

430. *A Normal Co-ordinate Analysis of MeCN, BX₃, and its Relevance to the Thermodynamic Stability of Co-ordination Compounds.*

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A normal co-ordinate analysis of MeCN, BX₃ for general angles has been carried out, and the G-matrix elements are tabulated. This analysis is used to calculate "C-N and B-N stretching frequencies" for a variety of force constants with X = F, Cl, or Br. The "C-N stretching frequency" is remarkably insensitive to variations of the mass of X or the force constant of the B-N bond, even when a relatively large coupling constant is incorporated between the B-N and the C-N bond stretches. It is probable that the force constant of the C-N bond increases on co-ordination to BX₃. The present vibrational analysis does not entirely agree with an earlier analysis for WXY₃.

It is the purpose of this Paper to examine the common assumption¹ that frequency shifts in the Raman or infrared spectra of ligand and acceptor on co-ordination are indicative of the strength (measured by the force constant) of the donor-acceptor bond. As an illustration of the behaviour to be expected in co-ordination compounds we have chosen the molecule MeCN, BX₃ because (a) the "CN" stretching frequencies of the fluoride, chloride, and bromide are known,² (b) the molecular symmetry of the fluoride is known³ (C_{3v}), and (c) the results obtained in this system are likely to be of direct interest in other systems. The vibrational analysis of this molecule, on which the following discussion is based, is given in the Appendix. In Table I we record the a₁ modes most nearly approximating to the C-N and B-N bond stretches. The contributions of the relevant force constants to the total potential energy of the chosen vibrations are also given. We have allowed the C-N force constant to assume the values 15, 10, and 5 millidynes Å⁻¹ in order that the bond may be representative of triple, double, and single bonding between C and N.

In the case of a force constant of 15 millidynes Å, that is to say with chemically significant acetonitrile, the C-N frequency is remarkably insensitive to variations of the halogen attached to the boron, and to the B-N force constant. The frequency shift from free MeCN (calculated) is about +25 cm.⁻¹ whereas that observed experimentally² is in the range +70—110 cm.⁻¹. This increase in frequency on co-ordination is rare, and according to our simple (simple valence-force field) calculations, is not solely a kinematic effect due to coupling in the G-matrix. If the off-diagonal terms in the potential-energy matrix which relate to coupling of the B-N stretch with the C-N stretch ($F_{23} = F_{32} = +fr_4r_5$) are given the value -10⁵ dynes cm.⁻¹ the calculated "C-N frequency" is 2192 cm.⁻¹, giving a shift of about +90 cm.⁻¹ from that in free acetonitrile (calculated), which is of the order of magnitude of the shift observed in practice. It is, however, difficult to justify this high

¹ See, e.g., Lappert, *J.*, 1962, 542.

² Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2182; the value for the C-N stretching frequency of MeCN, BCl₃ does not agree with that given by Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

³ Hoard, Owen, Buzzell, and Salmon, *Acta Cryst.*, 1950, **4**, 405.

TABLE 1.

Calculations of "B-N" and "C-N" stretching frequencies for MeCN, BX₃, and including main contributors to the potential-energy function for the vibrations selected.

Force constants *	Halide	Frequency (cm. ⁻¹)	Contributions (%)	Force constants *	Halide	Frequency (cm. ⁻¹)	Contributions (%)
15, 2	BF ₃	2126	85 CN, 12 CC	10, 2	BF ₃	1803	77 CN, 20 CC
		291	59 BN, 33 BF ₃ def.			289	58 BN, 32 BF ₃ def.
	BCl ₃	2125	85 CN, 12 CC		BCl ₃	1802	77 CN, 20 CC
		1010	34 BN, 39 CC			1004	37 BN, 33 CC,
	BBr ₃	214	31 BN, 65 BCl ₃ def.		BBr ₃	213	17 BCl ₃ str.
		2125	85 CN, 12 CC			1802	31 BN, 64 BCl ₃ def.
5, 2	BF ₃	983	30 BN, 57 CC	15, 2.5	BF ₃	974	77 CN, 20 CC
		266	36 BN, 60 BBr ₃ str.			265	35 BN, 50 CC
	BCl ₃	1440	51 CN, 40 CC		BCl ₃	2133	85 CN, 12 CC
		280	55 BN, 29 BF ₃ def.			310	52 BN, 39 BF ₃ def.
	BBr ₃	1434	53 CN, 43 CC		BBr ₃	2132	85 CN, 12 CC
		997	43 BN, 22 BCl ₃ str.			1053	41 BN, 32 CC
10, 2.5	BF ₃	1434	53 CN, 43 CC	5, 2.5	BF ₃	2132	85 CN, 12 CC
		953	47 BN, 28 CC			1021	39 BN, 47 CC
	BCl ₃	1811	76 CN, 19 CC		BCl ₃	1453	48 CN, 35 CC
		307	51 BN, 37 BF ₃ def.			297	48 BN, 34 BF ₃ def.
	BBr ₃	1810	76 CN, 19 CC		BBr ₃	1442	53 CN, 41 CC
		1052	43 BN, 28 CC			1048	47 BN, 20 CC
15, 2	GaCl ₃	1809	76 CN, 19 CC	GaCl ₃	1441	53 CN, 41 CC	
		1017	43 BN, 41 CC		1007	52 BN, 27 CC	
		2124	86 CN, 12 CC				
		335	72 GaN, 10 GaCl ₃ str.				

* Refers to force constants for C-N and B-N (or Ga-N) bonds respectively (in millidynes Å).

TABLE 2.

Calculated "C-N stretching frequencies" for MeCN, BX₃, using a C-N, B-N stretch-stretch interaction term of -0.5×10^5 dynes cm.⁻¹.

Acceptor	BF ₃	BF ₃	BCl ₃	BCl ₃	BCl ₃	BCl ₃	BBr ₃	BBr ₃
B-N force constant (10 ⁵ dyne cm. ⁻¹) ...	2.5	2.0	3.5	3.0	2.5	2.0	2.5	2.0
Frequency (cm. ⁻¹)	2162	2154	2178	2169	2161	2154	2161	2155

The following force constants were used:

Halide	CC	CN	BN	BX str.	∠XBX	∠NBX
BF ₃	5	5,10,15	2,2.5	8.36	1.47	0.625
BCl ₃	5	5,10,15	2,2.5	4.38	1.28	0.487
BBr ₃	5	5,10,15	2,2.5	3.47	1.01	0.456

with stretching constants in mdyne Å⁻¹, deformational in mdyne Å radian⁻².

B-X bond lengths: BF₃ 1.33, BCl₃ 1.79, BBr₃ 1.91 Å.

All angles were assumed to be tetrahedral or 180°.

For GaCl₃ the same force constants as those taken for BCl₃ were assumed.

negative value, and we consider that the force constant of the C-N bond increases to some extent on co-ordination. In Table 2 we record "C-N stretching frequencies" for MeCN, BX₃, on the assumption of a coupling constant of -0.5×10^5 dynes cm.⁻¹, and it is evident that this frequency is still insensitive to the force constant of the B-N bond.

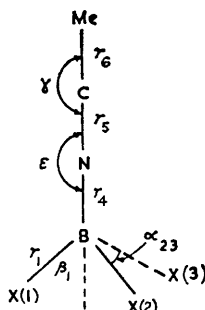
The slight increase in the force constant of the C-N bond on co-ordination of acetonitrile is surprising and in the reverse direction to shifts normally found with donor molecules involving >C=O or >P=O, for example. The apparent lowering of the force constant of the carbonyl group in >C=O on co-ordination through the oxygen is usually interpreted in terms of electron flow from the multiple bond to the co-ordinate link, and

it is difficult to see initially why such an explanation should not apply equally well to acetonitrile. However, in adducts such as $>C=O \rightarrow AX_n$, where the COA angle is approximately tetrahedral, X will be close to the electrons forming the C-O link and close to the carbon, so that repulsions from X may effectively weaken the C-O link. The CNB angle in $MeCN, BX_3$ is 180° , and it appears that the effect of X may be to repel electrons from the nitrogen into the C-N link, possibly causing an increased force constant. Similarly, the difference of 40 cm.^{-1} between the observed "C-N stretching frequencies" in $MeCN, BF_3$ and $MeCN, BBr_3$ could be accounted for in terms of the effect of the size of the halogen on the electron distribution within the molecule.

The second point that arises from the analysis is the expected one, namely, that it becomes progressively more difficult to talk of "a C-N stretching frequency" as the force constant is lowered from 15 through 10 to 5. Thus in $MeCN, BX_3$, with the C-N force constant at 5, the "C-N stretching frequency" is about 40% C-C stretch. Similar difficulties occur in assignment of a B-N stretch. We may conclude by noting that for acetonitrile the C-N stretching frequency is remarkably insensitive to the residue to which it is attached, and even to the strength of the bond by which it is attached to this residue. Similar conclusions will apply to adducts with double bonds. With a single bond the frequency is becoming more sensitive but less capable of exact description. A study of the variation of a fundamental frequency of a ligand in a series of co-ordination compounds will be meaningful in terms of donor strength where a closely related series of compounds are being examined. That is where the nature of the bonding and the size and stereochemistry of the adduct are sensibly constant. Such examples occur in the first, second, or third transition series, and studies here have been rewarding.⁴ It is doubtful if such examination will be found to be of general value for halides of the non-transition elements where, for example, $SbCl_3, Me_3PO$ and $SbCl_5, Me_3PO$ differ greatly in their heat of formation but have similar shifts for the P-O stretching frequency from that in pure trimethylphosphine oxide.⁵

APPENDIX

Normal Co-ordinate Analysis of $MeCN, BX_3$ for General Angles; Symmetry C_{3v} (and including WXY_3).—Our choice of internal co-ordinates is shown in the Figure [γ and ϵ lying in the plane through $X(1)$]. With cartesian co-ordinates, the representation of the molecule after removal



of translational and rotational degrees of freedom is $\Gamma_{mol} = 5a_1 + 5e$, whereas, with internal co-ordinates we find $\Gamma_{mol} = 6a_1 + 5e$, so that there will be one redundant co-ordinate of the a_1 type.

Our orthonormal symmetry co-ordinates were:

$$a_1 \quad S_1 = \Delta r_6; \quad S_2 = \Delta r_5; \quad S_3 = \Delta r_4; \quad S_4 = (1/\sqrt{3})(\Delta r_1 + \Delta r_2 + \Delta r_3); \\ S_5 = [1/\sqrt{3(1+n^2)}][\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 + n(\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{13})];$$

⁴ See, e.g., Fronæus and Larsson, *Acta Chem. Scand.*, 1962, **16**, 1433; Cotton and Zingalesse, *J. Amer. Chem. Soc.*, 1961, **83**, 351; Sacconi and Sabatini, *Nature*, 1960, **186**, 549.

⁵ Zackrisson and Alden, *Acta Chem. Scand.*, 1960, **14**, 994.

$$S_5^* = [1/\sqrt{3(1+n^2)}][\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{13} - n(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)].$$

$$e^\dagger S_6 = \Delta\gamma; S_7 = \Delta\varepsilon; S_8 = (2/\sqrt{6})[\Delta r_1 - \frac{1}{2}(\Delta r_2 + \Delta r_3)];$$

$$S_9 = [2/\sqrt{6}][\Delta\alpha_{23} - \frac{1}{2}(\Delta\alpha_{12} + \Delta\alpha_{13})]; S_{10} = -(2/\sqrt{6})[\Delta\beta_1 - \frac{1}{2}(\Delta\beta_2 + \Delta\beta_3)].$$

By use of standard techniques the G-matrix elements are found to be:

$$a_1 G_{11} = \mu_{Me} + \mu_c; G_{12} = -\mu_c; G_{13} = 0; G_{14} = 0; G_{15} = 0; G_{22} = \mu_c + \mu_N;$$

$$G_{23} = -\mu_N; G_{24} = 0; G_{25} = 0; G_{33} = \mu_N + \mu_B; G_{34} = -\sqrt{3} \cos \beta \mu_B;$$

$$G_{35} = (\sqrt{3(1+n^2)}/r_1) \sin \beta \mu_B; G_{44} = \mu_X + 3 \cos^2 \beta \mu_B;$$

$$G_{45} = -(3\sqrt{(1+n^2)}/r_1) \cos \beta \sin \beta \mu_B;$$

$$G_{55} = [(1+n^2)/r_1^2] \mu_X + [3(1+n^2)/r_1^2] \sin^2 \beta \mu_B.$$

$$e G_{66} = \mu_{Me}/r_6^2 + \mu_c(1/r_6 + 1/r_5)^2 + \mu_N/r_5^2;$$

$$G_{67} = -(\mu_N/r_5)(1/r_5 + 1/r_4) - (\mu_c/r_5)(1/r_5 + 1/r_6) G_{68} = 0;$$

$$G_{69} = 0; G_{6,10} = (\sqrt{6}/2r_5 r_4) \mu_N; G_{77} = \mu_c/r_5^2 + \mu_N(1/r_5 + 1/r_4)^2 + \mu_B/r_4^2;$$

$$G_{78} = (\sqrt{6}/2r_4) \sin \beta \mu_B; G_{79} = (\sqrt{6}/2r_1 r_4) m \mu_B;$$

$$G_{7,10} = -(\sqrt{6}/2r_4)(1/r_4 + 1/r_5) \mu_N - (\sqrt{6}/2r_4)(1/r_4 + \cos \beta/r_1) \mu_B;$$

$$G_{88} = \mu_X + (3/2) \sin^2 \beta \mu_B; G_{89} = (3 m \sin \beta/2r_1) \mu_B;$$

$$G_{8,10} = (-3/2)(1/r_4 + \cos \beta/r_1) \sin \beta \mu_B;$$

$$G_{99} = (3/p^2 r_1^2) \mu_X + (3/2)(m^2/r_1^2) \mu_B + (n^2/4r_1^2) \mu_X;$$

$$G_{9,10} = (n/2r_1^2) \mu_X - (3/2)(m/r_1)(1/r_4 + \cos \beta/r_1) \mu_B;$$

$$G_{10,10} = (\mu_X/r_1^2) + (3/2)(\mu_N/r_4^2) + (3/2)(1/r_4 + \cos \beta/r_1)^2 \mu_B$$

where $n = \sqrt{3} \cos \beta / \cos(\alpha/2)$; $p = 2 \cos(\alpha/2)$;
 $m = (\sqrt{3}/2)[\sin^2 \beta / \cos(\alpha/2)] = \sin \beta \tan(\alpha/2).$

The F-matrix elements for simple valence-force field may be written by the appropriate matrix multiplication as:

$$a_1 F_{11} = f_r; F_{22} = f_s; F_{33} = f_r; F_{44} = f_r; F_{55} = [1/(1+n^2)](f_x + n^2 f_\beta).$$

$$e F_{66} = f_\gamma; F_{77} = f_\varepsilon; F_{88} = f_r; F_{99} = f_x; F_{10,10} = f_\beta.$$

A glance at the analysis by Ziomek and Piotrowski⁶ will indicate that our G-terms involving S_8 , S_9 , and S_{10} should be identical with their G-terms involving S_{1a} , S_{2a} , and S_{3a} . Aside from a number of misprints in their Paper, this is essentially true, when their expressions are reduced by means of the trigonometrical relationship $2 \cos \alpha = 3 \cos^2 \beta - 1$. However, for the a_1 modes the terms in our analysis involving S_3 , S_4 , and S_5 should also be similar to theirs except for the inclusion (appropriately) of the factor n allowing for non-tetrahedral angles. This is by no means always true. Their expressions in many cases can be considerably reduced, but in the case of their G_{33} term there is a factor involving μ_N (μ_X in their terminology). This is clearly impossible from group theoretical considerations. By use of the terms involving S_3 , S_4 , S_5 , S_8 , S_9 , and S_{10} in the G-matrix our analysis can be directly applied to WXY_3 with general angles.

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* Redundant co-ordinate.

† The additional co-ordinates γ^1 and ε^1 are necessary to describe the second symmetry co-ordinates associated with S_6 and S_7 .

⁶ Ziomek and Piotrowski, *J. Chem. Phys.*, 1961, **34**, 1087.