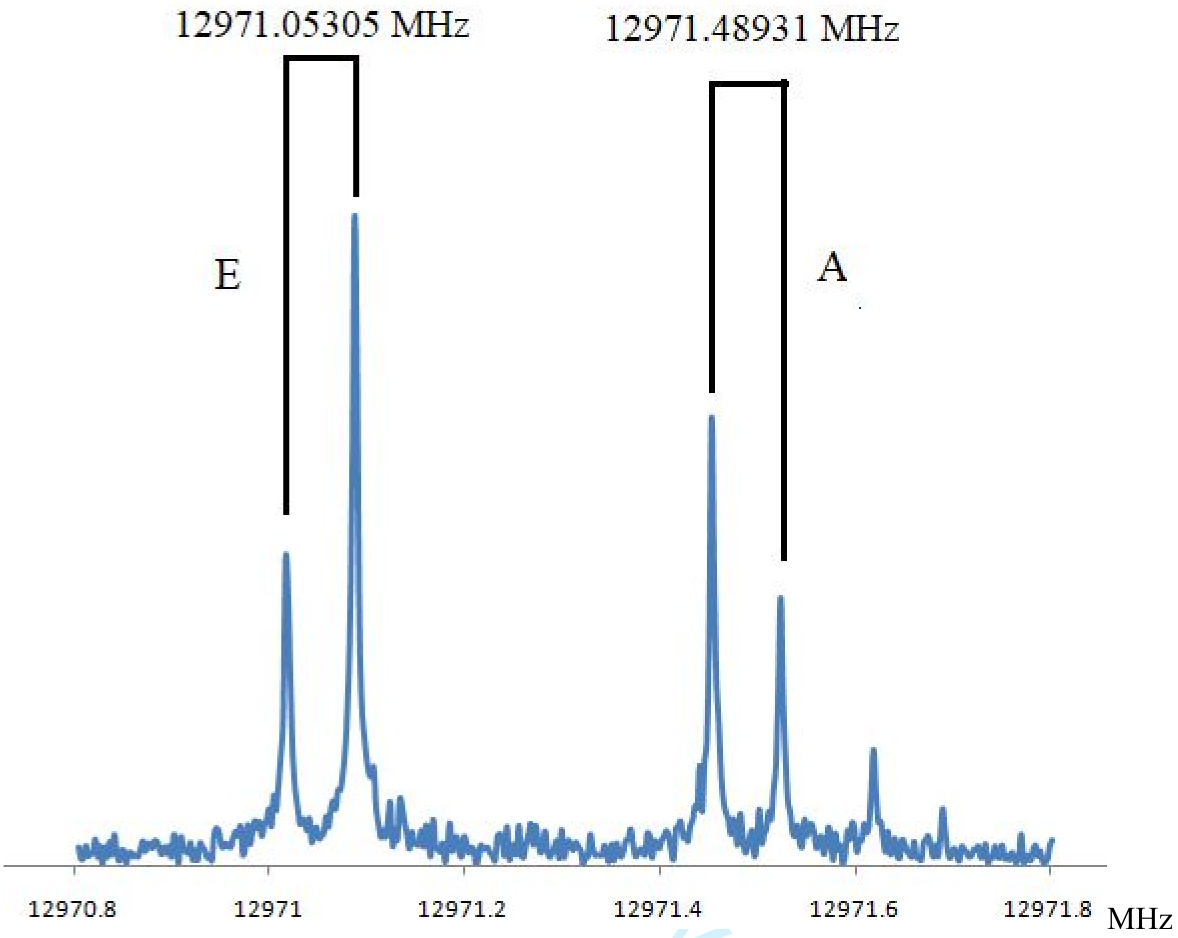


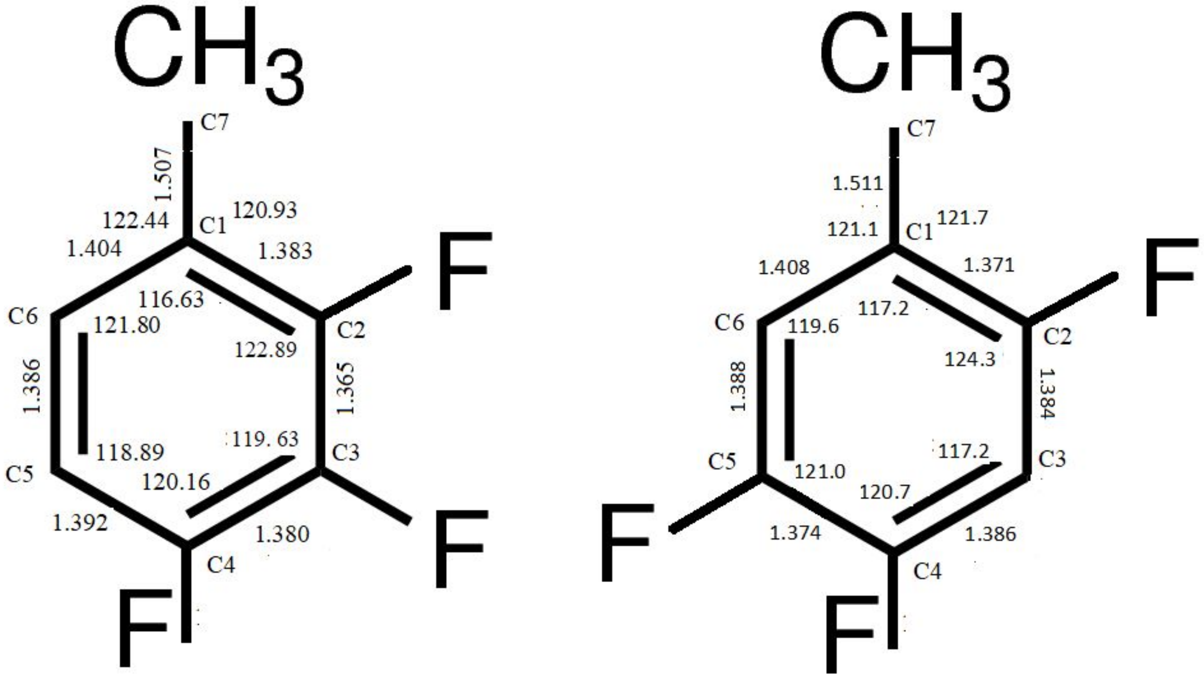
Figure 3: The Doppler components for the A and E components of the internal rotation splitting of the $8_{1,8} - 7_{0,7}$ transitionof the 2,3,4-trifluorotoluene ^{13}C-isotopologue substituted at position 1.

3. Molecular Structure

The molecular structures of the title compounds were derived from all isotopic data acquired for the two molecules. The rotational constants obtained for seven ^{13}C isotopologues, substituting at all six carbon ring positions and the methyl carbon, are collected in Table 3. Together with those of the parent molecule, the rotational constants were used to obtain the r_s and r_0 structures of 2,3,4-trifluorotluene and, similarly, the rotational constants given in Table 2 and 4 are used for the determination of molecular structure of 2,4,5-trifluorotoluene.

The position of each substituted carbon atom was first calculated using the substitution method (r_s) of Kraitchman, which provides the absolute atomic coordinates in the principal axes system [21-23]. Kraitchman's equations are analytical solutions for the absolutes of the Cartesian coordinates of the substituted atom. However, these equations are only exact for equilibrium structures within the Born-Oppenheimer approximation and the assumption that atoms can be treated as point masses. The neglect of vibrational effects can lead to pronounced anomalies, such as imaginary coordinates or strong distortions, if the substituted atom is close to one of the principal axes. Compared to least squares fit r_0 structures, the r_s structures benefit from a partial compensation of zero-point contributions to ground state moments of inertia, since the coordinates are derived from differences between the isotopologues rather than their absolute values of the moments of inertia. It should be noted that two of the substitution coordinates in 2,4,5-triflurotoluene, marked with asterisks, are imaginary due to vibrational changes when a substitution coordinate is near to one of the principal axes (see Figure 2). In those cases, the values from the DFT calculated coordinates are taken as more reliable in order to estimate the bond lengths and bond angles. In the case of 2,3,4-triflurotoluene such a situation did not arise as all atomic coordinates were away from the principal axes (see Figure 1).

The resulting atomic coordinates are compared with the *ab initio* data in Table 5 and 6. The derived bond lengths and valence angles are collected in Table 7 and 8 for 2,3,4-trifluorotoluene and 2,4,5-trifluorotluene, respectively, and compared with their *ab initio* values. We also provide a semi-experimental r_0 structure determined with the program STRFIT [24], in which several parameters were fixed to values from the B3LYP/6-311++g(2d,2p) geometry optimization. Hydrogen related coordinates cannot be expected to be well determined, since no deuterated species were measured. Also it should be highlighted here, that r_0 and r_s structures are not directly comparable to equilibrium r_e structures, since they are influenced by vibrational effects.The theoretical equilibrium (r_e) *ab initio* values are given in Table 4 along with derived bond lengths and valence angles. The $r_s$structures of 2,3,4-triflurotoluene and 2,4,5-trifluorotoluene are shown in Figure 4.



2,3,4-triflurotoluene

2,4,5-trifluorotoluene

Figure 4:The r_s substitution structure of 2,3,4- and 2,4,5-trifluorotoluenes

4. Theoretical Predictions

To support this work, we have made calculations using the Kohn-Sham density functional theory [25] employing Becke's three parameter hybrid exchange functional [26] and the Lee-Yang-Parr correlation functional [27] (B3LYP), which is assumed to be adequate for our purposes [28]. For comparison, those calculations were replicated using the second order Møller-Plesset perturbation method (MP2) [29]. The calculations were performed with the

GAUSSIAN09 package [16] and the split-valence triple-ζ basis set 6-311++G(2d,2p), previously used in the analysis of difluorotoluenes [6-10], allowing for a direct comparison. The agreements of the rotational parameters with the experimental constants in Table 1 and 2 are quite satisfactory and the isotopic dependence is well reproduced in both cases. Following a vibrational frequency calculation in the harmonic approximation we additionally calculated the quartic centrifugal distortion coefficients. Finally, we have also calculated the torsional barrier at the MP2/6-311++G(2d,2p) level of theory by a relaxed potential energy surface scan. The observed barrier V_3(exp)= 2.5878(80)kJ/mol in 2,3,4-difluorotoluene is well reproduced by the *ab initio* calculations, which predicts a barrier V_3(theor) =2.79 kJ/mol and in the case of 2,4,5-trifluorotoluene the observed barrier V_3 = 2.2809 (23) kJ/mol also compares well with V_3 = 2.45 kJ/mol from the *ab initio* calculation. The results of the relaxed potential energy surface scan to determine the potential barrier are illustrated in Figures 5 and 6

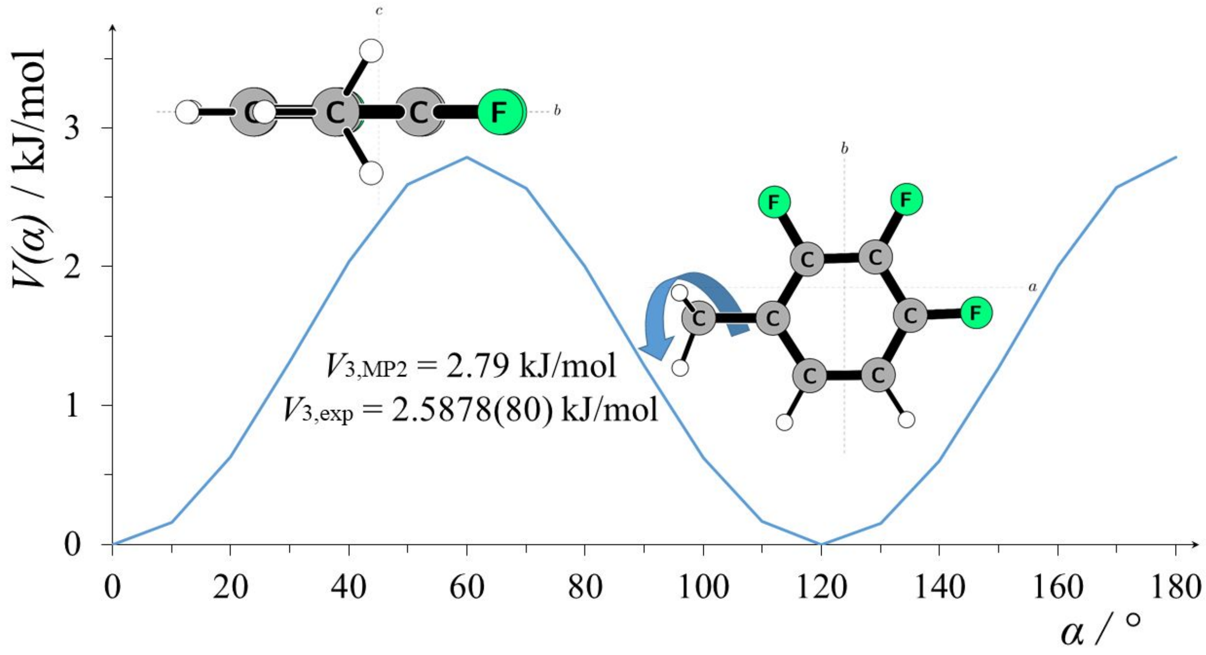


Figure 5: Potential barrier of the methyl torsion in 2,3,4-trifluorotoluene.

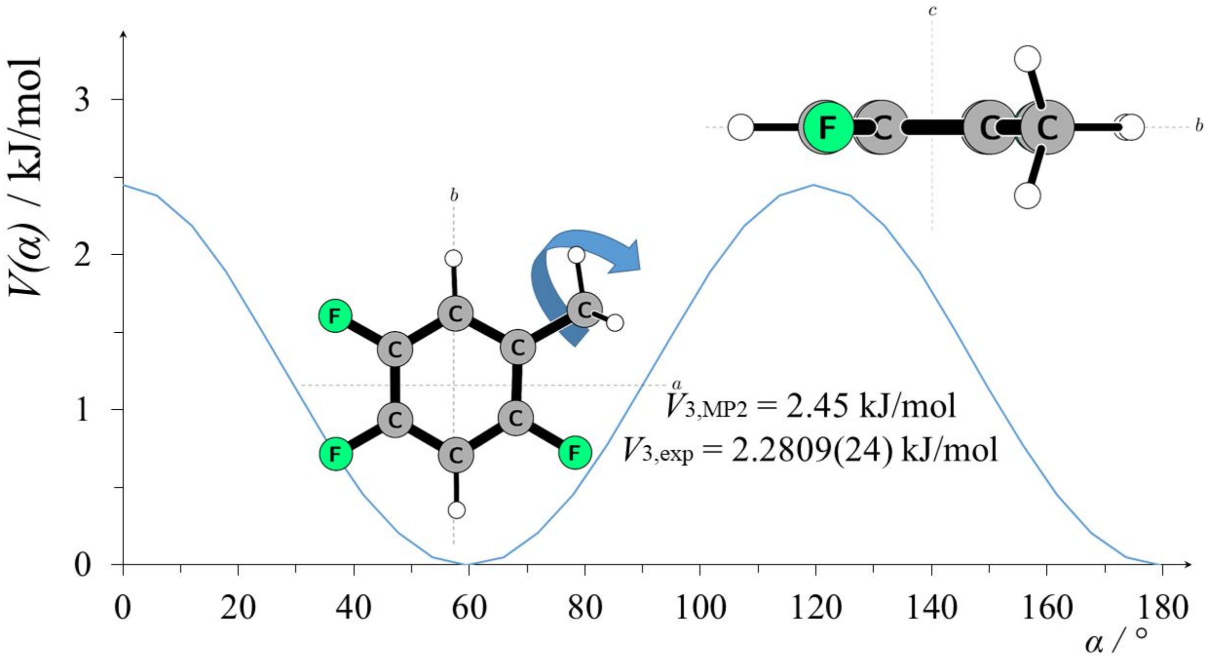


Figure 6: Potential barrier of the methyl torsion in 2,4,5-trifluorotoluene

5. Conclusion/Discussion

This work provides the rotational assignments, including successful determination of molecular structures and internal rotation barriers in 2,3,4-trifluorotoluene and 2,4,5-trifluorotoluene.The *ab initio* predictions allow for a reasonable description of the rotational parameters. The *ab initio* prediction of the internal rotation barrier (2.79 kJ/mol) is almost the same as the experimental value (2.5856 kJ/mol) in 2,3,4-trifluorotluene and the corresponding values in 2,4,5-trifluorotoluene are 2.45 kJ/mol (theoretical) and V_3= 2.2809(29) kJ/mol (experimental). Comparison of the V_3 internal rotation potential barrier with those of other mono- and disubstituted toluenes is aided in Table 9. The fluorines at the 2,3,and 4 positions in 2,3,4-trifluorotoluene require a higher potential barrier for internal rotation compared to 2,4 and 5 positions in 2,4,5-trifluorotluene. One can deduce that the fluorines at the ortho- and meta-positions cause an increase or decrease, respectively, of the potential barrier. In 2-flurotoluene the potential barrier is 2.71887 kJ/mol, in 2,3-difluorotluene it is 2.51870 kJ/mol and in 2,3,4-triflurotoluene 2.5878 kJ/mol which shows, that the addition of another F in the para-methyl position of 2,3-diflurotoluene gives only a small increase in the potential barrier.

The investigation of internal rotation barriers and structures in methylated halobenzenes will broaden the empirical data prerequisite for a general description of the substituent effects towards intramolecular dynamics in conjugated bond systems such as aromatic molecules.

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Table 1. Experimental and theoretical rotational parameters for the most abundant isotopologue (parent species) of 2,3,4-trifluorotoluene using Watson's S-reduction in the I^r representation.

Molecular Parameter	Experiment	Theory	
	XIAM	B3LYP/ 6-311++g(2d,2p)	MP2/ 6-311++g(2d,2p)
A (MHz)	2085.9101(31)	2087.380	2084.415
B (MHz)	1201.434445(36)	1200.646	1199.312
C (MHz)	765.974221(30)	765.800	764.855
D_J (kHz)	0.015840(58)	0.080859	0.081075
D_{JK} (kHz)	0.06782(41)	-0.107219	-0.107451
D_K (kHz)	0.06201(109)	0.032686	0.032739
d_1 (kHz)	-0.007055(20)	-0.028954	-0.029006
d_2 (kHz)	-0.002359(8)	-0.005546	-0.005537
$D_{\pi 2-}$(kHz)	-10.759(54)		
$D_{\pi 2K}$(kHz)	119(22)		
V_3(kJ/mol)	2.5878(79)		2.79
V_3(cm^{-1})	216.32(66)		233
V_3(cal/mol)	618.07(190)		666
δ*(radian)*	0.0118(21)	0.0088	0.0046
F_0(GHz)	159.52(50)		
σ (kHz)	2.4		
N	627		
$\lvert\mu_a\rvert$(D)		2.089	2.013
$\lvert\mu_b\rvert$(D)		2.592	2.522
$\lvert\mu_c\rvert$(D)		0.0	0.0
$\lvert\mu\rvert$(D)		3.329	3.226

The program XIAM is used in the fit of the lines to optimize the spectroscopic constants and the potential barrier. N is the number of lines used in the fit and σ denotes the standard deviation.

Table 2. Experimental and theoretical rotational parameters for the most abundant isotopologue (parent species) of 2,4,5-trifluorotoluene using Watson's S-reduction in the I^r representation.

Molecular Parameter	Experiment	Theory	
	XIAM	B3LYP/ 6-311++g(2d,2p)	MP2/ 6-311++g(2d,2p)
A (MHz)	2269.3534(13)	2268.0	2269.3
B (MHz)	1032.193000(98)	1031.5	1028.8
C (MHz)	712.627827(22)	712.1	710.9
D_J (kHz)	0.012986(50)	0.01257	0.01258
D_{JK} (kHz)	0.02653(29)	0.02515	0.02621
D_K (kHz)	0.2787(45)	0.30762	0.31305
d_1 (kHz)	-0.004514(39)	-0.00442	-0.00440
d_2 (kHz)	-0.000831(21)	-0.00080	-0.00080
$D_{\pi 2J}$(kHz)	-16.04(24)		
$D_{\pi 2K}$(kHz)	305(6)		
$D_{\pi\text{-}K}$(kHz)	23.46(24)		
V_3(kJ/mol)	2.2809(23)		2.45
V_3(cm^{-1})	190.67(20)		205
V_3(cal/mol)	540.77(56)		586
δ(radian)	0.525847(80)	0.517	0.514
F_0(GHz)	159.22(17)		
σ (kHz)	1.8		
N	386		
$\|\mu_a\|$(D)		1.89	1.83
$\|\mu_b\|$(D)		1.03	0.98
$\|\mu_c\|$(D)		0.0	0.0
$\|\mu\|$(D)		2.15	2.07

The program XIAM is used inthe fit of the lines to optimize the spectroscopic constants and the potential barrier. N is the number of lines used in the fit and σ denotes the standard deviation.

Table 3: Rotational Constants of the ^{13}C-isotopologues of 2,3,4-trifluorotoluene from a fit by Xiam optimizing the rotational constants while all other parameters are kept fixed at the parent molecule's value.

Species	A_0 /MHz	B_0 /MHz	C_0 /MHz	σ/kHz	N
Parent	2085.9101(31)	1201.434445(36)	765.974221(30)	1	627
13C1	2082.7023(10)	1195.46081(14)	763.112200(14)	0.5	48
13C2	2083.1198(21)	1199.87423(88)	764.964370(45)	0.8	39
13C3	2082.6350(49)	1200.3230(11)	765.082533(71)	3	54
13C4	2083.2674(16)	1196.27981(35)	763.521542(23)	0.9	34
13C5	2059.0178(11)	1200.06247(25)	761.765888(19)	0.6	26
13C6	2058.5583(23)	1200.02589(53)	761.687636(34)	1	32
13C7	2082.8237(14)	1176.99639(26)	755.560593(32)	2	34

Table 4: Rotational Constants of the ^{13}C-isotopologues of 2,4,5-trifluorotoluene from a fit by Xiam optimizing the rotational constants while all other parameters are kept fixed at the parent molecule's value.

Species	A_0 /MHz	B_0 /MHz	C_0 /MHz	Δ(u.Å^2)	σ/kHz	N
Parent	2269.3534(13)	1032.193000(98)	712.627827(22)	3.13749(13)	1.8	386
13C1	2263.7192(72)	1028.8396(22)	710.49982(23)	3.1636(25)	2.6	14
13C2	2265.2381(15)	1029.0963(27)	710.74454(25)	3.1362(13)	4.9	16
13C3	2250.183(10)	1032.2150(20)	710.74034(21)	3.1410(14)	3.8	14
13C4	2264.7700(37)	1029.42271(84)	710.856187(81)	3.13834(55)	1.4	15
13C5	2264.3957(37)	1029.40582(92)	710.811555(71)	3.13864(57)	1.3	15
13C6	2249.2041(47)	1032.23095(90)	710.639175(89)	3.12990(53)	1.9	15
13C7	2247.9333(72)	1018.3259(17)	703.899962(14)	3.1336(11)	2.8	23

Table 5 Atomic substitution (r_s) coordinates of 2,3,4-trifluorotoluene

	MP2			DFT			Kraitchman r_s		
Atom	x (Å)	z(Å)	Y (Å)	x(Å)	z(Å)	Y(Å)	x(Å)	z(Å)	Y(Å)
C1	-1.4539	-0.6265	0.0	-1.4540	-0.6230	0.0	-1.4508	-0.6150	0.0
C2	-0.7531	0.5763	0.0	-0.7505	0.5766	0.0	-0.7402	0.5711	0.0
C3	0.6357	0.6264	0.0	0.6356	0.6235	0.0	0.6245	0.6177	0.0
C4	1.3523	-0.5655	0.0	1.3493	-0.5666	0.0	1.3475	-0.5577	0.0
C5	0.6954	-1.7850	0.0	0.6907	-1.7808	0.0	0.6886	-1.7842	0.0
C6	-0.7001	-1..8031	0.0	-0.7007	-1.7969	0.0	-0.6976	-1.7998	0.0
C7	-2.9568	-0.6178	0.0	-2.9590	-0.6201	0.0	-2.9575	-0.6151	0.0
H8	-1.2160	-2.7527	0.0	-1.2158	-2.7472	0.0			
H9	-3.3374	-1.6347	0.0	-3.3411	-1.6387	0.0			
H10	-3.3445	-0.1035	0.8762	-3.3546	-0.1059	0.8767			
H11	-3.3445	-0.1035	-0.8762	-3.3546	-0.1059	-0.8767			
F12	2.6944	-0.5066	0.0	2.6923	-0.5126	0.0			
F13	-1.4281	1.7402	0.0	-1.4204	1.7444	0.0			
F14	1.2712	1.8030	0.0	1.2725	1.7996	0.0			
H15	1.2761	-2.6946	0.0	1.2682	-2.6931	0.0			

Kraitchman's r_s coordinates are unsigned, however for brevity the signs are given obtained from *ab initio*

Table 6 Atomic substitution (r_s) coordinates of 2,4,5-trifluorotoluene

	MP2			DFT			Kraitchman r_s		
Atom	x (Å)	z(Å)	Y (Å)	x(Å)	z(Å)	Y(Å)	x(Å)	z(Å)	Y(Å)
C1	1.2635	0.7493	0.0	1.2634	0.7472	0.0	1.2642(13)	0.7302(22)	0.0
C2	1.2239	-0..6425	0.0	1.2195	-0.6430	0.0	1.2150(12)	-0.6399(23)	0.0
C3	0.0473	-1.3766	0.0	0.0449	-1.3735	0.0	0.1020*	-1.3785(11)	0.0
C4	-1.1533	-0.6822	0.0	-1.1522	-0.6800	0.0	-1.1489(13)	-0.6735(22)	0.0
C5	-1.1599	0.7073	0.0	-1.1554	0.7060	0.0	-1.1523(13)	0.7004(22)	0.0
C6	0.0333	1.4137	0.0	0.0355	1.4101	0.0	0.1339*	1.4175(11)	0.0
C7	2.5763	1.4800	0.0	2.5760	1.4828	0.0	2.5764(6)	1.4785(10)	0.0
H8	3.1656	1.2196	0.8760	3.1721	1.2258	0.8765			
H9	3.1656	1.2196	-0.8760	3.1715	1.2266	-0.8765			
H10	2.4131	2.5534	0.0	2.4136	2.5586	0.0			
H11	-0.0063	2.4936	0.0	-0.0050	2.4901	0.0			
H12	0.0599	-2.4553	0.0	0.05756	-2.4526	0.0			
F13	2.3967	-1.3177	0.0	2.3901	-1.3247	0.0			
F14	-2.3165	-1.3524	0.0	-2.3168	-1.3492	0.0			
F15	-2.3335	1.3616	0.0	-2.3294	1.3642	0.0			

See Figure 4 for atomic numbering. Kraitchman's r_s coordinates are unsigned and signs given are obtained from *ab initio.* Starred quantities are ill determined from Kraitchman equations (imaginary).

Table 7: Substitution (r_s) semi empirical zero point (r_0) and B3LYP/6-311++g(2d,2p) predicted equilibrium (r_e) structure of 2,3,4-trifluorotoluene. Errors in r_0 are 1-σ deviations. Bond lengths (r) in Å, angles (A) and dihedral angles (D) in degrees. The highest deviation between calculated and experimental rotational constants in the r_0 structure is 110 kHz for the *A* rotational constant of C1.

Parameter	r_s (KRA)	MP2	DFT	r_0 (STRFIT)
$r_{C1\text{-}C2}$	1.3827(3)	1.3921	1.3907	1.3927(derived)
$r_{C2\text{-}C3}$	1.3655(4)	1.3897	1.3869	1.3871(20)^a
$r_{C3\text{-}C4}$	1.3800(3)	1.3907	1.3877	1.3879(20)^a
$r_{C4\text{-}C5}$	1.3923(1)	1.3852	1.3811	1.3815(20)^a
$r_{C5\text{-}C6}$	1.3863(1)	1.3956	1.3915	1.3916(20)^a
$r_{C6\text{-}C1}$	1.4040(1)	1.3974	1.3948	1.3908(20)^a
$r_{C7\text{-}C1}$	1.5067(5)	1.5029	1.5051	1.5081(22)
$r_{C7\text{-}H}$		1.0858	1.0872	1.0956(9)^b
$r_{C7\text{-}H}$		1.0874	1.0929	1.0983(9)^b
$r_{C7\text{-}H}$		1.0874	1.0929	1.0983(9)^b
$r_{C6\text{-}H}$		1.0807	1.0809	1.0887(9)^b
$r_{C5\text{-}H}$		1.0792	1.0797	1.0875(9)^b
$r_{C2\text{-}F}$		1.3455	1.3463	1.3470(41)^c
$r_{C3\text{-}F}$		1.3372	1.3375	1.3382(41)^c
$r_{C4\text{-}F}$		1.3434	1.3441	1.3448(41)^c
$A_{C1\text{-}C2\text{-}C3}$	122.89(4)	122.29	122.33	122.17(derived)
$A_{C2\text{-}C3\text{-}C4}$	119.63(4)	118.95	119.01	119.01(fixed)
$A_{C3\text{-}C4\text{-}C5}$	120.16(4)	120.68	120.57	120.57(fixed)
$A_{C4\text{-}C5\text{-}C6}$	118.89(2)	119.05	119.14	119.14(fixed)
$A_{C5\text{-}C6\text{-}C1}$	121.80(1)	121.90	122.03	122.03(fixed)

$A_{C6-C1-C2}$	116.63(3)	117.13	116.92	117.07(derived)
$A_{C6-C1-C7}$	122.44(11)	122.98	122.80	123.34(derived)
$A_{C7-C1-C2}$	120.93(11)	119.90	120.28	119.59(20)
$A_{H-C7-C1}$		110.18	110.45	110.45(fixed)
$A_{H-C7-C1}$		111.05	111.32	111.32(fixed)
$A_{H-C7-C1}$		111.05	111.32	111.32(fixed)
$A_{H-C6-C1}$		118.84	118.85	118.85(fixed)
$A_{H-C5-C6}$		121.81	121.67	121.67(fixed)
$A_{F-C4-C5}$		120.83	120.79	121.36(23)
$A_{F-C2-C3}$		118.05	117.90	117.84(21)
$A_{F-C3-C4}$		120.61	120.61	121.02(25)

a,b,c–differences fixed on B3LYP/6-311++G(2d,2p) prediction.

Table 8: Substitution (r_s) semi empirical zero point (r_0) and B3LYP/6-311++g(2d,2p) predicted equilibrium (r_e) structure of 2,4,5-trifluorotoluene. Errors in r_0 are 1-σ deviations. Bond lengths (r) in Å, angles (A) and dihedral angles (D) in degrees. The highest deviation between calculated and experimental rotational constants in the r_0 structure is 110 kHz for the *A* rotational constant of C1.

Parameter	r_s (KRA)	MP2	DFT	r_0 (STRFIT)
r_{C1-C2}	1.371(3)	1.392	1.391	1.3934(20)^a
r_{C2-C3}	1.383(4)	1.387	1.383	1.3858(20)^a
r_{C3-C4}	1.386(4)	1.387	1.383	1.3860(20)^a
r_{C4-C5}	1.374(3)	1.390	1.386	1.3886(20)^a
r_{C5-C6}	1.387(2)	1.387	1.383	1.3860(20)^a
r_{C6-C1}	1.408(2)	1.398	1.395	1.3979(derived)
r_{C7-C1}	1.511(2)	1.502	1.505	1.5032(22)
r_{C7-H}		1.087	1.090	1.0980(11)^b
r_{C7-H}		1.087	1.090	1.0980(11)^b

r_{C7-H}		1.086	1.088	1.0954(11)^{b}
r_{C6-H}		1,081	1.081	1.0883(11)^{b}
r_{C3-H}		1.079	1.079	1.0867(11)^{b}
r_{C2-F}		1.353	1.354	1.3480(35)^{c}
r_{C4-F}		1.342	1.343	1.3365(35)^{b}
r_{C5-F}		1.344	1.346	1.3393(35)^{b}
$A_{C1-C2-C3}$	124.3(5)	123.59	123.69	123.69(fixed)
$A_{C2-C3-C4}$	117.2(4)	118.00	118.04	118.04(fixed)
$A_{C3-C4-C5}$	120.7(5)	120.31	120.21	120.21(fixed)
$A_{C4-C5-C6}$	121.0(3)	120.35	120.46	120.46(fixed)
$A_{C5-C6-C1}$	119.6(2)	121.00	121.05	121.05(derived)
$A_{C6-C1-C2}$	117.2(3)	116.74	116.55	116.55(derived)
$A_{C7-C1-C6}$	121.1(2)	122.53	122.36	122.49(derived)
$A_{C7-C1-C2}$	121.7(3)	120.73	121.08	120.96(26)
$A_{H-C7-C1}$		110.92	111.19	111.19(fixed)
$A_{H-C7-C1}$		110.92	111.19	111.19(fixed)
$A_{H-C7-C1}$		110.45	110.71	110.71(fixed)
$A_{F-C2-C1}$		118.30	118.41	118.41(30)
$A_{F-C2-C3}$		118.11	117.91	117.90(derived)
$A_{H-C6-C5}$		118.52	118.44	118.44(fixed)
$A_{F-C4-C5}$		119.67	119.75	119.68(derived)
$A_{F-C4-C3}$		120.01	120.03	120.11(31)
$A_{F-C5-C6}$		120.24	120.14	120.20(derived)
$A_{F-C5-C4}$		119.41	119.40	119.34(32)
$A_{H-C3-C4}$		120.71	120.76	120.76(fixed)

a,b,c–differences fixed on B3LYP/6-311++G(2d,2p) prediction.

Table 9: Comparison of V_3 Potential barriers for some substituted toluenes in kJ/mol

Molecule	Experimental	MP2	Reference
o-fluorotoluene	2.71887(24)	2.78	30,31
m-fluorotoluene	0.202506	0.185	32
o-chlorotoluene	6.146 (32) 5.6417(50)	6.517 5.76	31,33,34
m-chlorotoluene	0.038757(60)	0.029341	35
2,3-difluorotoluene	2.51870(14)	2.736	9
2,4-difluorotoluene	2.80144(82)	2.8335	8
2,5-difluorotoluene	2.580(12)	2.568	7
3,4-difluorotoluene	0.384786(39) 0.406280(37)	0.366755	10
2,3,4-trifluorotoluene	2.5878(80)	2.79	this study
2,4,5-trifluorotoluene	2.3809(23)	2.45	this study