Spectroscopic Studies of Charge Transfer Complexes

XIII. Dimethylcyanamide and Iodine, Iodine Monochloride and Iodine Monobromide

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The interactions between dimethylcyanamide and iodine, iodine monochloride, and iodine monobromide have been studied by spectroscopic methods in the ultraviolet, visible and infrared regions. Spectral data and the thermodynamic functions $\Delta G_{25}°$, $\Delta H°$, and $\Delta S°$ for the complex formation have been determined. These data revealed that dimethylcyanamide is a stronger base than the nitriles. The complex bond was probably formed from the nitrile nitrogen. Comparisons have been made with hydrogen bond formation to phenol and to methanol.

A mong the donor-acceptor complexes, those formed between iodine and nitrogen bases have been extensively studied. Thus, the amines [1-4] form very strong complexes with iodine when dissolved in unpolar solvents, as inferred from the large formation constants and enthalpies of formation. On the other hand, the nitriles are less basic and interact weakly with iodine [5-11] or phenol.[12] With this in mind, the basicity of cyanamide appeared to be of interest, since it contains both an amine and a nitrile group. However, the solubility of this molecule in unpolar solvents is very low and prevented any quantitative studies. Therefore we turned to dimethylcyanamide (DMCA) which is soluble in carbon tetrachloride, carbon disulphide and heptane. In the course of this study we hoped to establish the stoichiometry of the halogen complexes and the preferred site of the halogen attack. Also a comparison of the basicity to that of amines and nitriles seemed to be of interest.

EXPERIMENTAL

Chemicals. DMCA from Fluka AG was purified by four times fractional distillation in a Vigreux column under reduced pressure, b.p. 41−41.5°C at 10 mm Hg. The infrared spectrum was checked with the one reported by Davies and Jones.[13] The halogens were purified as described earlier,[7] and the solvents, carbon tetrachloride, carbon disulphide and heptane, *Uvasole* from Merck were used without further purification. Stock solutions

of the halogens and DMCA were prepared by weighing into 100 ml volumetric flasks. The mixed solutions were prepared by pipetting into 25 ml flasks immediately before the spectra were recorded.

Instrumental. The ultraviolet and visible spectra were obtained with the aid of a Beckman DK-1 recording spectrophotometer equipped with a thermostated cell holder. Matched pairs of ground glass stoppered silica cells of path lengths 1 cm and 5 cm were used.

A Perkin-Elmer model 21 spectrophotometer with sodium chloride optics and sealed cells of path lengths 0.05 and 1.0 cm were used for recording the infrared spectra.

RESULTS

Visible region. DMCA dissolved in carbon tetrachloride has negligible absorption in the visible region, but iodine, iodine monochloride and iodine monobromide have peaks at 517, 465, and 492 mμ, respectively. When DMCA was added to iodine or any of the interhalogens, blue shifted halogen bands (*BS*-bands) appeared. For each of the halogens series of mixed solutions were recorded at constant halogen and varying DMCA concentrations. The set of curves obtained at 20°C for the iodine monobromide system is shown in Fig. 1.
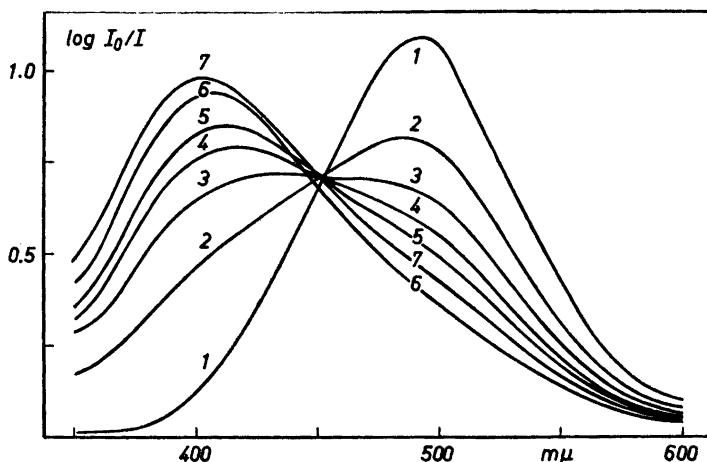

Fig. 1. Visible absorption spectra of DMCA- and iodine monobromide (3.072 × 10^{-3} M) in carbon tetrachloride at 20°C for 1 cm cell. The concentrations (M) of DMCA are: (1) zero; (2) 0.02642; (3) 0.05284; (4) 0.07925; (5) 0.1057; (6) 0.1585, and (7) 0.2113.

For DMCA concentrations below 0.2 M the curves passed through isosbestic points, situated at 489, 410, and 451 mμ in the iodine, iodine monochloride, and iodine monobromide systems, respectively. At higher donor concentrations, however, the absorption curves passed below the isosbestic point as previously reported for other iodine complexes.[14],[15] The *BS*-bands had maxima at 450, 353, and 397 mμ for the iodine, iodine monochloride, and iodine monobromide systems, respectively. To check the stability of the complexes, the mixed solutions were rescanned after 1, 4, and 24 h. In each of the systems

the absorption at the short wave length wing of the *BS*-bands increased with time, suggesting an irreversible chemical reaction involving polyhalide ions.[16] The spectral changes occurred faster for high DMCA and halogen concentrations and more rapidly for the interhalogens than for iodine. However, if the solutions were kept in darkness, negligible changes took place within ½ h after preparation.

The stoichiometry of the DMCA-halogen complexes was studied by the method of continuous variation.[17] Separate sets of curves were recorded in the visible and the ultraviolet regions. Because the ultraviolet absorption bands have higher extinction coefficients than the *BS*-bands, more dilute solutions were prepared for this region. These curves are shown in Figs. 2 and 3 for the iodine monochloride and the iodine monobromide systems, respectively. Distinct maxima occurred at the mole fraction 0.5, characteristic of 1:1 complexes. For the iodine system the complex was too weak to permit any conclusions, but it seems reasonable to assume 1:1 stoichiometry also in this case.

We obtained the thermodynamic functions by recording each series of the DMCA-halogen solutions at three temperatures in the visible region. Whenever a large excess of DMCA could be employed the molecular formation constants (K_c) and extinction coefficients (ε) could be calculated by the
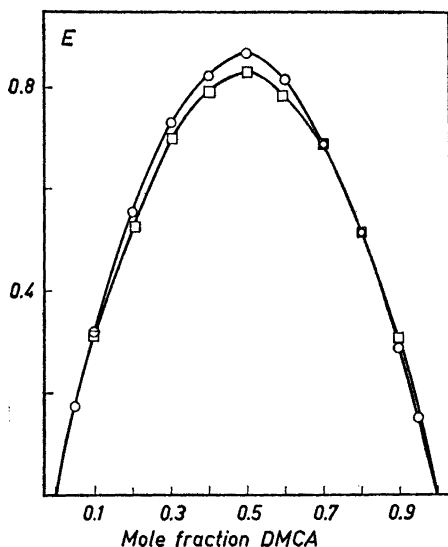

Fig. 2. Method of continuous variation of the DMCA-iodine monochloride system in carbon tetrachloride at 20°C, 1 cm cell. (O) 359 mμ, [DMCA] + [ICl] = 0.01997 M. (□) 265 mμ, [DMCA] + [ICl] = 0.004680 M.
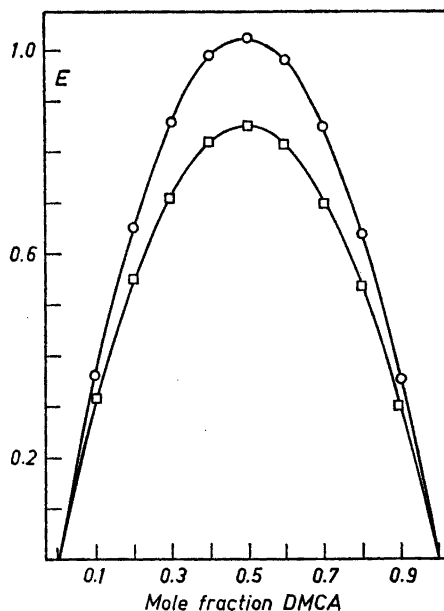
Fig. 3. Method of continuous variation of the DMCA-iodine monobromide system in carbon tetrachloride at 20°C, 1 cm cell. (O) 397 mμ [DMCA] + [IBr] = 0.02842 M. (□) 265 mμ [DMCA] + [IBr] = 0.006214 M.

simple Benesi-Hildebrand,[18] Scott,[19] or Nash [20] representations. However, this was not feasible for the DMCA-iodine monochloride system because of the low absorbance and high K_c value for this complex. The algebraic procedure of Liptay [21] was adopted for this system and the Scott representation was applied to the other systems. The values for K_c and ε as calculated from absorption data at the BS peaks are listed in Table 1. From these data the thermodynamic functions $\Delta H°$, $\Delta G_{25}°$, and $\Delta S°$ were obtained by standard procedure.

Ultraviolet region. In the region above 260 mμ DMCA has low intensity bands at 262 mμ ($\varepsilon = 1.9$ l mole^{-1} cm^{-1}) and 269 mμ ($\varepsilon = 0.9$ l mole^{-1} cm^{-1}). The mixed solutions of DMCA and iodine, iodine monochloride or iodine monobromide in carbon tetrachloride showed strong absorption around 260 mμ superposed on the DMCA and the halogen absorption. However, the maxima were beyond the cut-off region for carbon tetrachloride. The absorption curves for the DMCA-iodine system in heptane are given in Fig. 4. It appears that the complex absorption peak was situated at 259 mμ. In the iodine monobromide system the maximum was observed at 247 mμ and in the iodine monochloride system around 244 mμ. However, the latter was not stable in heptane and the absorption curves changed rapidly with time. Another difficulty arose from the DMCA absorption below 265 mμ. Therefore carbon tetrachloride was chosen as the solvent in the quantitative studies.

Table 1. Formation constants, extinction coefficients, and thermodynamic functions for the dimethyl cyanamide complexes with iodine, iodine monochloride, and iodine monobromide in carbon tetrachloride obtained from the BS bands.

DMCA complexes with	Temp °C	K_c l/mole	ε^a l/mole cm	Thermodynamic functions		
$I_2{}^b$	13	2.14	1110	$-\Delta H°$	=	2.8 kcal/mole
	23	1.82	1095	$-\Delta G_{25}°$	=	0.34 kcal/mole
	43	1.48	1080	$-\Delta S°$	=	8.2 e.u.
ICl^c	13	216	196	$-\Delta H°$	=	7.3 kcal/mole
	26	120	190	$-\Delta G_{25}°$	=	2.9 kcal/mole
	44	60	188	$-\Delta S°$	=	15.1 e.u.
IBr^d	9	27.5	409	$-\Delta H°$	=	5.6 kcal/mole
	20	18.8	396	$-\Delta G_{25}°$	=	1.64 kcal/mole
	40	10.0	390	$-\Delta S°$	=	13.3 e.u.

^{a} Extinction coefficients at the BS peaks.

^{b} The values were calculated from the absorption data at 450 mμ at 11 different DMCA$-I_2$ solutions using the Scott representation. [I_2] = 0.001089 M, [DMCA] varied from 0.06564 M to 1.3127 M, using 1 cm cells.

^{c} The values were calculated from the absorption data in the region 360$-$340 mμ, normalized at 353 mμ, using the Liptay algebraic method on 9 different DMCA$-$ICl solutions. [ICl] = 0.005439 M, [DMCA] varied from 0.004408 M to 0.03967 M, using 1 cm cells.

^{d} The values were calculated from the absorption data at 397 mμ of 10 different DMCA$-$IBr solutions using the Scott representation. [IBr] = 0.0005166 M, [DMCA] varied from 0.01214 M to 0.2185 M, using 5 cm cells.
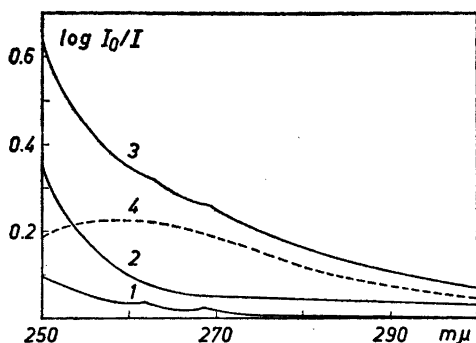
Fig. 4. The ultraviolet absorption spectra of DMCA-iodine solutions in heptane at 20°C for 1 cm cell: Curves (1) 0.01674 M DMCA; (2) 1.402 × 10⁻⁴ M iodine; (3) 0.01674 M DMCA and 1.402 × 10⁻⁴ M iodine, and (4) constructed absorption curve of the complex.
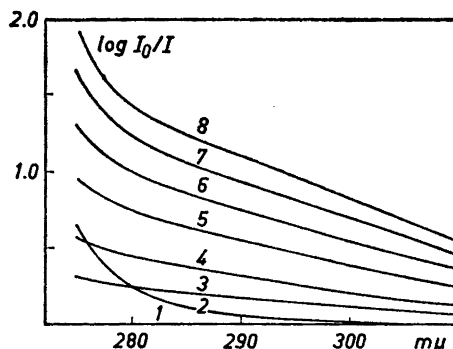
Fig. 5. Ultraviolet absorption spectra of DMCA and iodine (2.968 × 10⁻⁴ M) in carbon tetrachloride at 20°C for 1 cm cell. The concentrations (M) of DMCA are: (1) zero; (3) 0.09763; (4) 0.1953; (5) 0.3905; (6) 0.5858; (7) 0.7810, and (8) 0.9763. Curve (2) represents the absorption of 0.9763 M DMCA.

Mixed solutions of the three DMCA-halogen systems were recorded in the region 285—265 mμ at 20°C and the DMCA-iodine system is given in Fig. 5. The considerably higher complex absorption in this region permitted the use of lower halogen concentrations than formerly in the visible spectra. The Scott equation was well satisfied under these conditions and K_c and ε were calculated from absorption data at various wave lengths.

Obviously, higher DMCA concentrations were needed in the iodine than in the interhalogen solutions resulting in greater interference from DMCA

Table 2. Formation constants and extinction coefficients for the dimethyl cyanamide complexes with iodine, iodine monochloride, and iodine monobromide in carbon tetrachloride at 20°C obtained in the ultraviolet region by the Scott representation.

Wave length mμ	I₂[a]		ICl[b]		IBr[c]	
	K_c l/mole	ε l/mole cm	K_c l/mole	ε l/mole cm	K_c l/mole	ε l/mole cm
265			158	1600		
270			155	1120	16.5	4.200
275	1.65	5.200	153	735	15.8	3.300
280	1.60	4.300			15.4	2.500
285	1.56	3.550				

[a] The values were calculated from absorption data of 8 different DMCA—I₂ solutions. [I₂] = 3.343 × 10⁻⁴ M, [DMCA] varied from 0.06060 M to 0.7273 M, using 1 cm cells.

[b] The values were calculated from absorption data of 8 different DMCA—ICl solutions. [ICl] = 7.241 × 10⁻⁴ M, [DMCA] varied from 0.008446 M to 0.03378 M, using 1 cm cells.

[c] The values were calculated from 9 different DMCA—IBr solutions. [IBr] = 2.462 × 10⁻⁴ M, [DMCA] varied from 0.01321 M to 0.1585 M, using 1 cm cells.

absorption in the former system. The data are listed in Table 2 and it appears that the K_c values for each system are lower than those calculated from the visible spectra. Moreover, absorption data closer to the CT peak give higher K_c values and better agreement with the data in Table 1.

Infrared region. The infrared spectrum and vibrational assignments for DMCA have been reported by Davies and Jones.[13] We recorded solutions of DMCA in carbon tetrachloride and carbon disulphide in the region 4000—650 cm⁻¹ and studied the spectral changes on addition of iodine, iodine monochloride, or iodine monobromide. Iodine showed no effect, while the interhalogens caused perturbation of some infrared bands. DMCA has the $C\equiv N$ stretching frequency at 2219 cm⁻¹ in carbon tetrachloride[13] and we observed that this peak was shifted approximately 5.5 cm⁻¹ to higher frequencies with added iodine monochloride. Moreover, the integrated intensity was considerably enhanced and the half intensity width increased from 14 cm⁻¹ to approximately 31 cm⁻¹. In a mixed solution of 0.02 M DMCA and 0.08 M iodine monochloride, nearly 90 % of the donor should be complexed at approx. 25°C. If the halogen concentration was increased further, a new shoulder appeared at 2195 cm⁻¹. However, at these high halogen concentrations the infrared spectra were not stable with time. A few other spectral changes occurring at high iodine monochloride concentrations also indicated irreversible reactions.

Similar but smaller perturbations of the $C\equiv N$ stretching band appeared with iodine monobromide. The integrated intensity and the half intensity width increased, and a slight displacement of approximately 1 cm⁻¹ towards shorter wave length was observed. For comparison the corresponding shifts for acetonitrile and benzonitrile were 7 and 5 cm⁻¹, respectively. In the DMCA spectrum iodine monobromide concentrations exceeding approx. 0.2 M produced a shoulder at 2195 cm⁻¹ as in the iodine monochloride system. However, spectral changes with time suggested irreversible reactions also in this case.

It is well known that the nitriles can act as proton acceptors in hydrogen bond formation[12] to phenol and to alcohols. However, they form weaker hydrogen bonds than the amines.[22] We found it of interest to study qualitatively the hydrogen bonding properties of DMCA in comparison with the data reported for the nitriles.[12] Neither methanol nor phenol have infrared absorption bands in the $C\equiv N$ stretching region around 2250 cm⁻¹. In mixed solutions of DMCA (0.06 M) with phenol (0.2 M) and methanol (0.2 M) in carbon tetrachloride the $C\equiv N$ stretching band was shifted upwards by 5 and 2 cm⁻¹, respectively. The corresponding shifts in the acetonitrile systems were 8 and 2 cm⁻¹ with phenol and methanol, respectively, and in the benzonitrile system 5 and 1 cm⁻¹.

The enthalpies of formation associated with the hydrogen bonding between phenol and the nitriles can be estimated from the well known frequency shift correlations[23] of the O—H stretching vibration. Pimentel *et al.*[24] have reported large deviations from straight line plots between $\Delta H°$ and $\Delta \nu_{OH}$ for phenol associating with bases having different structures. For structurally related bases, however, the correlation is approximately valid as shown by Mitra[12] for the nitriles. The monomeric species of phenol in carbon tetrachloride has

its ν_{OH} (free) at 3611 cm^{-1}. The ν_{OH} (associated) was observed in mixtures of phenol (0.005 M) and acetonitrile, benzonitrile and DMCA. The shifts $\Delta\nu_{OH}$ had the following values: 160 cm^{-1} in the acetonitrile and the benzonitrile systems and 245 cm^{-1} in the DMCA-phenol system. By extrapolating Mitra's line the enthalpies of formation for the acetonitrile, benzonitrile and DMCA hydrogen bonds with phenol are: -3.9, -3.9 and -5.8 kcal/mole, respectively.

DISCUSSION

The spectroscopic data observed in the visible, ultraviolet and infrared regions are compatible with the formation of (n,σ) charge transfer complexes between DMCA and the halogens. Thus, characteristic blue shifts of the visible halogen bands occurred on complex formation. Moreover, these shifts were larger than those observed for the corresponding benzonitrile,[7] propionitrile [8] and acrylonitrile [10] systems suggesting considerably stronger interactions with DMCA.[25] The ultraviolet absorption bands observed in the region $240-300$ mμ have been interpreted as the charge transfer absorption of the complexes. It should be noted that for the aliphatic nitriles charge transfer absorption with the halogens have not been reported [6,8,11] as expected from the high ionization potentials of these donors. In benzonitrile [7] the band may be covered by the strong aromatic absorption, and in acrylonitrile [10] an absorption tail below 230 mμ might be interpreted as a charge transfer absorption. The ionization potential of DMCA is not known, but applying the linear relationship of McConnel, Ham and Platt [26] it should be approximately 10.0 eV. This value is close to that observed for benzonitrile [27] and considerably lower [27] than for acetonitrile and propionitrile. The aliphatic amines have ionization potentials in the region $8-9$ eV [28] and their charge transfer bands with iodine are situated in the region $245-285$ mμ.[3]

The continuous variation plots in Figs. 2 and 3 show that the DMCA-interhalogen complexes have 1:1 stoichiometry. This assumption is supported by the existence of isosbestic points in the visible region observed for each of the three systems. However, the inconsistent values for the formation constants in Table 2 might indicate the existence of more than one complex. In absorption matrix schemes after Liptay [21] the ζ_{ik} elements increased with higher K_c-values in the region $265-290$ mμ. These variations were most prominent at the high DMCA concentrations employed in the iodine complex. Similar changes in the ζ_{ik} of the DMCA-iodine monochloride system were hardly noticeable. As discussed by Liptay [21] such variations may indicate the existence of more than one complex, but can equally well be caused by changes in the ε of the complex with concentration. We have reported similar observations in different sulphoxide-iodine systems [29] and for dimethyl sulphoxide the CT-band was shown to shift towards longer wave lengths with higher donor concentrations. This displacement will result in a considerable change in ε at the steep slope of the band $15-30$ mμ from the peak, but in very small changes at the peak itself. K_c values calculated from absorption data at the side of the CT band will therefore give highly erroneous results. These conditions are likely to appear in weak complexes of strongly polar donors. The high donor

concentrations employed in these systems give rise to a considerable change in the bulk dielectric constant of the solutions. This effect may offer an explanation to the inconsistencies in Table 2.

It should be noted that bases with two or more donor sites generally form only 1:1 complexes with the halogens. Thus, the amides,[30] the cyclic disulphides and diselenides,[31] the sulphoxides [29] are all reported to form 1:1 complexes with iodine. Apparently the donation of a lone pair electron to iodine from one donor site effectively reduces the availability of the other lone pair electrons. In DMCA as well as in the other bases mentioned, the formation constants for eventual higher complexes must be very small compared to the K_c values for the 1:1 complexes.

According to Davies and Jones [13] DMCA as well as cyanamide itself do not have the pyramidal structure of the amines. The vibrational spectra of these compounds can be interpreted in terms of a planar configuration. This geometry is also in agreement with the assumption of strong delocalization of the lone pair electrons on the amine nitrogen. A planar arrangement of the skeleton $C_2=N-C\equiv N$ is a prerequisite for effective overlap of the amine lone pair orbitals with p-orbitals on the nitrile carbon and nitrogen atoms, resulting in a considerable gain in delocalization energy. The high stretching frequency and large force constant obtained by a normal coordinate treatment of cyanamide [13] suggest a high bond order for the $N-C\equiv$ bond as expected from the delocalization.

This structural model for DMCA can account for the spectral features observed on complex formation to the halogens and to phenol. Thus, the resonance structure of the type $>\overset{+}{N}=C=N^-$ will greatly increase the tendency of DMCA to act as an n donor from the nitrile nitrogen. The standard enthalpies of formation $\Delta H°$, the standard free energies of formation $\Delta G_{25}°$ or the formation constants K_c listed in Table 1 are considerably higher than the corresponding values reported for other nitriles.[6-11] Person, Golton and Popov [11] have obtained straight lines when log K_c for saturated, aliphatic nitriles with ICl, IBr, and I_2 were plotted *versus* the Taft σ^* constants. These linear correlations strongly suggest that mainly polar effects determine the base strength of these donors. However, the formation constants observed for the complexes between benzonitrile [7,9] or acrylonitrile [9,10] and the halogens are higher than predicted from these plots. In these molecules as well as in DMCA resonance effects undoubtedly contribute to the basicity. The fairly low ionization potential of DMCA, as inferred from the position of the CT band with iodine, is also in agreement with the delocalization of the orbitals.

The infrared data revealing an increase in the $C\equiv N$ stretching frequency on complex formation agree with earlier work on nitrile complexes with various Lewis acids.[9] This parallel behaviour of DMCA and aliphatic and aromatic nitriles strongly suggests that also DMCA forms complex bonds over the nitrile nitrogen. Furthermore, the lack of spectral changes in the region 1400—650 cm^{-1} on addition of iodine monochloride supports this conclusion. According to Davies and Jones [13] the normal vibrations mainly connected with stretching modes of bonds between the amine nitrogen and the neighbouring carbon atoms are found in this region. These infrared bands

should be perturbed if the bonding took place over the amine nitrogen. The possibility of a complex bond from this nitrogen at very high halogen concentrations cannot be ruled out completely, because irreversible reactions obscure the spectrum.

It appears that the $C \equiv N$ stretching frequency of DMCA was shifted less on complex formation with iodine monochloride than in the 17 different nitriles studied previously.[9] This supports the conclusion drawn earlier that there is no monotonic relationship between the frequency shifts ($\Delta \nu$) and the formation constants (K_c). The shift is undoubtedly caused by two opposing effects: a kinematic coupling of two oscillators which increases the frequency and a decrease in the bond order and force constant which tends to lower the frequency. We have reported [9] that the aromatic nitriles in which the π-electrons in the ring interact with the nitrile group show smaller shifts on complex formation to iodine monochloride than the aliphatic nitriles. The results obtained in the present study suggest that bonding to iodine monobromide and to phenol follow the same trend. For each Lewis acid the shift decreases in the order acetonitrile, benzonitrile, and DMCA, which is the same as that of increasing stability. Thus the enhanced mechanical interaction in the stronger acid base bond is more than outweighed by the decreased nitrile bond order.

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