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Microwave Spectrum, Conformational Equilibria, Intramolecular Hydrogen Bonding and Centrifugal Distortion of 3-Phosphinopropionitrile

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The microwave spectrum of 3-phosphinopropionitrile, $N{\equiv}CCH_2CH_2PH_2$, has been investigated in the 19.2–36.4 GHz spectral region at about −10 °C. Three conformations, denoted II, IV and V, were assigned. The heavy-atom *gauche* conformation II is stabilized by a weak hydrogen bond formed between one of the phosphino group hydrogen atoms and the π-electrons of the cyano group. No hydrogen bond is possible for the two heavy-atom *anti* conformations IV and V.

II is more stable than V by 0.3(20) kJ/mol. V is more stable than IV by 3(2) kJ/mol. Further rotameric forms are at least 2 kJ/mol less stable than II.

The CCCP dihedral angle is 66(3)° and the CCP angle is 117.0(15)° in II. The CCP angle was determined to be 109.0(15)° in IV, and to be 114.0(15)° in V.

Several vibrationally excited states were assigned for the three rotamers. The C–C torsional frequency of II was determined to be 108(30) cm^{-1} by relative intensity measurements and 107(10) cm^{-1} using the centrifugal distortion constants in a force-field calculation.

In recent years, ethanol derivatives of the form XCH_2CH_2OH, where X=F,[1] Cl,[2a] Br,[2a] OH,[3] NH_2,[4] SH,[5] $HC{=}CH_2$,[6] $C{\equiv}C{-}H$,[7] OCH_3,[8] $NH(CH_3)$[9] and $N(CH_3)_2$,[10] have been studied in the gaseous state by microwave spectroscopy. In each of these cases, the hydrogen-bonded conformation has been found to predominate to such an extent that no further rotamers have been identified by this method. Similar findings have been made for ethylamine derivatives, $XCH_2CH_2NH_2$, with X=F,[11] NH_2,[12] $C{\equiv}N$,[13] and OCH_3.[14]. However, at higher temperatures the heavy-atom *anti* conformation of CH_2ClCH_2OH is present in the gaseous state in considerable amounts as shown by electron diffraction.[2b]

The intramolecular hydrogen bonding ability of the hydroxyl and the amino groups thus seems to be well-documented and relatively strong in these molecules. Few investigations have been made for ethyl thiols of the form XCH_2CH_2SH. The mercapto group is considered to be a considerably poorer proton donor than the hydroxyl and amino groups. The results obtained for CH_2ClCH_2SH,[15] $H_2NCH_2CH_2SH$[15] and $N{\equiv}CCH_2CH_2SH$[16] are in keeping with this view. In the case of CH_2ClCH_2SH,[15] only one heavy-atom *anti* conformation without an internal hydrogen bond was identified. Two conformations were found for $HSCH_2CH_2NH_2$.[15] The one with the highest energy was found to have an intramolecular hydrogen bond with the mercapto group acting as proton donor and the amino group as acceptor. Two rotamers, one with and the other (the heavy-atom *anti* rotamer) without a hydrogen bond were assigned for $N{\equiv}CCH_2CH_2SH$.[16] The hydrogen-bonded conformation was found to be the more stable by 1.3(20)kJ/mol.

No microwave studies have previously been made for ethylphosphines of the type $XCH_2CH_2PH_2$, where X is some proton-accepting group. The phosphino group is presumably even a slightly weaker proton donor than the mercapto group. In order to investigate the

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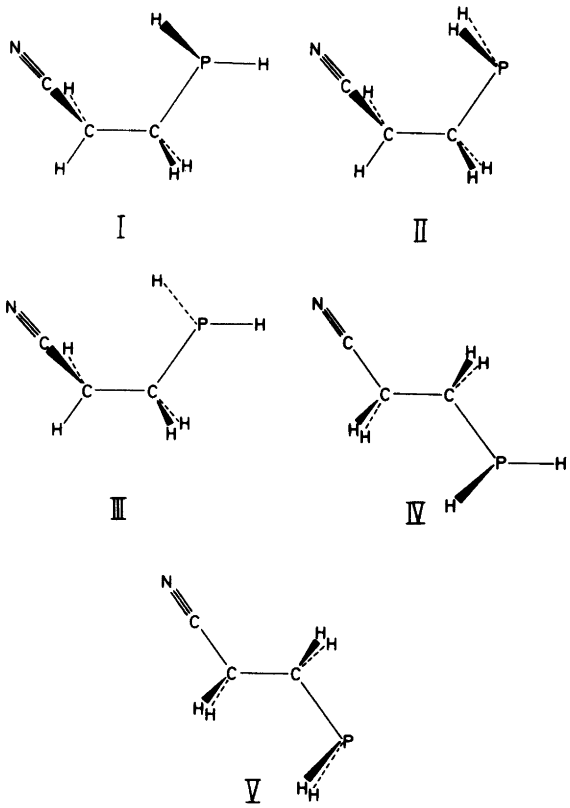

Fig. 1. Possible conformations of $NCCH_2CH_2PH_2$ with all-staggered atomic arrangements. The hydrogen-bonded heavy-atom *gauche* conformation II as well as the two heavy-atom *anti* conformations IV and V were assigned. II is the most stable conformation. It is more stable than V by 0.3(20) kJ/mol. V is more stable than IV by 3(2) kJ/mol.

internal hydrogen bonding ability of the phosphino group, $N{\equiv}CCH_2CH_2PH_2$ was chosen for study.

Five all-staggered conformations are possible for $NCCH_2CH_2PH_2$ as shown in Fig. 1. Weak hydrogen bonds formed between the phosphino group and the π electrons of the cyano group are possible for the heavy-atom *gauche* conformations I and II shown in this figure, while hydrogen bonding is not possible in the three further rotamers III, IV and V. Three rotamers, *viz.* II, IV and V, were found in this work. II is the most stable. It is 0.3(20)kJ/mol more stable than V which again is 3.0(15)kJ/mol more stable than IV. I and III are each less stable than II by at least 2 kJ/mol if they exist at all as stable conformations of $NCCH_2CH_2PH_2$.

EXPERIMENTAL

3-Phosphinopropionitrile was purchased from Aldrich-Europe, Beerse, Belgium, and used as received. Small amounts of CH_3CN, CH_3CH_2CN and $CH_2{=}CHCN$ impurities were noted by their microwave spectra. Spectra were recorded in the 19.2–36.4 GHz region at a pressure of about 0.5 Pa. A few measurements were also made above 36.4 GHz. The cell was cooled to about −10 °C. Lower temperatures could not be employed due to insufficient vapour pressure of $NCCH_2CH_2PH_2$.

The spectrum of 3-phosphinopropionitrile was found to be very dense. Most lines are very weak (peak absorption coefficients being less than roughly $5{\times}10^{-8}$ cm^{-1}). The strongest lines were the *b*-type *Q*-branch ground vibrational state lines of conformation II with *J* between 20 and

Table 1. Microwave spectrum of the ground vibrational state of conformation V of $NCCH_2CH_2PH_2$.

Transition	Observed frequency[a] (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion (MHz)
$6_{0,6}\rightarrow 7_{0,7}$	19933.73	−0.09	−0.26
$6_{1,6}\rightarrow 7_{1,7}$	19770.28	0.07	−0.20
$7_{0,7}\rightarrow 8_{0,8}$	22779.72	−0.08	−0.39
$7_{1,6}\rightarrow 8_{1,7}$	22976.01	−0.01	−0.32
$7_{1,7}\rightarrow 8_{1,8}$	22594.11	0.07	−0.32
$8_{0,8}\rightarrow 9_{0,9}$	25624.97	−0.14	−0.55
$8_{1,7}\rightarrow 9_{1,8}$	25847.55	0.16	−0.48
$8_{1,8}\rightarrow 9_{1,9}$	25417.69	0.02	−0.48
$9_{0,9}\rightarrow 10_{0,10}$	28469.70	0.06	−0.76
$9_{1,9}\rightarrow 10_{1,10}$	28241.11	0.03	−0.68
$9_{2,7}\rightarrow 10_{2,8}$	28494.51	−0.03	−0.44
$10_{0,10}\rightarrow 11_{0,11}$	31313.18	−0.15	−1.01
$10_{2,8}\rightarrow 11_{2,9}$	31346.49	0.09	−0.66
$11_{0,11}\rightarrow 12_{0,12}$	34156.22	0.13	−1.31
$11_{1,11}\rightarrow 12_{1,12}$	33887.16	−0.01	−1.22
$11_{2,9}\rightarrow 12_{2,10}$	34198.87	−0.09	−0.93
$11_{2,10}\rightarrow 12_{2,9}$	34175.87	−0.03	−0.93

[a] ±0.10 MHz.

30. The peak absorption coefficients of these transitions were roughly 3×10^{-7} cm^{-1}.

RESULTS

Assignment of conformation V. In our work on $NCCH_2CH_2SH$[16] one heavy-atom *anti* conformation not possessing internal hydrogen bonding, was found to make up a large fraction of the gas. The phosphino group was presumed to be a slightly weaker proton donor than the mercapto group. The existence of heavy-atom *anti* conformations was therefore considered to be quite probable for $NCCH_2CP_2PH_2$. Moreover, in the case of $CH_3CH_2PH_2$[17] a conformation having the phosphino group in a position similar to that of V was found to predominate. Conformation V was therefore assumed to be a likely candidate to search for.

Model calculations of the rotational constants indicated that V should be almost a symmetric top with Ray's asymmetry parameter[18] $\kappa \approx -0.99$. The dipole moment components along the principal inertial axes were predicted to be $\mu_a=3.2$ D, $\mu_b=1.6$ D and $\mu_c=0.0$ D (for symmetry reasons), using, with one exception, the bond moments of Ref. 19. In this reference, no value for the C−P bond moment is given. In our computations this bond moment was arbitrarily assigned a value of 0.0 D, because the electronegativity values of carbon and phosphorous are fairly similar.

A series of relatively strong lines, the *a*-type *R*-branch high-$K_1\neq1$ pile-ups, separated by almost exactly $B+C$ was therefore expected to occur for the heavy-atom *anti* conformation V. This simple series was immediately identified. The K_{-1} pair of lines were then assigned after some searching as were a few other low K_{-1}-transitions. The spectrum is shown in Table 1, which contains 17 well-resolved low K_{-1}-transitions used to derive the spectroscopic constants presented in Table 2. A large correlation matrix element of −0.895 was found to exist between Δ_J and A_0.

The low K_{-1}-transitions were too weak to allow quantitative Stark effect studies to be made both for this conformation as well as for the two further assigned rotamers. Unfortunately, no dipole moments could thus be determined.

The A_0 rotational constant is not accurately determined as can be seen in Table 2. Identification of *b*-type transitions would have produced a much more accurate value for this constant.

Table 2. Spectroscopic constants[a] of the ground vibrational state of conformation V of $NCCH_2CH_2PH_2$.

Root-mean-square (MHz)	0.104
A_0 (MHz)	22607(117)
B_0 (MHz)	1448.0610(67)
C_0 (MHz)	1400.3103(64)
Δ_J (kHz)[b]	0.190(26)
Δ_{JK}(kHz)[b]	−4.0(20)
κ[c]	−0.9955
$I_a+I_b-I_c$ (10^{-20} u m^2)	10.45(12)

[a] Uncertainties represent one standard deviation. [b] Further centrifugal distortion constants kept at zero in the least squares fit. [c] Ray's asymmetry parameter.[18] [d] Conversion factor 505376×10^{-20} u m^2 MHz.

Searches were made for the strongest of the low-J b-type lines, but none were found. The above-mentioned bond moment computations predict that μ_a is roughly twice as large as μ_b. The b-type lines should thus be very weak, and this is assumed to be the reason why they were not identified.

The rotational constants predicted for IV and V were quite similar as were the a-axis dipole moment components for each of these conformations. With no isotopic species studied and no dipole moment determined, there are three reasons why the spectrum of Table 1 is attributed to V and not to IV. Firstly, $I_a+I_b-I_c=10.45(11)\times10^{-20}$ u m^2. This is almost the same as $I_a+I_b-I_c=10.56\times10^{-20}$ u m^2 found for the corresponding conformation of $CH_3CH_2PH_2$.[17] Secondly, the structure calculations described below reproduce the B_0 and C_0 rotational constants satisfactorily. Thirdly, V is more stable than IV by 3.0(15) kJ/mol (see section on energy difference determination). This is close to 2.3(12) kJ/mol found for the corresponding conformational equilibrium of $CH_3CH_2PH_2$.[17]

Vibrationally excited states of V. The ground vibrational state spectrum was accompanied by a relatively strong satellite spectrum presumably belonging to vibrationally excited states of V. These spectral features were similar to those observed for the *anti* II form of $NCCH_2CH_2SH$,[16] as expected. Due to low intensities, only the high-K_{-1} pile-ups were assigned. Four such lumps of lines were identified; three of which presumably belong to successively excited states of the C−C torsional mode. $B+C\approx2853.35(5)$ MHz for the first excited state of the C−C torsional frequency; $B+C\approx2858.22(5)$ MHz for the second; and $B+C\approx2863.18(7)$ MHz for the third vibrationally excited state of this mode. The fact that $B+C$ increases almost linearly upon excitation is typical for a harmonic mode.

The intensity of the first excited state of the C−C torsional frequency is roughly 50 % of that of the ground state at −10 °C as judged by the high-K_{-1} pile-ups. The C−C torsional frequency is then calculated to be *ca.* 130 cm^{-1} which is similar to 121(20) cm^{-1} found for the correspond-

Table 3. Microwave spectrum of the ground vibrational state of conformation IV of $NCCH_2CH_2PH_2$.

Transition	Observed frequency[a] (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion (MHz)
$7\rightarrow8^b$	22957.48	–	−0.45
$8\rightarrow9^b$	25827.22	–	−0.64
$9\rightarrow10^b$	28697.12	–	−0.88
$10\rightarrow11^b$	31567.87	–	−1.17
$11\rightarrow12^b$	34436.64	–	−1.53
$12\rightarrow13^b$	37307.69	–	−1.93
$7_{1,6}\rightarrow8_{1,7}$	23152.63	−0.16	−0.45
$8_{1,7}\rightarrow9_{1,8}$	26046.47	0.26	−0.64
$9_{1,8}\rightarrow10_{1,9}$	28939.26	−0.13	−0.88
$10_{1,9}\rightarrow11_{1,10}$	31832.45	0.15	−1.17
$11_{1,10}\rightarrow12_{1,11}$	34724.79	−0.12	−1.52

[a] ±0.15 MHz. [b] Centre frequencies of high-K_{-1}-pile-ups.

ing vibrational mode of $NCCH_2CH_2SH$.[16]

The fourth identified vibrationally excited state was found to have $B+C\approx2852.01(10)$ MHz. Its intensity is roughly 30 % of that of the ground state. This corresponds to a vibrational frequency of *ca.* 200 cm^{-1}. This might be the C–P torsional frequency, or, perhaps, a low-frequency bending mode.

Assignment of conformation IV. The rotational constants predicted for the heavy-atom *anti* conformation IV were quite similar to those predicted for V. The dipole moment components were predicted in the same manner as reported above to be $\mu_a=3.5$ D, $\mu_b=0.8$ D and $\mu_c=0.3$ D, respectively. A series of *a*-type *R*-branch high-K_{-1} pile-ups similar to those found for V was therefore expected to occur for conformation IV and predicted to lie close to the lines identified for the former rotamer.

A series of high-K_{-1} pile-ups with $B+C\approx2869.7$ MHz was noted at the same time as V was assigned. It is most unlikely that this series is a vibrationally excited state of V, because this would have required an enormous – and highly unexpected – vibrational amplitude. Rather, it is assigned as belonging to the heavy-atom *anti* conformation IV (see Fig. 1). The intensity of this series is roughly 50 % of the corresponding series of V described above. The $J_{1,J}\rightarrow J+1_{1,J}$ series falling at higher frequencies than the $K_{-1}\neq1$ pile-ups was identified (Table 3). These transitions are quite weak. Unfortunately, only a few more low-K_{-1} transitions could be tentatively assigned due to the fact that they are weak and fall in regions where overlapping lines often occur. Use of the $K_{-1}\neq1$ pile-up frequencies (Table 3) with the $J_{1,J}\rightarrow J+1_{1,J}$ series was therefore made in order to calculate the spectroscopic constants of conformation IV which appear in Table 4. The A_0 rotational constant is quite inaccurately determined, whereas accurate values were obtained for B_0 and C_0, as can be seen from this table.

Table 4. Spectroscopic constants [a] of the ground vibrational state of conformation IV of $NCCH_2CH_2PH_2$.

Root-mean-square (MHz)	0.187
A_0 (MHz)	23271(1274)
B_0 (MHz)	1459.523(31)
C_0 (MHz)	1410.162(43)
Δ_J (kHz) [b]	0.220(42)
κ [c]	−0.9955

[a,b,c] Comments as for Table 2.

The bond moment calculations described above predict μ_a to be much larger than the two other dipole moment components. No search was made for the *b*- or *c*-type lines, because the *a*-type lines themselves are so weak.

There are two equivalent, mirror image forms of IV. Tunneling resulting in large splittings might thus be expected for the *c*-type transitions. Much smaller splittings might perhaps occur for the *a*- and *b*-type lines. No such splittings were observed for the identified *a*-type transitions. A similar finding was also made for the *a*-type lines of the *gauche* form of $CH_3CH_2PH_2$.[17] (However, some low-*J* *b*-type transitions of $CH_3CH_2PH_2$ were found to be split by a small amount).

The high-K_{-1} pile-ups of one vibrationally excited state were tentatively assigned. $B+C\approx2875.95(15)$ MHz was determined for this mode which is presumed to be the first excited C–C torsional mode for similar reasons as described for the corresponding mode of V.

Assignment of conformation II. After the completion of the assignments of conformations IV and V, it became clear that most of the strongest lines of the spectrum could in no way be ascribed to any one of these two rotamers. The heavy-atom *gauche* conformations I and/or II (see Fig. 1) were therefore suspected of producing these so-far unidentified transitions. Conformation III might also be present, but this rotamer was not assumed to be so energetically favoured as either I or II, because III is not capable of forming weak internal hydrogen bonds.

Moreover, II was assumed to be somewhat more stable than I because it can be produced by a rotation of about 120° from the more stable V conformation, whereas I is similarly formed from the less stable IV. As discussed below, the hydrogen-bonding conditions of II also appear to be a bit more favourable than those of I, and this was another reason why searches were next made for conformation II.

The dipole moment components of II were predicted to be $\mu_a=1.90$, $\mu_b=3.1$ D and $\mu_c=0.3$ D, respectively, using the same procedure as above. In the case of $NCCH_2CH_2SH$,[16] a CCCS dihedral angle of 65(3)° from *syn* was found for

Table 5. Microwave spectrum of the ground vibrational state of conformation II of $NCCH_2CH_2PH_2$.

Transition	Observed frequency[a] (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion (MHz)
a-type			
$6_{1,6}\rightarrow 7_{1,7}$	27292.11	0.06	−1.19
$6_{1,5}\rightarrow 7_{1,6}$	29930.67	0.14	−2.75
$7_{1,7}\rightarrow 8_{1,8}$	31119.86	0.09	−1.78
$7_{0,7}\rightarrow 8_{0,8}$	31617.68	0.00	−1.96
$7_{2,6}\rightarrow 8_{2,7}$	32760.28	−0.10	−2.42
$7_{1,6}\rightarrow 8_{1,7}$	34065.30	−0.14	−3.94
$8_{1,8}\rightarrow 9_{1,9}$	34928.96	0.10	−2.50
b-type			
$5_{0,5}\rightarrow 6_{1,6}$	26585.58	0.11	−0.01
$5_{1,5}\rightarrow 6_{0,6}$	20950.73	−0.07	−1.76
$6_{0,6}\rightarrow 7_{1,7}$	29785.47	−0.12	−0.17
$6_{1,6}\rightarrow 7_{0,7}$	25386.31	−0.11	−2.48
$7_{0,7}\rightarrow 8_{1,8}$	33025.50	0.10	−0.49
$8_{0,8}\rightarrow 9_{1,9}$	36336.43	−0.16	−1.03
$8_{1,8}\rightarrow 9_{0,9}$	33918.75	0.12	−4.04
$6_{2,4}\rightarrow 6_{3,3}$	26515.14	0.02	1.13
$8_{2,5}\rightarrow 8_{3,5}$	25089.53	0.01	4.60
$9_{1,9}\rightarrow 9_{2,8}$	25604.78	−0.07	−2.04
$10_{0,10}\rightarrow 10_{1,9}$	27635.03	0.02	−3.59
$10_{2,9}\rightarrow 10_{3,8}$	29852.08	−0.03	1.50
$12_{2,10}\rightarrow 12_{3,9}$	21501.25	0.10	11.66
$13_{0,13}\rightarrow 13_{1,12}$	31209.16	0.08	−22.76
$13_{2,12}\rightarrow 13_{3,11}$	33257.46	−0.02	−2.98
$14_{1,13}\rightarrow 14_{2,12}$	22997.94	−0.09	−27.16
$14_{3,11}\rightarrow 14_{4,10}$	33618.21	0.16	28.52
$15_{2,13}\rightarrow 15_{3,12}$	21166.59	0.14	1.75
$16_{2,13}\rightarrow 16_{3,13}$	21952.00	0.03	−7.85
$17_{1,16}\rightarrow 17_{2,15}$	33032.92	0.17	−61.55
$17_{3,14}\rightarrow 17_{4,13}$	29669.35	−0.18	44.35
$18_{2,16}\rightarrow 18_{3,15}$	25119.16	0.12	−39.71
$19_{2,17}\rightarrow 19_{3,16}$	27509.02	−0.06	−62.05
$19_{3,16}\rightarrow 19_{4,15}$	27876.98	−0.12	38.05
$21_{2,19}\rightarrow 21_{3,18}$	33707.38	−0.10	−115.54
$21_{3,18}\rightarrow 21_{4,17}$	27761.81	0.10	6.22
$23_{3,20}\rightarrow 23_{4,19}$	29868.71	0.05	−57.99
$24_{3,21}\rightarrow 24_{4,20}$	31826.03	−0.08	−102.65
$24_{4,20}\rightarrow 24_{5,19}$	35446.98	−0.10	114.82
$25_{3,22}\rightarrow 25_{4,21}$	34371.28	0.11	−154.30
$25_{4,21}\rightarrow 25_{5,20}$	34503.24	0.05	96.29
$26_{4,22}\rightarrow 26_{5,21}$	34040.82	0.01	63.88
$27_{4,23}\rightarrow 27_{5,22}$	34143.58	−0.08	16.50
$28_{4,24}\rightarrow 28_{5,23}$	34870.36	0.11	−46.31
$29_{4,25}\rightarrow 29_{5,24}$	36253.09	−0.05	−124.31

[a] ±0.10 MHz.

Table 6. Spectroscopic constants[a] of conformation II of $NCCH_2CH_2PH_2$.

Vibrational state	Ground	First ex. C–C-torsion
No. of transitions	66	46
Root-mean-square (MHz)	0.098	0.111
A_v (MHz)	7555.255(11)	7612.678(14)
B_v (MHz)	2257.9275(65)	2250.909(10)
C_v (MHz)	1868.7073(63)	1864.1739(98)
Δ_J (kHz)	1.837(46)	2.051(66)
Δ_{JK} (kHz)	−13.866(63)	−15.783(80)
Δ_K (kHz)	36.0(10)	55.9(11)
δ_J (kHz)	0.5908(14)	0.5829(21)
δ_K (kHz)	2.983(65)	4.47(10)

[a] Comments as for Table 2.

the intramolecularly hydrogen–bonded conformation. The same value was used for the CCCP dihedral angle to predict the rotational constants of this conformation.

The *b*-type *Q*-branch $K_{-1}=2\rightarrow3$ series with *J* between 15 and 20 was first found. The remainder of strong *b*-type *Q*-branch transitions, as well as the weaker *a*- and *b*-type *R*-branch lines with $J<11$ were then readily assigned. No *c*-type lines were seen. A total of about 70 transitions were measured; 42 of which are listed in Table 5.* The spectroscopic constants derived from 66 lines are shown in Table 6. A large number of high-*J*-, *P*- and *R*-branch *b*-type lines occur in the investigated spectral region, but they are so weak that no assignments could be made.

Vibrationally excited state of II. 46 *b*-type transitions of what is presumed to be the first excited state of the C–C torsional mode of II were measured as indicated in Table 6. The changes of the rotational constants upon excitation are similar to what was observed for the corresponding mode of $NCCH_2CH_2SH$.[16]

Relative intensity measurements yielded 105(30) cm^{-1} for this C–C torsional mode, similar to 118(20) cm^{-1} found for the corresponding frequency of $NCCH_2CH_2SH$. A rough diagonal force field (Table 7) was assumed for II in order to calculate the C–C torsional frequency utilizing the quartic centrifugal distortion constants in the manner described previously.[20] A frequency of 107 cm^{-1} was found, as compared to 105(30) cm^{-1} obtained by relative intensity measurements. It is difficult to estimate uncer-

Table 7. Assumed diagonal force field,[a] centrifugal distortion constants and torsional frequency of conformation II of $NCCH_2CH_2PH_2$.

Stretching (10^2 N m^{-1})			
C≡N	17.4	H_2C–CH_2	4.6
C–CN	5.5	C–P	1.7
P–H	3.5	C–H	4.8
Bending (aJ rad^{-2})			
P–C–C	1.0	C–C≡N	0.16
P–C–H	0.76	H–C–H	0.50
C–P–H	0.58	H–C–CN	0.67
H–P–H	0.45	C–C–H	0.61
C–C–C	1.1		
Torsion (aJ rad^{-2})			
C–P	0.25		
C–C	0.346[b]		

Centrifugal distortion constants (kHz)

	Obs.	Calc.
Δ_J	1.837	1.924
Δ_{JK}	−13.86	−12.59
Δ_K	36.0	36.4
δ_J	0.5908	0.5301
δ	2.983	3.149

C–C torsional frequency (cm^{-1})
From force-field calculations 107(10)[b]
Relative intensity 108(30)

[a] See text. [b] Obtained from least-squares fit.

* The complete spectra of the ground and the first excited state of conformation II are available from the authors upon request, or from the Molecular Spectra Data Center, National Bureau of Standards, Bld. 221, Rno. B 265, Washington D.C. 20234, U.S.A., where they have been deposited.

tainty limits for the computed value, but ± 10 cm^{-1} appears to be reasonable. All five quartic centrifugal constants are fairly well reproduced in the computations as can be seen in Table 7.

Further vibrationally excited states were searched for, but not assigned presumably because they are relatively weak and also involve high-J with significant centrifugal distortions.

Searches for further conformations. The assignments made as described above include all the strongest lines of the spectrum. However, there remained a few lines whose intensities at most were approximately 1/3 of the strongest transitions of II. In addition, a rich background of weaker and much weaker lines remained unaccounted for.

The existence of I seemed quite probable, and attempts were now made to find this conformation. Its principal inertial axes dipole moment components were predicted in the same manner as above as μ_a=2.3 D, μ_b=3.1 D and μ_c=0.2 D, respectively. The CCCP dihedral angle was guessed to be close to 65° from *syn* and the CCP angle assumed to be 110° in the predictions of the rotational constants. No *a*- type *R*-branch lines were found, and none of the relatively strong *b*-type *Q*-branch transitions were located, despite quite considerable efforts made to this end.

The unassigned lines need not belong to I. They could belong to unidentified vibrationally excited states of II, − which is considered to be quite probable, at least for many of them − or impurities. Their intensities make it possible to estimate a minimum energy difference between I and any further forms. Since the strongest unidentified lines possess roughly 1/3 of the intensity of the strongest transition of II, conformation II should be at least about $RT \ln 3 \approx 2$ kJ/mol more stable than I, if it is assumed that the dipole moment components are similar, which seems reasonable.

Energy difference between II, IV *and* V. Unfortunately, the dipole moments of the three conformations assigned in this work could not be determined. This precludes the determination of accurate energy differences between them. The calculated dipole moments given above had to be used in order to derive an energy difference.

Because the K_{-1}=1 lines of IV are so weak, the intensities of the K_{-1}-pile-ups of IV were used and compared to the corresponding pile-ups of V. K_{-1}=1 or K_{-1}=0 lines of V were compared to *b*-type *Q*-branch lines of conformation II. Moreover, the statistical weight of II and IV was assumed to be twice that of V.

Conformation II was thus found to be the most stable. It is more stable than V by 0.3 kJ/mol. The error limit is liberally estimated to be ± 2 kJ/mol. V is more stable than IV by 3 kJ/mol with an uncertainty of ± 2 kJ/mol. Any further form of the molecule, such as for example conformation I or III, is less stable than II by at least 2 kJ/mol.

Structure. As only one isotopic species has been studied, no complete structure can be calculated for any one of the three rotamers assigned in this work. Restrictions have to be made. In the cases of IV and V, only the CCP angle was fitted, because the rotational constants strongly depend on this angle and because it is prone to change from one conformation to another as evidenced for $CH_3CH_2PH_2$.[17]

The CCP angles of IV and V were fitted in steps of 0.5° to the *B* and *C* rotational constants. Smaller steps were not considered to be warranted in view of the fact that all further structural parameters were kept fixed at the values shown in Table 8. The fixed structural parameters were selected from recent, accurate studies of related compounds. The C−C≡N angle was assumed to be exactly 180°, although it is realized that small deviations from this have been observed.

Good fits were obtained for both conformations IV and V as indicated in Table 8. The CCP angle was found to be 109.0° in IV and 114.0° in V. Error limits are estimated to be ± 1.5° in both these cases, taking into consideration the inherent uncertainties of the assumed structural parameters. It is reassuring to note that 109.0(15)° found for IV and 114.0(15)° found for V are close to 110.1(2) and 115.2(2)°, respectively, determined for CCP angles of the two corresponding conformations of $CH_3CH_2PH_2$[17] as expected.

The CCP angle as well as the CCCP dihedral angle were fitted to all three rotational constants in steps of 0.5 and 1°, respectively, in the case of conformation II. The CCP angle was found to be 117.0(15)° and the CCCP dihedral angle to be 66(3)°. The fit is again good as can be seen in Table 8. The uncertainty limits were estimated in the same manner as described above.

The mass of the phosphino group hydrogen

Table 8. Plausible molecular structure[a] (bond lengths in pm; angles in degrees) of conformations II, IV and V of $NCCH_2CH_2PH_2$.

Structural parameters kept fixed for II, IV and V			
C–P	188.0	∠CCN	180.00
C≡N	115.7	∠CCC	110.50
C–C	153.0	∠CPH	95.50
C–CN	147.4	∠HPH	93.40
P–H	141.4	∠CCH	109.48
C–H	109.3	∠HCH	109.48
Fitted CCP angle for IV			109.0(15)
Fitted CCP angle for V			114.0(15)
Fitted CCP angle for II			117.0(15)
Fitted CCCP dihedral angle for II from *syn*			66(3)
Rotational constants (MHz)			
Conformation IV			
	Obs.	Calc.	Diff. (%)
A_0	23271(1274)	22912	–
B_0	1459.523(31)	1458.34	0.08
C_0	1410.162(43)	1410.39	0.02
Conformation V			
	Obs.	Calc.	Diff. (%)
A_0	22607(117)	22681	0.32
B_0	1448.0610(67)	1446.48	0.11
C_0	1400.3103(64)	1400.04	0.02
Conformation II			
	Obs.	Calc.	Diff.(%)
A_0	7555.255(11)	7537.47	0.23
B_0	2257.9275(65)	2253.593	0.19
C_0	1868.7073(63)	1870.221	0.08
Hydrogen bond parameters			
$P\cdots C_N$	335	$P\cdots N$	406
$C\cdots H_P$	270	$N\cdots H_P$	305
∠P–H···C	105	∠P–H···N	127
∠C≡N, P–H[b]	14.2		
Sum of van der Waals radii[c]			
C···P	360	H···C[d]	290

[a] See text. [b] Angle between C≡N bond and P–H bond involved in hydrogen bonding. [c] Taken from Ref. 21. [d] van der Waals radius of carbon assumed to be 170 pm as for aromatic carbon atoms.

atoms constitute only about 2 % of the mass of the entire 3-phosphinopropionitrile molecule. Without making isotopic substitutions in the phosphino group, one cannot discriminate between the three heavy-atom *gauche* conformations I, II, and III of Fig. 1 using only the rotational constants. Exploratory fits of the CCP angle and the CCCP dihedral angle were made for I and III. The results were ∠114.5(15)° and ∠CCCP=66(3)° for I, and ∠CCP=114.5(15)° and ∠CCCP=63(3)° for III, respectively. These two fits were insignificantly different from that of II (Table 8). This was, of course, expected.

However, no internal hydrogen bond is possible for conformation III. Moreover, the exploratory fit revealed that the hydrogen bond parameters of I would be less favourable than those of II which appear in Table 8. This is caused by the fact that the CPH and HPH angles both are more than 10° less than the dihedral angle. In addition, the phosphino group seems to prefer the conformation present in II as already noted above. Confusion of conformation II with either I or III is thus considered to be unlikely, although it cannot be completely ruled out.

DISCUSSION

3-Phosphinopropionitrile takes the II conformation as its most stable rotamer. This conformer is presumably stabilized by a weak intramolecular hydrogen bond formed between the phosphino group hydrogen atom and the π-electrons of the cyano group. The hydrogen bond is characterized by having the $H\cdots C_N$ distance about 20 pm shorter than the sum of the van der Waals radii of aromatic carbon and hydrogen,[21] and a $P-H\cdots C_N$ angle of about 105° (Table 8). Any covalent interaction of this bond must thus be marginal. Electrostatic interaction between the P–H and C≡N bonds is, however, favourable as the two bonds are approximately 14° from being parallel. The weak intramolecular hydrogen bond is thus mainly electrostatic in origin.

The fact that the phosphino and cyano groups are capable of interacting in a hydrogen-bonding-like manner parallels the finding made for mercapto and cyano groups as exemplified by $NCCH_2CH_2SH$.[16] The interactions seem to be of similar strengths in both $NCCH_2CH_2PH_2$ and $NCCH_2CH_2SH$. It would be interesting to see if this holds also for other examples.

Finally, ethylphosphines seem to prefer to have the phosphino group in a conformation similar to that of II and V as shown in the case of

$CH_3CH_2PH_2$,[17] as well as for the title compound. Ethyl thiols too, seem to have a similar propensity for forming HSCC *gauche* conformations as already noted.[16] No explanation can be offered for these tendencies, which are not paralleled by alcohols and amines.

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