Ab initio Study of Stretch–Bend Coupling in HOOH

Coral Getino,† Bobby G. Sumpter,‡ Jesus Santamaria,§ and Gregory S. Ezra*†
Department of Chemistry, Cornell University, Ithaca, New York 14853 (Received: September 25, 1989)

Ab initio calculations are used to investigate the dependence of the OOH bend force constants on the OO and OH bond lengths in HOOH. The calculations were performed using second-order Müllerm–Plesset perturbation theory with a split-valence triple-ζ basis set augmented with multiple polarization functions on both the oxygen and hydrogen atoms [6-311G(3d,2p)]. Analytical functions describing the variation of the bending force constants with the bond lengths are obtained by fitting the ab initio data and are found to be significantly different from the switching functions previously used in trajectory studies of HOOH.

I. Introduction

There has been considerable experimental1 and theoretical2 interest in the vibrational overtone induced decomposition of polyatomic molecules. The possibility of inducing unimolecular dissociation in state-specific fashion has provided the stimulus for many of the studies. Hydrogen peroxide is an attractive polyatomic molecule for study of overtone-induced unimolecular dissociation.3-4 The O–H bonds are good local modes and provide well-defined sites for overtone excitation; classical trajectory simulations5-15 are feasible, and the relatively small size (four atoms) makes it possible to perform ab initio calculations with large basis sets.16-25

Early work on the spectroscopy of HOOH established the nonplanar geometry and the existence of a hindered internal rotational mode.26-30 Some of the earlier studies indicated the importance of torsion–vibration interactions and the dependence of the torsional potential on the degree of excitation of the OH stretch.30-32 Several valence force fields were proposed which gave reasonable fits to the experimental data,1623 and some ab initio calculations16-19 were also performed.

More recently, several experimental studies of the vibrational overtone initiated decomposition of HOOH have been reported.3-8 The vibrationally mediated photodissociation of HOOH and HOOD34 and UV-induced photodissociation of hydrogen peroxide35 have also been investigated.

On the theoretical side, both ab initio and semiempirical quantum mechanical potential surface calculations21,26,24,28 and classical trajectory calculations of the OH overtone induced dissociation6-12 have been carried out. We briefly discuss some of the more recent studies below.

The equilibrium structure of hydrogen peroxide has been the subject of controversy for several years.36-42 Although it is known that the equilibrium dihedral angle is between 110° and 120°, the exact value has not been well established until very recently.38 Khachkurov and Przhavezskii39 reported a dihedral angle of 119.1° obtained by fitting rotational constants from microwave studies, while Hunt and co-workers3 obtained a value of 111.5° by fitting torsional frequencies. Koput40 determined a value of 111.83° by solving the torsional Schrödinger equation for a fixed OH bond distance of 0.965 Å and then fitting the solution to the experimental data. Koput argues that the value reported by Khachkurov and Przhavezskii corresponds to an average dihedral angle for the torsional ground state and that 111.83° is the correct equilibrium dihedral angle. More recently, experimental studies41,42 also indicate that the dihedral angle in HOOH is near the value reported by Koput.

There is a long history of ab initio calculations on the structure and torsional barriers of HOOH. A comprehensive account of the ab initio studies of HOOH before 1978 can be found in refs 18 and 19, while more recent work is discussed in refs 22 and 23.

16) Getino, C.; Sumpter, B. G.; Santamaria, J.; Ezra, G. S. To be submitted for publication.
structure of HOOH. They employed the Hartree-Fock approach using a [4s3p1d/2s1p] basis set and showed the necessity of using geometry optimization and polarization functions in order to obtain good geometries and torsional barrier heights.

Cramer18 undertook a systematic study of the dependence of the torsional barriers and molecular geometry on the basis set and level of theory and made a critical comparison of theory and experimental results. He concluded that 2p polarization functions at the H are important to accurately describe the cis configuration, and inclusion of correlation is necessary to obtain good agreement with the experimental geometry.

Bair and Goddard21 calculated the equilibrium geometry for HOOH using the generalized valence bond (GVB) plus CI method. They obtained a geometry in good agreement with that reported by Cramer18 and stressed the importance of inclusion of electron correlation in obtaining the correct equilibrium geometry.

Botvichina, Meyer, and Semkow (BMS)16 derived the first ab initio quadratic force field for HOOH using a small basis set and then scaled the diagonal F matrix to obtain estimated vibrational frequencies. The BMS semiempirical global surface was subsequently used in modified form in classical trajectory studies by Uzer et al.9,10

Carpenter and Weinhold23 have carried out high-level ab initio calculations to characterize the OH overtone vibration–torsion potential coupling on the ground-state potential surface. They have provided a detailed analysis of the effect of the level of theory and basis set on the equilibrium structure and torsional barrier height, and the results support the need for a thorough examination of the potential energy surface.

While the classical trajectories of Uzer et al. indicate that the torsional mode plays an insignificant role in the vOH = 6 overtone-induced dissociation of rotationless HOOH molecules, the work of Sumpter and Thompson5 has shown that the potentials describing the attenuation of the OOH bend force constants by the OO and OH stretches (nonlinear coupling). The torsional motion was found to play an insignificant role in the intramolecular dynamics of nonrotating hydrogen peroxide. The unimolecular decay rate calculated by Uzer et al. for an overtone excitation of vOH = 6 was consistent with statistical calculations,57 although vibrational energy redistribution was not complete in the time scale for dissociation. In particular, the initially unexcited OH bond remains unexcited and does not receive a statistical proportion of the total energy prior to reaction.

We have recently studied the classical dynamics of HOOH for various potential energy surfaces and initial excitations (vOH = 4, 5, 6, 7).13-15 Unimolecular decay lifetimes of HOOH were found to be sensitive to details of the potential energy surfaces. In the case of CH overtone relaxation in benzene, it is known that it is important to include switching functions in the potential to attenuate the CCH bending force constants as a function of the CH bond length.46 Such attenuation induces a potential coupling which leads to increased localization of energy in the CH bond by an effective cancellation of the kinetic and potential couplings.47 Similarly, we have found that the overtone-induced unimolecular decay lifetime of HOOH is strongly dependent on the rate at which the HOO bend force constant is attenuated by OO stretching.13-15 It is therefore important to determine an accurate switching function for the torsional mode also, and quantitatively accurate torsional energy levels were obtained.

There have been several classical trajectory studies of the unimolecular decomposition of hydrogen peroxide.9-15 These studies have shown the importance of the bending degrees of freedom in the flow of energy out of the initially excited OH stretch overtone and also provided some evidence for incomplete redistribution of energy on the time scale for dissociation.5

Uzer et al.9,10 have carried out several classical trajectory studies of the unimolecular decomposition of HOOH, using a potential energy surface that incorporated spectroscopic and thermodynamic data. The OH and OO bond stretches were modeled as Morse oscillators and the OOH bends as harmonic oscillators. Potential coupling between the various modes was taken into account by off-diagonal F matrix elements (linear coupling) and by switching functions describing the attenuation of the OOH bend force constants by the OO and OH stretches (nonlinear coupling).

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function for the attenuation of the bending force constant as a function of the OO bond length. Appropriately switching functions can be obtained by ab initio calculations, and this method has previously been used to obtain switching functions for methane,\(^{48}\) propylene,\(^{49}\) methanol,\(^{49}\) benzene,\(^{49}\) and the hydroperoxyl radical\(^{49,50}\).

The purpose of the present paper is to determine the dependence of the HOO bending force constants on the OO and OH bond lengths for the ground-state potential surface of HOOH. In particular, we obtain analytical switching functions describing the stretch-bend couplings in HOOH. The switching function approach\(^{46-50}\) combined with ab initio calculations yields global potential energy functions which describe both the low- and high-energy regimes, in which mode-mode potential couplings are included in a reasonable fashion. In particular, potential couplings decrease to zero as the molecule dissociates\(^{43,51}\) in a physically reasonable way. The details of the ab initio calculations are given in section II, and results on the switching functions are presented in section III. Conclusions are given in section IV.

II. Ab Initio Calculations: Basis Set Selection

We have carried out several calculations at different levels of theory and for various sizes of basis set to determine an appropriate method and basis set for studying the dependence of the bending force constants on the OO and OH bond lengths. We require that the method used should provide both torsional barrier heights and equilibrium geometries in good agreement with experiment.

The equilibrium geometries and torsional barrier heights (energies of the fully optimized cis or trans configurations relative to the equilibrium energy) obtained for basis sets ranging from 6-31G* to 6-311G(3df,3pd) for HF and MP2 levels of theory are given in Table I along with some of those discussed in section I. All of the calculations reported here were carried out using the GAUSSIAN suite of programs.\(^{51}\)

In order to obtain reasonable torsional barrier heights, it is necessary to include multiple polarization functions on all the atoms and to fully optimize the geometry. Inclusion of electron correlation is very important in obtaining an accurate equilibrium geometry for a given basis set. These points have also been stressed in previous ab initio studies of HOOH.\(^{17-19}\) Inclusion of f orbitals on the oxygen atoms and d orbitals on the hydrogen atoms leads to an important stabilization of the equilibrium cis and trans configurations, compared to the results for smaller basis sets (see Table I). The torsional barrier heights obtained for MP2/6-311G(3df,2pd) are in very good agreement with experiment. On the other hand, smaller basis sets at the MP2 level of theory yield equilibrium geometries in better accord with the experimental results. The MP2/6-311G(3df,2pd) calculation gives both reasonable barrier heights and geometry and was chosen as a suitable compromise for the study of the dependence of the OOH bending force constant on the OH and OO bond lengths.

The quadratic internal coordinate force constants, the harmonic normal-mode frequencies, and the rotational constants obtained in the present work for the different basis sets and levels of theory are summarized in Table II, together with those obtained by Harding.\(^{25}\) The MP2/6-311G(3df,2pd) calculation gives force constants and vibrational frequencies that are in reasonable agreement with Harding’s calculations. Whereas the force constants for the MP2/6-311G(2d,p) calculation appear to be in better agreement, the smaller basis set yields a relatively poor description of the equilibrium geometry, torsional barrier heights for the torsion (see Table I). The largest deviations for the MP2/6-311G(3d,2p) force constant matrix are for the O-O bond stretch force constant \(F_{RR}\) and for the coupling between the OH and adjacent OOH bond \(f_{AC}\). Although the calculations of Harding give a negative sign on the coupling constant \(F_{AC}\), our constant is positive. \(F_{AC}\) is in fact the only coupling constant for which the sign changes as a function of the basis set and level of calculation, and its magnitude is small. We therefore do not consider the discrepancy with Harding’s calculation to be significant.

The experimentally determined fundamental frequencies\(^{36,40}\) are \(v_1\) (symmetric OH stretch) = 3614 cm\(^{-1}\), \(v_2\) (symmetric bend) = 1393 cm\(^{-1}\), \(v_3\) (OO stretch, \(v_3\) = 863 cm\(^{-1}\)), \(v_4\) (asymmetric OH stretch) = 1615 cm\(^{-1}\), and \(v_5\) (asymmetric bend) = 1269 cm\(^{-1}\). As is well-known,\(^{22}\) harmonic frequencies \((\omega)\) obtained by ab initio calculations give a poor description of the experimental normal-mode frequencies and need to be corrected for anharmonicity. Using the correction for anharmonicity (\(\omega - \nu\)) obtained by Harding\(^{22}\) (for GVB+1+2+QD), we obtain for the MP2/6-311G(3d,2p) calculation the following fundamental normal-mode frequencies: \(v_1 = 3638 \text{ cm}^{-1}\), \(v_2 = 1418 \text{ cm}^{-1}\), \(v_3 = 893 \text{ cm}^{-1}\), \(v_4 = 3632 \text{ cm}^{-1}\), and \(v_5 = 1300 \text{ cm}^{-1}\). The largest deviation from experiment is 3.5% and is for the OO stretch. A reason for this could be the underestimation of the electron correlation energy\(^{52}\).


\(^{51}\) Fisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Mielicki, C. F.; Martin, R. L.; Stewart, J. P.; Bobrowicki, F. W.; Robb, C. M.; Kahn, L. R.; Defrees, D. J.; Seagar, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Topeol, S.; Pople, J. A. This work (GAUSSIAN 82 system of programs) is based on the GAUSSIAN 82 system, which is copyright 1983 by Carnegie-Mellon University.

TABLE II: Harmonic Force Constants, Calculated Harmonic Normal-Mode Frequencies, and Rotational Constants for Hydrogen Peroxide

<table>
<thead>
<tr>
<th></th>
<th>HF/II</th>
<th>HF/IV</th>
<th>HF/V</th>
<th>MP2/II</th>
<th>MP2/III</th>
<th>MP2/IV</th>
<th>MP2/V</th>
<th>GVB+QC*</th>
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<tr>
<td>$F_{02}$</td>
<td>1.149</td>
<td>1.166</td>
<td>1.177</td>
<td>1.002</td>
<td>0.901</td>
<td>0.965</td>
<td>0.988</td>
<td>0.957</td>
</tr>
<tr>
<td>$F_{03}$</td>
<td>0.0389</td>
<td>0.0453</td>
<td>0.048</td>
<td>0.0353</td>
<td>0.0048</td>
<td>0.0391</td>
<td>0.0427</td>
<td>0.039</td>
</tr>
<tr>
<td>$F_{12}$</td>
<td>-0.0085</td>
<td>-0.0027</td>
<td>-0.0038</td>
<td>-0.0133</td>
<td>-0.0241</td>
<td>-0.0018</td>
<td>-0.0051</td>
<td>-0.0134</td>
</tr>
<tr>
<td>$F_{13}$</td>
<td>-0.0704</td>
<td>-0.0601</td>
<td>-0.0440</td>
<td>-0.1354</td>
<td>-0.2143</td>
<td>-0.1515</td>
<td>-0.1494</td>
<td>-0.092</td>
</tr>
<tr>
<td>$F_{23}$</td>
<td>-0.0112</td>
<td>-0.0178</td>
<td>-0.0116</td>
<td>-0.0124</td>
<td>0.1032</td>
<td>0.0037</td>
<td>0.0043</td>
<td>-0.028</td>
</tr>
<tr>
<td>$F_{00}''$</td>
<td>0.0083</td>
<td>0.0083</td>
<td>0.0050</td>
<td>0.0100</td>
<td>0.0215</td>
<td>0.0121</td>
<td>0.0059</td>
<td>0.003</td>
</tr>
<tr>
<td>$F_{01}''$</td>
<td>0.654</td>
<td>0.659</td>
<td>0.669</td>
<td>0.625</td>
<td>0.574</td>
<td>0.633</td>
<td>0.650</td>
<td>0.575</td>
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<tr>
<td>$F_{02}''$</td>
<td>0.104</td>
<td>0.094</td>
<td>0.088</td>
<td>0.096</td>
<td>0.199</td>
<td>0.085</td>
<td>0.075</td>
<td>0.076</td>
</tr>
<tr>
<td>$F_{03}''$</td>
<td>-0.024</td>
<td>-0.018</td>
<td>-0.010</td>
<td>-0.018</td>
<td>-0.00001</td>
<td>-0.013</td>
<td>-0.005</td>
<td>-0.0012</td>
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<tr>
<td>$F_{12}''$</td>
<td>0.015</td>
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<td>0.016</td>
<td>0.015</td>
<td>0.00002</td>
<td>0.016</td>
<td>0.016</td>
<td>0.020</td>
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<tr>
<td>$F_{13}''$</td>
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<td>0.041</td>
<td>0.038</td>
<td>0.039</td>
<td>0.00004</td>
<td>0.036</td>
<td>0.031</td>
<td>0.026</td>
</tr>
</tbody>
</table>

*Units of force are mdyn, units of length angstroms, angles radians, frequencies and rotational constants wavenumbers. The basis sets used are as follows: I, 6-31G*; II, 6-31G**; III, 6-311G; IV, 6-311G(2d,p); V, 6-311G(3d,2p). Reference 25.

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** Minimum-energy paths along O0 (circles) and OH (stars) bond stretch coordinates. Potential energy is calculated at the MP2/6-31G(3d,2p) level with full optimization of all geometric parameters for fixed O0 or OH bond lengths. Energies are in hartrees and bond displacements in angstroms.

as calculated by second-order Møller–Plesset perturbation theory, which also leads to an O0 equilibrium bond length which is too short (see Table I).

### III. Switching Functions

Figure 1 shows the MP2/6-311G(3d,2p) potential energy along the minimum-energy paths (MEPs) for dissociation along the O0 (circles) and OH (stars) bond stretch coordinates, obtained by full optimization of all of the geometric parameters for fixed O0 or OH bond lengths, respectively. The O0 MEP is energetically more favorable and is the reaction coordinate pathway for overtone-induced unimolecular dissociation of HOOH; we are interested in accurately describing the potential couplings along this coordinate. The OH stretch–bend potential coupling is also important in determining overtone decay dynamics, and the OH stretch–OOH bend coupling is therefore also of interest.

The O0H bending potential is determined from energies calculated by varying one of the bond angles over 20° about the equilibrium angle for fixed values of the O0 or OH bond lengths along the MEPs. (The remaining geometric parameters are fully optimized.) The energies obtained are fit by using the nonlinear least-squares method to a quadratic

\[ V_0 = 0.5K_0(\theta - \theta_0)^2 \]  

or a quadratic–quartic function

\[ V_0 = 0.5K_0(\theta - \theta_0)^2 + f_0(\theta - \theta_0)^4 \]  

The force constants calculated as a function of the bond lengths are then fit to a suitable functional form. Figure 2 shows the quartic force constant ($f_0$) dependence on the O0 bond length.

Quadratic force constants ($K_0$) obtained from both fits (eqs 1a and 1b) are very similar, and the small magnitude of the quartic correction suggests that deviations from harmonicity are small for the bending angle displacements studied here.

Figure 3 shows the calculated switching function (a) for the O0 bond compared to that used in previous dynamics calculations of HOOH. In this figure, the circles are the ab initio data ($K/K_0$, where $K_0$ is the force constant at equilibrium) and the solid line is the fit given by

\[ S(\Delta r) = \exp[-1.468\Delta r_{OOH}] \]  

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The second switching function (b) describes the HCH bend attenuation for methane and corresponds to

$$S(r_{\text{CH}}) = 1 - \tanh \left[ 1.35 \times 10^{-7} \Delta r_{\text{OH}} (r_{\text{OH}} + 4.67) \right]$$

This function has been used by Uzer et al. in classical trajectory studies of HOOH. The third switching function (c) was obtained by ab initio calculations at the Hartree-Fock level for a 6-31G** basis:

$$S(r_{\text{CH}}) = 1 - \tanh \left[ 0.1205 \Delta r_{\text{OH}} \right]$$

We have previously used this function in a study of the dissociation dynamics of HOOH.

There are substantial differences between the various switching functions. The switching function (Figure 3a) calculated in the present paper shows very strong stretch-bend coupling in the region of small bond displacements (-0.5 < \Delta < 0.5) as compared to the other functions, but decreases relatively slowly at large distances. On the other hand, curve c of Figure 3 shows very weak coupling for moderate bond displacements and abruptly decreases to zero at larger displacements. The stretch-bend coupling described by Figure 3b is of a type intermediate between the other two; this function was, however, derived for the HCH bend of methane and not for HOOH. The transferability of switching functions from one molecule to another has been seriously questioned by several authors. As the intramolecular dynamics of HOOH and other polyatomic molecules is sensitive to changes in the rate of attenuation of bending force constants as described by switching functions of the type shown in Figure 3, it is clearly important to use functions that correctly describe this type of stretch-bend coupling.

Figure 4 illustrates the switching function for the OH bond stretch. Curve a is the best fit to the ab initio points (stars) and corresponds to a function of the form

$$S(r_{\text{OH}}) = 0.076(1 - \tanh \left[ 5.752 \Delta r_{\text{OH}} - 0.450 \right] + 0.892 \exp(-0.364 \Delta r_{\text{OH}}))$$

although a simpler function

$$S(r_{\text{OH}}) = 1 - \tanh \left[ 0.00823 \Delta r_{\text{OH}} (r_{\text{OH}} + 1.757) \right]$$

was found to give a reasonable fit. The switching function used by Uzer et al. (curve b)

$$S(r_{\text{OH}}) = 1 - \tanh \left[ 1.531 \times 10^{-7} \Delta r_{\text{OH}} (r_{\text{OH}} + 4.67) \right]$$

and one appropriate for the hydroperoxyl radical (curve c)

$$S(r_{\text{OH}}) = 1 - \tanh \left[ 1.0279 \Delta r_{\text{OH}} (r_{\text{OH}} - 0.797) \right]$$

are also shown in Figure 4. The parameters in eqs 2-7 are appropriate for distances measured in angstroms.

The differences between these switching functions are not as striking as for the OH bond coordinate. The rate of attenuation of curve a is slower for the large bond displacements than either curve b or c.

In the simplest statistical adiabatic channel (SAC) approach to unimolecular bond fission and the reverse association reaction, the shape of the potential surface governing dissociation depends on two parameters. The first parameter, \( \beta \), is the usual Morse parameter describing the radial interaction potential, while the second parameter, \( \alpha \), determines the function used to interpolate the adiabatic channel eigenvalues between their equilibrium and asymptotic eigenvalues. In fact, \( \alpha \) is directly related to the radial dependence of the bending force constant:

$$K(r) = K_0 \exp(-2\alpha \Delta r)$$

(cf. eq 2; note the factor of 2).

Application of SAC theory to a large number of neutral radical reactions leads to an approximately constant value of the ratio \( \alpha/\beta \) close to 0.5, implying a correlation between the range of the radial interaction potential and the switching function (8). Wolf et al. have recently pointed out such a correlation for the HO bond rupture in the hydroperoxyl radical. The short range of the switching function (Figure 4c) correlates with the short-range interaction of the H + O2 association potential, where the latter can be understood by noting that the double bond in O2 must be broken to form the OH bond. The bending switching function for HOOH (Figure 4a) has a longer range than the function (c), which is consistent with the longer range radial interaction expected for the association of H and HO2 radicals to form hydrogen peroxide.

From the switching function exponent \( 2\alpha = 1.4683 \) Å\(^{-1} \) (cf. eq 2) and a fit of the MEP for OO dissociation to a Morse function with \( \beta = 2.005 \) Å\(^{-1} \), we obtain a ratio of \( \alpha/\beta = 0.37 \). This number should be compared with the value (0.44) used in the SAC calculation of the HOOH dissociation rate of ref. 57.

**IV. Conclusions**

We have reported ab initio calculations of the OO and OH bond length dependence of HOO bending force constants in HOOH at the MP2/6-311G(3d,2p) level and have determined switching functions describing the stretch-bend potential couplings. The switching functions differ markedly from those used previously in classical trajectory calculations of HOOH dissociation. In particular, the attenuation of the bending force constant by OO...
bond stretching is of BEBO form and is more rapid than for the functions previously used.

We believe that the present ab initio results give an accurate description of the stretch-bend coupling in HOOH. As the HOOH dissociation rate is strongly dependent on the rate of attenuation of the bending force constants, it will be important to study the unimolecular reaction dynamics using the switching functions determined here. Preliminary classical trajectory calculations for rotationless HOOH, using the switching functions of the present paper in the potential surface of refs 14 and 15, give a lifetime for $\tau_{OH} = 6$ of around 8 ps. Further details of both the ab initio potential surface and the classical trajectory calculations will be given elsewhere.

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**Dipolar-Chemical Shift NMR Spectra of the Carbon-Nitrogen Linkage in Benzylideneaniline. Carbon and Nitrogen Chemical Shielding Anisotropes**

Ronald D. Curtis, Glenn H. Penner, William P. Power, and Roderick E. Wasylishen*

*Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3 (Received: September 26, 1989)

The magnitudes and orientations of the principal components of the carbon and nitrogen chemical shift tensors for the "localized" imine moieties of the Schiff base benzylideneaniline have been determined by the analysis of dipolar-chemical shift NMR spectra. The carbon chemical shift anisotropy was determined to be $156 \pm 2$ ppm with $\eta = 0.88 \pm 0.02$ whereas the nitrogen shift anisotropy was found to be $545 \pm 2$ ppm with $\eta = 0.92 \pm 0.01$. The most shielded component of both the carbon and nitrogen shift tensors is approximately perpendicular to the imine fragment. For the imine carbon the intermediate component of the shift tensor is approximately along the C=N axis. The corresponding component of the nitrogen chemical shift tensor is oriented along the direction of the nitrogen lone pair. These results are compared to those available in the literature for related molecules. For the $^{13}$C,$^{15}$N spin pair, the $^{13}$C dipolar-chemical shift NMR spectrum cannot be accurately simulated if the high-field approximation for the $^{15}$N nucleus is assumed. To circumvent this problem, a general equation is described that can be used to calculate the dipolar-chemical shift NMR spectrum of a spin 1/2 nucleus dipole coupled to a spin 1 nucleus where the high-field approximation is not invoked.

In order to characterize the carbon and nitrogen chemical shift tensors of the imine fragment, we have analyzed the $^{13}$C and $^{15}$N dipolar-chemical shift NMR powder spectra of the $^{13}$C=$^{15}$N and $^{13}$C=$^{15}$N spin pairs in benzylideneaniline (I). This compound was chosen since it is easy to prepare with selective enrichment at either the imine carbon or nitrogen or both simultaneously. Also, the availability of X-ray diffraction data greatly facilitates

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