# Shapes of Molecules by Millimeter-Wave Spectroscopy: 2-Phenylethanol

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We have detected one conformer of 2-phenylethanol and determined its shape using Stark-modulated free jet microwave spectroscopy. By comparing observed and ab initio predicted spectroscopic rotational constants and hydroxyl-deuteration isotopic substitution coordinates, the species has been identified with a gauche conformer, designated as **1**, in which the hydroxyl hydrogen atom is involved in an intramolecular hydrogen bond with the $\pi$-electron cloud of the aromatic ring. Stark effect measurements yielded electric dipole moment values of $\mu_a = 1.251(3)$ D and $(\mu_b^2 + \mu_c^2)^{1/2} = 1.102(10)$ D, and hence $\mu_{total} = 1.667(10)$ D. Previously published molecular mechanics and RHF level ab initio calculations predict that other conformers are of comparable stability to **1**. However, when electron correlation is included at the MP2/6-31G(d,p) level, the predicted energy of **1** is substantially (ca 8 kJ mol$^{-1}$) lower than that of all the other conformers. This is in full accord with our identification of only one conformer in our spectroscopic searches at a pre-expansion temperature of 363 K.

## Introduction

2-Phenylethanol is a 1,2-disubstituted ethane, the oxygen analogue of the neurohormone 2-phenylethylamine (PEA), and is structurally related to numerous other amines that have neurochemical activity. Information regarding the molecular shape[1] of such compounds is of particular interest in the context of gaining improved insights into structure-dependent biological activity. It has been suggested that the most stable shapes of such species may be stabilized by a nonclassical hydrogen bond interaction between a hydrogen attached to a nitrogen or oxygen on the side chain and the $\pi$-electron cloud of an aromatic or heterocyclic ring. Such interactions have been found to stabilize the observed lowest energy conformers of both 2-phenylethylamine[2] and histamine.[3]

An intramolecular hydrogen bond interaction of this kind was first suggested for 2-phenylethanol in the 1950s.[4] The authors of most of the subsequent studies[5] agreed with the hypothesis, but not all.[6] Later, IR studies found the intramolecular bond energy in 2-phenylethanol to be ca. 11 kJ mol$^{-1}$ in the gas phase,[7] compared with ca. 6.7 kJ mol$^{-1}$ in $CCl_4$ solution.[8]

Conflicting results were obtained in two recent studies involving 2-phenylethanol. Both of the investigations studied dilute solutions of 2-phenylethanol in organic solvents using $^1$H NMR and IR spectroscopy. The first concluded that the influence of a hydroxyl−aromatic interaction in stabilizing the conformational geometry of 2-phenylethanol was negligible.[8] The conclusion of the second study[9] was that 2-phenylethanol was stabilized to the extent of ca. 5.8 kJ mol$^{-1}$. On the basis of a comparison of the IR hydroxyl stretching bands with those of other unsaturated alcohols, the interaction was determined to be intramolecular hydrogen bonding between the hydroxy hydrogen atom and the $\pi$-electrons of the benzene ring.

The present study aims to contribute both via experiment and theory to a more informed general picture of the potential energy surface encompassing the various conformers of disubstituted ethanes and on the energetics of hydrogen bonds involving $\pi$-electron systems specifically exemplified by 2-phenylethanol. Such increased understanding has broader implications in fields such as supramolecular chemistry and crystal engineering, where extended hydrogen bonded networks to $\pi$-systems are involved in shape-specific complexation[9] and in relation to the long-standing problem of protein folding. The issue of the role of hydrogen bonds to $\pi$-systems such as tyrosine and phenylalanine in determining the ultimate structure of proteins remains an area of some controversy.[10] Additionally, a study of such hydrogen bonds in an intramolecular context helps illuminate the related small molecule studies of intermolecular bonds in the bimolecular complexes linking small polar hydrides such as water and ammonia with the $\pi$-electron systems ethylene and benzene.

## Previous Work

The conformations of 2-phenylethanol have been explored theoretically in an earlier study using the semiempirical MNDO method and two molecular mechanics methods.[11] The conformer believed to involve an intramolecular hydrogen bond was predicted to be the lowest energy conformer for only one of these methods (and in this calculation a second conformer also was predicted to be of comparable energy). The conformational energies also were determined by performing frozen structure Hartree−Fock calculations (using STO-3G and 4-31G basis sets) on geometries determined by the MNDO method. In each case, these calculations predicted the all-trans conformer **5** to be the lowest in energy.

## Methodology

**Experimental.** The free-jet expansion, Stark-modulated spectrometer used in the present study is based on a design that has previously been described.[12] Liquid 2-phenylethanol (99%), obtained from Aldrich and used without further purification, was vaporized at temperatures ranging from 90 to 200 °C in a stream of argon at a pressure of ca. 30 kPa. Following free-jet expansion, the rotational temperature was found to be ca. 2−5 K under the conditions employed. O-deuterated 2-phenylethanol

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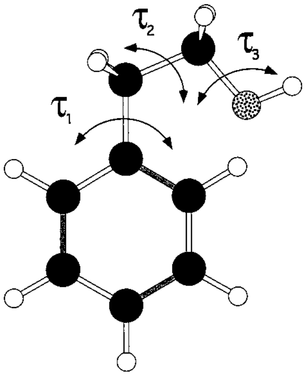

**Figure 1.** Definition of the "1,2-disubtituted ethane" torsional angles that distinguish the conformers of 2-phenylethanol.

**TABLE 1: Experimentally Derived Rotational and Centrifugal Distortion Constants[a] for the Observed Conformer of 2-Phenylethanol and for the Corresponding O-Deutero Isotopomer**

| | normal isotopomer | O-deutero species |
|---|---|---|
| *A*/MHz | 3338.01076(99) | 3285.8709(27) |
| *B*/MHz | 1083.49102(85) | 1075.2363(29) |
| *C*/MHz | 958.89987(92) | 952.4135(35) |
| $D_j$/kHz | 0.21612(82) | 0.2127(30) |
| $D_{jk}$/kHz | 0.8077(22) | 0.8313(75) |
| $D_k$/kHz | 0.4076(64) | 0.328(20) |
| $d_1$/kHz | −0.00215(15) | |
| $d_2$/kHz | −0.00544(11) | |
| no. of lines in fit | 86[b] | 65[b] |
| rms residual/MHz | 0.015 | 0.038 |

[a] The numbers in parentheses are one standard deviation in units of the least significant quoted digit. [b] Observed frequencies, assigned quantum numbers, and residuals from the fitting calculations are listed in Tables 1S and 2S of the Supporting Information.

was prepared by shaking 2-phenylethanol with acidified $D_2O$/$H_2O$ = 1:1 for 5 min, making the solution slightly alkaline, and separating the organic layer.

The microwave absorption spectrum was first investigated via an extended spectral search scan over a wide frequency range (48−72 GHz). In these strip chart recorded wide searches, the pre-expansion temperature was 90 °C and the sensitivity limit was ca. 10% of the strongest line detected. Once located via the wide search scan, each detected line was digitally acquired via repetitively averaged narrow band scans, and line frequencies measured by least-squares fitting of a Lorentzian function to each line profile.

The 33 kHz square wave Stark modulation system employed parallel-plate electrodes with a separation of ca. 3.5 cm. The square wave modulation field was established by opposed polarity equal amplitude ground-clamped voltage waveforms applied to the opposing electrodes. For dipole moment measurements, the various $M_J$ lobes for selected transitions were scanned and digitally acquired and the Stark frequency shift was measured by least-squares fitting a Lorentzian line shape profile. The preset Stark voltages were measured via a precision a/d converter. The effective electrode spacing, which includes allowance for any scale factor error in the voltage measurement, was calibrated from a series of Stark shift measurements on $SO_2$ for which a precise dipole moment has been determined via molecular beam electric resonance.[13]

**Theoretical.** Predictive ab initio calculations of molecular structure, conformational energy, and electric dipole moments were performed on all the feasible 2-phenylethanol conformers to assist in the rotational assignment of the observed spectrum and to serve as a guide to the identification of the species present in the expanding jet. The three important torsional angles that distinguish the different conformers of 2-phenylethanol are defined in Figure 1. Ab initio calculations were performed using the GAUSSIAN 94 package.[14] To add to our knowledge of the relative reliability of different quantum chemical methods, the structure optimizations were repeated over a sequence of increasingly more elaborate (and computationally more expensive) methods, ranging from HF/STO-3G to MP2/6-31G(d,p). Past experience led us to anticipate that only the latter level of approximation (or better) with the additional inclusion of vibrational zero-point energy would suffice to predict the relative energies of the conformers with adequate reliability (i.e., with probable errors less than *RT* at 400 K).[3b,15] Furthermore, the inclusion of thermal Gibbs energy and a more general exploration of the conformational potential energy surface may be needed to predict the relative abundances of the conformers occurring in the jet spectrometer. To this end, ab initio vibrational frequency calculations were performed on all conformers studied and the energy barriers between adjacent conformers were explored via constrained optimizations.

## Results and Discussion

**Identification.** We observed a total of 86 lines (primarily $\mu_b$ or $\mu_c$ type) in the frequency range 48−68 GHz that we were able to assign an asymmetric rotor. No moderate or strong unassigned lines were detected in the wide band search scans. It is a characteristic of the collisional cooling process in the free-jet expansion that all low-frequency vibrational modes are efficiently cooled, and hence the torsional vibrational satellites that are a major complicating feature of past conventional microwave spectrometer studies of disubstituted ethanes are not detected in our spectrometer. Table 1 lists the spectroscopic constants ($I^R$ representation, *S* reduction[16]) derived by a least-squares fit to these lines. A full listing of the observed transitions and the least-squares fit residuals is given in Table 1S of the Supporting Information. Similarly are listed in Table 1 the spectroscopic parameters derived from the measurement of 66 lines assigned to the O-deutero isotopomer of the same species for which the full listing of observed transitions is given in Table 2S of the Supporting Information.

Principal axis dipole moment component values were determined from the analysis of Stark effect measurements on the $M_J = 1$ and 2 lobes of the prolate-degenerate paired $\mu_c$-type transitions $\{10_{73}-9_{63}; 10_{74}-9_{64}\}$ and $\{8_{80}-7_{70}; 8_{81}-7_{71}\}$. The much larger linear Stark shifts of the Stark lobes from the merged pairs of degenerate $\mu_b$ transitions corresponding to the same zero-field frequency depended only upon $\mu_a$ and were not measured. As with all transitions for 2-phenylethanol with resolvable Stark effects in the 48−72 GHz band, the measured Stark shifts from prolate-degenerate levels had identical dependence on $\mu_b$ and $\mu_c$, and hence it was possible to determine only the combination $(\mu_b^2 + \mu_c^2)^{1/2}$. The resulting best-fit dipole moment component values are listed in Table 2. The details of the 50 individual Stark shift measurements and the fit residuals are listed in Table 3S of the Supporting Information.

The predicted ab initio structures of the five distinct conformers of 2-phenylethanol are shown, together with the nomenclature adopted in this work, in Figure 2. The relative energies are listed in Table 3, which also gives relative energies including vibrational zero-point energy (i.e., Gibbs free energies at 0 K) and the Gibbs energies at 363 K, the pre-expansion temperature used for the experimental search scan of the rotational spectrum. The most stable species is predicted to be the gauche conformer (**1**). Then, there is a clustering of comparable energies for a

**TABLE 2: Experimentally Derived Principal Axis Dipole Moment Components for the Observed Conformer of 2-Phenylethanol**[a]

| | |
|---|---|
| $\mu_a$/D | 1.251(3) |
| $(\mu_b2 + \mu_c2)^{1/2}$/D | 1.102(10) |
| $\mu_{total}$/D | 1.667(10) |
| number of transitions used | 4 |
| number of Stark shift measurements | 50 |
| rms residual/MHz | 0.069 |

[a] The numbers in parentheses are one standard deviation in units of the least significant quoted digit. Stark shifts at a series of voltages were measured for the transitions $10_{7,3}-9_{6,3}$, $10_{7,4}-9_{6,4}$, $8_{8,0}-7_{7,0}$, and $8_{8,1}-7_{7,1}$. Voltages, observed Stark shifts, $M_J$ quantum numbers, and residuals from the dipole moment fitting calculation and from the Stark electrode spacing calibration are detailed in Tables 3S and 4S of the Supporting Information, respectively.

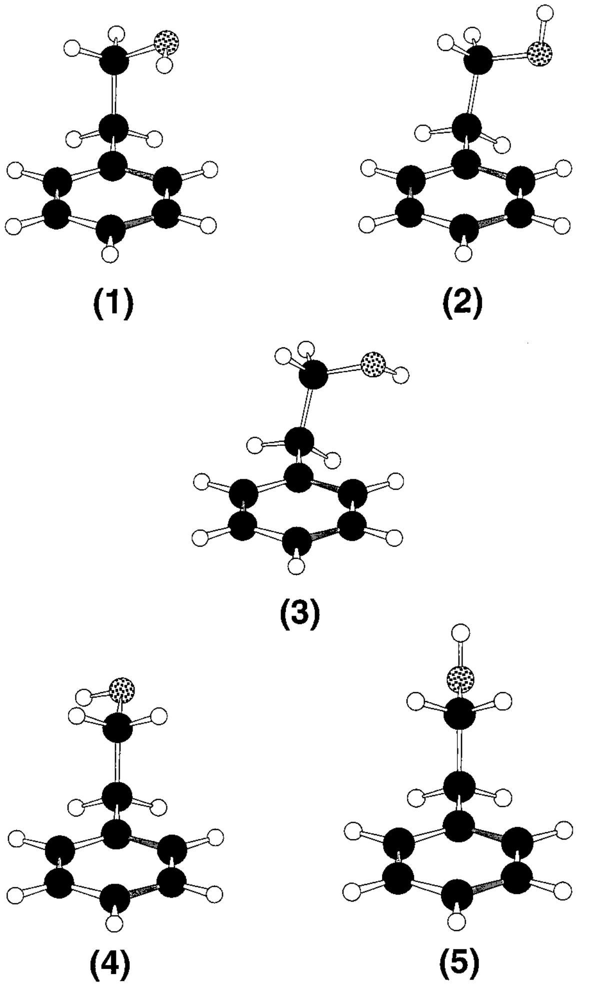

**Figure 2.** Theoretically predicted structures from ab initio MP2/6-31G(d,p) calculations of the stable conformers of 2-phenylethanol.

trans species (**4**) and another gauche conformer (**2**), with relative energies predicted to be in the range 7.8−8.3 kJ mol$^{-1}$ followed by the second trans species **5** and the final gauche species **3**, which are of highest energy, approaching 9.6 kJ mol$^{-1}$.The spectroscopic constants predicted from the ab initio optimized structures for these conformers are listed in Table 4. It is evident that for **1** the predicted rotational constants are in best agreement with those observed for the observed 2-phenylethanol species. Clearly the two trans conformers, **4** and **5**, can be ruled out as having very different rotational constants from those observed. Of the three gauche conformers, the one with predicted constants closest to those observed is **1**. The measured rotational constants are within 3% of those calculated for conformer **1** and within 5% and 6% for conformers **2** and **3**. We thus have an indication on just this basis that the observed conformer is **1**.

**TABLE 3: Predicted Relative ab Initio Energies and Abundances for the Conformers of 2-Phenylethanol Optimized at the MP2/6-31G(d,p) Level**

| species | $\Delta E_{MP2}$ (kJ mol$^{-1}$) | $\Delta E_{MP2}$ + ZPE[a] (kJ mol$^{-1}$) | $\Delta G_{363K}$[a] (kJ mol$^{-1}$) | mole fraction[b] ($T$ = 363 K) |
|---|---|---|---|---|
| **1** | 0.00 | 0.00 | 0.00 | 0.57 |
| **2** | 8.29 | 6.98 | 5.23 | 0.10 |
| **3** | 9.58 | 8.67 | 6.36 | 0.07 |
| **4** | 7.78 | 6.81 | 4.49 | 0.13 |
| **5** | 8.80 | 7.35 | 4.60 | 0.13 |

[a] The vibrational zero-point and thermal Gibbs energy contributions are predicted from Gaussian 94 harmonic force field calculations performed at the MP2/6-31G(d,p) level. [b] Calculated from the theoretical relative Gibbs energies.

The measured electric dipole moment components also listed for comparison in Table 4 are not decisive, especially since $\mu_b$ and $\mu_c$ could not be measured independently through the Stark effect. At best, the measured dipole moment components serve to eliminate **5** as the observed species because of its significantly smaller than observed value of $\mu_a$.

As further confirmation of the identity of the observed conformer, we considered the assigned O-deutero species. The substitution coordinates for the hydroxyl hydrogen were calculated via Kraitchman's equations[17] and are listed in Table 5. This provides the clearest identification of the observed species as **1**, with the value of $|a|$ being particularly indicative.

The identification of the observed vapor-phase conformer with **1** is consistent with the most elaborate of our ab initio calculations, the latter predicting conformer **1** to be more stable than the next most stable by 7.8 kJ mol$^{-1}$. For this species, the lowest vibrational frequency is calculated (harmonic approximation, MP2/6-31G(d,p) level) to be 53 cm$^{-1}$. Given that no vibrational satellites were detected at signal levels >0.1 of the observed ground state spectrum, this implies an upper limit to the post-expansion vibrational temperature of ca. 35 K. This is entirely consistent with previous observations that excited states of the low-frequency vibrational modes (which are the excited states that are likely to be significantly populated at the preexpansion temperature) are efficiently cooled in the free-jet expansion when argon is used as the carrier gas.

**Geometry.** The geometrical parameters predicted by the molecular orbital optimizations showed no unexpected values for bond lengths and angles. The most subtle effect noted was in the methylene C−H lengths adjacent to the hydroxyl group. For those conformers where one of the hydrogen atoms is trans to the OH, i.e., **1**, **3**, and **4**, that C−H length is 108.95−108.98 pm, while otherwise these C−H lengths fall in the range 109.61−109.66 pm. Such an effect for C−H trans to OH has been reported in calculations on methanol.[18,19]

The most stable conformer of 2-phenylethanol is **1**, in which the hydroxyl hydrogen is poised above the benzene ring. This suggests that the weak interaction ("hydrogen bond") between the external hydroxyl and the benzene ring is important, as has been discussed by earlier workers.[4,5] Analogous stabilizing effects of side-chain amino groups with aromatic or heterocyclic rings have been adduced in studies of 2-phenylethylamine[2] and of histamine.[3] If the greater stability of conformer **1**, as compared with the other four conformers, can be attributed primarily to this interaction, then the molecular orbital calculations imply that its strength is about 8 kJ mol$^{-1}$. This is to be compared with the value, based on IR studies,[7] of 11 kJ mol$^{-1}$. It also is of some interest to compare this estimate of bond

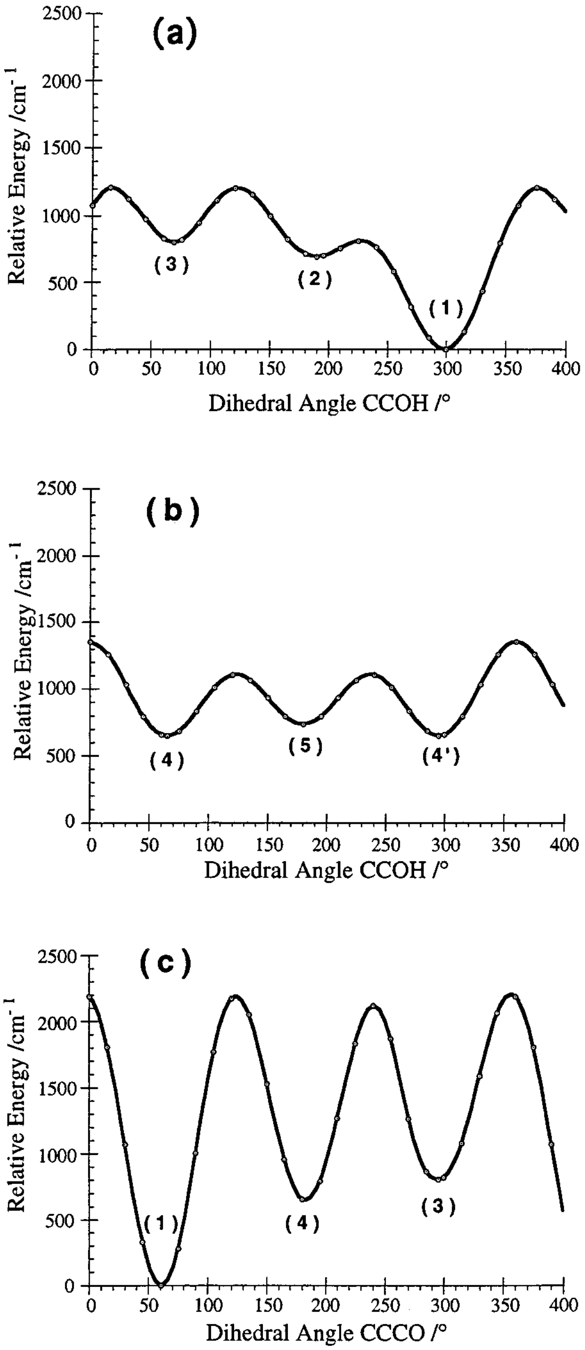

**Figure 3.** Interconformational energy profiles predicted from ab initio MP2/6-31G(d,p) calculations on 2-phenylethanol constrained in a single geometric parameter. The low barriers shown in (a) for the gauche conformers will enable efficient relaxation of both **2** and **3** to the lower energy hydrogen bonded **1**. The low barriers shown in (b) for the trans conformers enable rapid relaxation from **5** to **4**. The significantly higher barriers shown in (c) preclude efficient relaxation from the trans conformer **4** to the gauche conformer **1**.

**TABLE 4: Predicted Geometric and Spectroscopic Parameters from ab Initio MP2/6-31G(d,p) Calculations**

| | 2-phenylethanol conformer | | | | | |
|---|---|---|---|---|---|---|
| parameter[a] | **1** | **2** | **3** | **4** | **5** | observed |
| $\tau_1$/deg | 88.3 | 99.4 | 101.8 | 88.7 | 88.6 | |
| $\tau_2$/deg | 60.6 | 67.2 | 64.9 | 177.0 | 180.0 | |
| $\tau_3$/deg | 298.8 | 189.8 | 68.4 | 65.0 | 180.0 | |
| $E_{rel}$/kJ mol$^{-1}$ | 0 | 8.29 | 9.58 | 7.78 | 8.80 | |
| $A$/MHz | 3335.9 | 3470.4 | 3469.2 | 4384.9 | 4421.8 | 3338.0 |
| $B$/MHz | 1112.1 | 1088.2 | 1077.3 | 856.8 | 859.2 | 1083.5 |
| $C$/MHz | 964.0 | 915.9 | 905.1 | 767.0 | 769.4 | 958.9 |
| rms(O−C)[b] | 17 | 80 | 82 | 628 | 648 | |
| $\mu_a$/D | 1.4 | 1.1 | 1.4 | 1.0 | 0.3 | 1.25 |
| $\mu_b$/D | 1.0 | 0.8 | 1.0 | 1.2 | 0.0 | |
| $\mu_c$/D | 0.1 | 1.1 | 0.1 | 0.5 | 1.5 | |
| $\mu_{tot}$/D | 1.8 | 1.7 | 1.8 | 1.6 | 1.6 | 1.67 |

[a] A complete listing of ab initio predicted geometric parameters is given in Table 5S of the Supporting Information. [b] Root-mean-square deviation in megahertz between the observed and ab initio rotational constants.

**TABLE 5: Principal Axis Coordinates of the Hydroxyl H Atom for the Conformers of 2-Phenylethanol Predicted at the MP2/6311++G(d,p) Level Shown in Comparison with the Corresponding Values Obtained from the Application of Kraitchman's Equations to the Experimental Moments of Inertia Found for the Normal and OD Isotopomers of the Observed Species**

| species | $\|a\|$ (pm) | $\|b\|$ (pm) | $\|c\|$ (pm) |
|---|---|---|---|
| **1** | 153 | 112 | 103 |
| **2** | 304 | 116 | 127 |
| **3** | 304 | 127 | 25 |
| **4** | 387 | 76 | 16 |
| **5** | 414 | 7 | 98 |
| observed[a] | 154.0(5) | 109.4(2) | 110.8(2) |

[a] Calculated via Kraitchman's equations from the rotational constant values for the observed species and its O-deutero isotopomer as listed in Table 1.

strength with the experimental upper bound of 11.7 kJ mol$^{-1}$ established by Gotch and Zwier for the benzene···water complex.[20]

The aromatic carbon atom closest to the oxygen atom in conformer **1** of 2-phenylethanol is at a distance of 295 pm. We have little data for comparison, but we judge this interaction to be similar to that in 2-phenylethylamine where the N···C distance in the bent intramolecular hydrogen bond also is computed to be 295 pm.[2] Again it is useful to contrast this with the experimentally determined c.m. distance between the two molecules in the benzene···water complex of 310 pm[20] and for the case of the benzene···ammonia complex, where the distance from the nitrogen atom to the benzene plane also was found to be somewhat larger at 359 pm.[21]

However, because the internal hydrogen bond is constrained by the rest of the molecule so that it is bent rather than linear, it is more relevant to consider the H···C distances. In 2-phenylethylamine,[2] the internuclear distance of the interacting amino hydrogen to the nearest aromatic C was computed to be (see Table 4 of ref 2) 264 and 269 pm for the two most stable conformers. These two species were detected in the jet spectrometer. They are predicted to be lower in internal energy by more than 7 kJ mol$^{-1}$ than the third gauche conformer, for which no such internal interaction is present. In conformer **1** of phenylethanol, the corresponding H···C distance is 255 pm. For this compound also the computed relative energies of the conformers imply that the interaction produces a stabilization of about 7 kJ mol$^{-1}$, although the shorter C···H distance in phenylethanol would indicate an energetically stronger interaction than for the amine.

**Reliability of Less Elaborate Quantum Chemical Methods.** As part of the predictive phase of this study, an extended series of quantum chemical structure optimizations were performed. Increasing levels of sophistication were employed within the Gaussian basis family with SCF calculations ranging from minimal basis HF/STO-3G through to the much larger split valence 6-31G and 6-31G(d,p) basis sets, a density functional calculation at the B3LYP/6-31G(d,p) level and finally the MP2/6-31G(d,p) calculation that was used to assign the experimental

**TABLE 6: Comparative Reliability of Predicted Geometric and Spectroscopic Parameters for Conformer 1 from ab Initio Calculations at Different Levels**[a]

| | HF/STO-3G | HF/3-21G | HF/4-31G | HF/6-31G | HF/6-31G(d) | HF/6-31G(d,p) | BLYP/6-31G(d,p) | MP2/6-31G(d,p) | obsd |
|---|---|---|---|---|---|---|---|---|---|
| $A$ | 3402.1 | 3421.9 | 3441.6 | 3429.8 | 3460.6 | 3462.6 | 3372.8 | 3335.9 | 3338.0 |
| $B$ | 1043.6 | 1110.0 | 1078.6 | 1067.9 | 1070.0 | 1069.6 | 1057.1 | 1112.1 | 1083.5 |
| $C$ | 929.5 | 947.8 | 941.3 | 934.2 | 938.1 | 937.9 | 904.4 | 964.0 | 958.9 |
| $\Delta A\%$ | 1.9 | 2.5 | 3.1 | 2.8 | 3.7 | 3.7 | 1.0 | −0.1 | |
| $\Delta B\%$ | −3.7 | 2.4 | −0.5 | −1.4 | −1.2 | −1.3 | −2.4 | 2.6 | |
| $\Delta C\%$ | −3.1 | −1.2 | −1.8 | −2.6 | −2.2 | −2.2 | −5.7 | 0.5 | |
| rms | 3.0 | 2.1 | 2.1 | 2.3 | 2.6 | 2.6 | 3.6 | 1.6 | |
| $\|a\|$ | 166 | 161 | 170173 | 168 | 169 | 168 | 153 | 154.0 | |
| $\|b\|$ | 97 | 124 | 118116 | 108 | 108 | 123 | 112 | 109.4 | |
| $\|c\|$ | 127 | 111 | 122125 | 122 | 123 | 102 | 103 | 110.8 | |
| $\Delta\|a\|\%$ | 7.8 | 4.5 | 10.4 | 12.3 | 9.1 | 9.7 | 9.1 | −0.6 | |
| $\Delta\|b\|\%$ | −11.3 | 13.3 | 7.9 | 6.0 | −1.3 | −1.3 | 12.4 | 2.4 | |
| $\Delta\|c\|\%$ | 14.6 | 0.2 | 10.1 | 12.8 | 10.1 | 11.0 | −7.9 | −7.0 | |
| rms | 11.6 | 8.1 | 9.5 | 10.8 | 7.9 | 8.5 | 10.0 | 4.3 | |
| lowest | **1** | **1** | **1** | **1** | **1** | **1** | **1** | **1** | **1** |
| next | **4** | **2** | **5** | **5** | **5** | **5** | **4** | **4** | |
| $\Delta E$(N−L) | 0.72 | 2.92 | 2.12 | 1.52 | 3.43 | 3.19 | 4.73 | 7.78 | >7[b] |

[a] The parameters compared are: the rotational constants ($A$, $B$, $C$ (MHz)); the hydroxyl hydrogen principal axis coordinates ($|a|$, $|b|$, $|c|$ (pm)); the identity of the lowest-energy and the next lowest conformer and the energy interval $\Delta E$(N−L)/kJ mol$^{-1}$ between these. The data are extracted from a comprehensive listing of results from the series of ab initio calculations for all conformers given in Tables 6S−13S of the Supporting Information. [b] Based on the observed absence of a second conformer spectrum implying an abundance of <10% at 363 K.

spectrum. This series also represented a steeply rising progression in computational cost, and thus it is of some interest to assess the cost effectiveness of the MP2 calculation. Comprehensive listings of the key predicted parameters—torsional angles, rotational constants, electric dipole moment components, and hydroxyl hydrogen coordinates—are given in Tables 6S−13S of the Supporting Information. The reliability of calculated parameter values relating only to the observed conformer **1** are compared in Table 6. It can be seen that the density functional method B3LYP/6-31G(d,p) is no more reliable than the Hartree−Fock calculations. Within the Hartree−Fock calculations, there is no obvious correlation between reliability and the size of the basis set employed. However, it is apparent that the MP2/6-31G(d,p) calculation is significantly more accurate than the remainder. This is particularly noticeable for the relative energies of the conformers, where all the other methods imply that a second conformer should be of sufficiently low relative energy so as to be readily detectable.

**The Search for Other Conformers.** Free expansion jet spectroscopy enables chemical equilibration at elevated temperatures, providing the possibility of investigating higher energy conformers than are accessible with other forms of microwave spectroscopy.[15] The ab initio relative energies and dipole moment components for these conformers can be used to predict the feasibility of detecting such conformers. However, previous cases have drawn attention also to the need to recognize the possibility of conformational relaxation during the collisional cooling process in the jet expansion. Studies of somewhat similar compounds[3b,22,23] have shown that during a free-jet expansion such as that occurring in our spectrometer it is possible for certain conformers to interconvert into others with lower zero-point energy levels, this appearing to happen whenever the barrier to interconversion is lower than around 1000 cm$^{-1}$. We investigated this possibility theoretically by computing MP2/6-31G(d,p) energy profiles between selected 2-phenylethanol species with stepped constrained values of the H−O−C−C angle, embracing the interconversion between the three gauche forms, **1**, **2**, and **3**, and separately between the two trans forms **4** and **5**. Relaxation between the trans and gauche forms is precluded by the very high energy barriers that invariably accompany passing through an eclipsed ethane-type barrier.

The results for **1**, **2**, and **3**, shown in trace a of Figure. 2, indicate that the barriers are particularly low, no more than 400 cm$^{-1}$, so that we expect rapid relaxation during the expansion from **2** and **3** to the species of lowest energy, namely **1**. It can be seen that conformer **2** is separated from the well containing **1** by a particularly low barrier of ca. 100 cm$^{-1}$, meaning that **2** is probably better described as an excited vibrational state of **1** rather than as a distinct conformer. The possibility of interconversion between forms **4** and **5** was likewise investigated, with the results being shown in trace b of Figure 2. Again, in this case, the barriers are predicted to be quite low, less than 400 cm$^{-1}$, and so we expect rapid interconversion from **5** to **4** during the expansion.

Thus, it is predicted that the only higher energy detectable species via free jet spectroscopy would be conformer **4**. As such, it is a good candidate for future studies using either microwave absorption or other methods such as UV laser spectroscopy. Making suitable allowances for conformational relaxation, a readily detectable post-expansion mole fraction of 25% for **4** would require a pre-expansion temperature of more than 500 K.

## Conclusion

We have detected via microwave spectroscopy and rotationally assigned the spectrum of a single conformer of 2-phenylethanol. Through comparison of measured and ab initio MP2/6-31G(d,p) predicted theoretical rotational constants, deuterium substitution coordinates and dipole moment components we have shown that the new conformer is the gauche form **1**. This conformer appears to be stabilized by an intramolecular hydrogen bond from the OH hydrogen to the aromatic $\pi$-bond charge cloud. Our failure to identify any of the other conformers **2**−**5** in the jet-expanded microwave spectrum is consistent with the relative energies predicted at the MP2/6-31G level, but not at lower quality calculations such as HF/6-31g(d,p) or for the density functional method at the BLYP/6-31G(d,p) level.

Within a broader perspective, this study supports the view that ab initio calculations at the MP2/6-31G(d,p) level can provide adequately reliable structural and energetic predictions for conformers of organic molecules.

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**Supporting Information Available:** This collection of Tables 1S−13S contains all the measured and assigned microwave transition frequencies used to derive the rotational constants reported in this work, all the measured and assigned Stark shifts used to derive the dipole moment components reported in this work, and the complete ab initio optimized geometries for each structural form of 2-phenylethanol. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) By "shape" we mean approximate three-dimensional structure, such as represented by traditional ball-and-stick models. The shape is considered established if one can identify a domain of the multidimensional potential energy surface containing one local minimum sufficiently deep compared with *RT* for it to persist as a definite species long enough to be studied experimentally.

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