The significant asymmetry in torsional angles between chemically equivalent parts of the LL molecule is probably caused by packing forces, though it is difficult to ascribe this to any specific short intermolecular contacts. Since the LL molecules are laced together by fairly strong N–H···O hydrogen bonds, the energy of each bond amounting to several kilocalories per mole, one might expect major conformational adjustments to accommodate these bonds. However, the hydrogen bonds established in LL do not result in any short intermolecular contacts that might be responsible for the observed distortion. Chemically equivalent parts of the molecule have slightly different environments in the crystal. Especially the methyl group C(3) has a much "looser" packing than the equivalent group C(6), as reflected in the thermal ellipsoids (Figure 1). The methyl group C(6) is fairly tightly surrounded by neighboring molecules, and the interaction between C(6) and, *e.g.*, O(2)(i), though not critical, may be sufficient to cause the observed asymmetry in the ring. If that is the case, the normal conformation of a LL molecule in solution would be a regular twist boat. However, this assumption has to be tested by structure analysis of other substituted diketopiperazines. As to the difference in hydrolysis rate between the DL and LL isomers, it might be ascribed to the slight twist of the amide bonds in the LL molecule.[21]

Acknowledgments. The author wishes to thank cand. real. Otto Grahl-Nielsen for samples of the compounds and Dr. Lyle H. Jensen for helpful discussions. Financial support under U. S. Public Health Service Research Grant AM-3288 from the National Institutes of Health is gratefully acknowledged.

(21) NOTE ADDED IN PROOF. The complete reports on the parallel, independent structure determinations of the DL and LL compounds have just appeared (E. Benedetti, P. Corradini, and C. Pedone, *J. Phys. Chem.*, 73, 2891 (1969); *Biopolymers*, 7, 751 (1969)). A comparison with the present investigation revealed some quite significant differences in molecular dimensions obtained. The largest discrepancies appear in the bond length C—C′ of the DL structure where the value 1.470 ± 0.005 Å is quoted as compared to 1.509 ± 0.001 Å in the present determination. The difference of 0.04 Å is highly significant (8σ), and a comparison with the chemically equivalent bond length in the LL compound strongly indicate that the value 1.470 Å is in error.

The Circular Dichroism of 3-Methylpyrrolidin-2-one[1]

Norma J. Greenfield[2] and Gerald D. Fasman

Contribution No. 682 from the Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02154. *Received April 29, 1969*

Abstract: (+)-(*R*)-3-methylpyrrolidin-2-one has been prepared, and its circular dichroism spectra studied in various solvents. The compound shows a positive ellipticity band at 210–220 nm, which is red shifted upon going from water to solvents with lower polarity, which probably arises from an $n \rightarrow \pi^*$ transition. The sign of this transition, however, does not obey the simple quadrant rule for the sign of the $n \rightarrow \pi^*$ transition of amides proposed by Litman and Schellman. A second negative ellipticity band is centered at 189–196 nm and may be due to the $\pi \rightarrow \pi^*$ transition. However, the circular dichroism spectra of the compound cannot be resolved by only two Gaussian bands, so the assignment of this lower band is not absolute. The compound associates in *n*-hexane to produce an additional band at 202 nm, which is lost upon dilution.

In the past few years there have been extensive theoretical studies on the optical properties of polypeptides in ordered conformations.[3-14] This work has concerned itself with the interactions among transitions of the amide chromophores of peptides aligned in regular arrays. Unfortunately, there are relatively few studies on simple, rigid, optically active amide monomers, which are suitable reference compounds for the elucidation of the optically active transitions of the peptide bond.

In 1964, Litman and Schellman[15] studied the ORD[16] of 3-aminopyrrolidin-2-one. They reported a positive Cotton effect centered near 220 nm which red shifted upon changing the solvent from water to acetonitrile and dioxane. They assigned this band to an $n \rightarrow \pi^*$ transition of the amide. The ultraviolet absorption spectra indicated the beginning of a transition centered at a lower wavelength which blue shifted under the same conditions. They assigned this to the $\pi \rightarrow \pi^*$ transition of the amide. Litman and Schellman[15] postulated that the sign of the $n \rightarrow \pi^*$ transition was controlled by a quadrant rule which depended upon the charge on the nearest atom perturbing the peptide bond. However, the quadrant rule for peptides refers only to a

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(2) Predoctoral trainee on training grant No. GM-212 from the National Institute of General Medical Sciences, National Institutes of Health.

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(16) Abbreviations used in this paper: ORD, optical rotatory dispersion; CD, circular dichroism.

fraction of the rotatory strength of the n → π* transition. When this is the major contributing factor, one expects agreement between experiment and the rule; otherwise agreement is not expected.[17]

Recently several workers have examined substituted 5′-pyrrolidinones and other rigid amide monomers by ORD and CD. Urry[18a,b] studied a series of L-5′-pyrrolidinones by CD and found that all these model compounds showed an n → π* ellipticity band near 215 nm, which was red-shifted with decreasing solvent polarity. The sign of this transition obeyed the quadrant rule of Schellman. Goodman, *et al.*,[19] studied L-3-aminocaprolactam and found that it had an n → π* transition which also obeyed the quadrant rule of Schellman. In the pyrrolidinones the positive n → π* transition was followed by a transition of opposite sign at 190 to 195 nm, which was assigned to the π → π* transition.[18a,b,19] Urry[18a,b] also found that 5-methylpyrrolidin-2-one associated in cyclohexane to give a third CD band. This band had the same sign as the n → π* transition, was centered near 202 nm, and was diminished in dilute solutions. Unfortunately, it was impossible to dilute the material sufficiently to observe a monomer form and still have sufficient CD signal to see if the band persisted. Basch, *et al.*,[20] and Barnes and Rhodes[21] have recently found a new band, centered near 200 nm in the ultraviolet vacuum spectra of several amides. This band has been called the "mystery" transition and its assignment is unclear.[20,21] Urry was not able to rule out contributions of this new band to the CD spectrum of 5-methylpyrrolidin-2-one in cylohexane. Goodman, *et al.*,[19] have also recently studied the CD and ORD spectra of two bicyclic amides, 1,7,7-trimethyl-3-azabicyclo[2.2.1]heptan-2-one and 1,7,7-trimethyl-2-azabicyclo[2.2.1]heptan-3-one. These amides have spectra similar to those of 5-methylpyrrolidin-2-one and also associate in cyclohexane with the formation of a CD band near 200 nm; however, this band disappears upon dilution. Goodman, *et al.*,[19] did not correlate the sign of the n → π* transition with the configuration of the bicyclic lactams.

In a recent paper we[22] reported the CD of L-3-aminopyrrolidin-2-one. The CD spectra obtained in water and alcohols confirm the ORD results of Litman and Schellman.[15] This compound has a positive ellipticity band centered near 217 nm in water, which was red shifted and increased in magnitude with decreasing solvent polarity, probably due to the n → π* transition; this was followed by a negative band centered below 190 nm in water. However, this negative band did not blue shift with decreasing solvent polarity as might be expected for a π → π* transition. Moreover, a third band appeared in acetonitrile, which was centered near 200 nm. This band was opposite in sign from the n → π* transition and was not concentration dependent; the pyrrolidinone is monomeric in acetonitrile.[15,22] Furthermore, when the amino group of the molecule was protonated, the spectrum changed greatly. At acidic pH the two-band spectrum present at basic pH was replaced by a single negative band centered at 210 nm. Either the positive n → π* transition was entirely lost or masked upon protonation or it changed sign and no longer obeyed Schellman's quadrant rule. It is possible that the proton on the amino group forms a hydrogen bond to the lone pair electrons of the oxygen of the amide and greatly increases the energy of the n → π* transition.

Urry[18b] has recently studied the CD spectra of several substituted L-2,5-diketopiperazines and found that the sign of the n → π* transition of these compounds in acetonitrile, trimethylphosphate, water, and trifluoroethanol was positive and appeared not to follow Schellman's quadrant rule. We[22] have also reported the CD spectra of L-3-methyl-2,5-diketopiperazine and could not detect a positive n → π* transition in most hydroxylic solvents, although there was a positive band in acetonitrile at 228 nm and a small positive tail evident in water and methanol at 236 nm. The CD bands overlapped greatly, however, and the overlap could obscure a small positive n → π* band. Positive n → π* transitions have not been reported in the ORD spectra of several diketopiperazines.[23-25] Urry suggested that the quadrant rule which determines the sign of an n → π* transition contains terms which are distance dependent.[18a] When the closest perturbing atom is very close to the amide, the sign would be reversed. Protonation of the amino group would decrease the distance from the closest perturbing hydrogen atom of the amino group to the chromophore (the carbonyl group of the amide in 3-aminopyrrolidin-2-one), and therefore might reverse the sign of the n → π* transition. Schellman has pointed out, however, that in the diketopiperazines the sign of the n → π* transition depends on the sum of several mechanisms that cause optical rotation, and that in a dimer there are more mechanisms producing optical activity than in a monomer. Thus, it is difficult to compare the optical activity of the n → π* transition of diketopiperazine, a dimer, with that of a pyrrolidinone.[26]

In this paper we report the CD of (+)-3-methylpyrrolidin-2-one. This work was undertaken for two reasons. First, it was of interest to see if the spectrum of (+)-3-methylpyrrolidin-2-one showed the same spectral characteristics as the corresponding aminopyrrolidinone, or if the band at 200 nm in acetonitrile of the latter was due to some transition peculiar to the lone-pair electrons of an amino group. Note that the configuration of the (+)-3-methylpyrrolidin-2-one studied herein is opposite to the configuration of L-3-aminopyrrolidin-2-one. Second, we wished to see if the sign of the n → π* transition of the (+)-3-methylpyrrolidin-2-one obeyed the simple quadrant rule proposed by Litman and Schellman.[15]

Experimental Section

Synthesis. (+)-3-Methylpyrrolidin-2-one was prepared and purified according to the procedure of Fles and Ghyczy[27] from

(17) We wish to thank a referee for bringing this point to our attention.

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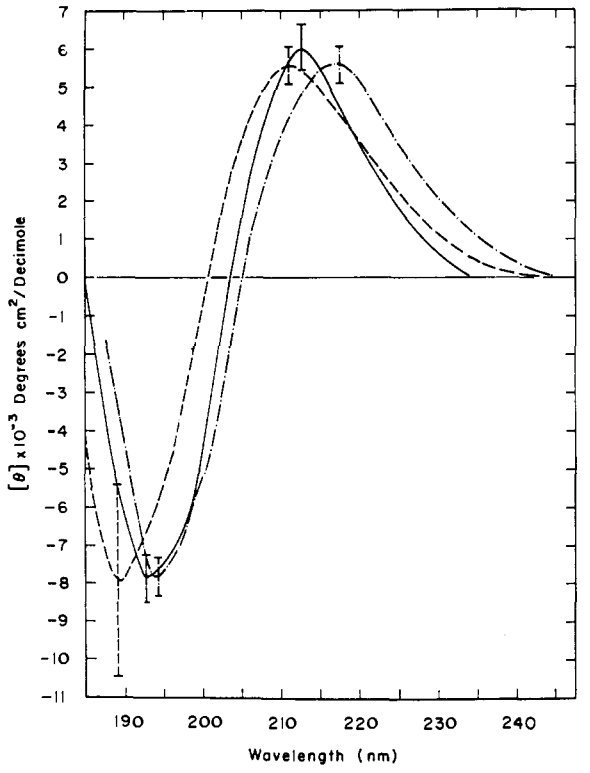

Figure 1. The CD of (+)-3-methylpyrrolidin-2-one in (a) water (——); (b) trifluoroethanol (– – – –); (c) methanol (– · – · –).

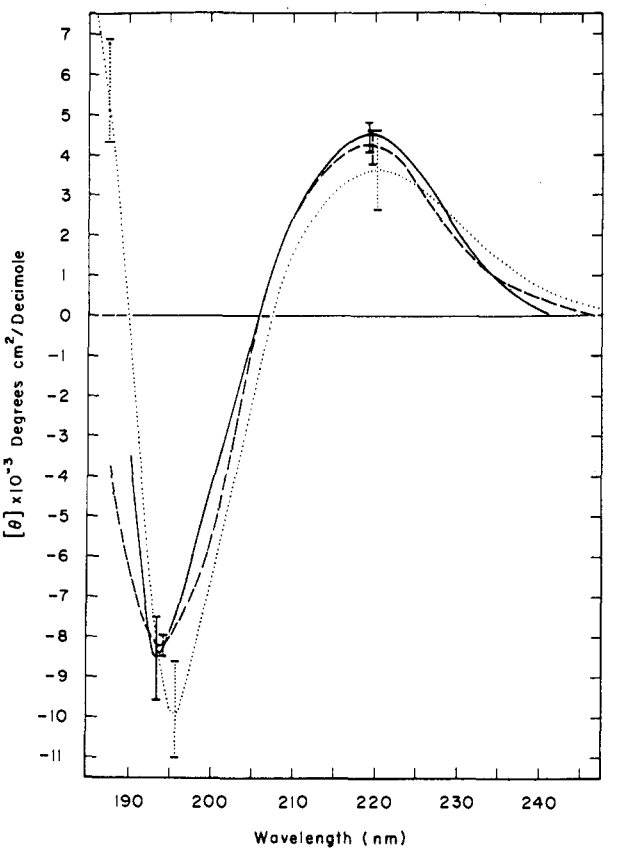

Figure 2. The CD of (+)-3-methyl-pyrrolidin-2-one in (a) ethanol (——); (b) 2-propanol (– – –); (c) acetonitrile (· · · ·).

(−)-2-methyl-4-phthalimidobutyric acid. (±)-2-methyl-4-phthalimidobutyric acid (I) was prepared from 2-methylbutyrolactone (Chem. Procurement Co.) and potassium phthalimide (Chem. Procurement Co.), as described by Adams and Fles,[28] mp 113–115°, lit.[28] value 114–115°. (−)-2-Methyl-4-phthalimidobutyric (II) was resolved from I with quinine (Chem. Procurement Co.), as described by Adams and Fles;[28] $[\alpha]^{22}D$ −21.4 ± 0.2° (0.65% in benzene), lit. value = $[\alpha]^{24}D$ −21.5 ± 0.4° (1.75% in benzene);[28] mp 102–104°, lit. value 102–104.[28] (+)-3-Methylpyrrolidin-2-one (III) was prepared according to the method of Fles and Ghyczy[27] for the enantiomer from II. It was purified by distillation *in vacuo* (at approximately 100°, 10^{-2} mm), as described by Fles and Ghyczy.[27] The specific rotation of the product was $[\alpha]^{22}D$ 61.6° (0.1% in benzene), lit. value $[\alpha]^{20}D$ −58.3 for the enantiomer (4.0% in benzene). The product had a molecular weight of 102 in water, as determined by vapor pressure osmometry on a Hewlett-Packard Mechrolab, Model 301A vapor pressure osmometer. This value is in experimental agreement with the calculated molecular weight of 99. *Anal.* Calcd: C, 60.6; H, 9.2; N, 14.1. Found: C, 60.4; H, 9.4; N, 14.2. The product was identical with a sample kindly sent by Dr. Dragutin Fles.

Solvents. Distilled water, spectrograde methanol (Matheson Coleman and Bell) and absolute ethanol were redistilled. In addition, spectrograde 2-propanol (Matheson Coleman and Bell), spectrograde acetonitrile (Matheson Coleman and Bell), spectroquality *n*-hexane (Fisher Scientific Co.) and trifluoroethanol (Eastman Organic Chemicals) were used without further purification.

CD measurements were performed on a Cary 60 recording spectropolarimeter fitted with a Model 6001 CD attachment with the slit programmed for a half-band width of 15 Å. Measurements were made at path lengths ranging from 0.1 to 1.0 mm and for concentrations ranging from 0.5 to 2.0 × 10^{-2} *M*, except where indicated. The CD is reported as molar ellipticity, $[\theta]$, in deg cm²/dmol.

Ultraviolet absorption spectra were taken on a Cary 14 recording spectrophotometer, equipped with nitrogen flushing, in cells of 0.1-mm path length, at concentrations of 0.5–2.0 × 10^{-3} *M*.

Apparent molecular weights in solutions were measured on a Hewlitt-Packard Mechrolab Division Model 301A vapor pressure osmometer in water, 2-propanol, acetonitrile, and *n*-hexane at concentrations of 0.5–2.0 × 10^{-2} *M*.

Sample concentrations were determined by Kjeldahl-Nesslers determination of nitrogen.[29–31]

Curve resolution was performed on a Du Pont Model 310 curve resolver. The rotational strength was calculated from the equation[32]

$$R_k = 0.696 \times 10^{-42} \sqrt{\pi [\theta]_k^\circ} \frac{\Delta_k^\circ}{\lambda_k^\circ}$$

where $[\theta]_k^\circ$ is the maximum ellipticity of the kth band occurring at λ_k° nm and Δ_k° is the wavelength interval over which θ falls from its maximum value to e^{-1} times its maximum value.

Results

The CD spectra of (+)-3-methylpyrrolidin-2-one in water, trifluoroethanol, and methanol are shown in Figure 1 and in ethanol, 2-propanol, and acetonitrile in Figure 2. In these solvents the CD spectra all exhibit a positive ellipticity band centered at 210–220 nm and a negative band centered at 189–196 nm. The spectra are independent of concentration. The positive band shows a large red shift and a slight decrease in magnitude with decreasing solvent polarity. The negative band also shows a red shift. The shifts in the negative band are not seen in the ultraviolet spectra. The ultraviolet peak remains at 190 ± 1 nm for all solvents, except in *n*-hexane, where it is blue shifted to below 187 nm. The molar ellipticities at the observed maxima

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Table I. The Observed Maxima and Molar Ellipticities of (+)-3-Methylpyrrolidin-2-one in Various Solvents

Solvent	Wavelength, nm	Molar ellipticity, deg cm²/dmol	Wavelength, nm	Molar ellipticity, deg cm²/dmol
Trifluoroethanol	211	5,500	189	−8,000
Water	212.5	6,000	192.5	−7,900
Methanol	217.5	5,600	193	−7,800
Ethanol	218	4,400	193	−8,600
2-Propanol	219	4,200	194	−8,200
Acetonitrile	220	3,700	196	−9,800
n-Hexane				
Concn = $1\text{–}2 \times 10^{-2}$ *M*	225	2,300		
	202	+2,700	192.5	−6,000
2×10^{-4} *M*	227.5	2,200 (±1,000)	197.5	−12,000 (±2,000[a])

[a] Signal-to-noise ratio 2:1.

Table II. Resolved Spectra of (+)-3-Methylpyrrolidin-2-one[a]

Solvent	λ, nm	θ in deg cm²/dmol	$R \times 10^{40}$ [b]	λ, nm	θ in deg cm²/dmol	$R \times 10^{40}$	λ, nm	θ in deg cm²/dmol	$R \times 10^{40}$
Water	210	6,100	6.1	194	−11,300	−8.0	176	39,400	16.8
Trifluoroethanol	210	5,800	4.2	191	−8,300	−6.5	166	21,200	17.6
Methanol	216	5,600	3.9	192	−8,600	−6.4	173	31,300	21.2
Ethanol	216	4,300	3.2	193	−10,800	−6.1	173	23,400	21.4
2-Propanol	217.5	4,200	2.2	191	−12,300	−7.8	174	47,500	22.4
Acetonitrile	220	3,600	2.7	195	−10,700	−5.2	179	37,100	22.8
Alternate acetonitrile[c]	220	3,600	2.2	195	−10,000	−3.6	180	15,900	4.6

[a] Resolved on a Du Pont 310 curve resolver. [b] Calculated as in ref 32. [c] Has an additional band at 202.5 nm, $\theta = -3100$, $R = -0.9 \times 10^{4}$

and minima of the bands are shown in Table I. The positive band is probably the n → π* transition, as deduced from its position and from the effect of solvent polarity; however, its sign does not obey the simple rule proposed by Litman and Schellman.[15] The spectra of the compound, moreover, are somewhat different from the spectra of the aminopyrrolidinone under the same conditions; the long and short wavelength bands are similar in magnitude in the methyl compound and no third band is apparent for it in acetonitrile. The curves were resolved with a Du Pont Model 310 curve resolver, and the results are shown in Table II. It was impossible to resolve the curves with only two Gaussian bands. In order to fit the curves it was necessary to include either a large band at a wavelength near 175 nm, or a small band near 175 nm plus a small band near 200 nm. The latter resolution is shown for the case where the solvent was actonitrile (Table II). Unfortunately, the signal-to-noise ratio at low wavelength is small, and there is as yet no information on the true strength of the bands below 190 nm. The maxima of the resolved bands and the rotational strengths, *R*, of each are shown in Table II. The rotational strengths were estimated, as described by Urry.[18b] There is a very slight decrease in rotational strength and a pronounced red shift for the n → π* transition as solvent polarity decreases, while there is no regular shift in the position of the 190–195-nm wavelength band, and the rotational strength remains constant. However, the position of the resolved negative band near 195 nm is dependent on the choice of position and magnitude for the band below the recorded spectra, so it should be treated with skepticism.

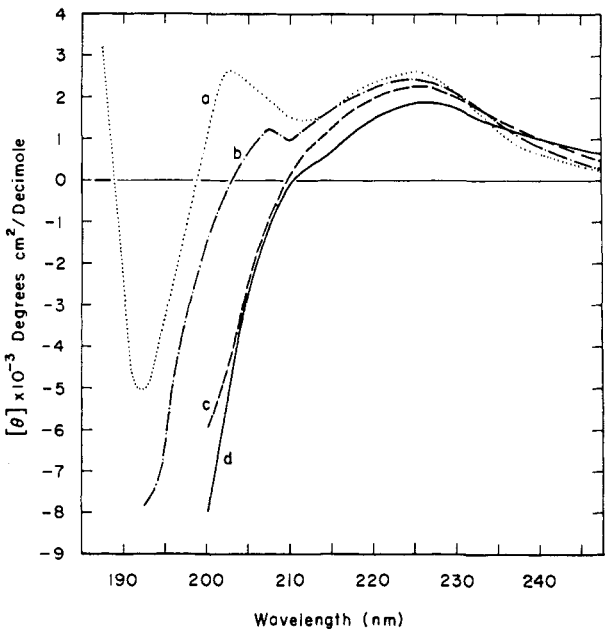

Figure 3. The CD of (+)-3-methylpyrrolidin-2-one in *n*-hexane at various concentrations: a = 1.68×10^{-2} *M* (····); b = 1.68×10^{-3} *M* (·–·–); c = 3.36×10^{-4} *M* (– – – –); d = 1.68×10^{-4} *M* (—).

The CD spectra of 3-methylpyrrolidin-2-one, at various concentrations in *n*-hexane, are shown in Figure 3. The compound associates to form a dimer in this solvent at 0.01 *M*. This was shown by vapor pressure osmometry. The spectra are similar to those of 5-methylpyrrolidinone found by Urry,[18a] in that there is a new band at 202 nm found in concentrated solutions in *n*-hexane. This band is lost upon dilution of the compound. Unfortunately, the CD signal is not high enough to obtain a good full spectrum of the diluted monomeric compound.

In summary, (+)-3-methylpyrrolidin-2-one has been prepared. The compound shows a positive ellipticity band at 210–220 nm, which is red shifted upon going from water to solvents with lower polarity, which probably arises from an n → π* transition. The sign of this transition does not obey the simple quadrant rule postulated for amides by Litman and Schellman.[15] A second negative ellipticity band centered at 189–196 nm also red shifts with decreasing solvent polarity; it may be due to a π → π* transition despite its solvent dependence. The spectra of the compound cannot be resolved by only two Gaussian curves; however, the position of a third band at lower wavelength is not unique. Therefore, no conclusions can be drawn about the presence of transitions other than the n → π* and π → π*. The compound associates in *n*-hexane to produce an additional band at 202 nm which is lost upon dilution. The CD spectrum of (+)-3-methylpyrrolidin-2-one exhibits striking differences from that of 3-aminopyrrolidinone; however, it is difficult to determine if this is due solely to differences in charge and orientation of the amino group compared to the methyl group, or if the amino group has additional optical activity due to the presence of lone-pair electrons.

Acknowledgment. We thank Dr. Dragutin Fles for his interest in this project and his gracious gift of a sample of (+)-3-methylpyrrolidin-2-one and Professor Sherman Beychok for the use of his Du Pont curve resolver.

Photodimerization of Thymine and Uracil in Acetonitrile

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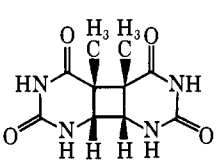
Contribution from the Chemistry Department, Michigan State University, East Lansing, Michigan 48823. *Received June 30, 1969*

Abstract: Studies on the photodimerization of thymine and uracil in acetonitrile reveal the following facts. At low pyrimidine concentrations, the reaction occurs almost entirely from the triplet state. All four *cis*-fused cyclobutane dimers are formed. The very low quantum yields reflect primarily the existence of a metastable dimeric species, most of which dissociates into two ground-state pyrimidine molecules before proceeding on to stable dimer. Rates of radiationless decay of the triplet states are 2×10^5 sec^{-1}; rate constants for addition of triplet pyrimidine to ground-state pyrimidine are 6×10^8 M^{-1} sec^{-1} for thymine and 2×10^9 M^{-1} sec^{-1} for uracil; fractions of metastable dimers which yield stable dimers are 2% for thymine and 6% for uracil. This self-quenching of the triplet may be partially responsible for the low quantum yields of photodimerization in DNA.

Photodimerization of the pyrimidine bases thymine and uracil is of interest for two reasons: the reaction is responsible for the photodeactivation of the nucleic acids;[2,3] and cycloaddition of α,β-unsaturated carbonyl compounds is an important and confusing general class of photoreactions.

The nature of the excited states responsible for these photoreactions is of basic mechanistic interest. It is known that frozen aqueous solutions of thymine yield one major photodimer, the *cis–syn* head-to-head "ice-dimer" I.[4] The reaction proceeds in high quantum efficiency,[5] apparently from the singlet-excited state[6] *via* excimers.[7] The high stereoselectivity is due to precise stacking of the thymine molecules in frozen crystallites.[8] The thymine dimer obtained from irradiated DNA is



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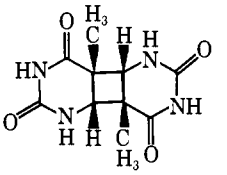

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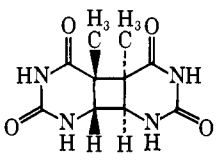
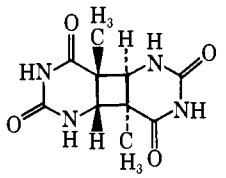


III



IV

I;[9] the uracil dimer from irradiated RNA also possesses a *cis–syn* head-to-head structure.[10] Here, too, the stereoselectivity must reflect the fixed relative configurations of the bases in the macromolecules. Since the thymine in DNA udergoes dimerization upon both direct and sensitized[11] irradiation, it is important to determine whether the product stereochemistry is affected by excited state multiplicity.

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