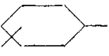
electron densities are expressed in units of the electronic charge.

Equation 1 was then used in the reverse direction to calculate the values of $\delta q_{CH_2^-}$ induced by introduction of substituents into the benzyl anion. Localization energy changes were calculated by equation 2.[17]

$$\delta L = \delta L^0 + \delta q_b \alpha_b + \alpha_a \Sigma_s \mathcal{E}_s \delta q_s \qquad (2)$$

Here, δL° is the difference in localization energy between the substituted and unsubstituted reference structures, in this case  $—CH_2^-$ and $C_6H_5CH_2^-$, and the δq_r are the difference in electron density at atom r between the unperturbed non-localized and localized structures, IV and V, respectively. All localization energies are expressed in units of β, the CC resonance integral appropriate for a ring bond.

Inductive Effect.—Throughout this paper the inductive effect has been treated in the manner proposed in the earlier papers of this series.[6] It was there shown that the inductive effect is of major importance in the electron density method. This is apparent from equation 1, where the terms in powers of $\mathcal{E}$ decrease with n_s, but the polarizabilities are largest for s = r, and generally the less important the farther s and r are separated. In the localization method the results do not depend greatly on the assumptions made about the inductive effect. This can be understood since again the powers of $\mathcal{E}$ decrease strongly with increasing n_s, while all the non-vanishing δq_s terms are roughly of the same order of magnitude.

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(17) Terms in δp_{rs} were neglected, *cf.* above.

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Infrared Studies of the Association of Secondary Amides in Various Solvents

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The infrared spectra of N-ethylacetamide, N-*n*-butylacetamide and γ-butyrolactam have been measured in the regions 3500 to 3000 cm.$^{-1}$ and 1700 to 1600 cm.$^{-1}$ as a function of concentration in carbon tetrachloride, and as a function of solvent at fixed concentration. Significant spectral changes are observed with seemingly similar solvents. It is suggested that changes in the spectrum are caused primarily by variation of the polymerization constant with solvent. Evidence is presented for weak hydrogen bond formation between chloroform and the carbonyl group of the amide.

The association of amides has been well known for a number of years[1] and much infrared spectral study[2,3] has been devoted to these compounds. Yet the conditions under which dimeric association, rather than higher polymerization, occurs are not well known. It has been clearly shown that the functional groups responsible for the association are the amino and the carbonyl groups by formation of NH–OC bonds.[3] Beyond this point the situation is less clear. For primary amides there is considerable evidence of polymers higher than dimers.[1,4,5] It has been suggested that secondary amides associate in cyclic dimers, as do the carboxylic acids, and consequently dimeric units should be favored over higher polymers.[6] In apparent support of this suggestion are the studies of δ-valerolactam,[7-9] where only dimeric units were found. In conflict with this suggestion is the definitive work of Mizushima, *et al.*,[10] on N-methylacetamide in carbon tetrachloride solutions. The high dielectric constant indicates chain polymers, and the frequency shift of the bonded NH absorption with concentration shows existence of several species.

In addition to consideration of the polymeric species resulting from hydrogen bonding, the present work includes study of the influence of several solvents, usually considered to be intercomparable, upon the spectra of the amides. This appeared important in view of previous work[3] which showed that oxygenated solvents have large effects upon amides not explainable in terms of the dielectric constants of the solvents.

Experimental

A Perkin-Elmer Model 21 infrared spectrometer was used to obtain the spectrograms. The spectra of the amides in carbon tetrachloride as a function of concentration were obtained with NaCl optics. The spectra of N-ethylacetamide in different solvents were obtained with a CaF_2 prism. For NaCl optics frequency accuracy is estimated as 25 cm.$^{-1}$ at 3000 cm.$^{-1}$ and 7 cm.$^{-1}$ at 1700 cm.$^{-1}$. For CaF_2 optics the accuracy is higher, namely, 10 cm.$^{-1}$ at 3000 cm.$^{-1}$ and 3 cm.$^{-1}$ at 1700 cm.$^{-1}$. In each region, frequency reproducibility is better than the absolute accuracies quoted above. Cell lengths are shown in the tables.

Results and Discussion

The results of measurements in carbon tetrachloride as a function of amide concentration are presented in Table I. In all cases the location of the absorption maximum ν, and the apparent molal extinction coefficient e of the absorption maximum have been corrected for overlapping absorption by the wings of neighboring bands. Frequency and intensity reproducibility were checked by the CH absorption. The apparent molal extinction coefficient refers to stoichiometric concentration. The units are moles^{-1} cm.^{2}, and it is computed from absorption measurements, using $\log_{10} I_0/I$ at the absorption maximum.

The data in Table I strongly support the hypothesis that the only polymeric species in carbon tetrachloride solutions of butyrolactam is a cyclic dimer.

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TABLE I

THE CONCENTRATION DEPENDENCE OF AMIDE SPECTRA IN CARBON TETRACHLORIDE

		NaCl optics										
		Free NH		Bonded NH				CH		CO		
Cell length, mm.	Concn., moles/l.	ν, cm.$^{-1}$	e	ν, cm.$^{-1}$	e	ν, cm.$^{-1}$	e	ν, cm.$^{-1}$	e	ν, cm.$^{-1}$	$Ce^2_{\rm m}/e_{\rm d}$
					N-*n*-Butylacetamide						
1.0	0.0161	3447	39	3349	16	3084	1.5[b]	2953	106	1681	1.5
1.0	.0399	3450	38	3339	32	3084	3.5	2951	116	1675	1.8
1.0	.0807	3451	20	3319	60	3089	6.9	2951	102		0.54
					N-Ethylacetamide						
103	0.00078	3472	26	3372	1.9[b]	3084	0.7[c]	3002	42		0.28
103	.00158	3478	22	3376	2.1	3084	0.6[c]	3002	35		0.36
103	.00239	3464	19	3372	2.3	3094	0.5[c]	3002	33		0.38
1.0	.0200	3469	23	3362	8.0	3084	5.0[c]	3000	38		1.3
1.0	.0400	3469	20	3354	15	3094	3.7[c]	3000	39	1680	1.1
1.0	.080	3472	15	3332	33	3114	7.0	3000	39		0.55
1.0	.160	3472	10	3322	49	3114	9.5	2997	34		0.33
0.07	(.31)[a]	3472	12[b]	3309	72	3104	17	2997		1649	0.62
					γ-Butyrolactam						
1.0	0.0112	3457	25	3224	108	3114	36	2994	80	1698	0.065
1.0	.0224	3452	15	3219	117	3114	34	2992	78		.043
1.0	.0448	3451	12	3219	125	3119	36	2991	80		.052
1.0	.090	3451	7.9	3219	120	3119	39	2990	73		.047
1.0	.1792	3452	5.9								
0.07	.1792			3219	90	3116	19	2989	55	1693	.069
0.07	.389	3454	5[c]	3224	119			2994	48		

[a] Saturated solution, concentration calculated from CH intensity. [b] Absorption less than 5%. [c] Absorption less than 2%.

The ratio $Ce^2_{\rm m}/e_{\rm d}$ is constant to 20% with no apparent drift. C = stoichiometric concentration, $e_{\rm m}$ and $e_{\rm d}$ are the apparent molal extinction coefficients of the 3450 and 3220 cm.$^{-1}$ bands, respectively. The above ratio will be a constant if the 3450 cm.$^{-1}$ band is entirely caused by monomer and the 3220 cm.$^{-1}$ by dimer. It is important to note that the 3220 cm.$^{-1}$ band remains constant in frequency over the entire concentration range.

In both of the secondary amides studied, the frequency location of the 3350 cm.$^{-1}$ bonded NH band is strongly dependent upon concentration, as was the case in N-methylacetamide[7,10,11] and other secondary amides. For N-ethylacetamide the previously published absorption curves of Buswell, Rodebush and Roy[2] indicate this shift. Neither the 3350 cm.$^{-1}$ nor the 3100 cm.$^{-1}$ bands give constant $Ce^2_{\rm m}/e_{\rm d}$, indicating neither band arises from a cyclic dimer. The intensities of these two bands have the same concentration dependence as shown by the constancy of the ratio of the apparent molal extinction coefficients at any concentration. The change of location of the 3350 cm.$^{-1}$ band with concentration indicates that there is more than one polymeric species in solutions of monosubstituted amides.

In all cases studied the carbonyl stretching frequency moved to higher frequency upon dilution, as is expected, under low spectral resolution, for polymers formed by hydrogen bonding to the carbonyl oxygen. When the carbonyl stretching frequency was studied under higher resolution two absorption maxima were found for butyrolactam in carbon tetrachloride (1716 and 1703 cm.$^{-1}$), while four were found for N-ethylacetamide (1688, 1674, 1655 and 1651 cm.$^{-1}$). This supports the contention that there is not a unique polymeric species in solutions of secondary amides.

In Table II are summarized the results of studies of N-ethylacetamide in several solvents which are frequently regarded as inert. In our interpretation we will assume that the true molal extinction coefficient is unaffected by change of solvent. In view of this assumption, small changes of intensity cannot be unambiguously attributed to change of the equilibrium between monomer and polymer.[12,13]

TABLE II

EFFECT OF SOLVENT UPON THE SPECTRUM OF N-ETHYLACETAMIDE

			CaF$_2$ optics					
			Free NH		Bonded NH		Free C=O	
Solvent	Concn., moles/l.	Cell length mm.	ν, cm.$^{-1}$	e	ν, cm.$^{-1}$	e	ν, cm.$^{-1}$	$e_{\rm m}/e_{\rm p}$
CCl_4	0.3	0.07	3461	9.5	3305	63		0.15
CCl_4	.04	1.0	3465	23.2	3357	8.5	1687	2.7
CS_2	.3	0.07	3448	10.5	3347	4.8		0.22
CS_2	.04	1.0	3448	23.7	3300	11.8	1687	1.9
CH_3CCl_3	.4	0.22	3455	21.6	3325	39.6		0.55
CH_3CCl_3	.04	1.0	3455	30.8	3352	5.5	1685	5.6
C_6H_6	.4	0.07	3440	26.0	3332	26.0		1.0
C_6H_6	.04	1.0	3442	31.3	3357	5.3	1684	6.0
$CHCl_3$	.4	0.07	3457	34.0	3342	11.4		3.0
$CHCl_3$	.04	1.0	3452	38.5			1667	>10
$CHBr_3$	.4	0.07	3442	36.3	3332	16.1		2.3
$CHBr_3$	.04	1.0	3443	37.5			1663	>10
CH_2Cl_2	.4	0.07	3443	41.0	3333	14.0		2.9
CH_2Cl_2	.04	1.0	3442	41.5			1671	>10
Vapor			3472				1715	

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The ratio e_m/e_p permits segregation of the solvents into three classes, (I) CCl_4 and CS_2, (II) CH_3CCl_3 and C_6H_6, and (III) $CHBr_3$, $CHCl_3$, CH_2Cl_2. The ratio indicates that polymerization is greatest in Class I and least in III. The solvents in Class I will be regarded as reference solvents. They have zero dipole moment and no hydrogen atoms. In comparing the effects of the remaining solvents, interactions of the type C–H · · · O–C, C–Cl · · · H–N, and dielectric effects might be influential. The dielectric effect should be larger in the solvent methylchloroform than in chloroform, while the chlorine–amide hydrogen interactions should be quite similar (as is suggested by the monomeric NH stretching frequencies in these two solvents). Consequently the large change in e_m/e_p indicates the dominant influence of the hydrogen bonding, C–H · · · O–C.

The difference in e_m/e_p between the reference solvents in Class I and methylchloroform indicates the combined effects of dielectric constant and chlorine–hydrogen bonding in stabilizing the monomeric species relative to polymers. With the exception of benzene the remaining solvents are considered to have hydrogens which are capable of competing with the amide hydrogen in bonding to the carbonyl oxygen. The possibility of arranging the solvents of Class III according to hydrogen bonding energy is precluded for a number of reasons. (1) There is a significant uncertainty in the intensity because of the use of peak intensities rather than integrated intensities. (2) The absorption coefficient of the monomeric NH stretching mode may vary with solvent.[13] (3) The halogen–hydrogen interactions vary with the solvent as shown by the frequency differences of the monomeric NH stretching mode in the several solvents. (4) The entropy change on depolymerization will depend upon the solvent, hence comparisons using a quantity determined by the equilibrium constant do not directly indicate the hydrogen bond energies. (5) Although the location of the carbonyl stretching frequency of the monomeric N-ethylacetamide presumably indicates hydrogen bonding with the solvent the large shift of this vibration frequency upon going from gaseous amide to a solution in carbon tetrachloride indicates large van der Waals interaction of the amide with solvent. This large shift precludes the possibility of quantitatively correlating carbonyl frequency with hydrogen bond energy.

Benzene appears to interact with the amide hydrogen to a considerable extent, since the free NH frequency is lowest where benzene is used as solvent. This frequency effect is in agreement with results on aromatic amines.[12]

The comparison of the dimerization constant of δ-valerolactam in carbon tetrachloride and benzene gives an indication of the magnitude of these solvent effects. The cryoscopic data of Jenkins and Taylor[9] give a dimerization constant in benzene at 5° of about 40, while 900 is obtained by extrapolation of the data of Tsuboi[8] for the same constant in carbon tetrachloride at 5°. This shows the order of magnitude of changes to be expected in going from a solvent in Class I to one of Class II.

The frequency shift of free NH to bonded NH is roughly constant, indicating that the actual energy of the hydrogen bond is the same in all solvents. The energy measured from the temperature coefficient of the polymerization constant will vary with solvent. Davies and Hallem[5] obtained 1.1 kcal. per bond for NH–OC in acetamide trimer dissolved in chloroform, while Tsuboi[8] obtained 5.1 kcal. per bond for NH–OC in δ-valerolactam in carbon tetrachloride. The frequency shift upon hydrogen bond formation is 210 cm.$^{-1}$ in δ-valerolactam and 125 cm.$^{-1}$ in acetamide $(3533 + 3415/2 - 3351)$. Assumption of a linear relation between frequency shift and energy obtains 3.0 kcal. for the energy of NH–OC of the acetamide trimer in carbon tetrachloride. This yields an energy of 1.9 kcal. for the energy of interaction of chloroform with an amide. The heat of mixing of chloroform with N,N-dimethylacetamide is 1.84 kcal. per mole chloroform at a mole fraction of $^1/_2$.[14]

Conclusions

1. The spectra of amides and lactams are affected considerably by both concentration and solvent. Comparison of spectra in carbon tetrachloride and chloroform is likely to be misleading, especially if used for identification purposes.
2. The conclusions of Mizushima[10] that secondary amides form several polymers while lactams form dimers are supported.
3. Hydrogen atoms attached to poly-halogenated carbon atoms are capable of forming hydrogen bonds to carbonyl oxygens.
4. The energy of interaction of chloroform with an amide is estimated at 2 kcal.

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