

## Crystal Structures of Chloro and Bromo Cyanoacetylene

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The crystal structures of chloro and bromo cyanoacetylene have been determined by X-ray crystallographic methods. The compounds are isomorphous with space group  $P2_1/m$ . The lattice constants for the chlorine compound are:  $a = 6.19 \text{ \AA}$ ,  $b = 6.14 \text{ \AA}$ ,  $c = 4.96 \text{ \AA}$ ,  $\beta = 95.5^\circ$ , and for the bromine compound:  $a = 6.28 \text{ \AA}$ ,  $b = 6.35 \text{ \AA}$ ,  $c = 5.16 \text{ \AA}$ ,  $\beta = 94.4^\circ$ . The compounds form linear chain structures with intermolecular  $N \cdots Cl$  and  $N \cdots Br$  distances equal to  $2.970(0.008) \text{ \AA}$  and  $2.956(0.018) \text{ \AA}$ , being about  $0.35 \text{ \AA}$  and  $0.50 \text{ \AA}$  shorter than expected for van der Waals' separations. The intramolecular bond lengths are for chloro cyanoacetylene:  $Cl-C = 1.634(0.009) \text{ \AA}$ ,  $C \equiv C = 1.176(0.012) \text{ \AA}$ ,  $C-C = 1.382(0.013) \text{ \AA}$ ,  $C \equiv N = 1.133(0.013) \text{ \AA}$ , and for bromo cyanoacetylene:  $Br-C = 1.766(0.015) \text{ \AA}$ ,  $C \equiv C = 1.190(0.021) \text{ \AA}$ ,  $C-C = 1.399(0.022) \text{ \AA}$ ,  $C \equiv N = 1.116(0.024) \text{ \AA}$ . The shortening in the  $C \equiv N$  distances from the value  $1.158 \pm 0.001 \text{ \AA}$  generally accepted for gaseous cyanides appears to be real when comparing with similar non-metallic cyanides where the nitrogen is involved in donor-acceptor interaction.

In studies of solid state complexes between n-donors and halogens a lengthening of the halogen-halogen distance appears to be quite general.<sup>1</sup> The lengthening increases with the donor strength and is about  $0.1-0.2 \text{ \AA}$  for the relatively strong amine complexes. Change in intramolecular bond lengths may also be expected in adducts where the acceptor is a halogen atom linked to a non-halogen atom, like iodine in iodoform or antimony triiodide. Iodoform and antimony triiodide are poorer acceptors than molecular iodine and the change should accordingly be smaller. Such change has also been reported in one case, namely for the addition compound containing antimony triiodide and sulphur( $S_8$ ) in the proportion 1:3 with the  $Sb-I$  distances  $0.03 \text{ \AA}$  longer than in the free molecule.<sup>2</sup> In the charge transfer complexes studied so far, no significant difference in the donor from that of the free molecule has been observed. The present structure determination of chloro cyanoacetylene (ClCCCN) and bromo cyanoacetylene (BrCCCN) was undertaken in order to study the effect of the charge transfer bond on the donor and acceptor groups as well as the general geometry of the complexes. The compounds

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were expected to contain linear chains of molecules with short intermolecular nitrogen-halogen distances, like the structure of iodo cyanoacetylene (ICCCN) studied by Borgen, Hassel and Rømming.<sup>3</sup>

### EXPERIMENTAL

Samples of ClCCCN and BrCCCN were generously supplied by Dr. E. Kloster-Jensen.<sup>4</sup> Needle shaped crystals were prepared by sublimation at about  $-40^{\circ}\text{C}$  for ClCCCN and  $4^{\circ}\text{C}$  for BrCCCN. The crystals sublime and decompose easily in air and were therefore sealed in thin walled glass capillaries during the X-ray exposure. The diagrams of the bromine compound were recorded at room temperature and those of the more unstable chlorine compound at  $-25^{\circ}\text{C}$ . The crystals used in the experiments had a nearly circular cross section with diameters about 0.20 mm. Oscillation and Weissenberg photographs showed that the compounds were isomorphous and formed monoclinic crystals with the needle axes parallel with  $[10\bar{1}]$ . The space group derived from the X-ray extinctions can either be  $P2_1$  or  $P2_1/m$ . The latter was assumed to be the correct one and this was eventually confirmed in the course of the structure determinations. The X-ray material collected for BrCCCN consisted of  $h0l$ - and  $hkh$ -zone precession diagrams ( $\mu = 30^{\circ}$ ) and a set of equi-inclination integrated Weissenberg diagrams with rotation about the needle axis ( $h-l = 0$  to  $h-l = 6$ ). Because of the volatility of the crystals, a new crystal had to be used for each equi-inclination level. The number of independent reflections obtained were 278 out of 445 possible under the actual experimental conditions. The X-ray material collected for ClCCCN consisted of  $h0l$ - and  $hkh$ -zone precession diagrams. 81  $h0l$ - and

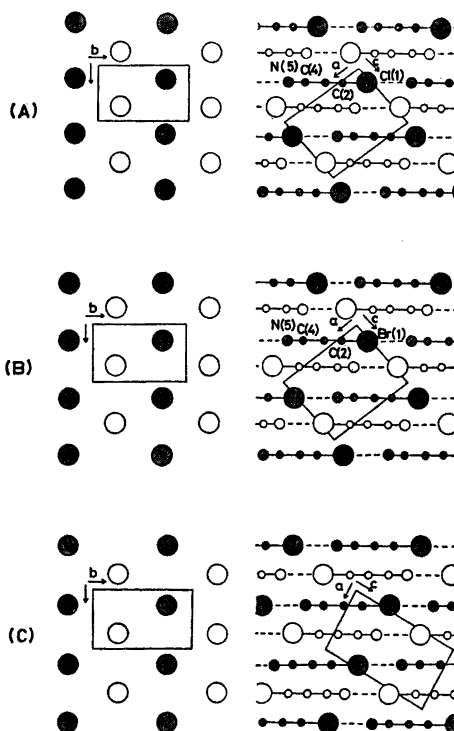


Fig. 1. Structures of the halogeno cyanoacetylenes as seen along the chains and along the  $b$ -axes: (A) ClCCCN, (B) BrCCCN, (C) ICCCN.

39  $hkh$ -reflections were measured; the corresponding maximum numbers are 92 and 42. The intensities of the reflections were measured photometrically. No corrections for absorption or secondary extinctions were applied.  $\text{MoK}\alpha$ -radiation was employed for all the intensity diagrams. In Table 1 cell constants and calculated density are compared with the corresponding values for the monoclinic form of ICCCN.<sup>3</sup>

Table 1. Cell constants and calculated densities.

	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	Diagonal parallel with [101]	Density
CICCCN	6.19 Å	6.14 Å	4.96 Å	95.5°	8.30 Å	1.51 g cm <sup>-3</sup>
BrCCCN	6.28	6.35	5.16	94.4	8.42	2.11
ICCCN <sup>3</sup>	4.43	6.72	7.65	86.1	8.58	2.59

### STRUCTURE ANALYSIS

The number of molecules in the unit cell is two and the molecules are therefore situated in the mirror planes at  $y = 1/4$  and  $y = 3/4$ . The structures were determined using Patterson and Fourier calculations and the parameters

Table 2. Final atomic coordinates ( $\times 10^4$ ) with standard deviations.  $y = 1/4$ .

	CICCCN				BrCCCN			
	<i>x</i>	( <i>x</i> )	<i>z</i>	( <i>z</i> )	<i>x</i>	( <i>x</i> )	<i>z</i>	( <i>z</i> )
Cl(1), Br(1)	381	3	2302	4	290	2	2455	3
C(2)	2329	13	313	15	2321	25	289	31
C(3)	3725	13	-1129	15	3775	24	-1043	29
C(4)	5364	14	-2826	16	5361	29	-2796	33
N(5)	6716	13	-4205	16	6697	30	-4099	36

Table 3. Final thermal parameters ( $\times 10^4$ ). The number below each parameter is its standard deviation. The expression used in the calculations is  $\exp-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})$ .  $B_{12} = B_{23} = 0$ .

	CICCCN				BrCCCN			
	$B_{11}$	$B_{22}$	$B_{33}$	$B_{13}$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{13}$
Cl(1), Br(1)	276	364	432	258	314	343	438	298
	6	11	10	10	5	5	7	8
C(2)	262	330	364	119	314	287	443	185
	20	41	29	36	44	43	68	90
C(3)	276	289	349	93	304	349	359	196
	21	31	29	37	43	49	62	85
C(4)	294	340	437	57	350	479	442	250
	24	0	37	44	50	64	74	97
N(5)	329	386	561	320	530	571	770	585
	22	40	36	44	64	69	106	141



refined by a full matrix least squares program.<sup>5</sup> The final  $R$ -factors were 0.045 for ClCCCN and 0.047 for BrCCCN. Unobserved reflections were not included in the  $R$ -factors or the least squares refinements. Anisotropic temperature factors were used for all the atoms. For ClCCCN the  $B_{22}$  parameters of C(4) and Cl (Fig. 1) are strongly correlated because of overlapping in the [101] projection and could not be refined independently of each other. The chlorine  $B_{22}$  parameter was therefore refined and the corresponding carbon parameter estimated assuming rigid body motion of the molecule. The atomic scattering factors used were those of Hanson *et al.* for halogen and nitrogen.<sup>6</sup> For carbon the  $C(\text{valence})$  values<sup>7</sup> were used. The weighting scheme used was that of Hughes<sup>8</sup> with  $4F_o(\text{min})$  equal to 5 for ClCCCN and 15 for BrCCCN. The final refined parameters and their standard deviations are listed in Tables 2 and 3, and observed and calculated structure factors for the two compounds in Tables 4 and 5.

Table 5. Observed and calculated structure factors for ClCCCN. The three columns in each group list values of either  $l$ ,  $10F_o$  and  $10F_c$  or  $k$ ,  $10F_o$  and  $10F_c$ . Unobserved reflections are indicated by an asterisk and the values of  $10F_o$  given correspond to the minimum observable intensities.

H = 0 K = 0	-2 137 -133	-4 21 14	-2 7* 0	H = 0 L = 0	H = 3 L = -3
1 85 84	-1 79 78	-3 32 -32	-1 20 19	2 516 -537	0 168 -176
2 145 -147	0 146 153	-2 70 -68	0 16 13	4 232 222	1 75 -78
3 26 -21	1 96 -91	-1 112 118	1 42 -43	6 91 -84	2 140 144
4 71 72	2 295 -304	0 71 71	2 16 -14	8 28 27	3 50 52
5 24 22	3 12 -11	1 55 -53	3 14 13		4 82 -85
6 29 -28	4 49 46	2 45 -44	4 7 6		5 22 -25
	5 74* -3	3 39 37		H = 1 L = -1	6 35 38
	6 10 -17	4 56 61		0 171 166	7 8 9
H = 1 K = 0		5 7* 3	H = 7 K = 0	1 170 172	
-6 7* 2	H = 3 K = 0		-4 22 -22	2 120 -116	H = 4 L = -4
-5 84 80	-6 20 -17	H = 5 K = 0	-3 35 -32	3 101 -100	0 17 14
-4 69 70	-5 59 54	-6 13 12	-2 7* -1	4 53 50	1 71 -72
-3 52 -51	-4 9 -12	-5 44 39	-1 44 -44	5 48 46	2 6 -13
-2 224 -230	-3 179 -176	-4 18 16	0 20 -18	6 17 -17	3 47 50
-1 165 166	-2 83 -84	-3 85 -82	1 49 -47	7 17 -16	4 9 9
0 73 78	-1 95 91	-2 27 27	2 7* -5	8 6* 4	5 23 -25
1 47 -45	0 165 173	-1 142 142	3 6* 13		6 4* -5
2 78 -80	1 102 -102	0 35 32		H = 2 L = -2	
3 36 -38	2 25 -26	1 51 -52	H = 8 K = 0	0 131 -133	H = 5 L = -5
4 74 76	3 35 34	2 37 -37	-3 19* -22	1 81 75	0 34 39
5 11 11	4 24 24	3 24 23	-2 22 22	2 103 104	1 17 -19
6 24 -24	5 8* 0	4 8* 0	-1 28 27	3 52 -51	2 29 -33
	6 13 -12		0 7* -3	4 57 -56	3 11 14
H = 2 K = 0		H = 6 K = 0	1 6* -2	5 26 26	4 18 20
-6 17 -16	H = 4 K = 0	-5 34 34	2 2 2	6 24 23	
-5 18 19	-6 10 11	-4 29 -26		7 10 -10	
-4 74 72	-5 58 57	-3 63 -63		8 4* -7	
-3 95 -99					

Rigid body analyses of the molecules were carried out by the method of Cruickshank<sup>9</sup> and with refinement of the centres of the angular oscillations.<sup>10</sup> The translational motion for the molecules indicated by these analyses are not markedly anisotropic (*cf.* Table 6). The angular oscillations in directions normal to the chains vary between  $2.5^\circ$  and  $3.5^\circ$  for ClCCCN, and between  $3.8^\circ$  and  $4.1^\circ$  for BrCCCN. Distances corrected for angular oscillations<sup>11</sup> are listed in Table 8. The least squares planes through the molecules and normal to the XZ-planes were calculated with the results given in Table 7. Both molecules are linear within two times the standard deviations of the atomic positions. The deviation of the least squares planes from [10 $\bar{1}$ ] are  $0.70^\circ$  for ClCCCN and  $0.65^\circ$  for BrCCCN.

Table 6. Rigid-body thermal parameters referred to orthogonal axes  $a_1$ ,  $a_2$ ,  $a_3$  with  $a_1$  parallel with the chain axis and  $a_2$  parallel with the monoclinic  $b$ -axis. The coordinates (monoclinic) of the centres of angular oscillations are (0.3179, 0.25, -0.0563) for ClCCCN, and (0.2326, 0.25, 0.0372) for BrCCCN. Numbers below  $U_{ij}$  are differences ( $\times 10^4$ ) of  $U_{ij}$  derived from  $B_{ij}$ <sup>12</sup> and those calculated from rigid-body parameters.  $U_{12} = U_{21} = 0$ .

	ClCCCN				BrCCCN			
	$U_{ij} \times 10^4 \text{ \AA}^2$				$U_{ij} \times 10^4 \text{ \AA}^2$			
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{13}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{13}$
Cl(1), Br(1)	433 -61	688 6	674 -9	27 1	448 -49	724 -23	768 14	59 -6
C(2)	433 -1	596 34	487 26	26 10	448 52	594 -7	615 86	57 -24
C(3)	433 30	590 -39	477 18	26 28	448 -20	657 55	690 -50	57 24
C(4)	433 131	649 -1	595 -52	27 -17	448 39	888 92	961 -186	65 13
N(5)	433 25	748 -12	798 35	29 -23	448 172	1194 -26	1322 81	65 16
T	$\begin{pmatrix} 433 & 0 & 25 \\ & 587 & 0 \\ & & 469 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$				$\begin{pmatrix} 448 & 0 & 58 \\ & 594 & 0 \\ & & 615 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$			
$\sigma(T)$	$\begin{pmatrix} 14 & 0 & 14 \\ & 25 & 0 \\ & & 25 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$				$\begin{pmatrix} 17 & 0 & 17 \\ & 26 & 0 \\ & & 26 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$			
$\omega$	$\begin{pmatrix} 0 & 0 & 0 \\ & 123 & 0 \\ & & 60 \end{pmatrix} \times 10^{-1} (^{\circ})^2$				$\begin{pmatrix} 0 & 0 & 0 \\ & 168 & 0 \\ & & 143 \end{pmatrix} \times 10^{-1} (^{\circ})^2$			
$\sigma(\omega)$	$\begin{pmatrix} 0 & 0 & 0 \\ & 16 & 0 \\ & & 16 \end{pmatrix} \times 10^{-1} (^{\circ})^2$				$\begin{pmatrix} 0 & 0 & 0 \\ & 15 & 0 \\ & & 15 \end{pmatrix} \times 10^{-1} (^{\circ})^2$			

Table 7. Distances from the least squares plane through the molecule and normal to the  $XZ$ -plane.

	Cl(1), Br(1)	C(2)	C(3)	C(4)	N(5)
ClCCCN	-0.001 \AA	0.004 \AA	0.001 \AA	-0.003 \AA	0.001 \AA
BrCCCN	0.002 \AA	-0.030 \AA	0.030 \AA	-0.018 \AA	0.007 \AA

## DISCUSSION

The halogeno cyanoacetylenes all form linear chain structures with short nitrogen-halogen distances between the molecules in a chain. Each chain is surrounded by two parallel and four antiparallel chains at distances 3.69, 3.65, and 3.51 \AA for ClCCCN, 3.83, 3.81, and 3.62 \AA for BrCCCN, and 3.94, 3.97, and 3.91 \AA for ICCCN.<sup>3</sup> The structures thus approximate close packing of cylinders. Distances between atoms in adjacent chains are equal to or

Table 8. Bond lengths and CN-acceptor angles. Standard deviations are given in parentheses. The bond lengths for the free molecules are based on microwave measurements.

	Donor-acceptor bond	Angle (°), CN-acceptor	Bond lengths(Å)					References
			Donor-acceptor	C≡N	C—C	C≡C	C—X (X = Cl, Br, I)	
1. Molecular complexes								
ClCCN	N—Cl	178.3(.7)	2.983(.008)	1.131(.013)	1.379(.013)	1.173(.012)	1.630(.009)	This work
ClCCN(corrected)			2.970	1.133	1.382	1.176	1.634	This work
BrCCN	N—Br	179.6(1.6)	2.976(.018)	1.114(.024)	1.394(.022)	1.184(.021)	1.758(.015)	This work
BrCCN(corrected)			2.956	1.116	1.399	1.190	1.766	This work
ClCN	N—Cl	180	3.008(.014)	1.138(.024)				This work
(CH <sub>3</sub> CN) <sub>2</sub> Br <sub>2</sub>	N—Br	171.6(.4)	2.837(.004)	1.138(.008)				15
CH <sub>3</sub> CN, BF <sub>3</sub>	N—B	176.5	1.627(.010)	1.133(.009)				This work
(CH <sub>3</sub> CN) <sub>2</sub> B <sub>2</sub> H <sub>12</sub>	N—B	178.0	1.523(.007)	1.137(.006)				16
CH <sub>3</sub> CN, B <sub>2</sub> H <sub>13</sub>	N—B	175.7	1.507(.010)	1.126(.008)				17
ICCCN	N—I		2.93	1.20	1.39	1.27	1.79	3
HCCCN	N—H—C	180	3.27(.02)	1.14(.02)	1.38(.02)	1.18(.02)		18
2. Free molecules								
ClCN				1.159			1.631	19
BrCN				1.158			1.789	19
ICN				1.159			1.994	19
CH <sub>3</sub> CN				1.157				20, 21
HCCCN				1.159			1.205	19

longer than the sum of the corresponding van der Waals' radii. The structures of ClCCCN and BrCCCN are isomorphous but ICCCN has a somewhat different unit cell imposing a reorientation of either the *a*- or the *c*-axis if the usual rule  $\beta \geq 90^\circ$  is followed. The cell data in Table 1 for ICCCN correspond to the same orientation of the molecule as for ClCCCN and BrCCCN with the chain parallel with  $[10\bar{1}]$  which is the needle axis. The principal intermolecular interaction is between nitrogen and halogen in the chain with the distances equal to  $2.95 \pm 0.03$  Å for the three compounds. The N...halogen distances are about 0.35, 0.50, and 1.00 Å shorter than expected for van der Waals' separations for the chlorine, bromine, and iodine compounds. The difference in size of the halogen is thus nearly compensated by an increase in bond strength accompanying the replacement of a lighter halogen by a heavier one.

The more interesting angles and interatomic distances within the chains have been listed in Table 8 together with the corresponding values for other comparable non-metallic cyanides where the nitrogen is involved in donor-acceptor interaction. In these examples the C—N-acceptor atoms nearly lie on a straight line. Intramolecular distances found from microwave spectra of some of the free gaseous cyanides have also been listed for comparison. For the two complexes acetonitrile-borontrifluoride and cyanogen chloride the author found it worth while to refine the structures by a full matrix least squares program<sup>5</sup> on the basis of the X-ray data in the literature.<sup>13,14</sup> For the boron compound the C≡N distance was altered from 1.13(0.03) Å to 1.133(0.009) Å and for cyanogen chloride from 1.16(0.03) Å to 1.138(0.024) Å. Except for ICCCN, all the C≡N distances for the donor-acceptor complexes in Table 8 lie between 1.114 Å and 1.140 Å. As a basis of discussion a weighted mean value was calculated for the seven first C≡N distances not corrected for angular oscillations. No standard deviations are quoted in the structure study of ICCCN,<sup>3</sup> but owing to the presence of the heavy atom, the uncertainty of the light atom positions is rather large. This compound was therefore deleted in the calculation of the weighted mean value. The formulas used for distance ( $\mu_{av}$ ) and standard deviation ( $\sigma_{av}$ ) were<sup>22</sup>

$$\mu_{av} = (\sum \mu_i / \sigma_i^2) / \sum 1 / \sigma_i^2, \quad \sigma_{av} = (\sum 1 / \sigma_i^2)^{-1/2}$$

and the values found were  $\mu_{av} = 1.133$  Å,  $\sigma_{av} = 0.0035$  Å. This indicates that the C≡N distances for the linear complexes are significantly shorter than the value  $1.158 \pm 0.001$  Å found from microwave spectra of the free molecules. The corrections due to angular oscillations are believed to be small in these complexes because of the external bond to the N atom of the cyanide group. The correction actually found for ClCCCN and BrCCCN is 0.002 Å. The decrease in C≡N bond length may thus be used as a criterion for a donor-acceptor interaction.

Energetically the difference between charge transfer bonds and hydrogen bonds appears to be rather small.<sup>23</sup> A decrease in C≡N bond distance may therefore also be expected when the cyanide group is involved in hydrogen bonding. An example in Table 8 is cyanoacetylene containing linear chains of molecules with intermolecular C—H...N distances equal to 3.27 (0.02) Å.<sup>18</sup> The C≡N distance is 1.14(0.02) Å compared with  $1.159 \pm 0.001$  Å in the gaseous state.<sup>19</sup>



The decrease in C≡N bond length which results when donor-acceptor interactions take place may be accompanied by an increase in bond order and stretching frequency around 2250 cm<sup>-1</sup>. A shift of 111–13 cm<sup>-1</sup> in this direction has been observed for nitrile complexes with Lewis' acids such as metal halides,<sup>24,27</sup> boron halides,<sup>24,28</sup> or iodine monochloride.<sup>29</sup> Infrared or Raman spectra of nitrile complexes with weaker acceptors are, however, rather rare in the literature because of the low formation constants in solution. Also the halogeno cyanoacetylenes may be considered as individual molecules in solution.<sup>30</sup> The few available data on the C≡N stretching frequency in these complexes are obtained from the pure liquid or solid state. Some examples

Table 9. (C≡N) stretching frequencies (in cm<sup>-1</sup>).

	Gas (IR)	Liquid (Raman)	Solid (IR)	References
CICN	2219	2206	2212	31
BrCN	2200	2191	2194	31
ICN	—	2158	2176	31
		(in methanol)		
HCN	2089	—	2097	32
HCCCN	2271	2270	2271.3	33, 34

have been listed in Table 9. Only HCN containing strong hydrogen bonds has a higher frequency in the solid than in the gas phase.<sup>32</sup> The reason for this is probably the condensed phase shift which displaces the vibrational bands from those found at low gas pressure; thus all simple stretching vibrations are displaced to lower frequency in the order:<sup>35</sup>

$$\nu_{\text{gas}} > \nu_{\text{solution(non-polar solvent)}} > \nu_{\text{liquid}} > \nu_{\text{solid}}$$

For example, the shift recorded for  $\nu(\text{C}\equiv\text{N})$  is 12 cm<sup>-1</sup> for acetonitrile in carbon tetrachloride.<sup>36</sup> The condensed phase shift may explain the constant C≡N frequency found for HCCCN in the vapour, liquid and solid state (Table 9), where this effect probably outweighs the increase in frequency due to higher C≡N bond order. For BrCN and CICN the C≡N frequency is lower in the solid than in the gaseous state but the shift is smaller than that expected for the condensed phase shift. A factor which might be expected to make an important contribution to the frequency increase is the kinematic coupling of the CN and N-acceptor bonds when the complex is formed. It is, however, shown by experiments<sup>37</sup> and by normal coordinate analyses<sup>38,39</sup> that this effect is of minor importance. The infrared and Raman spectra are thus indicative of increasing C≡N bond strength even for a weak donor-acceptor interaction and support the results from the structure analyses.

The increase in the C≡N bond strength may be understood if the rehybridization of the nitrogen valence orbitals is taken into account.<sup>37,40</sup> In the free nitrile the  $\sigma$ -bond is established by a nitrogen orbital intermediate between  $sp$  and  $p$  and the unshared electrons are located in an orbital intermediate between  $sp$  and  $s$ . On the formation of donor-acceptor bonds, both these orbitals approach equivalent  $sp$  orbitals, which is accompanied by an increase

in *s*-character of the orbital participating in the  $\sigma$ -bond. The overlap integral for different CN  $\sigma$ -bonds, as calculated according to the data of Mulliken and coworkers,<sup>41</sup> increases with an increase in the *s*-character of the nitrogen orbitals from 0 to approximately 65 % and falls thereafter. Consequently this rehybridization must lead to an increase in the C $\equiv$ N bond strength of the donor-acceptor complex. Purcell and Drago have carried out molecular orbital calculations on the C $\equiv$ N bonding in acetonitrile and some of its adducts and come to the same conclusion.<sup>39,42</sup>

If the change in C $\equiv$ N bond length is due to rehybridization, one might also expect this effect to be important for C $\equiv$ C bonds. It is therefore interesting to note that the mean C $\equiv$ C distance for solid ClCCCN, BrCCCN, and HCCCN is as low as 1.182 Å, although none of the individual values is significantly different from the distance 1.205 Å reported for HCCCN in the gaseous state (Table 8). The C-halogen and C—C bonds are not significantly different from the corresponding distances in the cyanogen halides and cyanoacetylene obtained from microwave spectra of the vapours.

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