$(CO)_{12}$ are asymmetric, the feasibility of this arrangement in the case of iron is probably marginal.

It should be noted that in the above calculations it has been assumed that all iron–carbon bonds are σ bonds with a bond order of 1, and all π bonding has been neglected. Also the interactions which were neglected could no doubt be used to break the degeneracy of the nonbonding orbitals. Such crude approximations might suffice for checking the feasibility of a certain structure, but we recognize their limited application for a detailed description of electronic arrangement.

A treatment of the correct structure which did not neglect most of the small interactions was also carried out. In this case the energies of the orbitals which had been bonding and antibonding before were unchanged, but the seven nonbonding orbitals became three bonding and four weakly antibonding orbitals.

There are several p orbitals on carbon atoms which have the proper symmetry to π-bond with the iron atoms. Therefore, it seems reasonable that much of the electron density in these iron–iron antibonding orbitals will be transferred to iron–carbon π bonds, thereby increasing the net strength of the iron–iron bonds. If one then replaces a carbonyl with a lesser π-bonding triphenylphosphine, these antibonding orbitals should be given additional electron density. This would weaken the iron–iron bonds and result in the longer iron–iron distances noted in this structure determination.

Acknowledgment. We thank Mr. Edwin Siefert for preparing the single crystals used in this study and Professor Robert J. Angelici for calling the existence of this compound to our attention and for his helpful discussions concerning its structure.

The Electronic Structure and Donor Properties of Cyanamides[1]

H. Fred Henneike and Russell S. Drago

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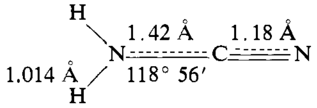
Abstract: Extended Hückel calculations have been carried out on dimethylcyanamide [$(CH_3)_2NCN$], cyanamide (H_2NCN), and acetonitrile. The minimum energy geometry is calculated for the nonplanar structure in agreement with the results from microwave studies. Various molecular properties are calculated in an attempt to understand why dimethylcyanamide is a better donor than acetonitrile toward a whole series of Lewis acids. Calculations on the BF_3 adducts of these donors are most illuminating. By examining the energies of the empty π orbitals of acetonitrile and dimethylcyanamide, we gain support for our previous qualitative rationalization of the fact that, in contrast to their donor properties, the spectrochemical parameter *Dq* toward nickel(II) for acetonitrile is larger than that for dimethylcyanamide.

Structural investigations on the cyanamides have been confined almost exclusively to cyanamide itself. A crystal structure study of cyanamide[2,3] yielded the paremeters below.



HNH angle (not shown) = 106° 47′

All of the parameters except possibly the N–H distance are at serious variance with the results of microwave studies on cyanamide in the vapor phase. Tyler, *et al.*,[4] find the total N–C–N distance to be 2.507 ± 0.003 Å and the HNH angle equal to 120 ± 1°. The authors present evidence for the bond lengths $r_{C\equiv N} = 1.16 \pm 0.01$ Å and $r_{N-C} = 1.35 \pm 0.01$ Å. A more complete analysis[5,6] substantiated the microwave findings and further suggested that superimposed on the parabolic potential function of the NH_2 out-of-plane bending vibration there is a small symmetric hump centered at the planar position causing cyanamide to have a nonplanar (C_s) equilibrium configuration. Fletcher and Brown[7] were able to fit all their observations of infrared and Raman bands through use of a Manning[8] potential for this vibration with a barrier height of 660 ± 20 cm^{-1} and an equilibrium out-of-plane bending angle of approximately 20°. It does not seem possible to reconcile the mutually longer bond lengths of the crystal-structure study with these results even by invoking various modes of hydrogen bonding in the crystal. It seems likely that the microwave data are the more accurate. Other authors[9-11]

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[1] Abstracted in part from the Ph.D. thesis of H. F. Henneike, University of Illinois, 1967. Address inquiries to Chemistry Department, University of Minnesota, Minneapolis, Minn.

[2] C. L. Christ, *Acta Cryst.*, 4, 77 (1951).

[3] "Cyanamide," American Cyanamid Co., Applied and Process Chemicals Department, 1963, p 13.

[4] J. K. Tyler, L. F. Thomas, and J. Sheridan, *Proc. Chem. Soc.*, 155 (1959).

[5] D. R. Lide, Jr., *J. Mol. Spectry.*, **8**, 142 (1962).

[6] D. J. Millen, G. Topping, and D. R. Lide, Jr., *ibid.*, **8**, 153 (1962).

[7] W. H. Fletcher and F. B. Brown, *J. Chem. Phys.*, **39**, 2478 (1963).

[8] M. F. Manning, *ibid.*, **3**, 136 (1935).

have studied this molecule and come to conclusions which are very probably incorrect.

In view of the interest in the structure of the cyanamides, it is a little surprising that more work has not been done on their donor properties. Klaeboe[12a] has studied the interaction between DMCA and I_2, ICl, and IBr, while Bock[12b] has prepared a novel series of compounds from nickel carbonyl and various cyanamides. The bonding in the latter appears to involve donation from the filled π orbitals of the $C{\equiv}N$ group of the cyanamide.[12c] We have extended the study of the donor properties of DMCA to a wider range of acceptors including BF_3, phenols, $(CH_3)_3SnCl$, and transition metal ions.[13] It appears that in all its σ donor interactions DMCA is a significantly better donor than is acetonitrile. In view of this it was suggested that the major contributing factor to the much lower value of $10Dq$ for the Ni^{2+} complex of DMCA compared to that in the acetonitrile complex is decreased metal–ligand π bonding in the DMCA complex. As a further check on the reasonableness of our conclusions and for a better understanding of the bonding in DMCA and of its donor properties, we undertook some extended Hückel-type molecular orbital calculations on DMCA. Calculations were also carried out on acetonitrile for purposes of a comparison of various calculated parameters between the two molecules. Because various additional facts are known about the parent cyanamide (H_2NCN) and because it is isoelectronic with acetonitrile, simpler in structure and much cheaper to carry out calculations for, while retaining all the essential bonding features of DMCA, it was included in this study. The agreement between our calculated parameters and experimental observations gives added confidence to certain applications of extended Hückel theory results. The analysis of Allen and Russell provides added theoretical justification[14] for investigating problems concerned with angular dependence.

Calculations

The extended Hückel theory (EHT) calculations were carried out by both of two methods previously described.[15,16] In both approaches the Coulomb integrals, H_{ii}, were approximated by charge-adjusted valence-state ionization potentials,[17] and the orbital exponents were taken from Burns[18] without any adjustment for charge. An exponent of 1.2 was used for hydrogen. The off-diagonal elements were approximated by both the Wolfsberg–Helmholz[19] (WH) and Cusachs[16] approach. Although the Cusachs method offers some apparent improvements, its successes and failures are not yet as widely investigated as are those of the WH method. More confidence can be placed in those results and conclusions that are independent of which method is employed.

The coordinate systems used were such that any rotational axes in the molecules were along the x axis, and any planar systems were wholly in the xy plane. Using the information from the microwave studies and the fact that[20] the length of $C{\equiv}N$ triple bonds generally falls in the range of 1.15–1.20 Å (and it is known that the length of the C–N partial double bond in amides[20] and thioamides[21] is 1.34 ± 0.02 Å), a reasonable choice of bond lengths and bond angles for the purposes of this study would seem to be as follows: $r_{C\equiv N}$ = 1.17 Å, r_{N-C} = 1.34 Å, r_{N-H} = 1.01 Å, HNH = 120°. Calculations made with $r_{C\equiv N}$ = 1.15, 1.19 and r_{N-C} = 1.36, 1.32, respectively, indicate that the predicted energies of the two lowest unoccupied and three highest occupied orbitals are not in either instance changed by more than 0.22 eV which will not affect the validity of the conclusions to be drawn later.

The geometry used for acetonitrile is as given by Sutton.[20] The B–N bond distances for both the $BF_3 \cdot CH_3CN$ and $BF_3 \cdot (DMCA)$ adducts were taken as 1.64 Å.[22]

Results

Although Hoffman has successfully used the Wolfsberg–Helmholz approximation in extended Hückel-type calculations to predict conformations[23] of saturated hydrocarbons, this method has been notably unsuccessful when applied to polar molecules with lone pairs, such as ammonia and water. In contrast the Cusachs approach has been reasonably successful in predicting the correct equilibrium configurations for water and H_2S.[24] In view of this, a series of calculations was performed on cyanamide in which the degree of nonplanarity (measured by θ) was varied. The other structural parameters were held constant. Some of the results of these calculations are shown in Figure 1 and Tables I–III. Figure 1 summarizes the results as a function of angle. The calculations were carried out by using the Cusachs parameters and varying only θ, the out-of-plane bend angle. A minimum of 4.5 ± 0.5 kcal/mole near θ = 22° is indicated by points which represent calculations for ten separate values of θ. Nine other points representing the second minimum are then placed by symmetry. The resultant curve qualitatively resembles the Manning curve.[8] Since the changes in such parameters as atomic charges and π-overlap populations as well as orbital energies are not very sensitive to the degree of nonplanarity for cyanamide as reflected in these calculations, we chose to carry out calculations on DMCA using planar geometry. In addition, we

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(9) G. P. Shipulo, *Opt. Spectry.* (USSR), 10, 288 (1961).

(10) M. Davies and W. J. Jones, *Trans. Faraday Soc.*, **54**, 1454 (1958).

(11) B. I. Sukhorukov and A. I. Finkelshtein, *Opt. Spectry.* (USSR), 7, 393 (1959).

(12) (a) E. Augdahl and P. Klaeboe, *Acta Chem. Scand.*, **19**, 3 (1965); (b) H. Bock and H. T. Dieck, *Chem. Ber.*, **99**, 215 (1966).

(12c) NOTE ADDED IN PROOF. A recent single crystal X-ray investigation is at variance with the structural conclusions of this work: K. Krogmann and R. Mattes *Angew. Chem.*, **78**, 1064 (1966).

(13) H. F. Henneike and R. S. Drago, submitted for publication.

(14) L. C. Allen and J. D. Russell, *J. Chem. Phys.*, **46**, 1029 (1967).

(15) P. C. Van der Voorn and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3255 (1966).

(16) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, S160 (1965).

(17) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, 84, 540 (1962).

(18) G. Burns, *J. Chem. Phys.*, **41**, 1521 (1964).

(19) M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952).

(20) L. E. Sutton, Ed., "Tables of Interatomic Distance and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(21) H. W. Dias and M. R. Truter, *Acta Cryst.*, **17**, 937 (1964).

(22) J. L. Hoard, T. B. Owen, A. Buzzell, and O. N. Salmon, *ibid.*, 3, 130 (1950).

(23) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).

(24) L. C. Cusachs, *ibid.*, **43**, S157 (1965).

Table I. Cusachs MO's for Planar Cyanamide

MO[a]	$-E$, eV	Nitrile nitrogen s	Nitrile nitrogen p_x	Nitrile nitrogen p_y	Nitrile nitrogen p_z	Carbon s	Carbon p_x	Carbon p_y	Carbon p_z	Amino nitrogen s	Amino nitrogen p_x	Amino nitrogen p_y	Amino nitrogen p_z	H^b
π_z^{**}	4.34				+0.856				−0.986				+0.565	
π_y^{*}	5.24			+0.919				−0.954				+0.167		±0.204
π_z^{*}	11.50				+0.671				+0.279				−0.683	
σ	12.39	+0.380	+0.774			−0.215	−0.319			+0.169	+0.241			=0.088
π_y	12.67		−0.604				−0.569				+0.251			±0.178
π_z	15.19				+0.196				+0.557				+0.588	
11	17.77	+0.324	+0.147			−0.304	+0.243			−0.078	−0.541			∓0.286
12	17.98			+0.030				−0.279				−0.487		±0.393
13	24.51	+0.653	+0.032			+0.216	+0.122			−0.376	+0.094			=0.134
14	29.17	+0.251	+0.031			+0.401	−0.007			+0.561	−0.002			∓0.098

[a] The symbols here have the same significance as those in Figures 2 and 5 for DMCA. The numbers are those arrived at when ordering the MO's from highest (unfilled) to lowest (filled) in energy. [b] The two signs correspond to the two hydrogen atomic orbitals.

Table II. Wolfsberg–Helmholz MO's for Planar Cyanamide

MO[a]	$-E$, eV	Nitrile nitrogen s	Nitrile nitrogen p_x	Nitrile nitrogen p_y	Nitrile nitrogen p_z	Carbon s	Carbon p_x	Carbon p_y	Carbon p_z	Amino nitrogen s	Amino nitrogen p_x	Amino nitrogen p_y	Amino nitrogen p_z	H^b
π_z^{**}	5.44				+0.715				−0.918				−0.459	
π_y^{*}	6.26			−0.769				+0.912				−0.130		±0.168
π_z^{*}	13.15				−0.615				−0.093				+0.789	
σ	14.42	+0.327	+0.802			−0.089	−0.239			+0.063	+0.288			=0.050
π_y	14.80			−0.700				−0.475				+0.264		±0.163
π_z	16.12				+0.463				+0.550				+0.465	
11	18.11			+0.128				+0.274				+0.598		±0.325
12	19.29	−0.279	−0.255			+0.311	−0.299			−0.064	+0.536			=0.157
13	29.10	+0.532	+0.007			+0.163	+0.226			−0.453	+0.052			=0.157
14	33.63	+0.390	−0.013			+0.428	+0.007			+0.444	+0.032			∓0.093

[a] The symbols here have the same significance as those in Figures 2 and 5 for DMCA. The numbers are those arrived at when ordering the MO's from highest (unfilled) to lowest (filled) in energy. [b] The two signs correspond to the two hydrogen atomic orbitals.

Table III. Cusachs MO's for Nonplanar Cyanamide

MO[a]	$-E$, eV	Nitrile nitrogen s	Nitrile nitrogen p_x	Nitrile nitrogen p_y	Nitrile nitrogen p_z	Carbon s	Carbon p_x	Carbon p_y	Carbon p_z	Amino nitrogen s	Amino nitrogen p_x	Amino nitrogen p_y	Amino nitrogen p_z	H^b
π_z^{**}	4.46	+0.010	−0.020		+0.862	−0.015	+0.014		−0.981	+0.142	−0.088		+0.518	=0.092
π_y^{*}	5.15			−0.916				+0.962				−0.185		±0.199
π_z^{*}	11.57	+0.049	+0.155		+0.649	−0.014	−0.084		+0.284	−0.091	+0.166		−0.648	∓0.043
σ	12.37	−0.371	−0.755		+0.136	+0.208	+0.313		+0.109	−0.174	−0.233		−0.090	∓0.093
π_y	12.62			+0.610				+0.561				−0.261		±0.177
π_z	15.20	+0.091	+0.075		+0.191	−0.085	+0.029		+0.539	+0.115	−0.170		+0.564	=0.014
11	17.78	−0.313	−0.147		+0.009	+0.301	−0.237		+0.075	+0.086	+0.513		+0.155	=0.289
12	18.01			−0.033				−0.287				−0.482		±0.391
13	24.49	−0.653	−0.032			−0.209	−0.124		−0.002	+0.3841	−0.092		−0.009	∓0.131
14	29.17	+0.258	+0.031			+0.404	−0.007			+0.557	−0.004			∓0.095

[a] The symbols here have the same significance as those in Figures 2 and 5 for DMCA. The numbers are those arrived at when ordering the MO's from highest (unfilled) to lowest (filled) in energy. [b] The two signs correspond to the two hydrogen orbitals.

simplify the form of all molecular orbitals to a large extent since we gain σ–π separability.

Results for similar calculations on DMCA and acetonitrile (for comparison purposes) are presented in Figures 2–4 and Tables IV and V. The C_{3v} axis of acetonitrile and the C_{2v} axis of DMCA are both along the x axis for these calculations. DMCA has all its heavy atoms in the xy plane. All energy levels below −10 eV are occupied, and those above this value are unoccupied. The composition of certain of these

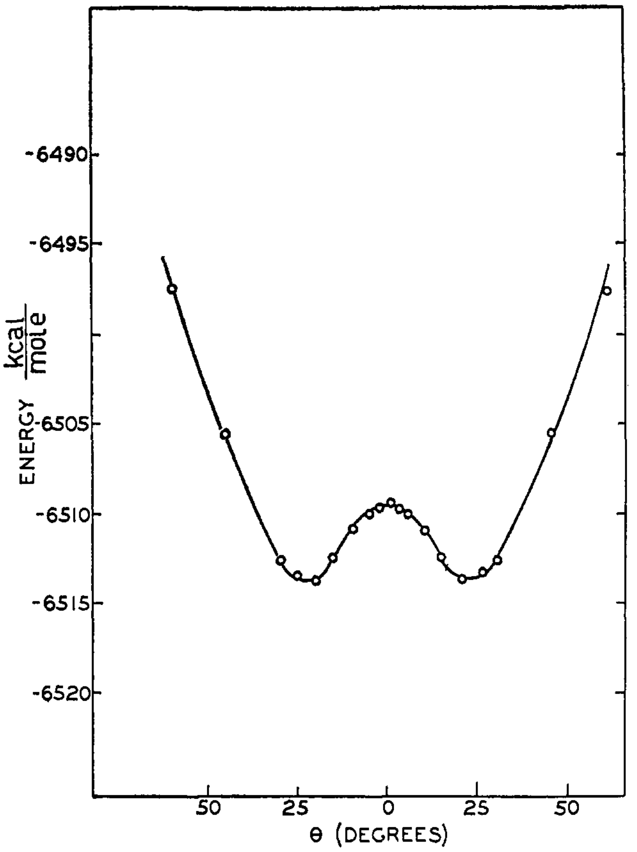

Figure 1. Cyanamide total energy as a function of conformation.

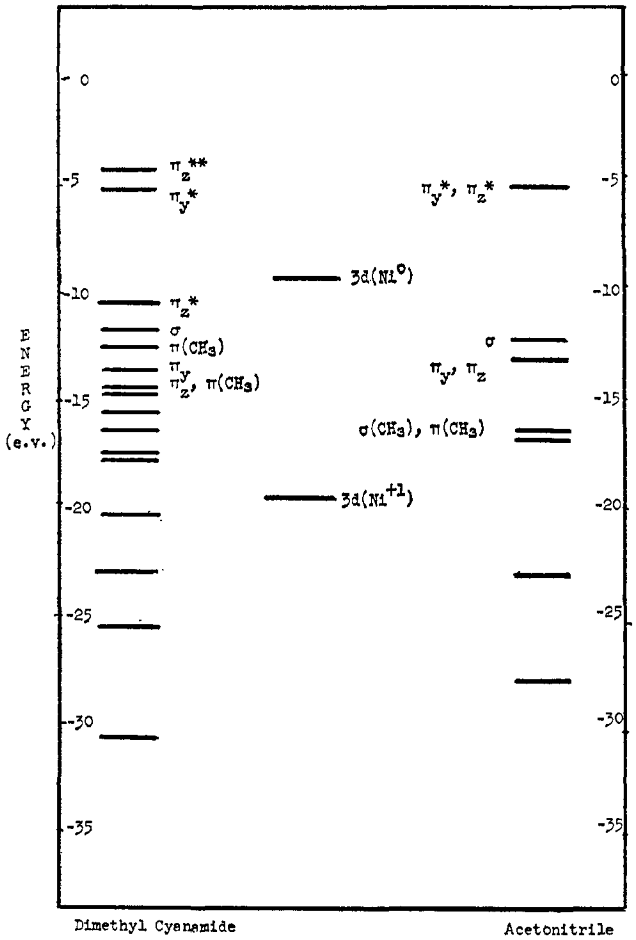

Figure 2. Orbital energy levels for acetonitrile and planar DMCA (Cusachs' parameters).

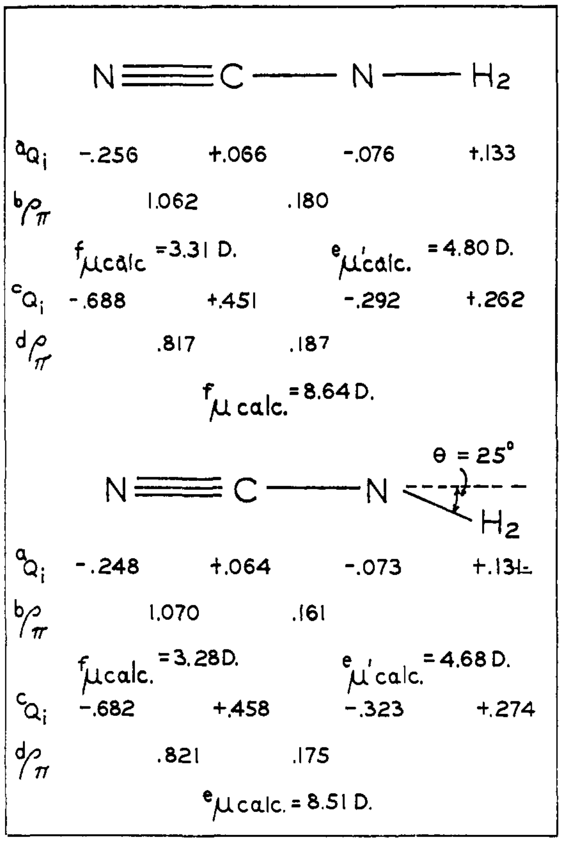

Figure 3. Atom charges and π-overlap populations in planar and nonplanar (θ = 25) cyanamide molecules: (a) atom charges by Cusachs method; (b) π-overlap population by Cusachs method; (c) atom charges by Wolfsberg-Helmholz method; (d) π-overlap population by Wolfsberg-Helmholz method; (e) point-charge dipole moment plus σ orbital polarization moment (J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, 5136 (1965); (f) dipole moment by point-charge model. The π overlap populations in the nitrile groups are for both π_y and π_z orbitals while those for the C–C or C–N bonds are for only the π_z orbitals.

molecular orbitals in terms of atomic orbital coefficients are given in Table IV. Reported[25] energies for the 3d levels of Ni^0 and Ni^+ have been added to the figure.

The orbital energy levels for acetonitrile and planar DMCA resulting from the Wolfsberg-Helmholz approximation and a constant factor of 2.00 eV/ionic charge for the charge dependence of the diagonal Hamiltonian matrix elements were also calculated.

Discussion

One of the more obvious results of the calculation is the expected splitting of the energies of the degenerate π orbitals in acetonitrile into nondegenerate orbitals in the cyanamides. The π_z system consisting of bonding, nonbonding, and antibonding orbitals (see Figure 2 and Table V), hereafter referred to as the three-center π system, has its π-bonding orbital greatly lowered in energy compared to that of the π_y system, or, as it is hereafter referred to, the two-center π-bonding orbital. The nonbonding π^* orbital of the three-center system is the highest filled molecular orbital and is the one that will be referred to as the amino nitrogen lone-pair

[25] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 1004 (1964).

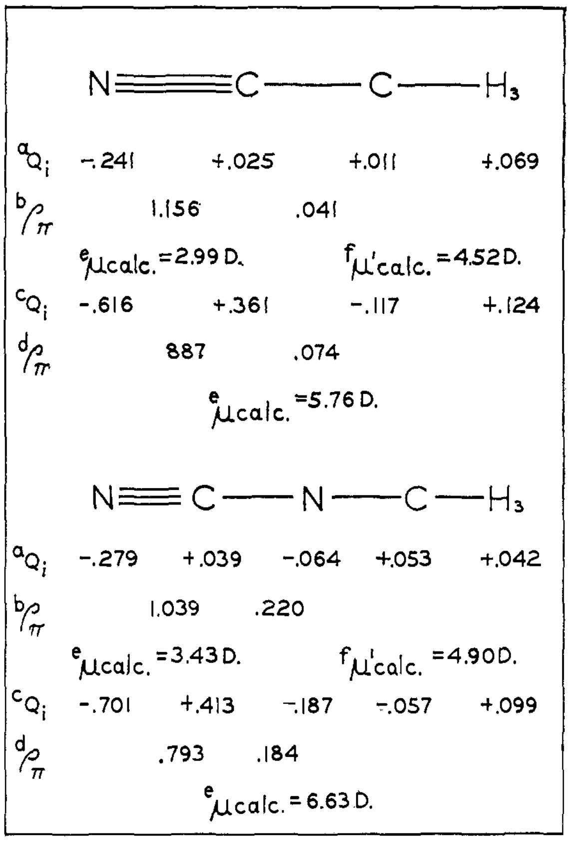

Figure 4. Atom charges and π-overlap populations in acetonitrile and DMCA. The letters a, b, c, etc., have the same connotation as in Figure 3.

molecular orbital, although it is only approximately 50% localized on the amino nitrogen.

The fact that the highest filled molecular orbital is not the lone pair σ orbital on the nitrile nitrogen is a little surprising. Calculations on formamide, thioformamide, and nitrosamine (unpublished results)[1] indicate that in these molecules the highest filled orbital is a lone-pair orbital largely on the oxygen, sulfur, and oxygen atoms, respectively, and not the nitrogen. In cyanamide the lone-pair orbital contains a relatively large contribution of the 2s orbital of the nitrogen atom, and the resulting molecular orbital lies at a significantly lower energy.

Somewhat more unexpected is the behavior of the π-orbital energies as the out-of-plane angle θ is varied. For instance, the two filled π_z orbitals become more stable as θ increases while the single filled π_y orbital becomes markedly less stable. This result is in contrast to a Hückel calculation on the π_z system only, which indicated an energy loss of about 10 kcal due to the bending, decreasing the overlap between the nitrile π system and the lone-pair orbital on the amino nitrogen.[9]

The over-all sum of the orbital energy changes is indicated in Figure 1. We see that they result in a minimum in the energy *vs.* θ curve of about 4.5 kcal at $\theta = 22°$ which are to be compared with the values 2.0 kcal at $\theta = \sim 18°$ which were obtained experimentally. The agreement in general is quite good for this type of calculation, the most significant point being the prediction of a nonplanar form of cyanamide for the ground state. As expected, those orbitals for which the contributions of individual atomic orbitals is affected the most by change in θ are the two three-center π orbitals which begin to acquire significant contributions from the s and p_z orbitals of the three heavy atoms along with the contribution from the hydrogens. Somewhat surprisingly, the nitrile nitrogen lone-pair orbital is also strongly affected in that it, in the nonplanar cases, has significant contributions from the p_z orbitals of all three heavy atoms.

Figure 3 and Tables I–III also allow comparisons to be drawn between the Cusachs and Wolfsberg–Helmholz approaches as they apply to cyanamide. The results are essentially the same in that the ordering of energy levels is the same in both cases, the coefficients of atomic orbitals in the molecular orbitals correspond quite closely, and the relative atomic charges generally correspond. However, the orbital energies in the Wolfsberg–Helmholz method generally lie an electron volt or so lower in energy, and even lower in the case of σ-type molecular orbitals, changing significantly the relative energies of the σ and π orbitals. In the Cusachs approach, the π orbitals are stabilized compared to the separation of σ and π levels in the Wolfsberg–Helmholz treatment.

It is interesting to compare the π overlap population values in Figures 3 and 4. For instance, in Figure 3 we see that both the Wolfsberg–Helmholz and Cusachs type calculations indicate that a small decrease in the amount of π bonding in the amino nitrogen–nitrile carbon region accompanies nonplanarity. The π overlap population ($\rho\pi$) for the nitrile group is the total of the ${}^{N}p_y$–${}^{C}p_y$ and ${}^{N}p_z$–${}^{C}p_z$ atomic orbital overlap populations. If we take half this then as a "standard" π-bond overlap population, we see that the Cusachs calculations on cyanamide indicate that there is 0.35 π bond in the amino nitrogen–nitrile carbon region for the planar form, and this decreases to 0.31 π bond in this region in the nonplanar form, compared to values of 0.47 π bond in the planar form and 0.43 π bond in the nonplanar form from WH calculations.

Both calculational methods do predict the order acetonitrile > cyanamide > DMCA for decreasing values of $\rho\pi$ in the nitrile group. It is also interesting that the nitrile stretching frequencies for these three molecules decrease in the same order.

While the charge distributions resulting from the Wolfsberg–Helmholz approach give point-charge dipole moments that are in the proper order (cyanamide > DMCA > acetonitrile), the Cusachs approach gives dipole moments which are of the right magnitude. The μ' dipole moments include the contributions from the nitrile lone pairs which are on the order of 1.5 D (Table VI) and nearly constant for all three molecules. These lone-pair dipole moments arise from hybridization of the s and p_z atomic orbitals in the lone-pair molecular orbital. The observed order of decreasing μ can be traced to the fact that the contribution of the nitrogen 2s atomic orbital in the σ molecular orbital decreases in the same order. As the σ molecular orbitals become less and less stable, the 2s atomic orbital, which is assigned a VSIE more negative than that assigned to the 2p atomic orbital on the nitrogen, makes a smaller contribution. This seems to be a reasonable trend.

The real goal in these studies is an insight into the donor properties of DMCA. As shall be seen, differ-

Table IV. The Highest Filled and Lowest Unfilled MO's of DMCA[d]

MO[a]	E, eV	Atomic orbital coefficients[b,c]			
π_z^{**}	−4.136	−0.845 NZ	−0.006 CS	+0.970 CZ	+0.00 CX
		+0.013 N′S	−0.581 N′Z	−0.012 N′X	+0.008 C′S
		−0.016 C′Z	+0.016 CX	−0.019 C′Y	+0.104 5H
		−0.074 6H	−0.047 7H	+0.008 C°S	−0.033 C°Z
		+0.020 C°X	+0.023 C°Y	+0.111 9H	−0.063 10H
		−0.069 11H			
π_y^*	−4.846	+0.921 NY	−0.974 CY	+0.188 N′Y	+0.002 N′S
		+0.003 N′Z	−0.100 C′S	+0.013C′Z	−0.098 C′X
		−0.086 C′Y	+0.015 5H	+0.067 6H	−0.068 7H
		+0.093 C°S	−0.019 C°Z	+0.090 C°X	−0.091 C°Y
		+0.001 9H	−0.078 10H	+0.069 11H	
π_z^*	−10.533	−0.643 NZ	+0.011 NX	−0.003 NY	−0.003 CS
		−0.112 CZ	−0.014 N′S	+0.742 N′Z	+0.013 N′X
		−0.003 N′Y	−0.009 C′S	−0.092 C′Z	+0.008 C′X
		+0.011 C′Y	−0.199 5H	+0.162 6H	+0.059 7H
		−0.012 C°S	−0.089 C°Z	+0.013 N′X	−0.011 C°Y
		−0.196 9H	+0.139 10H	+0.093 11H	
σ	−11.815	+0.339 NS	+0.738 NX	+0.005 NY	−0.153 CS
		−0.359 CX	+0.074 N′S	−0.014 N′Z	+0.358 N′X
		−0.041 C′S	−0.070 C′X	−0.037 C′Y	+0.064 6H
		+0.092 6H	−0.075 7H	−0.041 C°S	−0.007 C°Z
		−0.076 C°X	+0.035 C°Y	+0.052 9H	+0.111 10H
		−0.075 11H			
π_y	−12.308	−0.004 NS	−0.003 NZ	−0.008 NX	+0.606 NY
		+0.003 CS	−0.003 CZ	+0.003 CX	+0.566 CY
		−0.003 N′S	−0.002 N′X	−0.236 N′Y	−0.069 C′S
		+0.008 C′Z	+0.134 C′X	+0.073 C′Y	−0.039 5H
		−0.073 6H	+0.048 7H	−0.064 C°S	−0.006 C°Z
		−0.134 C°X	+0.075 C°Y	+0.028 9H	+0.078 10H
		−0.046 11H			
π_z	−13.773	−0.012 NS	−0.325 CZ	−0.023 NX	+0.021 CS
		−0.604 CZ	−0.009 CX	−0.002 CY	+0.007 N′S
		−0.308 N′Z	+0.011 N′X	+0.012 N′Y	+0.003 C′S
		+0.168 C′Z	−0.031 C′X	−0.012 C′Y	+0.201 5H
		−0.153 6H	−0.060 7H	+0.013 C°S	+0.171 C°Z
		−0.046 C°X	+0.192 9H	−0.120 10H	−0.105 11H
σ_{CH}	−14.712	−0.017 NS	+0.006 NZ	−0.016 NX	+0.008 NY
		−0.017 CS	+0.017 CZ	−0.006 CX	+0.037 CY
		−0.012 N′S	+0.012 N′Z	+0.022 N′X	+0.391 N′Y
		−0.076 C′S	+0.076 C′Z	+0.120 C′X	−0.378 C′Y
		+0.071 5H	−0.195 6H	+0.325 7H	+0.075 C°S
		−0.077 C°Z	−0.145 C°X	−0.375 C°Y	−0.120 9H
		+0.250 10H	−0.304 11H		
π_y'	−16.600	−0.016 NS	−0.009 NX	+0.045 NY	+0.017 CS
		−0.012 CX	+0.251 CY	+0.027 N′X	+0.186 N′Y
		+0.023 C′S	+0.063 C′Z	−0.339 C′X	−0.123 C′Y
		+0.257 5H	+0.175 6H	−0.127 7H	−0.035 C°S
		−0.048 C°Z	+0.327 C°X	−0.104 C°Y	−0.216 9H
		−0.183 10H	+0.126 11H		
π_z'	−17.496	+0.099 NS	−0.014 NZ	+0.038 NX	−0.085 CS
		−0.138 CZ	+0.071 CX	+0.086 N′S	−0.288 N′Z
		−0.169 N′X	−0.047 C′S	−0.220 C′Z	−0.067 C′X
		+0.207 C′Y	−0.209 5H	+0.162 6H	−0.139 7H
		−0.050 C°S	−0.227 C°Z	−0.047 C°X	−0.224 C°Y
		−0.250 9H	+0.159 10H	−0.098 11H	

[a] The designations correspond to those of Figure 5. [b] The abbreviations and numbering system are as follows: H = a hydrogen 1s atomic orbital, Z = a $2p_z$ atomic orbital, X = a $2p_x$ atomic orbital, Y = a $2p_y$ atomic orbital, S = a 2s atomic orbital, N = nitrile nitrogen atom, C = nitrile carbon atom, N′ = amino nitrogen in DMCA, C′, C° = methyl carbons, 5, 6, 7, 9, 10, 11 = methyl hydrogens. [c] In all calculations reported, Burns orbital exponents and Hinze and Jaffé's VSIE values were used. [d] Cusachs calculational method. The methyl groups (all tetrahedral angles) were oriented so that a CH bond of one was rotated (about C–N axis) 30° from the *XY* plane and a CH bond in the other methyl group was rotated 45° from the *XY* plane.

ences between planar cyanamide and the predicted equilibrium nonplanar form are slight. Actually we might expect the increased steric repulsions between methyl groups in DMCA compared to the protons in cyanamide to favor a more nearly planar form. Also, when DMCA is acting as a donor through the nitrile lone pair, the planar form of DMCA may be additionally favored. Figure 3 (Figure 4 is included here for convenience in making comparisons) shows that as θ increases there is a slight reduction in the negative charge on the nitrile nitrogen and a decrease in the net π-overlap density between the amino nitrogen and the

Table V. Comparison of the Energy Levels for Acetonitrile and DMCA Using both Calculational Procedures[a]

Wolfsberg–Helmholz				Cusachs			
CH_3CN		DMCA		CH_3CN		DMCA	
Orbital	Energy	Orbital	Energy	Orbital	Energy	Orbital	Energy
1	−32.121	1	−34.359	1	−27.172	1	−30.683
2	−26.028	2	−30.218	2	−22.798	2	−25.257
3	−17.615	3	−26.048	3	−16.792	3	−22.933
4	−16.531	4	−23.434	4	−16.438	4	−20.653
5	−16.531	5	−18.402	5	−16.438	5	−17.655
6	−14.548	6	−17.456	6	−12.496	6	−17.496
7	−14.548	7	−16.900	7	−12.496	7	−16.600
8	−14.137	8	−15.690	8	−12.165	8	−15.475
9	−6.142	9	−15.482	9	−5.243	9	−14.871
10	−6.142	10	−15.274	10	−5.243	10	−14.712
11		11	−14.710	11		11	−13.773
12		12	−14.609	12		12	−12.308
13		13	−14.087	13		13	−11.815
14		14	−11.865	14		14	−10.533
15		15	−6.308	15		15	−4.846
16		16	−5.294	16		16	−4.136

[a] The four highest energy empty orbitals are not indicated. Energies in electron volts.

Table VI. Values for Nitrile "Lone-Pair" Parameters

Parameter	Cyanamide	Aceto-nitrile	DMCA	DMCA′[a]
"Lone-pair" dipole moment, D	1.56	1.53	1.47	0
Total dipole moment, D	4.80	4.52	4.89	. . .
σ_{MM} energy, eV	−12.36	−12.16	−11.81	−10.53
Q_N	−0.248	−0.244	−0.279	−0.064
% localization	75.8	71.2	66.4	49.1
ΔQ_{CN}	. . .	−0.518	−0.529	. . .
$\Delta Q_{molecule}$	. . .	−0.541	−0.626	. . .

[a] Parameters for the amino nitrogen.

nitrile carbon. These results suggest that in the planar form there is not only more electron density on the nitrile nitrogen for donation, but also the "lone-pair" electrons on the amino nitrogen are more easily polarized into the nitrile group. The importance of the amino nitrogen lone pair in making the nitrile group of DMCA a stronger base than in acetonitrile was suggested by the results of WH-type calculations on the $BF_3\cdot$acetonitrile and $BF_3\cdot$DMCA adducts which will be briefly discussed later. The observation that the nitrile lone-pair orbital is much more effectively localized, not only on the nitrile nitrogen but in a particular orientation (s and p_x orbitals) parallel to the molecular dipole moment also, suggests that distortion toward the planarity might arise on complexation.

In Table VI are collected the results for various parameters which should be related to the donor ability of the nitrile lone pairs in cyanamide, acetonitrile, and DMCA. While a larger lone-pair dipole moment and increased atomic charge on the nitrile nitrogen Q_N should lead to increased donor ability, because of a greater electrostatic interaction, the results are also so similar as to preclude a valid relative ordering on this basis alone. The total dipole moments of DMCA and acetonitrile are in accord with the greater donor ability of DMCA. The over-all moment for cyanamide is the largest for all three molecules both experimentally and from the Wolfsberg–Helmholz calculations. Although the Cusachs calculations lead to a larger over-all moment for DMCA than for cyanamide, the small difference of 0.1 D between planar forms of the two molecules may well be reversed for the equilibrium forms if both are nonplanar.

From a comparison of the energies of the three lone-pair, σ orbitals, the order of increasing donor ability is predicted to be cyanamide < acetonitrile < DMCA. According to Koopman's theorem these orbital energies are comparable to the energy necessary to ionize an electron from the respective orbital. Each of these differences is, however, less than 4% of the total energy and too small to be employed as a reliable criterion of donor strength.

The percentage localization parameter of Table VI refers to the fraction of an electron pair in the σ molecular orbital which would be found in the s and p_x atomic orbitals on the nitrogen. As the percentage localization increases, the nitrile lone-pair molecular orbital should overlap more effectively with the empty orbital of an acid and thus improve in donor ability. Such a criterion does not take into consideration the ease with which the molecule can be polarized. It seems evident that from the experimentally observed[13] order of donor strengths, DMCA > acetonitrile, that the percentage localization alone is not a very effective measure of donor ability even for lone pairs of a very similar nature.

The last two parameters in Table VI differ from the others in that they are derived from calculations on the BF_3 adducts of the nitrile rather than on the nitriles themselves. ΔQ_{CN} and $\Delta Q_{molecule}$ are the changes in the net electron density of these atom groups upon coordination by BF_3 at the nitrile lone pair. That is, the net electron density in the nitrile group of acetonitrile decreases by 0.518 electron in going from acetonitrile to the BF_3·acetonitrile adduct while acetonitrile as a whole loses 0.541 electron.

In contrast to the other results in this table the calculations on the adducts were not carried out by the Cusachs method, because the large basis set would involve a considerably greater expense to iterate to charge self-consistency in the Cusachs approach. Most trends in the series cyanamide, acetonitrile, and DMCA, which were indicated by calculations on these molecules using the Cusachs method, were also evident in calculations employing the Wolfsberg–Helmholz approach. It seems likely then that the relative magnitude of Q_{CN} and $Q_{molecule}$ for DMCA and acetonitrile would also be independent of which method is applied. The values in Table VI indicate that while the nitrile groups in DMCA and acetonitrile transfer almost the same amount of electron density to BF_3 in their adducts, DMCA considered as a whole is able to transfer significantly more electron density than is acetonitrile. The dimethylamino group of DMCA released more than four times as much electron density as the methyl group in acetonitrile. Of the 0.097 electron released by the dimethylamino group in DMCA, the major portion, or 0.068 electron, comes from the nitrogen atom and the other 0.019 from the two methyl group carbons and none from the hydrogens. Of the 0.068 electron released by the nitrogen atom, 0.047 electron comes from the p_z atomic orbital, *i.e.*, the amino nitrogen lone-pair atomic orbital. The largest single factor contributing to DMCA's ability to transfer more electron density in an acid–base interaction can thus be traced to the presence of the lone pair of electrons on the amino nitrogen. It is further interesting to note that the π overlap density between the p_z orbital of the amino nitrogen and the nitrile carbon increases from 0.1843 in DMCA to 0.2038 in the DMCA·BF_3 adduct. Since this overlap density in cyanamide decreases as the degree of nonplanarity increases, it seems reasonable that nitrile coordination in DMCA should increase the relative stability of the planar form.

To summarize the comparison of the σ donor abilities of DMCA and acetonitrile, we note that of the parameters listed in Table VI only the lone-pair dipole moments and per cent localization of the nitrile lone pairs do not agree with the observed order DMCA greater than acetonitrile. The differences in the lone-pair dipole moments are small and do not represent a serious disagreement. It also seems reasonable that the percentage localization would be more than compensated for by the lower σ molecular orbital energy, larger Q_N, and $\Delta Q_{molecule}$ for DMCA. It is of interest to compare the donor properties of the amino nitrogen "lone pair" and nitrile nitrogen "lone pair" of DMCA, both for a planar molecule. It appears that the differences in per cent localization between these two orbitals now plays an important part in leading to reduced donor strength of the amino nitrogen. Values for several of these "lone-pair" parameters for the amino nitrogen lone pair in DMCA are indicated in Table VI in the column headed DMCA′. On the basis of the energies of these two orbitals in DMCA, it would be expected that the one labeled amino nitrogen lone pair would be by far the better donor orbital. However, this orbital has no dipole moment associated with it since it gives a charge distribution symmetric with respect to the plane of the molecule. Judging from the results on cyanamide, reasonable deviations from planarity at the amino nitrogen would not produce a "lone pair" moment of any significant magnitude. In addition, the net atomic charge on the amino nitrogen is only about one-quarter of that on the nitrile nitrogen. Although this molecular orbital has been termed a lone-pair orbital on the amino nitrogen, it is obvious from the per cent localization that it is far from localized on this atom. In cyanamide itself this molecular orbital is approximately 46% localized on the amino nitrogen in the planar form, and this is decreased to 41% localized on the amino nitrogen for $\theta = 25°$. Since there is no evidence for DMCA coordinating through other than the nitrile nitrogen lone pair in all of its monodentate σ interactions, it is evident that the large difference in orbital energies alone is not enough to make the amino nitrogen lone-pair molecular orbital a better orbital. Another factor which almost certainly plays a part in reducing the donor strength of the amino nitrogen is that, although this π_z molecular orbital is essentially nonbonding considered as a whole,[26] the π_z bonding orbital at lower energy is strongly bonding in both regions, and this would probably be impaired by coordination at the amino nitrogen.

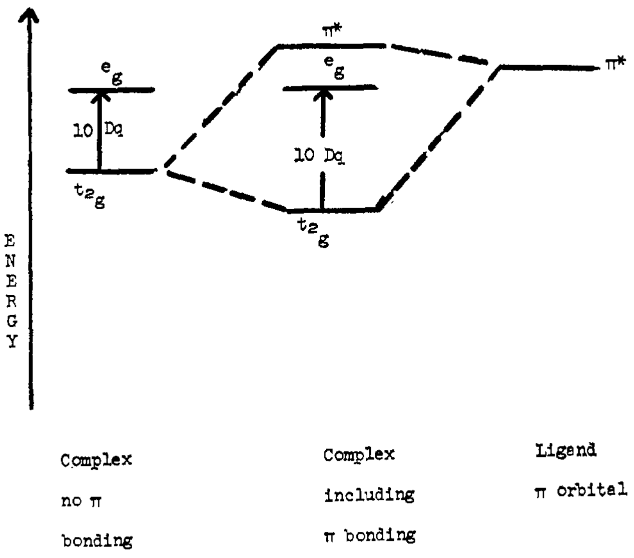

Figure 5. Effect of metal π bonding to empty ligand π orbitals.

We come finally to that particular facet of DMCA's donor properties which gives rise to the anomalously low *Dq* value for the $Ni(DMCA)_6^{2+}$ ion.[13] Figure 5 indicates the effect which overlap of an empty π^* ligand orbital with the t_{2g} metal orbitals has on the separation of the t_{2g} and e_g levels in an octahedral complex. From Figure 5 we expect that the effect of the π^* level on the parameter 10*Dq* will decrease as the stability of the π^* orbital decreases providing the energy of the metal t_{2g} orbitals remains approximately the same. As the stability of the π^* orbital decreases, the energy mismatch

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(26) It is weekly antibonding between the amino nitrogen and the nitrile carbon and weakly bonding between the nitrile nitrogen and the nitrile carbon according to the Cusachs calculations and the opposite according to Wolfsberg–Helmholz calculations.

between the π^* and t_{2g} orbitals increases. Energy mismatch would lead to less effective interaction between the two orbitals, thus a smaller lowering of t_{2g} in the complex and a smaller degree of π bonding between the t_{2g} metal orbitals and the π^* orbital.

From Figure 2 we see that the Cusachs method indicates that both empty π orbitals in DMCA lie higher in energy than the empty π orbitals of acetonitrile. Interaction between either of the DMCA π orbitals and the metal t_{2g} orbitals then would lead to the prediction of a decreased value for *Dq* in the DMCA complex of nickel because of the increased energy mismatch. The π_z^{**} orbital is raised the largest amount (1.11 eV) while the π_y^* orbital lies 0.40 eV higher in energy.

The coefficient of the p_π atomic orbital on the nitrile nitrogen in the π_y^* orbital is larger than that of the corresponding atomic orbital in the $p_z\pi^{**}$ molecular orbital of DMCA. The coefficients are 0.9205 and 0.8451, respectively. The Cusachs calculations on acetonitrile give 0.9011 for the coefficient of the nitrogen p_π atomic orbitals in the empty π^* orbitals. From the Cusachs calculations then, a poorer energy match for both empty π orbitals of DMCA and the metal t_{2g} orbitals would contribute to a lower *Dq* for the DMCA complex than for the acetonitrile complex. In addition, the overlap between the π_z^{**} molecular orbital in DMCA and the metal t_{2g} orbitals should be smaller than the overlap between an empty π^* orbital in acetonitrile and the t_{2g} orbitals. This also should lead to a lower *Dq* for CH_3CN. The better overlap between the π_y^* molecular orbital of DMCA and the t_{2g} metal orbitals compared to the overlap between an acetonitrile π orbital and the t_{2g} metal orbitals is not enough to overcome the other three factors.

Prediction of the relative degree of metal–ligand π bonding from the WH calculations is essentially the same. The results of either calculational method then can be used qualitatively to explain the lower *Dq* value for the DMCA complex and the better donor strength of DMCA compared to CH_3CN.[13]

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Thermodynamics of Ion Association. XVII. Copper Complexes of Diglycine and Triglycine

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Abstract: A sensitive differential calorimeter has been used to measure the enthalpy changes at 25° associated with the formation of copper diglycine and copper triglycine complexes and with the dissociations of the peptide hydrogen atoms at higher pH. The data have been combined with potentiometric measurements to yield ΔG, ΔH, and ΔS values at an ionic strength of 0.10 *M* for the various equilibria involved. At low pH, the values of the thermodynamic functions favor a bidentate structure for the species CuL^+ similar to that in the solid state, in which the copper is bonded to the terminal $-NH_2$ and the oxygen of the first peptide group. At higher pH, the thermodynamic data are discussed in terms of the important factors involved in the labilization of the peptide hydrogen atoms when the ligands are bound to the copper ion.

In recent years there has been considerable interest in the elucidation of the structures of the complex species formed in aqueous solutions of metal peptides because of their biological significance in enzyme reactions. The copper complexes of the polyglycines are of particular importance since dissociation of the peptide hydrogen atoms is facilitated in reactions which take place in the physiological range of pH. The structures of the complexes formed have been characterized in the solid state by X-ray methods.[2,3] In solution, however, there has been considerable disagreement as to the nature of the ligand atoms involved in coordination with the copper ion. In the absence of any unequivocal method for the determination of the structures in solution, they have generally been inferred from free-energy, kinetic, and spectral measurements.[4–10] There is now strong evidence, both from infrared absorption studies and from the observation that the peptide hydrogen atoms in some of the metal complexes readily undergo ionization, that the peptide group is involved

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(2) (a) H. C. Freeman, J. C. Schoone, and J. G. Sime, *Acta Cryst.*, **18**, 381 (1965); (b) H. C. Freeman, G. Robinson, and J. C. Schoone, *ibid.*, 17, 719 (1964); (c) B. Strandberg, I. Linqvist, and R. Rosenstein, *Z. Krist.*, **116**, 266 (1961).

(3) H. C. Freeman, "The Biochemistry of Copper," J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press Inc., New York, N. Y., 1966, p 77.

(4) M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 3080 (1963).

(5) M. K. Kim and A. E. Martell, *Biochemistry*, **3**, 1169 (1964).

(6) M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **88**, 914 (1966).

(7) S. P. Datta and B. R. Rabin, *Trans. Faraday Soc.*, **52**, 1123 (1956).

(8) B. R. Rabin, *ibid.*, **52**, 1130 (1956).

(9) W. L. Koltun, R. H. Roth, and F. R. N. Gurd, *J. Biol. Chem.*, **238**, 124 (1963).

(10) C. B. Murphy and A. E. Martell, *ibid.*, **226**, 37 (1957).