here; as the carbonyl group conjugates less with the ring nitrogen, it can conjugate more with the benzene ring so the extinction of this band increases.

These data show how a methylene group can have a large effect on the conformation, dipole moment and ultraviolet spectra of semicyclic imides.

Experimental

All dipole moments were measured in dioxane at 30° and calculations were made using the equation and method of Halverstadt and Kumler.[14] We wish to thank Dr. H. K. Hall, Jr., of du Pont for providing the compounds.[5] We wish to thank Mr. M. K. Hrenoff of the Spectrographic Laboratory for all spectrographic measurements. Infrared spectra were run on a Perkin-Elmer model 21 in KBr disks 1:250, 0.6 mm. thick. Ultraviolet spectra were run on a Cary model 11 or model 14 in ethanol in concentrations of 2.5 mg. %.

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[14] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2933 (1942).

[15] H. K. Hall, Jr., M. K. Brandt and R. M. Mason, *ibid.*, **80**, 6420, 6424 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, SCHOOL OF PHARMACY, UNIVERSITY OF CALIFORNIA, SAN FRANCISCO MEDICAL CENTER, SAN FRANCISCO, CALIF.]

The Dipole Moment and Structure of the Imide Group. III. Straight Chain Imides $>N{-}H\cdots O{=}C<$ Hydrogen Bonding and a Case of $\underset{O}{>}C{-}H\cdots O{=}C<$ Hydrogen Bonding

BY CALVIN M. LEE[1] AND W. D. KUMLER

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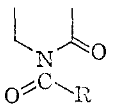
Table I gives the dipole moments for N-methyldiacetamide (I), diacetamide (II) and N-methyldiformamide (III). Compound I has the expected moment for the *cis-trans* conformation of imides; its moment varies only slightly (Δ0.2 D.) in going from dioxane to benzene to heptane; II, while having the expected moment for the *cis-trans* conformation in dioxane, has a much lower moment in benzene (Δ1.0 D.) and heptane (Δ1.6 D.), suggesting hydrogen bonding in a cyclic dimer of low moment. Examination of physical properties and infrared frequency shifts substantiate this conclusion. The low moment of III also suggests hydrogen bonding in a cyclic dimer of low moment. The only possibility for hydrogen bonding is with the hydrogen attached to the amide carbon. We propose that N-methyldiformamide (III) forms a cyclic dimer (Fig. 4) with $\underset{O}{>}C{-}H\cdots O{=}C<$ bonding. Theoretical considerations, examination of physical properties and molecular weight determinations support the proposed dimer. Infrared studies of the >C=O stretching frequency show a greater shift to lower frequency (from solution to pure liquid) for III than for I which cannot hydrogen bond. Nuclear magnetic resonance studies on III show the usual H-bond shift to higher field from the pure liquid to CCl_4 solution (17 c.p.s. at 60 mc.). Calculations based on this shift indicate about 2.2 kcal./mole is involved in holding the dimer together.

Introduction

In previous papers[2,3] we have discussed the three possible conformations in which an imide might be found (Fig. 1), namely, the *cis-cis*, *cis-trans* and *trans-trans* (named for the carbonyl groups relative to the group on nitrogen). Only the *cis-cis* conformation is possible in the five- and six-membered cyclic imides. The six-membered ring imides have a dipole moment of 2.6–2.9 D., while the five-membered ring imides have dipole moments of 1.5–2.2 D.[2] The lower moment of the five-membered ring imides is an indication of smaller ring angles which causes the angle between the carbonyl groups to increase. The semicyclic imides are in the *cis-trans* conformation and the dipole moments



depend both on ring size and the nature of the R group (methyl or phenyl).[3] N-Acetyl lactams are in the *cis-trans* conformation and have a moment of 3.0–3.2 D. The *trans-trans* conformation is unfavorable due to electrostatic repulsion; an estimation of its dipole moment gives a value of over 6.0 D.

It was expected that the aliphatic straight chain imides would be in one of the three possible conformations whose moment is known experimentally or theoretically.

Results and Discussion

The dipole moments of N-methyldiacetamide, diacetamide and N-methyldiformamide have been measured in dioxane, benzene and heptane at 30° (Table I). The dipole moments of N-methyldiacetamide, 3.0–3.2 D., are well in agreement with the experimental value for the expected *cis-trans* conformation (3.0–3.2 D.).[2,3] The presence of the bulky methyl group does not allow the compound to assume the otherwise more favored *cis-cis* conformation (Fig. 1) which would have a lower moment of about 2.6 to 2.9 D.

The dipole moment of diacetamide in dioxane, 2.9 D., is what one would predict for the compound

TABLE I

DIPOLE MOMENTS OF STRAIGHT CHAIN IMIDES AT 30° (IN DEBYES)

Compound	Dioxane	Benzene	Heptane
I, N-Methyldiacetamide	3.22	2.98	2.97
II, Diacetamide	2.91	1.89	1.33
III, N-Methyldiformamide	1.76	1.63[a]	2.16

[a] Ref. 10 gives a value of 1.51 D. at 20°.

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[1] Department of Pharmacology, Yale University School of Medicine, New Haven, Conn. Requests for reprints should be sent to W. D. Kumler at San Francisco.

[2] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4586 (1961), paper I.

[3] C. M. Lee and W. D. Kumler, *ibid.*, **84**, 565 (1962), paper II.

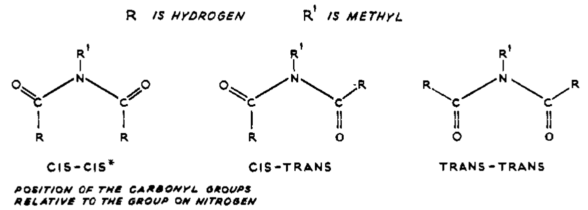


Fig. 1.—Three possible conformations for the imide group.

in the *cis-trans* conformation. N-Methyldiacetamide has a moment about 0.3 D. higher than that of diacetamide and this effect appears to be general with imides. The moment of N-methyldiacetamide varies only slightly in going from dioxane to benzene and heptane while the moment of diacetamide itself varies appreciably in going to solvents of lower dielectric constant. The difference between the moments in dioxane and benzene is about 1.0 D. and the difference between moments in dioxane and heptane is about 1.6 D. The only change between the two compounds is the substitution of a hydrogen for a methyl group on the central nitrogen atom. The decreased moment of diacetamide in benzene and heptane is paralleled by similar behavior in amides. Acetamide decreases by 0.7 D. in going from dioxane to benzene (Table II). This decrease has been attributed to hydrogen bonding between the hydrogen on the nitrogen with the carbonyl oxygen in a cyclic dimer.

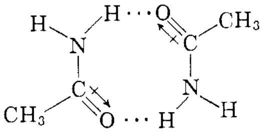


TABLE II

DIPOLE MOMENTS OF IMIDES AT 30° (IN DEBYES)

Compound	Dioxane	Benzene	Heptane
IV, Acetamide	3.70	3.07	Insol.
V, N,N-Dimethylformamide	3.95	3.92[a]	3.90

[a] Ref. 10 gives a value of 3.82 D. at 20°.

A dimer of this nature would have zero or low moment as the carbonyl, N^+O^- and other dipoles tend to cancel. One would expect the experimental moment of such a structure to be low.[4,5] Dimethylformamide, which does not hydrogen bond, changes its dipole moment very little in going from dioxane to benzene to heptane (Table II).

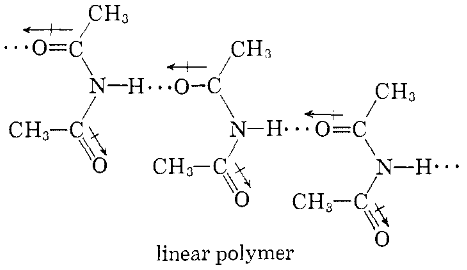
Table III shows that even though N-methyldiacetamide has a higher molecular weight than diacetamide (115–101), it boils and melts at a lower temperature than diacetamide. The difference between the melting and boiling points of these two compounds is due to the possibility of hydrogen bonding in diacetamide. Even though N,N-diethylformamide, and diacetamide, have the same molecular weight, diacetamide boils and melts at a higher temperature. This difference is also due to the hydrogen bonding possible in diacetamide, but not in N,N-diethylformamide. Hydrogen bonding in acetamide is indicated by its high melting and boiling points (81° and 222°, respectively) compared to its low molecular weight (59).

TABLE III

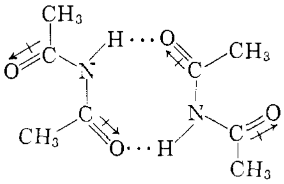
PHYSICAL PROPERTIES OF IMIDES AND AMIDES

Compound	Mol. wt.	B.P., °C.	M.p., °C.
N,N-Diethylformamide	101.1	178	<−20
Diacetamide	101.1	217	81
Acetamide	59.1	222	81
N,N-Dimethylbutyramide	115.2	190	−40
N-Methyldiacetamide	115.2	192	<−20
n-Valeramide	115.2	255	101
N,N-Dimethylacetamide	87.1	165	−20
N-Methyldiformamide	87.1	183	14
n-Butyramide	87.1	216	115

Like N-methyldiacetamide, diacetamide cannot be in the *cis-cis* conformation, but must be in the *cis-trans* conformation. It would conceivably be hydrogen bond in two different forms as a linear polymer or as a cyclic dimer



linear polymer



cyclic dimer

The linear polymer would be expected to have a high dipole moment because of the addition of dipoles. The cyclic dimer would be expected to have a low dipole moment because of partial or full cancellation of dipoles.[4,5]

Uno and Machida[6] have published a detailed analysis of the infrared spectra of diacetamide. There are two crystalline forms of diacetamide; one, form A, is found upon crystallization from CCl_4, while form B is obtained upon crystallization from water at 30–35° under 5–10 mm. pressure. The more stable form A is said to have the *cis-trans* conformation, while metastable form B is said to have the *trans-trans* conformation. The work presented was done on form A and confirms Uno and Machida's assignment of the *cis-trans* conformation. X-Ray diffraction studies[6,7] show that diacetamide had the dimeric structure in the solid state.

Hydrogen bonding has been detected by changes in the infrared carbonyl and N-H frequencies in going from CCl_4 solution to the pure liquid or pure solid (in KBr). Acetamide shows a large shift of 48 cm.$^{-1}$ (1712–1664) in the infrared carbonyl fre-

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[4] R. Huisgen and H. Walz, *Chem. Ber.*, **89**, 2616 (1956).

[5] S. I. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, pp. 117–152.

[6] T. Uno and K. Machida, *Bull. Chem. Soc. Japan*, **34**, 545 (1961).

[7] T. Watanabe and K. Osaki, unpublished.

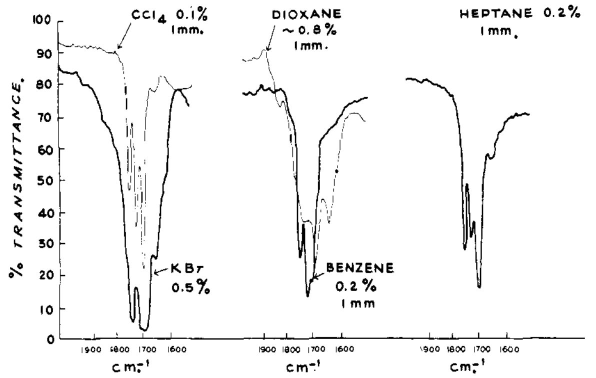

Fig. 2.—Infrared frequency shifts of diacetamide carbonyl frequency in various solvents (*cf*. Table IV).

quency in going from CCl_4 solution to KBr disc (Fig. 3). The data for diacetamide are given in Table IV (*cf*. Fig. 2)

TABLE IV

INFRARED FREQUENCIES IN CM.$^{-1}$ FOR >C=O AND >N—H BANDS OF DIACETAMIDE IN VARIOUS SOLVENTS

State	Hexachlorobutadiene pastes[6]	KBr. 0.5%	CCl_4, 0.1%	Dioxane. 0.8%	Benzene. 0.2%	Heptane. 0.2%
>C=O	1734	1736	1748	1818	1742	1745
	1700	1706	1721	1736	1712	1724
		1689	1698	1698	1698	1692
>N—H	3270	3226	3401	3497	3390	3040
	3245	3185	3205	3175	3279	
	3190	3135	3165		3941	
μ D.	..	..	..	2.91	1.89	1.33

While Uno and Machida[6] reported two bands for the infrared carbonyl frequency of form A of diacetamide, we are able to resolve three bands (especially in CCl_4) in the carbonyl region (Fig. 2). The dipole moment data suggest that the cyclic dimer of diacetamide is present in benzene and heptane solutions. X-Ray data[6,7] suggest that the dimer is also present in the solid. One would not expect an appreciable shift between the solid in KBr and the solution in CCl_4, benzene and heptane. This proves to be the case. The dipole moment of diacetamide in dioxane suggests that the expected *cis-trans* conformation is present. The large infrared shifts (1736 to 1818 and 1706 to 1736 cm.$^{-1}$) from KBr to dioxane solutions are indicative of the reduction of hydrogen bonding in dioxane. It is interesting to note that a 0.8% solution of diacetamide in dioxane gives a less intense carbonyl band than a 0.1 or 0.2% solution in other solvents indicating some type of interaction between dioxane and diacetamide. The >N–H band of diacetamide is at its highest frequency (3497 cm.$^{-1}$) in dioxane and its lowest in heptane (3040 cm.$^{-1}$), again suggesting less hydrogen bonding in dioxane in agreement with the dipole moment data.

Infrared frequency shifts and examination of physical properties show that diacetamide hydrogen bonds strongly. The low dipole moment of diacetamide in benzene and heptane leads one to conclude that the hydrogen bonding is in the form of a cyclic dimer rather than in a linear polymer.

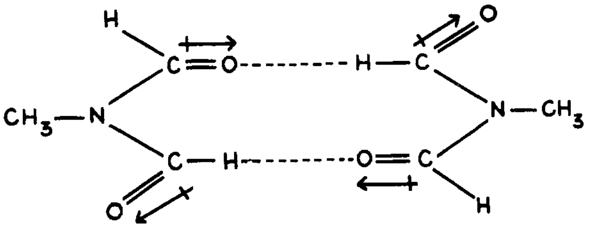

Fig. 3.—Proposed dimer of N-methyldiformamide.

Dipole Moment and Structure of N-Methyldiformamide.—The experimental moments for the three imide conformations are *cis-cis* 2.6–2.9 D., *cis-trans* 3.0–3.2 D. and *trans-trans* more than 6.0-D. (theoretical). One would expect N-methyldiformamide to be in the *cis-cis* conformation, for Stuart–Briegleb models indicate that this is the most favorable conformation when R is hydrogen since the carbonyl oxygens are farthest apart and electrostatic repulsions least (Fig. 1). The dipole moment of N-methyldiformamide in dioxane, 1.76 D., is less than the experimental value for the *cis-cis* conformation (2.6–2.9 D.) and is also less than N-methyldiacetamide, 3.22 D., which is in the *cis-trans* conformation.

The only difference here is the substitution of a hydrogen for a methyl group on the amide carbonyl group carbon. In dioxane at 30° acetamide has a moment of 3.70 D.[8] and formamide has a moment of 3.90 D.[9] Removal of a methyl group from the carbonyl carbon would thus not be expected to cause any great change in the dipole moment. In diacetamide it was suggested that the low moments in benzene and heptane are due to hydrogen bonding between the carbonyl group and the free hydrogen on the nitrogen. This is not possible in N-methyldiacetamide so the moment changes only slightly in going from dioxane to benzene to heptane.

In N-methyldiformamide there is no free hydrogen on the nitrogen, yet the dipole moment is lower than would be predicted and decreases slightly in going from dioxane to benzene. (George and Wright[10] obtained a value of 1.51 D. for N-methyldiformamide in benzene at 20°.) Furthermore, the moment increases in going from benzene to heptane. The only possibility here for hydrogen bonding is with the hydrogen attached to the carbonyl group. Examination of Stuart–Briegleb models shows that *a cyclic dimer* with zero or low moment can be formed (Fig. 3). We propose, therefore, that hydrogen bonding between the formyl group hydrogen and the carbonyl group is present in N-methyldiformamide.

N-Methyldiformamide is not very soluble in heptane, so the dipole moment calculated is based on low weight fractions (up to 0.0012). The increased moment, however, indicates that there is less dimer formed in heptane than in benzene. In this case one would expect a lower moment with increased hydrogen bonding. The results are not perfect, but indicate that the higher the dipole moment the less hydrogen bonding there is.

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[8] W. D. Kumler and C. W. Porter, *J. Am. Chem. Soc.*, **56**, 2549 (1934), obtained a value of 3.72 D. in dioxane at 30°.

[9] W. W. Bates and M. E. Hobbs, *ibid.*, **73**, 2151 (1951).

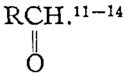
[10] M. V. George and G. F. Wright, *Can. J. Chem.*, **36**, 189 (1958).

INFRARED CARBONYL FREQUENCIES IN DIPOLE SOLVENTS

Solvent	Dipole moment, D.	Infrared >C=O ν cm.$^{-1}$
Benzene	1.63	1686
Dioxane	1.76	1684
Heptane	2.16	1698

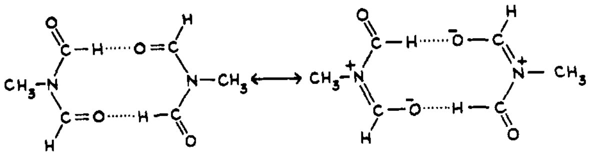
From the dipole moment data it would seem that more of the dimer is present in benzene than in dioxane or in heptane. While it appears that dioxane breaks up the diacetamide dimer, the situation apparently is different with regard to the proposed dimer. The formation of the proposed dimer of N-methyldiformamide appears to be assisted by solvents of a more polarizable nature. Benzene with its π-sextet is more polarizable than dioxane with its "lone pair" electrons which is more polarizable than heptane. The refractive index gives some indication of this as the $n^{20}\mathrm{D}$ values for heptane, dioxane and benzene are 1.3876, 1.4221 and 1.5001, respectively. Thus the amount of dimer present increases with the polarizability of the solvent from heptane to dioxane to benzene.

Theoretical Considerations.—There are a number of reasons why one would expect this proposed dimer to be fairly stable. A hydrogen bond is formed between a proton donor or acidic group A, and an electron donor or basic group B. The carbonyl group is a well known electron donor and participant in hydrogen bonding. The hydrogen in the dimer is attached to a carbon with two adjacent electronegative groups and would be expected to be more acidic than the usual hydrogen on a carbon. Weak hydrogen bonding has been demonstrated with the acidic hydrogen on carbon in chloroform and acetylene.[11] Less positive evidence exists for hydrogen bonding in aldehydes



$\underset{\underset{\mathrm{O}}{\|}}{\mathrm{R}}\mathrm{CH}$.[11–14]

Resonance in the proposed dimer forces the molecule into a planar conformation and places a partial negative charge on the oxygen and a partial positive charge on the nitrogen.



Both effects increase hydrogen bonding; the negative charge on the oxygen makes it a better electron donor, while the plus charge on the nitrogen makes the hydrogen more acidic. Normal carbonyl resonance also makes the hydrogen more acidic

The linear arrangement —A—H· · ·B— is energetically favored. In the case of the proposed dimer (Fig. 3) there is a perfect fit with both bonds linear. Coulson[15] has pointed out that the variation of electrostatic energy in hydrogen bonds with the angle of non-linearity (θ) is probably of the type $E = E_0 \cos \theta$, provided θ is not too large. Pauling[16] has discussed the idea of complementariness in structure as the basis of the specificity of interaction of antibodies and antigens. This is the idea that weak intermolecular forces, which individually would not be enough to produce a significant bond, may coöperate between molecules that are complementary in structure in such a way as to produce a strong bond. Here is such a case where two weak hydrogen bonds are so disposed as to reinforce each other and form a fairly stable bond.

Physical Properties.—The three compounds in group 2 of Table III have the same molecular weight (115) and all contain the amide group. N-Methyldiacetamide, which cannot hydrogen bond, boils and melts at about the same temperature as N,N-dimethylbutyramide, which is also unable to hydrogen bond. *n*-Valeramide, which can hydrogen bond, boils and melts higher than either compound.

All compounds in group 3 have a molecular weight of 87 and contain the amide group. N-Methyldiformamide, which can hydrogen bond weakly, boils and melts higher than N,N-dimethylacetamide, which cannot hydrogen bond. *n*-Butyramide which can hydrogen bond strongly boils and melts at a higher temperature than either compound.

N-Methyldiacetamide, which has a higher molecular weight than N-methyldiformamide boils only slightly above (9°) and melts below the latter compound. Diacetamide boils and melts above N-methyldiacetamide even though the latter has the higher molecular weight. These data suggest that there is strong hydrogen bonding in diacetamide and weak hydrogen bonding in N-methyldiformamide.

Molecular Weight Determinations.—Initial determinations of molecular weight based on the increase in the boiling point of benzene gave the following results (about 0.06 to 0.20 g. in 7 g. of benzene).

Compound	Mol. wt. Exptl.	Calcd.
N-Methyldiacetamide	113, 115	115
N-Methyldiformamide	175, 153, 186	87
Benzoic acid	261	122

These data give reasonable evidence of association in N-methyldiformamide and benzoic acid, but reproducibility of the data was difficult.

Independent determinations were made by the Microanalytical Laboratory of the Department of Chemistry, University of California, Berkeley, using an Osmometer (Mechrolab #301). The results for N-methyldiformamide in benzene at 37° give an average molecular weight of 161 (147–178). The calculated molecular weight of the compound is 87.08 so the dimer proposed would have a molecular weight of 174.16. These data show that there is pronounced association of N-methyldiformamide in benzene solution at 37° which confirms the evidence from the dipole moment work.

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[11] G. Pimentel and A. McClellan, "The Hydrogen Bond," Freeman, San Francisco, Calif., 1960, pp. 197–201.

[12] S. Pinchas, *Anal. Chem.*, **27**, 2 (1955).

[13] S. Pinchas, *ibid.*, **29**, 334 (1957).

[14] S. Pinchas, *Chemistry & Industry*, 1451 (1959).

[15] C. A. Coulson, in "Proceedings of Symposium on Hydrogen Bonding," Pergamon Press, London, 1959, p. 339.

[16] L. Pauling, in "Molecular Structure and Biological Specificity," Am. Ins. of Biol. Sci., Washington, D. C., 1957, p. 187.

Ray, *et al.*,[17] reported a molecular weight of 86.8 for N-methyldiformamide from vapor density at 240°. As the boiling point of the compound is 183°, one might anticipate the breaking up of the dimer at the more elevated temperature.

Ultraviolet Spectra.—Ultraviolet data show how the inductive effect of the methyl group facilitates transition from the ground to the excited state. There is no band for diacetamide above 200 mμ; the replacement of the hydrogen by a methyl group causes a peak at 216 mμ. The substitution of formyl for acetyl in N-methyldiacetamide causes the wave length to decrease to 207 mμ in N-methyldiformamide.

	EtOH		Hexane	
Compound	$\lambda_{\max.}$ mμ	ε	$\lambda_{\max.}$ mμ	ε
N-Methyldiformamide	207	10,500	207	11,250
N-Methyldiacetamide	216	10,400	213	10,000
Diacetamide	Nothing above 200 mμ			

Infrared Data (Fig. 4, Table V).—Comparison of the infrared spectra of the pure compound and a dilute solution in carbon tetrachloride might show hydrogen-bonding shifts of the C–H frequency. In the proposed dimer, however, only 20% of the C–H groups are hydrogen bonded, so clearcut C—H shifts are not expected. In another system (acetone–chloroform) where weak hydrogen bonding has been detected by other means (n.m.r., heat of formation) >C–H frequency shifts are not observed.[18]

TABLE V

INFRARED CARBONYL FREQUENCIES AND BAND WIDTHS OF STRAIGHT CHAIN IMIDES (CM.$^{-1}$)

Compound	State A, CCl_4	State B, pure	$\frac{\Delta\nu\ ^1/_2 \text{ state A}}{\Delta\nu\ ^1/_2 \text{ state B}}$
V. Acetamide	0.02% (2 mm.)	0.25% KBr	
	1712	(1730)	
	(1686)	1664	
	1600	1661	$\frac{36 \text{ cm.}^{-1}}{10 \text{ cm.}^{-1}} = 3.6$
	$\Delta\nu$ = 48 cm.$^{-1}$		
I. N-Methyldi-	0.1% (1 mm.)	Liquid	
acetamide[a]	1706	1706	$\frac{32 \text{ cm.}^{-1}}{12 \text{ cm.}^{-1}} = 2.7$
	$\Delta\nu$ = 14 cm.$^{-1}$	1692	
III. N-Methyldi-	0.1% (1 mm.)	Liquid	
formamide	(1739)	(1730)	$\frac{37 \text{ cm.}^{-1}}{8 \text{ cm.}^{-1}} = 4.6$
	1684	1695	
	$\Delta\nu$ = 25 cm.$^{-1}$	1669	Corrected
IV, Dimethyl-	0.1% (1 mm.)	Liquid	
formamide	1689	1678	$\frac{25 \text{ cm.}^{-1}}{9 \text{ cm.}^{-1}} = 2.8$
	$\Delta\nu$ = 11 cm.$^{-1}$		

[a] H. K. Hall, Jr., and R. Zbinden, *J. Am. Chem. Soc.*, **80**, 6430 (1958), give $\Delta\nu$ = 13 cm.$^{-1}$ (1708–1695).

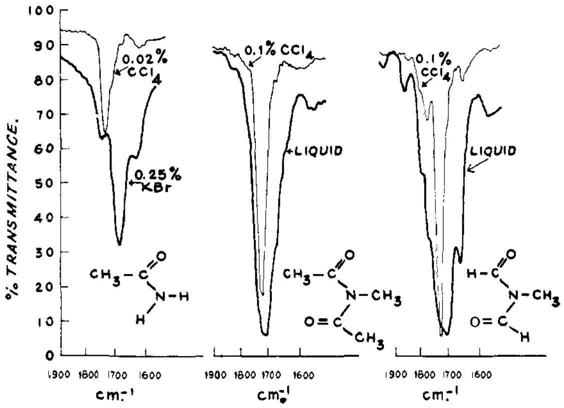

Fig. 4.—Infrared spectra of acetamide, N-methyldiacetamide and N-methyldiformamide, neat, and in CCl_4 solution (*cf*. Table V).

The carbonyl stretching frequency is a more sensitive indicator since with acetamide there is a shift of 48 cm.$^{-1}$ (1712–1611) going from the dilute CCl_4 solution to the KBr disk. The carbonyl stretching frequency of pure liquid N-methyldiformamide is a strong band with two peaks at 1695 and 1669 cm.$^{-1}$, both about the same intensity. This is expected as the proposed dimer has two free carbonyl groups and two hydrogen-bonded carbonyl groups. Upon dilution to 0.2% in CCl_4 the carbonyl band sharpens to one peak at 1689 cm.$^{-1}$ with a greater intensity. The hydrogen-bonded carbonyl groups represented at the lower frequency, 1669 cm.$^{-1}$, are partly broken up in CCl_4 and there is one peak for all four non-bonded carbonyl groups. Other peaks remain in the same position or are shifted to slightly lower frequency. The shift to lower frequency upon hydrogen bonding is indicative of the weaker force constant of the carbonyl stretch due to the interaction. This shift of 25 cm.$^{-1}$ (1694–1669) is contrasted to the shift of 48 cm.$^{-1}$ for the acetamide and the shift of 14 cm.$^{-1}$ for N-methyldiacetamide. Dimethylformamide shows a shift of 11 cm.$^{-1}$ from the pure liquid to the 0.1% CCl_4 solution (1689–1678). This is probably a solvent effect but still indicates that the N-methyldiformamide shifts a greater amount upon dilution than do compounds that do not hydrogen bond such as N-methyldiacetamide and dimethylformamide. The difference between the extremes of the carbonyl frequencies for N-methyldiacetamide and N-methyldiformamide in the pure liquid state is 37 cm.$^{-1}$ (1706–1669). The difference between the two sharp carbonyl peaks in the carbon tetrachloride solution is only 12 cm.$^{-1}$ (1706–1694).

In the four cases cited, the half width of the CCl_4 solution band is considerably less than that of the pure liquid (neat or KBr). The ratio of the half width of the pure compounds to the half width of the solution in cm.$^{-1}$ for N-methyldiacetamide and dimethylformamide is 2.7 and 2.8, respectively. For acetamide and N-methyldiformamide this ratio is 3.6 and 4.6, respectively. The latter is corrected so that the band at 1629 cm.$^{-1}$ is not included (uncorrected ratio is 5.4). The greater breadth of the acetamide and the N-methyldiformamide band (KBr or neat) is another indication of hydrogen bonding.

Nuclear Magnetic Resonance Studies.[19]—While >C–H stretching shifts are not observed in the infrared, n.m.r. is particularly useful in the detection of weak hydrogen bonding, for one "sees" only hydrogen. The formyl hydrogen $(\mathrm{H}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{N}<)$

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(17) J. D. Ray, *et al.*, *J. Org. Chem.*, **21**, 1052 (1956).

(18) C. Huggins, G. Pimentel and J. Shoolery, *J. Chem. Phys.*, **23**, 1244 (1955).

(19) We wish to thank Dr. James Shoolery and Mr. Norman Bhacca of Varian Associates, Palo Alto, Calif., for running the spectra and for consultation. The spectra were run on Varian Spectrometer A-60 (60 mc. at room temperature with tetramethylsilane as internal reference).

resonates at very low field due partly to the combined inductive effect of the oxygen and **nitrogen** which reduces local diamagnetic shielding. Paramagnetic circulations at the aldehydic carbonyl group also diminish the shielding of the proton.[20,21] The spectrum of pure liquid N-methyldiformamide consists of two sharp lines of area ratio 3:2, as Ray, *et al.*,[17] and George and Wright found.[10] A peak at low field 531 c.p.s. from $SiMe_4$ is the absorption from the two formyl hydrogens, while a peak at 182 c.p.s. represents the absorption from the three equivalent hydrogens of the N-methyl group. Dimethylformamide as the pure liquid shows the HCO peak, 480 c.p.s. from $SiMe_4$.

The n.m.r. spectrum of N-methyldiacetamide shows two peaks of area ratio 2/1. The larger peak, 138 c.p.s. from $SiMe_4$, is the absorption of the six acetyl hydrogens, while the other peak, 189 c.p.s. from $SiMe_4$, is the absorption of the three N-methyl hydrogens.

In the infrared studies, it is possible sometimes to see vibrational bands for both the associated and non-associated carbonyl groups simultaneously in the liquid but with n.m.r. at room temperature, H-bonding solutions usually display only one line for both the associated and non-associated protons due to the large difference in frequencies involved in the two methods.[22,23]

Nuclear magnetic resonance hydrogen bonding shifts are really "shifts in the chemical shifts." The formyl proton in liquid N-methyldiformamide appears 546 c.p.s. from $SiMe_4$. A dilute solution (*ca.* 2.5%) in CCl_4 finds a shift to higher field, 529 c.p.s. of $\Delta\nu$ = 17 c.p.s. with broadening of the band. No correction for bulk diamagnetic susceptibility need be made as an internal standard, $SiMe_4$, is used. Warming of the pure liquid causes the same effect, namely, broadening of the band and a shift toward higher field. Other things being equal, the resonance is sharper the more the rate of exchange exceeds the ν separation.[24] Thus dilution in carbon tetrachloride, in contrast to infrared, broadens the line as there is less opportunity for rapid exchange in the more dilute solution. The sharpness and position of the N-methyl peak (183 c.p.s.) is affected neither by dilution nor warming.

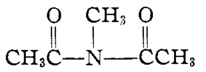
The n.m.r. spectra of dimethylformamide, both as the pure liquid and in 10% solution in carbon tetrachloride, have the HCO peak within 1 c.p.s. of 480 c.p.s. from $SiMe_4$, indicating no significant shift or dilution effect. Since one would expect the formyl hydrogen in dimethylformamide and N-methyldiformamide to act the same, this shows that the shift in N-methyldiformamide is real.

Nuclear magnetic resonance proton signals are displaced to lower fields by the formation of hydrogen bonds, the exception being those associated with some aromatic molecules. The presence of the electron donor (carbonyl group) draws the protons away from its bonding electrons and reduces the electron density immediately around it. The frequency shift is small, 17 c.p.s., indicating that the strength of the bond is small. Schneider[24] has shown the shift for the self association of chloroform (liquid and solution in hexane and cyclohexane and

TABLE VI

DIPOLE MOMENTS OF STRAIGHT CHAIN IMIDES AND AMIDES AT 30°

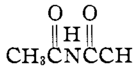
I,



$CH_3C(=O)—N(CH_3)—C(=O)CH_3$

	ω_2	ϵ_{12}	ν_{12}
In dioxane	0.0010245	2.20849	0.97818
	.0014033	2.21198	.97815
	.0018429	2.21633	.97814
	.0023456	2.22165	.97811
μ = 3.22 ± 0.04 D.	.0029379	2.22862	.97806
Mol. wt. 115.15	.0034666	2.23481	.97803
ϵ_1 = 2.19682	ν_1 = 0.97824	P_{2_0} = 237.87	
α = 10.82788	β = −0.06069	P_{E_2} = 29.03 calcd.	
In benzene	0.00	2.26279	.....
	.0005380	2.26793	.....
	.0009698	2.27116	1.15194
	.0012325	2.27308	1.15177
μ = 2.98 ± 0.03 D.	.0017494	2.27752	1.15163
Mol. wt. 115.15	.0022080	2.28127	1.15146
ϵ_1 = 2.26323	ν_1 = 1.15227	P_{2_0} = 207.63	
α = 8.20244	β = −0.36854	P_{E_2} = 29.03 calcd.	
In heptane	0.00	1.90992	1.47566
	.0003657	1.91198	1.47554
	.0008463	1.91455	1.47509
	.0013285	1.91744	1.47486
	.0015768	1.91857	1.47463
μ = 2.97 ± 0.01 D.	.0019935	1.92054	1.47452
Mol. wt. 115.15	.0031298	1.92722	1.47372
ϵ_1 = 1.90982	ν_1 = 1.47560	P_{2_0} = 210.28	
α = 5.56821	β = −0.55732	P_{E_2} = 29.03 calcd.	

II,



$CH_3C(=O)NHC(=O)CH_3$

	ω_2	ϵ_{12}	ν_{12}
In dioxane	0.00	2.20875	0.97450
	.0007721	2.21535	.97450
	.0024247	2.23298	.97450
	.0034385	2.24231	.97450
μ = 2.91 ± 0.03 D.	.0042503	2.25190	.97450
Mol. wt. 101.12	.0052019	2.25960	.97450
ϵ_1 = 2.20839	ν_1 = 0.97450	P_{2_0} = 194.88	
α = 9.97965	β = 0.00	P_{E_2} = 24.28 calcd.	
In benzene	0.00	2.26671	1.14870
	.0009716	2.27099	1.14794
	.0025326	2.27646	1.14764
	.0050354	2.28451	1.14673
μ = 1.89 ± 0.02 D.	.0068890	2.29204	1.14658
Mol. wt. 101.12	.0085752	2.29881	1.14597
ϵ_1 = 2.26694	ν_1 = 1.14843	P_{2_0} = 95.79	
α = 3.66101	β = −0.29128	P_{E_2} = 24.28 calcd.	
In heptane	0.00	1.91215	1.47785
	.0008371	1.91352	1.47634
	.0024093	1.91592	1.47559
	.0030881	1.91722	1.47409
μ = 1.33 ± 0.02 D.	.0031843	1.91763	1.47459
Mol. wt. 101.12	.0042868	1.91908	1.47333

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[20] L. H. Meyer, *et al.*, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

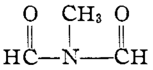
[21] J. A. Pople, *Proc. Roy. Soc.* (*London*), **A239**, 550 (1957).

[22] Reference 11, pp. 142–157.

[23] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution NMR," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 400–421.

[24] W. G. Schneider, ref. 15, p. 61.

$\epsilon_1 = 1.91209 \quad \nu_1 = 1.47764 \quad P_{2_0} = 59.57$
$\alpha = 1.66459 \quad \beta = -1.01895 \quad P_{E_2} = 24.28$ calcd.

III, 
$$\mathrm{H\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{N}-\overset{\overset{O}{\|}}{C}H}$$

	ω_2	ϵ_{12}	ν_{12}
In dioxane	0.00	2.20747	0.97385
	.0009521	2.21201	.97376
	.0030300	2.22040	.97318
	.0048351	2.22801	.97299
	.0063069	2.23426	.97278
$\mu = 1.761 \pm 0.01$ D.	.0088221	2.24436	.97241
Mol. wt. 87.08	.0102128	2.25241	.97203

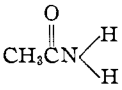
$\epsilon_1 = 2.20747 \quad \nu_1 = 0.97384 \quad P_{2_0} = 81.72$
$\alpha = 4.29243 \quad \beta = -0.17216 \quad P_{E_2} = 19.73$ calcd.

In benzene	0.00	2.26251	1.14700
	.0011109	2.26576	1.14661
	.0033074	2.27270	1.14608
	.0059752	2.28109	1.14501
$\mu = 1.63 \pm 0.01$ D.	.0071921	2.28451	1.14461
Mol. wt. 87.08	.0087422	2.29084	1.14382

$\epsilon_1 = 2.26223 \quad \nu_1 = 1.14708 \quad P_{2_0} = 72.94$
$\alpha = 3.8360 \quad \beta = -0.35496 \quad P_{E_2} = 19.73$ calcd.

In heptane	0.00	1.91061	1.47428
	.0003381	1.91215	1.47379
	.0004288	1.21224	1.47368
$\mu = 2.16 \pm 0.03$ D.	.0010334	1.91438	1.47357
Mol. wt. 87.08	.0012085	1.91523	1.47335

$\epsilon_1 = 1.91070 \quad \nu_1 = 1.47562 \quad P_{2_0} = 113.18$
$\alpha = 3.69787 \quad \beta = -0.49080 \quad P_{E_2} = 19.73$ calcd.

IV, 
$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}N\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H}}$$

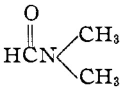
	ω_2	ϵ_{12}	ν_{12}
In dioxane	0.0009837	2.23656	0.97820
	.0014874	2.25223	.97814
	.0020301	2.26637	.97813
$\mu = 3.70 \pm 0.03$ D.	.0024229	2.27770	.97810
Mol. wt. 59.07	.0034426	2.30611	.97803

$\epsilon_1 = 2.20956 \quad \nu_1 = 0.97825 \quad P_{2_0} = 289.96$
$\alpha = 28.0872 \quad \beta = -0.06334 \quad P_{E_2} = 14.9$ calcd.

In benzene	0.00	2.26114	1.14700
	.0007579	2.27852	1.14672
	.0014070	2.28853	1.14644
	.0024174	2.30600	1.14617
$\mu = 3.07 \pm 0.02$ D.	.0031840	2.31884	.....
Mol. wt. 59.07	.0035459	2.32440	.....

$\epsilon_1 = 2.26484 \quad \nu_1 = 1.14698 \quad P_{2_0} = 203.06$
$\alpha = 16.91850 \quad \beta = -0.34777 \quad P_{E_2} = 14.9$ calcd.

In heptane: insoluble

V, 
$$\mathrm{H\overset{\overset{O}{\|}}{C}N\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown CH_3}}$$

	ω_2	ϵ_{12}	ν_{12}
In dioxane	0.00	2.20640	.....
	.0008836	2.22836	0.97891
	.0014040	2.24240	.97900
	.0024834	2.27003	.97906
$\mu = 3.95 \pm 0.02$ D.	.0030097	2.28293	.97914
Mol. wt. = 73.09	.0034602	2.29522	.97916

$\epsilon_1 = 2.20617 \quad \nu_1 = 0.97884 \quad P_{2_0} = 333.66$
$\alpha = 25.649 \quad \beta = +0.09464 \quad P_{E_2} = 19.79$ calcd.

In benzene	0.00	2.26480	.....
	.0010338	2.28685	1.15218
	.0016434	2.30052	1.15209
	.0021561	2.31212	1.15207
	.0029478	2.32964	1.15196
$\mu = 3.92 \pm 0.01$ D.	.0033072	2.33758	1.15193
Mol. wt. = 73.09	.0033931	2.33932	1.15190

$\epsilon_1 = 2.26445 \quad \nu_1 = 1.15230 \quad P_{2_0} = 329.30$
$\alpha = 22.07751 \quad \beta = -0.11107 \quad P_{E_2} = 17.79$ calcd.

In heptane	0.00	1.90874	1.48191
	.0013982	1.92748	1.48150
	.0021219	1.93663	1.48124
	.0026244	1.94369	1.48111
	.0035458	1.95781	1.48084
$\mu = 3.90 \pm 0.02$ D.	.0041558	1.96583	1.48057
Mol. wt. = 73.09	.0046563	1.97324	1.48048

$\epsilon_1 = 1.90803 \quad \nu_1 = 1.48192 \quad P_{2_0} = 315.67$
$\alpha = 13.9042 \quad \beta = -0.31332 \quad P_{E_2} = 19.79$ calcd.

cyclopentane) is 12 c.p.s. at 40 mc. which is equivalent to 18 c.p.s. at 60 mc.

Huggins and Pimentel[18] found a shift of 20.4 c.p.s. for chloroform and acetone solution at 30 mc. or 40.8 c.p.s. at 60 mc. They estimated a value of 2.5 kcal. (uncertainty of 2) for the heat of formation of the acetone–chloroform complex from the n.m.r. shift and other data. Campbell and Kartzmark[25] determined the enthalpies of mixing of acetone and chloroform and calculated the energy of hydrogen bonding in the system as 2.7 ± 0.1 kcal. From our shift of 17 c.p.s. and the value of 2.7 kcal. corresponding to a shift of 40.8 c.p.s., one calculates a value of 1.1 kcal. for each hydrogen bond in the dimer. Because of the complementary nature of the dimer, the total energy would be of the order of 2.2 kcal./mole of dimer. Thermal energy (*RT*) at room temperature is about 0.6 kcal./mole, so one would expect the dimer to be reasonably stable in the pure liquid at room temperature.

Summary.—We propose that N-methyldiformamide forms a cyclic dimer VI where the formyl hydrogen is bonded to the carbonyl group. Dipole moments of the compound are lower than N-methyldiacetamide which has the expected moment for the *cis-trans* conformation. Comparison of melting and boiling points of the compound suggests interaction. Molecular weight determinations indicate appreciable association in benzene at 37°. Both ends of the proposed hydrogen bond have been investigated. The Δν for N-methyldiformamide is 11 cm.$^{-1}$ greater than the Δν of N-methyldiacetamide and dimethylformamide in going from CCl_4 solution to pure liquid; n.m.r. studies show a broadening and a shift to higher field of the formyl hydrogen upon dilution; the methyl hydrogens remain unchanged both in position and sharpness. Calculations from the n.m.r. shift indicate a strength of 1.1 kcal./hydrogen bond or 2.2 kcal. per mole of dimer.

Experimental

Dipole moments were measured using an apparatus described previously[26] and on a WTW Dipolmeter model DM 01 with DFL 2 cell. The solvents were purified as before.[26] Dipole moments were calculated using the method

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[25] A. N. Campbell and E. M. Kartzmark, *Can. J. Chem.*, **38**, 652 (1960).

[26] W. D. Kumler, *J. Am. Chem. Soc.*, **62**, 3292 (1940).

and equation of Halverstadt and Kumler[27]

$$p_{20} = \frac{3\alpha\nu_1}{(\epsilon_1 + 2)^2} + \frac{(\nu_1 + \beta)(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

$$P_{20} = p_{20}M \qquad M = \text{mol. wt.}$$

$$\mu = 0.01281\sqrt{(P_{20} - P\epsilon)T}$$

The plots of ϵ_{12} *versus* ω_2 and γ_{12} *versus* ω_2 were straight lines within the limits of experimental error. The values of ϵ_1 and γ_1 were obtained by the method of least squares. The standard errors in the dipole moments were calculated from the equation

$$\delta_\mu = 0.0046\,\frac{M}{\mu}\,\delta_\alpha{}^{28}$$

and the standard error in α. $\delta\alpha$, from the equation[28,29]

$$\delta_\alpha = \pm\left[\frac{n}{n-2}\left(\frac{\Sigma(\epsilon_1 - \epsilon_{12})^2}{n\Sigma(\omega_2)^2 - (\Sigma\omega_2)^2}\right)\right]^{1/2}$$

The errors from scatter of the points for specific volume do not need to be considered since even large errors in β produce only very small errors in the dipole moment.[30]

Diacetamide was prepared by acetylation of acetamide with acetic anhydride in the presence of ammonium chloride.[31] It was recrystallized several times from CCl_4 (m.p. 81°).

Acknowledgment.—We wish to thank Dr. H. K. Hall, Jr., of du Pont[32] for providing N-methylformamide and N-methyldiacetamide. Gas chromatograpy and n.m.r. showed the original sample of N-methyldiformamide had a small amount of impurity, probably N-methyldiacetamide. N-Methyldiformamide was synthesized by the method of Ray and Ogg[17] and found to contain the same impurity. Purification was effected by gas chromatography using a preparative Apiezon column on an Aerograph model A110-C. All work reported on N-methyldiformamide was done on the purified compound. Dimethylformamide was Eastman Kodak Co., purified by shaking with solid potassium hydroxide, then lime, and distilled.[33]

We wish to thank Mr. M. K. Hrenoff of the Spectrographic Laboratory for all infrared and ultraviolet studies. Infrared spectra were run on Perkin–Elmer model 21 and ultraviolet spectra were run on Cary model 11. Portions of this study were aided by Public Health Grant CY-3211 (C4).

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[27] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2933 (1942).

[28] Private communication, E. W. Randall and Roger Rabb.

[29] R. J. W. Le Fevre, *J. Chem. Soc.*, 404 (1953).

[30] K. B. Everard, R. A. W. Hill and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

[31] D. Davidson and M. Karten, *J. Am. Chem. Soc.*, **78**, 1068 (1956).

[32] H. K. Hall, Jr., M. K. Brandt and R. M. Mason, *J. Am. Chem. Soc.*, **80**, 6424 (1958).

[33] G. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

Polymerization and Copolymerization of N-Vinylpyridinium Salts

BY IRL N. DULING[1] AND CHARLES C. PRICE

RECEIVED AUGUST 21, 1961

Several new salts of the N-vinylpyridinium ion have been prepared and their physical and chemical properties briefly described. The salts were found to polymerize or copolymerize with both ionizing radiation and free radical initiation. From the copolymerizations it was calculated that $Q = 0.31$–1.9, $e = +1.7$–2.4. It is suggested that the uncertainty in these values may be explained by variation of the separation between radical and ion due to electrical repulsions in the transition state. The existence of resonance interactions between the pyridinium ring and the vinyl group was established by observation of tritium exchange in the rearrangement of N-allylpyridinium salts to N-propenylpyridinium salts.

Introduction

Simple unsubstituted N-vinylpyridinium salts (I) have been reported only twice,[2a,b] and in neither case were any except the most obvious physical properties mentioned. Substituted salts (II) have been extensively investigated,[3–5] but principally with physiological objectives in mind. This paper reports the preparation and properties of several new N-vinylpyridinium salts. The principal portion, however, reports our investigation of the homopolymerization and copolymerization of these salts.

Gillis[6] attempted to copolymerize styrene and methyl methacrylate with vinyltrimethylammonium salts and vinyldimethylsulfonium salts without success. This result can be attributed to a lack of resonance stabilization of the radical derived from these monomers, although it may also be due to electrostatic repulsions. In this regard, it is interesting to note that, although N-allylammonium salts have been polymerized,[7] there are no reported polymerizations of vinyl compounds which carry an electrostatic charge α to the carbon–carbon double bond. It seemed interesting, therefore, to investigate an example in which resonance stabilization of the radical derived from the monomer was possible but which retained the electrostatic charge adjacent to the vinyl group. N-Vinylpyridinium salts provide such a case.

Experimental

N-Vinylpyridinium Fluoroborate.—A solution of 18.8 g. (0.1 mole) of 1,2-dibromoethane in 20 ml. of absolute alcohol was refluxed while 7.9 g. (0.1 mole) of pyridine was added dropwise during 6 hours. After refluxing an additional hour and standing overnight, the precipitated 1,2-(N,N-dipyridinium)-ethane bromide was filtered out and the filtrate evaporated to dryness under vacuum. Drying over phosphorus pentoxide gave 4.9 g. (56%) of crude **N-(2-bromoethyl)-pyridinium bromide**. Recrystallization from absolute ethanol yielded colorless hygroscopic needles, m.p. 126–128° (lit.[2] 100–103°). *Anal.* Calcd. for $C_{13}H_{11}N_4O_7Br$: C, 37.61; H, 2.67; N, 13.49; Br, 19.25. Found: C, 37.76; H, 2.86; N, 12.83; Br, 19.38.

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[1] Sun Oil Co. Fellow, 1959–1961.

[2] (a) F. Cappolla, *Gazz. chim. ital.*, **15**, 333 (1885); (b) E. Schmidt, *Arch. Pharm.*, **251**, 183 (1913).

[3] P. Pfeiffer and A. Longenberg, *Ber.*, **43**, 2935 (1910).

[4] L. C. King and W. B. Brownell, *J. Am. Chem. Soc.*, **72**, 2507 (1950).

[5] R. Kröhnke, *Angew. Chem.*, **65**, 605 (1953).

[6] R. G. Gillis, Ph.D. Thesis, University of Notre Dame, 1952.

[7] G. B. Butler and R. L. Bunch, *J. Am. Chem. Soc.*, **71**, 3120 (1949); D. S. Trifan and J. J. Hoglen, *ibid.*, **83**, 2021 (1961).