The Infrared Intensities of Stretching Fundamentals in Gaseous and Crystalline Cyanoacetylene

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The absolute intensities of the stretching fundamentals of cyanoacetylene and cyanoacetylene-d were measured in gaseous and crystalline (77 K) states. As had been expected from the previous result for hydrogen cyanide, a striking intensity increase upon crystallization was observed not only for $\nu_{CH(CD)}$ but also for the other fundamentals. The observed intensities were reduced to dipole-moment derivative with respect to the internal coordinates, $\partial\mu/\partial r$. Then, by taking advantage of the strictly linear geometry of hydrogen-bonded chains in the crystals, it was demonstrated that the derivative with respect to the hydrogen-bonded distance, $[\partial\mu/\partial r_{N\cdots H}]$, was primarily responsible for the remarkable change in $\partial\mu/\partial r$; this was in accordance with the previous conclusion for hydrogen cyanide. A discrepancy from this view which appeared for $\partial\mu/\partial r_3$ was interpreted as being mainly caused by the vibronic behavior of π-electrons.

The infrared intensity characteristics of hydrogen-bonded systems are well known and have generally been interpreted in terms of a charge-transfer mechanism.[1-4] However, since there have been rather few quantitative intensity studies of those systems so far, there still seems to be need for such detailed investigations as will give positive evidence for the importance of the charge-transfer contribution. In a previous study of crystalline HCN and DCN, particular attention was given to the fact that not only the C–H (C–D) stretching but also the C≡N stretching absorption was remarkably intensified compared with gaseous ones; the analysis of those changes was then able to deduce a very large dipole-moment derivative properly attributable to the intermolecular charge transfer.[5] In that case, a strictly linear structure of hydrogen-bonded chains in the crystal furnished a very favourable condition for interpreting the results. In order to confirm the above conclusion for the N···H–C hydrogen-bonded system, cyanoacetylene and its deuterated derivative were studied from the same point of view, as these linear molecules are known to form linear hydrogen-bonded chains in a crystal just like hydrogen cyanide.[6]

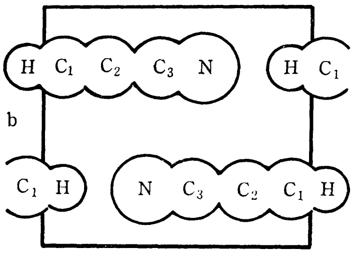

Fig. 1. Crystal structure of cyanoacetylene.

The crystal structure of cyanoacetylene determined by X-ray diffraction at 248 K is shown in Fig. 1, which belongs to the space group $C_{2h}{}^2$—$P2_1/m$ and which has two molecules per unit cell. In this structure, a linear hydrogen-bonded chain is surrounded by four parallel and two anti-parallel identical chains at intervals of 3.6 Å, and the $R_{N\cdots H-C}$ distance, 3.27 Å, is slightly longer than that of hydrogen cyanide ($R_{N\cdots H-C}$=3.18 Å).[6]

TABLE 1. CORRELATION DIAGRAM FOR CRYSTALLINE CYANOACETYLENE

	Molecule $C_{\infty v}$	Site C_s	Factor C_{2h}	Activity
ν_1, ν_2	Σ^+	A′	A_g	(*R*)
ν_3, ν_4			B_g	(*R*)
ν_5, ν_6	Π	A′′	A_u	(*IR*)
ν_7			B_u	(*IR*)

According to the correlation diagram, Table 1, each stretching fundamental is predicted to give only one infrared active crystal component, while each degenerate bending has two active components caused by the site-group splitting. The present work deals with the intensities of only stretching fundamentals, because our instrument was not able to cover the whole bending region. As we are primarily interested in the vibrations accompanying hydrogen-bonded stretching, the present result is not affected by the lack of intensity data on bending fundamentals.

Experimental

The HCCCN was kindly offered by Takeda Chemical Industries, Ltd., from their stock. The DCCCN was obtained by mixing the HCCCN with weakly alkaline D_2O, and both samples were distilled within a vacuum line just before the spectroscopic measurements, in order to remove any residual water and colored impurities. Their infrared spectra showed no indication of impurities except for a minute amount of HCCCN in the DCCCN sample, whose deuterium concentration was determined to be 98 mole% in both gas and crystal by measuring the intensity of the residual C–H stretching band.

The gaseous intensities were determined by the Wilson-Wells method.[7] The area of absorption

$$B' = \int \ln(T_0/T)d\nu$$

was measured using a 10 cm-length cell, with helium gas for pressure broadening. Sufficient broadening was achieved at a pressure of less than 170 Torr for every stretching band with a spectral slit width of 1 cm^{-1} or somewhat less. It was confirmed by observing the intensity by varying the total

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pressure; the intensity increase from 9 Torr to 170 Torr was a little less than 5%. The good linearity of Beer's law plots obtained to very low concentration seems to support it also. The ν_1, ν_2, and ν_3 frequencies of gaseous HCCCN were essentially identical with those reported by Turrell *et al.*[8] A weak absorption was observed in the ν_4 fundamental region of gaseous HCCCN, whereas no well-defined absorption band was observed in the ν_4 region (750~900 cm^{-1}) of gaseous DCCCN, even under its saturated vapor pressure.

The crystalline spectra were obtained at 77 K by an experimental procedure similar to that used for hydrogen cyanide.[5] In the process of evaluating intensities, the density at 248 K from the X-ray experiment[6] was used temporarily because no value was available for 77 K. The refractive index of the crystal at the wavelength of one micron, where the interference fringes were recorded for measuring the film thicknesses, was tentatively calculated based on the Lorentz-Lorenz formula using the atomic refraction data for the Na-D line.[9]

Results

The observed frequencies are shown in Table 2, together with those reported earlier.[8] In the ν_4 fundamental region of gaseous HCCCN, a broad and weak absorption attributable to the overlap of two parallel bands was observed. We provisionally assigned the 863 cm^{-1} band to ν_4 and the 887 cm^{-1} to $\nu_5+\nu_7$, following Job and King for the latter assignment[8] (Fig.

Table 2a. Observed and calculated frequencies of gaseous cyanoacetylene (cm^{-1})

HCCCN	Observed			Calculated
	Turrell *et al.*[a]	Job *et al.*[a]	This work	
ν_1(C-H)	3328.5±3	3328	3327	3329
ν_2(C≡C)	2271.0±0.8	2271	2272	2275
ν_3(C≡N)	2078.0±4	2078	2077	2081
ν_4(C-C)	—	—	863	868
DCCCN				
ν_1(C-D)		2608	2607	2604
ν_2(C≡C)		2250	2251	2248
ν_3(C≡N)		1968	1956	1953
ν_4(C-C)		—	—	855

Table 2b. Observed and calculated frequencies of crystalline cyanoacetylene (cm^{-1})

HCCCN	Observed		Calculated
	Turrell *et al.*[a]	This work	
ν_1(C-H)	3204±5	3204	3208
ν_2(C≡C)	2271.3±1	2271	2277
ν_3(C≡N)	2066±1	2066	2072
ν_4(C-C)	879.5±4	882	881
DCCCN			
ν_1(C-D)		2544	2538
ν_2(C≡C)		2246	2240
ν_3(C≡N)		1932	1927
ν_4(C-C)		868	869

a) Ref. 8.

Table 2c. Force constants of cyanoacetylene (md/Å)

	Gas[b]	Crystal[c]
K_1	5.904	5.338
K_2	16.92	17.17
K_3	6.866	7.006
K_4	16.05	15.39
K_{23}	1.55	1.74
K_{34}	−0.208	−0.501
K_5	—	0.149 (assumed)[c]

b) Potential function was assumed as follows;

$$2V=K_1r_1^2+K_2r_2^2+K_3r_3^2+K_4r_4^2+2K_{23}r_2r_3+2K_{34}r_3r_4.$$

For the definition of internal coordinates, see Ref. 15.

c) Potential function for the optically-active normal mode in crystal was assumed as follows, where r_i signifies the translationally invariant sum of internal coordinates as defined by Eq. (3). Hydrogen bond stretching force constant K_5 was estimated from Lippincott-Schroeder's potential.[14]

$$2V=(K_1+K_5)r_1^2+(K_2+K_5)r_2^2+(K_3+K_5)r_3^2 +(K_4+K_5)r_4^2+2(K_{23}+K_5)r_2r_3+2(K_{34}+K_5)r_3r_4.$$

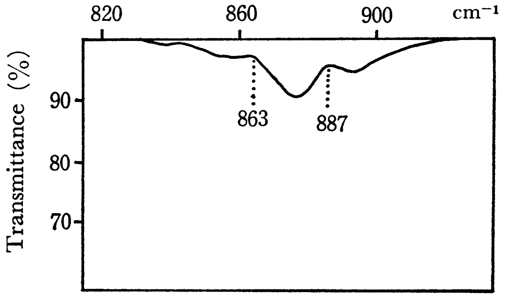

Fig. 2. Spectrum of ν_4 in gaseous HCCCN.

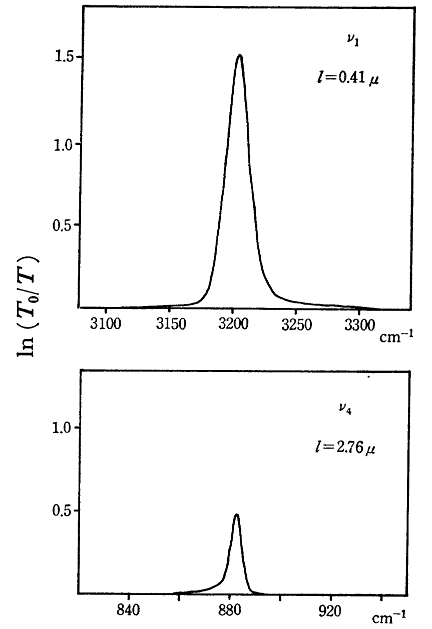

Fig. 3. Spectra of ν_1 and ν_4 in crystalline HCCCN.

2). Although Turrell *et al.* reported two additional broad absorptions at about 3200 cm^{-1} and 800 cm^{-1} in an HCCCN crystal, neither of these nor any of the corresponding bands in DCCCN was found in the present study (Fig. 3). The frequencies and breadth of these bands seem to suggest that they originate from the H_2O in HCCCN.[4]

The integrated absorption coefficient, A, was determined from Beer's law plots shown in Figs. 4 and 5, except for the gaseous ν_4 bands, which were so weak under the present observing conditions that no significant plots were obtainable. The $A(\nu_4)$ value of gaseous HCCCN was roughly estimated by comparing the peak height of the P-branch with that of ν_3, while no appreciable intensity was detected for ν_4 of DCCCN, as has been stated before. The values of the intensities thus determined are given in Table 3, in which the effective field correction by means of Polo-Wilson's equation[10] has already been incorporated in the crystalline values.

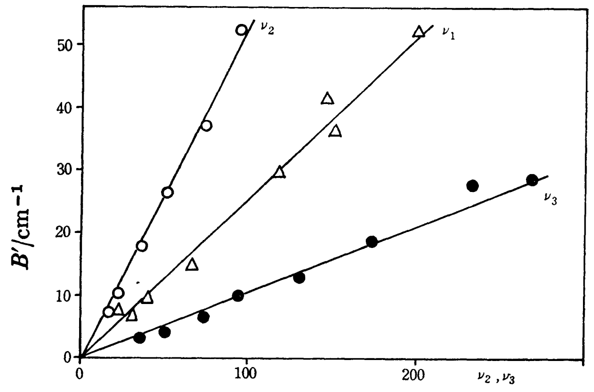

Fig. 4a. Beer's law plots of gaseous HCCCN.

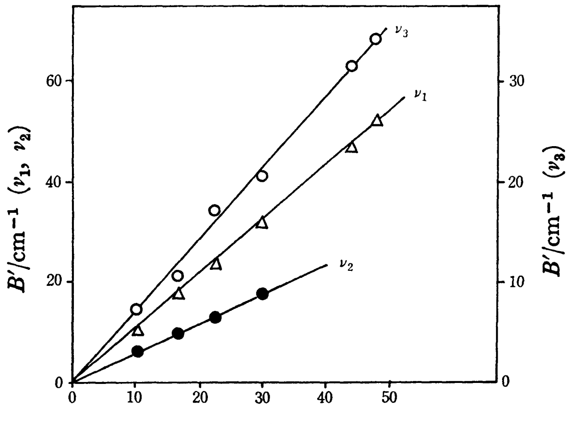

Fig. 4b. Beer's law plots of gaseous DCCCN.

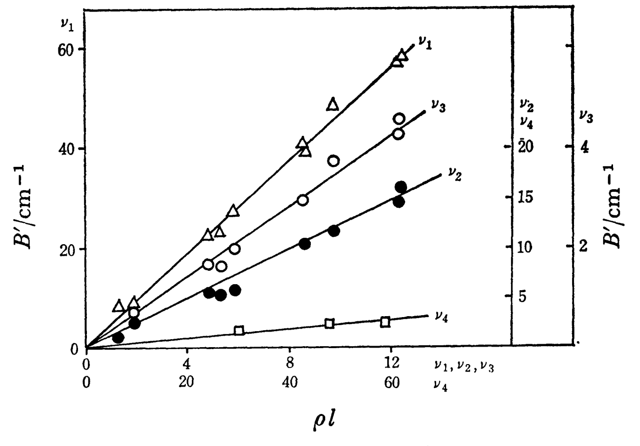

Fig. 5a. Beer's law plots of crystalline HCCCN (ρl in 10^{-4} mM cm^{-2}).

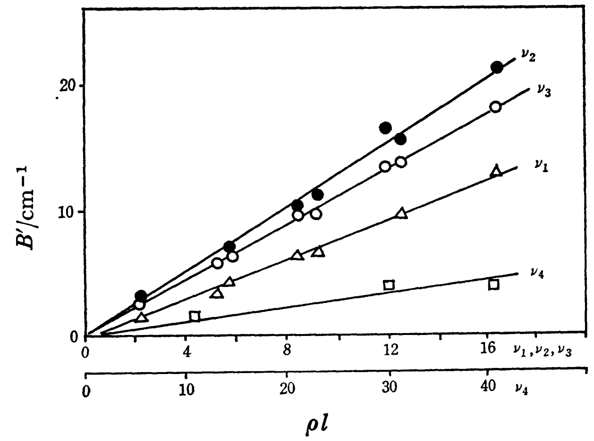

Fig. 5b. Beer's law plots of crystalline DCCCN (ρl in 10^{-4} mM cm^{-2}).

It should be noticed that the above intensities include errors from various sources; the accuracy of crystalline values can be especially seriously influenced by the slit width used and by the finite range of the frequency in integration. In the present observation, the slit width was normally much less than, or, at most, equal to, one-half of the band-width, and the integration was carried out over ten times the band width or more. Assuming a Lorentzian shape of the band, the maximum errors due to these sources are estimated at 6% and 7% respectively.[11] Taking other factors into consideration, the composite error is estimated at about 20% for crystals and about 15% for gases, considering some additional sources of error (for example, the uncertainty of the density at 77 K, the inhomogeneity of the film thicknesses, *etc*) in the former case. A criterion of the accuracy may be obtained by examining the validity of the intensity F-sum rule;[12] then, it is seen that the sums:

$$\sum_i (1/\lambda_i)\,|\partial\mu/\partial Q_i|^2$$

for H and D species agree within an error of 9% for the gas and 4% for the crystal, where λ_i is an eigenvalue ($\lambda_i=4\pi^2\nu_i^2$); $\partial\mu/\partial Q_i$ is given immediately below.

The integrated intensity, A, is related to the derivative of the dipole moment with respect to a normal coordinate, Q_i, by:[13]

$$A(\nu_i) = (N\pi/3c^2)\,|\partial\mu/\partial Q_i|^2 \qquad (1)$$

For crystalline intensities, Q_i should be an optically-active (wave vector $K=0$) normal coordinate of the crystal. The transformation to the derivatives with respect to the internal coordinates, r_i, is expressed as;[13]

TABLE 3. OBSERVED INTENSITIES $A(\nu_i)$ OF CYANOACETYLENE (10^4 DARKS)

		ν_1	ν_2	ν_3	ν_4
Gas	HCCCN	0.604±0.091	0.0992±0.0149	0.0193±0.0029	~0.0006
	DCCCN	0.202±0.030	0.110 ±0.016	0.133 ±0.020	<0.0002
Cryst.	HCCCN	3.53 ±0.71	0.933 ±0.187	0.271 ±0.054	0.035±0.007
	DCCCN	0.577±0.115	0.963 ±0.193	0.824 ±0.165	0.076±0.015

TABLE 4. POSSIBLE COMBINATIONS OF RELATIVE SIGNS IN
$(\partial\mu/\partial Q_1, \partial\mu/\partial Q_2, \partial\mu/\partial Q_3, \partial\mu/\partial Q_4)$ (D/Å)

Gas		++++	+−++	++−+	+++−	+−−+	++−−	+−+−	+−−−[a]
$\partial\mu/\partial r_1$	HCCCN	0.989	1.137	1.100	0.976	1.249	1.088	1.124	1.236
	DCCCN	0.048	0.392	0.980	0.032	1.324	0.964	0.964	1.310
$\partial\mu/\partial r_2$	HCCCN	−1.250	−0.245	−0.383	−1.401	0.614	−0.535	−0.405	0.461
	DCCCN	−1.985	−1.664	0.215	−2.078	0.538	0.124	−1.756	0.446
$\partial\mu/\partial r_3$	HCCCN	0.463	−0.173	0.447	0.210	−0.188	0.193	−0.427	−0.442
	DCCCN	0.629	−0.006	0.345	0.483	−0.290	0.199	−0.152	−0.437
$\partial\mu/\partial r_4$	HCCCN	−0.438	1.222	−1.061	−0.602	0.599	−1.225	1.058	0.436
	DCCCN	−0.527	1.504	−1.564	−0.620	0.465	−1.658	1.409	0.373
Cryst.		++++	+−++	++−+	+++−	+−−+[a]	++−−	+−+−	+−−−
$\partial\mu/\partial r_1$	HCCCN	2.255	2.721	2.709	2.155	3.176	2.610	2.622	3.077
	DCCCN	−0.588	0.492	1.962	−0.897	3.042	1.652	0.183	2.733
$\partial\mu/\partial r_2$	HCCCN	−3.630	−0.733	−0.284	−4.811	2.612	−1.466	−1.915	1.430
	DCCCN	−3.546	−3.052	1.932	−5.400	2.426	0.079	−4.906	0.572
$\partial\mu/\partial r_3$	HCCCN	2.012	−0.080	2.110	0.000	0.018	0.098	−2.092	−1.994
	DCCCN	2.994	0.897	2.470	−0.003	0.367	−0.532	−2.106	−2.636
$\partial\mu/\partial r_4$	HCCCN	−0.748	4.269	−2.944	−2.086	2.073	−4.281	2.931	0.735
	DCCCN	−0.870	5.084	−3.497	−2.853	2.458	−5.480	3.101	0.476

a) Best combination.

$$\partial\mu/\partial r_i = \textstyle\sum_j L^{-1}_{ji} \partial\mu/\partial Q_j, \tag{2}$$

where r_i for the crystalline case stands for a translationally-invariant linear combination of molecular r_i's. According to the crystal structure given before, the interaction between different chains of molecules may be much smaller than that due to hydrogen bonding, so that the crystal may be approximated by a one-dimensional chain in the following considerations. Then, the r_i in Eq. (2) for the crystal may be:

$$r_i = (1/\sqrt{n}) \textstyle\sum_j r_i^j \tag{3}$$

where r_i^j is the i-th coordinate of the j-th molecule of a chain and where n represents the number of molecules conforming to the periodic boundary condition.

The L^{-1}_{ji} in Eq. (2) was calculated based on the force constants given in Table 2, which reproduce the observed frequencies with deviations less than 0.5%. The force constant of a hydrogen-bond K(N···H), was obtained assuming a Lippincott-Schroeder potential.[14] Since the sign of $\partial\mu/\partial Q_i$ is not determinable experimentally, eight different sets of values are possible for $\partial\mu/\partial r_i$'s, corresponding to eight different combinations of relative signs among the four $\partial\mu/\partial Q_i$'s. It may be seen in Table 4 that the best consistencies between HCCCN and DCCCN are obtained in the (+ − − −) combination for the gas and in the (+ − − +) combination for the crystal. The final values of $\partial\mu/\partial r_i$ are given in Table 5, where two alternative sets of the signs are still present. Hereafter, the absolute sign of the derivatives will be defined so that a positive $\partial\mu/\partial r_{st}$ represents the increase in the dipole moment in the $^+$HCCCN$^-$ or $^+$HCN$^-$ direction caused by the s-t stretching.

TABLE 5. $\partial\mu/\partial r_i$ IN GASEOUS AND CRYSTALLINE CYANOACETYLENE AND CHANGE OF $\partial\mu/\partial r_i$ (D/Å)

	Gas	Cryst.	Change of $\partial\mu/\partial r_i$
$\partial\mu/\partial r_1$	1.28	3.11	1.83
$\partial\mu/\partial r_2$	0.45	2.52	2.07
$\partial\mu/\partial r_3$	−0.44	0.19	0.63
$\partial\mu/\partial r_4$	0.41	2.27	1.86

Finally, it must be pointed out that the observed $\partial\mu/\partial r_3$ value of cyanoacetylene may contain a larger error than the others. That is, the intensity of ν_4, to which C–C stretching is mainly responsible, is extremely weak, so that the major contribution to $\partial\mu/\partial r_3$ comes from the other fundamental intensities through L^{-1} matrix elements, *i.e.* L^{-1}_{i3} (i=1,2,3).

Discussion

Since the criterion of Table 4 does not disclose the absolute sign of $\partial\mu/\partial r$, it has to be determined on other bases. In the case of hydrogen cyanide, the sign of the gaseous derivatives was already known through the analysis of the vibration-rotation bands;[16] the crystalline one was chosen so that the observed differences, $\Delta(\partial\mu/\partial r) = (\partial\mu/\partial r)_{\text{crystal}} - (\partial\mu/\partial r)_{\text{gas}}$, which were remarkable not only in $\partial\mu/\partial r_{CH}$ but also in $\partial\mu/\mu r_{C\equiv N}$, could be interpreted consistently in terms of an intermolecular contribution $[\partial\mu/\partial r_{\mathrm{N\cdots H}}]$, given below. In fact, only such a choice of the sign made possible a reasonable interpretation; the resulting large negative $[\partial\mu/\partial r_{\mathrm{N\cdots H}}]$ value was attributed to the vibrational contribution of the charge-transfer effect in hydrogen bonding.[5]

As for the absolute signs of $\partial\mu/\partial r_1$ in cyanoacetylene,[15] it seems most reasonable to assume that they are positive both in gas and in the crystal, so as to give similar values to those of hydrogen cyanide, because the C–H bond properties cannot be much different between these molecules and the effects of hydrogen bonding may also be alike in view of their similar crystal structures. In fact, any other sign combination proves to give quite an unintelligible situation regarding the interpretation of $\partial\mu/\partial r_1$ and $\partial\mu/\partial r$'s. Table 5 shows the results obtained assuming the absolute sign proposed above.

According to considerations similar to those made before,[5] the observed crystalline derivatives may be expressed as:

$$\partial\mu/\partial r_i = [\partial\mu/\partial r_i] - [\partial\mu/\partial r_{\mathrm{N\cdots H}}], \tag{4}$$

where the brackets signify that the derivative is unconstrained by the condition for the optically-active coordinates:[17]

$$r_1 + r_2 + r_3 + r_4 + r_{\mathrm{N\cdots H}} = 0. \tag{5}$$

Then, we obtain

$$\begin{aligned}\Delta(\partial\mu/\partial r_i) &= (\partial\mu/\partial r_i)_{\mathrm{crystal}} - (\partial\mu/\partial r_i)_{\mathrm{gas}} \\ &= \Delta[\partial\mu/\partial r_i] - [\partial\mu/\partial r_{\mathrm{N\cdots H}}],\end{aligned} \tag{6}$$

where the change of a derivative is resolved into a purely intramolecular part ($\Delta[\partial\mu/\partial r_i]$) and a concurrent intermolecular term ($[\partial\mu/\partial r_{\mathrm{N\cdots H}}]$).

Now, it may be noted in Table 5 that the three $\Delta(\partial\mu/\partial r_i)$ values are fairly close each other and comparable to the corresponding values in hydrogen cyanide with the exception of $\Delta(\partial\mu/\partial r_3)$. Therefore, if the previous conclusion that $[\partial\mu/\partial r_{\mathrm{N\cdots H}}]$ is primarily responsible for $\Delta(\partial\mu/\partial r_i)$ is essentially valid here, there must be adequate reasons for the abnormally small value of $\Delta(\partial\mu/\partial r_3)$. Therefore, it may be proper to investigate such reasons in (a) the behavior of conjugated π-electrons during vibration, (b) the polarization of σ-electron due to the electrostatic field by neighboring molecules, and (c) the polarization of σ-electrons due to the intermolecular charge transfer through the hydrogen bond. In these effects, the behavior of conjugated π-electrons seems to be most significant, as will be shown below.

Assuming that the dipole moment is simply given by:

$$\mu = \textstyle\sum_i q_i x_i, \tag{7}$$

where q_i and x_i are the charge density and the coordinate of the i-th atom, its derivative with respect to s-t stretching is:

$$\partial\mu/\partial r_{\mathrm{st}} = \textstyle\sum_i\{(\partial q_i/\partial r_{\mathrm{st}})x_i + q_i(\partial x_i/\partial r_{\mathrm{st}})\}, \tag{8}$$

In a simple MO consideration for π-electrons, it may be appropriate to represent the effect of s-t stretching by a change in the resonance integral, β_{st}. Thus, confining ourselves to π-electrons, we may obtain

$$\partial q_i/\partial r_{\mathrm{st}} = (\partial q_i/\partial\beta_{\mathrm{st}})(\partial\beta_{\mathrm{st}}/\partial r_{\mathrm{st}}) = \pi_{i,\mathrm{st}}(\mathrm{d}\beta_{\mathrm{st}}/\mathrm{d}r_{\mathrm{st}}), \tag{9}$$

where $\pi_{i,\mathrm{st}}$ is the atom-bond polarizability.[18] It may be noticed here that always $\mathrm{d}\beta_{\mathrm{st}}/\mathrm{d}r_{\mathrm{st}} > 0$. In the present approximate consideration, the hydrogen-bonding perturbation to π-electrons may be represented by the change in the Coulomb integrals of C_1 and N; $\Delta\alpha_1$ and $\Delta\alpha_4$. Then, we obtain:

$$\begin{aligned}\Delta\left(\frac{\partial\mu}{\partial r_{\mathrm{st}}}\right)_\pi &= \textstyle\sum_i\left(\frac{\partial\pi_{i,\mathrm{st}}}{\partial\alpha_1}\Delta\alpha_1 + \frac{\partial\pi_{i,\mathrm{st}}}{\partial\alpha_4}\Delta\alpha_4\right)\frac{\partial\beta_{\mathrm{st}}}{\partial r_{\mathrm{st}}}x_i \\ &\quad + \textstyle\sum_i(\pi_{i,1}\Delta\alpha_1 + \pi_{i,4}\Delta\alpha_4)\frac{\partial x_i}{\partial r_{\mathrm{st}}},\end{aligned} \tag{10}$$

where $\pi_{i,j}$ is the atom-atom polarizability;[18] an explicit form of $(\partial\pi_{i,\mathrm{st}}/\partial\alpha_j)$ is given in the Appendix. The use of the π-wave function based on a CNDO calculation gives the numerical expression in Table 6.

In Table 6, it is notable that the first term of $\Delta(\partial\mu/\partial r_3)_\pi$ is of a sign opposite to those of the other two. Since the perturbation may be taken such that $\Delta\alpha_1 > 0$ and $\Delta\alpha_4 < 0$, because of either electrostatic and charge-transfer interactions, the first term above may certainly serve to lower the value of $\Delta[\partial\mu/\partial r_3]$, while it raises the other two.

TABLE 6. π-ELECTRON CONTRIBUTION TO $\Delta[\partial\mu/\partial r]$ CALCULATED BY USING CNDO WAVE FUNCTIONS (in atomic units)[a]

r_{st}	$\Delta[\partial\mu/\partial r_{\mathrm{st}}]$
r_2	$(18.1\Delta\alpha_1 - 6.1\Delta\alpha_4)(\partial\beta_2/\partial r_2) + (2.4\Delta\alpha_1 - 0.4\Delta\alpha_4)$
r_3	$-(15.5\Delta\alpha_1 - 15.6\Delta\alpha_4)(\partial\beta_3/\partial r_3) + (0.3\Delta\alpha_1 - 0.3\Delta\alpha_4)$
r_4	$(6.0\Delta\alpha_1 - 17.3\Delta\alpha_4)(\partial\beta_4/\partial r_4) + (0.4\Delta\alpha_1 - 2.3\Delta\alpha_4)$

a) The resonance integrals are numbered in the same way as r_i. See Ref. 15.

Besides the π-electron contribution (a) mentioned above, $\Delta[\partial\mu/\partial r_i]$ should be influenced by the σ-electron polarization, which is caused by the electrostatic field (b) and also by the intermolecular charge transfer (c) as described by such resonance structures:

$$\equiv\mathrm{N}\quad \mathrm{H{-}C{\equiv}C{-}C{\equiv}}\overset{+}{\mathrm{N}}\mathrm{{-}H}\quad \overset{-}{\mathrm{C}}$$

$$\equiv\overset{+}{\mathrm{N}}\mathrm{{-}H}\quad \overset{-}{\mathrm{C}}\mathrm{{\equiv}C{-}C{\equiv}N}\quad \mathrm{H{-}C}$$

However, in view of the fact that C–H bending intensity was almost unchanged in hydrogen cyanide,[5] as is generally observed in hydrogen-bonded systems, the (b) effect does not seem very important. On the other hand, the (c) effect may reduce $\Delta[\partial\mu/\partial r_i]$ more or less except in the case of C–H, resulting in a rather large negative $\Delta[\partial\mu/\partial r_3]$ value in cooperation with the (a) effect. On the other hand, $\Delta[\partial\mu/\partial r_2]$ and $\Delta[\partial\mu/\partial r_4]$ may become less important because the (c) and (a) effects tend to cancel each other out.

The consideration given above, though it is only qualitative, seems to explain the discrepancy in $\Delta(\partial\mu/\partial r_3)$ rather convincingly. We may, then, consider that, in all probability, the present result further demonstrates the importance of the intermolecular dipole-moment derivative $[\partial\mu/\partial r_{\mathrm{N\cdots H}}]$. As a rough estimate, the value of $[\partial\mu/\partial r_{\mathrm{N\cdots H}}]$ may be comparable to the observed $\Delta(\partial\mu/\partial r_1)$ value with a negative sign, because the previous estimate, -1.4 D/Å, for hydrogen cyanide seems to be too low because the effect of $\Delta[\partial\mu/\partial r_{\mathrm{C{\equiv}N}}]$ was ignored then.

The authors wish to thank the Takeda Chemical Industries, Ltd., for giving them the cyanoacetylene sample.

Appendix

The atom-bond polarizability, $\pi_{r,\mathrm{st}}$, is given in terms of the LCAO MO coefficients as:[18]

$$\pi_{\mathrm{r,st}} = \partial q_r/\partial\beta_{\mathrm{st}}$$

$$= 4\sum_{j=1}^{m}\sum_{k=m+1}^{n} C_{rj}C_{rk}(C_{sj}C_{tk}+C_{tj}C_{sk})/(\varepsilon_j-\varepsilon_k)$$

$$(1{\sim}m\text{: occuppied MO, } m+1{\sim}n\text{: vacant MO}) \qquad \text{(A1)}$$

Now, for a small perturbation, $\boldsymbol{J}$, in the Hamiltonian matrix, the perturbed orbital energy and LCAO MO coefficients are given by:

$$\varepsilon_j = \varepsilon_j^\circ + \tilde{\boldsymbol{C}}_j^\circ \boldsymbol{J}\boldsymbol{C}_j^\circ,$$

$$\boldsymbol{C}_j = \boldsymbol{C}_j^\circ + \sum_{k\mp j}\{\tilde{\boldsymbol{C}}_k^\circ \boldsymbol{J}\boldsymbol{C}_j^\circ/(\varepsilon_j^\circ-\varepsilon_k^\circ)\}\boldsymbol{C}_k^\circ \qquad \text{(A2)}$$

where $\boldsymbol{C}_j$ is a column vector of coefficients for the j-th MO and where the superscript ° denotes unperturbed values. On the basis of these equations, the following expressions are obtained straightforwardly for a diagonal term, $J_{\mathrm{u,u}}=\Delta\alpha_{\mathrm{u}}$:

$$\partial\pi_{r,\mathrm{st}}/\partial\alpha_{\mathrm{u}} = 4\sum_{j=1}^{m}\sum_{k=m+1}^{n}\frac{C_{rj}C_{rk}}{\varepsilon_j-\varepsilon_k}\Bigg\{(C_{sj}C_{tk}+C_{tj}C_{sk})$$

$$\times\left[\frac{C_{rj}^{(u)}}{C_{rj}}+\frac{C_{rk}^{(u)}}{C_{rk}}-\frac{C_{uj}^2-C_{uk}^2}{\varepsilon_j-\varepsilon_k}\right]+C_{sj}^{(u)}C_{tk}$$

$$+C_{sj}C_{tk}^{(u)}+C_{tj}^{(u)}C_{sk}+C_{tj}C_{sk}^{(u)}\Bigg\}, \qquad \text{(A3)}$$

$$C_{rj}^{(u)} = \sum_{\substack{l=1\\ l\neq j}}^{n}\{C_{rl}C_{ul}C_{uj}/(\varepsilon_j-\varepsilon_l)\} \qquad \text{(A4)}$$

where the superscript ° is omitted from every symbol for the sake of brevity.

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