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The Dipole Moment and Structure of the Imide Group. II. Semicyclic Imides: N-Acetyl Lactams, Effect of Ring Size on Dipole Moment; N-Benzoyl Lactams, Ring Size, Dipole Moment and Ultraviolet Spectra

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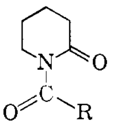
Ring size affects the moment of N-acetyl lactams by determining the amount of *s*-character in the exocyclic bond and by changing the angle between the two carbonyl groups. The first effect is noted in the dipole moment of five-, six- and seven-membered N-acetyl cyclic amines. A relationship between the dipole moments of N-acetyl cyclic amines and the carbonyl frequency of the same ring size cyclic ketones is demonstrated. The low dipole moments of N-acetyl lactams, 3.0–3.2 D., indicate that the semicyclic imides are in the *cis-trans* conformation.

The dipole moments of N-benzoyl lactams, in contrast to N-acetyl lactams, increase with increasing ring size. Examination of models indicates that the ring nitrogen and phenyl group cannot be coplanar with the free carbonyl group at the same time. Competition for the lone pair of electrons on the carbonyl oxygen is shown in the higher dipole moment of the seven-membered ring where the phenyl group can resonate more with the free carbonyl group. This shifts the position of the free carbonyl group closer to the ring carbonyl so the moment is increased. The ultraviolet spectra of N-benzoyl lactams show two bands: one band, also found in N-acetyl lactams, represents the imide resonance and decreases in intensity with increasing ring size. The other band increases in intensity with ring size and represents the increased conjugation of the benzene ring with the carbonyl group. A relationship between dipole moment and extinction of N-benzoyl and N-acetyl lactams is shown.

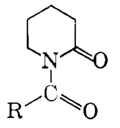
Introduction

Of the three possible conformations for the free imide group[1] the *cis-cis*, *cis-trans*, *trans-trans*, only the latter two are possible in the semicyclic imides

cis-trans[a]



trans-trans



[a] Position of carbonyl groups relative to the group on nitrogen.

An estimation of the *trans-trans* conformation gives a moment of more than 6.0 D.; electrostatic repulsions render this conformation unlikely. (The *cis-cis* conformation in six-membered rings was found to have a dipole moment of 2.7–2.9 D.[1])

Most molecules of semicyclic imides would be expected to be in the *cis-trans* conformation and have a moment slightly higher than the *cis-cis* conformation. Data on N-acetyl and N-benzoyl lactams bears this out and shows that the dipole moment is determined by two factors; one is the size of the ring, the other is the size and nature of the R group.

Results and Discussion

Effect of Ring Size on N-Acetylamines.—Ring size can affect the moment in two ways. One is by changing the angle between the two carbonyl groups so the five-membered ring has a lower moment than the six- or seven-membered ring. This is due to the smaller ring angles in the five-membered ring which creates a larger angle between the two carbonyl groups. Besides this, the size of the ring affects the exocyclic bond between the nitrogen and acetyl group by rehybridization of bonds.

An examination of N-acetyl cyclic amines allows us to investigate this effect of ring size on the dipole moment and other physical properties. Table I shows that the dipole moment of the N-acetyl cyclic amines decreases from the five- to the six- to the seven-membered ring. The cause of the higher moment of the five-membered ring as compared to the six- and the lower moment of the seven-membered ring lies in the ring size, for that is all that changes.

Bartlett and Stiles and others[2-4] have correlated the carbonyl stretching frequency of cyclic ketones with ring size. Wiberg and Nist[5] have published the vibrational frequencies of 10% solutions of cycloalkenes, cycloalkanones and methylenecycloalkenes in carbon tetrachloride. The results (Table II) in all three cases show that the six-membered ring has about the normal frequency while smaller rings have higher frequencies and larger rings lower frequencies.

Bartlett and Stiles[2] attribute this to rehybridization of the bonds forming the ring. In the strained ring systems below six members there is more *p*-character in the C–C–C bonds forming the ring with a concomitant increase in *s*-character in the exocyclic bond. This increase in *s*-character in the exo bond causes an increase in the force constant of the $>C{=}O$ or $>C{=}C$ or $=CH$ bond and an increased frequency. In the more flexible seven- and eight-membered rings mutual repulsion between hydrocarbon groups tends to spread the C–C–C angles and results in absorption of the *exo* bond at lower frequency.

H. K. Hall, Jr., and R. Zbinden[6] measured the infrared carbonyl frequencies for a variety of carbonyl compounds. The five-membered ring

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

[2] P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2809 (1955).

[3] Reference 8, pp. 387–389.

[4] D. Bladon, *et al.*, *J. Chem. Soc.*, 2410 (1951).

[5] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

[6] H. K. Hall, Jr., and R. Zbinden, *ibid.*, **80**, 6428 (1958).

TABLE I

DIPOLE, ULTRAVIOLET AND INFRARED DATA[a]

		μ in Debyes	Ultraviolet in EtOH λ_{max}	ϵ	Infrared carbonyl frequency in cm.$^{-1}$
I	N-Acetylpyrrolidine	4.28	[b]	....	1639
II	N-Acetylpiperidine	4.07	[b]	....	1639
III	N-Acetylhexamethyleneamine	3.99	[b]	....	1639
IV	N-Acetylpyrrolidone	3.00	216	11,300	1730, 1686
V	N-Acetylpiperidone	3.22	218	8,900	1686
VI	N-Acetyl caprolactam	3.13	219	9,400	1686
VII	N-Isobutyrylpyrrolidone	2.38	217	13,300	1730, 1689
VIII	N-Carbethoxypyrrolidone	3.42	204?	10,400?	1786, 1748, 1706
IX	5-Methyl-N-acetyl caprolactam	3.35	218	10,400	1686

[a] Compounds courtesy of Dr. H. K. Hall, Jr., du Pont. [b] Nothing above 200 mμ.

TABLE II

VIBRATIONAL FREQUENCIES FOR SOME CYCLIC COMPOUNDS[a]

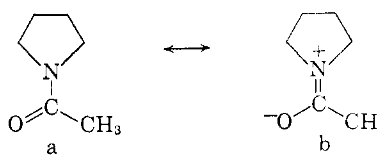
Ring size	=CH[c]	>C=O	>C=CH$_2$
3	3076	1815	1730
4	3048	1788	1678
5	3061	1746	1657[b]
6	3024	1715	1651[b]
7	3020	1703	..
8	3016	1702	..
Straight chain	3023 (*cis*-2-butene)	1720 (diethyl ketone)	1654 (isobutene)

[a] K. Wiberg and B. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961). [b] Raman frequencies. [c] Values in cm.$^{-1}$ for CCl$_4$ solutions (10%) using calcium fluoride prism.

compounds absorbed about 40 cm.$^{-1}$ higher than the six-membered rings. This is due to hybridization effects rather than ring strain as no correlation with polymerizability was noted.

It has been calculated for cyclopropane[7] that there is about 9% more *s*-character in the exocyclic bond than the usual *sp*^{3}-bond. The C–H stretching frequency of cyclopropane is 3030 cm.$^{-1}$ as compared to the usual CH$_2$ stretching frequency[8] of 2926 and 2853 cm.$^{-1}$.

Utilizing this general concept in the five-membered ring, we would expect the exocyclic C–N bond to have more *s*-character with the ionic structure b favored and thus it would have a higher dipole moment. On this basis one would



predict that the six-membered ring would have the normal tertiary amide moment while the seven-membered ring would have a slightly lower moment. Bellamy[9] has shown that the carbonyl frequency of tertiary amides is about 30 cm.$^{-1}$ less than that of secondary amides and 40 cm.$^{-1}$ less than primary amides (all dilute solutions). All three N-acetylamines show a carbonyl frequency of 1639 cm.$^{-1}$. The low frequency of tertiary amides is due to the ability of R groups to stabilize the partial positive charge on the nitrogen and should increase the dipole moment of the tertiary amide over that of the primary amide. Dimethylformamide in dioxane at 30° has a dipole moment of 3.95 D., while formamide under the same conditions has a dipole moment of 3.86 D.[10] The moment of the six-membered ring compound N-acetylpiperidine is about 0.1 D. higher than dimethylformamide due to the inductive effect of the ring. The five-membered ring compound has a moment 0.2 D. higher than the six-membered ring compound, while the seven-membered ring compound is about 0.1 D. less.

If the carbonyl frequency is an indication of the amount of *s*-character in an exocyclic bond and if the dipole moment is increased by the extra *s*-character stabilizing resonance form b, then one might expect a relationship between the two quantities. Figure 1 shows a plot of Wiberg's data for the carbonyl stretching frequency of five-, six- and seven-membered cyclic ketones against our dipole moment values obtained for the five-, six- and seven-membered ring N-acetyl cyclic amines. The correlation is excellent and suggests that rehybridization of ring bonds does indeed affect the dipole moment.

N-Acetyl Lactams and Related Compounds.—The dipole moments of the N-acetyl lactams (Table I) demonstrate the two ways ring size can affect the moment: one, by varying the amount of *s*-character in the exocyclic bond and, two, by varying the angle between the two carbonyl dipoles.

From the work on the N-acetyl cyclic amines one would expect the five-membered ring compound to have a slightly higher moment than the six-membered ring compound, that is, about 3.4 D. in contrast to 3.2 D. The widening of the angle between the two carbonyls caused by the more acute ring angles overcomes the effect of increased resonance stabilization and decreases the moment from the expected 3.4 to 3.0 D. (An increased angle of 5° between two dipoles of 3.8 D. will decrease the resultant dipole moment by 0.3 D.)

The seven-membered ring would be predicted to have a lower moment by about 0.1 D.; this is the case. The six-membered ring compound would be expected to have the moment of the normal *cis-trans* conformation. The *trans-trans* conforma-

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(7) L. L. Ingraham, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 519.

(8) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen, London, 1958, pp. 15, 387.

(9) Reference 8, pp. 209–213.

(10) W. W. Bates and M. E. Hobbs, *J. Am. Chem. Soc.*, **73**, 2153 (1951).

tion is not indicated, for its calculated dipole moment is much higher than the experimental value of 3.22 D. Thus imides in the *cis-trans* conformation have a dipole moments of 3.0–3.2 D.

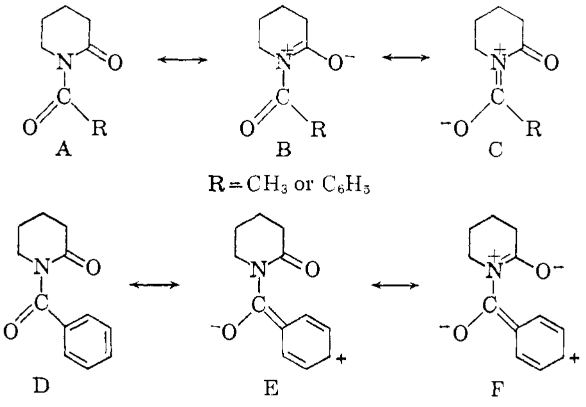
The methyl group being relatively small sterically does not affect the moment greatly. When a bulky group such as isopropyl is substituted there is a decrease in the moment; N-isobutyrylpyrrolidone (VII) has a moment 0.6 D. less than N-acetylpyrrolidone (IV). This is probably a steric effect in which the bulky isopropyl group increases the angle between the two carbonyl groups. One would expect the inductive effect of the isopropyl group to be greater than the methyl, and ultraviolet spectra indicate this is the case (Table I); the extinction of the N-acetylpyrrolidone is 11,300 at 216 mμ, while the N-isobutyrylpyrrolidone has an extinction of 13,300 at 217 mμ. The increase in angle between the carbonyl groups overcomes this inductive effect, however, and the resultant moment is lower.

The insertion of a methyl group two methylene groups removed from the nitrogen and oxygen in N-acetyl caprolactam (VI) would not be expected to have a significant effect except to increase the moment slightly. The increase (0.2 D.) in the moment of 5-methyl-N-acetyl caprolactam (IX) is also reflected in the increased extinction of the compound (10,400 compared to 9,400).

In going from acetone (μ 2.8 D.), to ethyl acetate (μ 1.9 D.), the moment decreases by 0.9 D. In the case of N-carbethoxypyrrolidone (VIII) as compared to N-acetylpyrrolidone (IV) there is an increase in the moment (3.42 D. compared to 3.00 D.) as the C–O–C dipole is in the general direction of the ring carbonyl dipole and adds to the resultant moment.

The infrared spectra of both five-membered ring compounds, N-acetyl- and N-isobutyrylpyrrolidone, show two sharp carbonyl peaks at 1730 and 1686–1689 cm.$^{-1}$. The N-acetyl substituted six and seven-membered rings show only one peak at 1686 cm.$^{-1}$. The normal tertiary amide I frequency of 1639 cm.$^{-1}$ is shown by all three N-acetyl cyclic amines.

N-Benzoyl Lactams.—Ring size affects the dipole moment of semicyclic imides by varying the angle between the carbonyl groups and by varying the amount of *s*-character in the exocyclic bond. As a result, the dipole moments of N-acetyl lactams vary (0.1–0.2 D.) with the size of the lactam.



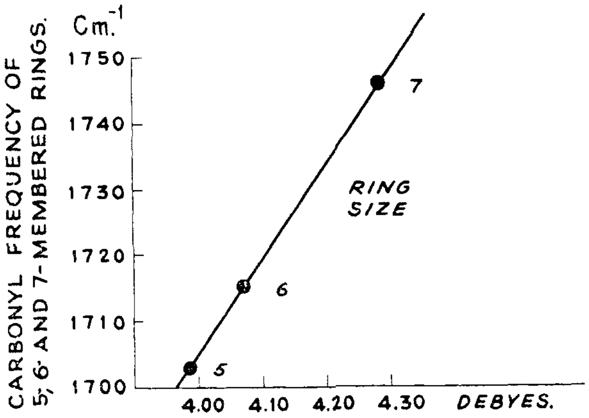
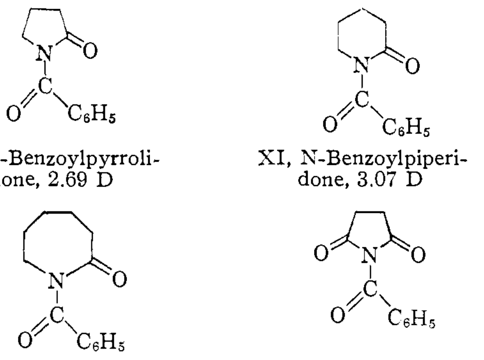


Fig. 1.—Relationship between dipole moment of N-acetyl cyclic amines and the carbonyl frequency of the same ring size cyclic ketone.

Ring size	>C=Oν, cm.$^{-1}$ cycloalkanones (ref. 5)	Dipole moment of N-acetyl amines in Debyes in dioxane at 30°
5	1746	4.28
6	1715	4.07
7	1703	3.99

Another factor in altering the dipole moment is a steric effect due to the bulkiness of a group; while the methyl group is relatively small, the benzene ring is large. Furthermore, the benzene ring can conjugate with the carbonyl group (D ↔ E ↔ F), while with R = alkyl only normal imide resonance is possible (A ↔ B ↔ C). Conjugation can affect both the dipole moment and ultraviolet spectra of imides.

The usual moment for the *cis-trans* conformation is 3.0 to 3.2 D. The dipole moments of the N-benzoyl lactams (Fig. 2) show that the moment of the six-membered ring appears normal, while the moment of the five seems low and the seven high. From the work on N-acetyl lactams one might have predicted just the reverse. The difference is due to the inductive, steric and resonance effects of the benzene ring which replaces the methyl group.


X, N-Benzoylpyrrolidone, 2.69 D

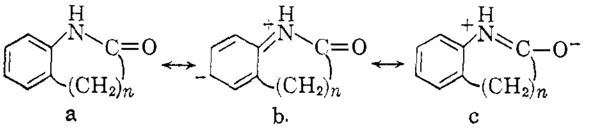
XI, N-Benzoylpiperidone, 3.07 D

XII, N-Benzoyl caprolactam, 3.47 D

XIII, N-Benzoylsuccinimide, 4.10 D

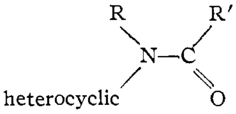
Fig. 2.—Dipole moments of N-benzoyl lactams in dioxane at 30°.

Examination of Stuart–Briegleb models of the five-, six- and seven-membered ring compounds shows that the carbonyl group cannot become coplanar with the ring nitrogen and the benzene ring at the same time. There is "competition" between the benzene ring and the ring nitrogen for the lone pair of electrons on the carbonyl oxygen; *i.e.*, resonance between structures C ↔ E (R = C_6H_5) cannot occur without shifting the position of the carbonyl group. Huisgen, *et al.*,[11,12] have shown in 1,2-benzalactams that the carbonyl frequency is a function of the number of methylene groups, *n*. When *n* is one, the carbonyl frequency is 1710 cm.$^{-1}$; this falls to 1660 cm.$^{-1}$ when *n* is five. As *n* becomes larger the lactam ring becomes more puckered so that the resonance of the nitrogen with the benzene ring (a → b) decreases and the normal amide resonance (a ↔ c) increases.



Bellamy[12] has shown in N-acetyl heterocyclics that there is a smooth relationship between the resonance energy of the heterocyclic ring and the carbonyl frequency. The greater the resonance energy of the ring the more unavailable is the lone pair on the ring nitrogen. Consequently, there is less normal amide resonance and the carbonyl frequency increases because of decreased single bond character. Tetrazole has a resonance energy of 65 kcal./mole and its N-acetyl derivative absorbs at 1779 cm.$^{-1}$; the usual tertiary amide frequency is 1639 cm.$^{-1}$. Katritzky and Jones[13] have discussed competition in compounds when R′ is changed from methyl to phenyl; there is an increase in the conjugation of the carbonyl group and the carbonyl frequency is lowered by 12 ± 3 cm.$^{-1}$. Also, the more electronegative the heterocyclic ring, the higher is the carbonyl frequency.

R = H or CH_3



Examination of models of N-benzoyl lactams shows that as the ring size increases from five to six to seven, the free carbonyl group can become more coplanar with the benzene ring. One would predict that the larger the ring the more likely is conjugation with phenyl and less likely is conjugation with the ring nitrogen. Coplanarity between the free carbonyl group and phenyl results in a smaller angle between the direction of the dipole moments of the two carbonyl groups and consequently a higher dipole moment.

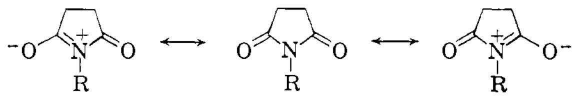
In N-isobutyrylpyrrolidone (VII) the bulk of the group causes a decreased moment, as the angle between the carbonyl groups is greater; the moment of the N-acetyl compound is 3.00 D., that of the N-isobutyryl is 2.38 D. In five-membered ring lactams steric factors play a prominent role. In N-benzoylpyrrolidone (XI) the carbonyl group is conjugated primarily with the ring nitrogen, the benzene ring not being coplanar with the five-membered ring. The bulk of the benzene ring causes an increased angle between the two carbonyls and the moment is low, 2.69 D. Being almost perpendicular to the ring the phenyl group does not cause as much steric hindrance as the isopropyl group and does not decrease the moment as much (0.3 D. compared with 0.6 D.).

The moment of the six-membered ring compound XI, 3.07 D., is about that of the normal *cis-trans* conformation. From previous examples one might have expected the seven-membered ring XII to have a moment 0.1 D. less than the six-membered ring. Increased conjugation of the benzene ring with the free carbonyl groups shifts the position of the free carbonyl nearer the ring carbonyl and there is a higher dipole moment (3.47 D. for the seven-membered ring compared to 3.07 D. for the six-membered ring).

The dipole moment of succinimide is 1.47 D.[1]; the dipole moment of N-benzoylsuccinimide (XIII) is considerably higher, 4.10 D. The moment is also higher than that of N-benzoylpyrrolidone (X), 2.69 D., because the free carbonyl group adds to the moment no matter which way it is pointed.

In going from the five- to six- to seven-membered ring the carbonyl stretching frequency changes from 1692 cm.$^{-1}$ to (1739 cm.$^{-1}$ and) 1684 cm.$^{-1}$, to 1672 cm.$^{-1}$ (Table III). This suggests increasing conjugation with the benzene ring is permitted by the larger ring size. The six-membered ring compound has two sharp carbonyl bands while the other compounds have only one band.

The Ultraviolet Spectra of N-Acetyl and N-Benzoyl Lactams. Relationship between Dipole Moments and Extinction.—The ultraviolet spectra of succinimide and N-methylsuccinimide[1] consist of one sharp peak at about 196 and 206 mμ, respectively, with an extinction of 12,000–13,000. The spectra of N-benzoylsuccinimide, in contrast, show two bands, a broad one at 242 mμ with an extinction of 11,000 and a shoulder at 288 mμ with an extinction of 1500. From a minimum at 220 mμ there is increasing absorption up to 195 mμ, the limit on the Cary 14. The normal imide resonance is strong here, for there are two equivalent structures and the benzene ring can resonate with the free carbonyl group. The high extinction of the band at 252 mμ probably is of the benzaldehyde type (λ 242 mμ, ε 14,000). The unresolved band below 195 mμ probably is the imide chromophore:



The infrared spectra shows three distinct carbonyl bands at 1783, 1724 and 1681 cm.$^{-1}$.

Evidence that there is increasing conjugation between the free carbonyl and the phenyl group with increasing ring size is found in the ultraviolet spectra of the compounds. Ultraviolet spectra of N-acetyl lactams (Table III) show a peak at 216–219 mμ with ε of 8900 to 11,300. This is due to resonance A ⟷ B ⟷ C; there is little change in position and extinction with ring size.

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[11] R. Huisgen, I. Ugi, H. Brade and E. Ravenbusch, *Ann.*, **586**, 30 (1956).

[12] L. J. Bellamy, *Spectrochim. Acta*, **13**, 60 (1958).

[13] A. R. Katritzky and R. A. Jones, *J. Chem. Soc.*, 2067 (1959).

TABLE III

ULTRAVIOLET AND INFRARED SPECTRA OF SEMICYCLIC IMIDES[a]

	U.v. spectra in EtOH					
	Band I		Band II			
	λ_{max}, mμ	ε	λ_{max}, mμ	ε	μ in Debyes	Infrared carbonyl freq. in cm.$^{-1}$
N-Acetyl						
Pyrrolidone	216	11,300	..	....	2.00	1730, 1686
Piperidine	218	8,900	..	....	3.22	1686
Caprolactam	219	9,400	..	....	3.13	1686
N-Benzoyl						
Pyrrolidone	228	16,100	280 274	1,000 1,200	2.69	1692
Piperidine	230	11,400	268	4,100	3.07	1739, 1684
Caprolactam	232	7,200	248	6,700	3.47	(1695),[b] 1672
Succinimide	..	....	252 288	12,900 1,500	4.10	1783, 1724, 1681
Benzaldehyde	..	....	242	14,000	2.96	1704
Succinimide	194?	12,000	..	....	1.47	1770, 1686

[a] Compounds courtesy of H. K. Hall, Jr., of du Pont.
[b] Shoulder.

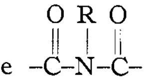
The ultraviolet spectra of N-benzoyl lactams (Fig. 3) show a remarkable shift in extinction and maxima considering the fact that the compounds differ only by a methylene group. In contrast to the N-acetyl lactams there are two bands, one between 228 and 232 mμ and another that varies from 280 to 268 to 248 mμ for the five-, six- and seven-membered rings, respectively. Band I, around 230 mμ, is like the band of the N-acetyl lactams at 218 mμ and must be from the chromophore  $-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-$ as it is present in both series. Band II, not present in the N-acetyl lactams, must be due to the new resonance between the benzene ring and the free carbonyl group.

TABLE IV

DIPOLE MOMENTS OF N-ACETYL AMINES IN DIOXANE AT 30°

	ω_2	ϵ_{12}	ν_{12}
I, N-Acetylpyrrolidine	0.0011715	2.22592	.....
	.0017253	2.23638	0.97908
	.0021136	2.24431	.97912
μ = 4.28 ± 0.03 D.	.0026187	2.25312	.97913
Mol. wt. = 113.06	.0029989	2.26192	.97915
	.0034356	2.26976	.97917

ϵ_1 = 2.20298 ν_1 = 0.97901 P_{2_0} = 398.81
α = 19.44875 β = +0.04570 P_E = 31.55 calcd.

	ω_2	ϵ_{12}	ν_{12}
II, N-Acetylpiperidine	0.0011581	2.22244	0.97926
	.0017968	2.23385	.....
	.0020422	2.23656	0.97921
μ = 4.07 ± 0.04 D.	.0026000	2.24632	.97917
Mol. wt. = 127.07	.0031095	2.25408	.97912
	.0034701	2.25939	.97915

ϵ_1 = 2.20444 ν_1 = 0.97976 P_{2_0} = 370.30
α = 15.94486 β = −0.05646 P_E = 37.42 calcd.

	ω_2	ϵ_{12}	ν_{12}
III, N-Acetylhexamethyleneamine	0.00	2.20293	0.97433
	.0010181	2.21723	.97433
	.0026518	2.24060	.97433
	.0039340	2.25800	.97433
μ = 3.99 ± 0.01 D.	.0053271	2.27561	.97433
Mol. wt. = 141.14	.0057225	2.28160	.97433
	.0068229	2.29752	.97433

ϵ_1 = 2.20332 ν_1 = 0.97433 P_{2_0} = 361.56
α = 13.79880 β = 0.00 P_E = 40.95 calcd.

As the size of the lactam ring increases from five to six to seven members the extinction of band I decreases and the maxima moves to longer wave length. At the same time, band II increases in intensity and it moves to shorter wave length. The decrease in the intensity of band I is an indication of a decrease in resonance between the ring nitrogen and the free carbonyl (A ⟷ B ⟷ C). The increase in the extinction of band II is due to the increase in the competitive resonance between the benzene ring and the free carbonyl (D ⟷ E ⟷ F).

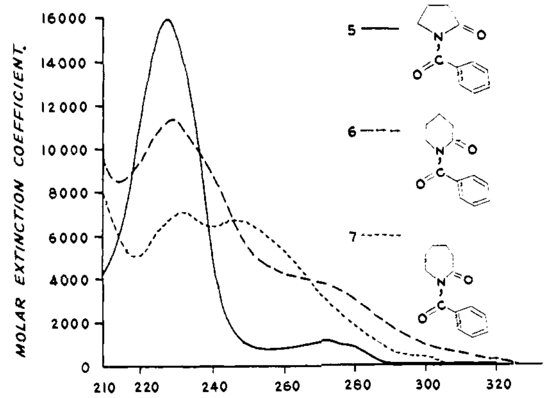


Fig. 3.—Ultraviolet spectra of N-benzoyl lactams in C_2H_5OH.

The dipole moment in these compounds is an indication of the position of the two carbonyl groups. A low dipole moment is indicative of the *cis-trans* conformation with little resonance permitted between the phenyl ring and the free carbonyl. The carbonyl group is coplanar with the ring nitrogen and the benzene ring is almost perpendicular to the carbonyl group due to steric hindrance. As noted before, the low moment also indicates a widening of the angle between the carbonyl groups due to steric bulk. As the lactam becomes larger and more flexible there is less steric interference and more opportunity for the phenyl ring to become coplanar with the carbonyl group. The ultraviolet spectra confirm the dipole and infrared data, which suggests that there is more conjugation between the benzene ring and the carbonyl group as ring size becomes greater.

The position of maxima hardly changes for the band I in both N-acetyl and N-benzoyl compounds (216 to 219 and 228 to 232 mμ, respectively). With band II, however, there is a large shift from 280 and 274 mμ to 268 to 248 mμ, with a shift in extinction of 1300 to 4100 to 6700. This shift in extinction and wave length is toward that of benzaldehyde, which has a maximum at 242 mμ, ε 14,000.

Ultraviolet extinction is a measure of the relative resonance between the two competitive chromophores, one between the free carbonyl and ring nitrogen and one between the free carbonyl and benzene ring. The dipole moment of the compounds is determined *inter alia* by the position of the carbonyl groups which depends upon the relative resonance in the two chromophores. If resonance is predominantly with the ring nitrogen the carbonyl groups are farthest apart and the dipole moment is low. If resonance is primarily with the benzene ring steric factors force the ring

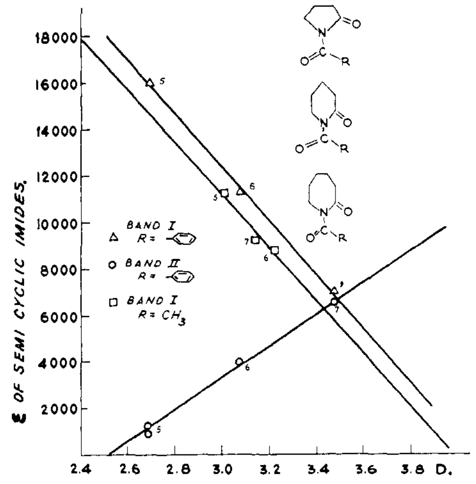


Fig. 4.—Plot of dipole moments of N-acetyl and N-benzoyl lactams *vs.* ε of band I and band II (ultraviolet).

and free carbonyl dipoles closer together with a resultant high moment.

Figure 4 shows a plot of ultraviolet extinction *versus* the dipole moment of the N-acetyl lactams and N-benzyl lactams. All three plots show good correlation though the dipole moment does not change appreciably in some cases. The relationship is between the dipole moment of the compounds, not ring size, and extinction. In the N-acetyl series the moment goes up five, seven, then six, while in the N-benzoyl series it goes up five, six and seven. The important factor is not ring size but how ring size affects the compound *via* steric and rehybridization effects. The dipole moment is a resultant of these effects plus the opportunity for increased conjugation in the N-benzoyl series.

The linear increase in band II of the N-benzoyl lactams indicates that there is true competition

TABLE V

DIPOLE MOMENTS OF N-ACETYL LACTAMS AND RELATED COMPOUNDS IN DIOXANE AT 30°

	ω_2	ϵ_{12}	ν_{12}
IV, N-Acetylpyrrolidone	0.0011380	2.20727	0.97857
	.0016089	2.21163	.97852
	.0020373	2.21520	.97845
$\mu = 3.00 \pm 0.03$ D.	.0025096	2.21947	.97844
Mol. wt. = 127.06	.0030344	2.22392	.97840
	.0036091	2.22828	.97831
$\epsilon_1 = 2.19780$ $\nu_1 = 0.97869$ $P_{2_0} = 212.52$			
$\alpha = 8.53523$ $\beta = -0.10098$ $P_E = 31.51$ calcd.			
V, N-Acetylpiperidone	0.0009276	2.20805	0.97860
	.0012398	2.21084	.97856
	.0017158	2.21511	.97854
$\mu = 3.22 \pm 0.05$ D.	.0023234	2.22052	.97849
Mol. wt. = 141.07	.0028270	2.22479	.97844
	.0033208	2.22915	.97839
$\epsilon_1 = 2.19994$ $\nu_1 = 0.97868$ $P_{2_0} = 244.21$			
$\alpha = 8.88065$ $\beta = -0.18510$ $P_E = 36.12$ calcd.			
VI, N-Acetyl caprolactam	0.0009763	2.20640	0.97867
	.0013923	2.20988	.97862
	.0020799	2.21511	.97860
$\mu = 3.13 \pm 0.05$ D.	.0023478	2.21782	.97856
Mol. wt. = 155.08	.0028702	2.22043	.97853
	.0035709	2.22662	.97848
$\epsilon_1 = 2.19914$ $\nu_1 = 0.97873$ $P_{2_0} = 238.09$			
$\alpha = 7.66212$ $\beta = -0.07050$ $P_E = 40.73$ calcd.			
VII, N-Isobutyrylpyrrolidone	0.00	2.20457	.....
	.0008512	2.20814	0.97810
	.0011637	2.21023	.97809
$\mu = 2.38 \pm 0.03$ D.	.0017764	2.21302	.97807
Mol. wt. = 155.19	.0021803	2.21476	.97806
	.0025383	2.21651	.97805
$\epsilon_1 = 2.20447$ $\nu_1 = 0.97812$ $P_{2_0} = 164.60$			
$\alpha = 4.7468$ $\beta = -0.02612$ $P_E = 50.81$ calcd.			
VIII, N-Carbethoxypyrrolidone	0.00	2.20073	.....
	.0010050	2.20954	0.97808
	.0014325	2.21342	.97801
$\mu = 3.42 \pm 0.64$ D.	.0019429	2.21825	.97794
Mol. wt. = 157.17	.0023548	2.22139	.97788
	.0035863	2.23316	.97771
$\epsilon_1 = 2.20056$ $\nu_1 = 0.97822$ $P_{2_0} = 273.52$			
$\alpha = 9.02330$ $\beta = -0.14004$ $P_E = 37.94$ calcd.			
IX, 5-Methyl-N-acetyl caprolactam	0.0009805	2.21407	0.97909
	.0015209	2.21851	.97905
	.0021205	2.22374	.97902
$\mu = 3.35 \pm 0.06$ D.	.0025023	2.22732	.97897
Mol. wt. = 170.90	.0030063	2.22993	.97896
	.0035730	2.23516	.97893
$\epsilon_1 = 2.20640$ $\nu_1 = 0.97914$ $P_{2_0} = 273.46$			
$\alpha = 8.05075$ $\beta = -0.06070$ $P_E = 47.06$ calcd.			

TABLE VI

THE DIPOLE MOMENTS OF N-BENZOYL LACTAMS AND N-BENZOYLSUCCINIMIDE IN DIOXANE AT 30°

	ω_2	ϵ_{12}	ν_{12}
X, N-Benzoylpyrrolidone	0.0007255	2.19838	0.97839
	.0010549	2.19969	.97839
	.0014294	2.20221	.97826
$\mu = 2.69 \pm 0.05$ D.	.0021233	2.20588	.97807
Mol. wt. = 189.17	.0024808	2.20718	.97802
	.0028226	2.20849	.97780
$\epsilon_1 = 2.19480$ $\nu_1 = 0.97857$ $P_{2_0} = 194.07$			
$\alpha = 4.98273$ $\beta = -0.24210$ $P_E = 51.06$ calcd.			
XI, N-Benzoylpiperidone	0.0009521	2.20396	0.97843
	.0014219	2.20657	.97837
$\mu = 3.07 \pm 0.03$ D.	.0019165	2.20919	.97822
Mol. wt. = 203.17	.0028995	2.21538	.97805
	.0034877	2.21886	.97801
$\epsilon_1 = 2.19815$ $\nu_1 = 0.97859$ $P_{2_0} = 246.86$			
$\alpha = 5.91907$ $\beta = -0.17603$ $P_E = 56.94$ calcd.			
XII, N-Benzoyl caprolactam	0.0008981	2.20309	0.97841
	.0014648	2.20675	.97832
	.0021991	2.21198	.97826
$\mu = 3.47 \pm 0.02$ D.	.0025717	2.21459	.97818
Mol. wt. = 217.17	.0032283	2.21904	.97810
	.0034281	2.22078	.97808
$\epsilon_1 = 2.19668$ $\nu_1 = 0.97853$ $P_{2_0} = 304.86$			
$\alpha = 6.97257$ $\beta = -0.13126$ $P_E = 62.82$ calcd.			
XIII, N-Benzoylsuccinimide	0.0015158	2.21276	0.97819
	.0020014	2.21712	.97805
$\mu = 4.10 \pm 0.05$ D.	.0024454	2.22235	.97795
Mol. wt. = 203.17	.0029072	2.22679	.97785
	.0034224	2.23202	.97773
$\epsilon_1 = 2.19711$ $\nu_1 = 0.97854$ $P_{2_0} = 388.63$			
$\alpha = 10.20969$ $\beta = -0.23737$ $P_E = 51.08$ calcd.			

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).

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[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···O=C< Hydrogen Bonding and a Case of $\mathrm{\underset{O}{>}C{-}H\cdots O{=}C<}$ Hydrogen Bonding

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

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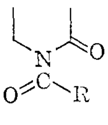
Table I gives the dipole moments for N-methyldiacetamide (I), diacetamide (II) and N-methyldiformamide (III). Compound I has the expected moment for the *cis-trans* conformation of imides; its moment varies only slightly (Δ0.2 D.) in going from dioxane to benzene to heptane; II, while having the expected 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 $\mathrm{\underset{O}{>}C{-}H\cdots O{=}C<}$ 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.

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°.

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

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(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.