Council of Canada. The authors also wish to express their appreciation to Professor C. A. McDowell for his encouragement and interest in the work, to Mr. D. A. Vroom for enthusiastic cooperation in the laboratory, and to Dr. F. G. Herring for assistance with computer programming.

An Investigation into the Source of C≡N Vibrational Frequency Shifts

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Abstract: The results of normal coordinate analyses and molecular orbital calculations are utilized to explain the increase in C≡N vibrational frequency when either the carbon or nitrogen atom acts as a Lewis base. The molecules included in this study are CN^-, CH_3CN, CH_3NC, ClCN, BrCN, ICN, and HCN. Detailed comparisons are made for CN^- and HCN, and CH_3CN and CH_3NC.

In a recent report[1] the utility of an approximate LCAO-MO method was demonstrated in augmenting normal coordinate analyses in a study of the bonding in acetonitrile and its adducts. The primary question there was the source of the increase in energy of the "C≡N" normal mode upon coordinate bond formation by the N "lone pair." We wish to report analogous calculations here for the C and N lone pairs of CN^- which are in agreement with the earlier computations and which substantiate the earlier interpretation.

Calculational Methods

The molecular orbital calculations were carried out in a manner previously described.[1] Briefly, a modification of the extended Hückel method was used with Slater exponents and valence-state ionization potentials[2] for neutral atoms as initial values. Off-diagonal elements of the H matrix were calculated from the overlap integrals and the arithmetic mean of the diagonal elements using a proportionality constant of 1.75.[3] (The use of the geometric mean does not alter any of our conclusions.) Valence-state ionization energies were adjusted for atom charge by 2.0 ev/atomic unit and the Slater exponents by Slater's formula.[4] The calculations were iterative with respect to self-consistent atom charges to within 0.01 charge unit.

The results of these calculations have been analyzed *via* the Mulliken overlap population procedure[5] to yield, for example, the overlap populations themselves and the overlap energies (Ω). The magnitude of Ω_{ij} for a pair of interacting atomic orbitals (X_i, X_j) depends on the definition[5] of β in

$$\Omega_{ij} = n(i,j)\beta_{ij}/S_{ij}$$

For $\beta_{ij} \equiv H_{ij}$ the overlap energies are larger, of course, than for $\beta_{ij} \equiv H_{ij} - S_{ij}\bar{\alpha}$. Qualitatively our results do not depend upon which definition we use; only the magnitudes of the numbers differ. Since the definition given by Mulliken bears a closer relationship to what one thinks of when one uses the term "covalent energy," we report only those values of Ω calculated from the latter definition. Finally these energy terms are analyzed at the "subtotal" and "total" levels.

Results and Discussion

The results of our calculations in terms of total overlap energies and overlap populations are presented, along with other pertinent data, in Table I and in terms of subtotal energies in Table II. All of the neutral molecules may be thought of as arising from CN^- by coordination of X^+ through the carbon or nitrogen lone pair. In every instance an increase in the C≡N force constant is observed which is in part[1] responsible for the higher C≡N vibrational frequencies relative to CN^-. This behavior is quite common for the cyano group where back-donation from an electron-rich acceptor is not possible, but is quite unusual for coordination at a multiply bound donor atom site. In the case of doubly and singly bound atoms, polarization of π and σ molecular orbitals appears to be the major effect and bond weakening occurs.

Table I

Compound	$-\Omega_{CN}$, ev	F_{CN}, mdynes/A	n_{CN}	$R_{CN}{}^e$
CN^-	19.628	16.4^a	1.805	1.140
CH_3NC	19.661	16.7^b	1.715	1.167
BrCN	19.738	17.8^c	1.718	1.160
ICN	19.954	17.9^c	1.754	1.159
CH_3CN	20.350	18.1^b	1.759	1.157
ClCN	20.361	17.6^c	1.730	1.163
HCN	20.939	18.7^d	1.809	1.156

[a] This work. [b] J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1964). [c] E. E. Aynsley and R. Little, *ibid.*, **18**, 667 (1962). [d] H. C. Allen, Jr., E. D. Tidwell, and E. K. Plyler, *J. Chem. Phys.*, **25**, 302 (1956). [e] L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

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(2) (a) J. Hinze and H. H. Jaffé, *ibid.*, **84**, 540 (1962); (b) *J. Phys. Chem.*, **67**, 1510 (1963).

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397, 2745; **40**, 2474, 2480 (1964).

(4) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(5) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

Table II. Subtotal Overlap Energies by Atomic Orbital Pairs

Compound	X_i	X_j	$\Delta\Omega_{ij}$	$-\Delta\Omega\sigma$
CH_3NC	N_s	C_s	1.283	
	N_s	C_σ	−1.516	
	N_σ	C_s	−0.690	0.553
	N_σ	C_σ	0.370	
	N_π	C_π	0.519	
BrCN	C_s	N_s	0.846	
	C_s	N_σ	−1.714	0.931
	C_σ	N_s	−0.313	
	C_σ	N_σ	0.250	
	C_π	N_π	0.821	
ICN	C_s	N_s	1.096	
	C_s	N_σ	−1.573	1.061
	C_σ	N_s	−0.758	
	C_σ	N_σ	0.174	
	C_π	N_π	0.735	
CH_3CN	C_s	N_s	−0.191	0.848
	C_s	N_σ	−2.043	
	C_σ	N_s	1.042	
	C_σ	N_σ	0.344	
	C_π	N_π	0.126	
ClCN	C_s	N_s	0.686	
	C_s	N_σ	−2.574	1.091
	C_σ	N_s	0.094	
	C_σ	N_σ	0.703	
	C_π	N_π	0.358	
HCN	C_s	N_s	0.746	
	C_s	N_σ	−1.954	1.098
	C_σ	N_s	−0.323	
	C_σ	N_σ	0.433	
	C_π	N_π	−0.214	

As discussed in the earlier paper,[1] simple electronegativity arguments predict a decrease in force constant for the bond(s) involving the Lewis donor atom. It is apparent from Table I that the overlap populations themselves reflect this decrease in bonding electron density for "nitrile" donors. However, the direct comparison of overlap populations is valid only when the ratio β_{ij}/S_{ij} remains constant for each pair of interacting atomic orbitals (X_i, X_j) before and after coordination.[5] When constancy of β/S fails, one must resort to full calculation of the overlap energies (Ω_{ij}'s).

It is to be expected on the basis of intuitive arguments that the overlap energy will parallel or reflect the magnitude of a stretching force constant, at least within a series of related molecules. If an increase of the force constant for a bond is observed, one concludes the bond is energetically more stable and resistant to distortion. This latter concept is not directly derivable from the definition of the force constant as the quadratic term in the Taylor expansion of molecular energy as a function of the defining coordinate; on the basis of experience, however, the correlation is a useful and valid one. The analytical relation between force constant and bond energy is, at best, extremely complicated.

A. General. The overlap energies in Table I confirm the utility of this correlation when applied to "coordinate bond" formation. The formation of a new bond by means of the carbon or nitrogen lone pair results in strengthening of the C≡N link as required by the force constants.

The source of this strengthening may be found from analysis of the data in Table II. It is seen that in every case the σ "system" is responsible for the increased stability in the C≡N link. Within the σ system it is further apparent that both the C 2s and N 2s orbitals in overlapping with the N 2pσ and C 2pσ orbitals, respectively, are responsible for this increase in all but CH_3CN and ClCN. Furthermore, it is *always* the donor atom s orbital which makes the largest contribution to the energy change.

These arguments somewhat parallel an argument based on Bent's isovalent hybridization model:[6] the p character in the formerly "lone-pair orbital" increases while the s character in the C–N σ bond increases upon lone-pair donation. While the hybrid model visualizes localized lone-pair and CN σ orbitals (a model inconsistent with these and other molecular orbital treatments[1,7]), it is interesting that the two ultimately "put the finger" on the same source, *i.e.*, the donor atom "s" orbital.

It is interesting to note also that the correlation of force constant with overlap energy is quite good. The two measures of bond strength predict, with one exception, the same order throughout this series of molecules. The two predict the same order of $CN^- < CH_3NC < BrCN < ICN < CH_3CN < HCN$ with only ClCN out of order. A very likely source of error in this case may be inadequate handling of ClC π bonding by the molecular orbital treatment and/or inaccuracy of the force constant due to the problems inherent in these calculations.

Two other interesting correlations are to be found in Table I with the possible exception of ClCN. Within the series of neutral molecules, the overlap populations follow the force constants very well. This is perhaps to be expected since constancy of β/S should be more nearly true for a series such as XCN. Difficulty is found only on going from CN^- to XCN. Furthermore, the CN bond distance correlates with the other quantities measuring bond strength within the series. It is to be noted, however, that $R_{C\equiv N}$ increases upon coordination of CN^- and this is reflected in a decreased overlap population but interestingly enough as an increase in Ω_{CN} and F_{CN}.

B. Detailed Comparison of CN^- and HCN. The transformation from CN^- to HCN may be visualized as coordination of the C lone pair by a proton. The effect of this on the energies of the σ-type orbitals (the C lone pair (φ_4 of CN^-), the N lone pair (φ_7 of CN^-), and the CN σ bond (φ_8 of CN^-)) and the π-type orbitals (φ_5, φ_6) is shown in Table III. The fallacy in the use of the term "lone pair" is strikingly pointed out in Table III. Overlap populations by molecular orbitals are given in Table IV.

Both φ_4 and φ_8 orbitals move to lower energy as expected and φ_7 moves to higher energy. The effect on the π-type orbitals is much less, but in the expected direction. The population analyses show an over-all shift of electron density out of the σ-type atomic orbitals. The total CN overlap population barely increases as the *net* result of an *increase* in CN σ overlap population and a nearly equal *decrease* in π population.

Looking at the population analysis by molecular orbitals, we observe the following changes. (1) Electron density in the N lone-pair (φ_7) orbital is drawn further into the C–N binding region with an accompanying increase in N pσ character and decrease in N s character (note the opposite prediction on the basis of

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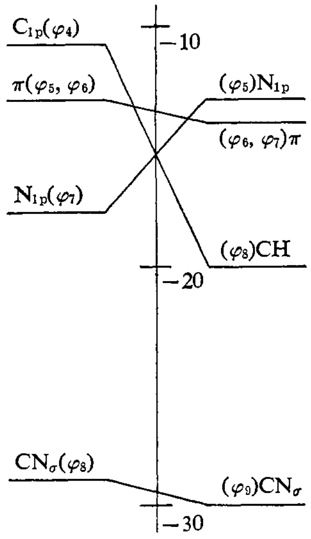
(6) (a) H. A. Bent, *Chem. Rev.*, 61, 275 (1961); (b) *J. Chem. Educ.*, 37, 616 (1960).

(7) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 88, 2367 (1966).

Table III. Orbital Energy Level Diagram and Gross Atomic Orbital Populations



$C\equiv N^-$ C_s	C_σ	C_π	N_s	N_σ	N_π		E, ev		H—C≡N H	C_s	C_σ	C_π	N_s	N_σ	N_π
0.08	1.01	...	0.00	0.92	...	$C_{lp}(\varphi_4)$	−10								
...	...	1.41	...	...	2.58	$\pi(\varphi_5, \varphi_6)$		$(\varphi_5)N_{lp}$	0.18	0.02	0.31	...	0.06	1.43	...
								$(\varphi_6, \varphi_7)\pi$	...	...	...	1.62	...	...	2.38
0.62	0.37	...	0.27	0.74	...	$N_{lp}(\varphi_7)$									
							−20	$(\varphi_8)CH$	0.61	0.42	0.50	...	0.30	0.18	...
0.70	0.04	...	1.26	0.00	...	$CN_\sigma(\varphi_8)$	−30	$(\varphi_9)CN_\sigma$	0.04	0.72	0.05	...	1.19	0.00	...

Table IV. Overlap Populations by Molecular Orbitals

CN^-	HCN
φ_4, 0.02	φ_5, CH = 0.10; CN = 0.21
$\varphi_5 + \varphi_6$, 0.96	$\varphi_6 + \varphi_7$, CN = 0.92
φ_7, 0.15	φ_8, CH = 0.62; CN = 0.04
φ_8, 0.68	φ_9, CH = 0.03; CN = 0.65

isovalent hybridization[6]) and the resultant *increase* in orbital energy. Note that the electron drift in this orbital has been in a direction to stabilize the CN link (whether or not it actually does, however, depends on the changes in β/S values). (2) The carbon lone pair (φ_4), while only slightly binding for CN^-, becomes the CH bond and remains slightly binding for the CN link in HCN. There has been a drift of electrons out of the C and N pσ orbitals toward the proton, and the populations of the C and N 2s orbitals have increased in this molecular orbital (note the opposite prediction on the basis of isovalent hybridization[6]). (3) The CN σ bond (φ_8) is perturbed very little upon formation of the HC bond as evidenced by the slight CN overlap population decrease and a very slight change in the populations of the C and N s orbitals. (4) The π orbitals (φ_5, φ_6) reflect the increase in the electronegativity of the carbon atom by a decrease in N π population and an increase in C π population. The overlap population was found to decrease very slightly while the π overlap energy was found to increase somewhat (Table II). This is what might be expected for coordination at the *less electronegative* donor atom since, in resonance theory

$$\underset{\text{I}}{:C{=}\bar{N}:} \longleftrightarrow \underset{\text{II}}{:C\equiv N:}$$

form II should contribute more highly upon C lone-pair donation than in CN^-. A similar interpretation has been implied[8] for sulfur lone-pair donation in heavy metal complexes of $(CH_3)_2SO$ for which an increase in ν_{S-O} has been observed. (Refer to the discussion of CH_3NC below for an example of coordination at the more electronegative donor atom, N.)

A few comments about the accuracy of these molecular orbital calculations may be made at this point since SCF results[9] are available for HCN. In comparing our results with those in the literature, we find good agreement with regard to C–H overlap population (our 0.77 with their 0.80) and C–N π overlap population (our 0.92 with 0.92); however, our CN σ population of 0.89 is quite a bit higher than the SCF value of 0.54. On the other hand, our molecular orbital energies compare within a few per cent of theirs except for the π orbitals which appear at a lower energy in our calculation. These discrepancies should not come as a surprise. It would be desirable to have available complete results of SCF calculations for both CN^- and HCN. A check of our *overlap energies* would then be possible. We believe that any discrepancies in overlap energies will largely cancel when one computes the *change* in overlap energies for similar molecules if the molecular orbital calculations have been handled in a similar manner for the molecules under comparison. The good agreement between the change in F_{CN} and change in Ω_{CN} should be taken as support for this hypothesis. Strictly speaking, however, the ultimate test will be a comparison with SCF results when they are published in sufficient detail.

C. Comparison of CH_3CN and CH_3NC. Comparison of these two molecules is interesting because we are able to compare the effects of coordination of the carbon lone pair with that of the nitrogen lone pair. That the carbon lone pair of CN^- is much more easily involved in bond formation is a well-known and established fact.

With regard to the more gross features of the bonding in these two molecules, we note from Table I that the $C\equiv N$ force constant and overlap energy of the cyano group suggest a much more stable situation for CH_3CN. The results in Table II afford a little more insight into

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[8] F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

[9] (a) A. D. McLean, *J. Chem. Phys.*, **37**, 627 (1962); (b) W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966).

this comparison. As mentioned previously, the act of coordination by the donor atom lone pair results in increased binding energy in the σ systems in both molecules. The stabilization effect is much larger for CH_3CN. On the other hand, the π systems in both molecules are destabilized, this effect being much larger for CH_3NC.

Further evidence for the greater "basicity" of the carbon lone pair comes from a comparison of the H_3C–C and H_3C–N bonds, respectively. The overlap energies for these links are −9.70 and −8.65 ev while the overlap populations are 0.84 and 0.70.

Comparison of the energies of the C and N lone-pair orbitals in these two compounds indicates CH_3NC should be the stronger base in agreement with experiment.[10]

In the case of CH_3NC we find a situation with regard to the π orbitals very analogous to that of acyl group donors such as ketones and amides. These Lewis bases undergo a marked decrease in C=O bond strength upon coordination of the oxygen lone pair. This has generally been attributed to strong polarization of the π cloud resulting in a more singly bonded nature for the C–O link. Coordination of the N lone pair of CN^- by CH_3^+ appears to nearly produce the same effect. The π-bond weakening, moreover, nearly offsets the σ-system strengthening, and very little change in CN binding energy occurs. Note the small increase in F_{CN} relative to the parent CN^-.

D. C_2^{2-}, H_2C_2. Calculations were carried out for C_2^{2-} and H_2C_2 with essentially the same trends as noted for CN^- and HCN. The redistribution of electron density in the lone pairs and C–C σ orbital of C_2^{2-} upon protonation is quite similar to the cyanide case. One exception here, however, is a slight *decrease* in π overlap energy, where before a slight increase in overlap energy was found. This, perhaps, is not unexpected. No comparison with F_{CC} is possible here since the Raman spectrum of C_2^{2-} has not been reported. Our molecular orbital calculations predict an increase in F_{CC}.

Conclusions

To summarize our findings we note the following. (1) A good correlation is found between F_{CN} and Ω_{CN} when coordination of *either* lone pair of CN^- occurs. Within the series of substituted cyanides both overlap energies and overlap populations afford a good correlation with the CN force constant and the C–N internuclear distance. (2) Analysis of the overlap energies at the subtotal level indicates that stronger binding occurs within the CN σ system as a result of electron-pair donation, and this effect, through an increase in CN force constant, explains the observed increase in ν_{CN} upon coordination. The increased strength of the σ bonds arises from a greater dominant contribution from the donor atom s orbital. The π-orbital perturbation is subordinate to this. (3) The effect of coordination of the C lone pair of CN^- on the N lone pair appears to be such as to make the N lone pair more basic in the Lewis sense since this orbital is found to lie at higher energy in HCN and CH_3CN, for example, than in CN^-. A similar statement may be made for the C lone pair in CH_3NC. (4) Comparison of CH_3CN and CH_3NC shows the carbon lone pair in CH_3NC is more readily available for coordination than the N lone pair of CH_3CN. This greater basicity of CH_3NC is masked to some extent in practice by its general instability relative to CH_3CN. Both the C—C and C≡N links are stronger in CH_3CN than the C—N and N≡C links of CH_3NC.

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A Study of the HF_2^- Ion by Fluorine Magnetic Resonance[1a]

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Abstract: Studies of the fluorine chemical shift changes in the following salts have been measured in water as a function of concentration: KHF_2, NH_4HF_2, $NaHF_2$, KF, NH_4F, and NaF. The changes in chemical shift observed for the salt KHF_2 can be satisfactorily interpreted according to the equilibrium: $HF_2^- \rightleftharpoons HF + F^-$. An equilibrium constant has been obtained for this dissociation, and chemical shifts of the species $HF_2^-(H_2O)_x$, $HF(H_2O)_y$, and $F^-(H_2O)_z$ are compared. The subscripts x, y, and z denote unknown solvation numbers in water.

A study of KHF_2[2] in the solid state by infrared spectroscopy was followed by detailed measurements of heat capacity and dielectric properties.[3] The linearity of the HF_2^- ion has been shown by Ketelaar and Vedder[4a] and Newman and Badger.[4b] Pimentel[5] has sug-

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[1] (a) This research was supported by the National Research Council of Canada and Petroleum Research Fund of the American Chemical Society in grants to L. W. R.

[2] J. A. A. Ketelaar, *Rec. Trav. Chim.*, 60, 523 (1941).

[3] E. F. Westrum and K. S. Pitzer, *J. Am. Chem. Soc.*, 71, 1941 (1949).

[4] (a) J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.*, 19, 654 (1951); (b) R. Newman and R. M. Badger, *ibid.*, 19, 654 (1951).

[5] G. C. Pimentel, *ibid.*, 19, 446 (1951).