tographed on Woelm neutral alumina with benzene and recrystallized from ethanol by evaporation, mp 107–108°.

Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.2; H, 5.04; N, 8.75; O, 15.0. Found: C, 71.8; H, 5.11; N, 8.30; O, 14.7.

7. 2-Chlorotriphenylamine was prepared from diphenylamine and *o*-iodochlorobenzene. The crude product was chromatographed on basic alumina. An oil was obtained repeatedly on attempted recrystallizations, so this oil was vacuum distilled, bp ~200° (~1 mm).

Anal. Calcd for $C_{18}H_{14}NCl$: C, 77.4; H, 5.07; N, 5.05; Cl, 12.6. Found: C, 78.1; H, 5.11; N, 5.22; Cl, 11.5.

8. 3-Methoxytriphenylamine was prepared from diphenylamine and *m*-iodoanisole. The product was chromatographed on basic alumina with benzene. An oil was obtained upon attempted recrystallization.

Anal. Calcd for $C_{19}H_{17}NO$: C, 82.9; H, 6.22; N, 5.09; O, 5.80. Found: C, 83.3; H, 6.18; N, 5.32; O, 5.33.

9. Tri-*m*-anisylamine was prepared from *m*-anisidine and *m*-iodoanisole. The crude product was chromatographed on basic alumina with benzene and an oil was obtained from ethanol upon evaporation.

Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.3; H, 6.33; N, 4.18; O, 14.2. Found: C, 75.1; H, 6.17; N, 4.24; O, 14.5.

10. Tris(*m*-nitrophenyl)amine was prepared from *m*-nitroaniline and *m*-iodonitrobenzene. The tar was dissolved by refluxing with benzene for 48 hr. The crude product was chromatographed on neutral alumina with benzene. The first band to come off was a side product, 3,3′-dinitrobiphenyl. The next fraction was collected and passed through a column again, and most of the remaining biphenyl was removed. The second band was collected and the pure product was obtained by recrystallization from benzene–ethanol, mp 232–233°.

Anal. Calcd for $C_{18}H_{12}N_4O_6$: C, 56.8; H, 3.18; N, 14.7; O, 25.3. Found: C, 57.2; H, 3.41; N, 13.6; O, 25.8.

B. Substituted Benzidines. 1. N,N′-Di-*p*-tolyl-N,N′-diphenylbenzidine was prepared from N,N′-diphenylbenzidine and *p*-iodotoluene. The product was chromatographed on basic alumina with benzene and recrystallized from methanol, mp 154–156°.

Anal. Calcd for $C_{38}H_{32}N_2$: C, 88.3; H, 6.24; N, 5.42. Found: C, 88.1; H, 6.28; N, 5.53.

2. N,N′-Di-*p*-anisyl-N,N′-diphenylbenzidine was prepared from N,N′-diphenylbenzidine and *p*-iodoanisole. The crude product was chromatographed on basic alumina with benzene and recrystallized from benzene–methanol by evaporation, mp 154–156°.

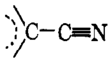
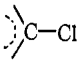
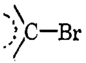
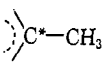
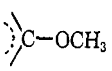
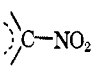
Anal. Calcd for $C_{38}H_{32}N_2O_2$: C, 83.2; H, 5.88; N, 5.11; O, 5.83. Found: C, 83.4; H, 5.98; N, 4.94; O, 5.71.

3. N,N′-Di-*p*-nitrophenyl-N,N′-diphenylbenzidine was prepared from N,N′-diphenylbenzidine and *p*-iodonitrobenzene. The product was chromatographed twice on neutral alumina with benzene and recrystallized from benzene–methanol, mp 186–189°.

Anal. Calcd for $C_{36}H_{26}N_4O_4$: C, 74.7; H, 4.53; N, 9.68; O, 11.1. Found: C, 75.5; H, 4.77; N, 9.16; O, 10.6.

Parameters for HMO Calculations. For all calculations, the following values were taken for the "central" triphenylamine nitrogen: $h_N = 1.0$, $k_{N-Cl} = 0.8$ (for all three N-phenyl carbon bonds). For a mono-*ortho*-substituted triphenylamine, the resonance integral for the pertinent N-C bond was varied from $k_{N-C} = 0.8$ *via* the usual twisting calculations. For the tri-*ortho*-substituted compounds, all three k_{N-C} values were varied simultaneously by the same amount to account for twisting.

The following heteroatom parameters were employed for the various substituents indicated.

	$k_{CC} = 0.9$, $k_{CN} = 2.0$, $h_N = 1.0$, $h_{C(cyano)} = 0.0$
	$k_{CCl} = 0.4$, $h_{Cl} = 2.0$
	$k_{CBr} - 0.3$, $h_{Br} = 1.5$
	$h_{C^*} = -0.3$ (inductive model, neglecting methyl C)
	$h_{CO} = 0.8$, $h_O = 2.0$ (methyl carbon neglected)
	$k_{CN} = 1.2$, $h_N = 2.2$, $k_{NO} = 1.67$, $h_O = 1.4$

Far-Infrared Intensity Studies of Complexes of Some Pyridine Bases with Iodine Monochloride

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Received December 2, 1967

Abstract: Studies are reported of the far-infrared spectra of complexes of ICl with pyridine, 3-picoline, and 2,6-lutidine. The frequencies and the intensities are given for both the I-Cl stretching vibration (~290 cm^{-1}) and the N-I stretching vibration (115–140 cm^{-1}) measured for complexes dissolved in benzene. The measurements were made with a Beckman IR-11 far-infrared spectrometer, using polyethylene cells. Experimental techniques for intensity measurements in this region of the spectrum are discussed. Attempts to obtain normal coordinates are described. Some interpretation is given of these results in terms of the theory presented by Friedrich and Person.

Studies of the changes in the vibrational spectra of the donor (D) and acceptor (A) molecules when they combine to form a complex have been a powerful aid in elucidating structural changes occurring in that process.[3] For example, earlier studies[4,5] of the I-Cl stretching vibration in complexes of ICl with different electron donors revealed a characteristic decrease of frequency and increase in intensity of that vibration as

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[2] Reprint requests should be sent to Dr. Person at this address.

[3] See (a) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964; (c) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, 13, 107 (1962).

[4] W. B. Person, R. E. Humphrey, W. A. Deskin, and A. I. Popov, *J. Am. Chem. Soc.*, 80, 2049 (1958).

[5] W. B. Person, R. E. Erickson, and R. E. Buckles, *ibid.*, **82**, 29 (1960).

Table I. Analytical Data for ICl Complexes

Compound	Mp, °C		% C		% H		% N	
	Found	Lit.[a]	Found	Calcd	Found	Calcd	Found	Calcd
Pyridine–ICl	131–133	132	25.1	24.8	2.5	2.1	5.6	5.8
3-Picoline–ICl[b]	55–56	. . .	28.3	28.2	2.9	2.7	4.9	5.5
2,6-Lutidine–ICl	112–114	112–113	32.6	31.2	3.6	3.3	5.0	5.2

[a] From ref 17. [b] Previously unreported compound.

the strength of the donor increased. These changes were interpreted in terms of the Mulliken theory[6] by Friedrich and Person,[7] following ideas first presented by Ferguson and Matsen.[8] However, the early experimental data[4,5] were not as accurate as can be expected from the new far-infrared spectrometers which are now available.

Furthermore, it has recently become possible to make measurements in the far-infrared region of the spectrum more or less routinely. As a result, there has been a flurry of activity in this field of research, aimed especially at locating the vibrations of the donor against the acceptor. For example, Ginn and Wood have recently reported studies of pyridine complexes with I$_2$, ICl, and IBr; they have located the intermolecular N–I stretching vibration near 150–180 cm^{-1} in the latter two complexes.[9] Other far-infrared work on complexes of pyridine bases with halogens by Yada, Tanaka, and Nagakura,[10] by Watari,[11] by Maki and Nelson,[12] and by Yagi, Popov, and Person[13] and in the Raman spectrum by Klaboe[14] verify and extend these results for the frequency shift of the I–X band and the new frequency of the N–I band.

The intensity change of the I–X band has been of considerable importance,[3–5,7,8] and the intensity of the intermolecular N–I band should be of as much interest. Recently the latter has been measured in pyridine complexes of I$_2$,[15] and we have also reported studies of I$_2$ complexes.[16] Some of the results which we found for the intensities of I–I stretch in the latter study were inconsistent with our earlier work,[4,5,7] but the data for the pyridine–I$_2$ complexes were quite reasonable.

We report here the study of the intensities of both the I–Cl stretch and the N–I stretch for complexes of ICl with pyridine, 3-picoline, and 2,6-lutidine. These complexes are easily prepared and are quite stable (with formation constants, $K_c = 4.8 \times 10^5$, 8.9×10^5, and 8.9×10^4 l./mole, respectively).[17] We had thought that the intensity or frequency of the N–I band, in particular, might show some interesting variation paralleling the small changes in K_c.

Experimental Section

Preparation and Purity of Materials. The pyridine, 2,6-lutidine (both Eastman), and 3-picoline (Matheson) were all reagent grade chemicals and were used without further purification apart from drying. The ICl had been prepared by the method of Cornog and Karges.[18] The amine–ICl complexes were prepared from solutions in CCl$_4$.[17] However, a much better yield of 2,6-lutidine–ICl complex was obtained on precipitating from *n*-heptane solution, presumably because of its lower solubility. The complexes were recrystallized repeatedly from CCl$_4$ solution until the melting points were reasonably constant at the values listed in Table I, which also summarizes other relevant analytical data. Although the bulk solid appeared to the eye to melt sharply at the temperatures listed in Table I, subsequent examination of the picoline–ICl and lutidine–ICl samples under a microscope revealed that small amounts of the solid melted 5–10° below the melting point of the bulk solid, even after repeated recrystallization. The low-melting crystals were more deeply colored than the very pale yellow "complex" crystals. No low-melting component was detected in samples of pyridine–ICl. The compounds were stored in a vacuum desiccator over barium oxide.

The benzene and CCl$_4$ used as solvents were both Eastman "Spectroquality." They were dried over Linde Molecular Sieve ($^1/_{16}$ in. pellets) before use in the far-infrared region, where minute traces of dissolved water can cause large background absorbance shifts. For example, the apparent absorbance at 250 cm^{-1} of undried benzene from a newly opened bottle was about 8% greater than that for a carefully dried sample.

Cells and Instruments. The problem of constructing cells for making quantitative measurements on halogen solutions in the region between 100 and 400 cm^{-1} is formidable. The window material must be rigid and transparent, but CsBr or CsI plates are clearly inadequate because of their reactivity.[4,5] Our cells were constructed from high-density polyethylene, 2.5 mm thick (obtained from Cadillac Plastic and Chemical Co., Chicago, Ill.). This material is virtually unaffected by many organic solvents and has only one weak absorption band below 500 cm^{-1} (at 72 cm^{-1}). It is sufficiently transparent and rigid so that standard Perkin-Elmer demountable liquid cells with these polyethylene windows are quite satisfactory. Spacers and gaskets were cut from thinner sheets of polyethylene or Teflon. The assembled cells were clamped in their holders tightly enough to prevent leaking. Thus, the only metal parts which came into contact with the solutions were the stainless steel syringe adapters of the standard Perkin-Elmer cell entry and exit ports. The empty polyethylene cells transmitted about 45% of the double-beam energy at 180 cm^{-1}; filled with benzene, the transmittance was about 40%. Absorption measurements were made on solutions of complex in benzene for which the transmittance (against air) varied from 15 to 40%.

A Beckman IR-11 spectrometer was used, continuously purged with clean, dry air from the Gilbarco drier. The spectrometer was calibrated using atmospheric water vapor and carbon dioxide lines found between 50 and 700 cm^{-1}.[19] The wavenumber accuracy was about ±0.5 cm^{-1}. The intensity and position of the very strong water band at 202.6 cm^{-1} was measured daily as a check on the purge and calibration. The purge was considered to be satisfactory when the absorption of this band was less than 30%. Frequent checks also were made to ensure that the 0 and 100% transmission reference points were correct. The reference comb was found to be linear within 1% at 50% transmission. The false energy was tested by measuring the apparent transmittance of a totally absorbing sample and found to be less than 3% above 100 cm^{-1}.

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(11) F. Watari, *Spectrochim. Acta*, **23A**, 1917 (1967).

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(13) Y. Yagi, A. I. Popov, and W. B. Person, *J. Phys. Chem.*, **71**, 2439 (1967).

(14) P. Klaboe, *J. Am. Chem. Soc.*, **89**, 3667 (1967).

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(16) J. Yarwood and W. B. Person, *J. Am. Chem. Soc.*, **90**, 594 (1968).

(17) A. I. Popov and R. H. Rygg, *ibid.*, **79**, 4622 (1957).

(18) J. Cornog and R. A. Karges, *Inorg. Syn.*, **1**, 165 (1939); see also A. I. Popov and R. E. Buckles, *ibid.*, **5** 172 (1959).

(19) K. N. Rao, R. V. de Vore, and E. K. Plyler, *J. Res. Natl. Bur. Std.*, **A67**, 351 (1963); L. R. Blaine, E. K. Plyler, and W. S. Benedict, *ibid.*, **A66**, 223 (1962).

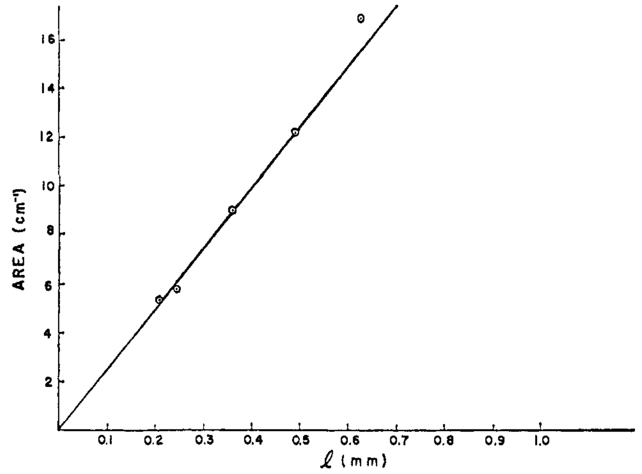

Figure 1. Calibration plot of band area *vs.* path length, using the 264-cm^{-1} band in pure liquid chloroform. (Note: for path lengths larger than 0.6 mm, the absorbance is greater than 1.0 near the peak at 264 cm^{-1}.)

The Golay detectors for the IR-11 easily developed faults, and only rarely were we able to obtain a detector which operated within the noise and energy specifications for longer than a few weeks. In many of our measurements reported here the noise level was higher than it should have been. However, modification of the slit program, speed of scan, gain, and time constant of the instrument permitted us to achieve satisfactory operating conditions.

We did not have linearity disks at the University of Iowa, so we did not test linearity of the absorbance scale reading. Subsequent tests of its linearity on a similar instrument at the University of Florida suggest that this error may have been systematic and about ±10%. This error may in fact account for the discrepancy between our results[16] and those of Lake and Thompson[15] for the I_2 complexes.

The spectra of the solutions were recorded using the IR-11 in the double-beam mode and using the spectrum of the cell plus solvent as the background. We use the linear absorbance scale, so that the integrated intensities, $B = (1/nl)\int \ln (I_0/I)\, d\nu$, could be obtained by measuring directly from the spectrum with a planimeter. (Here n is the concentration in moles/liter, l is the path length in centimeters, obtained as described below, I_0 is the background transmission, and I is the sample transmission. Hence, B is given in centimeters/millimole, or "darks.") The solid samples of complex were weighed into a volumetric flask, which was then filled with solvent to form the solution at the appropriate concentration, computed assuming no dissociation of the complex as it dissolved. These solutions were then transferred immediately to the polyethylene cells described above and the spectra measured.

The spectra of freshly recrystallized solids were obtained using Nujol mulls 1 mm thick, held between polyethylene plates.

Path-Length Calibration. Because polyethylene cells are not uniform enough so that their path lengths can be measured interferometrically,[20] and because the polyethylene and the Teflon used for spacers are both compressible to some extent, it was necessary to devise some alternative method of measuring the path lengths of these cells after construction. We have used the known intensities of three bands in common organic solvents in the 250–350-cm^{-1} region to obtain calibration graphs from which the path length of any polyethylene cell can be determined. The bands used for this purpose and their intensities are given in Table II. These intensities were easily measured using cells made from polished CsI plates and a metal spacer, whose path lengths *could* be determined by the interferometric method.[20] On plotting path length (l) against band area (in cm^{-1}) for one of these standards in the CsI cells, a straight line was obtained; from these plots, the path length of the polyethylene cell can be obtained from the band area measured for a standard sample. A typical Beer's law plot is shown in Figure 1 for the 264-cm^{-1} band of chloroform. For this pure liquid the background is chosen to match the absorbance in the wings of the band; this procedure is not expected to introduce any appreciable error in l since the error in choosing the background should be the same in both the CsI and the polyethylene cells. We believe that the path length of a polyethylene cell is accurate to about ±2–5%.

Table II. Far-Infrared Bands Used for Path-Length Calibration of Polyethylene Cells

Spacer thickness, mm	Band used (liquid phase)	Intensity,[a] cm mmole^{-1}
0.1–0.6	262-cm^{-1} band in $CHCl_3$	20.2
0.6–1.2	312, 330-cm^{-1} doublet in CCl_4	39.1[b]
1–5	300-cm^{-1} band in C_6H_6	16

[a] Measured here, using a cell with CsI windows (see text). [b] Notice that this value agrees well with the value (34 cm/mmole) obtained by C. F. Cook, W. B. Person, and L. C. Hall, *Spectrochim. Acta*, **23A**, 1425 (1967).

The path lengths of *thick* polyethylene cells (>1.5 mm) were measured with a micrometer, since the error caused by the compressibility of spacers of this thickness is very small.

Stability of the Complexes in Solution. The solubility of these complexes in carbon tetrachloride ($<1 \times 10^{-3}$ *M* at room temperature) is too small for quantitative measurements to be made in the infrared region; hence, direct comparison with the stabilities found in earlier studies[17] is not possible. Since the complexes usually decompose in common polar solvents (see below), the intensity measurements were made in benzene solutions. We found, however, that some slow decomposition of complex does take place even in benzene. The solutions are a bright yellow when made up, but they gradually turn pink over a period of 2–4 hr (depending on the concentration of complex). The reaction produces iodine (probably complexed with the benzene solvent) which we have identified by examination of the visible spectra of these solutions. No trace of absorption due to the ICl_2^- ion (at ~220 cm^{-1}) was found in the infrared spectrum of these complexes except when a polar solvent was used[4,5] or when cells with CsI plates were used. In the absence of CsI, very little decomposition of the complex occurs in benzene solution during the time periods used for quantitative measurements.

Results

Spectra of Complexes in Different Media. Relatively large changes in the frequencies of these vibrations [ν(I–Cl) and ν(N–I)] of these complexes have been reported from studies in different solvents, or as solids.[9,12] A summary of our frequency data for these complexes in Table III verifies these remarkable "solvent effects."

Solid-State Spectra. The solid complexes deteriorate somewhat over a long period of time. The spectra of Nujol mulls of freshly recrystallized material are given in Figure 2. The solid-state frequencies and band shapes vary somewhat from one mull to another. The I–Cl stretching band in both pyridine–ICl and 3-picoline–ICl is very broad ($\Delta\nu_{1/2}$ = 25–40 cm^{-1}), and the frequency of maximum absorption is somewhat difficult to locate, especially in view of the splitting of this band observed in some samples of the solid pyridine–ICl complex. The ICl band is remarkably narrow ($\Delta\nu_{1/2}$ only ~7 cm^{-1}) with no sign of any splitting for all samples of solid 2,6-lutidine–ICl. Furthermore, in samples of solid pyridine–ICl and 3-picoline–ICl, a broad doublet is observed for the N–I stretching band ($\Delta\nu_{1/2}$ = 20–25 cm^{-1}), split by 8–10 cm^{-1}, whereas the narrower 140-cm^{-1} band in 2,6-ludidine–ICl is apparently unsplit (Figure 2). There is, however, also a resolved weaker shoulder at about 118 cm^{-1} in the

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[20] See W. J. Potts, Jr., "Chemical Infrared Spectroscopy," Vol. I, "Techniques," John Wiley and Sons, Inc., New York, N. Y., 1963.

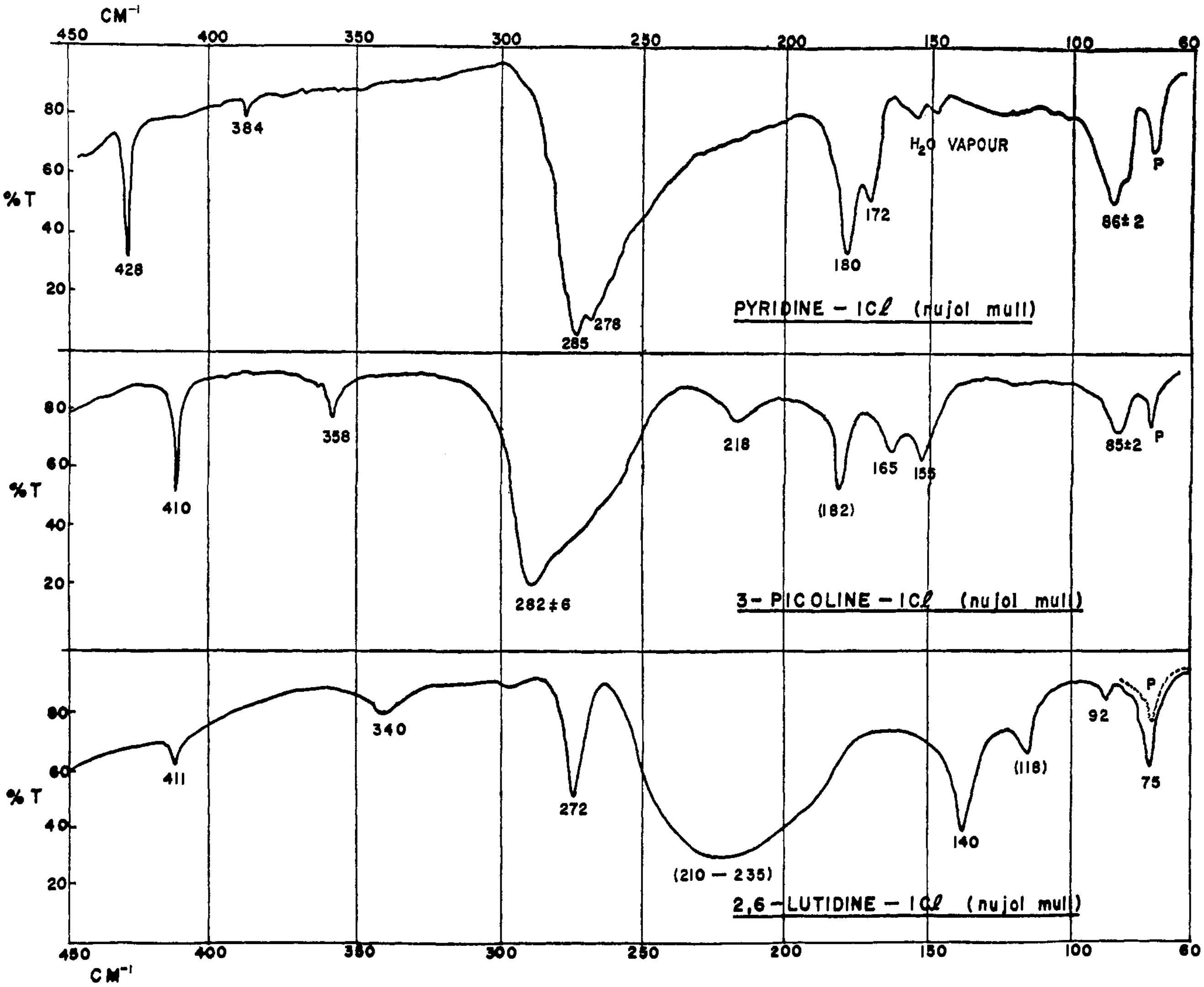

Figure 2. Spectra of some solid pyridine base–ICl complexes (in Nujol mulls) from 60 to 450 cm^{-1}.

Table III. Summary of Low-Frequency Data for ICl Complexes with Pyridine Bases

Complex	Vibration (approx description)	Solid (this work)		Solid M–N[a]	Benzene soln		Pyridine soln	
		ν_1, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ν_1, cm^{-1}	ν_1, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ν_1, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}
Pyridine–ICl	ν(I–Cl)	285 278 db[c]	25	277 db	292 ± 1 290[b]	20 ± 1	278 277[b]	30
	ν(N–I)	180 172 db	25	181 172 db	140 ± 1 147[b]	20 ± 1	(151) 160[b]	
	(N–I–Cl) bend	86 ± 2	. . .	. . .	. . .	. . .	. . .	. .
3-Picoline–ICl	ν(I–Cl)	282 ± 5	~43	270	290 ± 1	21 ± 1	278	24
	ν(N–I)	165 155 db	20	155	133	19 ± 1	. . .	
	(N–I–Cl) bend	85 ± 2	. . .	. . .	. . .	. . .	. . .	. .
2,6-Lutidine–ICl	ν(I–Cl)	272	7	273	290 ± 1	23 ± 1	278	23
	ν(N–I)	140	18	140	117	20 ± 1		
	(N–I–Cl) bend	75 ± 1(?)	. . .	. . .	. . .	. . .	. . .	. .

[a] Maki and Nelson, ref 12. [b] Work of Ginn and Wood, ref 9. [c] db = doublet.

spectrum of the latter which we cannot explain. The 3-picoline–ICl complex has a band at 180 cm^{-1} which is also of unknown origin.

The bands tentatively assigned in Table III to the bending vibration of the linear N–ICl group in these compounds are clearly defined for the pyridine and 3-picoline complexes, but in the lutidine complex this band is shifted to lower frequency somewhat and is, we believe, overlapped by the polyethylene absorption at 72 cm^{-1}.

From the details given in the Experimental Section, it is clear that our samples of pic–ICl and lut–ICl were not pure. (We shall use the abbreviations py, pic, and lut to mean pyridine, 3-picoline, and 2,6-lutidine, respectively.) From the analytical data given in Table I, we see that any appreciable amounts of impurities

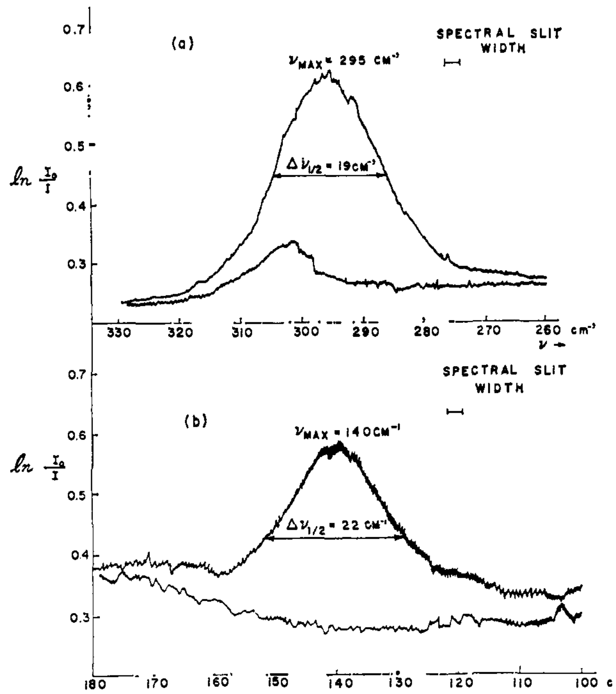

Figure 3. Spectra of pyridine–ICl in benzene solution. (a) ν(I–Cl): path length, 1.10 ± 0.03 mm; [py–ICl] = 0.0132 *M*. (b) ν(N–I): path length, 1.13 ± 0.04 mm; [py–ICl] = 0.0412 *M*.

existing in these samples must also have 1:1 stoichiometry. It seems possible that the absorption in pic–ICl near 180 cm^{-1} may be due to (pic–I–pic)$^+$ ions[21] formed in a reaction on the solid. To preserve the 1:1 stoichiometry, ICl_2^- ions might be expected to form; the strong absorption at 220 cm^{-1} (and weaker absorption near 260 cm^{-1}) expected for this anion[22,23] is not observed. Similar difficulties are encountered in attempting to explain the bands in solid lut–ICl, although it seems likely that some ICl_2^- is absorbing in our sample.

Since these bands are not observed in the spectra of solutions of the complexes in nonpolar solvents, and since their appearance does vary from sample to sample,[24] we believe them to be due to impurities of the type suggested above. We should emphasize that the spectrum of our sample of py–ICl exhibits bands which are attributable only to the 1:1 complex.[21] Table III includes only the bands which we believe are due to the complexes.

Solution Spectra. An attempt was made to study ν(I–Cl) and ν(N–I) in solutions of the complex in benzene and in pyridine. It may be seen from the gaps in Table III that these studies were only partially successful because of the overlapping intense absorption by these solvents in some regions of interest.

In solutions of the complex in pyridine, ν(I–Cl) comes at about 278 cm^{-1} in all three complexes, or about 12–14 cm^{-1} lower than in benzene solutions. Although this change is not very large, the percentage change in frequency (5%) is relatively much larger than those usually observed for such small environmental changes. Ginn and Wood[9] have interpreted this unusual frequency shift as an indication of an increase in stability of the complex in pyridine solution. This interpretation is supported by the parallel increase of about 11–15 cm^{-1} in the N–I stretching frequency of the py–ICl complex on going from benzene to pyridine solution (see Table III). Unfortunately we were unable to observe ν(N–I) in pyridine solution for comparison, either for pic–ICl or for lut–ICl because of the strong absorption by pure liquid pyridine below 140 cm^{-1}. In benzene solution the frequency of the N–I band decreases from py–ICl to lut–ICl, suggesting that the strength of the interaction affecting the frequency shift decreases in the order py–ICl > pic–ICl > lut–ICl. This order is to be contrasted with that found[17] for the formation constants, pic–ICl > py–ICl > lut–ICl, which presumably reflect the balance between enhancement of base strength (which affects the frequency) and steric repulsion by the methyl group substituent (which may have less effect on the frequency).

The visible spectra of all three complexes in benzene solution show a weak band at about 492 ± 3 mμ which gradually grows in intensity as the solution is allowed to stand. After a period of 2–4 hr (depending on the complex and concentration), the solutions are pinkish in color. The lut–ICl solutions in either benzene or carbon tetrachloride become pink within an hour if relatively large concentrations of complex are used. This visible band is almost certainly caused by iodine, shifted from 520 mμ[25] probably because of the interaction between iodine and the benzene solvent. The visible I_2 band is observed in lut–ICl solutions in CCl_4 but not for solutions of py–ICl or pic–ICl in CCl_4, nor for any of the complexes dissolved in pyridine. In pyridine solutions, however, the infrared band of ICl_2^- at 224 ± 2 cm^{-1} is observed with all three complexes. We should emphasize that neither this band nor the free ICl band at about 375 cm^{-1} is observed in benzene solutions, indicating that only 1:1 complex species are present in this solvent.

Intensity Measurements. The results from the intensity measurements are given in detail in Table IV and summarized in Table V. Measurements were made using between five and nine different *nl* values for each band. Each band area listed in Table IV is the average value from four or five separate measurements of the band under similar (or identical) instrumental conditions.

Figure 3 shows a typical spectrum from which intensities were measured. We see there that the background absorbance matches the absorbance of the solution in the wings of the band fairly well.

For each band a Beer's law plot was made to determine the "best" value of B_i listed in Table V (see Figure 4). For ν(I–Cl) in py–ICl, B_i in Table V was obtained from the plot using a least-squares treatment. However, B_i values for the other bands in Table V are obtained from a visual fit of a straight line to the data, since the extra work of a least-squares analysis was not justified by the quality of the data.

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[21] (a) J. A. Creighton, I. Haque, and J. L. Wood, *Chem. Commun.*, 229 (1966); (b) I. Haque and J. L. Wood, *Spectrochim. Acta*, 23A, 959 (1967).

[22] W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, and R. Forneris, *J. Chem. Phys.*, 35, 908 (1961).

[23] A. G. Maki and R. Forneris, *Spectrochim. Acta*, 23A, 867 (1967).

[24] Private discussions with Dr. A. G. Maki, National Bureau of Standards, indicate that he also observed these bands in his studies of solid ICl complexes,[12] although the bands were much weaker in his samples. The difference in relative intensities in the spectra of our two samples confirms the assignment of these bands to impurities, although we did not observe any variation in the spectra of samples which we attempted to purify further.

[25] C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, 76, 3869 (1954).

Table IV. Intensity Results for Pyridine Base–ICl Complexes in Benzene Solution

Complex	Band	ν_{max}, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	Run no.	*l*, mm	*nl* × 10^6, mole cm^{-1}	*Bnl* (av) area, cm^{-1}	B_i, cm mmole^{-1} (darks)
Pyridine–ICl	ν(I–Cl)	292	20	1	0.67 ± 0.03	0.79 ± 0.04	9.9 ± 0.4	12500 ± 1200
				2	0.67 ± 0.03	1.21 ± 0.06	16.1 ± 0.4	13300 ± 1000
				3	0.67 ± 0.03	1.82 ± 0.08	23.9 ± 0.7	13100 ± 900
				4	0.70 ± 0.02	1.63 ± 0.05	19.0 ± 0.5	11700 ± 700
				5	0.70 ± 0.02	1.04 ± 0.03	12.6 ± 0.4	12100 ± 900
				6	1.10 ± 0.03	1.07 ± 0.03	11.8 ± 0.4	11000 ± 500
				7	1.10 ± 0.03	2.05 ± 0.06	23.5 ± 0.7	11500 ± 800
				8	1.10 ± 0.03	1.45 ± 0.04	17.2 ± 0.8	11900 ± 900
				9	1.10 ± 0.03	0.83 ± 0.03	9.6 ± 0.5	11600 ± 1100
	ν(N–I)	140	20	1	1.10 ± 0.03	3.12 ± 0.08	13.4 ± 0.7	4295 ± 340
				2	1.13 ± 0.03	3.87 ± 0.10	13.3 ± 0.9	3426 ± 320
				3	1.13 ± 0.03	3.13 ± 0.07	11.8 ± 0.7	3756 ± 320
				4	1.13 ± 0.04	4.66 ± 0.11	17.4 ± 1.0	3750 ± 300
				5	2.32 ± 0.02	7.41 ± 0.07	30.7 ± 0.5	4150 ± 100
				6	2.32 ± 0.02	6.13 ± 0.05	19.6 ± 0.5	3190 ± 140
3-Picoline–ICl	ν(I–Cl)	290	21	1	1.13 ± 0.04	0.96 ± 0.06	12.5 ± 0.3	13000 ± 1200
				2	1.13 ± 0.04	1.58 ± 0.05	18.0 ± 0.7	11400 ± 800
				3	1.13 ± 0.04	1.21 ± 0.07	14.5 ± 1.0	12000 ± 1600
				4	1.13 ± 0.04	2.00 ± 0.07	23.7 ± 0.4	11900 ± 600
				5	1.06 ± 0.02	1.72 ± 0.03	20.9 ± 1.3	12200 ± 900
				6	1.06 ± 0.02	0.71 ± 0.02	7.3 ± 0.5	10300 ± 1000
	ν(N–I)	133	19	1	1.06 ± 0.02	2.57 ± 0.04	6.6 ± 0.3	2570 ± 150
				2	2.32 ± 0.02	5.62 ± 0.05	13.4 ± 0.9	2380 ± 190
				3	1.06 ± 0.02	3.98 ± 0.08	11.9 ± 0.5	2990 ± 190
				4	2.32 ± 0.02	8.71 ± 0.08	24.3 ± 0.1	2790 ± 40
				5	2.32 ± 0.02	10.51 ± 0.09	26.6 ± 0.8	2530 ± 100
				6	1.06 ± 0.02	4.80 ± 0.09	11.6 ± 0.3	2410 ± 110
2,6-Lutidine–ICl	ν(I–Cl)	290	23	1	1.06 ± 0.02	1.05 ± 0.02	11.3 ± 0.4	10760 ± 600
				2	1.06 ± 0.02	1.97 ± 0.03	18.7 ± 1.0	9490 ± 700
				3	1.06 ± 0.02	1.29 ± 0.03	12.9 ± 0.6	10000 ± 700
				4	1.06 ± 0.02	1.49 ± 0.02	14.2 ± 0.6	9530 ± 500
				5	1.06 ± 0.02	2.82 ± 0.06	28.6 ± 2.0	10100 ± 1000
				6	1.06 ± 0.02	2.38 ± 0.05	23.8 ± 0.4	10000 ± 400
	ν(N–I)	117	20	1	2.32 ± 0.02	5.21 ± 0.05	9.8 ± 0.6	1880 ± 120
				2	2.32 ± 0.02	6.02 ± 0.06	10.6 ± 0.3	1760 ± 70
				3	2.32 ± 0.02	8.06 ± 0.07	19.4 ± 0.8	2400 ± 120
				4	2.32 ± 0.02	11.71 ± 0.10	24.9 ± 1.1	2130 ± 110

Table V. Summary of Intensity Measurements for Pyridine–ICl Complexes

Complex	Vibration	Frequency, ν_{max}, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	Average B_i, cm mmole^{-1} (darks) ± scatter	$\partial\mu/\partial Q_i$, cm$^{3/2}$ sec^{-1}
Pyridine–ICl	ν(I–Cl)	292	20	12,100 ± 1000	131.2 ± 5.3
	ν(N–I)	140	20	3,760 ± 500	73.2 ± 4.6
3-Picoline–ICl	ν(I–Cl)	290	21	11,900 ± 1100	130.2 ± 5.9
	ν(N–I)	133	19	2,610 ± 310	61.0 ± 4.2
2,6-Lutidine–ICl	ν(I–Cl)	290	23	10,000 ± 1000	119.3 ± 6.3
	ν(N–I)	117	20	2,050 ± 350	54.0 ± 4.4

Errors in Intensity Measurements. The error estimates listed in Table V for the B_i values are from the maximum and minimum slopes of lines which fit reasonably the Beer's law plots (Figure 4). It should, however, be emphasized that these error estimates are for *random* errors caused by the *scatter* of data. In addition, there are several possible sources of *systematic* error which should at least be considered when trying to evaluate the accuracy of these intensity values. (a) The error in the photometric accuracy of the IR-11 *may* be as high as ±10% in the low-frequency region (especially below 100-cm^{-1}). (b) Background shifts occur, often caused by extremely minute quantities of water in the benzene. Such shifts may result in failure of the solution and solvent traces to match in the wings of the band. Spectra on which this shift was obvious were discarded. Furthermore, this error might be expected to be random. (c) Concentration errors could be caused by chemical reactions in solutions giving iodine and *possibly* also polyhalide ions (such as ICl_2^-) in *small* concentrations. (d) Finally an error might occur owing to the finite resolution of the instrument. This error should be small for our measurements since the spectral slit width was generally less than one-third of the apparent half-width of the bands.

In spite of all the potential sources of error, we believe that our intensity values should be accurate within ±15–20%, and are as good as can be expected for such systems using presently available techniques.

Discussion

Force Constants. Several attempts have been made previously to calculate the force constants for halogen complexes with pyridine bases.[9,10,12–16] Even if the

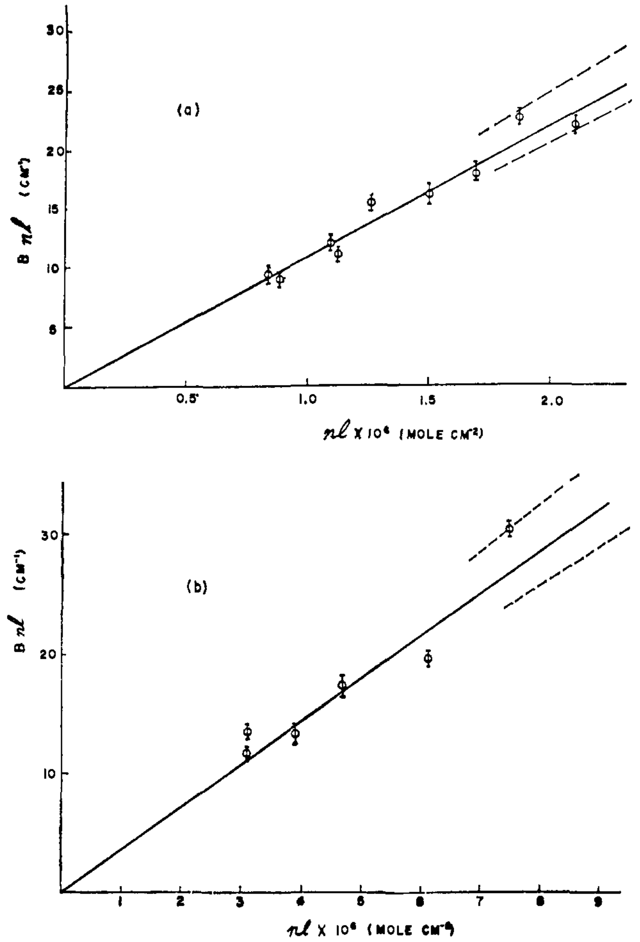

Figure 4. Beer's law plots for the pyridine–ICl complex in benzene: (a) ν(I–Cl) at 290 cm⁻¹; (b) ν(N–I) at 140 cm⁻¹.

simplifying assumption is made that the complex is a linear triatomic molecule [*i.e.*, D–I–X (X = I, Cl, Br) with symmetry $C_{\infty v}$], there are two observable stretching frequencies, with three force constants necessary to define the general quadratic force field. Hence, it is necessary to make some additional assumption about the force field, particularly the value of the interaction constant, k_{12}. Maki and Nelson[12] have suggested by analogy with trihalide ions[22,23] that it may be reasonable to assume that k_{12} is 0.4 mdyn/Å for all halogen complexes. They have also found that k_{NI} is relatively insensitive to the value assumed for k_{12}.

The force constants (k_{NI} and k_{ICl}) have been calculated from the observed frequencies and the equations given by Herzberg[26] for k_{12} values ranging from 0 to 1.0 mdyn/Å. Calculations were made using the frequencies for the solid complexes and also for the benzene solutions, in order to give an idea of the changes in force constants for this environmental change. The values obtained using solid-state frequencies agree with these given previously[12] for k_{NI} and k_{ICl}. The results are presented in Table VI, and diagrammatically in Figure 5.

We note in Figure 5a that for every value of k_{12} there are two values for each of the force constants k_{NI} and k_{ICl}. These force constants are not all independent of each other, but they go in pairs. Thus, for a given value of k_{12}, one solution (a) gives the higher value for k_{ICl} paired with the lower value of k_{NI}; the other solution (b) gives a high value of k_{NI} paired with the lower value of k_{ICl}. These two solutions correspond to quite different normal coordinates; for solution a the normal coordinate corresponding to the high-frequency vibration of the complex is predominantly I–Cl stretching, with only a little N–I stretching; for solution b that normal coordinate is predominantly the N–I stretch. We believe that the results from solution a (high k_{ICl}, low k_{NI}) are correct for these complexes, and in further discussion (and in Figure 5b) we consider only that solution. The situation is not so clear for the I_2 complexes,[16] however, and the alternate assignment should be considered there.

Table VI. Force Constants Calculated for ICl Complexes in the Solid Phase and in Benzene[a]

Solid			Benzene solution		
k_{12}	k_{NI}	k_{ICl}	k_{12}	k_{NI}	k_{ICl}
		Pyridine–ICl			
0.0	1.04	1.22	0.0	0.63	1.36
0.1	0.99	1.29	0.1	0.62	1.41
0.2	0.97	1.34	0.2	0.62	1.45
0.3	0.98	1.38	0.3	0.64	1.48
0.4	1.01	1.41	0.4	0.68	1.51
0.5	1.07	1.42	0.5	0.73	1.52
0.6	1.14	1.42	0.6	0.80	1.52
		3-Picoline–ICl			
0.0	0.94	1.23	0.0	0.64	1.34
0.1	0.90	1.30	0.1	0.62	1.39
0.2	0.89	1.35	0.2	0.61	1.43
0.3	0.90	1.38	0.3	0.64	1.47
0.4	0.94	1.41	0.4	0.68	1.49
0.5	0.99	1.43	0.5	0.73	1.51
0.6	1.06	1.43	0.6	0.80	1.52
		2,6-Lutidine–ICl			
0.0	0.78	1.16	0.0	0.53	1.35
0.1	0.75	1.22	0.1	0.52	1.40
0.2	0.75	1.26	0.2	0.53	1.44
0.3	0.77	1.30	0.3	0.55	1.47
0.4	0.80	1.32	0.4	0.59	1.50
0.5	0.86	1.34	0.5	0.64	1.51
0.6	0.94	1.35	0.6	0.71	1.53

[a] All values in mdyn/A; $k_{ICl}{}^0$ = 2.27 (ref 4). Only the solution with high k_{ICl} and low k_{NI} values is given here for selected values of k_{12} ranging from 0.0 to 0.6 mdyn/Å (see Figure 5, and related discussion in text).

The following general trends in the force constants are evident from the curves in Figure 5b.

(1) All three complexes have the same ICl force constant in benzene solution (reflecting the fact that ν(ICl) is the same also), but the N–I force constant for lut–ICl is lower than that for the other two complexes. This behavior parallels the intensity behavior, although there is more variation in the intensity of the N–I stretch than is found for k_{NI}.

(2) In the solid phase k_{NI} is different for all three complexes, but k_{ICl} is the same for py–ICl and pic–ICl. The latter appears to differ significantly in lut–ICl from the other values.

(3) From Figure 5b, it seems clear that k_{NI} and k_{ICl} have about the same dependence on k_{12}. Both constants are relatively independent of the choice of k_{12}, providing only that the latter is positive and less than about 0.6 mdyn/Å. Watari[11] has estimated for the solid complexes that k_{ICl} = 1.18 mdyn/Å from Badger's rule. If so, then he finds k_{NI} = 0.91 and k_{12} = 0.22

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(26) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

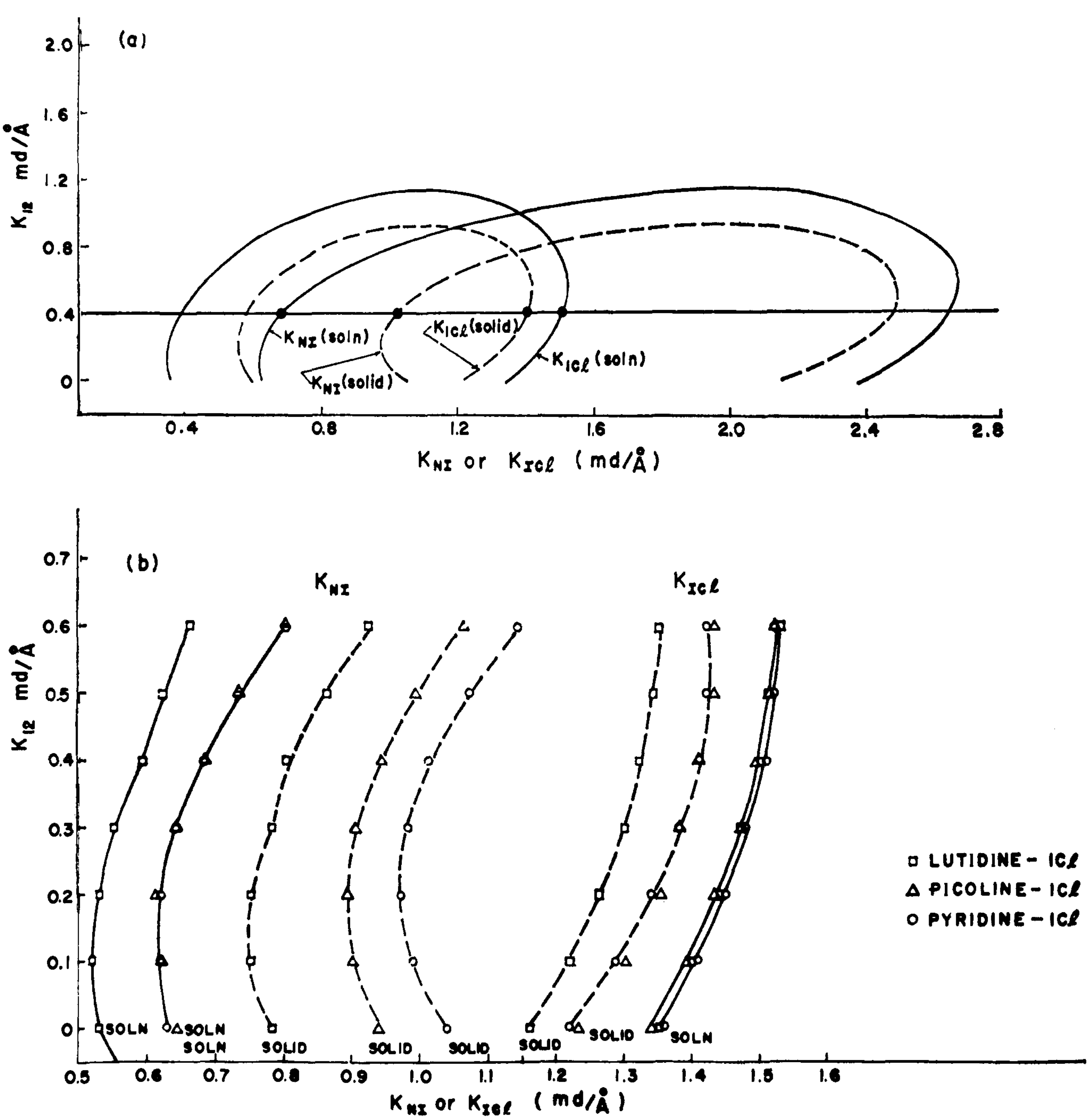

Figure 5. Force constants for the pyridine base–ICl complexes. (a) The force constant ellipses for pyridine–ICl, showing k_{12} as a function of k_{NI} and k_{ICl}, for solid-phase samples (– – –), and for data from benzene solution (———). Preferred solutions are indicated by ●, for k_{12} = 0.4, as an example. (b) Portions of the force constant ellipses for solid and solution data for pyridine–ICl (○), for picoline–ICl (△), and for lutidine–ICl (□) complexes.

mdyn/Å. This estimate reinforces the expectation that k_{12} is in this range.

(4) There is a significant change, both in k_{NI} and in k_{ICl}, on changing the environment of the complex from the benzene solution to the pure solid. We see that k_{NI} increases and k_{ICl} decreases, consistent with the idea that these changes in force constants occur because of the changes in the weight of the dative structure.[7,15] Again, we emphasize that the observed changes are larger than those usually expected for these relatively minor changes in environment. Specifically, we note that $\Delta k/k$ [$=(k_{ICl}{}^0 - k_{ICl})/k_{ICl}{}^0$] is about 0.4 for the solid complexes, and about 0.3 for the complexes in benzene solution. This conclusion that the importance of the dative structure is greater in the solid phase is not unreasonable; it supports some other interpretations of the "solvent effects" found when properties of gas-phase complexes are compared to those of the same complexes measured in solution.[27]

It is interesting to pursue the hypothesis advanced earlier[13,16] that the force constant $k_{NI}{}^0$ for the N–I band in the *pure* dative structure is about 2.5 mdyn/Å. For the solid complexes, we see that k_{NI} in the complexes studied here ranges from about 0.6 to 1.1, corresponding to values of $b^2 + abS_{01}$ (computed from $k_{NI}/k_{NI}{}^0$) of

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[27] See, for example, M. Kroll, *J. Am. Chem. Soc.*, 90, 1097 (1968); M. Tamres and J. M. Goodenow, *J. Phys. Chem.*, 71, 1982 (1967).

0.24 to 0.44, in agreement with the range indicated by the values of $(k_{ICl}^0 - k_{ICl})/k_{ICl}^0$. Repeating the reasoning used for the I_2 complexes,[16] we may use the relatively constant value of k_{NI} to compute $b^2 + abS_{01}$ for a given complex and then choose k_{12} so that we obtain a value of k_{ICl} which gives a consistent value of $b^2 + abS_{01}$. In this way we find the results listed in Table VII. The values of the force constants chosen in this way are reasonable; the values of $b^2 + abS_{01}$ are perhaps higher than one might expect intuitively, but they are perhaps a bit more reasonable than those found from the corresponding calculation for the I_2 complexes.[15] However, the failure of this simple procedure to give completely consistent results emphasizes its approximate nature. It would be possible to obtain consistency by choosing a slightly different value for k_{NI} (about 2.0 mdyn/Å, for example). However, it does not seem profitable at this time to press ideas further. The results presented here seem quite reasonable, but they can be proved only if some method is found independently to evaluate k_{12} and hence pin down the exact experimental force constants.

Table VII. Values of Force Constants Chosen to Give Consistent Estimates of the Weight of the Dative Structure, $b^2 + abS_{01}$ (See Text)

Complex	State	k_{NI}[a]	$k_{NI}/2.5$[b]	k_{12}[c]	k_{ICl}[d]	$b^2 + abS_{01}$[e]
py–ICl	Solid	0.98	0.39	0.3	1.38	0.39
py–ICl	Benzene	0.68	0.27	0.4	1.65[f]	0.25–0.35
pic–ICl	Solid	0.94	0.37	0.4	1.42	0.37
pic–ICl	Benzene	0.68	0.27	0.4	1.65[f]	0.25–0.35
lut–ICl	Solid	0.80	0.32	0.4	1.54[f]	0.3–0.4
lut–ICl	Benzene	0.59	0.24	0.4	1.73[f]	0.24–0.34

[a] Value from Table VI. [b] Assumed value for k_{NI}^0; see text. [c] Value from Table VI corresponding to k_{NI}. [d] Value computed by setting $k_{NI}/2.5$ ($\approx b^2 + abS_{01}$) equal to $\Delta k/k$ [or $(2.27 - k_{ICl})/2.27$] and solving. [e] Consistent both with $k_{NI}/2.5$ and with $\Delta k/k$. [f] These values are not consistent, implying that k_{ICl} should be smaller for solutions in benzene.

In spite of all these difficulties with details of this analysis, it would seem safe to draw several conclusions from these results. (1) The change in force constant, and hence probably the weight of the dative structure, is considerably greater (by about a factor of 2) for complexes of ICl with pyridine bases than for the corresponding complexes of I_2. This conclusion is consistent with the much greater stability of the ICl complexes, and it implies other properties, such as a much greater increase in static dipole moment than for I_2 complexes. (2) The weight of the dative state is probably somewhat greater in solid ICl complexes than in solution in the nonpolar solvent, benzene. This conclusion seems consistent with the postulate of a similar decrease on changing the environment of the complex from nonpolar solvent to the gas phase. (3) The value of k_{NI}^0 seems quite definitely to be between 2.0 and 3.0 mdyn/Å. The theory may be so approximate that a more exact estimate may not be possible. Furthermore, it may well be different for pyridine complexes from the value for lutidine complexes, for example.

Intensities. Next, let us consider the estimation of the vibronic contribution to the intensity of ν(I–Cl) for these complexes. Following the procedure for the I_2 complexes, we attempt to compute the value of M'. From the discussion above, $b^2 + abS_{01}$ is about 0.3 for these complexes in solution; since S_{01} is about 0.3, $b \approx 0.43$ and $a \approx 0.78$. Person and Friedrich estimated[7] $(\partial E_A^V/\partial r)$ to be 5.70 eV/Å. In order to obtain $\mu_{EN}/\Delta W$, we need the intensity (to get μ_{EN}) and the frequency (to get ΔW) of the charge-transfer band of py–ICl. We have attempted, unsuccessfully, to determine these parameters. Lacking better information, we assume that $\mu_{EN}/\Delta W$ is about the same for py–ICl as for py–I_2, or $\mu_{EN}/\Delta W = 1.43$ D/eV.[16] Hence, M' is computed to be 9.0 D/Å. Since ϵ_0 for ICl is 2.5 D/Å,[4] we conclude that $(\partial\mu/\partial R_1)$ [where R_1 is the symmetry coordinate describing the I–Cl stretch (just Δr_{ICl})] should be equal to ±11.5 D/Å° if M' has the same sign as $(\partial\mu/\partial R_1)_0$ which would be expected from the arguments given earlier.[15] In spite of all the uncertain parameters, we do not think this estimate is likely to be wrong by more than about ±30%.

Let us now compare this computed value with the value measured experimentally. In order to do so, we may simply use the "diatomic approximation" to compute $\partial\mu/\partial R_1$ ($\equiv 1.537 \times 10^{-2} \times \sqrt{B/0.0365}$).[4] From this, for the py–ICl complex in benzene solution, $\partial\mu/\partial R_1 = 9.7$ D/Å.

However, as we have discussed previously,[13,16] it is necessary to obtain the normal coordinates for these strong complexes in order to sort out the mixing of symmetry coordinates in the high-frequency "I–Cl stretching" vibration. In particular, R_1, the I–Cl stretching symmetry coordinate, is expected to mix rather strongly with R_2, the N–I stretching vibration. The difficulty with doing a full normal coordinate analysis, however, is that we do not know k_{12}, so that the normal coordinate transformation, **L**, cannot be uniquely determined. In spite of this, it is of some interest to compute this transformation as a function of k_{12} in order to examine the range of possible solutions. The results of that calculation are given in Table VIII.

Table VIII. Normal Coordinate Transformation Matrix Elements' L_{ij}^{-1} ($\mathbf{Q} = \mathbf{L}^{-1}\mathbf{R}$) for Some Pyridine–ICl Complexes[a]

	Pyridine–ICl		3-Picoline–ICl		2,6-Lutidine–ICl	
	Solid	Bz soln	Solid	Bz soln	Solid	Bz soln
$k_{12} = 0.4$						
L_{11}^{-1}	7.034	7.042	7.037	7.047	7.071	7.059
L_{12}^{-1}	1.552	1.622	1.522	1.598	1.740	1.625
L_{21}^{-1}	0.905	0.853	1.099	1.046	1.091	1.172
L_{22}^{-1}	9.263	9.249	9.794	9.780	10.202	10.228
$k_{12} = 0.2$						
L_{11}^{-1}		6.792		6.872		6.893
L_{12}^{-1}		0.407		0.415		0.506
L_{21}^{-1}		1.753		2.159		1.931
L_{22}^{-1}		9.381		9.897		10.340
$k_{12} = 0.0$						
L_{11}^{-1}		6.574		6.501		6.616
L_{12}^{-1}		−0.880		−0.872		−0.688
L_{21}^{-1}		2.677		2.747		2.709
L_{22}^{-1}		9.355		9.856		10.331

[a] Units are 10^{-12} $g^{1/2}$; assumed mass for D is the entire molecular weight of D.

There is surprisingly little change in the normal coordinates on changing from solid to solution. On the other hand, the normal coordinates are quite sensitive to the assumption made for k_{12}; in fact the relative sign of L_{11}^{-1} to L_{12}^{-1} changes from positive to negative as k_{12} changes from 0.4 to 0.0 mdyn/Å.

From these values of the normal coordinate transformation coefficients, we compute the values of $\partial\mu/\partial R_j$ from the intensities of Table IV using equations given earlier.[16] The results are tabulated in Table IX. As before,[16] we expect $\partial\mu/\partial R_1$ and $\partial\mu/\partial R_2$ to have opposite signs. Hence the second set of solutions is preferred as indicated in Table IX. Thus, we find that $\partial\mu/\partial R_1$ for py–ICl ranges from +8.62 to +6.66 D/Å over a "reasonable" range for k_{12} from 0.4 to 0.0 mdyn/Å, in moderately satisfactory agreement with the calculated value of 11.5 D/Å. The agreement is even better with the value of 6.5 D/Å calculated assuming M' and $(\partial\bar{\mu}/\partial r_{\mathrm{ICl}})$ have opposite signs. However, if we assume in the latter case that M' has the same direction for all complexes, weak and strong, then we should observed a *decrease* followed by an *increase* in the intensity of the I–Cl stretch as the strength of the complex is increased systematically, instead of a monotonic increase. Hence, we conclude that the difference between the observed $\partial\mu/\partial R_1$ values and the calculated value is probably due to an estimate for $\partial E_{\mathrm{A}}^{\mathrm{V}}/\partial r$ which is too large, as suggested earlier.[7]

Table IX. "Bond Moment Derivatives," $\partial\mu/\partial R_j$,[a] Calculated for Some Pyridine–ICl Complexes in Benzene Solution

	Py–ICl		Pic–ICl		Lut–ICl	
	++[b]	+−	++	+−	++	+−
k_{12} = 0.4						
R_1 (ICl)	9.86 or	*8.62*	9.82 or	*8.54*	9.05 or	*7.79*
R_2 (NI)	8.90 or	*−4.64*	8.04 or	*−3.88*	7.47 or	*−3.59*
k_{12} = 0.2						
R_1 (ICl)	10.19 or	*7.63*	10.27 or	*7.63*	9.26 or	*7.18*
R_2 (NI)	7.40 or	*−6.34*	6.58 or	*−5.50*	6.19 or	*−4.97*
k_{12} = 0.0						
R_1 (ICl)	10.58 or	*6.66*	10.14 or	*6.78*	9.36 or	*6.54*
R_2 (NI)	5.60 or	*−8.00*	4.87 or	*−7.15*	4.76 or	*−6.40*

[a] Units are D/A. Calculated from the $\partial\mu/\partial Q_i$ values listed in Table V and the L_{ij}^{-1} values from Table VIII. Note that $\partial\mu/\partial R_1 = \partial\mu/\partial r_{\mathrm{ICl}} \equiv \epsilon_{\mathrm{ICl}}$ and $\partial\mu/\partial R_2 = \partial\mu/\partial r_{\mathrm{NI}} \equiv \epsilon_{\mathrm{NI}}$. [b] The signs of $\partial\mu/\partial Q_1$ and $\partial\mu/\partial Q_2$, respectively. Because of the sign ambiguity in the normal coordinate transformation, we cannot know whether $\partial\mu/\partial R_1$ for py–ICl is positive (corresponding to ++) or negative (corresponding to −−). We do know that the relative signs of $\partial\mu/\partial R_1$ and $\partial\mu/\partial R_2$ are as given here. The preferred solutions are italicized.

The comparison of the values of $\partial\mu/\partial R_2$ found here with those found in the study of I_2 complexes is most interesting. For the same choice of k_{12} in the two complexes, the agreement is remarkable. Thus, for k_{12} = 0.4, 0.2, and 0.0, we find $\partial\mu/\partial R_2 = -4.64$, -6.34, or -8.0 D/Å here for the py–ICl complex compared to values of -4.49, -5.85, or -7.45 D/Å for the py–I_2 complex. Such close agreement is to be expected if the intensity of this vibration *is* primarily due to the vibronic contribution, resulting from the change in overlap between N and I during this vibration, and if the weight of the dative structure is indeed about the same for these two complexes as indicated by the force constants.

Intuitively, the most reasonable values both for $\partial\mu/\partial R_1$ and for $\partial\mu/\partial R_2$ occur for the solution with $k_{12} \approx 0.4$ mdyne/Å. This set of force constants also seems the most reasonable from the interpretation of $\Delta k/k$ in terms of the weight of the dative structure, $b^2 + abS_{01}$ (see Table VIII and the related discussion).

The results presented earlier[16] for the I_2 complexes cast some doubt on the theory[6] used to interpret them. Many more studies are needed before these ideas should be accepted fully. Some method must be found to evaluate k_{12} and to determine the force field for the complexes. Nevertheless, the experimental results so far for most halogen complexes seem satisfactorily explained by the ideas given earlier[7,13,16] and applied here.

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