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Bifurcated Hydrogen Bonding in 2-Trifluoromethylphenol Confirmed by Gas Electron Diffraction

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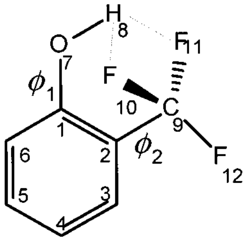
The molecular structure of 2-trifluoromethylphenol has been determined by gas-phase electron diffraction. The analysis, aided by constraints from ab initio molecular orbital calculations, yielded the following bond lengths (r_g) and bond angles: $(C-C)_{Ar,mean}$, 1.395 ± 0.004 Å; $C-C(F_3)$, 1.510 ± 0.005 Å; C−O, 1.362 ± 0.011 Å; $(C-F)_{mean}$, 1.358 ± 0.006 Å; $\angle O-C_1-C_2$, 121.0 ± 1.2°; $\angle C-O-H$, 105 ± 6°; $\angle C(F_3)-C_2-C_1$, 120.7 ± 0.8°; $(C-C-F)_{mean}$, 113.2 ± 0.3°; CF_3 torsion, 10.1 ± 0.8°. Weak intramolecular bifurcated hydrogen bonding between the hydroxy hydrogen and two of the CF_3 fluorines is indicated by the H···F nonbonded distances 2.05 ± 0.06 and 2.42 ± 0.06 Å. Compared with the freely rotating CF_3 group in trifluoromethylbenzene, the well-defined conformer of 2-trifluoromethylphenol indicates the constraining effect of hydrogen bonding.

Introduction

Hydrogen bonding is a significant factor contributing to the structures and interactions of molecules in various states.[1,2] Especially interesting are the bifurcated hydrogen bonds, where two acceptor groups are involved in simultaneous interaction with a single hydrogen donor. Bifurcated hydrogen bonds in the solid phase have been recognized as early as 1939,[3] and today they are known to be quite common in the crystal structures of many biological molecules. Surveys of hydrogen bonding in peptides,[4] carbohydrates,[5−7] amino acids,[8] purines and pyrimidines,[9] as well as nucleosides and nucleotides[10] indicate that between 25% and 40% of the bonds in the sample structures are of this type. Bifurcated hydrogen bonds were observed in oligo- and polynucleotide crystal structures[11−13] and are believed to stabilize the DNA molecule. Recent ab initio molecular orbital calculations on base-pair models have pointed to the importance of amino group nonplanarity in these interactions.[14,15]

Beyond the biological examples, bifurcated hydrogen bonds have also been found in several simple systems (mostly in the solid phase). It is a common feature of crystalline hydrates,[16−20] hydrogen peroxide,[21] and alcohols,[22] and has been suggested to be responsible for some peculiar bulk properties of liquid water.[23] Somewhat special cases are the bifurcated $C-H\cdots(N)_2$ interactions in pyrazole and *s*-triazine,[24] the $C-H\cdots(O)_2$ one in flutamide,[25] the bifurcated $O-H\cdots(\pi)_2$ hydrogen bond in 4-nitro-2,6-diphenylphenol,[26] and the $N-H\cdots(Cl)_2$ interaction in 4-chloropyridinium hexachlorostannate(IV).[20] Fluorine has been observed to share the role of acceptor in bifurcated hydrogen bonding with a stronger (mostly oxygen) acceptor.[27]

CHART 1



The above examples refer to intermolecular interactions. Information on intramolecular bifurcated hydrogen bonds is more scarce. Such interactions were proposed for solutions of 1,3-dioxan-5-ols,[28,29] bis(*b*-acylvinyl)amines,[30] and 1,1,1,3,3,3-hexafluoro-2-propanol.[31] Combinations of inter- and intramolecular interactions have been suggested in other cases.[32−34]

Our literature search resulted only in one gas-phase study, by microwave spectroscopy, with evidence for bifurcated intramolecular hydrogen bonding: the only conformer observed in the vapor above 1,3-dioxan-5-ol is stabilized by $O-H\cdots(O)_2$ hydrogen bonding.[35] This observation was supported by a semiempirical INDO study.[36]

In trifluoroethylamine and 2,2-difluoroethylamine, intramolecular double hydrogen bonding, rather than bifurcated hydrogen bonding, was observed between the amino hydrogens and two fluorines of the CF_3 and CF_2 groups, respectively.[37,38] Intramolecular hydrogen bonding in small gaseous molecules is summarized in the review of Wilson and Smith.[39]

Our recent theoretical study of 2-trifluoromethylphenol[40] (**1**) found weak intramolecular hydrogen bonding accompanied by characteristic changes in the geometry of the rest of the molecule, compared with the structures of the parent phenol and trifluoromethylbenzene. In agreement with available experimental results[41−44] the ab initio calculations predicted the hydrogen-bonded syn conformer (Chart 1) to be more stable than the anti form in which the hydroxy hydrogen points away

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from the CF_3 group. At the MP2/6-31+G**//MP2/6-31G** level, corrected for *zero-point vibrational energy*, the energy difference is 7.65 kJ/mol.[40] However, the most interesting result of this investigation was the bifurcated hydrogen bonding, as depicted in Chart 1.

To extend our theoretical study, we decided to perform an experimental investigation of the molecular geometry of **1** by gas electron diffraction. Although better suited for symmetrical molecules,[45,46] this method has been successfully employed for benzene derivatives of lower symmetry, especially when augmented with ab initio calculations.[47,48]

The only experimental study of the molecular geometry of **1**, prior to our work, was by microwave spectroscopy,[44] indicating one major conformer in the vapor. On the basis of the rotational constants, it was suggested to be the syn form.

Experimental Section

A commercial Aldrich product (purity 99%) served as the sample for the electron diffraction experiment in our modified EG-100A apparatus[49] with a membrane nozzle system.[50] Nozzle-to-plate distances of about 50 and 19 cm and nozzle temperatures of about 317 and 319 K were used with six and seven plates selected for analysis, respectively. The electron wavelength was calibrated with TlCl polycrystal.[51] The tracing and data reduction were carried out as in ref 52. The ranges of intensity data used were $1.875 \leq s \leq 13.875$ Å^{-1} and $8.50 \leq s \leq 35.25$ Å^{-1}, with data intervals of 0.125 and 0.25 Å^{-1}, respectively. The numbering of atoms in the molecular model is depicted in Chart 1.

A listing of the total experimental electron diffraction intensities has been deposited as Supporting Information.

Computational Details. Ab initio molecular orbital calculations were carried out on two conformers of 2-fluoromethylphenol using the Gaussian 94 series of programs.[53] The standard 6-31G basis set, augmented with polarization functions, was used at the second-order Møller−Plesset (MP2)[54] level of theory with only the valence orbitals active. HF/6-31G** geometry optimizations followed by vibrational frequency analyses verified the energy minimum and transition-state character of the computed geometries.

Structure Analysis. The least-squares method was applied to the molecular intensities, using a modified version of the program by Andersen et al.[55] The electron scattering factors were taken from available compilations.[56]

The geometry of the molecule was described by bond lengths, bond length differences, bond angles, bond angle differences, angles of torsion (ϕ), and dihedral angles of two planes (ψ) as independent parameters: $C_1{-}C_2$, $(C{-}H)_{mean}$, $\Delta(C_1{-}C_2/C_2{-}C_3)$, $\Delta(C_1{-}C_2/C_3{-}C_4)$, $\Delta(C_1{-}C_2/C_6{-}C_1)$, $\Delta(C_1{-}C_2/C_5{-}C_6)$, $\Delta(C_1{-}C_2/C_1{-}O_7)$, $\Delta(C_1{-}C_2/C_2{-}C_9)$, $\Delta(C_1{-}C_2/(C{-}F)_{mean}$, $\Delta(C_9{-}F_{12}/C_9{-}F_{10})$, $\Delta(C{-}H/O{-}H)$, $C_6{-}C_1{-}C_2$, $C_1{-}C_2{-}C_3$, $C_2{-}C_3{-}C_4$, $C_5{-}C_6{-}C_1$, $O_7{-}C_1{-}C_2$, $C_9{-}C_2{-}C_1$, $C_1{-}O_7{-}H_8$, $(C_2{-}C_9{-}F)_{mean}$, $\Delta(C_2{-}C_9{-}F_{10}/C_2{-}C_9{-}F_{12})$, $H{-}O{-}C_1{-}C_2$ (ϕ_1), $F_{12}{-}C_9{-}C_2{-}C_3$ (ϕ_2), $F_{12}{-}C_9{-}C_2/F_{10}{-}C_9{-}C_2$ (ψ_1), $F_{12}{-}C_9{-}C_2/F_{11}{-}C_9{-}C_2$ (ψ_2) (for numbering of atoms see Chart 1). The initial vibrational amplitudes were estimated by a scaled quantum mechanical (SQM) analysis. The harmonic force field of **1** was computed by density functional theory (DFT, Becke3−Lee−Yang−Parr/6-31G*).[57,58] Scaling of the computed force field and calculation of vibrational amplitudes were done using the program SCALE3.[59] The scale factors were taken from ref 60.

Multistart Monte Carlo global optimizations[61] were carried out with 1000 initial sets. The parameter ranges covered were as follows: for bond lengths and bond angles ±5% from the value of the best single-start results; for angles of torsion the full range of possible values; for amplitudes of vibration ±10% from the value of the single-start results except for the amplitudes of rotation-dependent distances, where the ranges covered were ±50%. An automatic rearrangement scheme was applied to the so-called group refinement approach, which prescribes assumed differences between the amplitudes of closely spaced distances. Least-squares refinements continued until the change in the R factor was less than 0.01 in two consecutive refinements.

Preliminary refinements using local symmetries of D_{6h} and C_{3v} assumed for the benzene ring and the trifluoromethyl group, respectively, and OH and CF_3 torsions constrained in the plane of the benzene ring showed the inadequacy of such simple models to approximate the experimental data. The constraints on local symmetries and the CF_3 torsion were released in subsequent refinements. Constraints from our recent MP2/6-31G** molecular orbital calculations[40] were used for the similar geometrical parameters, viz., for differences in the ring C−C and C−F bond lengths and in the C−C−F bond angles. Such a model was used to test the effects of the hydroxy hydrogen's syn and anti position, the CF_3 rotation, and the variation of the ring Δ(C−C) and CF_3 group constraints. The orientation of the hydroxy hydrogen exerted negligible influence on the geometrical parameters as well as on the R factor. Similarly, variation of the ring Δ(C−C) and the CF_3 constraints resulted only in minor effects. However, both the geometry and the R factor proved to be very sensitive to CF_3 rotation.

Refinements of this model kept producing unreasonable values for the C−O bond lengths and for the dependent ring parameters. This situation did not improve upon introducing multistart Monte Carlo global optimizations[61] or upon employing models consisting of two conformers.[62] We note that the inadequacy of the two-conformer model is in agreement with the computed results.[40] On the basis of the calculated energy difference between the syn and anti forms, only a very small amount (ca. 6%) of the anti conformer can be expected in the gas-phase at the temperature of the electron diffraction experiment.

Reasonable values for all the geometrical parameters were obtained when the benzene ring was constrained at the MP2/6-31G** geometry,[40] corrected by offset values.[63] These empirical corrections represent the error of this computational level for the impact of OH and CF_3 groups on the benzene ring.[64]

A slight but conspicuous discrepancy appeared in the region $r > 4.5$ Å of the experimental and theoretical radial distributions. To account for possible shrinkage effects, we introduced the three $C_5{\cdots}F$ distances as additional independent parameters. Of the geometrical parameters, only the C−O bond length changed appreciably because of this change in the refinement scheme. According to our recent theoretical study,[40] the C−O bond length is expected to be shorter by about 0.007 Å with respect to the C−O bond in phenol (1.381 ± 0.004 Å[65]). The decrease of the C−O bond length upon extension of the independent parameters in **1** is in agreement with the expectations; however, its magnitude appears to be somewhat exaggerated (cf. Table 1). We note, however, the large experimental error for this parameter.

Selected geometrical parameters of **1** are given in Table 1. The total experimental errors were estimated as described in ref 66. The experimental data yielded too short O−H and C−H bond distances, which may be a consequence of background effects. To alleviate the importance of the actual values, their

TABLE 1: Selected Geometrical Parameters[a] of 2-Trifluoromethylphenol

	distance (r_g, Å)		angle (deg)
$(C-C)_{Ar,mean}$	1.395(4)	$O-C_1-C_2$	121.0(12)
$C-O$	1.362(11)	$C-O-H$	105(6)
C_2-C_9	1.510(5)	$C_9-C_2-C_1$	120.7(8)
$(C-F)_{mean}$	1.358(6)	$(C-C-F)_{mean}$	113.2(3)
$(C-H)_{mean}$	1.074(10)	ϕ_2	10.1(8)
$O-H$	0.94(2)		
$H_8 \cdots F_{10}$	2.05(6)		
$H_8 \cdots F_{11}$	2.42(6)		
$O \cdots F_{10}$	2.792(13)		
$O \cdots F_{11}$	3.098(21)		
R	3.66%		

[a] Estimated total errors[66] in parentheses.

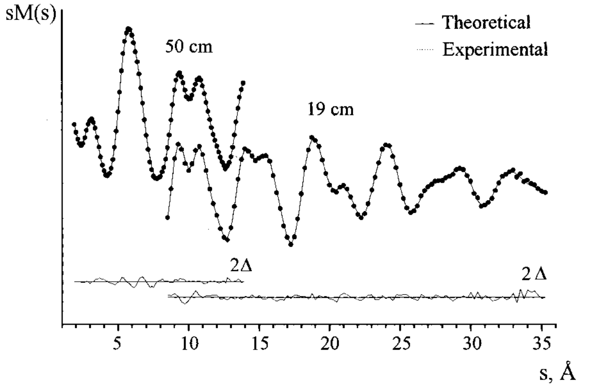

Figure 1. Molecular intensity curves for the two camera distances (Δ = experimental − theoretical).

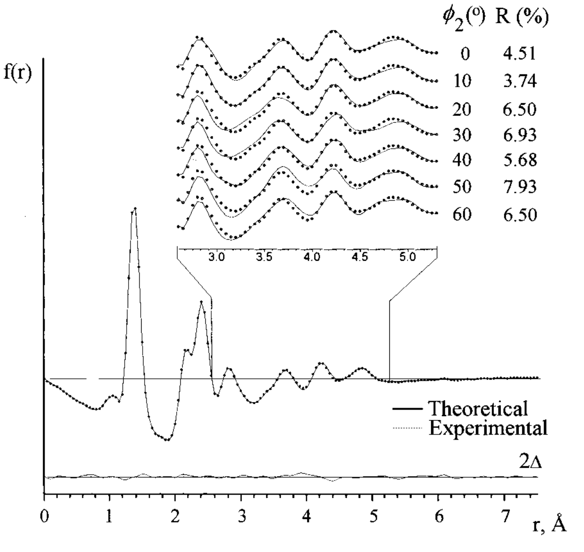

Figure 2. Radial distribution curves (Δ = experimental − theoretical).

estimated errors were doubled. The uncertainty of these bond lengths does not have any bearing on the conclusion of this investigation. The molecular intensity and radial distribution curves from the final refinements are shown in Figures 1 and 2, respectively. The correlation coefficients, ρ_{ij}, having absolute values greater than 0.6 are listed in Table 2.

Discussion

The most interesting feature of the molecular geometry of **1** is the angle of CF_3 torsion. According to our DFT-based SQM analysis (vide supra), the CF_3 torsional motion is represented by the lowest frequency fundamental of the molecule and is a large-amplitude motion. This hinders the determination of the equilibrium value of the torsional angle. Our prior quantum chemical calculations[40] indicated a slightly nonsymmetrical equilibrium geometry for the syn conformer of **1**, in which both the OH and CF_3 groups are twisted from the coplanar position with the benzene ring (ϕ_1 by 14° and ϕ_2 by 12° at the MP2/6-31G** level). However, the saddle-point structure with both groups being in the plane of the benzene ring, representing the symmetric bifurcated hydrogen bonding, lies only marginally higher in energy, by 0.11 kJ/mol (10 cm^{-1}) at the MP2/6-31+G**//MP2/6-31G** level. The frequency of the CF_3 torsional vibration was estimated to be about 50 cm^{-1} by our SQM analysis, with a much higher frequency of OH torsion, ca. 300 cm^{-1}. Relatively large uncertainties can be assigned to these values because of the difficulties in the description of the flat potential energy surface (PES) and the anharmonicity of large-amplitude vibrations. Nevertheless, it is reasonable to suppose that the ground-state vibrational level of the CF_3 torsion may lie above the saddle point of the PES, corresponding to the symmetrical bifurcated configuration. Furthermore, the higher CF_3 torsional levels are considerably populated at room temperature, owing to the small excitation energy. At room temperature, and certainly at the temperature of the electron diffraction experiment, the molecule may be characterized by OH and CF_3 torsional vibrations about the symmetric bifurcated equilibrium geometry.

TABLE 2: Elements of the Correlation Matrix Exceeding 0.6 in Absolute Value

i	j	ρ_{ij}
C_1-C_2	$\Delta(C_1-C_2/C_1-O_7)$	0.713
	$\Delta(C_1-C_2/C_2-C_9)$	0.691
	$\Delta(C_1-C_2/(C-F)_{mean})$	0.872
	$(C_2-C_9-F)_{mean}$	−0.637
	$l(C_1-C_2)$	−0.873
	$l(C_1 \cdots C_3)$	−0.622
$\Delta(C_1-C_2/C_1-O_7)$	$\Delta(C_1-C_2/C_2-C_9)$	0.619
	$l(C_1-C_2)$	−0.620
	$l(C_5 \cdots C_9)$	−0.624
$O_7-C_1-C_2$	$C_9-C_2-C_1$	−0.886
	ϕ_2	0.753
	$l(C_5 \cdots C_9)$	0.722
$\Delta(C_1-C_2/C_2-C_9)$	$l(C_1-C_2)$	−0.664
$C_9-C_2-C_1$	$l(C_5 \cdots C_9)$	−0.808
$\Delta(C_1-C_2/(C-F)_{mean})$	$(C_2-C_9-F)_{mean}$	−0.901
	$l(C_1-C_2)$	−0.778
	$l(C_1 \cdots C_3)$	−0.715
$(C_2-C_9-F)_{mean}$	$l(C_1 \cdots C_3)$	0.600
$C_5 \cdots F_{10}$	$C_5 \cdots F_{11}$	−0.992
	$C_5 \cdots F_{12}$	−0.998
$C_5 \cdots F_{11}$	$C_5 \cdots F_{12}$	0.986
$l(C_1-C_2)$	$l(C_1 \cdots C_3)$	0.683

Investigation of the CF_3 torsion was performed with the original parameter set, i.e., applying the geometrical constraints on all dependent distances, including the $C_5 \cdots F$ distances. Seven rotamers were refined with constrained CF_3 angle of torsion, ϕ_2, in the interval 0−60° in steps of 10°. Variation of the torsional angle can be monitored quite sensitively in the outer region, $r > 2.5$ Å, of the radial distributions (Figure 2). Consistent with the theoretical results (vide supra), the agreement is rather poor between the theoretical and experimental radial distribution curves for the rotamers with angles of CF_3 torsion between 20 and 60°. The best agreement is observed for $\phi_2 = 10°$, corresponding to the refined value. The agreement worsens again at $\phi_2 = 0°$. However, it is impossible to distinguish between a relatively rigid form with $\phi_2 = 10°$ and a flexible form with $\phi_2 = 0°$ on the basis of electron diffraction data alone. In any case, the electron diffraction data provide a

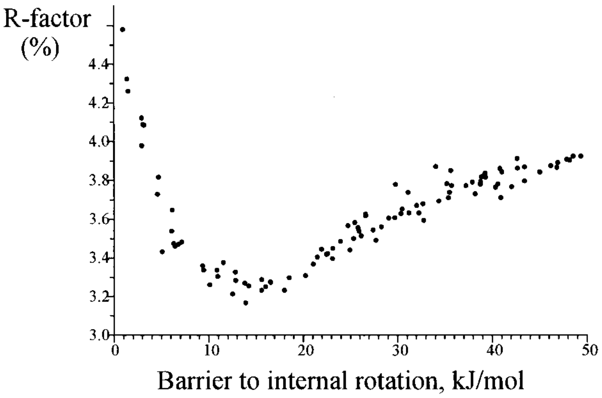

Figure 3. Graphical estimation of the barrier height to internal rotation of the CF_3 group in 2-trifluoromethylphenol.

strong support for the bifurcated character of the intramolecular hydrogen bonding in 2-trifluoromethylphenol.[40,44]

For the rotational barrier of the CF_3 group, 6 kJ/mol was estimated from MP2/6-31+G**//MP2/6-31G** calculations corrected for *zero-point vibrational energy*.[40] The determination of the rotational barrier from electron diffraction data requires knowledge of the potential function of this large-amplitude motion including the equilibrium value of the torsional angle. Assuming the symmetric bifurcated structure (Chart 1) for the equilibrium geometry, the average angle of torsion (Table 1) leads to an estimated barrier of the CF_3 rotation of 12 ± 2 kJ/mol.[67]

In addition, another method[68] has also been used to estimate the rotational barrier, the so-called dynamic model.[45] Seven pseudoconformers were considered with the CF_3 angle of torsion, ϕ_2, in the interval 0−60° in steps of 10°, with double statistical weights for all conformers except the one with the coplanar $-C_1-O_7-H_8\cdots F_{10}-C_9-C_2-$ moiety ($\phi_2 = 60°$). The contributions of the rotation-dependent distances to the molecular scattering were calculated from a Boltzmann distribution. Different values of the barrier height were assumed in the interval of 0−50 kJ/mol utilizing a wide array of initial geometries in our Monte Carlo optimization routine.[61] The results of the calculations are presented in Figure 3. The barrier to internal rotation was derived by fitting a parabolic function around the minimum of the curve formed by the scatter (*R* factor) points. This suggested a barrier of 15 ± 3 kJ/mol. When the data from the different sources are assessed, there is satisfactory agreement between the computed and the experimental barriers. Compared with the free rotation of the CF_3 group in trifluoromethylbenzene,[69] the present results point unambiguously to a well-defined conformer and, accordingly, to the constraining effect of hydrogen bonding.

According to our literature search, such a bifurcated interaction of the CF_3 group is very scarce. Only one report is known to us, an IR study of 1,1,1,3,3,3-hexafluoro-2-propanol.[31] In molecules containing CF_3 and CF_2 groups, single hydrogen bonds have been found.[70−72] The formation of the bifurcated interaction in **1** may be the result of several effects. Steric and electronic influence of the benzene ring may contribute to making the two weaker interactions more advantageous rather than a single and stronger one.

To account for the effects of the benzene ring, we carried out a theoretical study of 2-fluoromethylphenol (**2**) at the MP2/6-31G** level.[73] This compound models the hydrogen-bonding interaction between the OH hydrogen and a single fluorine in the presence of the benzene ring. The global minimum on the PES of **2** corresponds to a structure in which the hydrogen-bonded $-O-H\cdots F-C-$ moiety is out of the plane of the benzene ring, the $H-O-C_1-C_2$ and $F-C_9-C_2-C_1$ torsions being 22.6° and 50.4°, respectively. The length of the hydrogen bond was calculated to be 1.91 Å. The planar arrangement with the shortest (O)H···F distance (1.80 Å) is a transition state, being higher in energy by 8.4 kJ/mol than the hydrogen-bonded global minimum.[74] Hence, an "out-of-plane" type interaction is preferred even with one fluorine acceptor, indicating considerable forces against the coplanar arrangement. The main effects contributing to the arrangement of the interacting groups may be orbital overlaps as well as ligand−ligand repulsion of the ortho-positioned substituents.

Conclusions

The formation of bifurcated intramolecular hydrogen bonding in 2-trifluoromethylphenol was confirmed by the present electron diffraction analysis. The joint analysis of theoretical and experimental results indicates that the H···F bonds are weak and that the large-amplitude torsional vibration of the CF_3 group appears in a flat valley of the potential energy surface, possibly around the symmetrically bifurcated arrangement. Compared with the freely rotating CF_3 group in trifluoromethylbenzene, the well-defined conformer of 2-trifluoromethylphenol indicates the constraining effect of intramolecular hydrogen bonding.

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Supporting Information Available: Table of experimental electron diffraction intensities of hydrogen bonding in 2-trifluoromethylphenol (2 pages). Ordering information is given on any current masthead page.

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(74) MP2/6-31G** energy corrected for *zero-point vibrational energy* (ZPVE) from HF/6-31G** frequency analysis. The ZPVE was scaled by a factor of 0.89, taking care of the known overestimates at this level.[76]

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