Prediction of IR Intensities of Bending Fundamentals in 2,4-Pentadiynenitrile by the Combination of ab Initio Calculation and Experimental Parameters

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2,4-Pentadiynenitrile is a H(C≡C)$_n$C≡N-type molecule. Molecules with n=0 to n=5 are known as interstellar molecules. Infrared spectra have not been observed yet, because the synthesis of a molecule of this type becomes more difficult as the molecular size increases. In the present study, the frequencies and infrared intensities of bending fundamentals in 2,4-pentadiynenitrile were predicted from an ab initio calculation coupled with empirical corrections. Calculation errors have been estimated by comparing calculated and experimental values in small reference molecules which have local structures similar to those of 2,4-pentadiynenitrile. The errors in 2,4-pentadiynenitrile have also been estimated.

Molecules designated as H(C≡C)$_n$C≡N are known as interstellar molecules and the microwave spectra for those with n=1 to 5 have been identified by radio-telescope observations.[1–5] The spectroscopic parameters of these molecules, especially those for the bending vibrations, are essential for an analysis of the radio-telescope data,[6] but laboratory infrared spectra are available only for hydrogen cyanide (n=0) and 2-propynenitrile (n=1). In the present work, the frequencies and the infrared intensities for the bending fundamentals of 2,4-pentadiynenitrile (n=2) were predicted based on an ab initio calculation. It is widely accepted that semiempirical MO theory, such as CNDO, is a powerful means for resolving sign ambiguities in dp/dQ. These are indeterminable from experiments alone.[7] However, the accuracy of semiempirical MO theory is still insufficient to predict infrared intensities with practical accuracy. Nowadays, ab initio MO theory has been applied to molecules of moderate size and it has become accepted that their accuracies are generally much superiror to those of semiempirical ones. In some cases, however, large discrepancies still remain between the calculated and experimental dipole-moment derivatives.[8] The major reason for these discrepancies is the fact that the electron repulsion is not properly taken into account in the Hartree-Fock MO theory. In fact, when elaborated CI calculations are performed, the above-mentioned discrepancies are significantly reduced.[9,10] Then, highly correlated wave functions are necessary for the accurate prediction of frequencies and infrared intensities. The ab initio calculation at this level, however, can be carried out at the present time only for small molecules (for example hydrogen cyanide) and can not be extended easily to larger molecules. Therefore, some alternate approaches must be explored. One of them may be an empirical correction of Hartree-Fock calculations, where the differences between calculated and experimental quantities are assessed. These are then used to obtain an empirical correction to the ab initio results. Essentially the same approaches have been employed in the determination of force fields, where the force constants from ab initio calculations were multiplied by empirical scale factors to obtain a more accurate prediction than the ab initio results themselves.[11,12] In the present study, the ab initio calculations were carried out to obtain the force fields and dipole-moment derivatives for bending vibrations of three H(C≡C)$_n$C≡N type molecules, i.e., HC≡N (n=0), HC≡CC≡N (n=1), and HC≡CC≡CC≡N (n=2), and two related molecules, i.e., HC≡CH and N≡CC≡N. First, the calculated values were compared with the experimental ones in cyanogen, acetylene, and hydrogen cyanide (hereafter, called reference molecules), in order to obtain the empirical correction parameters. Then, the frequencies and the infrared intensities in 2-propynenitrile were predicted and compared with the experimental values so as to estimate the error in the prediction employed here. Finally, the frequencies and the infrared intensities of the bending fundamentals in HC≡CC≡CC≡N and DC≡CC≡CC≡N were predicted in the same way by the use of empirical correction terms.

The same procedure can be applied, in principle, to other larger molecules. However, the CPU time available for each project is limited. Thus, the calculation of a large molecule can be performed at the sacrifice of the quality of the results. On the other hand, as described later, the error of an MO calculation is fairly large for the molecules treated in this work. Therefore, it is necessary to maintain a moderate calculation level for the purpose of this work. After all, the maximum-size molecule must be determined to take these conditions into account. Under the present computational condition, 2,4-pentadiynenitrile (n=2) is the largest member in this series of molecules that can be treated at the same calculation level as 2-propynenitrile (n=1) and other small reference molecules.

Calculation

The ab initio MO calculations were carried out after Hartree–Fock approximations using Pople's 4-31G** split valence plus polarization basis set. The alpha parameters for the polarization functions in H, C, and N were taken to be 1.0, 0.70, and 0.75 respectively.[13–15] The programs used are library programs IMSPAK and HONDOG at Computer Center of Institute for Molecular Science.

Force Fields. First, the theoretical equilibrium geometry was sought for each molecule; then, each atom was displaced 0.01 a.u. along a Cartesian coordinate perpendicular to the molecular axis. The energy gradients were calculated at every configuration; then these energy gradients were differentiated numerically with respect to atomic displacement to obtain $\boldsymbol{F}_x$ matrices. These calculations were performed using the program IMSPAK.

Internal coordinates $\boldsymbol{R}$ and laboratory fixed coordinates $\boldsymbol{X}$ are related by the following expression:[17]

$$\boldsymbol{X} = (\boldsymbol{A} \vdots \boldsymbol{\alpha})\begin{pmatrix}\boldsymbol{R}\\ \boldsymbol{\rho}\end{pmatrix} \qquad (1)$$

where $\boldsymbol{\rho}$ corresponds to the Eckart condition which must be fulfilled by molecular fixed coordinates $\boldsymbol{R}$. The inverse transformation of Eq. 1 is expressed as

$$\begin{pmatrix}\boldsymbol{R}\\ \boldsymbol{\rho}\end{pmatrix} = \begin{pmatrix}\boldsymbol{B}\\ \boldsymbol{\beta}\end{pmatrix}\boldsymbol{X}, \qquad (2)$$

where $\boldsymbol{B}$ matrices are defined by Wilson[18] and an explicit expression of the $\boldsymbol{\beta}$ matrices is shown in Ref. 17. The $\boldsymbol{F}$ matrices for each molecule were obtained from $\boldsymbol{F}_x$ matrices by

$$\boldsymbol{F} = \tilde{\boldsymbol{A}}\, \boldsymbol{F}_x\, \boldsymbol{A}, \qquad (3)$$

where $\tilde{\boldsymbol{A}}$ stands for the transpose of $\boldsymbol{A}$.

Atomic Polar Tensors (APTs). Atomic coordinates were displaced 0.01 a.u. along the Cartesian coordinate around the equilibrium geometry and the dipole moments were calculated at these geometries; then the dipole moments were differentiated numerically to obtain $\boldsymbol{P}_x$ matrices (APTs).[16,17]

Fundamental Frequencies ν_i, and Infrared Intensities A_i. The $\boldsymbol{F}$ matrices obtained from Eq. 3 and the $\boldsymbol{G}$ matrices were used to determine the fundamental frequencies ν_i and $\boldsymbol{L}$ matrices. $\boldsymbol{P}_x$ matrices are related to the dipole-moment derivatives with respect to the internal coordinates $\boldsymbol{P}_R$ by the following Eq.,

$$\boldsymbol{P}_R = \boldsymbol{P}_x\, \boldsymbol{A}, \qquad (4)$$

and $\boldsymbol{P}_R$ are related to $\boldsymbol{P}_Q$, i.e., the dipole-moment derivatives with respect to the normal coordiate, by

$$\boldsymbol{P}_Q = \boldsymbol{P}_R\, \boldsymbol{L}. \qquad (5)$$

Then, the integrated molar absorption coefficients A_i are expressed as;[19]

$$A_i = \frac{N g_i P_{Qi}^2}{3c^2(4\varepsilon_0)} \qquad (6)$$

where N is Avogadro's constant and g_i is the degree of degeneracy.

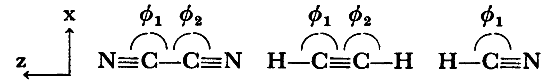
Results and Discussion

Force Fields. Calculated and experimental force constants for N≡CC≡N, HC≡CH, and HC≡N are shown in Table 1. The force fields of these molecules have been thoroughly studied and the experimental values in Table 1 were obtained from harmonic frequencies.[20–22] The relative errors found in the calculated values in these molecules are generally larger than those obtained in other molecules at a similar calculation level (Hartree-Fock approximation using split valence basis set).[12] At the same time, it may be noted that the errors depend to some extent on the local structure of the molecules where the internal coordinate is defined; for example, the ratios of experimental diagonal force constants to calculated ones are 0.67—0.64 for H-C≡C and H-C≡N bending coordinates, and 0.58 for C-C≡N bending respectvely, which seems to reflect the extent of the electron correlation in a triple bond. As for the

Table 1. Experimental and Calculated (4-31G**) Force Constants (10^2 N m^{-1}) of the Reference Molecules[a,b)]

	NCCN[c)]		HCCH[d)]		HCN[e)]
	$r_0\Delta\phi_1$	$r_0\Delta\phi_2$	$r_0\Delta\phi_1$	$r_0\Delta\phi_2$	$r_0\Delta\phi_1$
Exp.					
$r_0\Delta\phi_1$	0.2918		0.2510		0.2596
$r_0\Delta\phi_2$	−0.0133	0.2918	0.0925	0.2510	
Calc.					
$r_0\Delta\phi_1$	0.4976		0.3729		0.4054
$r_0\Delta\phi_2$	−0.0408	0.4976	0.1081	0.3729	
Exp./Calc.					
$r_0\Delta\phi_1$	0.5864		0.6731		0.6404
$r_0\Delta\phi_2$	0.326	0.5864	0.8557	0.6731	

a) Bending coordinates ϕs are defined as follows;



b) r_0 is a constant of 0.1 nm. c) Ref. 20. d) Ref. 21. e) Ref. 22.

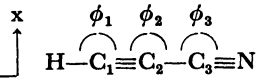
off-diagonal force constants, the ratios of experimental to calculated values vary to a large extent. In one case, the ratio of experimental to calculated values is close to unity, and far from unity in the other case. However, it must be noted that the absolute values of the off-diagonal force constants are much smaller than the diagonal ones, so that in the off-diagonal force constants a small absolute error gives a large relative one.

The bending force constants for HC≡CC≡N and HC≡CC≡CC≡N were obtained at the same calculation level. Then, the correction factors were multiplied by the calculated force constants to give the most accurate prediction for the force fields. These correction factors were taken from the ratios of the experimental to the theoretical force constants obtained for similar or same bending coordinates in the reference molecules, i.e., the correction factor for H–C≡C was taken from the mean value (0.657) of ratios both in H–C≡N of HC≡N and in H–C≡C of HC≡CH. As for the C–C≡C bending force constant, there is no corresponding value among the reference molecules. Therefore, the correction factor for this constant was assumed to be equal to that for C–C≡N in N≡CC≡N (0.586). These two force constants are similar in that they are bending coordinates around a carbon atom which is involved in a conjugated triple bond. As for the off-diagonal force constants in 2,4-pentadiynenitrile, only those which are related to adjacent bending coordinates were considered here, since others are less important for the calculation of vibrational frequencies. These constants are further classified into two groups. The first group (group A) is composed of those between C–C≡C and C≡C–C bending coordinates; both of which have common C≡C bond. Group B is composed of those between C≡C–C and C–C≡C or C–C≡N bending coordinates; both of which have common C–C bond. Experimental values of the force constants in group A are positive, and fairly correctly predicted by the ab initio method in the reference molecules (for example, the ratio of the experimental value to the calculated one is 0.86 in HC≡CH), whereas those in group B are negative and the predicted magnitudes are too large (the above-mentioned ratio is 0.33 in N≡CC≡N). These ratios were used as correction factors for the force constants in the two groups. The force constants of HC≡CC≡N predicted in this way are compared with the experimental ones in Table 2(a) and the experimental and predicted frequencies of 2-propynenitrile are summarized in Table 2(b). The predicted freqencies are in the range of 0.95—1.04 of the experimental ones. Here, it may be noted that the predicted force constants in Table 2(a) are based on empirical correction factors and these were derived from harmonic frequencies of reference molecules, whereas the experimental force constants of 2-propynenitrile are based on the observed experimental frequencies. It is well known that the observed frequencies are generally lower than the harmonic ones because of the anharmonicities in potential functions. On account of the above effect, it might be reasonable that the predicted force constant of H–C≡C bending is 5% larger than the experimental one. On the contrary, the predicted values for the C≡C–C and C–C≡N bending force constants are about 2 to 6% less than the experimental ones. These discrepancies will be explained from the following two reasons. First, the frequencies of ν_6 and ν_7 are fairly near so that relatively large correlations exist between these force constants (diagonal constants for C≡C–C and C–C≡N bending coordinates) and the experimental uncertainties are relatively large in these force constants. Second, there is no C≡C–C bending force constant in the reference molecules, so that the correction factor for this bending force constant was assumed to be equal to that for C–C≡N. The force constants of 2,4-pentadiynenitrile which were pre-

Table 2(a). Experimental and Predicted Force Constants (10^2 N m^{-1}) of 2-Propynenitrile[a)]

Experimental[d)]	$r_0\Delta\phi_1$	$r_0\Delta\phi_2$	$r_0\Delta\phi_3$
$r_0\Delta\phi_1$	0.2397		
$r_0\Delta\phi_2$	0.0977	0.2732	
$r_0\Delta\phi_3$	0.0[b)]	0.0[b)]	0.3556
Predicted	$r_0\Delta\phi_1$	$r_0\Delta\phi_2$	$r_0\Delta\phi_3$
$r_0\Delta\phi_1$	0.2525		
$r_0\Delta\phi_2$	0.0836	0.2678	
$r_0\Delta\phi_3$	0.0[c)]	−0.0160	0.3361
Exp./Pred.	$r_0\Delta\phi_1$	$r_0\Delta\phi_2$	$r_0\Delta\phi_3$
$r_0\Delta\phi_1$	0.9493		
$r_0\Delta\phi_2$	1.169	1.0202	
$r_0\Delta\phi_3$	—	—	1.0580

a) Bending coordinates ϕs are defined as follows;



b) Assumed. c) Assumed in the present prediction.
d) Ref. 23.

Table 2(b). Experimental and Predicted Bending Fundamental Frequencies (cm^{-1}) of 2-Propynenitrile

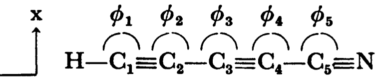
HCCCN	Exp.[a)]	Pred.	Exp.−Pred.
	663	690	−27
	499	504	−5
	223	215	8
DCCCN	**Exp.[a)]**	**Pred.**	**Exp.−Pred.**
	523	551	−28
	495	490	5
	213	205	8

a) Ref. 23.

Table 3. Rredicted Force Constants ($10^2\,\mathrm{N\,m^{-1}}$) of 2,4-Pentadiynenitrile[a)]

	$r_0\Delta\phi_1$	$r_0\Delta\phi_2$	$r_0\Delta\phi_3$	$r_0\Delta\phi_4$	$r_0\Delta\phi_5$
$r_0\Delta\phi_1$	0.2476				
$r_0\Delta\phi_2$	0.0712	0.3087			
$r_0\Delta\phi_3$	0.0[b)]	−0.0183	0.3275		
$r_0\Delta\phi_4$	0.0[b)]	0.0[b)]	0.0543	0.2678	
$r_0\Delta\phi_5$	0.0[b)]	0.0[b)]	0.0[b)]	−0.0181	0.3554

a) Bending coordinates are defined as follows;



$$\overset{\phi_1}{\text{H—C}_1}\equiv\overset{\phi_2}{\text{C}_2}\text{—}\overset{\phi_3}{\text{C}_3}\equiv\overset{\phi_4}{\text{C}_4}\text{—}\overset{\phi_5}{\text{C}_5}\equiv\text{N}$$

b) Assumed in the present prediction.

dicted in the same way are shown in Table 3.

Table 4. Experimental and Calculated (4-31G**) APTs of the Reference Molecules[a),b)]

Cyanogen	N	C	
Exp.[c)]	−0.245	0.245	
Calc.	−0.344	0.344	
Exp. − Calc.	0.099	−0.099	
Acetylene	**H**	**C**	
Exp.[d)]	0.205	−0.205	
Calc.	0.206	−0.206	
Exp. − Calc.	−0.001	0.001	
Hydrogen cyanide	**H**	**C**	**N**
Exp.[e)]	0.237	0.084	−0.321
Calc.	0.254	0.081	−0.337
Exp. − Calc.	−0.017	0.003	0.016

a) Among nine elements of APTs for each atom, only those which are responsible for the bending intensities, $\partial P_x/\partial_x$, are listed. b) APTs are shown in *e*. c) Ref. 24. d) Ref. 25. e) Ref. 26.

Table 5(a). Calculated (4-31 G**), Predicted and Experimental APTs of 2-Propynenitrile[a)]

	H	C_1	C_2	C_3	N
Calc.	0.210	−0.137	0.024	0.267	−0.355
Corr.	—	—	—	−0.099	0.099
Pred.	0.210	−0.137	0.024	0.168	−0.256
Exp.[b)]	0.199	−0.117	0.034	0.149	−0.265
Exp. − Pred.	−0.011	0.020	0.010	−0.019	−0.009

a) See the footnote a) and b) in Table 4. b) Ref. 23.

Table 5(b). Experimental and Predicted Infrared Intensities (A/km mol^{-1}) of 2-Propynenitrile

	Exp.[a)]	Pred.(1)[b),c)]	Pred.(2)[b),d)]
HCCCN			
ν_5	68.4	80.3 (1.17)	84.6 (1.24)
ν_6	8.0	12.5 (1.56)	8.1 (1.01)
ν_7	0.18	0.087 (0.48)	0.16 (0.88)
DCCCN			
ν_5	21.0	20.5 (0.97)	21.0 (1.00)
ν_6	24.5	30.3 (1.24)	29.7 (1.21)
ν_7	0.22	0.079 (0.36)	0.12 (0.55)

a) Ref. 23. b) Values in the parentheses are the ratios of predicted to experimental intensities. c) Based on the predicted force constants and predicted APTs. d) Based on the force constants fitted to the observed frequencies and the predicted APTs.

Atomic Polar Tensors (APTs). Calculated and experimental atomic polar tensors (APTs) for N≡CC≡N, HC≡CH, and HC≡N are shown in Table 4.[24–26] In acetylene, good agreements were obtained between the calculated and the experimental APTs. On the other hand, fairly large errors were found in H and N of hydrogen cyanide. These errors are due to an overestimation of H-C and C≡N bond moments. This trend is also found in cyanogen in a more exaggerated way, where the calculated APT for N is 0.099*e* larger than the experimental one. This error is about 6-times larger than that in hydrogen cyanide. This error difference regarding the APTs for the N which participate in the C≡N bonds reflects a difference in the bonding characteristics in these C≡N bonds. This might be caused by a conjugation difference in these molecules. Therefore, when these APTs are used to predict those for 2-propynenitrile and 2,4-pentadiynenitrile, it becomes necessary to decide which of the reference molecules they are similar to. In the following calculation, the bonding characters of C≡N in 2-propynenitrile and 2,4-pentadiynenitrile were assumed to be the same as that in cyanogen. This is because these C≡N bonds participate in the conjugation. In this respect, hydrogen cyanide must be classified in a different category. The differences between the calculated and experimental APTs in the reference molecules are largest in C and N in cyanogen (0.099*e*) and the other differences are much smaller. Therefore, as a first approximation, it may be reasonable to correct errors only for C and N in a C≡N bond which participates in conjugation. In the following prediction of the APTs for C and N in a C≡N bond, 0.099*e* was subtracted from APTs for C and was added to those for N in 2-propynenitrile and 2,4-pentadiynenitrile to compensate the overestimation of the C≡N bond polarity. The other APTs were not subject to corrections and the ab initio results were used as the predicted values for the APTs. The predicted APTs of 2-propynenitrile and 2,4-pentadiynenitrile are shown in Table 5(a) and Table 6 respectively.

The predicted infrared intensities in 2-propynenitrile are shown in Table 5(b). When the predicted values are used for both APTs and force fields (Pred. (1) in Table 5(b)) the ratios of the predicted to

Table 6. Predicted APTs of 2,4-Pentadiynenitrile[a)]

	H	C_1	C_2	C_3	C_4	C_5	N
Calc.	0.214	−0.149	−0.034	0.090	−0.026	0.248	−0.343
Corr.	—	—	—	—	—	−0.099	0.099
Pred.	0.214	−0.149	−0.034	0.090	−0.026	0.149	−0.244

a) See footnote a) and b) in Table 4.

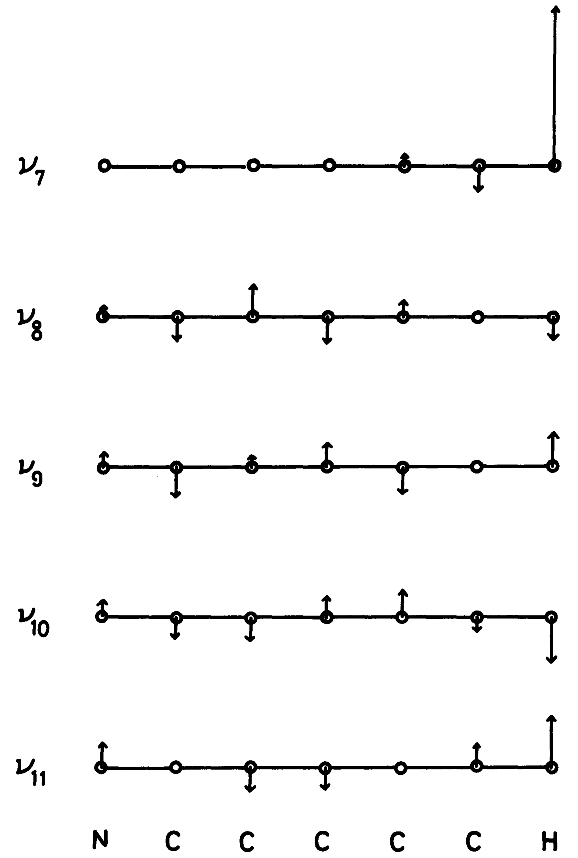


Fig. 1 (a). Normal modes of vibration in HCCCCCN.

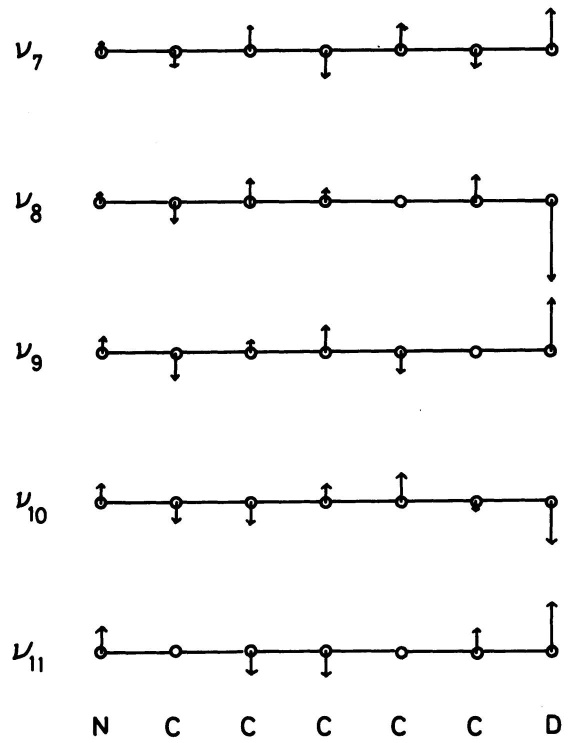


Fig. 1 (b). Normal modes of vibration in DCCCCCN.

experimental intensities lie between from 1.50 to 0.33. The value of this ratio for ν_5 in HCCCN is 1.17; this vibration results mainly from H–C≡C bending. The overestimated H–C polarity may be responsible for this overestimation. The errors in ν_7 intensities of HCCCN and DCCCN are much larger than those expected solely from the errors in APTs. In this mode, the molecules are bent mainly at the C–C≡N bending coordinate and the resultant changes of H–C and C≡N bond moments cancel each other. The net dipole-moment change becomes so small that a large relative error arises. Cancellations of this type occur more or less in ν_6 and ν_7 of HCCCN and DCCCN.

The sources of error in the predicted infrared intensities can be classified into two categories; one is the error in the APTs and the other is that in *L* matrices, which is mainly caused by the error in force fields. The *L* matrices determine the deformations of molecules, so that they determine the degree of cancellation or reinforcement of bond moments during the deformation. When this situation is taken into account, the general trend is well understood that the weak bands have large relative errors. To examine the influence of the error in the *L* matrix to the intensity *A*, another calculation was made for HCCCN and DCCCN, (Pred. (2) in Table 5(b)), where *L* matrices were determined from experimental force fields and the APTs were predicted as above. Here, it can be seen that the agreement between the experimental and predicted intensities of ν_6 and ν_7 in HCCCN and DCCCN have changed. This result seems to suggest that the errors in the predicted force fields are responsible to some extent for the errors in the predicted intensities, especially for low-intesity bands.

Fundamental frequencies ν_i and infrared intensities A_i of bending vibrations in HCCCCCN and DCCCCCN were calculated using the predicted force fields (Table 3), and APTs (Table 6). Normal modes of vibrations for HCCCCCN and DCCCCCN are shown in Fig. 1. It can be seen that the ν_7 in the HCCCCCN is mainly localized at the H–C≡C bending coordinate. In the other vibrations, however, the vibrations delocalize more or less over the molecule. In the lowest vibrations (ν_{11} of HCCCCCN and DCCCCCN), the molecules are bent; thus the large bond moments of H–C (or D–C) and C≡N are inclined in the opposite direction and their moments cancel each other to give very low intensities. This situation is similar to that in ν_7 in 2-propynenitrile. As the vibrational frequency increases from ν_{11} to ν_8, the number of nodes in normal modes also increases, so that bond moments of H–C (or D–C) and C≡N cancel or reinforce each other, depending on the number of nodes. The resultant infrared intensities give rise to a intensity alternation.

As for the accuracy of the predicted force fields in 2-propynenitrile and 2,4-pentadiynenitrile, there may be no essential difference between them. Therefore, the predicted fundamental frequencies of 2,4-pentadiynenitrile are expected to have a comparable accuracy with that of 2-propynenitrile. The predicted frequency of ν_7 (mainly comprised from H–C≡C bending) in HCCCCCN may be about 4% too large as in HCCCN, since the correction factors for the H–C≡C diagonal force constants for these molecules were assumed to be equal. The other vibrations mainly consist of C≡C–C and C–C≡N bendings. Thus, their vibrational frequencies may be predicted too small, since the diagonal force constants for the C≡C–C and C–C≡N bendings have been predicted to be smaller than the experimental ones in 2-propynenitrile. These same correction factors were used for the prediction in 2,4-pentadiynenitrile.

It is more difficult to estimate the errors involved in the infrared intensities than those related to frequencies. This is because the former include errors from both the force fields and the APTs. However, it may be noted that the APTs for H, C, and N in H–C and C≡N bonds in these molecules are 2- to 7-times larger than those for other atoms. Thus, the $\boldsymbol{P}_R$ are dominated by APTs for these atoms and fairly good agreement were obtained between experimental and predicted APTs for H, C, and N in H–C and C≡N bonds in 2-propynenitrile. Therefore, the predicted APTs in 2,4-pentadiynenitrile are expected to have almost the same accuracy as those in 2-propynenitrile. The highest bending vibration (ν_7 in HCCCCCN) is mainly localized at H–C≡C bending. Thus, the infrared intensity is mainly donimated by the APTs of the H and C in H–C bond. At this point, it might be remembered that the APTs of H and C in the H–C bond in 2-propynenitrile were calculated to give an overestimated polarity with the direction (+)H–C(−), i.e, the magnitudes of APTs of H and C have been calculated too large by 6 to 17 percent. The calculated APT values for H and C in H–C≡C of 2,4-pentadiynenitrile are close to those in 2-propynenitrile. From this similarity in the APTs, it is inferred that the intensities of ν_7 in HCCCCCN and ν_5 in HCCCN may be predicted about 15 to 20% larger. In the other bending vibrations, it is difficult to estimate the errors in the predicted intensities since these vibrations delocalize over a molecule. Therefore, cancellations of bond moments occur to a larger extent. In such cases, some correlation may exist between the relative errors and the predicted intensities. In moderately strong bands (ν_7 and ν_{10} in HCCCCCN), their relative errors are expected to be 50% at most. In the weaker bands (ν_9 and ν_{11}), the predicted values may be regarded as order estimations.

Table 7. Predicted Frequencies (ν/cm^{-1}) and IR Intensities (A/km mol^{-1}) of Bending Fundamentals in HCCCCCN and DCCCCCN

HCCCCCN	ν_i	A_i	DCCCCCN	ν_i	A_i
ν_7	691	77.2	ν_7	580	2.33
ν_8	565	13.4	ν_8	537	41.1
ν_9	457	0.19	ν_9	444	2.9
ν_{10}	249	10.5	ν_{10}	242	11.1
ν_{11}	101	0.087	ν_{11}	98	0.098

The preliminary results of this work have been published previously,[27] and we should note that the intensity of the ν_8 fundamental in Table 1 in Ref. 27 was unfortunately misprinted and that the radiative transition rate through the ν_8 band was overestimated in the calculation. However, the total pump rate through the ν_8 and ν_7 bands decreases only by 15% due to this mistake and the main conclusion of the paper does not change.

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References

1) L. E. Snyder and D. Buhl, *Astrophys. J.*, **163**, 147 (1971).

2) B. E. Turner, *Asptrophys. J.*, **163**, 138 (1971).

3) L. W. Avery, N. W. Broten, J. M. MacLeod, T. Oka, and H. W. Kroto., *Astrophys. J.*, **205**, L173 (1976).

4) N. W. Broten, T. Oka, L. W. Avery, J. M. MacLeod, and H. W. Kroto, *Astrophys. J.*, **223**, L105 (1978).

5) M. B. Bell, P. A. Feldman, S. Kwok, and H. E. Mattews, *Nature*, **295**, 389 (1982).

6) S. Deguchi, Y. Nakada, T. Onaka, and M. Uyemura, *Publ. Astron. Soc. Jpn.*, **31**, 105 (1979).

7) Roy E. Bruns, "Vibrational Intensities in Infrared and Raman Spectroscopy," ed by W. B. Person and B. Zerbi, Elsevier, Amsterdam (1982).

8) A. B. M. S. Bassi, *J. Chem. Phys.*, **68**, 5667 (1978).

9) B. Liu, K. M. Sando, C. S. North, H. B. Friedrich, and D. M. Chipman, *J. Chem. Phys.*, **69**, 1425 (1978).

10) J. E. Gready, G. B. Bacskay, and N. S. Hush, *J. Chem. Phys.*, **70**, 1071 (1979).

11) P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, and A. Vargha, *J. Am. Chem. Soc.*, **105**, 7037 (1983).

12) G. Fogarasi and P. Pulay, *Ann. Rev. Phys. Chem.*, **35**, 191, (1984).

13) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

14) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).

15) T. H. Dunning, Jr., and P. J. Hay "Modern Theoretical Chemistry," ed by H. F. Schaeffer III, Plenum, New York (1977), Vol. 3.

16) W. B. Person and J. H. Newton, *J. Chem. Phys.*, **61**, 1040 (1974).

17) W. B. Person, "Vibrational Intensities in Infrared and Raman Spectroscopy," ed by W. B. Person and B. Zerbi, Elsevier, Amsterdam (1982).

18) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York (1955).

19) D. Steele, *J. Mol. Struct.*, **117**, 163 (1984).

20) L. H. Jones, *J. Mol. Spectrosc.*, **49**, 82 (1974).

21) G. Strey and I. M. Mills, *J. Mol. Spectrosc.*, **59**, 103 (1976).

22) G. Strey and I. M. Mills, *Mol. Phys.*, **26**, 129 (1973).

23) M. Uyemura, S. Deguchi, Y. Nakada, and T. Onaka, *Bull. Chem. Soc, Jpn.*, **55**, 384 (1982).

24) K. Kim and W. T. King, *J. Chem. Phys.*, **80**, 974 (1983).

25) K. Kim and W. T. King, *J. Mol. Struct.*, **57**, 201 (1979).

26) K. Kim and W. T. King, *J. Chem. Phys.*, **71**, 1967 (1979).

27) S. Deguchi and M. Uyemura, *Astrophys. J.*, **285**, 153 (1984).