J. Phys. Chem. A **2006,** *110,* 8037−8043

Microwave Spectra, ab Initio Calculations, and r_0 Structural Parameters for (Methylamino)thiophosphoryl Difluoride

James R. Durig,*,† Chao Zheng,† Jinpeng Xiao,† Wayne Zhao,† R. S. Sanders,‡,§ and B. J. van der Veken‡

Departments of Chemistry, University of Missouri—Kansas City, Kansas City, Missouri 64110, and University of Antwerp, 171 Groenenborgerlaan, Antwerp 2020, Belgium

Received: March 27, 2006; In Final Form: May 2, 2006

The microwave spectra of (methylamino)thiophosphoryl difluoride, $CH_3NHP(=S)F_2$, and two deuterated species, $CH_3NDP(=S)F_2$ and $CD_3NHP(=S)F_2$, have been investigated in the region from 26.5 to 39.0 GHz. The rotational constants of the ground vibrational state have been determined and have been shown to be only consistent with the trans conformer (CH_3 group antiperiplanar to the P=S bond) with C_s symmetry. The a-type R branch transitions have been assigned for the trans conformer for the three isotopomers on the basis of the rigid rotor model. Near-trans and near-cis forms without molecular planes of symmetry are predicted by all ab initio calculations with the near-trans form being more stable. However, the double-well potentials governing the interchange between the two enantiomeric near-trans as well as the two near-cis forms are too shallow to accommodate the zero-point energies of the ν_{24} asymmetric torsion. Thus, the trans conformation with C_s symmetry may be more accurate in explaining the microwave experimental data. The "adjusted" r_0 structural parameters have been obtained by systematically adjusting the ab initio MP2(full)/6-311+G(d,p) structure of the trans conformer with C_s symmetry to fit the microwave rotational constants. The determined heavy atom distances are $r(\mathrm{C-N}) = 1.459(5)$, $r(\mathrm{P-N}) = 1.621(5)$, $r(\mathrm{P=S}) = 1.879(5)$, and $r(\mathrm{P-F}) = 1.550(5)$ Å, and the heavy atom angles are $\angle\mathrm{CNP} = 124.7(5)°$, $\angle\mathrm{NPS} = 118.3(5)°$, $\angle\mathrm{NPF} = 103.2(5)°$, $\angle\mathrm{FPS} = 117.0(5)°$, and $\angle\mathrm{FPF} = 94.6(5)°$. The adjusted r_0 parameters have also been obtained for aminodifluorophosphine, H_2NPF_2, with a slightly pyramidal $-PNH_2$ moiety. The results indicate that the previously reported short distance of 0.981(5) Å for the $N-H_o$(outer) bond from the microwave study is too short, and the adjusted r_0 value of 1.007(3) Å is obtained from the combined data. Adjusted r_0 parameters are also reported for (dimethylamino)difluorophosphine, $(CH_3)_2NPF_2$, with C_s symmetry with the PNC_2 portion of the molecule being planar. The previously reported C−H distances from the electron diffraction study are too long, and the $\angle PNC_i$ and $\angle C_oNC_i$ angles are also found to be in error. These results provide a reasonable explanation why the microwave and electron diffraction results differ for the structures of these latter two molecules.

Introduction

The structure and the conformational stabilities of phosphorus molecules which contain the $-P(=S)F_2$ group are of interest to chemists.[1−8] For ethylthiophosphoryl difluoride, $CH_3CH_2P(=S)F_2$, there is little difference between the conformational stabilities of the two forms where the gauche conformer (CH_3 group gauche to P=S bond) was determined to be more stable than the trans conformer (CH_3 group antiperiplanar to P=S bond) by 63 ± 37 cm^{-1} (0.75 ± 0.44 kJ/mol) from the microwave study[3] which is consistent with the more recently determined value[5] of 53 ± 7 cm^{-1} (0.63 ± 0.08 kJ/mol) from variable-temperature studies of krypton solutions by utilizing infrared spectral data. However, when the terminal methyl group is replaced by a halogen atom, the experimentally determined order of stability is reversed with values of 244 ± 16 cm^{-1} (2.92 ± 0.19 kJ/mol) for $ClCH_2P(=S)F_2$ in the krypton solution[7] and 250 ± 20 cm^{-1} (2.99 ± 0.24 kJ/mol) for $FCH_2P(=S)F_2$ in the liquid phase,[8] both having the trans conformer as the more stable form. Apparently, the nature of the substituent X on the methylene group of $XCH_2P(=S)F_2$ molecules determines the conformational stability along the C−P bond. We also investigated[9] the conformational stability of (dimethylamino)difluorophosphine, $(CH_3)_2NPF_2$, and found a single conformer in the gaseous, liquid, and solid states. About the same time, an electron diffraction study was reported for $(CH_3)_2NPF_2$ and it was also concluded that there was only one stable conformer present at ambient temperature.[10] As a continuation of our studies of conformational stabilities of substituted $-P(=S)F_2$ molecules, we have investigated the conformational stability of (methylamino)thiophosphoryl difluoride, $CH_3NHP(=S)F_2$.

In the initially reported[11] infrared spectral study of $CH_3NHP(=S)F_2$ it was inconclusive whether only one conformer or two exist in the fluid phases. In a recent study[6] of the infrared and Raman spectra of this molecule, two conformers were identified in the fluid phases (near-trans where the CH_3 group is nearly antiperiplanar to the P=S bond and near-cis where the CH_3 group is nearly cisperiplanar to the P=S bond) but only the near-trans conformer remains in the solid. On the basis of the temperature study of the Raman spectrum of the liquid as well as the asymmetric top infrared contour simulation of the vapor

---

* Corresponding author. Phone: 01 816-235-6038. Fax: 01 816-235-2290. E-mail: durigj@umkc.edu.

† University of Missouri—Kansas City.

‡ University of Antwerp.

§ Taken in part from the dissertation of R.S.S., which was submitted to the Department of Chemistry, University of Antwerp, Antwerp, Belgium, in partial fulfillment of the Ph.D. degree.

10.1021/jp061882c CCC: \$33.50

phase, it was concluded that the near-trans conformer is the more stable form in the fluid phases. To obtain more structural information on this molecule as well as to obtain additional conformational data, we have recorded the microwave spectra of (methylamino)thiophosphoryl difluoride and two deuterated derivatives, $CH_3NDP({=}S)F_2$ and $CD_3NHP({=}S)F_2$. Additionally we have carried out ab initio calculations using a variety of basis sets with valence and core electron correlation by the Møller−Plesset perturbation method[12] to the second order (MP2) as well as the density functional theory by the B3LYP method to predict the conformational stability, rotational constants, and structural parameters for comparison to the experimental values. In addition, the adjusted r_0 structure has been obtained by systematically varying the MP2(full)/6-311+G(d,p) structural parameters to fit the reported microwave rotational constants. Similar theoretical calculations of aminodifluorophosphine, H_2NPF_2, and (dimethylamino)difluorophosphine, $(CH_3)_2NPF_2$, have been carried out to obtain the adjusted r_0 structural parameters. The results of these experimental and theoretical studies are reported herein.

Experimental Section

(Methylamino)thiophosphoryl difluoride, $CH_3NHP({=}S)F_2$, was prepared according to the procedure of Cavell et al.[11] This method is based on the vapor phase reaction of methylamine with chlorothiophosphoryl difluoride (2:1 molar ratio). These compounds were mixed, and after a reaction time of 1−2 h, the mixture was transferred to a low-temperature, low-pressure fractional distillation column for purification. The isotopic species were prepared in the same manner by using CH_3ND_2 and CD_3NH_2 as the starting materials. CD_3NH_2 was obtained by the reaction of $CD_3NH_2{\cdot}HCl$ (Janssen Chimica) with NaOH in H_2O solution. CH_3ND_2 was prepared by several successive exchanges of CH_3NH_2 with concentrated NaOD in D_2O solution. The two different isotopic methylamines were purified by vacuum distillation and checked for isotopic purity by their infrared spectra of the vapor phase. Chlorothiophosphoryl difluoride was prepared by partial fluorination of thiophosphoryl trichloride with freshly sublimed antimony trifluoride (Janssen Chimica), followed by vacuum fractionation.

The microwave spectra of (methylamino)thiophosphoryl difluoride and its isotopomers were investigated in the frequency region between 26.5 and 39.0 GHz by using a Hewlett-Packard model 8460A MRR spectrometer with a Stark modulation frequency of 33.33 kHz. The Stark cells were maintained at dry ice temperature (−78 °C) for all measurements. Precise line positions were measured at reduced pressure, typically in the order of ~2 Pa. The accuracy and precision of the frequency measurements are estimated to be ±50 kHz.

Ab Initio Calculations

The LCAO−MO−SCF calculations were performed with the Gaussian-98 program[13] with Gaussian type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all the geometric parameters using the gradient method of Pulay.[14] We have carried out ab initio calculations using a variety of basis sets with valence and core electron correlation by the Møller−Plesset perturbation method[12] to the second order (MP2) as well as density functional theory by the B3LYP method to predict the conformational stability. These calculations converged to stable near-trans and near-cis conformers that do not possess molecular planes of symmetry. Full optimization was also performed at the trans and cis first-order saddle points with C_s symmetry (Figure 1). The calculated electronic energies and energy differences of the near-trans, trans, near-cis, and cis forms are listed in Table 1S (Supporting Information).

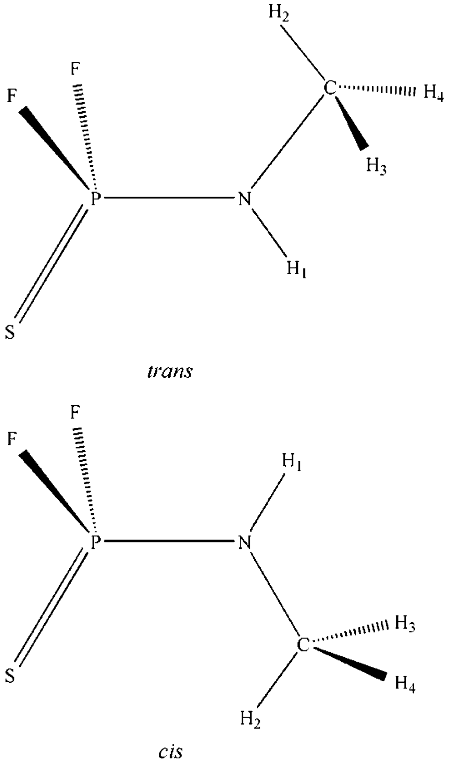

Figure 1. Illustrated trans and cis conformations of $CH_3NHP({=}S)F_2$.

The predicted energy difference between the near-trans and near-cis conformers ranges from 152 to 485 cm^{-1} from the MP2 calculations and from 286 to 389 cm^{-1} for B3LYP calculations with the near-trans conformer being more stable (Table 1S). The CNPS dihedral angle is approximately 6 and 30° from the planar structure for the near-trans and near-cis conformers, respectively. From the MP2 calculations, the energy of the trans structure with C_s symmetry is predicted 27−168 cm^{-1} higher than the near-trans form and that of the cis structure with C_s symmetry is predicted 5−189 cm^{-1} higher than the near-cis form. However, the molecule does not need to pass through the trans or cis orientation with C_s symmetry when interconverting between two enantiomeric near-trans or near-cis forms. When the SPNC dihedral angles are fixed at 180 and 0°, respectively, and all other geometric parameters and the symmetry constraint are relaxed, the resulting optimized structure has the methyl group rotating in one direction and the amino hydrogen bending in the opposite direction. Thus, the interconversion barriers between the two enantiomeric near-trans or near-cis forms are significantly smaller than the predicted energy differences between the trans and near-trans or the cis and near-cis forms. In both cases, the calculated double-well potentials at moderate-to-high levels are too shallow to accommodate the zero-point vibrational energy of the ν_{24} asymmetric torsion with MP2(full)/6-31G(d) predicted frequency of 82 cm^{-1} for the near-trans form and 73 cm^{-1} for the near-cis form. Therefore, (methylamino)thiophosphoryl difluoride in the trans conformation with C_s symmetry may be more accurate in explaining its experimental microwave data. For this reason, the structural parameters were optimized at the trans and cis C_s configuration by HF/6-31G(d), MP2(full)/6-31G(d), MP2(full)/6-311+G(d,p), and MP2(full)/6-311+G(2d,2p) calculations.

TABLE 1: Predicted Rotational Constants from MP2(full)/6-311G(2df,2pd) Structural Parameters for the Trans and Cis Forms with C_s Symmetry of (Methylamino)thiophosphoryl Difluoride[a]

isotopomer	param	trans	cis	obsd
	$\|\mu_a\|$	4.625	3.901	
	$\|\mu_b\|$	1.724	2.064	
	$\|\mu_c\|$			
	$\|\mu_{tot.}\|$	4.601	4.414	
$CH_3NHP(=S)F_2$	A	3817.7	2630.0	
	B	1768.4	2317.4	
	C	1614.5	1656.5	
	$B + C$	3382.9	3973.9	3384.5[b]
	k	−0.8604	0.3578	
$CH_3NDP(=S)F_2$	A	3710.3	2599.8	
	B	1764.7	2287.9	
	C	1592.0	1629.5	
	$B + C$	3356.7	3917.5	3358.2[b]
	k	−0.8370	0.3572	
$CD_3NHP(=S)F_2$	A	3705.5	2587.7	
	B	1621.8	2080.9	
	C	1487.8	1532.1	
	$B + C$	3109.6	3613.0	3111.0[b]
	k	−0.8791	0.0398	

[a] Dipole moment components in D; calculated and experimental rotational constants in MHz. [b] $B + C$ values from low-resolution microwave spectrum.

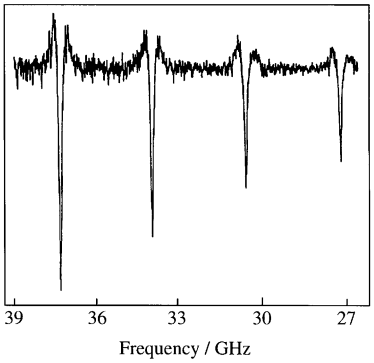

Figure 2. Low-resolution microwave spectrum of $CH_3NHP(=S)F_2$ in the region from 26.5 to 39.0 GHz.

Microwave Spectra

On the basis of the ab initio predictions, a microwave spectrum of a near-prolate asymmetric top, dominated by a-type transitions, with the spacing of approximately $B + C$ is expected for the trans conformer whereas the microwave spectrum of the cis conformer is expected to be that of an asymmetric top, containing a superposition of a-type and b-type transitions. For both conformers, structural parameters optimized at MP2(full)/6-311G(2df,2pd) level, together with calculated rotational constants, $B + C$ values, and the asymmetry parameter κ for the three isotopomers are summarized in Table 1. In this table, the dipole moment components in the principal axes system for the trans and the cis conformers are also given. From these data, it is clear that for the trans conformer a microwave spectrum of a near-prolate asymmetric top, dominated by a-type transitions, with a spacing of approximately 3383 MHz (3357 MHz for N-d_1 species and 3110 MHz for C-d_3 species) is expected.

The low-resolution microwave spectrum of the d_0 isotopomer between 26.5 and 39.0 GHz is shown in Figure 2. This spectrum shows a number of equidistant "pile-ups", characteristic of an a-type spectrum of a near symmetric top. Similar results were obtained for the other isotopomers. The $B + C$ values of all three isotopic species were determined (Table 1) from frequency differences between the maxima of the "pile-ups" in the low-resolution spectrum, and they are 3384.5, 3358.2, and 3111.0 MHz for the d_0, N-d_1, and C-d_3 species, respectively. These numbers agree extremely well with the $B + C$ values predicted by ab initio calculations for the trans conformer but not with the cis conformer; thus, these "pile-ups" are assigned to the trans conformer. Guided by these results and the rotational constants from the ab initio calculations, we identified a number of a-type ground-state transitions for the d_0, N-d_1, and C-d_3 derivatives, and they are listed in Table 2. Attempts to observe b-type transitions (expected to be one order of magnitude weaker than a-type transitions) or any transition due to the cis conformer were unsuccessful, presumably as a consequence of its expected complex microwave spectrum.

The effective rotational constants and moments of inertia for the trans conformer calculated from the transitions in Table 2 are listed in Table 3, along with the centrifugal distortion constants Δ_J. Other centrifugal distortion constants are not listed because their determined uncertainties were larger than their absolute values. Because only a-type transitions were observed, the accuracy of the rotational constant A is significantly lower than the other two rotational constants.

When we were trying to obtain the structural parameters from the eight rotational constants of three isotopic species by the usual process, great difficulties were encountered. Because the number of rotational constants is much smaller than the number of structural parameters, we initially fixed some parameters at assumed values to optimize the remaining ones. However, after several tests, the attempt to fit all three isotopic species by one set of geometrical parameters by this method was not successful. The fitting gave too large an error (about 1% or more) in the rotational constant A which is unacceptable even with the greater uncertainty of this constant. Therefore, we turned to the ab initio predicted values and combined them with the microwave rotational data.

Structural Parameters

We[15] have recently shown that ab initio MP2(full)/6-311+G(d,p) calculations predict the r_0 structural parameters for more than 50 carbon−hydrogen distances better than 0.002 Å of the experimentally determined values from isolated CH stretching frequencies[16] which were compared to previously determined values from earlier microwave studies. It has also been shown[17] that similar calculations predict the C−N distances very well for a number of methyl hydrazines and amines. Finally, we have found[18] that we can obtain good structural parameters by adjusting the structural parameters obtained from the ab initio calculations to fit the rotational constants (computer program A&M, Ab Initio and Microwave, developed in our laboratory) obtained from the microwave experimental data. To reduce the number of independent variables, the structural parameters are separated into sets according to their types. Bond lengths in the same set keep their relative ratio, and bond angles and torsional angles in the same set keep their differences in degrees. This assumption is based on the fact that the errors from ab initio calculations are systematic. Therefore it should be possible to obtain "adjusted r_0" structural parameters for (methylamino)thiophosphoryl difluoride from the eight determined rotational constants, particularly since the parameters associated with the CH_3NH- moiety should be transferable from the predicted values from the MP2(full)/6-311+G(d,p) calculations. These parameters are expected to be more accurate than those that could be obtained from an electron diffraction or microwave study alone.

TABLE 2: Rotational Transitions (MHz) of $CH_3NHP({=}S)F_2$, $CH_3NDP({=}S)F_2$, and $CD_3NHP({=}S)F_2$ in the Ground Vibrational State

transition	$CH_3NHP({=}S)F_2$		$CH_3NDP({=}S)F_2$		$CD_3NHP({=}S)F_2$	
	ν_{obs}	$\Delta\nu^a$	ν_{obs}	$\Delta\nu^a$	ν_{obs}	$\Delta\nu^a$
$8_{0,8} \leftarrow 7_{0,7}$	26 547.26	−0.02				
$8_{2,7} \leftarrow 7_{2,6}$	26 982.06	0.01	26 739.99	−0.08		
$8_{1,7} \leftarrow 7_{1,6}$	27 497.33	0.01	27 294.17	0.04		
$8_{2,6} \leftarrow 7_{2,5}$	27 508.25	−0.03	27 400.25	−0.02		
$9_{1,9} \leftarrow 8_{1,8}$	29 604.07	0.00	29 231.60	0.01	27 267.99	0.00
$9_{0,9} \leftarrow 8_{0,8}$	29 770.26	−0.01	29 371.74	0.05	27 453.16	0.06
$9_{2,8} \leftarrow 8_{2,7}$	30 322.92	−0.06	30 040.47	−0.10	27 897.03	−0.07
$9_{1,8} \leftarrow 8_{1,7}$	30 864.30	0.08	30 608.36	0.05	28 396.31	0.05
$9_{2,7} \leftarrow 8_{2,6}$	31 007.68	0.02	30 882.41	0.01	28 440.29	0.01
$10_{1,10} \leftarrow 9_{1,9}$	32 859.61	0.00	32 439.02	−0.01	30 270.36	0.04
$10_{0,10} \leftarrow 9_{0,9}$	32 987.91	0.03	32 540.91	0.02	30 421.05	0.00
$10_{2,9} \leftarrow 9_{2,8}$	33 653.40	−0.06	33 327.70	0.03	30 967.51	−0.12
$10_{1,9} \leftarrow 9_{1,8}$	34 202.03	0.02	33 883.73	−0.01	31 485.84	0.00
$10_{2,8} \leftarrow 9_{2,7}$	34 499.10	0.01	34 347.61	0.05	31 650.66	−0.01
$11_{1,11} \leftarrow 10_{1,10}$	36 109.64	0.02	35 640.74	0.00	33 267.64	0.05
$11_{0,11} \leftarrow 10_{0,10}$	36 204.91	0.05	35 712.14	0.04	33 385.67	0.03
$11_{2,10} \leftarrow 10_{2,9}$	36 972.92	−0.05	36 600.90	−0.09	34 029.55	−0.11
$11_{1,10} \leftarrow 10_{1,9}$	37 507.78	−0.05	37 119.47	−0.02	34 551.38	0.01
$11_{2,9} \leftarrow 10_{2,8}$	37 975.41	0.03	37 788.23	0.01	34 853.39	0.08
$12_{1,12} \leftarrow 11_{1,11}$			38 838.02	0.05	36 260.47	−0.03
$12_{0,12} \leftarrow 11_{0,11}$			38 886.50	−0.05	36 350.13	0.06
$12_{2,11} \leftarrow 11_{2,10}$					37 082.75	−0.08
$12_{1,11} \leftarrow 11_{1,10}$					37 590.97	0.00
$12_{2,10} \leftarrow 11_{2,9}$					38 043.17	0.04

[a] Observed − calculated utilizing the rotational constants listed in Table 3.

TABLE 3: Ground-State Rotational Constants (MHz), Centrifugal Distortion Constants (kHz), and Moments of Inertia ($u{\cdot}Å^2$) of Trans d_0, N-d_1, and C-d_3 (Methylamino)thiophosphoryl Difluoride[a]

param	$CH_3NHP({=}S)F_2$	$CH_3NDP({=}S)F_2$	$CD_3NHP({=}S)F_2$
A	3929.81(12)	3804.21(12)	(3800)
B	1768.173(3)	1764.717(3)	1621.98(5)
C	1616.318(3)	1593.434(4)	1489.06(5)
Δ_J	0.145(12)	0.142(14)	0.134(15)
I_A	128.601(4)	132.847(4)	(133.0)
I_B	285.8201(4)	286.3798(4)	311.5819(8)
I_C	312.6731(5)	317.1626(7)	339.3945(9)
σ^b	0.041	0.053	0.064
n^c	19	20	20

[a] Standard error in parentheses in units of last digit. [b] Standard deviation of frequency fit in MHz. [c] n is the number of fitted transitions.

The adjusted r_0 parameters for the $CH_3NHP({=}S)F_2$ molecule obtained by the ab initio MP2(full)/6-311+G(d,p) predicted parameters and the fit of the eight microwave rotational constants are listed in Table 4. First it should be noted that the adjusted P−F and P═S distances obtained by this method are significantly different from the predicted values at the MP2-(full)/6-311+G(d,p) level. The P−F distances are better predicted[5] from the HF calculations, and the adjusted r_0 values obtained for the $CH_3NHP({=}S)F_2$ molecule are within 0.005 Å of these predicted values. The other two heavy atom distances, r(C−N) and r(N−P), are only slightly smaller than the values predicted from the MP2(full)/6-311+G(d,p) calculations.

We have also determined the adjusted r_0 parameters for two other substituted aminodifluorophosphine molecules, aminodifluorophosphine, H_2NPF_2, and (dimethylamino)difluorophosphine, $(CH_3)_2NPF_2$, for comparison purposes. A microwave[19] and an electron diffraction[10] study of aminodifluorophosphine, H_2NPF_2, appeared at nearly the same time, but there were two major parameters which differ between the two studies. From the electron diffraction study[10] it was reported that the molecule adopted the conformation with a slightly pyramidal $-PNH_2$ moiety (C_1 symmetry) and a rather long N−P bond distance of 1.661(7) Å compared to a planar $-PNH_2$ moiety (C_s symmetry) and N−P bond distance of 1.650(4) Å from the microwave results[19] (Table 5), although taking into account the listed uncertainties they agree on the distance. We carried out ab initio calculations at five different levels, and all of the results predicted a slightly pyramidal $-PNH_2$ moiety (C_1 symmetry) as reported from the electron diffraction study.[10] We also obtained the adjusted r_0 parameters by combining the ab initio predicted values with the previously reported[19] microwave rotational constants. The largest difference between our results and those previously reported[19] is the $N-H_o$ (H atom outer from the PF_2 group) which is predicted to differ by not more than 0.003 Å from the value of the $N-H_i$ distance (H atom inner from the PF_2 group). Therefore, the difference of 0.021 Å from the microwave study[19] must be in error and the adjusted r_0 values of 1.007 and 1.010 Å for the $N-H_o$ and $N-H_i$ parameters, respectively, obtained from our results (Table 5) are expected to be much more accurate than the previously reported values.

In the same electron diffraction study[10] of the H_2NPF_2 molecule, the authors also carried out an investigation of (dimethylamino)difluorophosphine, $(CH_3)_2NPF_2$, and reported that this molecule also exists in a staggered conformation (C_1 symmetry) similar to that for H_2NPF_2. Therefore, we also carried out a structural study of this molecule and we found that some of the ab initio calculations predicted a slightly pyramidal $-PNC_2$ moiety (C_1 molecular symmetry) whereas others (including the two highest levels utilized) predicted a planar $-PNC_2$ moiety (C_s molecular symmetry) (Table 6). The r_0 structural parameters were obtained for both models. However, the fit of the asymmetric model resulted in a near-symmetric structure. This result suggested that the molecule may be more properly described with the symmetric model in analyzing the microwave data. We have also obtained the adjusted r_0 parameters by combining the predicted MP2(full)/6-311+G-(d,p) values and the previously reported[20] rotational constants (Table 6). The reported C−H distances from the electron

TABLE 4: Ab Initio Structure (Bond Lengths in Å, Bond Angles in Degrees, Rotational Constants in MHz, Dipole Moments in D) Obtained for the Trans and Cis Conformers of (Methylamino)thiophosphoryl Difluoride

	HF/6-31G(d)		MP2/6-31G(d)		MP2/6-311+G(d,p)		MP2/6-311+G(2d,2p)		
param	trans	cis	trans	cis	trans	cis	trans	cis	r_0: trans
r(C−N)	1.459	1.460	1.461	1.460	1.462	1.461	1.458	1.457	1.459(5)
r(N−P)	1.618	1.621	1.631	1.635	1.628	1.631	1.622	1.624	1.621(5)
r(P═S)	1.900	1.900	1.892	1.892	1.888	1.889	1.902	1.902	1.879(5)
r(P−F)	1.555	1.555	1.590	1.590	1.590	1.589	1.573	1.572	1.550(5)
r(N−H$_1$)	0.997	1.000	1.012	1.015	1.008	1.011	1.002	1.005	1.009(3)
r(C−H$_2$)	1.080	1.078	1.090	1.089	1.090	1.089	1.083	1.082	1.090(2)
r(C−H$_{3,4}$)	1.082	1.082	1.092	1.092	1.092	1.092	1.084	1.085	1.092(2)
∠CNP	126.3	128.1	125.6	126.6	126.2	126.6	125.5	126.1	124.7(5)
∠NPS	117.2	119.1	117.2	118.6	118.2	119.0	117.7	118.3	118.3(5)
∠NPF	104.4	103.7	103.8	103.4	103.5	103.4	103.6	103.5	103.2(5)
∠FPS	116.1	115.6	116.9	116.5	116.5	116.1	116.8	116.6	117.0(5)
∠FPF	95.8	95.8	95.2	95.2	95.4	95.4	95.1	95.1	94.6(5)
∠PNH$_1$	116.0	115.9	116.1	116.7	115.9	117.0	115.9	117.1	115.9(5)
∠CNH$_1$	117.7	116.0	118.4	116.7	118.0	116.5	118.6	116.8	119.5(5)
∠H$_2$CN	109.7	109.4	109.3	108.5	109.3	108.6	109.2	108.4	109.3(5)
∠H$_{3,4}$CN	110.4	110.2	110.6	110.5	110.6	110.5	110.8	110.7	110.6(5)
∠H$_2$CH$_{3,4}$	108.4	108.8	108.3	108.8	108.2	108.7	108.2	108.7	108.2(5)
∠H$_3$CH$_4$	109.5	109.5	109.6	109.6	109.9	109.8	109.6	109.5	109.9(5)
τ(SPNC)	180	0	180	0	180	0	180	0	180
τ(FPNS)	130.0	130.2	130.5	130.6	130.5	130.5	130.6	130.6	131.0(5)
τ(H$_2$CNH$_{3,4}$)	119.4	119.6	119.2	119.2	119.0	119.1	119.1	119.2	119.0(5)
$\|\mu_a\|$	4.779	4.470	4.402	4.239	4.001	4.335	3.943	3.998	
$\|\mu_b\|$	1.651	1.898	1.940	1.901	2.258	1.243	2.012	1.464	
$\|\mu_c\|$	0	0	0	0	0	0	0	0	
$\|\mu_{tot.}\|$	5.056	4.857	4.811	4.646	4.594	4.510	4.427	4.257	
A	3809.9	2645.9	3711.0	2579.6	3741.4	2591.5	3795.8	2590.2	3924.2[a]
B	1757.3	2264.9	1742.8	2257.9	1735.2	2255.0	1745.3	2297.7	1768.2
C	1599.6	1631.1	1587.8	1620.7	1589.1	1625.3	1593.3	1632.2	1616.2

[a] Difference between the rotational constants from microwave data and the adjusted r_0 structure: for $^{12}CH_3{}^{14}NHP(=^{32}S)^{19}F_2$, $\Delta A = 5.5$ MHz, $\Delta B = 0.0$ MHz, $\Delta C = 0.1$ MHz; for $^{12}CH_3{}^{14}NDP(=^{32}S)^{19}F_2$, $\Delta A = 5.1$ MHz, $\Delta B = 0.2$ MHz, $\Delta C = 0.1$ MHz; for $^{12}CD_3{}^{14}NHP(=^{32}S)^{19}F_2$, $\Delta(B + C) = 0.1$ MHz.

TABLE 5: Structural Parameters (Å, deg), Rotational Constants (MHz), and Dipole Moments (D) for the H_2NPF_2 with a Slightly Pyramidal −PNH$_2$ Moiety

param	HF/6-31G(d)	MP2/6-31G(d)	MP2/6-311+G(d,p)	MP2/6-311+G(2d,2p)	MP2/6-311+G(2df,2pd)	ED[a]	MW[b]	r_0[c]
r(N−P)	1.655	1.668	1.658	1.659	1.651	1.661(7)	1.650(4)	1.655(5)
r(P−F$_o$)	1.582	1.610	1.618	1.604	1.595	1.581(3)	1.587(4)	1.584(5)
r(P−F$_i$)	1.589	1.619	1.626	1.614	1.602	1.581(3)	1.587(4)	1.585(5)
r(N−H$_o$)	0.997	1.012	1.008	1.003	1.004		0.981(5)	1.007(3)
r(N−H$_i$)	1.000	1.016	1.011	1.006	1.008		1.002(5)	1.010(3)
∠NPF$_o$	98.5	97.6	98.5	97.9	98.7		100.6(2)	100.0(5)
∠NPF$_i$	102.3	103.2	101.9	102.4	102.2		100.6(2)	101.1(5)
∠FPF	94.3	94.4	94.2	94.2	94.3		94.6(2)	94.7(5)
∠PNH$_o$	118.3	117.7	118.3	117.0	118.0	118.3(6)	119.7(4)	118.2(5)
∠PNH$_i$	121.7	121.1	122.7	121.3	123.0	118.3(6)	123.1(2)	122.5(5)
∠H$_o$NH$_i$	114.4	114.1	114.9	114.1	114.9	111.8(15)	117.2(4)	114.5(5)
τ(FPNF)	96.3	96.4	96.1	96.1	96.3			96.9(5)
τ(HNPH)	152.2	148.7	156.0	147.9	155.9		180	154.0(5)
A	7794.3	7559.2	7483.4	7601.0	7687.4		7766.22(5)	7767.2
B	7037.3	6855.6	6888.4	6948.9	6996.5		7052.29(5)	7052.8
C	4610.2	4479.7	4479.5	4535.2	4567.2		4596.43(5)	4597.1
$\|\mu_a\|$	2.541	2.472	3.054	2.648	2.718		2.570(7)	
$\|\mu_b\|$	1.054	1.474	1.116	1.249	0.933		0.000	
$\|\mu_c\|$	0.060	0.024	0.321	0.000	0.105		0.18(1)	
$\|\mu_t\|$	2.751	2.878	3.267	2.928	2.876		2.576(7)	

[a] Reference 10. [b] Reference 19. [c] Adjusted from the MP2(full)/6-311+G(d,p) optimized structure, with the exception that the initial P−F distances are taken from optimized HF/6-31G(d) structure. Difference between the rotational constants from microwave data and the adjusted r_0 structure: for $H_2{}^{14}N^{31}P^{19}F_2$, $\Delta A = 1.0$ MHz, $\Delta B = 0.5$ MHz, $\Delta C = 0.6$ MHz; for $H_2{}^{15}N^{31}P^{19}F_2$, $\Delta A = 0.5$ MHz, $\Delta B = 0.3$ MHz, $\Delta C = 0.0$ MHz; for $H_oD_i{}^{15}N^{31}P^{19}F_2$, $\Delta A = 0.0$ MHz, $\Delta B = 0.3$ MHz, $\Delta C = 0.0$ MHz; for $H_iD_o{}^{15}N^{31}P^{19}F_2$, $\Delta A = 0.4$ MHz, $\Delta B = 0.2$ MHz, $\Delta C = 0.3$ MHz; for $D_2{}^{15}N^{31}P^{19}F_2$, $\Delta A = 1.2$ MHz, $\Delta B = 0.3$ MHz, $\Delta C = 0.3$ MHz.

diffraction study[10] are entirely too long, and there are several angles such as −PNC$_i$ and −C$_o$NC$_i$ which have unrealistic values so the listed uncertainties must be meaningless.

Discussion

The N−P distance of 1.621(5) Å in (methylamino)thiophosphoryl difluoride (Table 4) is significantly shorter than the ones in aminodifluorophosphine (1.655(5) Å, Table 5) and (dimethylamino)difluorophosphine (1.652(4) Å, Table 6), indicating conjugation between the lone pair of electrons of the nitrogen atom and the π orbital of the P═S bond. The structural parameters of the −P(═S)F$_2$ moiety calculated with different basis sets (Table 4) show large differences whereas the parameters of −NHCH$_3$ moiety are more consistent. A basis

TABLE 6: Structural Parameters (Å and Degree), Rotational Constants (MHz), and Dipole Moments (D) for $(CH_3)_2NPF_2$

param	HF/ 6-31G(d)	MP2/ 6-31G(d)	MP2/ 6-311+G(d,p)	MP2/ 6-311+G(d,p)	MP2/ 6-311+G(2d,2p)	MP2/ 6-311+G(2df,2pd)	ED[a]	MW[b]	r_0[d]
sym	C_s	C_1	C_1	C_s	C_s	C_s			C_s
r(N−P)	1.647	1.659	1.658	1.653	1.648	1.645	1.648(8)	1.6571(6)	1.652(4)
r(P−F$_o$)	1.591	1.620	1.624	1.631	1.617	1.607	1.589(3)	1.5945(7)	1.593(4)
r(P−F$_i$)	1.591	1.624	1.637	1.631	1.617	1.607		1.5945(7)	1.593(4)
r(N−C$_o$)	1.450	1.454	1.458	1.456	1.451	1.449	1.448(6)	1.4503(3)	1.453(4)
r(N−C$_i$)	1.453	1.457	1.459	1.458	1.453	1.447	1.448(6)	1.4503(3)	1.457(4)
r(C$_i$−H$_s$)	1.080	1.090	1.090	1.090	1.083	1.085	1.15(1)	1.090[c]	1.090(2)
r(C$_i$−H$_{ao}$)	1.086	1.095	1.094	1.095	1.088	1.090	1.15(1)	1.090[c]	1.095(2)
r(C$_i$−H$_{ai}$)	1.086	1.096	1.096	1.095	1.088	1.090		1.090[c]	1.095(2)
r(C$_o$−H$_s$)	1.083	1.092	1.093	1.092	1.085	1.087	1.15(1)	1.090[c]	1.093(2)
r(C$_o$−H$_{ao}$)	1.086	1.095	1.094	1.096	1.088	1.090	1.15(1)	1.090[c]	1.096(2)
r(C$_o$−H$_{ai}$)	1.086	1.097	1.097	1.096	1.088	1.090		1.090[c]	1.096(2)
∠NPF_o	100.9	99.6	99.1	100.9	101.0	101.1	97(4)	100.70(3)	100.8(5)
∠NPF$_i$	100.9	101.9	102.6	100.9	101.0	101.1		100.70(3)	100.8(5)
∠FPF	93.3	92.9	93.2	92.8	92.7	93.0	99(3)	93.49(5)	93.5(5)
∠PNC$_i$	123.4	122.8	123.5	124.5	124.0	124.1	118.3(6)	124.05(5)	124.1(5)
∠PNC$_o$	120.7	120.2	118.9	120.3	120.1	120.1	118.3(6)	119.73(2)	120.0(5)
∠C$_o$NC$_i$	115.9	116.0	114.6	115.2	115.9	115.7	111.8(15)	116.22(5)	116.0(5)
∠NC$_i$H$_s$	110.1	109.4	110.0	110.1	110.0	110.1	109.0(15)	110.6[c]	110.1(5)
∠NC$_i$H$_{ao}$	110.5	109.9	109.2	110.2	110.3	110.4	109.0(15)	110.6[c]	110.2(5)
∠NC$_i$H$_{ai}$	110.5	111.0	111.0	110.2	110.3	110.4		110.6[c]	110.2(5)
∠NC$_o$H$_s$	110.3	109.7	110.1	110.1	110.0	110.0	109.0(15)	110.6[c]	110.1(5)
∠NC$_o$H$_{ao}$	110.8	110.2	109.6	110.5	110.6	110.8	109.0(15)	110.6[c]	110.5(5)
∠NC$_o$H$_{ai}$	110.8	111.3	111.3	110.5	110.6	110.8		110.6[c]	110.5(5)
τ(FPNF)	95.4	95.0	95.3	95.1	94.8	95.2	86(2)	95.66(6)	95.7(10)
τ(C$_i$NPC$_o$)	180	167.9	159.2	180	180	180		180	180
A	4355.0	4259.1	4218.8	4241.9	4291.3	4322.7		4318.4(21)	4319.1
B	2172.8	2152.2	2170.4	2120.1	2146.4	2158.1		2164.684(18)	2164.9
C	2099.4	2069.2	2054.8	2062.3	2080.4	2191.5		2091.011(15)	2090.9
$\|\mu_a\|$	2.938	3.073	3.486	3.582	3.363	3.197		3.061(95)	
$\|\mu_b\|$	0.210	0.374	0.464	0.576	0.255	0.145			
$\|\mu_c\|$	0.000	0.295	0.295	0.000	0.000	0.000			
$\|\mu_t\|$	2.946	3.529	3.529	3.628	3.373	3.201			

[a] Reference 10. [b] Reference 20. [c] Assumed parameters. [d] Adjusted parameters obtained from MP2(full)/6-311+G(d,p) optimized structure with C_s symmetry, with the exception that the initial P−F distances are taken from the optimized HF/6-31G(d) structure. Difference between the rotational constants from microwave data and the adjusted r_0 structure: for $(^{12}CH_3)_2{}^{14}N^{31}P^{19}F_2$, ΔA = 0.7 MHz, ΔB = 0.2 MHz, ΔC = 0.1 MHz; for $(^{12}CD_3)_2{}^{14}N^{31}P^{19}F_2$, ΔA = 0.2 MHz, ΔB = 0.2 MHz, ΔC = 0.2 MHz; for $^{12}C_oD_3{}^{12}C_iH_3{}^{14}N^{31}P^{19}F_2$, ΔA = 0.4 MHz, ΔB = 0.1 MHz, ΔC = 0.1 MHz; for $^{12}C_oH_3{}^{12}C_iD_3{}^{14}N^{31}P^{19}F_2$, ΔA = 0.5 MHz, ΔB = 0.1 MHz, ΔC = 0.1 MHz.

TABLE 7: Calculated (Method/Basis Set) and Experimental Centrifugal Distortion Constants (in kHz) of $CH_3NHP({=}S)F_2$, $(CH_3)_2NPF_2$, and H_2NPF_2

	trans-$CH_3NHP({=}S)F_2$		$(CH_3)_2NPF_2$		
param	calcd with MP2(full)/6-311+G(d,p)	exptl[a]	calcd with MP2(full)/6-31G(d)	exptl[b]	H_2NPF_2: calcd with MP2(full)/6-311+G(d,p)
Δ_J	0.119	0.145(12)	0.404	0.508(107)	3.135
Δ_K	0.786		−2.388		−6.391
Δ_{JK}	1.183		3.264	2.47(48)	10.711
δ_J	0.012		0.062		0.903
δ_K	−0.419		−41.516	−35.4(82)	6.521

[a] This study. [b] Reference 20.

set larger than 6-311+G(2d,2p) is necessary to obtain a better predicted structure of the $-P({=}S)F_2$ moiety which contains phosphorus and sulfur and the double bond between them. In particular, it should be noted that the P−F distances are better predicted[5] from low-level HF calculations than MP2 calculations with even relatively large basis sets.

The centrifugal distortion constants were calculated with the Gaussian 98 programming package[13] for all three of the molecules investigated, and the predicted values are given in Table 7. For the H_2NPF_2 molecule, none of these constants were determined, but for the $(CH_3)_2NPF_2$ molecule, three of the five normally obtained constants were obtained experimentally.[20] For both the Δ_J and δ_K constants, the experimental values are in agreement with the predicted ones within the experimental error limits and Δ_{JK} does not differ significantly. In this study, only the Δ_J constant was obtained for the $CH_3NHP({=}S)F_2$ molecule experimentally (0.145(12) kHz) and it is in satisfactory agreement with the predicted value (0.119 kHz). These limited results indicate that ab initio calculations at the MP2(full) level with relatively small basis sets can provide excellent predictions for the values of the centrifugal distortion constants.

It should be noted that there are three coordinates, SPNC skeletal torsion, methyl torsion, and NH "out-of-plane" bend, that are important in determining the position of the energy minima. Therefore, a one-dimensional model can only approximately describe the potential function. Nevertheless, to obtain the potential function governing the asymmetric torsion, calculations were performed at the MP2(full)/6-311+G(2d,2p) level by fixing the SPNC dihedral angle at 15° intervals from 0 to 180° and optimizing the remaining geometric parameters. The resulting potential function is shown in Figure 3. The trans-to-cis barrier is predicted to be 1538 cm^{-1}. The potential

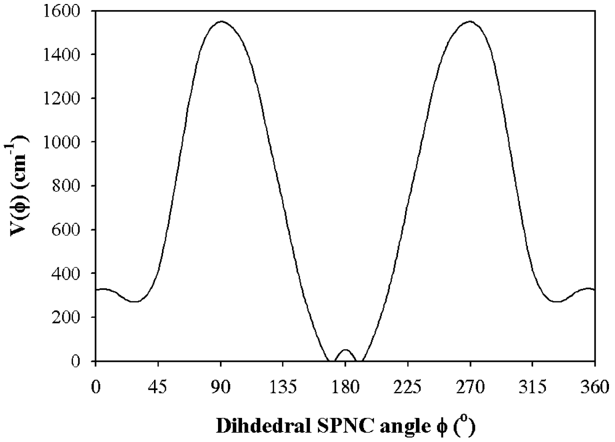

Figure 3. Asymmetric torsional potential function governing the τ-(SPNC) dihedral angle for $CH_3NHP(=S)F_2$ calculated at the MP2(full)/6-311+G(2d,2p) level.

function can be expressed by a Fourier cosine series:

$$V(\phi) = \sum_i V_i/2(1 - \cos i\phi)$$

Here ϕ and i are the SPNC torsional angle and foldness of the barrier for each individual term, respectively. When the small potential bumps at the trans and cis configurations are ignored, the first four potential coefficients, V_1−V_4, were calculated from the fit of the single point calculations with varying SPNC dihedral angles. The Fourier cosine coefficients are $V_1 = -184$, $V_2 = 1393$, $V_3 = -135$, and $V_4 = -93$ cm^{-1}.

In both the trans and the cis configurations, the in-plane hydrogen of the methyl group is cis-periplanar to the N−P bond. The predicted 3-fold barrier to methyl rotation at the MP2(full)/6-31G(d) level is only 36 cm^{-1} at for the trans form which indicates that nearly free rotation of the methyl group might be observed in the infrared spectrum of the vapor. In fact, a very broad nondescriptive band was observed in the region expected for the CH_3 antisymmetric deformation but it was not assigned as a fundamental.[6] In addition, it appears that a similar broad band was observed for the CH_3 antisymmetric stretch. Thus, a reinvestigation of the infrared spectrum of the gas would be of interest to evaluate the barrier to internal rotation of the methyl group.

A small barrier in the potential function governing a large amplitude vibration can frequently be determined by the nonlinearity of the change in the rotational constants of the excited states of such a vibration. For (dimethylamino)-difluorophosphine, the rotational constants for the excited states of the asymmetric torsion vary in a harmonic manner[20] which indicates that there is a plane of symmetry for this molecule. However for aminodifluorophosphine the authors[19] pointed out that the excited-state rotational constants of the lowest frequency vibration (ν_{12}, asymmetric torsion) do not vary in a harmonic manner. They[19] attributed this nonharmonic variation to vibrational−rotational interaction between $2 \times \nu_{12}$ and ν_8 since they have similar energies. However, it is very probable that the variation is due to the small barrier of the planar configuration of the nitrogen atom rather than the vibrational−rotational interaction.

Acknowledgment. J.R.D. acknowledges the University of Missouri−Kansas City for a Faculty Research Grant for partial financial support of this research. We thank the Flemish Community for financial support through the Special Research Fund (BOF) and the Scientific Affairs Division of NATO for travel funds between our two laboratories.

Supporting Information Available: Table 1S, listing calculated energies and energy differences for the near-trans, trans, near-cis, and cis forms of $H_3CNHP(=S)F_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Durig, J. R.; Meadows, J. A.; Li, Y. S.; Stanley, A. E. *Inorg. Chem.* **1983**, *22*, 4134.
(2) Van der Veken, B. J.; Coppens, P.; Johnson, R. D.; Durig, J. R. *J. Phys. Chem.* **1986**, *90*, 4537.
(3) Durig, J. R.; Johnson, R. D.; Nanaie, H.; Hizer, T. J. *J. Chem. Phys.* **1988**, *88*, 7317.
(4) Chatterjee, K. K.; Durig, J. R. *J. Mol. Struct.* **1995**, *351*, 25.
(5) Durig, J. R.; Robb, J. B., II; Xiao, J.; Gounev, T. K. *J. Mol. Struct.* **2000**, *516*, 131.
(6) Van der Veken, B. J.; Sanders, R. S.; Xiao, J.; Durig, J. R. *J. Mol. Struct.* **2001**, *560*, 57.
(7) Durig, J. R.; Xiao, J. *J. Mol. Struct.* **2001**, *562*, 145.
(8) Durig, J. R.; Daeyaert, F. F. D. *J. Raman Spectrosc.* **1998**, *29*, 191.
(9) Durig, J. R.; Casper, J. M. *J. Cryst. Mol. Struct.* **1972**, *2*, 1.
(10) Holywell, G. C.; Rankin, D. W. H.; Beagley, B.; Freeman, J. M. *J. Chem. Soc. A* **1971**, 785.
(11) Cavell, R. G.; Charlton, T. L.; Sim, W. *J. Am. Chem. Soc.* **1971**, *93*, 1130.
(12) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.2; Gaussian, Inc.: Pittsburgh, PA, 2001.
(14) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.
(15) Durig, J. R.; Ng, K. W.; Zheng, C.; Shen, S. *Struct. Chem.* **2004**, *15*, 149.
(16) McKean, D. C. *J. Mol. Struct.* **1984**, *113*, 251.
(17) Durig, J. R.; Yu, Z.; Zheng, C.; Guirgis, G. A. *J. Phys. Chem. A* **2004**, *108*, 5353.
(18) Van der Veken, B. J.; Herrebout, W. A.; Durig, D. T.; Zhao, W.; Durig, J. R. *J. Phys. Chem. A* **1999**, *103*, 1976.
(19) Brittain, A. H.; Smith, J. E.; Lee, P. L.; Cohn, K.; Schwendeman, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 6772.
(20) Durig, J. R.; Harlan, R. J.; Groner, P. *J. Phys. Chem.* **1989**, *93*, 3041.