J_{BX} or $J_{BX} \gg J_{AX}$. This question is unambiguously answered by the results of the deuteration experiment. It is seen that when the B proton (as well as the X proton) is replaced by deuterium, it is the upper doublet (at τ 3.47) which disappears, while the one centered at τ 3.28 collapses to a single line because of the loss of AB coupling. Thus it is clear that (1) the lower doublet is due mainly to the A proton, and (2) $J_{AX} \gg J_{BX}$. These are precisely the assumptions made in the study[2] of $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$, thus leading to the conclusion that 1,2 shifts accounted for the fluxional ("ring-whizzing") behavior of the $\sigma\text{-}C_5H_5$ ring in that molecule.

It is interesting to note that according to the detailed analysis of the spectrum of indene by Elleman and Manatt[11] $|J_{AX}| \approx |J_{BX}| \approx 2$ cps though the two coupling constants differ in sign. Also, the A proton absorbs at a higher field than the B proton. It is thus evident that attachment of indene at the 1 position to the $(\pi\text{-}C_5H_5)$-$Fe(CO)_2$ moiety, which may have considerable diamagnetic anisotropy, causes marked changes in both the spin–spin couplings (J_{BX} becoming very small, J_{AX} remaining of the same absolute magnitude) and in the relative chemical shifts. Manatt and Elleman, as quoted by Whitesides and Fleming,[10] have found for cyclopentadiene that $|J_{AX}| \approx |J_{BX}| \approx 1.3$ cps, whereas in the low-temperature spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2$-$(\sigma\text{-}C_5H_5)$ it was concluded[2] that $|J_{AX}|$ remained in the range 1–2 cps while J_{BX} became very small. Thus, in this respect there is a clear parallel between the $\sigma\text{-}C_5H_5$ and 1-indenyl systems suggesting that the two have generally similar behavior.

Acknowledgment. It is a pleasure to thank Professor George Whitesides for useful advice and for information on his work in advance of publication.

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[11] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962).

σ- and π-Bonding Effects in the Coordination of the Cyano Group

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Abstract: The effect of CN^- π^*-orbital occupation on the CN force constant and bond strength is examined by LCAO–MO computations. In addition to emphasizing the opposing influences of CN σ stabilization and π destabilization when the cyano group coordinates "electron-rich" acids, the LCAO–MO results are examined in relation to nuclear quadrupole resonance data and the Lewis-base properties of the free and coordinated cyano group. The molecules considered are NCN^{2-}, OCN^-, and SCN^-, and results for these molecules are compared with those obtained earlier for CN^-, ClCN, BrCN, and ICN as well as CH_3CN, CH_3NC, and HCN.

In continuing our investigations into the effects of coordination on the cyano group, we wish to report the results of modified Hückel calculations for NCN^{2-}, OCN^-, and SCN^-. The ion N^- and atoms O and S are examples of back-bonding "acids" which are capable of donating electron density to the π-antibonding orbitals of the CN^- ligand. One goal of this approach is to study the relative importance of σ- and π-bonding changes over a series of related cyano molecules with regard to their effects[2] on the CN vibrational frequency and force constant.

The nitrile group is particularly interesting for study since the CN stretching frequency generally increases upon either carbon or nitrogen coordination. Earlier studies[3] have shown that kinematic coupling is only partly responsible for the observation. In fact, molecular orbital calculations show that the increase in F_{CN} is due, in general, to σ strengthening although electron polarization effects are evident. In the adducts considered previously, only primarily σ-bonding acids were considered and back-bonding was not sufficiently important to offset σ-bond strengthening and bring about a decrease in F_{CN} and ν_{CN}. Because of the great interest in back-bonding to the cyano group in some of its complexes, we now wish to report a similar examination of the factors mentioned above for highly electron-rich or back-bonding acids and compare them to the "σ-bonding" acids. Forthcoming reports will deal with the equally interesting NO and CO ligands.

Calculations

The LCAO–MO method used here is the same in every respect as that used previously. An earlier report[3a] can be consulted for a discussion of the parameterization in the molecular orbital calculations and the method of analysis in terms of Mulliken's population procedure.

Overlap integrals were calculated from Slater-type orbitals. Initial, neutral atom H_{ii}'s were taken as valence-state ionization potentials[4] and the H_{ij} approximated from the MWH formula[5,6] with $K = 1.75$. The initial secular determinant was solved; atom charges were calculated, the H_{ii}'s corrected by 2.0 ev/unit charge, the Slater exponents adjusted by Slater's rules, the overlap integrals recomputed; and the new secular determinant was solved, etc. The iteration was halted when successive cycles yielded changes in charge on each atom of less than 0.01. The final results have been analyzed in terms of orbital populations and overlap energies.[7]

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[5] R. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).

[6] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[7] R. S. Mulliken, *ibid.*, **23**, 1833, 1841 (1955).

Table I. Bond-Strength Changes in the Coordinated Cyano Group

Compound	$\Delta\nu_{CN}$, cm^{-1}	$\Delta\Omega_{CN}$, ev	F_{CN}, mdynes/A	$\Delta\Omega^{\sigma}_{CN}$, ev	$\Delta\Omega^{\pi}_{CN}$, ev	n^{π}_{XC}	Δn^{π}_{CN}	$S^{\pi}_{X,C}$[g]	$\|\Delta E\|$, ev[g]
NCN^{2-}	40[a]	2.2	11.8[e]	−0.6	2.8	0.6	−0.3	0.33	0.1
OCN^-	85[b]	1.1	15.5[b]	−0.3	1.4	0.3	−0.2	0.27	3.5
SCN^-	−14[c]	0.9	16.0[c]	−0.8	1.7	0.3	−0.3	0.21	0.4
CN^-	0[d]	0.0	16.4[e]	0.0	0.0	0.0	0.0		
BrCN	120[d]	−0.1	17.8[f]	−0.9	0.8	0.2	−0.1	0.21	1.8
ICN	78[d]	−0.4	17.9[f]	−1.1	0.7	0.2	−0.1	0.20	1.7
ClCN	140[d]	−0.7	17.6[f]	−1.1	0.4	0.1	−0.1	0.16	2.9
HCN	17	−1.3	18.7	−1.1	−0.2		−0.02		

[a] Reference 8. [b] A. Maki and J. C. Decius, *J. Chem. Phys.*, **31**, 772 (1959). [c] L. H. Jones, *ibid.*, **28**, 1234 (1958). [d] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963. [e] This work. [f] E. E. Aynsley and R. Little, *Spectrochim. Acta*, **18**, 667 (1962). [g] Using final cycle entities.

Discussion of Results

Frequencies, Force Constants, and Overlap Energies. The possibility for error in using vibrational frequency shifts, rather than the force constants themselves, in estimating bond-strength changes is particularly striking from the data in Table I. The force constant–frequency discrepancies arise from kinematic coupling, changes of mass (though slight for acids with a mass greater than 10 amu),[3b] and interaction force constants in the adducts.

It is interesting to note that the "CN stretching frequency" (2120 cm^{-1}) of CN_2^{2-} is very much like that of the other coordinated cyanide adducts while the "adduct bond frequency" is quite high (1234 cm^{-1}).[8] However, the CN force constants of the other "adducts" and NCN^{2-} are not close at all (~17 *vs.* 12 mdynes/A). (The value of F_{CN} reported for NCN^{2-} in Table I is obtained by first solving the vibrational secular equation, in the symmetry coordinate basis set, for the Σ_g^+ and Σ_u^+ stretching modes. The symmetry force constants are then reduced to the corresponding internal coordinate quantities; $F_{CN} = 11.8$ and $F_{CN,CN} = 0.7$ mdynes/A.) This is an extreme example of kinematic coupling (the CN_2^{2-} stretching vibrations are properly treated as symmetric and asymmetric modes) but illustrates the danger in inferring bond orders from frequencies alone. In CN_2^{2-}, the large coordinate bond and interaction force constants (11.8 and 0.7 mdynes/A) produce a CN stretching frequency in the normal range for triply bound carbon and nitrogen. This rather strikingly emphasizes the opposing but related effects of kinematic coupling and σ-bond strengthening on the one hand and back-bonding on the other since in CN_2^{2-} the two factors do not quite offset each other and result in a net *increase* of 40 cm^{-1} in "ν_{CN}" relative to CN^-. Similar comments, on a less impressive scale, apply to the other molecules in this series.

The CN force constants for NCN^{2-}, OCN^-, SCN^-, CN^-, BrCN, ICN, and ClCN (Table I) indicate that the sequence of CN bond orders or bond strengths is ICN > BrCN > ClCN > CN^- > SCN^- > OCN^- > NCN^{2-}. The CN total overlap energies for these molecules (Table I) indicate, in good agreement with the force constants, the order ClCN > ICN > BrCN > CN^- > SCN^- > OCN^- > NCN^{2-}. The sole discrepancy in these orderings concerns the position of ClCN with respect to the other halogen cyanides. The halogen and nitrogen quadrupole resonance data to be discussed are compatible with the results of the molecular orbital calculations and suggest that the CN force constant of ClCN should be somewhat larger. The discrepancy may stem from insensitivity of the spectral data used in solving the vibrational secular equation to the force constants.[9]

The CN overlap energies and force constants are considerably lower for the anionic adducts than for CN^- while these quantities are larger than those for CN^- in the halogen cyanide series. By analyzing the overlap energy changes for the σ and π systems of CN in these molecules, the observed order of CN bond strengths is readily interpreted (Table I). In all cases the CN σ-overlap energy is lowered (becomes more negative) while the π overlap becomes less negative from occupation of the CN π* orbitals and related effects. For the halogen cyanides the σ stabilization is greater than the π destabilization, and the C and N atoms are more tightly bound as a result of coordination. In this instance, σ effects are seen to outweigh π effects on F_{CN}. For the anionic adducts just the opposite is the case. The π destabilization is by far the larger effect; it outweighs the σ stabilization, and the decrease in F_{CN} relative to CN^- is predicted. The XC and CN π-overlap populations also parallel the CN π-overlap energy changes. It also appears that σ strengthening is less when extensive π bonding occurs than when back-donation is minimal.

We found it interesting to compare the acids X in these XCN molecules with regard to a possible correlation between σ-electron withdrawal from CN^- and π back-donation, so-called synergism. The decrease in gross population of the C and N σ orbitals upon XCN formation very closely follows the electronegativity of X with a decrease in population of 1.3 for oxygen and 0.82 for hydrogen. σ electron withdrawal decreases in the order: O > Cl ~ N > Br > S > I ~ H. There is, therefore, no simple relation between σ polarization and change in CN σ-binding energy.

Back-bonding from X→C was not found to be related in any simple manner to σ withdrawal. The gross pπ population of CN decreases from 5.0 for nitrogen to 4.2 for Cl; the order is: N > S > O > Br > I > Cl. With regard to back-donation, the X pπ atomic depopulations, the C,X π overlap populations, the changes in C,N π populations, and the changes in C,N π overlap energies agree very well with one another. Furthermore, this back-bonding order does not follow σ withdrawal (synergism) but does follow an order based on X,C pπ overlap integrals and energy match (*S* and Δ*E* in Table I). In the one instance, oxygen, for which overlap integral and energy match

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(8) S. K. Deb and A. D. Yoffe, *Trans. Faraday Soc.*, **55**, 106 (1959).

(9) J. L. Duncan and I. M. Mills. *Spectrochim. Acta*, **20**, 523 (1964).

disagree on the position of X, the composite (observed) position more closely resembles the order base on overlap integrals.

A word of caution may be in order too at this point regarding the operation of synergism. The MO method used here most likely underestimates electron–electron repulsions and, hence, would tend to underestimate synergistic charge flow at an atom. It seems unlikely, in view of the compatibility of the force constants and overlap energies, that any major revision in these conclusions would be necessary after more rigorous calculations are performed. We hope to perform such computations in the near future for comparative purposes.

More important and significant are the changes in CN σ- and π-binding energies. From the overlap energy point of view, there is a correlation between $\Delta\Omega^{\sigma}_{\mathrm{CN}}$ and $\Delta\Omega^{\pi}_{\mathrm{CN}}$; an increase in CN σ binding (more negative σ-overlap energy) over the XCN series is generally accompanied by an increase (more negative π-overlap energy) in CN π-binding energy, *i.e.*, $\Delta\Omega_{\mathrm{CN}}$ becomes more negative. The order of increasing force constant is, therefore, the order of both increasing σ and increasing π binding.

It is also interesting to note again[3a] that protonation of CN$^-$ stabilizes the CN σ binding and also stabilizes the CN π binding (even though R_{CN} increases).

Quadrupole Coupling. While the correlation between the CN force constants and the CN overlap energies for these molecules, as well as those reported earlier, essentially assures us that the relative π and σ effects over this series have been correctly determined, nuclear quadrupole resonance data reaffirm the correctness, particularly in a relative sense, of the calculated σ *vs.* π factors.

The experimental field gradients at the nitrogen and halogen atoms in these molecules can be related to p-orbital occupation numbers by the following expression for the "excess p$_z$ electron density" (z is the principal field gradient and molecular figure axis; the field gradients are axially symmetric in these compounds)[10,11] (Table II).

$$f_z = N_\sigma - N_\pi/2 = (e^2qQ)_{\mathrm{mol}}/(e^2qQ)_{\mathrm{at}}$$

N_σ and N_π are the (gross) p-orbital populations and $(e^2qQ)_{\mathrm{at}}$ is the quadrupole constant for a single p electron in an orbital along the principal field gradient axis in the free atom.

Table II. Excess p$_z$ Electron Density

	f_z			
	Experimental[a]		Computed	
Compound	N^{14}	Halogen	N^{14}	Halogen
HCN	0.38		0.41	
CH$_3$CN	0.37		0.32	
BrCN	0.32	−0.88	0.27	−0.55
CN$^-$			0.37	
ClCN	0.30	−0.76	0.30	−0.48
ICN	0.28	−1.06	0.29	−0.69
SCN$^-$			0.21	
OCN$^-$			0.13	
NCN^{2-}			0.06	
CH$_3$NC	<0.5[b]		−0.32	

[a] For original references consult ref 11. [b] Sign unknown: M. K. Kemp, J. M. Pochan, and W. H. Flygare, *J. Phys. Chem.*, **71**, 765 (1967).

The values of $(e^2qQ)_{\mathrm{at}}$ are readily available for the halogens while this is not the case for N^{14}. Values from −9 to −12 Mc/sec appear reasonable.[11] The values of f_z under N^{14} of Table II were calculated with $(e^2qQ)_{\mathrm{at}} = -12$ Mc/sec. With regard to the ordering of these molecules according to decreasing f_z (relative σ and π populations of the nitrogen orbitals), both experiment and calculation give the same order: HCN > CH$_3$CN > BrCN > ClCN > ICN > CH$_3$NC, except for BrCN. A change in sign of the field gradient was calculated for CH$_3$NC; this reflects the effect of coordination of the nitrogen lone pair, but it appears that this LCAO–MO method has overdetermined depopulation of the p$_z$ and/or population of pπ orbitals to the extent that $N_\pi/2 > N_\sigma$. Resonances have not been observed (or reported), unfortunately, for the anionic "adducts" or the parent CN$^-$, probably because of very small field gradients at N^{14}.

The agreement, in an absolute sense, between the calculated and experimental f_z for the halogen atoms is not very satisfactory. The disagreement may, in part, result from the approximations[10,11] in setting $N_\sigma - N_\pi/2 = q_{\mathrm{mol}}/q_{\mathrm{at}}$. Nevertheless, the source of error does not upset the agreement between calculated and observed principal field gradients with regard to sign and the order I > Br > Cl or, more significantly, the relative field gradient values

	I	Br	Cl
Exptl	1.0	0.83	0.92
Calcd	1.0	0.80	0.70

These comparisons of the calculational results with experimental quantities indicate (not unexpectedly) some discrepancies on an absolute basis, but in comparing one molecule in the series to another the agreement is quite satisfactory. This is particularly encouraging in view of the small differences in the N^{14} coupling constants over this series.

Cyano Free Radical. In order to examine the fidelity of this LCAO–MO method under rather extreme conditions, we have examined the cyano free radical and find the results to be consistent with several lines of experimental evidence. The unpaired electron is found in the carbon "lone-pair" orbital, and the ground state of the molecule is therefore $X^2\Sigma^+$ as observed. The overlap population (1.652) and overlap energies (−19.455 ev) are less than the corresponding values (1.805 and −19.628 ev) for CN$^-$. The force constant is also smaller for the radical and has the value 15.9 mdynes/A calculated from the anharmonic frequency. The CN internuclear distance is greater in the radical (1.172 A) than in the anion (1.140 A). The ionization process has removed an electron from a σ symmetry orbital with only a small, positive (bonding) overlap population of 0.02 between the carbon and nitrogen atoms. It is not reasonable that removal of one electron from this orbital would explain[7] the decrease in F_{CN} and the increases in R_{CN} and Ω_{CN}. An analysis of the change in σ- and π-overlap energies indicates that the ionization results in stabilized σ bonding ($\Delta\Omega^{\sigma} = -0.40$) and destabilized π bonding ($\Delta\Omega^{\pi}$

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(10) T. P. Das and E. L. Hahn "Nuclear Quadrupole Resonance Spectroscopy," Academic Press Inc., New York, N. Y., 1958.

(11) C. T. O'Konski in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962.

= 0.57) the latter being the greater effect in this case. In relation to the results for XCN molecules, the ionization of an electron from the C lone pair of CN^- corresponds to the extreme case of σ withdrawal, and it is interesting that the total σ binding strengthens even in this limit of electron withdrawal. We hasten to repeat[3a] that the σ binding in CN^- and CN is due mostly to the lowest energy σ orbital and to some extent to the nitrogen "lone-pair" orbital. One obvious effect of electron withdrawal from the carbon "lone pair" is to reduce the excess negative charge on the CN moiety. This apparently allows more effective interaction of the carbon and nitrogen σ AO's and results in greater σ overlap energy.

In addition to the overlap energy–force constant correlation, the CN N^{14} quadrupole coupling constant supports the calculated σ- and π-electron redistribution following ionization of CN^-. A value for the quadrupole coupling constant has not been reported for the ground electronic state, but a value of -5 ± 5 MHz has been determined[12] for the excited B $^2\Sigma^+$ state. That author argued that the ground state should exhibit a smaller field gradient at the nitrogen nucleus than the excited state and this LCAO–MO method is in agreement with that prediction. The calculated coupling constant (assuming $(e^2qQ)_{at} = -12$ MHz) for $B^2\Sigma^+$ is -3.7 MHz in agreement with experiment and that for $X^2\Sigma^+$ is $+1.7$ MHz.

Chemical Implications. Bridging Cyanide. In further support of the general conclusions reached in this and preceding papers,[3] we wish to call attention to the recent work of King,[13] who has reported the preparation of the series of compounds $M(CO)_5CNX$ where X = H, $(CH_3)_3Si$, and $(CH_3)_3Sn$. The XNC molecules are stabilized by coordination of the carbon lone pair, and the complexes can be sublimed at a temperature of 100° and above. Similarly, Holzl and co-workers[14] found it possible to prepare alkylisonitriles by alkylation of metal cyanide complexes although these reactions apparently are not the simple addition reactions which lead to $M(CO)_5CNX$. In every instance studied so far by us, coordination of the carbon lone pair leads to a higher energy, greater p character (more "basic") nitrogen lone pair. Though difficult to prove experimentally, this should be a significant factor in the ease with which nitrogen is found to coordinate in forming the isonitrile ligands of King and Holzl. It is important to note that the simple inductive effect of carbon coordination would be expected to lead to a less basic nitrogen atom.

Another example[15] of bridging (linear) cyanide is the compound $[(NC)_5CoCNFe(CN)_5]^{6-}$, the structure of which is presumably similar to that of the activated complex for the electron-transfer reaction of $Fe(CN)_6^{3-}$ with $Co(CN)_5^{3-}$.

π-Acceptor Property. The CN force constants[13] for the compounds $M(CO)_5CNX$ fall in the range 16.7–17.3 mdynes/A in spite of the fact that the CN group is coordinated to an electron-rich acid. These complexes are similar, though the force constant increase is not so large, to conventional acetonitrile Lewis adducts[3b] where both lone pairs of CN^- are coordinated. The smaller F_{CN} increase in the carbonyl complexes is reasonably linked to back-bonding but may also be due in part to smaller σ stabilization. A smaller σ stabilization was found[3a] for CH_3NC than for CH_3CN and $M(CO)_5$ undoubtedly is a weaker σ-bonding acid than BF_3. An upper limit on the effect of back-bonding may be estimated by assuming the change in σ-overlap energy ($\sim$1 ev) found[16] for $CN^- \rightarrow CH_3CNBF_3$ to apply for $CN^- \rightarrow XNCM(CO)_5$. The maximum CN π destabilization (<1 ev) is therefore much less than that for SCN^- and suggests that $M(CO)_5$ is a poorer back-bonding acid to XNC than the sulfur atom is to CN^- and probably poorer than the halogens.

Jones[17] has examined the trivalent hexacyano complexes of Cr, Mn, Fe, Co, Rh, Ir, and Fe(II) and dicyano complexes of Ag(I), Au(I), and Hg(II) and found good correlations between CN integrated absorption coefficients, CN stretching frequencies, and metal formal charge, all of which are used to infer CN σ stabilization and MC π-bonding orders in this series. In only one instance, $Fe(CN)_6^{4-}$, is metal–carbon π bonding sufficiently extensive to offset σ stabilization and kinematic coupling and bring about a decrease in ν_{CN} and presumably F_{CN}.

In selecting a force-field model for cyano complexes it appears to be a good approximation to set $F_{MC,CN} = 0$. For the molecules included in this study this approximation would be inaccurate (Table III). In the event that the dominant contribution to f_i arises from π-system charge flow in vibrating XCN, the finding that $F_{MC,CN} \sim 0$ suggests that transition metals are inferior to sulfur and the halogens as back-bonding acids to CN^-. With the cyano compounds considered in Table III, a correlation between π bonding and interaction constant is questionable.

Table III. Stretch–Stretch Interaction Constants

Compound	$F_{XC.CN}$, mdynes/A	Compound	$F_{XC.CN}$, mdynes/A
NCN^{2-}	0.7[a]	BrCN	0.7[b]
OCN^-	1.4[b]	ICN	1.1[d]
SCN^-	0.9[c]	ClCN	0.5[d]

[a] This work. [b] Footnote *b*, Table I. [c] Footnote *c*, Table I. [b] Footnote *f*, Table I.

All these studies with transition metal complexes seem to indicate that back-bonding to the CN ligand from all but the most highly back-bonding acids is not of major consequence to the CN force constant, frequency, and bond strength. Nevertheless, the effect of XC multiple bonding in complexes shows up in the intensity of the "CN stretching" absorption and in the energies of metal atom d orbitals as evidenced by the unusually large d-orbital splitting in cyano complexes. The latter two observations are not at all inconsistent with the first. In this connection the data in columns 6 and 7 of Table I indicate that the decrease in CN π-overlap population is appreciably less than the CX π population—only about one-third of the *gross* CN population increase appears as antibonding electron density.

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(12) H. E. Radford, *Phys. Rev.*, **136A**, 1571 (1964).

(13) R. B. King, *Inorg. Chem.*, **6**, 25 (1967).

(14) (a) F. Holzl, T. Meir-Mohar, and F. Viditz, *Monatsh.*, **52**, 73 (1929); (b) *ibid.*, **53–54**, 237 (1929), and earlier references.

(15) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

(16) The value of $\Delta\Omega_{CN}$ reported in ref 3b is larger than the value given here. This is due to the use of different definitions of β_{ij} in ref 3b and the current work; refer to ref 3a for comments on this matter.

(17) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963), and references therein.

Conclusions

On the basis of these calculations for σ-bonding, weakly π-bonding, and strongly π-bonding situations for CN^-, we can draw the following conclusions. (1) One must exercise care in deducing a CN force constant change from a frequency shift. (2) On the basis of the correlation between F_{CN} and overlap energy, the LCAO-MO method used in these studies faithfully reproduces, at least within a related series, the changes in CN binding when CN^- coordinates a Lewis acid. (3) CN σ binding strengthens when either the carbon or nitrogen lone pair coordinates—though to a lesser extent with strongly back-bonding acids. (4) These computations provide no evidence for the operation of synergism in the coordination of CN^-, in the sense that the greater σ withdrawal by X the greater π donation by X. (4) The degree of back-bonding depends strongly on overlap integrals and energy matching of the π*- and acid π-type orbitals. (6) Estimates of electric field gradients at the nitrogen atom in XCN by this MO method are better than for those at halogens; nevertheless, the errors associated with the MO method and the model for analysis of quadrupole data do not invalidate any of the trends in field gradient magnitude. (7) The computations reveal an increased basicity of the nitrogen lone pair when carbon coordination occurs, and there is experimental justification of this prediction.

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Asymmetric Syntheses, Asymmetric Transformations, and Asymmetric Inductions in an Optically Active Solvent

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Abstract: Asymmetric syntheses, asymmetric transformations, and asymmetric inductions have been achieved using L-2,3-butanediol as a solvent. When a solution of the racemic *cis*-dichlorobis(ethylenediamine)cobalt(III) ion is heated in the optically active solvent, the ion slowly antiracemizes to give an optically active product. Similar asymmetric syntheses occur with the *cis*-dichlorobis(ethylenediamine)chromium(III) ion and with the α-*cis*-dichlorotriethylenetetraminecobalt(III) ion; at equilibrium the latter complex exists as a mixture of α- and β-*cis* isomers both of which are optically active. In this solvent *trans*-chlorohydroxobis(ethylenediamine)cobalt(III) chloride isomerizes to the *cis* isomer which is optically active. In all these asymmetric syntheses resolution appears to be total. Dissolution of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride in the active solvent results in the appearance of strong optical activity in the region of the d → d absorption of the ion. This is regarded as a first-order asymmetric transformation wherein the solvent constrains the puckered ethylenediamine–cobalt rings into one of their enantiomeric conformations. Benzil and benzophenone dissolved in L-2,3-butanediol show optical activity in the region of the n → π* carbonyl absorption. These effects are regarded as examples of asymmetric induction which, presumably, is evident because of hydrogen bonding between the solvent and the carbonyl group.

The equilibrium constant between the enantiomeric forms of an optically active substance dissolved in an optically inactive medium is unity, and thus the sum of the contributions to the optical activity by the two enantiomorphs is zero. In certain cases, however, the addition of an optically active substance to such solutions leads to a displacement of the equilibrium and hence to the observation that the racemic mixture, in solution, has been either partly or totally resolved. This effect was named by Kuhn[1] as an "asymmetric transformation of the first order (or kind)." Similarly he named the earlier observation of Leuchs and Wutke,[2] who found that brucine precipitated *chemically* quantitative amounts of only one enantiomer of 2-*o*-carboxybenzyl-α-hydrindone from acetone solution, as an "asymmetric transformation of the second order." These two phenomena have been observed extensively in both organic[3] and inorganic[4] systems. In the latter compounds these effects have been variously described as "configurational activity"[5] or simply as the "Pfeiffer effect"[6] although Werner[7] observed essentially the same effect almost 20 years before. There seems little doubt that, in general terms, in both the first- and second-order asymmetric transformations, the basic physical mechanism which controls these effects is the same, namely, that an asymmetric molecule, whether in the crystal or in solution, interacts differently with the left- and right-handed forms of the molecules undergoing the asymmetric transformation.

The recognition of this fundamental principle, that asymmetry begets asymmetry, leads naturally to the supposition that asymmetric transformations, asymmetric syntheses, and asymmetric inductions may be observed in a suitable asymmetric solvent. Although

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