

Lawrence Berkeley National Laboratory

Recent Work

Title

ULTRAVIOLET ABSORPTION SPECTRA OF OXAZOLONES AND RELATED COMPOUNDS

Permalink

<https://escholarship.org/uc/item/77314968>

Authors

Bennett, Edward L.
Hoerger, Earl.

Publication Date

1951-11-19

UCRL-1568

UNCLASSIFIED

UNIVERSITY OF CALIFORNIA - BERKELEY

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

RADIATION LABORATORY

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-1568
Unclassified-Chemistry Distribution

UNCLASSIFIED

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. W-7405-eng-48

ULTRAVIOLET ABSORPTION SPECTRA OF
OXAZOLONES AND RELATED COMPOUNDS

Edward L. Bennett and Earl Hoerger

November 19, 1951

Berkeley, California

ULTRAVIOLET ABSORPTION SPECTRA OF
OXAZOLONES AND RELATED COMPOUNDS¹

Edward L. Bennett² and Earl Hoerger

Radiation Laboratory and Department of Chemistry

University of California

Berkeley, California

November 19, 1951

ABSTRACT

The ultraviolet absorption spectra of substituted oxazolones and esters and acids derived therefrom are presented. The effect of the solvent on the absorption spectra and on the stability of the oxazolones has been studied. Trans-acylation has now been noted in the preparation of several oxazolones.

For publication in the Journal of the American Chemical Society

-
- (1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.
- (2) Present address, Institut for Cytofysiologi, Copenhagen, Denmark.
-

The ultraviolet absorption curves of a variety of substituted oxazolones have been investigated by Schueler and Wang³ who discussed the effect of substitution in the 2 and 4 position on the spectra. Recently Schueler and Hanna⁴ compared the spectra of substituted crotonlactones with the oxazolones studied earlier. Earlier investigations include those of T. Asahina⁵ who reported the ultraviolet absorption spectra of a number of compounds including 2-phenyl-4-benzal-5-oxazolone (I), 2-phenyl-4-fural-5-oxazolone and the α -benzamido acids derived from these oxazolones.

Schueler and Wang have reported only a small difference in the absorption spectra of (I) and 2-methyl-4-benzal-5-oxazolone (II).

Large differences have already been reported in the spectra of certain 2-phenyl oxazolones as compared with 2-methyl oxazolones^{6,7,8}. This discrepancy prompted us to investigate the ultraviolet absorption spectra of a number of compounds which we had prepared in connection with other research being carried out in these laboratories.

Experimental

Preparation of oxazolones. - The oxazolones were prepared by refluxing for 2 hours mixtures of the appropriate aldehyde with hippuric acid, sodium acetate and acetic anhydride with mole ratios of 1:1:1:10. The oxazolones

-
- (3) F. W. Schueler and S. C. Wang, *J. Am. Chem. Soc.*, 72, 2220 (1950).
 - (4) F. W. Schueler and C. Hanna, *J. Am. Chem. Soc.*, 73, 3528 (1951).
 - (5) T. Asahina, *Bull. Chem. Soc. Japan*, 4, 202 (1929); *ibid.*, 5, 354 (1930).
 - (6) E. L. Bennett and C. Niemann, *J. Am. Chem. Soc.*, 72, 1803 (1950).
 - (7) E. L. Bennett, Ph.D. Thesis, Calif. Inst. of Tech., Pasadena, Calif. (1949).
 - (8) S. N. Timasheff and F. F. Nord, *J. Am. Chem. Soc.*, 73, 2390 (1951).

were isolated either directly from the cooled reaction mixture or after addition of an equal volume of water and were recrystallized from benzene or benzene-ligroin.

Preparation of substituted cinnamic acid esters and acids. - The esters and acids were prepared from the oxazolones by the method of Carter, et.al.⁹ The acids were recrystallized from water.

Absorption spectra. - All spectra were determined with a Beckman quartz spectrophotometer model DU. Unless otherwise stated, all spectra were obtained within 30 minutes after solution of the sample in the appropriate solvent.

Results

The positions and intensities of the principal absorption maxima and minima of the oxazolones studied are shown in Table I and Fig. 1-9. Table II and Fig. 7, 10-12 present the data obtained for the esters and acids derived from several of the oxazolones¹⁰.

Discussion

The absorption spectra obtained for oxazolones studied show marked similarity; particularly noteworthy is the similarity of the curves

(9) H. Carter, C. Stevens, and L. Ney, J. Biol. Chem. 139, 255 (1941).

(10) The ultraviolet absorption spectra reported by Asahina⁵ are qualitatively similar to those reported here, although the fine structure present is not shown. Also, an error appears to have been made in the text; the absorption maximum of I is stated to be at 2760 Å (fig. indicates 362 μ) and the absorption maximum of 2-phenyl-4-fural-oxazolone-5 appears to be at 392 μ instead of 2550 Å as stated in the text.

Table I

Principal Absorption Maximum of
Some Substituted Oxazolones

Substituent on Oxazolone	Solvent	λ_{max} m μ	E_{max}
2-Phenyl-4-benzal-	Chloroform	365.5	38,600
	Ether	360	42,000
	Ethanol	361	36,500
2-Phenyl-4-(o-chlorobenzal)-	Chloroform	370	33,200
2-Phenyl-4-(p-chlorobenzal)-	Chloroform	370	43,000
	Ether	365	42,100
	Ethanol (95%)	365	39,800
2-Phenyl-4-(p-dimethylamino-benzal)-	Chloroform	472	54,500
	Ether	455	59,000
2-Phenyl-4-(α -fural)-	Chloroform	390	36,600
2-Phenyl-4-(3,5-diiodo-4-[4-methoxy-phenoxy]-benzal)-	Chloroform	376	41,800
2-Methyl-4-benzal-	Chloroform	332	28,000
2-Methyl-4-(o-chlorobenzal)-	Chloroform	335	21,000
2-Methyl-4-(p-chlorobenzal)-	Chloroform	350	30,900
2-Methyl-4-(3,5-diiodo-4-acetoxybenzal)-	Chloroform	336	29,200
	Ethanol (95%)	332	27,100

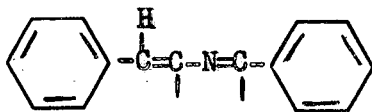
Table II

Principal Absorption Maxima and Minima
of Some Substituted Cinnamic and Acrylic Acids
and Esters in 95% Ethanol

Compound	μ	E
α -Acetamido-p-chlorocinnamic acid ethyl ester	288 (max.)	20,000
	236 (min.)	3,260
	218 (max.)	11,000
α -Acetamido-p-chlorocinnamic acid	284 (max.)	19,000
	236 (min.)	4,500
α -Acetamido- β -(3,5-diiodo-4-hydroxyphenyl)-acrylic acid	298 (max.)	17,200
	268 (min.)	10,000
	245 (max.)	22,600
	222 (min.)	15,900
α -Benzamido-cinnamic acid	280 (max.)	17,200
	248 (min.)	12,500
	224 (max.)	17,800
α -Benzamido-o-chlorocinnamic acid ethyl ester	279 (max.)	14,400
	251 (min.)	10,600
	220 (max.)	18,200
α -Benzamido-o-chlorocinnamic acid	278 (max.)	13,850
	250 (min.)	11,400
	220 (max.)	20,400
α -Benzamido-p-chlorocinnamic acid ethyl ester	288 (max.)	20,400
	250 (min.)	11,300
	224 (max.)	18,900
α -Benzamido-p-chlorocinnamic acid	284 (max.)	19,700
	248 (min.)	13,100
	224 (max.)	20,200
α -Benzamido- β -(α -furyl)-acrylic acid ethyl ester	313 (max.)	21,100
	260 (min.)	5,350
	228 (max.)	11,700
α -Benzamido- β -(α -furyl)-acrylic acid	311 (max.)	21,400
	256 (min.)	6,500
	228 (max.)	12,600

obtained for the oxazolones derived from halogen substituted aldehydes.⁶ The substitution of halogen in the 4-benzal group causes a displacement of the absorption maxima towards longer wave lengths. This shift is more for para substitution than for ortho substitution and is more for chlorine substitution than for fluorine substitution. The presence of one peak or shoulder on each side of the principal absorption maximum is to be noted. As is to be expected, the substitution of a p-dimethylamino group in the aromatic ring of the substituent in the 4 position causes a large bathochromic and auxochromic effect in the absorption spectrum. The substitution of fural for benzal in the 4 position produces a bathochromic displacement of about 30 μ . A similar displacement of approximately 30 μ has been observed for the ultraviolet absorption spectra of 2-phenyl-4-(2-thenal)-oxazolone-5 and 2-methyl-4-(2-thenal)-oxazolone-5.⁸ However, the authors fail to state in what solvent the determinations were made. As is shown in Table I and Fig. 1 and 2 for I and 2-phenyl-4-(p-chlorobenzal)-oxazolone-5, the ultraviolet absorption spectra show a bathochromic displacement of approximately 5 μ when determined in chloroform as compared to spectra obtained in ether or ethanol. The marked similarity between the data presented herein and that presented for the crotonlactones⁴ is to be noted.

The positions of the maxima of the oxazolones studied indicate that the resonating system involved in the absorption of light does include the following:



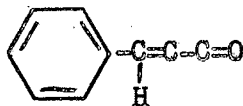
and the striking similarity between the spectra obtained for I and its derivatives and that obtained for trans-trans diphenylbutadiene¹¹ suggests that the predominating configuration of the above resonating system is similar to that of trans-trans diphenylbutadiene.

The ultraviolet absorption spectra data obtained for (II) and closely related derivatives show the expected differences from the 2-phenyl derivatives. A hypsochromic displacement of about 30 $m\mu$ is observed and the peaks on the side of the main maximum are not observed for the 2-methyl derivatives. The second main peak in the neighborhood of 240-250 $m\mu$ is also absent. Here again the substitution of chlorine in the aromatic ring produces a bathochromic displacement of 3-18 $m\mu$. The ultraviolet spectrum of 2-methyl-4-(2-thenal)-5-oxazolone⁸ shows a bathochromic displacement of 30 $m\mu$ as compared to (II) and thus it appears that similar bathochromic displacements will be obtained in the 2-methyl series of oxazolones as in the 2-phenyl oxazolones by substitution in the 4 position.

The absorption spectra of the acids and esters derived from several of the oxazolones exhibit absorption maxima at much shorter wave lengths (50-100 $m\mu$) than the parent compound.⁵ Only small differences are to be noted in the ultraviolet absorption spectra of the acids as compared to the corresponding ester. (cf. Table II and Fig. 7.) The substitution of an α -acetamido group for the α -benzamido group in α -benzamido-p-chlorocinnamic acid produces no significant change in the absorption maximum in the region of 288 $m\mu$, but as would be expected, a significant change is produced in the position of the minimum in the 230-250 $m\mu$ region and the maximum in the 218-224 $m\mu$ region (Fig. 10).

(11) J. H. Pinckard, B. Wille and L. Zechmeister, J. Am. Chem. Soc., 70, 1938 (1948).

The absorption data obtained for these compounds is similar to those obtained for α,β -unsaturated ketones¹² and is consistent with the idea that



is the principal resonating system.

Fig. 2 and 8 show that changes occur in the spectra of oxazolones when these compounds are dissolved in ethanol. This change is probably due to alcoholysis.

Other experiments indicate that oxazolones are relatively stable in chloroform or ether solutions; only slight changes in spectra are obtained in periods up to one month after preparation of solutions when stored under normal laboratory conditions. The marked similarity between the ultra-violet absorption data obtained for the esters derived from the oxazolones and the data presented in (3) makes it appear likely that many of the spectra reported by Schueler and Wang are actually those of the esters (or acids) derived from the oxazolones by alcoholysis (or hydrolysis).

The absorption spectrum of 2-phenyl-4-(p-dimethylaminobenzol)-5-oxazolone undergoes almost no change after solution for two weeks in 95% ethanol. This increased stability of the oxazolone ring is most probably attributable to the increased resonance resulting from the presence of the p-dimethylamino group. The spectrum shown in Fig. 6 is similar to that reported by Schueler and Wang. In the case of this compound, it appears that these authors were investigating the spectrum of a reasonably unaltered oxazolone.

(12) A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, Jr., T. L. Johnson, and C. H. Shunk, J. Am. Chem. Soc., 69, 1985 (1947).

Transacylation in the Erlenmeyer-Plöchl reaction has been observed previously when the reaction was carried out at refluxing temperatures.⁶ This phenomenon was again observed in the preparation of 2-phenyl-4-(o-chlorobenzal)-5-oxazolone and 2-phenyl-4-(p-chlorobenzal)-5-oxazolone. It is to be noted that the conditions used for the preparation of the oxazolones were more drastic than usually used. They were intentionally made more so in order to enhance any tendency for trans-acylation to occur. Further study is necessary to ascertain if trans-acylation actually did not occur in those cases in which it was not observed, or if the properties of the reaction mixture were not favorable for the isolation of the 2-methyl derivative.

The ultraviolet absorption data presented for 2-methyl-4-(o-chlorobenzal)-5-oxazolone and 2-methyl-4-(p-chlorobenzal)-5-oxazolone were obtained from these compounds isolated as byproducts from the preparation of the 2-phenyl derivatives. In each case, there is still about 5-15% of the 2-phenyl derivative in the preparations used to obtain absorption data. Fig. 4 also presents the absorption data of the crude reaction product obtained in the preparation of the p-chlorobenzal oxazolone. One-half of the crude product appears to be the 2-methyl derivative. The effect of variables such as time of heating and temperature on the rate of transacylation can now be readily investigated since it has been shown to occur with readily available compounds as well as with the more difficultly obtainable fluorobenzaldehydes.

Acknowledgment. - The authors wish to express their appreciation to Professor Melvin Calvin for his interest in the problem.

Captions to Figures

- Figure 1 - Ultraviolet absorption spectra of 2-phenyl-4-benzal-5-oxazolone in ether, _____; and in chloroform, _____.
- Figure 2 - Ultraviolet absorption spectra of 2-phenyl-4-benzal-5-oxazolone in abs. ethanol, 30 minutes after solution, _____; 1 day after solution, _____; 7 days after solution, _____; 7 days after solution (stored in dark),
- Figure 3 - Ultraviolet absorption spectra of 2-phenyl-4-(o-chlorobenzal)-5-oxazolone, _____; and 2-methyl-4-(o-chlorobenzal)-5-oxazolone, m.p. 95-99°, _____.
- Figure 4 - Ultraviolet absorption spectra of 2-phenyl-4-(p-chlorobenzal)-5-oxazolone, _____; 2-methyl-4-(p-chlorobenzal)-5-oxazolone, m.p. 133-138° _____; and crude oxazolone, m.p. 143-175°, _____.
- Figure 5 - Ultraviolet absorption spectrum of 2-phenyl-4-(3,5-diiodo-4-[4-methoxyphenoxy]-benzal)-5-oxazolone, _____.
- Figure 6 - Absorption spectrum of 2-phenyl-4-(p-dimethylaminobenzal)-5-oxazolone, _____.
- Figure 7 - Absorption spectra of 2-phenyl-4-(2-fural)-5-oxazolone, _____; α -benzamido- β -(2-furyl)-acrylic acid ethyl ester, _____; and α -benzamido- β -(2-furyl)-acrylic acid, _____.
- Figure 8 - Ultraviolet absorption spectra of 2-methyl-4-(3,5-diiodo-4-acetoxy-benzal)-5-oxazolone in 95% ethanol after 30 minutes, _____; 24 hours, _____; and 48 hours _____.
- Figure 9 - Ultraviolet absorption spectra of 2-methyl-4-(3,5-diiodo-4-acetoxybenzal)-5-oxazolone in chloroform after 30 minutes, _____; and 24 hours, _____.
- Figure 10 - Ultraviolet absorption spectra of α -benzamido-p-chlorocinnamic acid ethyl ester, _____ (in 95% ethanol); and α -acetamido-p-chlorocinnamic acid ethyl ester, _____ (in 95% ethanol).
- Figure 11 - Ultraviolet absorption spectra of α -benzamido-cinnamic acid _____ (in 95% ethanol; and α -benzamido-o-chlorocinnamic acid ethyl ester, _____ (in 95% ethanol).
- Figure 12 - Ultraviolet absorption spectra of α -acetamido- β -(3,5-diiodo-4-hydroxy-phenyl)-acrylic acid in 95% ethanol after 30 minutes _____; and 24 hours _____.

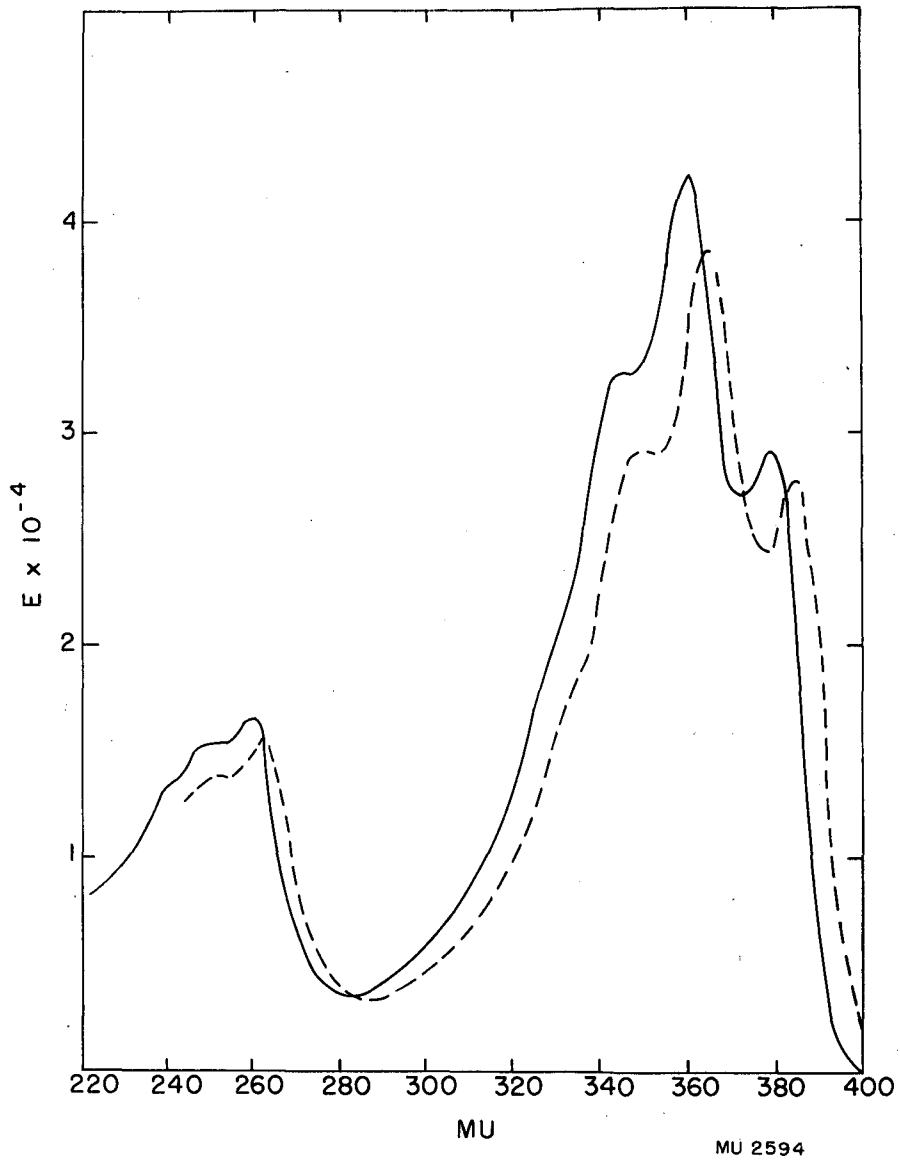


Figure 1

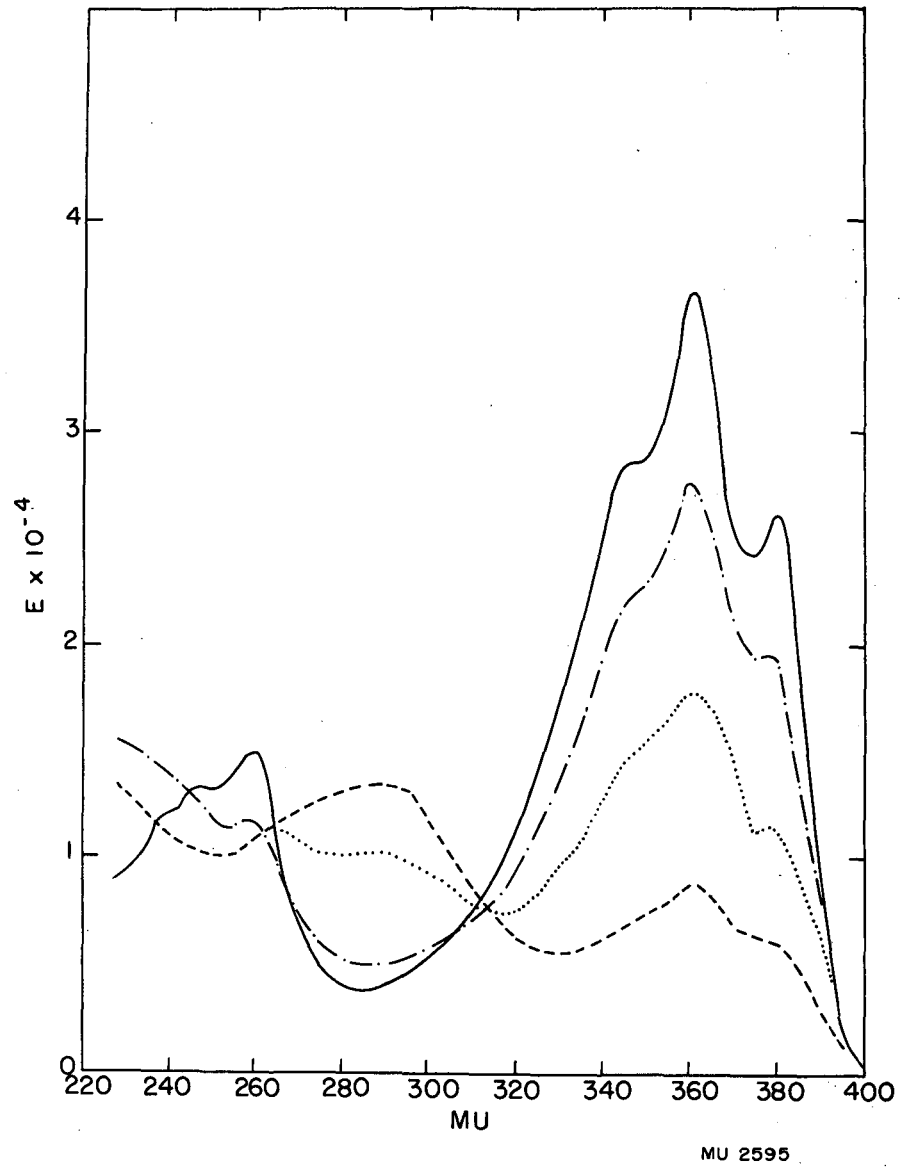


Figure 2

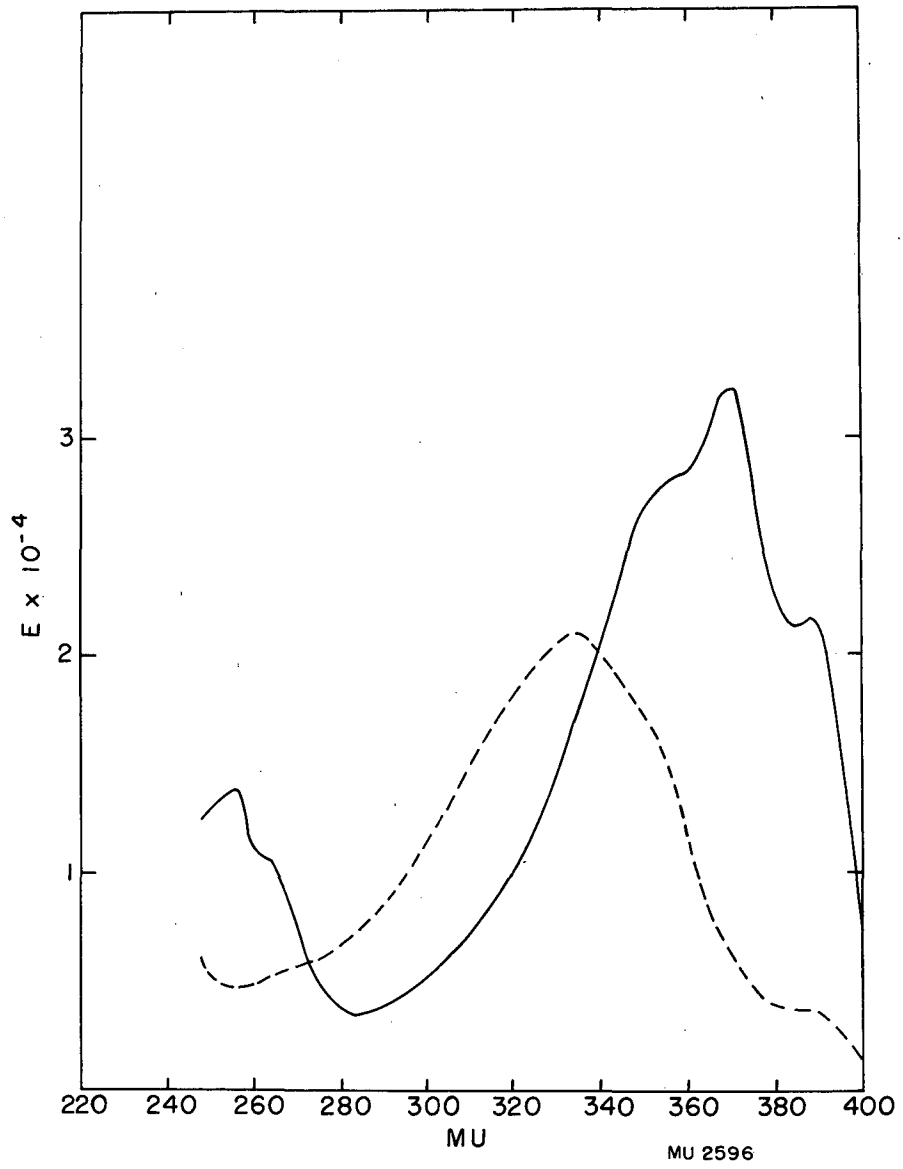


Figure 3

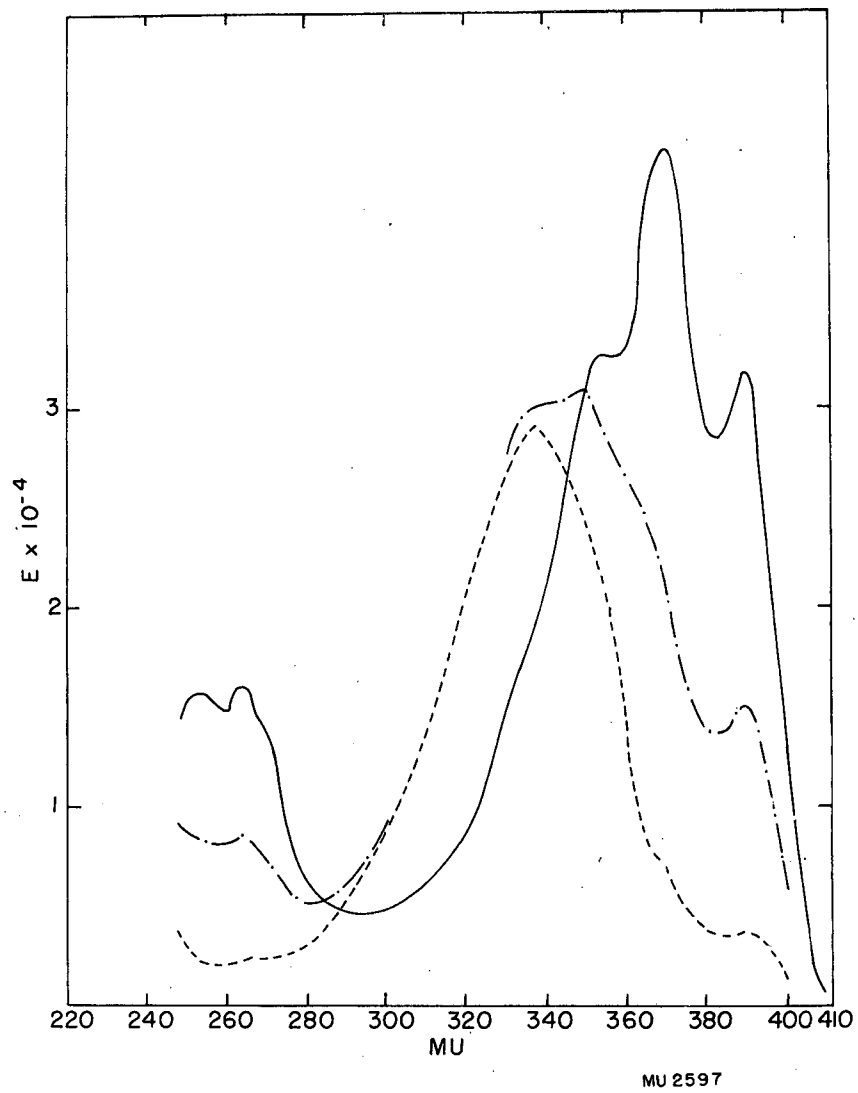


Figure 4

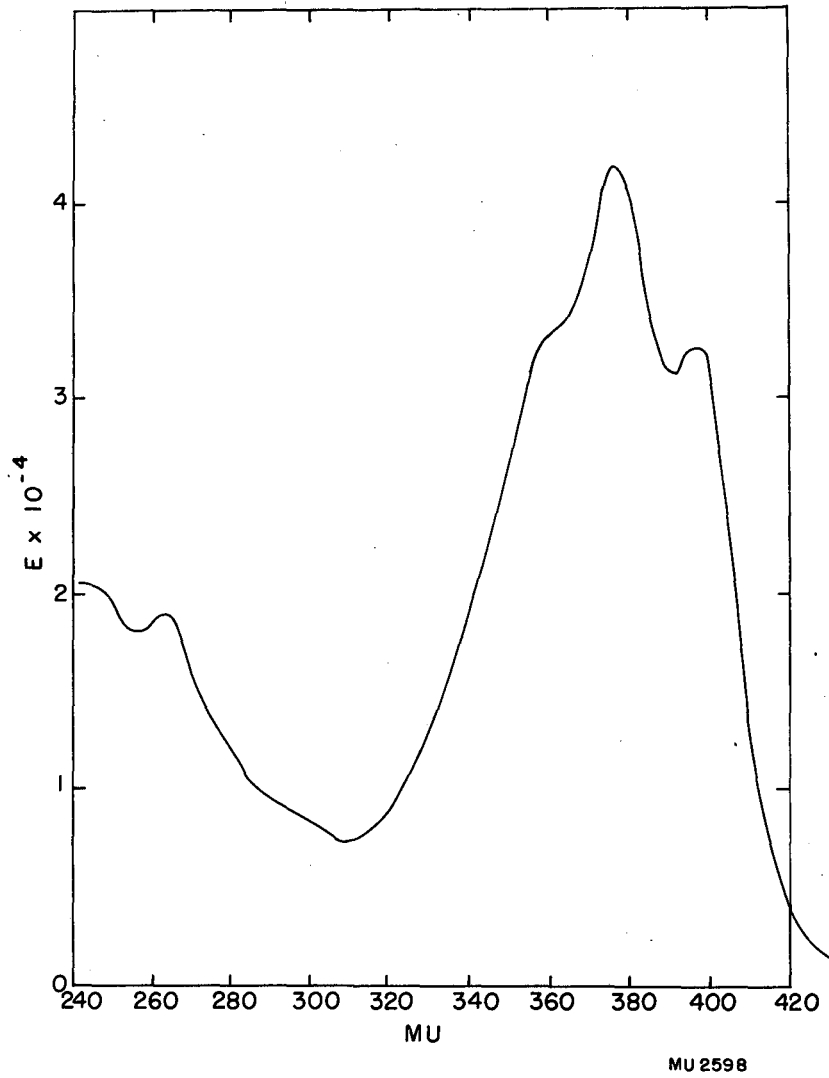
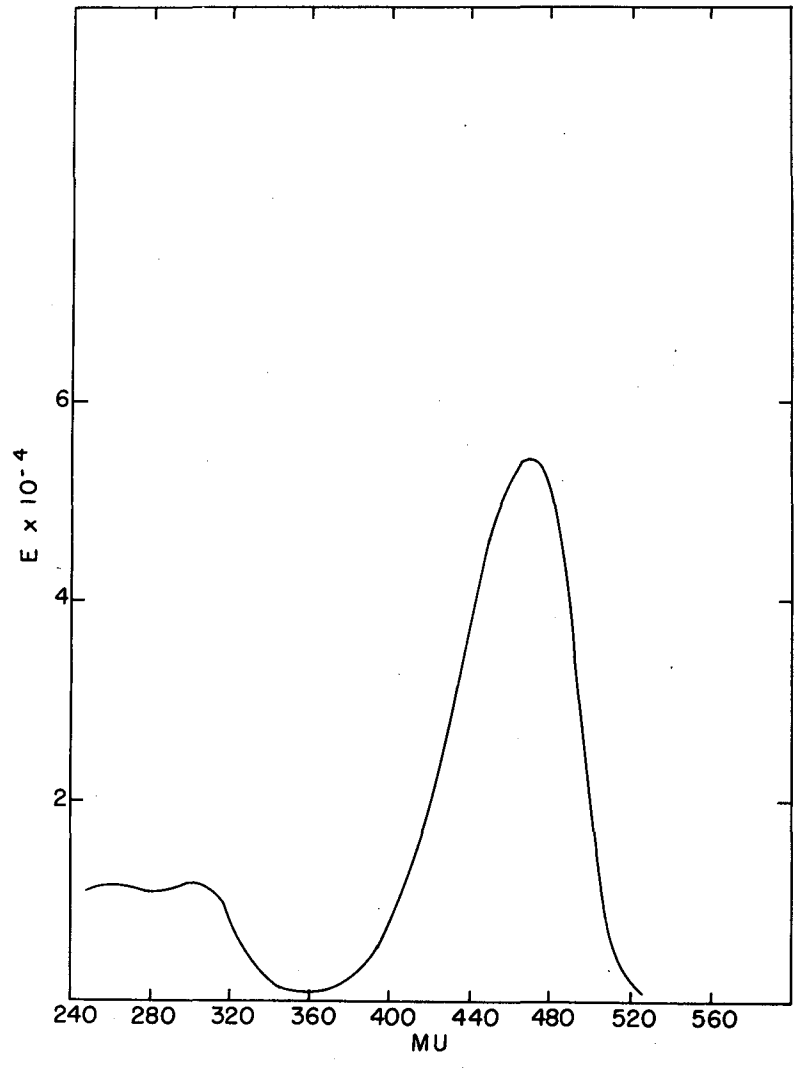


Figure 5



MU2599

Figure 6

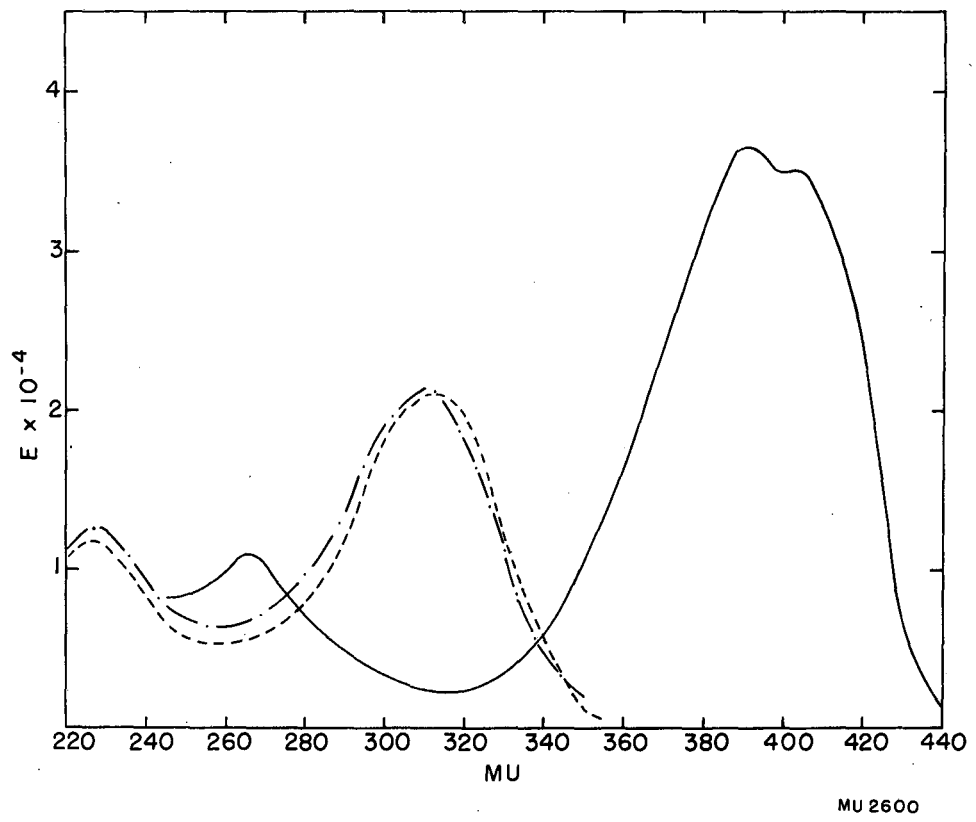


Figure 7

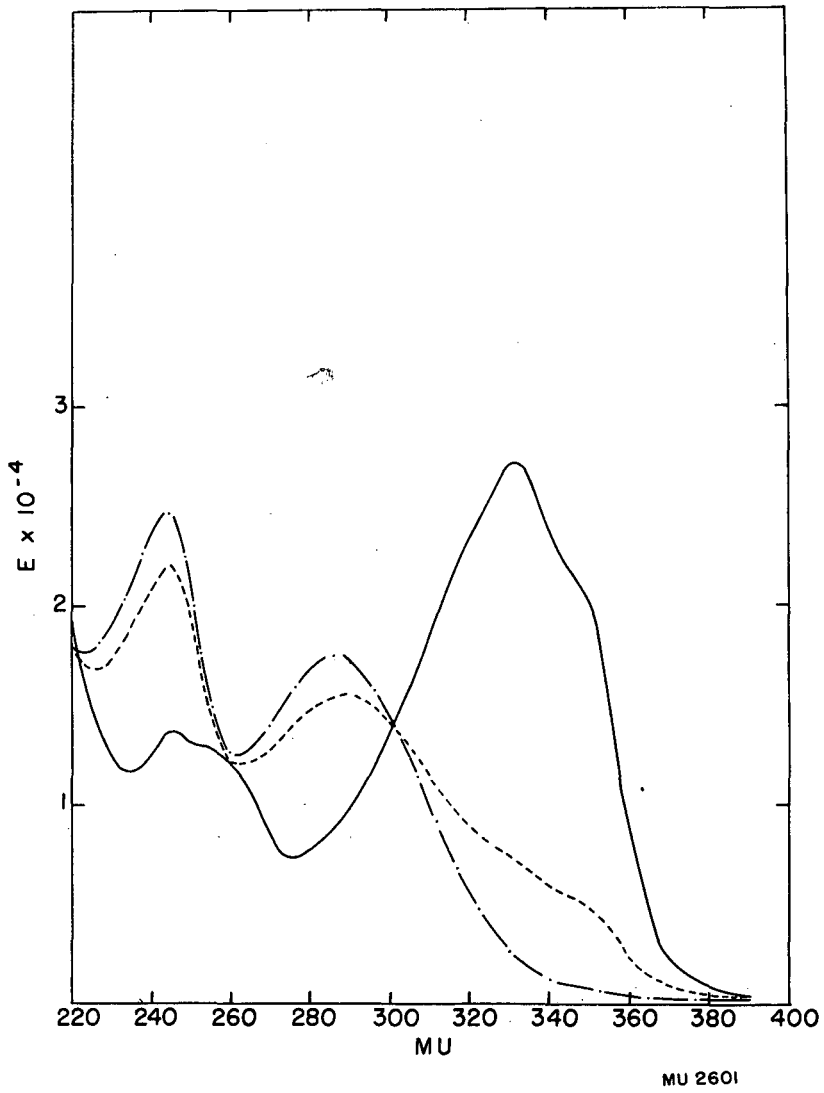


Figure 8

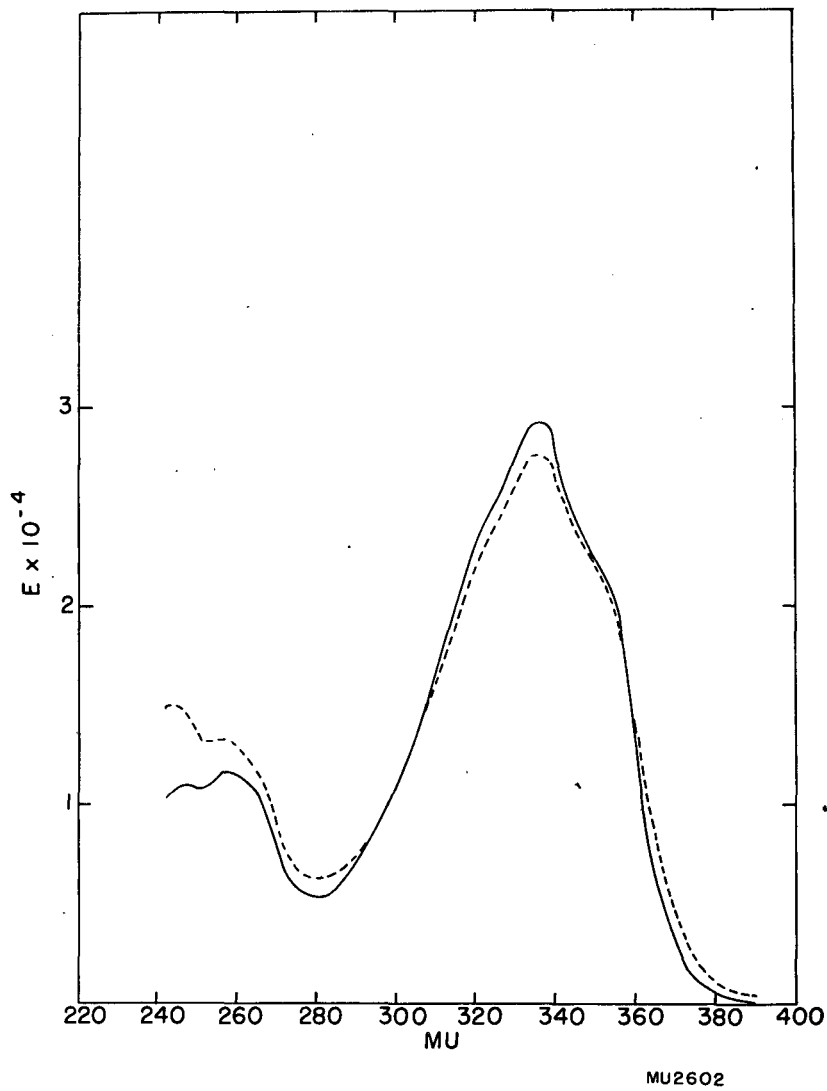


Figure 9

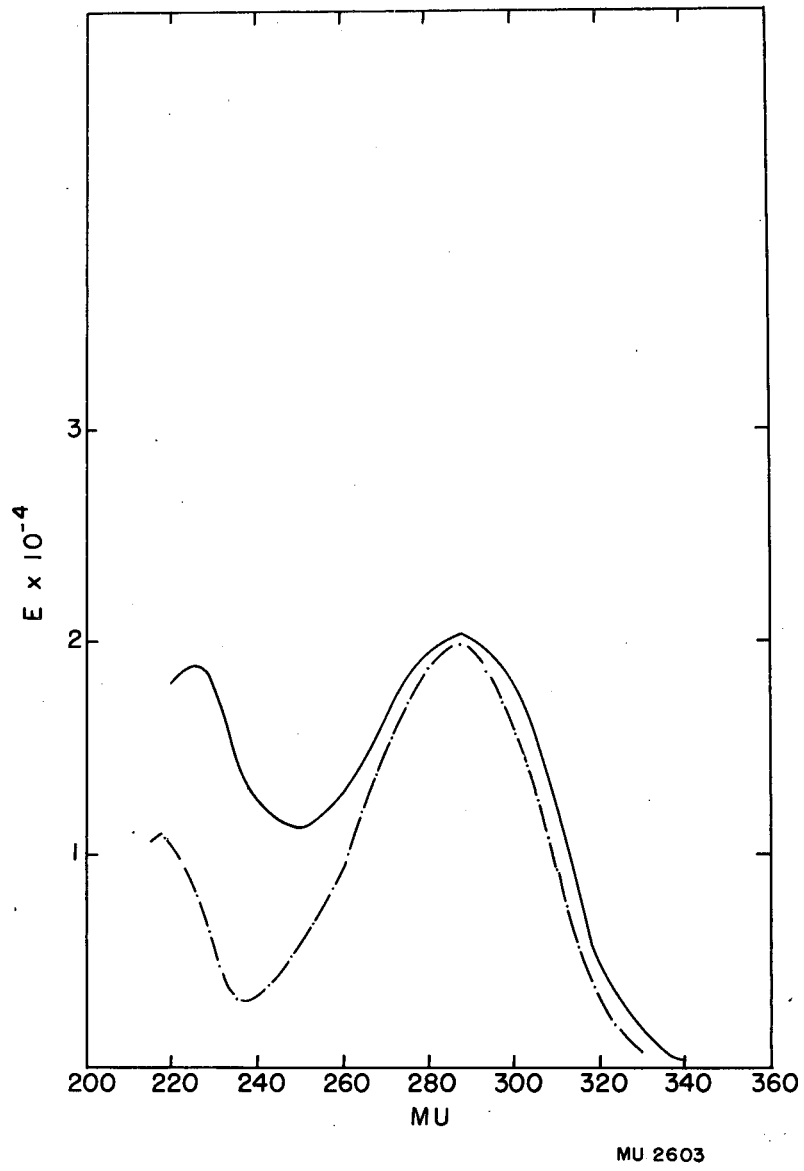
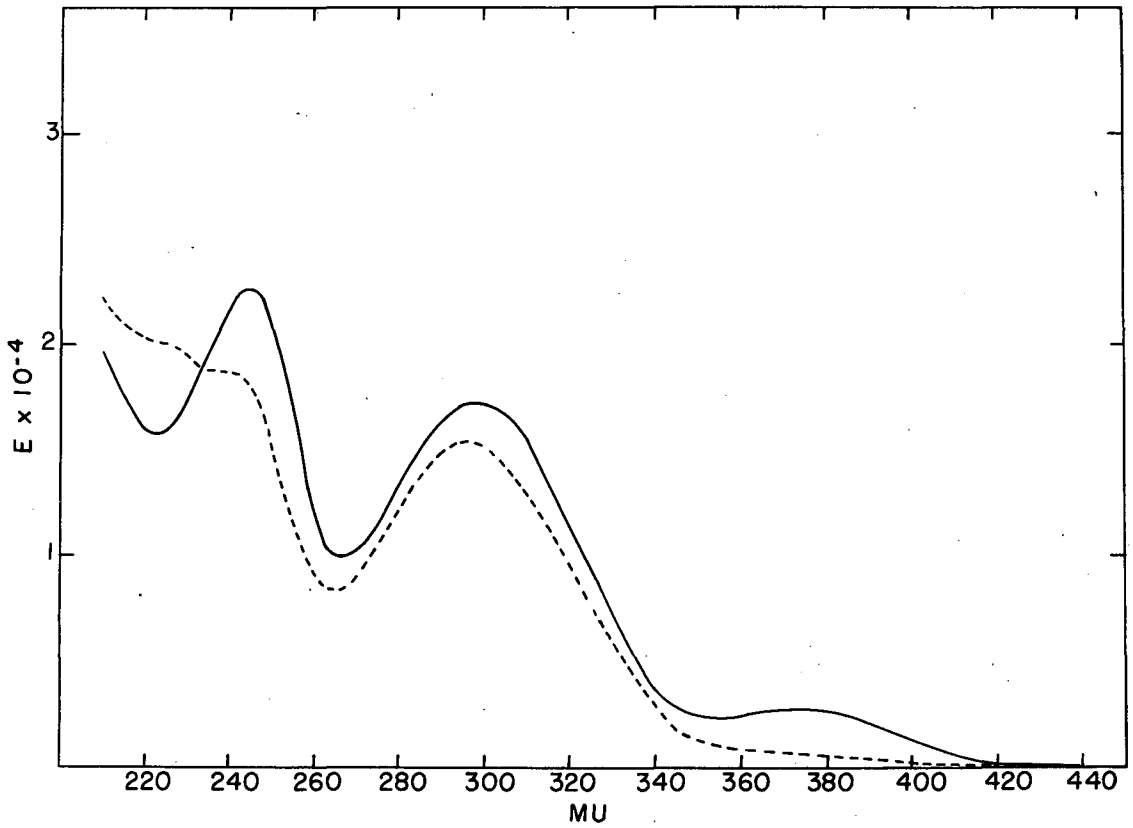


Figure 10.



MU 2605

Figure 12