spectrum in the infrared. We are not entirely satisfied with our work on this point and it will be investigated further.

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Molecular Addition Compounds of Tin(IV) Chloride. II. Frequency and Intensity of the Infrared Nitrile Absorption in Benzonitrile Complexes

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The infrared nitrile absorption in 1:1 complexes of a series of benzonitriles with tin(IV) chloride in benzene have been examined. The nitrile frequency is shifted to higher values, and the integrated band intensity is increased by at least tenfold in the complexes, as compared with the free nitrile. The results for the benzonitriles are compared with those for aliphatic nitriles, and the differences interpreted in terms of a simple molecular orbital model. The low frequency infrared spectra of tin(IV) chloride-bis-acetonitrile and tin(IV) chloride bis-p-methoxybenzonitrile as Nujol mulls are reported. From these it appears that the acetonitrile complex may be of cis symmetry, while the other is trans.

The first paper in this series dealt with the equilibria which obtain in benzene solutions of tin(IV) chloride and benzonitriles.[1] In the present paper the frequency and intensity of the infrared nitrile absorption of the complexed benzonitriles, and the low frequency (600–725 cm.$^{-1}$) infrared spectra of solid tin(IV) chloride-bis-acetonitrile and tin-(IV) chloride-bis-p-methoxybenzonitrile are reported and discussed.

Experimental

The data listed in Table I were obtained in the course of the experimental work reported in paper I.[1] The complex frequency, ν_c, listed for each benzonitrile is the frequency of maximum absorbance, after correction for overlap with the free nitrile band, of the band ascribed to complex formation. Under the conditions of the experiment this band is due almost entirely to 1:1 complex.[1]

The intensities of the complex band were estimated from use of Ramsay's equation.[2] The intensity is given by

$$A = K/cl$$

where

$$K = (1/2)2.303\pi\Delta\nu_{1/2} \log (T_0/T)_{max}$$

where $\Delta\nu_{1/2}$ is the half-intensity width of the complex band, $\log (T_0/T)_{max}$ is the observed absorbance at band maximum (corrected for overlap with the adjacent free base band). The concentration of the complex is taken to be just the concentration of the AB species alone, as calculated using K_{11} and K_{12} of paper I. The apparent values of intensity are then graphed vs. the calculated values of $[AB_2]/[AB]$ and the plot, which is roughly linear, extrapolated to zero value of the latter quantity. The limiting value of intensity is taken as the integrated intensity of the nitrile band in the 1:1 complex. The results probably are not very accurate, although the precision appears good. The uncertainty in the values of intensity for the complexes in benzene is perhaps ±10%.

The low frequency infrared data listed in Table II were obtained using a Perkin–Elmer model 112 spectrophotometer fitted with a CsBr prism. Thin polyethylene sheets were employed as windows for the spectrometer housing, which was thoroughly flushed with dry nitrogen gas. The instrument was calibrated using water vapor lines and a recommended calibration sample.[3] The frequencies listed probably are correct to within 2 cm.$^{-1}$, except where the

bands are very broad. The compounds examined in this region were studied as Nujol mulls.

TABLE I

FREQUENCIES AND INTENSITIES OF THE NITRILE ABSORPTION BANDS IN TIN(IV) CHLORIDE–BENZONITRILE COMPLEXES IN BENZENE SOLUTION

Substituent	$\nu_f{}^a$	ν_c	$\delta\nu$	$A_f{}^{b,c}$	$A_c{}^c$	ΔA	A_c/A_f
p-CH₃O–	2227	2249	22	0.34	3.3	3.0	9.7
p-CH₃–	2230	2254	24	.21	2.7	2.5	13
p-t-Butyl	2230	2253	23	..	..	..	..
m-CH₃–	2232	2256	24	.20	2.6	2.4	13
H	2231	2258	27	.15	1.95	1.8	13
p-F	2233	2258	25	.15	1.6	1.4	11
p-Cl	2233	2257	24	.14	1.8	1.7	13
p-NO₂	2235	2263	28	..	0.6	..	..

^{a} Frequencies in cm.$^{-1}$ ^{b} Free nitrile intensities for hexane solution. T. L. Brown, J. Am. Chem. Soc., **80**, 794 (1958). ^{c} Intensities in units of 1×10^4 mole^{-1} l. cm.$^{-2}$.

The solid complexes were prepared by addition of tin(IV) chloride to a slight excess of the base in carbon tetrachloride. The solids were filtered, washed a number of times with pentane and vacuum dried. All operations involved in the preparation of the compounds were conducted in a dry box.

Discussion

The effect of addition compound formation on the frequency and intensity of the nitrile absorption in benzonitriles may be understood in terms of a simple molecular orbital model for these properties of the nitriles themselves.[4] In this model a molecular orbital is formed from the highest occupied orbital in the phenyl (or substituted phenyl) ring and the lowest vacant orbital (π^*) in the nitrile group. To an extent which depends on the relative energies of these two orbitals, as effected by the meta or para substituent, electron density is "transferred" from the ring to the nitrile group.[5]

As the carbon–nitrogen bond distance changes in the characteristic nitrile vibration, the pi electron energy levels in the nitrile bond also change. This effect is responsible for the major contribution to the absorption intensity.[4]

(1) T. L. Brown and M. Kubota, J. Am. Chem. Soc., **83**, 331 (1961).
(2) D. A. Ramsay, ibid., **74**, 72 (1952).
(3) R. N. Jones, D. K. Faure, W. Zakarias, Revue Univ. Mines XV 417 (1959), cf. P. W. Behnke, Perkin–Elmer Corp. Reprint MPL-5603, 10505.
(4) T. L. Brown, J. Phys. Chem., **64**, 1798 (1960).
(5) S. Nagakura, J. Chem. Phys., **23**, 1441 (1955).

Addition compound formation can be thought of as the formation of a σ molecular orbital involving the occupied non-bonding orbital on the nitrogen atom and a vacant tin atomic orbital. The two orbitals are close enough in energy so that a fairly strong bond is formed, with a resultant transfer of electrons away from the nitrogen atom.[6] The energies of both the bonding and antibonding π orbitals in the nitrile group are lowered as a result of this interaction, because the coulomb integral of the nitrogen atom, which is already greater than that of the carbon atom, is increased. This has the effect of decreasing the energy difference between the nitrile orbital and the ring orbital, with the result that the interaction between these two increases.[7] It follows that the carbon–nitrogen bond order should decrease and that the intensity of the nitrile absorption should increase.[7] Benzonitrile addition compounds should show different behavior in some respects from the aliphatic nitrile compounds, since in the latter the interaction of the nitrile group with the ring is absent. In the discussion which follows these considerations will be measured against the experimental results.

TABLE II

LOW FREQUENCY (600–275 CM.$^{-1}$) INFRARED SPECTRUM OF NUJOL MULLS OF TIN(IV) CHLORIDE–NITRILE ADDITION COMPOUNDS (FREQUENCIES IN CM.$^{-1}$)[a]

SnCl₄·2CH₃CN	SnCl₄·2p-CH₃OC₆H₄CN	Assignment
397w	413w	Sn–Cl
393w	405w	Sn–Cl
367s	360vs	Sn–Cl
333–345vs	337vs	Asymm. Sn–N
305m	303w	Symm. Sn–N

[a] w, weak; s, strong; vs, very strong; m, medium.

The Nitrile Frequency.—An increase in the frequency of the nitrile absorption upon Lewis acid–base interaction appears to be quite general.[8–11] In at least one place the effect has been explained in terms of an increase in the carbon–nitrogen bond order.[10] Dows and co-workers have examined the effect of bridging on the frequency of cyanide groups[12] and have shown that the major part of the frequency increase is associated with the mechanics of the system and does not require an increase in the cyano bond force constant. In the general case of a bond Y–X: where the bond between Y and X may be a double or triple bond (there may be more than one unshared electron pair on X) and where X is more electronegative than Y, the donation of the unshared electron pair to a Lewis acid nearly always lowers the Y–X frequency.[9,13–15]

This result is directly interpretable in terms of a decrease in the Y–X stretching force constant. The nitrile interactions represent an exception, in that the C≡N stretching frequency increases on addition compound formation. It does not follow immediately that the nitrile force constant is thereby increased. The results of a simplified normal coördinate analysis given in the appendix show that in the aliphatic nitriles the C≡N force constant possibly increases a little, while in the benzonitriles it apparently decreases slightly on interaction with tin(IV) chloride (Table III).

It is interesting to note (Table I) that among the benzonitriles the change in frequency on addition compound formation decreases with increasing stability of the addition compound, as measured by the formation constant.[1] This trend appears to be the reverse of that which follows from comparison of a given nitrile with a series of Lewis acids,[8] in which the frequency change increases with increasing addition compound stability. The effect observed in the substituted benzonitriles follows from the molecular orbital model discussed earlier. Addition compound formation causes a lowering of the π^* orbital energy level in the nitrile group. The lowering results in greater contribution of this orbital to the MO formed with the highest occupied ring orbital, and, obversely, a lower nitrile bond order.[4]

This effect is most important when the energy difference between the ring and nitrile orbitals is smallest, as it is when electron-releasing groups are substituted on the ring. Addition compound formation on the part of the nitriles leads, then, to two different effects. The formation of the acid–base bond, merely because of the mechanical properties of the system tends to cause an increase in the nitrile absorption frequency. At the same time the interaction of the ring and nitrile orbitals is changed in such a way as to lead to a decrease in the nitrile frequency. The latter effect grows relatively more important with increased electron-releasing character of the substituents, as evidenced by the slightly smaller frequency increase for those benzonitriles (Table I). The fact that the nitrile frequency in the acetonitrile complex is much higher than in any of the aromatic nitrile complexes (Table III) lends support to this interpretation.

The Low Frequency Spectra.—The infrared spectral results listed in Table II deserve some comment. The frequencies assigned to the Sn–Cl bond are not far removed from those in SnCl₄.[16] The remaining two frequencies are assigned tentatively to the symmetric (303 cm.$^{-1}$) and asymmetric (337 cm.$^{-1}$) tin–nitrogen vibrations. These two frequencies are about the same in the two complexes; the indication is that the force constant of the tin–nitrogen bond is about the same in both (Table III). It is noteworthy that while the lower frequency band is fairly intense in the acetonitrile

(6) R. S. Mulliken, J. Am. Chem. Soc., 64, 811 (1952).

(7) It is also possible that a vacant tin atomic orbital (5d) of appropriate symmetry contributes to a molecular orbital involving the ring and nitrile orbitals; we ignore this possibility in the discussion which follows.

(8) H. J. Coerver and C. Curran, J. Am. Chem. Soc., 80, 3522 (1958).

(9) Y. N. Terenin, W. Filimonov and D. Bystrov, Z. Elektrochem., 62, 180 (1958).

(10) W. Gerrard, M. F. Lappert, H. Pyszora and J. W. Wallis, J. Chem. Soc., 2182 (1960).

(11) S. Califano, R. Moccia, R. Scarpati and G. Speroni, J. Chem. Phys., 26, 1777 (1957).

(12) D. A. Dows and A. Haim and W. K. Wilmarth (private comm.).

(13) B. P. Susz and P. Chelandon, Helv. Chim. Acta, 41, 1332 (1958).

(14) I. Lindqvist, Acta Chem. Scand., 13, 1159 (1959).

(15) J. C. Sheldon and S. Y. Tyree, J. Am. Chem. Soc., 81, 2290 (1959).

(16) Landolt-Börnstein, "Zahlen Werte und Funktionen," Pt. 2, Mol. 1, Springer-Verlag, Berlin, 1951.

complex, it is barely discernible in the p-methoxy compound. This suggests that the acetonitrile complex is of *cis* symmetry, while the p-methoxybenzonitrile complex is *trans*. The low intensity absorption which does appear at 303 cm.$^{-1}$ in the latter compound may be due to a small amount of the *cis* isomer or to lattice effects which remove slightly the selection rule restriction. This evidence regarding the geometry of the p-methoxybenzonitrile complex parallels the results of dielectric constant measurements of benzene solutions of benzonitrile and tin(IV) chloride,[1] although the evidence in both instances is weak. The much lower solubility of the acetonitrile complex in benzene may also be ascribed to its *cis* geometry.

The Nitrile Intensity.—The intensities of the complexed nitrile absorptions relate closely to the points just mentioned. The variation in the nitrile absorption intensity with substituent has been treated previously.[4] The same considerations apply to the complexed nitriles, with the exception that the lowering of the π^* level of the nitrile group upon addition compound formation results in an increased intensity. The intensity increase is much larger for the benzonitriles substituted with electron releasing substituents, a result which is consistent with the observed frequency variations, as discussed.

It is interesting that the square root of the complexed nitrile intensity correlates with the electrophilic substituent constants just as the free nitrile intensities[4]; the slope of the correlation line is, however, steeper. The extent to which the slope changes in this correlation as the Lewis acid is varied should provide an interesting measure of acid strength.

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Appendix

The vibrational system to be considered is the linear

$$
\begin{array}{cccc}
F_1 & F_2 & F_3 \\
M_1\!-\!M_2\!-\!M_3\!-\!M_4
\end{array}
$$

where M_1 equals 15 (CH_3) or 100 (p-$CH_3OC_6N_4$), $M_2 = 12$ (C), $M_3 = 14(N)$ $M_4 = \infty(SnCl_4)$. The axial vibrations only are considered. In a more precise treatment one would need to consider the interaction which leads to the symmetric-asymmetric Sn–N frequency difference in the 2:1 complexes. In the present case the frequency of the tin-nitrogen mode is taken as the mean of the two frequencies which are assigned to the symmetric and asymmetric tin-nitrogen vibrations. If the assignment of these two frequencies is correct the approximation is good, since the central group possesses a large mass. If the assignment is incorrect and only the higher frequency, for example, is a tin-nitrogen vibration, the results are not qualitatively changed. Only the value for the tin-nitrogen force constant, F_3, would be affected to any extent. Table III contains the requisite experimental information, as well as the results of the

TABLE III

RESULTS OF NORMAL COÖRDINATE ANALYSIS OF NITRILE–TIN VIBRATIONS IN TIN(IV) CHLORIDE–NITRILE ADDITION COMPOUNDS

Compound	$\nu_1{}^a$	ν_2	ν_3	$F_1{}^b$	$F_2{}^b$	$F_3{}^b$
CH_3CN	2248^c	920^d	..	5.2	17.4	0
$SnCl_4\cdot2CH_3CN$	2303^e	940^d	322^e	5.2	17.6	3.1
p-$CH_3OC_6H_4CN$	2227^e	..	..	5.5	17.1	0
$SnCl_4\cdot2p$-$CH_3OC_6H_4CN$	2249^f	..	320^e	5.5	16.9	3.1

^{a} Frequencies in cm.$^{-1}$. ^{b} Force constants in units of mdynes/Å. ^{c} Ref. 8; spectrum in benzene solution. ^{d} Ref. 9; spectrum of solid. ^{e} Present work; spectrum of solid as Nujol mull. ^{f} Present work; spectrum in benzene solution. This is essentially the nitrile frequency for the 1:1 complex, which differs very little, if at all, from that for the 2:1.

calculations. The values for F_1 were assumed. The results of interest, the values for F_3 and the *change* in F_2 on addition compound formation, are not sensitive to the choice of F_1. No interaction force constants were employed. A trial calculation was made with an interaction force constant F_{23} of $+0.5$ mdyne/Å. The result was slightly higher value for F_2 (about 0.2 mdyne/Å. higher) and a slightly lower value for F_3. It thus remains true that the force constant of the nitrile group in the addition compounds is lower for p-methoxybenzonitriles than for acetonitrile.

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On the Electronic Spectra of Some Substituted Benzenes

BY ASISH KUMAR CHANDRA

Conjugative and inductive effects in styrene, phenylacetylene, benzaldehyde and benzonitrile are determined by means of second order perturbation method based on the molecular orbital theory including electron interaction and neglecting overlap. It is shown that mixing of locally excited states and the electron transfer states arising from the transfer of electron from the benzene to the substituent and from the substituent to the benzene is of importance in determining the energies of lower electronic states of substituted benzenes. Inductive parameters for phenylacetylene, benzaldehyde and benzonitrile are also determined.

The electronic spectrum of a composite alternant hydrocarbon R–S was theoretically discussed by Longuet-Higgins and Murrell[1] in relation to the excited electronic states of the separate fragments RH and SH. It was shown that the mixing of the locally excited states and the electron transfer states plays an important role in the electron migration effect. In their calculations on the electronic spectra of composite hydrocarbons only one-electron transfer configurations were considered but interactions with two-electron transfer configurations are not negligible. It was shown by

(1) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **68A**, 601 (1955).