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Microwave Spectrum, Structure, Dipole Moment, and Vibrational Spectrum of Dimethylcyanophosphine

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The microwave spectrum of dimethylcyanophosphine has been recorded from 26.5 to 40.0 GHz. Only A-type transitions were observed. The R-branch assignments have been made for the ground state and three vibrationally excited states. It is shown that the heavy-atom skeleton is nonplanar from the magnitude of the μ_c component of the dipole moment as well as from the value of $I_a + I_b - I_c$. The following structural parameters were obtained: $r(\text{P}-\text{CN}) = 1.783$ Å, $\angle\text{CPC} = 101°$, and $\angle\text{CPC}(\equiv\text{N}) = 99°$ with reasonable assumptions made for the structural parameters of the dimethylphosphino moiety and the nitrile bond. These parameters are consistent with those previously reported for trimethylphosphine and tricyanophosphine. The dipole moment components were determined to be $\mu_a = 3.83 \pm 0.05$ D and $\mu_c = 1.5 \pm 0.1$ D with a total dipole moment of 4.11 ± 0.08 D. A vibrational assignment has been made, and from the low-frequency vibrational data of the solid, a tentative value of 2.2 kcal/mol was obtained for the barrier to internal rotation of the methyl groups.

Introduction

There have been many microwave studies of molecules containing the C≡N group, especially the group IVa and Va nitriles, for the purpose of determining the effect of the strong electron-withdrawing group CN on the molecular structure.[2-17] In addition, there is the possibility of bonding through the nitrogen of the CN group, to form the isocyanide compounds. Recently, in this laboratory, microwave and vibrational studies were completed on isopropyl cyanide, $(CH_3)_2CHCN$,[18] and dimethylcyanamide, $(CH_3)_2NCN$.[19] In the latter work, Li and Durig[19] found evidence of significant electron delocalization and a large contribution of sp^2 hybridization on the apex nitrogen. As an extension of this work, a microwave investigation of dimethylcyanophosphine has been undertaken.

A vibrational study of $(CH_3)_2PCN$ was conducted by Goubeau, *et al.*,[20] but their assignment was incomplete. Therefore, Raman, infrared and far-infrared data were obtained for the solid sample and a complete vibrational assignment is presented.

Experimental Section

The sample used in the present work was prepared by the method of Jones and Coskran[21] and purified on a low-temperature distillation column. Sample purity was confirmed by comparison of the ^{31}P nmr and mass spectral data with those previously reported.[21]

The microwave spectrum of $(CH_3)_2PCN$ was investigated in the frequency region 26.5–40.0 GHz using a Hewlett-Packard 8460A MRR spectrometer with a Stark modulation frequency of 33.33 kHz. The Stark cell was maintained at Dry Ice temperature for all measurements except those of relative intensity, which were performed at room temperature.

The infrared spectra were recorded from 4000 to 200 cm^{-1} with a Perkin-Elmer Model 621 spectrophotometer. The atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry air. In the higher frequency region, the instrument was calibrated with standard gases.[22] The lower wave number region was calibrated by using atmospheric water vapor and the frequencies reported by Hall and Dowling.[23] The spectrum of the solid was obtained by condensing the sample on a CsI plate maintained at −190° with boiling nitrogen.

The Raman spectrophotometer used was a Cary Model 82 equipped with a CRL Model 53A argon ion laser source. The spectrum of the room-temperature liquid was taken with the sample sealed in a capillary tube. The spectrum of the solid sample (−190°) was obtained by using a cell which was similar in design to a far-infrared cell which was described earlier.[24] Depolarization measurements in the liquid phase were made by using the analyzer in the monochromator when making such measurements.

The far-infrared spectrum was recorded from 33 to 590 cm^{-1} on a Beckman Model IR-11 spectrophotometer. The instrument was purged with dry nitrogen and calibrated with the frequencies reported for water vapor by Hall and Dowling.[23] The cell used for recording the spectrum of the solid at −190° has been described earlier.[24] The frequencies for all observed bands are expected to be accurate to ±2 cm^{-1}.

Microwave Spectrum and Results

Preliminary spectral predictions for dimethylcyanophosphine were made using the reported structures of $P(CN)_3$[25] and $(CH_3)_3P$.[26] These calculations indicated that the molecule was an asymmetry parameter $\kappa = -0.60$ with principally A-type transitions predicted. A diagram of the molecule in the principal axis system is given in Figure 1. There was no apparent hyperfine structure observed due to the nitrogen

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(1) Taken in part from the thesis of A. W. Cox, Jr., to be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

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Table I. Rotational Transitions (cm^{-1}), Rotational Constants (MHz), and Moments of Inertia (amu Å^2)^a of Dimethylcyanophosphine

	$\nu = 0$		$\nu_\alpha = 1$		$\nu_\beta = 1$		$\nu_\gamma = 1$	
	Obsd	Obsd − calcd	Obsd	Obsd − calcd	Obsd	Obsd − calcd	Obsd	Obsd − calcd
$5_{14} \leftarrow 4_{13}$	28,748.66	0.29	28,721.18	0.24			28,743.56	0.22
$5_{24} \leftarrow 4_{23}$	27,406.90	0.26	27,379.67	−0.05	27,437.90	0.09	27,400.64	0.05
$6_{06} \leftarrow 5_{05}$	30,675.86	0.12	30,637.08	0.14	30,730.31	0.18	30,662.15	0.04
$6_{15} \leftarrow 5_{14}$	33,995.45	0.03	33,959.05	0.02	34,045.63	0.28	33,986.87	0.18
$6_{16} \leftarrow 5_{15}$	30,447.41	0.13	30,410.79	0.13	30,495.27	0.13	30.434.95	0.13
$6_{25} \leftarrow 5_{24}$	32,676.67	−0.02	32,643.15	0.00	32,717.39	−0.07	32,668.38	−0.04
$7_{07} \leftarrow 6_{06}$	35,456.82	−0.03	35,412.09	−0.11	35,518.25	−0.02		
$7_{16} \leftarrow 6_{15}$	38,973.23	−0.22	38,927.34	−0.02	39,041.32	−0.17	38,960.16	−0.09
$7_{17} \leftarrow 6_{16}$	35,336.25	0.01	35,293.16	0.07	35,393.05	−0.10	35,321.32	0.09
$7_{26} \leftarrow 6_{25}$	37,849.14	−0.19	37,808.46	−0.29	37,900.65	−0.19	37,838.10	−0.40
A	5763.1 ± 0.3		5750.6 ± 0.2		5797.0 ± 0.3		5759.2 ± 0.4	
B	3116.55 ± 0.02		3114.57 ± 0.01		3117.95 ± 0.03		3116.78 ± 0.03	
C	2418.34 ± 0.01		2415.29 ± 0.01		2422.26 ± 0.01		2417.18 ± 0.01	
κ	−0.58250		−0.58067		−0.58771		−0.58134	
I_a	87.693		87.883		87.179		87.751	
I_b	162.159		162.262		162.087		162.147	
I_c	208.976		209.241		208.638		209.077	
$I_a + I_b - I_c$	40.875		40.904		40.628		40.820	
$I_a + I_c - I_b$	134.51		134.86		133.73		134.68	

^{a} Conversion factor 505,377 MHz amu Å^2.

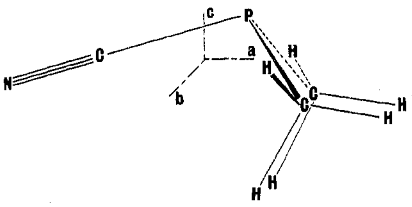

Figure 1. Projection of $(CH_3)_2PCN$ in its *ac* plane of symmetry.

quadrupole, and, therefore, no quadrupole coupling information was obtained from the present study.

The assignment was made mainly on the basis of the rigid-rotor model fit. The Stark effects were also used to check some of the assigned transitions. The microwave spectrum and a computer plot of the spectrum generated from the fitted rotational constants are shown in Figure 2. Around each ground-state line, there are many weaker satellite lines which arise from molecules in excited vibrational states of low-frequency modes.

The frequencies and assignments for the ground and three excited vibrational states and the differences between the observed and calculated frequencies are given in Table I. The observed rotational constants, moments of inertia, and inertial defect terms for the ground and three excited vibrational states are also given in Table I. The relative intensity of the three excited-state satellites was measured with respect to the ground-state line intensity for several transitions. The calculated energy level differences between the ground and excited vibrational states were $\nu_\alpha = 252 \pm 20$ cm^{-1}, $\nu_\beta = 201 \pm 10$ cm^{-1}, and $\nu_\gamma = 178 \pm 15$ cm^{-1}. The quoted error is derived from the standard deviation of the data.

A major problem of interest in the present study is the determination of the skeletal configuration of the $(CH_3)_2$-PCN molecule. From Table I, it can be clearly seen that the magnitude of $I_a + I_b - I_c$ is larger than that which would be observed from only the out-of-plane hydrogen atoms of the methyl groups. Thus, one can conclude that the heavy-atom skeleton is nonplanar.

A complete structural determination is not possible from the present experimental information. In order to obtain some quantitative values for the nonplanarity and the P–C(≡N) bond distance, assumptions have been made in dimethylphosphino parameters and the C≡N distance. An X-ray diffraction study of $P(CN)_3$ indicated a nonlinear P–C≡N angle of 172°.[25] This was attributed to requirements of crystal packing,[27] but recent work by Schwendeman, *et al.*,[16] determined the P–C≡N angle to be 171° in gaseous PF_2CN. The reason for this somewhat surprising angle is unclear, so for the purpose of this study, two sets of calculations were performed. In the first set, the P–C≡N angle was assumed to be 180°, and in the second set, 171.2°. For both cases, the other assumed parameters were r(P–C) = 1.843 Å, r(C–H) = 1.100 Å, r(C≡N) = 1.157 Å, and ∠HCH = 109.5°. A linear regression structure was calculated using the experimental rotational constants allowing the P–C(≡N) distance and the internal angle between the P–C(≡N) bond and the

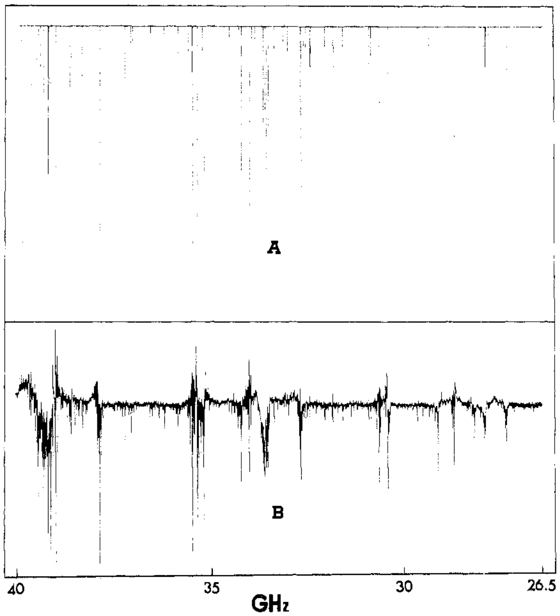

Figure 2. (A) Computer plot of the microwave spectrum of $(CH_3)_2PCN$ generated from the fitted rotational constants. (B) Microwave spectrum of $(CH_3)_2PCN$.

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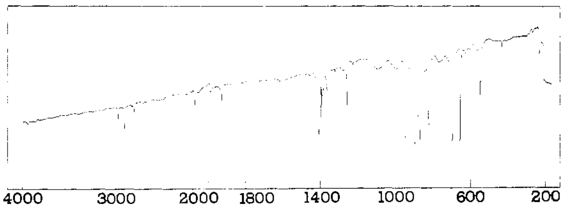

Figure 3. Infrared spectrum of $(CH_3)_2PCN$ at ~−190°.

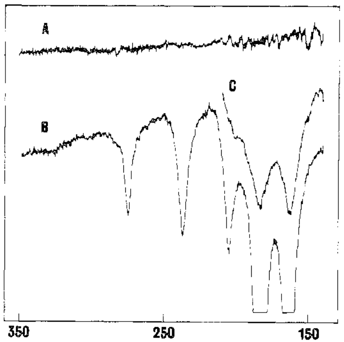

Figure 4. Far-infrared spectrum of $(CH_3)_2PCN$ at ~−190°: (A) cell background; (B) annealed sample; (C) some sample evaporated.

CPC plane to vary. Several calculations were carried out for each case assuming different values in the range 97-105° for the CPC angle in the dimethylphosphino moiety. Minimization of root sum square of the deviations between the observed and calculated moments of inertia, $[\Sigma_g \Delta I_g^2]^{1/2}$, $g = a, b, c$, gave the following results. The optimum value for the CPC angle in the dimethylphosphino moiety was found to be 101° for both the linear and bent configurations of the P–C≡N angle. The P–C(≡N) bond length was calculated to be 1.783 Å for the linear case and 1.771 Å for the bent case. The calculated internal angles for the linear and bent cases were 104.4 and 108.5°, respectively.

Dipole Moment

The quadratic Stark effect of $(CH_3)_2PCN$ has been measured for the $|M| = 1$ component of the $5_{14} \leftarrow 4_{13}$ transition, the $|M| = 2$ component of the $6_{16} \leftarrow 5_{15}$ transition, and the $|M| = 1$ and $|M| = 2$ components of the $6_{25} \leftarrow 5_{24}$ transition. The $|M| = 2$ component of the $6_{16} \leftarrow 5_{15}$ transition showed a perturbation due to higher order terms in the Stark effect and was appropriately corrected. The electric field was calibrated using the $3 \leftarrow 2$, $|M| = 2$, transition of OCS with its dipole moment taken to be 0.71521 D.[28] The components of the electric dipole moment along the a and c axes and estimated error limits are 3.83 ± 0.05 and 1.5 ± 0.1 D, respectively. The total dipole moment is 4.11 ± 0.08 D.

Vibrational Spectrum and Results

The mid-infrared, far-infrared, and Raman spectra of solid $(CH_3)_2PCN$ are shown in Figures 3-5. Since the heavy-atom skeleton is nonplanar, the molecule belongs to symmetry group C_s and 15 a′ and 12 a″ modes are expected. The observed frequencies and their assignments are given in Table II.

The assignment of the bands above 800 cm^{-1} is reasonably straightforward on the basis of relative intensities and expected frequencies. This leaves three skeletal stretches, five skeletal bends, and two CH_3 torsions to be assigned. The C-P stretches are expected to be the highest frequency bands

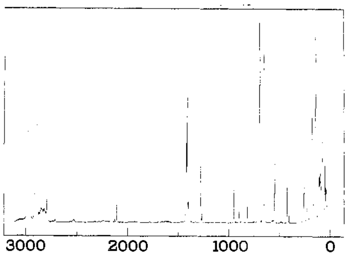

Figure 5. Raman spectrum of $(CH_3)_2PCN$ at ~−190°.

Table II. Frequencies (cm^{-1}) and Assignments for Dimethylcyanophosphine

Raman			
Solid	Liquid	Infrared Solid	Assignment
2990 vs	2987 vs	2986 m	ν_1, ν_2 (a′), ν_{16}, ν_{17} (a″) CH_3 str
2917 vs	2915 vs	2920 w	ν_3 (a′), ν_{18} (a″) CH_3 str
2168 vvs	2170 vs	2170 w	ν_4 (a′) C≡N str
1433 s		1432 s	ν_{19} (a″) CH_3 def
1424 s		1421 s	ν_5 (a′) CH_3 def
1412 m		1413 m	ν_{20} (a″) CH_3 def
1407 m	1403 w	1399 m	ν_6 (a′) CH_3 def
1293 s	1288 w	1283 m	ν_7 (a′) CH_3 def
1277 m		1274 m	ν_{21} (a″) CH_3 def
964 m	950 vw	963 s	ν_{22} (a″) CH_3 rock
915 w		913 s	ν_8 (a′) CH_3 rock
886 m		884 s	ν_{23} (a″) CH_3 rock
835 w		840 s	ν_9 (a′) CH_3 rock
713 vs	714 s, dp	713 s	ν_{24} (a″) C-P str
673 vs	668 vs, p	673 s	ν_{10} (a′) C-P str
560 s	565 w, p	561 s	ν_{11} (a′) P-CN str
439 m	435 w, p	441 w	ν_{12} (a′) skel def
421 vw			Two-phonon band
268 m	268 w, p	276 (275) w	ν_{13} (a′) skel def
238 w		238 (236) w	ν_{25} (a″) skel def
		206 (204) w	ν_{26} (a″) out-of-phase torsion (?)
191 s	190 s, p(?)	(184) s	ν_{14} (a′) skel def
180 vw			ν_{15} (a′) in-phase torsion (?)
158 s	160 s, dp(?)	(162) s	ν_{27} (a″) skel def
116 m			Lattice modes
107 m			
90 s			
86 s			
60 m			
51 w			

[a] Abbreviations used: m, medium; w, weak; s, strong; v, very; p, polarized; dp, depolarized.

in this region, and the 673- and 713-cm^{-1} bands are assigned to the symmetric, ν_{10}, and antisymmetric, ν_{24}, stretches of the methyl carbon–phosphorus bonds. The slightly lower band at 560 cm^{-1} is assigned as the P-CN stretch, ν_{11}, involving the nitrile carbon. Of the five remaining skeletal modes, the three a′ modes and the two a″ modes are expected to couple strongly, and, hence, in the absence of any data for

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isotopically substituted molecules, their assignment is tentative. One possibility is to assign the 439-cm^{-1} band to the in-plane P—C≡N bend, ν_{12}, and the band at 238 cm^{-1} to the out-of-plane bend, ν_{25}. The band at 435 cm^{-1} in the Raman spectrum of the liquid was polarized, but no depolarization data were obtained for the 238-cm^{-1} band, which was not resolved in the spectrum of the liquid phase. The three C_3P deformations could then be assigned to the bands at 268 cm^{-1}, ν_{13}, 191 cm^{-1}, ν_{14}, and 158 cm^{-1}, ν_{27}. The shoulder at 204 cm^{-1} in the far-infrared spectrum and the shoulder at 180 cm^{-1} in the Raman spectrum of the solid are tentatively assigned as the out-of-phase, ν_{26}, and in-phase, ν_{15}, torsions, respectively. The weakness of the bands, as well as their relative frequencies, is consistent with their being assigned as torsional motions.

Discussion

The results of the structural calculations indicated that the angle between the CPC plane and the P—C≡N linkage is not very sensitive to the CPC angle in the $(CH_3)_2P$ moiety and the P—C(≡N) distance increases smoothly with an increasing CPC angle. The CPC angle and the calculated CPC(≡N) angles of 99 and 101.7° for the linear and bent configurations, respectively, are comparable with those found in $(CH_3)_3P$[26] and $(CN)_3P$.[25] Thus, there is no evidence of electron delocalization of the nonbonded electron pair on the phosphorus atom. It is not possible to give meaningful error limits on the calculated structural parameters due to the relatively large number of assumed parameters. However, the calculations do seem to indicate the linear configuration of the P—C≡N bond as the appropriate one. This is reasonable, since two molecules in which a bent P—C≡N bond has been found[16,25] had strong electron-withdrawing groups as the other two substituents on the phosphorus (CN and F), whereas $(CH_3)_3PCN$ does not.

Since the nitrile group is more electronegative than the $(CH_3)P$ group, the dipole moment should be directed from the $(CH_3)_2P$ moiety to the negative center of the nitrile group. The dipole moment (4.11 D) is less than that of $(CH_3)_2NCN$ (4.77 D)[19] which is to be expected if the lone pair of electrons in the phosphorus compound contributes less to the dipole moment than the lone pair in the nitrogen compound, as previous work suggests.[17,29]

The calculated frequency of the excited vibrational state ν_α, 252 ± 20 cm^{-1}, corresponds to ν_{13}, 268 cm^{-1}, in the Raman spectrum of the solid. Also, ν_{13} is an a′ mode and the value of $I_a + I_c - I_b$ for ν_α is not very different from that of the ground state. The assignment of ν_β, 201 ± 10 cm^{-1}, and ν_γ, 178 ± 15 cm^{-1}, is not as clear. Consistent with $I_a + I_c - I_b$ values for ν_β and ν_γ, they could be excited states of the out-of-phase and in-phase torsional motions, respectively. Or, on the other hand, they could be excited states of the two lowest skeletal deformations.

We have been interested in the barriers to internal rotation of methyl groups attached to phosphorus.[30-33] Unfortunately, no barrier information was obtained from the microwave study of $(CH_3)_2PCN$. Barrier calculations[34] were performed using the data from the vibrational studies and an F value of 5.23 cm^{-1} calculated from the proposed structure. One can calculate a barrier to internal rotation by assuming the interaction between the two tops is negligible. Using 204 cm^{-1} as a torsional frequency, one calculates a harmonic barrier of 2.5 kcal/mol for the barrier in the solid sample. If one assumes the second torsion to correspond to the 180-cm^{-1} band, the internal rotational barrier is calculated to be 2.2 kcal/mol. These values are in qualitative agreement with the barriers to internal rotation of methyl groups of 3.58 kcal/mol reported for $(CH_3)_3P$[32] and 2.14 kcal/mol reported for $(CH_3)_2PH$.[35] However, it should be pointed out the internal rotational barrier in dimethylcyanophosphine is dependent on a correct assignment of the torsional modes, and because no studies were made on the deuterium compound, this assignment must be considered tentative.

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