

A Relationship between Infrared Band Intensity and Configuration of the Cyano Group in Simple and Fused Cyclohexanecarbonitriles

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Infrared spectral measurements were carried out to obtain the integrated intensity of the stretching vibration band of the cyano group in simple and fused cyclohexanecarbonitriles in carbon tetrachloride solution. A linear relationship was found between the integrated intensity and the square of the number (N) of $C_\beta-C_\gamma$ bonds parallel to the $C\equiv N$ bond. This result was theoretically supported by CNDO/2 calculations.

Nagata *et al.*¹ have reported a correlation between the configuration of the cyano group and the infrared molecular extinction coefficient (ϵ) of its stretching vibration band ($\nu_{C\equiv N}$) for some epimeric pairs of cyclohexanecarbonitriles. Experimentally, the ϵ value of an equatorial cyano group as in structures (IIIa) and (IIIb) was greater than that of the corresponding axial epimer as in (Ia) and (II), respectively.¹ Theoretically, the value of ϵ was shown to increase qualitatively with increasing number (N) of $C_\beta-C_\gamma$ bonds parallel to the $C\equiv N$ bond, [indicated by the thick lines in the illustrations (II), (IIIa), and (IIIb)].¹ This correlation has been utilized for determining the configuration of the cyano group in intermediates for syntheses of natural products.²

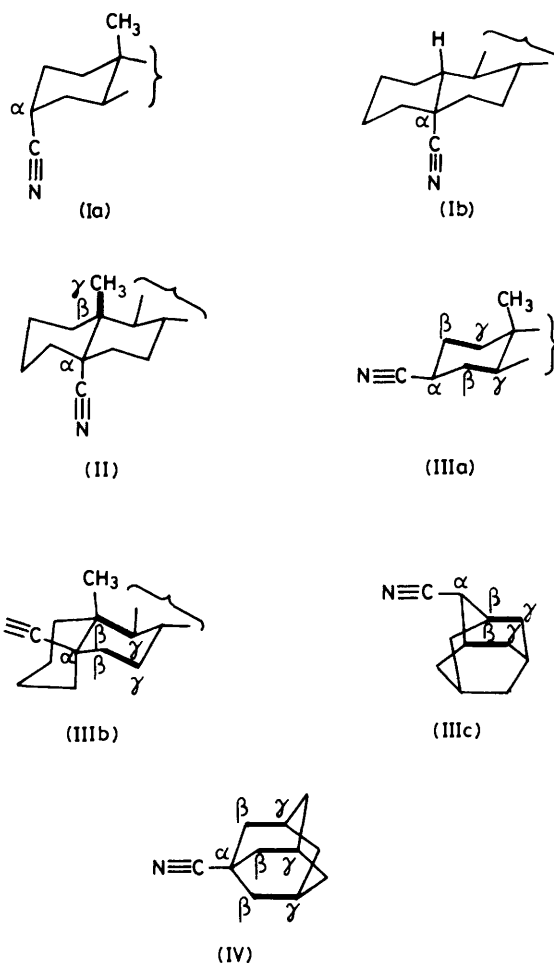
In this study, we have measured the integrated intensities (A) of the $\nu_{C\equiv N}$ bands of cyano compounds of types (Ia)—(IV), and have examined the relationship between the A value and the N value; the A value is more directly related to the molecular structural properties and to theoretical quantities than is ϵ . The effect of substituents on the integrated intensities of the $\nu_{C\equiv N}$ bands of benzonitriles has been studied previously by the CNDO/2 method, and satisfactory explanations have been provided.³ We have tried to elucidate interesting phenomena in this series by the same treatment.

Experimental

2,2-Dimethylpropionitrile and compound (14) were obtained commercially; compound (10) was prepared as reported elsewhere;⁴ compounds (1)—(9), (11)—(13), and (15) were supplied by Drs. Nagata, Yoshioka, and Narisada of our laboratory. These materials were purified by standard methods until their physical constants agreed with published values. I.r. spectra were recorded at room temperature (*ca.* 27 °C) with a JASCO DS-402G or a JASCO A702 spectrometer calibrated according to the rotational bands of both carbon monoxide and carbon dioxide gases. Nitriles were dissolved in carbon tetrachloride at three concentrations in the range 0.03—0.23M (cell length $l = 0.1$ cm). The integrated intensity is given by equation (1), where n is the number of molecules in 1 cm³ and ν is the frequency. The values of A

$$A = (1/nl) \int \ln(I_{0\nu}/I_\nu) d\nu \quad (\text{cm}^2 \text{ s}^{-1} \text{ molecule}^{-1}) \quad (1)$$

were obtained by graphical integration of the spectra, because the $\nu_{C\equiv N}$ band contour does not generally follow a Lorentz function. Because the values of A for 2,2-dimethylpropionitrile measured by the two spectrometers used differed slightly, all the A values for the other compounds are expressed as the values obtained from the JASCO A702 after correction using 2,2-dimethylpropionitrile as reference.



Calculation

The A_j value (that of the j th normal mode of vibration) is given by equation (2),⁵ where c is the velocity of light, Q_j is

$$A_j = (\pi/3c)(\partial\mu/\partial Q_j)^2 \quad (\text{cm}^2 \text{ s}^{-1} \text{ molecule}^{-1}) \quad (2)$$

$$(\partial\mu/\partial Q_j)^2 = [\partial\mu(x)/\partial Q_j]^2 + [\partial\mu(y)/\partial Q_j]^2 + [\partial\mu(z)/\partial Q_j]^2 \quad (3)$$

the j th normal co-ordinate, and μ is the total dipole moment. As described previously,³ $(\partial\mu/\partial Q_j)$ is approximated by equation (4) according to Brownlee *et al.*⁶ Then, when a

$$(\partial\mu/\partial Q_j) \approx (\Delta\mu/\Delta Q_j) \quad (4)$$

Table 1. Cartesian L matrix elements for the 2270.6 cm^{-1} band ^a in acetonitrile ^b

Atom ^c	$L_{Jz} = 20 \times \Delta z_j$ ^d
C*	-0.0347
C	0.2263
N	-0.1626

^a Ref. 9. ^b The bond lengths and bond angles of acetonitrile are from ref. 13. ^c C* is the carbon atom bonded by the nitrile group; C and N are the atoms in the nitrile group. ^d The Δz_j value (Å) is calculated as being 0.05 times the corresponding L_{Jz} value.

C-C≡N moiety is placed on the z -axis, all dipole moment derivatives of the $\nu_{\text{C}\equiv\text{N}}$ mode will be negligibly small except for the z -component. If the dipole moment derivatives can be assumed to consist approximately of only the z -component, and if cyano compounds of types (Ia)–(IV) have the same normal co-ordinate for the $\nu_{\text{C}\equiv\text{N}}$ mode, the square root of the relative intensities of molecules a and b is given theoretically by equation (5).

$$(A_b/A_a)^{\frac{1}{2}} = [\partial\mu(z)/\partial Q_j]_b / [\partial\mu(z)/\partial Q_j]_a \approx \Delta\mu_b(z) / \Delta\mu_a(z) \quad (5)$$

Each $\Delta\mu(z)$ value in equation (5) is obtained as $[\mu^+(z) - \mu^-(z)]$, where $\mu^+(z)$ and $\mu^-(z)$ are calculated using the co-ordinates $(z_j + \Delta z_j)$ and $(z_j - \Delta z_j)$, respectively. The Δz_j values are obtained from the Cartesian L matrix elements in Table 1. From the normal co-ordinate analysis, it is clear that the band characteristic of the C≡N stretching vibration is highly localized at a C-C≡N unit.^{1,3,7} As shown in Table 2, the position of the $\nu_{\text{C}\equiv\text{N}}$ band is scarcely changed by the configuration of the cyano group. Therefore, the Δz_j values obtained from the Cartesian L matrix of acetonitrile were used approximately as those of all compounds in this work. The normal co-ordinate analysis of acetonitrile was carried out by a modification of Gwinn's method.⁸ The force constants used were determined by referring to the values proposed by Duncan *et al.*⁹ The geometry of the model compounds is given in Table 3.^{10,11} The z -axis was taken to be parallel to the C≡N bond and the calculations were performed by the CNDO/2 method.¹²

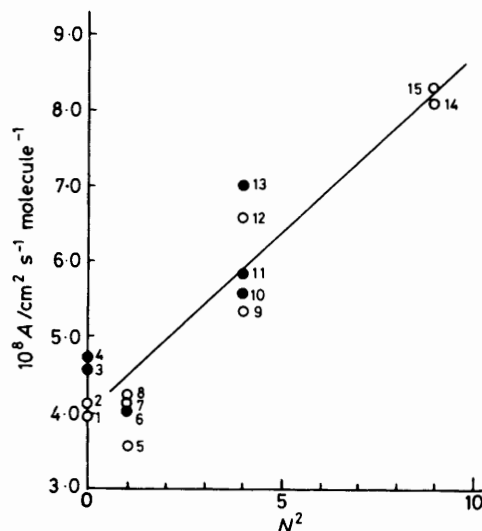
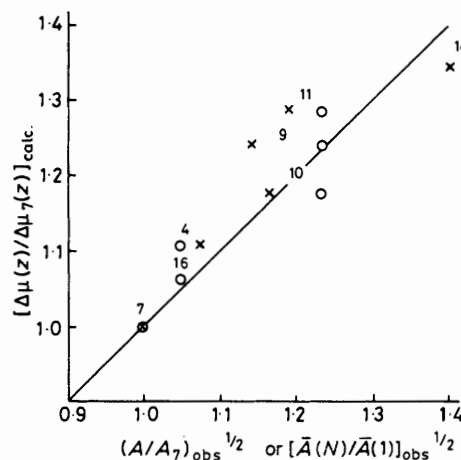
Results and Discussion

(a) *Relationship between the Integrated Intensity and the Number of Parallel C_β-C_γ Bonds.*—The i.r. parameters obtained for the carbon tetrachloride solutions of cyclohexanecarbonitriles are listed in Table 2, together with the numbers (N) of C_β-C_γ bonds parallel to the C≡N bond. The values of A or A_{rel} increase with increasing N in the order $N = 0$ or 1 through $N = 2$ to $N = 3$, but the values of A or A_{rel} for $N = 0$ are almost the same as those for $N = 1$. The average value of A or A_{rel} for $N = 0$ is slightly larger than that for $N = 1$. The compounds may be classified into three types; $N = 0$ or $N = 1$, $N = 2$, and $N = 3$. Thus the value of the integrated intensity of the $\nu_{\text{C}\equiv\text{N}}$ band provides useful information on the configuration of the cyano group in cyclohexanecarbonitriles.

The A values of the $\nu_{\text{C}\equiv\text{N}}$ band are given theoretically by equation (6), where $\mu_{\text{C}\equiv\text{N}}$, $\mu_{\text{C}\alpha-\text{C}}$, and $\mu_{\text{C}\beta-\text{C}\gamma}$ are the bond

$$A_j = (\pi/3c)[\partial/\partial Q_j(\mu_{\text{C}\equiv\text{N}} + \mu_{\text{C}\alpha-\text{C}} + N\mu_{\text{C}\beta-\text{C}\gamma})]^2 \quad (6)$$

moments of the C≡N, C_α-C, and C_β-C_γ bonds, respectively. Equation (6) indicates that the A value can be expressed by a quadratic equation in N . From the data for the 15 cyano

**Figure 1.** Plot of $10^8 A$ against N^2 for cyano compounds (for key see Table 2): (●) secondary nitrile; (○) tertiary nitrile**Figure 2.** Plots of $[\Delta\mu(z)/\Delta\mu_7(z)]_{\text{calc}}$ against $(A/A_7)_{\text{obs}}^{\frac{1}{2}}$ (×) or $[A(N)/A(1)]_{\text{obs}}^{\frac{1}{2}}$ (○) (for key see Table 4)

compounds shown in Table 2, equation (7) was obtained using the regression analysis method, where r is the correlation coefficient. This analysis shows statistically that the term in

$$A = 0.646N^2 - 0.545N + 4.28 \quad (r = 0.94) \quad (7)$$

N^2 has significance at the 99% confidence level, but the linear term has no significance at a confidence level above 75%. The regression analyses for A and A_{rel} shown in Table 2 were thus carried out for N^2 , and equations (8) and (9) were obtained. These indicate that both A and A_{rel} are mainly proportional to N^2 . Interestingly, the value of the constant term of equation

$$A = 0.467N^2 + 4.05 \quad (r = 0.93) \quad (8)$$

$$A_{\text{rel}} = 0.115N^2 + 1.00 \quad (r = 0.93) \quad (9)$$

(8) corresponds to that of A for 2,2-dimethylpropionitrile. Figure 1, a plot of A versus N^2 , gives a linear relationship as expressed approximately by equation (8). This suggests that the

Table 2. Infrared spectral data for the $\text{C}\equiv\text{N}$ stretching band for cyano compounds in carbon tetrachloride solution

No.	Compound	$\nu_{\text{C}\equiv\text{N}}/\text{cm}^{-1}$	$10^8 A^a$	A_{rel}^a	N^b
1	5 α -Cyanoestrane	2 228	3.97	0.98	0
2	5 α -Cyano-17 β -acetoxyestrane	2 229	4.25	1.05	0
3	3 α -Cyano-5 α -cholestane	2 238	4.66	1.15	0
4	<i>cis</i> -1-Cyano-4- <i>t</i> -butylcyclohexane	2 240	4.74	1.17	0
5	3 β ,20-Diacetoxy-9 α -cyano-5 α -pregnane	2 226	3.56	0.88	1
6	1 α -Cyano-5 α -cholestane	2 232	4.05	1.00	1
7	<i>trans</i> -4 α -Cyano-8 α -methylperhydronaphthalene	2 226	4.13	1.02	1
8	5 α -Cyanocholestane	2 227	4.25	1.05	1
9	<i>cis</i> -4 α -Cyano-8 α -methylperhydronaphthalene	2 231	5.35	1.32	2
10	2-Cyanoadamantane	2 236	5.59	1.38	2
11	<i>trans</i> -1-Cyano-4- <i>t</i> -butylcyclohexane	2 240	5.83	1.44	2
12	5 β -Cyanocholestane	2 229	6.60	1.63	2
13	3 β -Cyano-5 α -cholestane	2 240	7.01	1.73	2
14	1-Cyanoadamantane	2 239 ^c	8.10	2.00	3
15	1-Cyanobicyclo[2.2.2]octane	2 242	8.30	2.05	3

^a A in $\text{cm}^2 \text{s}^{-1} \text{molecule}^{-1}$. $A_{\text{rel}} = A/A_0$, where A_0 is the observed integrated intensity of the $\nu_{\text{C}\equiv\text{N}}$ band of 2,2-dimethylpropionitrile, *i.e.* $A_0 = 4.05 \times 10^{-8} \text{cm}^2 \text{s}^{-1} \text{molecule}^{-1}$. ^b The number of parallel $\text{C}_\beta\text{-C}_\gamma$ bonds with respect to the cyano group (such bonds are shown by heavy lines in structures (Ia)–(IV)). ^c The value of the centre of gravity frequency was adopted as $\nu_{\text{C}\equiv\text{N}}$ because the $\nu_{\text{C}\equiv\text{N}}$ band is split into three.

Table 3. Bond lengths (Å) and angles ($^\circ$)^{10,11} of molecules used in the CNDO/2 calculations

Bond	Length	Angle
$\text{C}\equiv\text{N}$	1.16	$\text{CC}'\text{N}$ 180
$\text{C}'\text{-C}$	1.46	$\text{C}'\text{CC}=\text{C}'\text{CH}=\text{CCC}=\text{C}'\text{C}$
C-C	1.54	$\text{CCH}=\text{HCH}$ 109.4667
C-H	1.11	All torsion angles 60

A value of the $\nu_{\text{C}\equiv\text{N}}$ band in this case is governed mainly by N^2 . Because the coefficient of N^2 in equation (8) is small, the contribution of the $\text{C}_\beta\text{-C}_\gamma$ bond to the A value for $N = 1$ is not very large. This may be the principal reason that no difference exists between the A values for $N = 0$ and $N = 1$. However, when N is 2 or 3, the contribution increases as A in equation (8) depends on N^2 .

(b) *Relative Dipole Moment Derivatives.*—The $[\Delta\mu(z)/\Delta\mu_7(z)]_{\text{calc}}$ values obtained from the CNDO/2 calculations on the model compounds [types (Ia)–(IV)] are given in Table 4, together with the corresponding experimental $(A/A_7)_{\text{obs}}$ values and the $[\bar{A}(N)/\bar{A}(1)]_{\text{obs}}$ values estimated from the average of *i.r.* parameters for the corresponding analogous compounds. The calculated $\mu'(z)$ values are also given in Table 4, where $\mu'(z)$ is the dipole moment caused by replace-

ment of a hydrogen atom by a cyano group. These values are almost proportional to the N values ($r = 0.92$), but not closely correlated with the dipole moment derivative as defined in equation (5) ($r = 0.72$). However, the calculated $[\Delta\mu(z)/\Delta\mu_7(z)]$ values agree reasonably well with the observed $(A/A_7)_{\text{obs}}$ or $[\bar{A}(N)/\bar{A}(1)]_{\text{obs}}$ values both in magnitude and in order as shown in Figure 2. A linear relationship ($r = 0.89$) was obtained between the square of $[\Delta\mu(z)/\Delta\mu_7(z)]_{\text{calc}}$ and N^2 in the model compounds [types (Ia)–(IV)]. This suggests theoretically that the A value of the $\nu_{\text{C}\equiv\text{N}}$ band is primarily governed by N^2 . Interestingly, the calculation also suggests that the A value for $N = 1$ is almost the same as (but smaller than) that for $N = 0$, as mentioned in the preceding paragraph.

Conclusion

The A values of the $\nu_{\text{C}\equiv\text{N}}$ bands in various cyclohexane-carbonitriles are adequately approximated by a linear relationship with N^2 . This is supported by CNDO/2 calculations. The calculations predict fairly accurately the values for the relative dipole moment derivatives of the $\nu_{\text{C}\equiv\text{N}}$ bands in the systems examined.

Table 4. Dipole moments and relative dipole moment derivatives for $\nu_{\text{C}\equiv\text{N}}$ bands of cyano compounds calculated by the CNDO/2 method and from experimental data

Type	Compound no.	N^a	$\mu(z)/\text{D}^b$	$\mu'(z)/\text{D}^b$	$[\Delta\mu(z)/\Delta\mu_7(z)]_{\text{calc}}^c$	$(A/A_7)_{\text{obs}}^{\pm d}$	$[\bar{A}(N)/\bar{A}(1)]_{\text{obs}}^{\pm e}$
(Ia)	4	0	2.964	2.666	1.109	1.071	1.049
(Ib)	16 ^f	0	3.062	2.762	1.063		
(II)	7	1	3.108	2.782	1.000	1.000	1.000
(IIIa)	11	2	3.126	2.832	1.287	1.188	
(IIIb)	9	2	3.122	2.822	1.240	1.138	1.232
(IIIc)	10	2	3.137	2.837	1.178	1.163	
(IV)	14	3	3.241	2.942	1.346	1.400	1.432

^a See Table 2, footnote b. ^b $\mu'(z) = \mu(z) - \mu(z)_0 - 0.30$, where $\mu(z)$ is the z -component of the dipole moment for the cyano compound, $\mu(z)_0$ is that for corresponding compound in which the cyano group is substituted by a hydrogen atom, and 0.30 is the bond moment of the $\text{C}(\text{sp}^3)\text{-H}$ bond.¹⁴ ^c $\Delta\mu_7(z)$ is the dipole moment derivative for the $\nu_{\text{C}\equiv\text{N}}$ band of compound 7 by CNDO/2 calculation, $\Delta\mu_7(z) = 0.13121 \text{D}$, and $\Delta\mu(z)$ is that of the model compound. ^d A_7 is the integrated intensity of the $\nu_{\text{C}\equiv\text{N}}$ band of compound 7 and A is that of the compound used. ^e $\bar{A}(0)$, $\bar{A}(1)$, $\bar{A}(2)$, and $\bar{A}(3)$ are the average values of $A_1\text{--}A_4$ ($N = 0$), $A_5\text{--}A_8$ ($N = 1$), $A_9\text{--}A_{13}$ ($N = 2$), and A_{14} and A_{15} ($N = 3$), respectively. ^f *trans*-4 α -Cyanoperhydronaphthalene.

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