ence of *cis* and *trans* isomers[7] and attendant conformations must be appreciated. The dissymmetry of most of the curves and the additional irregularities which are apparent in some made it advisable not to attempt a calculation of molecular extinctions for the interpolated maxima.

As a further check on the steric interference of the N-alkyl group with transannular N–C_{CO} interaction, we synthesized 1-isobutyl-1-azacyclononan-5-ol-6-one by the acyloin condensation of diethyl γ,γ'-isobutylimino-bis-butyrate, with the thought that the isobutyl group should provide hindrance intermediate between that of ethyl and isopropyl. The pure N-isobutylaminoacyloin exhibited two clear maxima, at 1703 and 1682 cm.$^{-1}$, even in concentrated solution in carbon tetrachloride. The infrared absorption for a dilute (1.23×10^{-2} *M*) solution, which has been included in Fig. 1, shows that the proportion of interacted (IVe) to non-interacted (IIIe) forms is smaller than that for the N-ethyl and greater than that for the N-isopropyl compound. The infrared carbonyl absorption of 1-cyclohexyl-1-azacyclononan-5-ol-6-one (IIIf), which was synthesized by the same general method, bears closest resemblance to that of the N-isopropyl compound.

Experimental[8]

Diethyl γ,γ'-Isobutylimino-bis-butyrate.—This compound was made in a manner similar to that employed for the isopropylimino-bis-butyrate,[3] using 36.6 g. (0.5 mole) of isobutylamine, 242 g. (1.0 mole) of ethyl γ-iodobutyrate, 138 g. (1.0 mole) of potassium carbonate, 500 ml. of absolute ethanol and a reflux time of 12 hours; b.p. 106–107° (0.04 mm.), $n^{19.5}\text{D}$ 1.4449, yield 82 g. (55%), characteristic infrared maxima at 1740 and 1179 cm.$^{-1}$ (liquid film).

Anal. Calcd. for $C_{16}H_{31}NO_4$: C, 63.75; H, 10.37; N, 4.65. Found: C, 63.72; H, 10.44; N, 4.65.

1-Isobutyl-1-azacyclononan-5-ol-6-one (IIIe).—The acyloin ring closure was effected in the usual way[3] using 10.1 g. (0.44 g. atom) of sodium and 30.1 g. (0.10 mole) of the diester in xylene under high dilution conditions; colorless oil, b.p. 83–85° (0.1 mm.), $n^{20}\text{D}$ 1.4907, yield 10.3 g. (48%), representative infrared maxima at 3470, 1703, 1682 and 1100 cm.$^{-1}$ for a 10% solution in carbon tetrachloride.

Anal. Calcd. for $C_{12}H_{23}NO_2$: C, 67.56; H, 10.87. Found: C, 67.65; H, 10.86.

1-Cyclohexyl-1-azacyclononan-5-ol-6-one (IIIf).—This compound was made by the same method; viscous, rather unstable oil, b.p. 124–126° (0.25 mm.), $n^{21}\text{D}$ 1.5177, yield 50%, infrared maxima at 3455 and 1691 cm.$^{-1}$ for a 5% solution in carbon tetrachloride, at 1687 cm.$^{-1}$ (unsymmetrical) for a 0.01 ± 0.005 *M* solution.

Anal. Calcd. for $C_{14}H_{25}NO_2$: C, 70.25; H, 10.53. Found: C, 70.58; H, 10.29.

The picrate was made in ether and recrystallized from ethanol–ether as yellow prisms, m.p. 146–148°, infrared maxima (Nujol mull) at 3480, 3075 and 1701 cm.$^{-1}$ among others.

Anal. Calcd. for $C_{20}H_{28}N_4O_9$: C, 51.27; H, 6.02; N, 11.96. Found: C, 51.36; H, 6.17; N, 12.15.

1-Methyl-, 1-ethyl-, 1-isopropyl- and 1-*t*-butyl-1-azacyclononan-5-ol-6-one[3] were freshly prepared and distilled prior to infrared spectral examination.

Infrared Absorption Spectra.—The spectra of the cyclic aminoacyloins were obtained with a Perkin–Elmer recording spectrophotometer, model 21. For high resolution with the dilute carbon tetrachloride solutions of the aminoacyloins, the wave number scale was expanded fourfold, and maximum response and a scanning speed of 120 cm.$^{-1}$ per minute were employed. The thickness of the sodium chloride cell was about 1.0 mm. and the thickness of the solvent cell was variable so that a match could be achieved. The concentration was $1.23 \pm 0.05 \times 10^{-2}$ *M* of aminoacyloin in Rascher and Betzold reagent carbon tetrachloride (except for the cyclohexyl compound) and the spectra were calibrated against water vapor.

The infrared spectra of the perchlorates in D_2O were determined with a Beckman IR-2T infrared spectrophotometer, using a silver chloride cell. We wish to thank Mr. Donald O. Woolf, Jr., of Eli Lilly and Company for these determinations in deuterium oxide.

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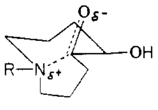
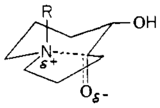
[7] *E.g.*



cis



trans

[8] Microanalyses by Mrs. R. Maria Benassi and Mr. Joseph Nemeth.

Cyclic Aminoacyloins and Aminoketones. VI. Effect of Transannular Interaction between N and C_{CO} on Ultraviolet Absorption[1]

BY NELSON J. LEONARD AND MICHINORI ŌKI

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Since it has been found possible to use infrared absorption spectra effectively[2] in the detection of transannular interaction between N and C_{CO} in cyclic aminocyloins and aminoketones,[3–6] it was of corollary interest to ascertain the relation of ultraviolet absorption spectra to this type of interaction. Ether was selected as the solvent for the ultraviolet spectral study because of the availability of information on the absorption of tertiary amines in ether[7] and because carbon tetrachloride, which was the solvent of choice for the infrared determinations, is reported to cut off at 265 mμ. 2-Hydroxycyclononanone[8] was selected as a model since it contains the acyloin function in a nine-membered carbocyclic ring, analogous to the 1-alkyl-1-azacyclononan-5-ol-6-ones here considered. The model I exhibited two distinct ultraviolet maxima (Table I), at 217 and 264 mμ. The position of the long wave length (carbonyl) maximum is probably determined by the geometry of the α-ketol system.[9] 1-Methyl-1-azacyclononan-5-ol-6-one (II) showed very weak absorption, with no detectable maximum, in the region of 264 mμ, and had a new maximum at 228 mμ. Since this compound probably occurs predominantly in the transannular interacted form[2] in

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[1] Presented at the Fourteenth National Organic Chemistry Symposium of the Am. Chem. Soc., Lafayette, Ind., on June 14, 1955. Supported in part by a grant from the University Research Board, University of Illinois.

[2] N. J. Leonard, M. Ōki, J. Brader and H. Boaz, THIS JOURNAL, **77**, 6237 (1955).

[3] N. J. Leonard, M. Ōki and S. Chiavarelli, *ibid.*, **77**, 6234 (1955).

[4] N. J. Leonard, R. C. Fox and M. Ōki, *ibid.*, **76**, 5708 (1954).

[5] N. J. Leonard and M. Ōki, *ibid.*, **76**, 3463 (1954).

[6] N. J. Leonard, R. C. Fox, M. Ōki and S. Chiavarelli, *ibid.*, **76**, 630 (1954).

[7] N. J. Leonard and D. M. Locke, *ibid.*, **77**, 437 (1955).

[8] A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).

[9] R. C. Cookson and S. H. Dandegaonker, *J. Chem. Soc.*, 352 (1955).

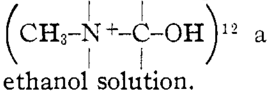
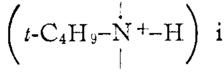
TABLE I

ULTRAVIOLET ABSORPTION MAXIMA[a]

	Compound	λ, mμ[b]	log ε	λ, mμ	log ε	λ, mμ	log ε
I	2-Hydroxycyclononanone[8]	217	2.65[c]			264	2.13[c]
II	1-Methyl-1-azacyclononan-5-ol-6-one[4,6]			228	3.77	[d]	
III	1-Ethyl-1-azacyclononan-5-ol-6-one[4,6]			226	3.62	[d]	
IV	1-Isobutyl-1-azacyclononan-5-ol-6-one[2]	217	3.49	[e]		[d]	
V	1-Isopropyl-1-azacyclononan-5-ol-6-one[5]	218	3.47	∼230[f]	3.45	[d]	
VI	1-*t*-Butyl-1-azacyclononan-5-ol-6-one[5]	217	3.43	∼231[f]	3.37	[d]	
VII	1-Methyl-1-azacycloheptadecan-9-ol-10-one[4]	216	3.51			∼270[f]	1.98
VIII	1-Methyl-1-azacycloöctan-5-one[3,6]			225	3.80	[d]	
IX	1-Methyl-1-azacyclodecan-6-one[3]			221	3.75	[d]	

[a] In diethyl ether. [b] The maxima reported below 220 mμ may be apparent maxima due to scattered light effects, although the opinion of the authors, based upon internal consistency of the present results and comparison with other results obtained in this Laboratory,[7] is that the figures in the first column represent real maxima. [c] The value of the molecular extinction coefficient may be slightly in error due to the presence of a small quantity of the 1,2-diketone. [d] Weak absorption in this region, no apparent maximum. [e] No inflection is observable, but log ε 3.38 at 230 mμ. [f] ∼ Indicates an inflection point.

ether solution, it is not surprising that the ultraviolet carbonyl absorption would be modified by the electronic interaction between the tertiary amino nitrogen and the carbonyl. For an aminoacyloin of ring size large enough so that transannular interaction does not occur,[4] 1-methyl-1-aza-cycloheptadecan-9-ol-10-one (VII) served as a model, showing an inflection point at 270 mμ and a short wave length maximum like that of I.[10]

It is therefore apparent that the appearance of an absorption maximum at 228 mμ can be associated with excitation of the interacting N–C_{CO} system. The bands at longer and shorter wave length observed for model compounds I and VII have disappeared or have been submerged under the strong 228 mμ band. As the interaction between nitrogen and carbonyl in the series of 1-alkyl-1-azacyclononan-5-ol-6-ones is diminished due to increasing steric hindrance of the N-alkyl group (III, IV, V, VI), the intensity of the absorption in the 228 mμ region is decreased and the 217 mμ band becomes evident as a maximum. The overlapping of two fairly close (10–15 mμ) absorption bands of varying intensity is suggested by the curves.[11] It might be hoped that a corresponding increase in the intensity of the 264 mμ absorption would accompany an increase in the proportion of cyclic aminoacyloin in the non-interacted form, but no clear maximum developed in this region for the series III, IV, V, VI. The necessity of availability of the pair of electrons on nitrogen for the absorption observed in the short wave length region was shown by the negligible ultraviolet absorption of the perchlorates of II  $\left(CH_3\text{–}\overset{|}{\underset{|}{N}}{}^{+}\text{–}\overset{|}{\underset{|}{C}}\text{–}OH\right)$[12] and VI  $\left(t\text{-}C_4H_9\text{–}\overset{\vdots}{\underset{|}{N}}{}^{+}\text{–}H\right)$ in ethanol solution.

The cyclic aminoketones, 1-methyl-1-azacyclooctan-5-one (VIII) and 1-methyl-1-azacyclodecan-6-one (IX), which exhibit different degrees of transannular N–C_{CO} interaction,[4] also showed maxima in the short wave length region and no detectable maxima in the longer wave length (carbonyl) region. It is an interesting analogy that the appearance of maxima in the 225–231 mμ region for α,β-unsaturated tertiary amines has been ascribed to the interaction of the unshared electron pair on nitrogen with the π-electrons of the C=C bond.[13]

While it has been shown that transannular nitrogen–carbonyl interaction in cyclic aminoacyloins and aminoketones has an effect on ultraviolet absorption, no generally applicable correlation can be made at this time.

Experimental[14]

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined using a Cary recording spectrophotometer, model 11. The solvent was diethyl ether, Merck reagent grade. The concentrations were 5.0–10.0 × 10^{-3} *M* for the 270 mμ region and 1.0–5.0 × 10^{-4} *M* for the 220 mμ region. The compounds were prepared as reported in the references provided in Table I.

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[10] The intensity at 216 mμ is greater due to the tertiary amine grouping, which is present in VII but not in I.

[11] J. M. Vandenbelt and C. Henrich, *Applied Spectroscopy*, **7**, 171 (1953).

[12] See also E. H. Mottus, H. Schwarz and L. Marion, *Can. J. Chem.*, **31**, 1144 (1953).

[13] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946); see also ref. 7.

[14] We wish to thank Miss Gerardine Meerman for determination of the ultraviolet absorption spectra.