

SYNTHESIS OF N-SUBSTITUTED BIS-ITACONIMIDE MONOMERS *file*

FOR USE AS THERMOSETTING POLYIMIDE RESINS

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SYNOPSIS

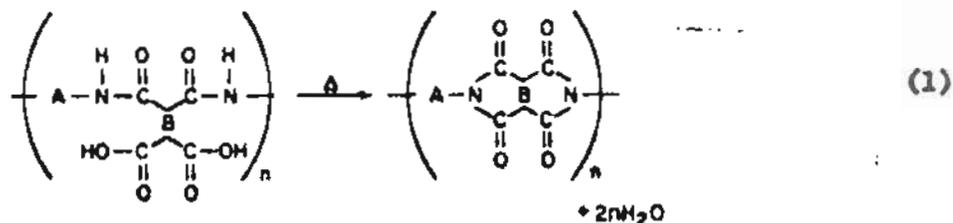
Two monomeric N-substituted bis-itaconimides, N,N'-bis-itaconimido-p,p'-diphenylmethane and N,N'-bis-itaconimido-p,p'-diphenylether, were synthesized from the corresponding diamines. The synthesis was accomplished by reaction of the diamine with itaconic anhydride and cyclocondensation of the resultant bis-itaconamic acid. Attempts to use p,p'-diamino-diphenylsulfone as the diamine gave N,N'-bis-citraconimido-p,p'-diphenylsulfone and N-citraconimido-N'-itaconimido-p,p'-diphenylsulfone instead of the bis-itaconimide. The two bis-itaconimides thermally polymerize at 180°C and 225°C, respectively, and yield tough polymers with very high thermal stability.

INTRODUCTION

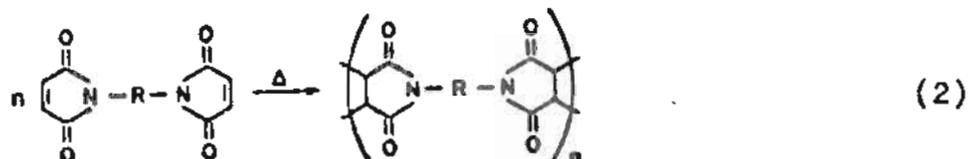
Polyimides are one of a growing number of classes of thermosetting resins which offer very high thermal stability and high temperature mechanical strength. The most common synthesis of polyimides takes place by the cyclocondensation of the corresponding polyamic acid.^{1,2} Unfortunately, volatile byproducts are evolved which interfere with the curing of the polymer:

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Here A and B can be a wide variety of organic moieties, usually aromatic for higher thermal stability. In recent years, the use of N-substituted bis-maleimide monomers has eliminated the problem of volatiles from polyimide synthesis.³ With the bis-maleimides, the imide bonds are pre-formed in the monomer, and the polymer is subsequently formed by an addition type reaction:



Here R is generally an aromatic structure to enhance the thermal stability of the polymer. However, it is a rather general rule that 1,2-disubstituted ethylenes, such as maleimides, do not readily homopolymerize,^{4,5} and it would be advantageous to use a more reactive species. It has been shown that itaconic derivatives homopolymerize by an addition type reaction more readily than maleic derivatives.⁶⁻⁹ Therefore, it is reasonable to speculate that itaconimides may be more suitable than maleimides as precursors for polyimides. There has been very little discussion

of itaconimides in the literature,¹⁰⁻¹⁴ and we wish to report the synthesis of several N-substituted bis-itaconimides, which yield polyimides upon thermal curing. These N-substituted bis-itaconimides have the general structure:



EXPERIMENTAL

Materials and Instrumentation

The N-substituted bis-itaconimides were prepared by the method of Searle.¹⁵ First, the bis-itaconamic acid was formed from a diamine and itaconic anhydride. Then the amic acid was dehydrated using acetic anhydride and sodium acetate to give the bis-itaconimide. All chemicals were reagent grade and were used directly as obtained from the supplier. Diamines and chloroform were obtained from Aldrich Chemical Company, itaconic acid from Pfizer Chemicals Division, acetic anhydride, silica gel, and phosphorus pentoxide from Baker Chemical Company, sodium acetate from Eastman Chemicals Division, and acetone from Mallinckrodt Chemical Company.

Melting point determinations were performed using a Thomas Hoover uni-melt apparatus and are uncorrected. Melting points were also determined by differential thermal analysis (DTA) using a DuPont 990 differential thermal analyzer. Infrared spectra were taken on a Perkin-Elmer Model 180 infrared spectrometer. NMR spectra were obtained using a 100-MHz Varian HA 100 spectrometer. The liquid chromatographs were run on a Waters Associates model 202/401 high-pressure liquid chromatograph equipped with a differential UV detector and an M6000 pumping unit. Thermogravimetric analysis (TGA) was performed using a DuPont 950 thermogravimetric analyzer. Elemental analysis was done by I. J. Wilk Associates, Stanford, California.

Synthesis of Itaconic Anhydride

Itaconic anhydride was prepared in the laboratory from itaconic acid using phosphorus pentoxide as the dehydrating agent.¹⁶ The reaction is carried out by mixing 2.0 moles of itaconic acid and 1.5 moles (excess) of phosphorus pentoxide in a 3-liter reaction flask containing 2 liters of chloroform. The mixture is allowed to reflux with stirring for 24 hr. After refluxing, the chloroform solution is decanted from the viscous brown residue at the bottom of the flask, and the volume of solution is reduced to 1 liter by rotary evaporation. The remaining chloroform solution is cooled to -10°C , resulting in crystallization of itaconic anhydride from the solution. Three crops of white crystals, m.p. 68°C , can be obtained in this manner. The average yield is about 85%.

General Synthesis of Bis-Itaconamic Acids

The synthesis of the bis-itaconamic acids is similar to the synthesis of the mono-itaconamic acids.¹¹ One half mole of the appropriate primary diamine is dissolved in 2 liters of acetone contained in a 3-liter round bottom flask, and 1.1 moles (10% excess) of itaconic anhydride is added slowly. A slight excess of the anhydride is used to assure complete reaction of the diamine so that no mono-amic acid is present. After addition of the itaconic anhydride, the mixture is refluxed with stirring for 24 hr. The bis-itaconamic acid that precipitates from the acetone is collected by suction filtration and washed with fresh acetone. After air drying at room temperature for 24 hr, the product is vacuum dried at 75°C to remove any remaining solvent. The yields of the different bis-itaconamic acids are given in Table I.

General Synthesis of Bis-Itaconimides

The bis-itaconimides are made by the cyclocondensation of the bis-itaconamic acids. First, 0.06 mole of the bis-itaconamic acid is suspended in 700 ml of acetone in a 1-liter round bottom flask. Next, 0.18 mole (excess) of acetic anhydride, the dehydrating agent, and 1.0 g of sodium acetate, as catalyst, are added to the suspension. The mixture is refluxed with stirring until the solution just becomes clear and no solid remains. Then the reaction mixture is poured into 8 liters of distilled water with vigorous stirring, causing the imide to precipitate. The imide is filtered and washed with copious quantities of distilled water. After air-drying at room temperature for 24 to 48 hr, the imide is vacuum dried at 75°C to remove any remaining solvent. The product, a mixture of bis-imides, is obtained in 80 to 90% yield.

Isolation of Pure Bis-Imides

The mixtures resulting from the cyclocondensation of the different bis-itaconamic acids were fractionated using a 4.9 cm (I.D.) x 100 cm chromatographic column filled with 60-200 mesh silica gel. For each mixture, 50 g of material was fractionated at a time using chloroform as the eluting solvent. Fractions were collected in 250 ml volumes and examined by high-pressure liquid chromatography (HPLC) to determine which fractions contained only one species and which fractions contained more than one. Pure compounds were obtained by rotary evaporation of the solvent from the pure fractions. The yields of the different bis-imides which were obtained by this process are given in Table II.

Figure 1 shows the 100-MHz ^1H -NMR spectra of the bis-itaconamic acids, I, II, and III. The different resonances in the spectra are assigned, but the absence of a resonance for the amide hydrogen indicates a very rapid equilibrium between amide bound hydrogen and solvated hydrogen ion. This rapid equilibrium broadens the peak to the point where it is unobservable. Also, there are two small peaks at 5.64 and 5.96 ppm. These small peaks may be due to the presence of small amounts of the isomer in which the amine has attached to the conjugated carbonyl. The small peaks do occur in the same region of the spectrum as the larger itaconic methylene hydrogen peaks.

Figure 2 shows the infrared spectra of the bis-itaconamic acids, I, II, and III. In each spectrum there is a broad absorption region from approximately 1600 to 1700 cm^{-1} . This broad absorption is due to overlap of the amide carbonyl and acid carbonyl stretching absorptions of the amic acid. It should be pointed out that even though there is a very broad absorption in the region 2500 to 3500 cm^{-1} due to the OH stretch of the amic acid, there is also a significant contribution in this region due to the OH stretch of H_2O . The H_2O could not be completely eliminated from the KBr pellets.

Figure 3 contains the DTA data for the bis-itaconamic acids, I, II, and III. These compounds exhibit normal melting behavior which was substantiated by using a standard melting point apparatus. The melting point data, elemental analysis, physical description, and yield of each compound are given in Table I. The slight coloration in compounds I and II could be due to slight amounts of impurity. The low yield of compound III is reproducible and cannot be accounted for.

Characterization of Bis-Itaconimides

Figures 4(a), (b) and (c) show the high-pressure liquid chromatographs (HPLC) of the reaction products which resulted from the cyclocondensation of the bis-itaconamic acids, I, II and III, respectively. Only the major component, IV, was isolated in the pure form from the cyclocondensation products of bis-itaconamic acid I. Compound IV corresponds to the peak appearing at 4.6 min in figure 4(a). Only the major component, V, was isolated in the pure form from the cyclocondensation products of bis-itaconamic acid II. Compound V corresponds to the peak appearing at 4.4 min in figure 4(b). Compounds VI(a) and VI(b) were both isolated in the pure form from the cyclocondensation products of bis-itaconamic acid III. Compounds VI(a) and VI(b) correspond to the peaks at 3.6 min and 4.8 min, respectively, in figure 4(c).

Figure 5 shows the 100-MHz $^1\text{H-NMR}$ spectra of compounds IV, V, VI(a) and VI(b). Figure 5(a) is the NMR spectrum of IV which was identified as *N,N'*-bis-itaconimido-*p,p'*-diphenylmethane:

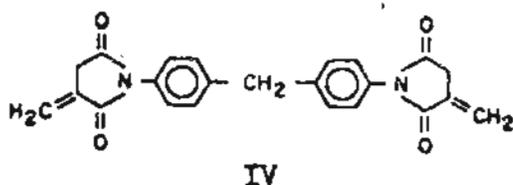


Figure 5(b) is the NMR spectrum of V which was identified as *N,N'*-bis-itaconimido-*p,p'*-diphenylether:

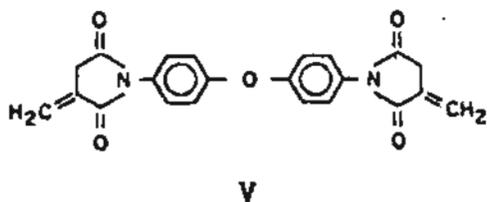


Figure 5(c) is the NMR spectrum of VI(a) which was identified as N,N'-bis-citraconimido-p,p'-diphenylsulfone:

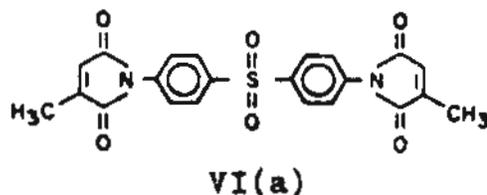
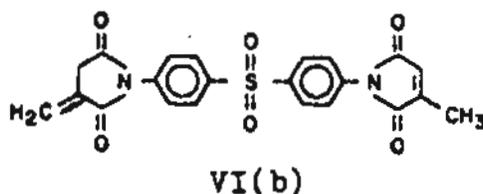


Figure 5(d) is the NMR spectrum of VI(b) which was identified as N-citraconimido-N'-itaconimido-p,p'-diphenylsulfone:



The low signal/noise level in figure 5(d) is a result of the low solubility of the bis-imide, VI(b), in CDCl_3 . Attempts to dissolve this compound in other solvents such as acetone- d_6 , acetonitrile- d_3 , and DMSO-d_6 produced a pink solution which gave an altered NMR spectrum.

The presence of citraconimide as a byproduct of itaconimide synthesis is not unexpected since the isomerization of itaconic anhydride to citraconic anhydride is known to take place readily,¹⁸



The citraconimide is distinguished in the NMR spectra by a peak at 6.44 ppm and another, approximately three times as large, at 2.15 ppm.

Figure 6 shows the infrared spectra of the bis-imides IV, V, VI(a) and VI(b). All of the spectra show the large absorption at 1710 cm^{-1} which is characteristic of imides. The spectral region from approximately $700\text{--}800\text{ cm}^{-1}$ is obscured by the absorption of the C-Cl stretch of the solvent.

The DTA data for the bis-imides IV, V, VI(a) and VI(b) are shown in figure 7. It is interesting to note that the bis-itaconimides, IV and V, show a strong exotherm just after the endotherm of melting. It is believed that this exotherm is caused by the thermally induced polymerization of double bonds in the bis-itaconimides. In correlating the DTA data with standard melting point tests, it was observed that the bis-itaconimide, V, did not melt when heated from room temperature to the $210\text{--}211^{\circ}\text{C}$ melting point shown in figure 7(b). However, the compound did melt when immersed directly into an oil bath at 211°C , but not less than that temperature. Apparently, if the compound is heated gradually, sufficient crosslinking occurs at lower temperatures so that melting does not occur at the normal melting temperature. The observation that the bis-itaconimide, IV, shows normal melting behavior when heated gradually is attributed to the fact that it has a lower melting point, and sufficient thermal crosslinking to prevent melting does not occur. Table II summarizes the melting point data of the bis-imides, IV, V, VI(a) and VI(b), determined by DTA and standard techniques, as well as elemental analysis, physical description, and yields of these compounds.

Thermal Polymerization of the Monomeric Bis-Itaconimides

The two bis-itaconimides, IV and V, were thermally polymerized by heating in a 1.25-inch-diameter, cylindrical press at

2500 psi for 24 hr. Bis-itaconimide IV was heated to 180°C and bis-itaconimide V was heated to 225°C. Both compounds yielded tough, light yellow, transparent discs with a density of approximately 1.3 g/cm³. Figure 8 shows the TGA data for the two polymers. These curves show that the bis-itaconimide polymers have very high thermal stability, which is comparable to the bis-maleimide polymers. Further physical tests are currently being conducted on the bis-itaconimide polymers.

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TABLE I. CHARACTERISTICS OF MONOMERIC BIS-ITACONAMIC ACID COMPOUNDS

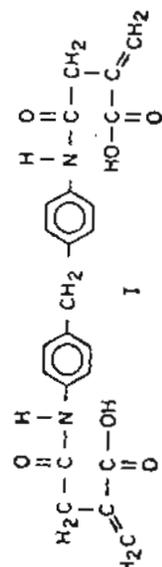
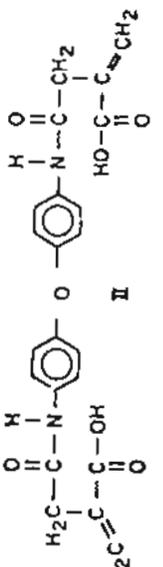
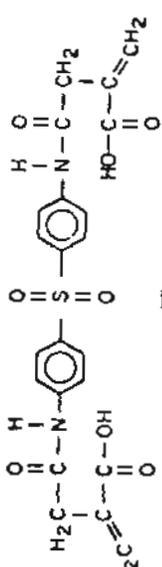
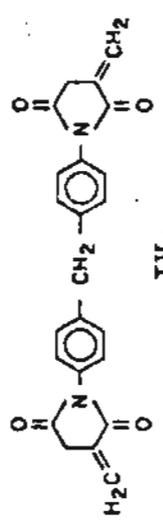
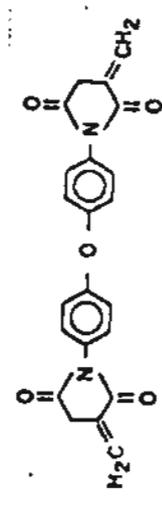
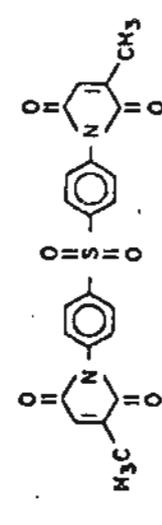
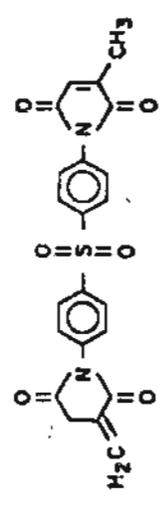
Bis-Itaconamic acid	Melting point, °C	Elemental analysis C, % H, % N, % O, % S, %	Physical description	Yield
 <p style="text-align: center;">I</p>	211-212	Calcd. 65.40 5.21 6.64 22.75 Found 64.96 5.25 6.51 22.29	Slightly yellow powder	94%
 <p style="text-align: center;">II</p>	195-196	Calcd. 62.26 4.72 6.60 26.42 Found 61.97 4.76 6.46 26.42	Slightly grey powder	91%
 <p style="text-align: center;">III</p>	201-202	Calcd. 55.93 4.24 5.93 27.12 6.78 Found 55.78 4.39 5.50 27.03 6.30	White powder	61%

TABLE II. CHARACTERISTICS OF MONOMERIC BIS-IMIDE COMPOUNDS

Bis-Imide	Melting point, °C	Elemental analysis						Physical description	Yield
		C, %	H, %	N, %	O, %	S, %	S, %		
 <p style="text-align: center;">IV</p>	160-161	Calcd. 71.51	4.66	7.25	16.58		White powder	32%	
Found	71.09	4.67	7.09	16.65					
 <p style="text-align: center;">V</p>	210-211*	Calcd. 68.04	4.12	7.22	20.62		White powder	44%	
Found	67.98	4.15	7.07	20.59					
 <p style="text-align: center;">VI(a)</p>	214-215	Calcd. 60.55	3.67	6.42	22.02	7.34	White powder	10%	
Found	60.35	3.67	6.18	22.00	7.25				
 <p style="text-align: center;">VI(b)</p>	240-241	Calcd. 60.55	3.67	6.42	22.02	7.34	White powder	26%	
Found	60.46	3.74	6.20	22.19	7.10				

*See discussion in text

FIGURE LEGENDS

- Figure 1. 100-MHz ^1H -NMR spectra of (a) N,N'-bis-(itaconamic acid)-p,p'-diphenylmethane, (b) N,N'-bis-(itaconamic acid)-p,p'-diphenylether, and (c) N,N'-bis-(itaconamic acid)-p,p'-diphenylsulfone in DMSO-d_6 .
- Figure 2. Infrared spectra of (a) N,N'-bis-(itaconamic acid)-p,p'-diphenylmethane, (b) N,N'-bis-(itaconamic acid)-p,p'-diphenylether, and (c) N,N'-bis-(itaconamic acid)-p,p'-diphenylsulfone in KBr pellet form.
- Figure 3. Differential thermal analysis plots of (a) N,N'-bis-(itaconamic acid)-p,p'-diphenylmethane, (b) N,N'-bis-(itaconamic acid)-p,p'-diphenylether, and (c) N,N'-bis-(itaconamic acid)-p,p'-diphenylsulfone with alumina as the reference and a heating rate of $10^\circ\text{C}/\text{min}$.
- Figure 4. High-pressure liquid chromatographs of the reaction products of the cyclodehydration reactions of (a) N,N'-bis-(itaconamic acid)-p,p'-diphenylmethane, (b) N,N'-bis-(itaconamic acid)-p,p'-diphenylether, and (c) N,N'-bis-(itaconamic acid)-p,p'-diphenylsulfone using a microporasil* column (*Waters Associates trade name).
- Figure 5. 100-MHz ^1H -NMR spectra of the products that were isolated pure from the cyclocondensation reaction of the bis-itaconamic acids I, II, and III: (a) N,N'-bis-itaconimido-p,p'-diphenylmethane, (b) N,N'-bis-itaconimido-p,p'-diphenylether, (c) N,N'-bis-citraconimido-p,p'-diphenylsulfone, and (d) N-citraconimido-N'-itaconimido-p,p'-diphenylsulfone in CDCl_3 .
- Figure 6. Infrared spectra of (a) N,N'-bis-itaconimido-p,p'-diphenylmethane, (b) N,N'-bis-itaconimido-p,p'-diphenylether, (c) N,N'-bis-citraconimido-p,p'-diphenylsulfone, and (d) N-citraconimido-N'-itaconimido-p,p'-diphenylsulfone in CDCl_3 using a matched 0.1-mm reference cell.

Figure 7. Differential thermal analysis plots of (a) N,N'-bis-itaconimido-p,p'-diphenylmethane, (b) N,N'-bis-itaconimido-p,p'-diphenylether, (c) N,N'-bis-citraconimido-p,p'-diphenylsulfone, and (d) N-citraconimido-N'-itaconimido-p,p'-diphenylsulfone with alumina as the reference and a heating rate of 10°C/min.

Figure 8. Thermogravimetric analysis of (a) poly (N,N'-bis-itaconimido-p,p'-diphenylmethane) and (b) poly (N,N'-bis-itaconimido-p,p'-diphenylether) with a heating rate of 10°C/min.

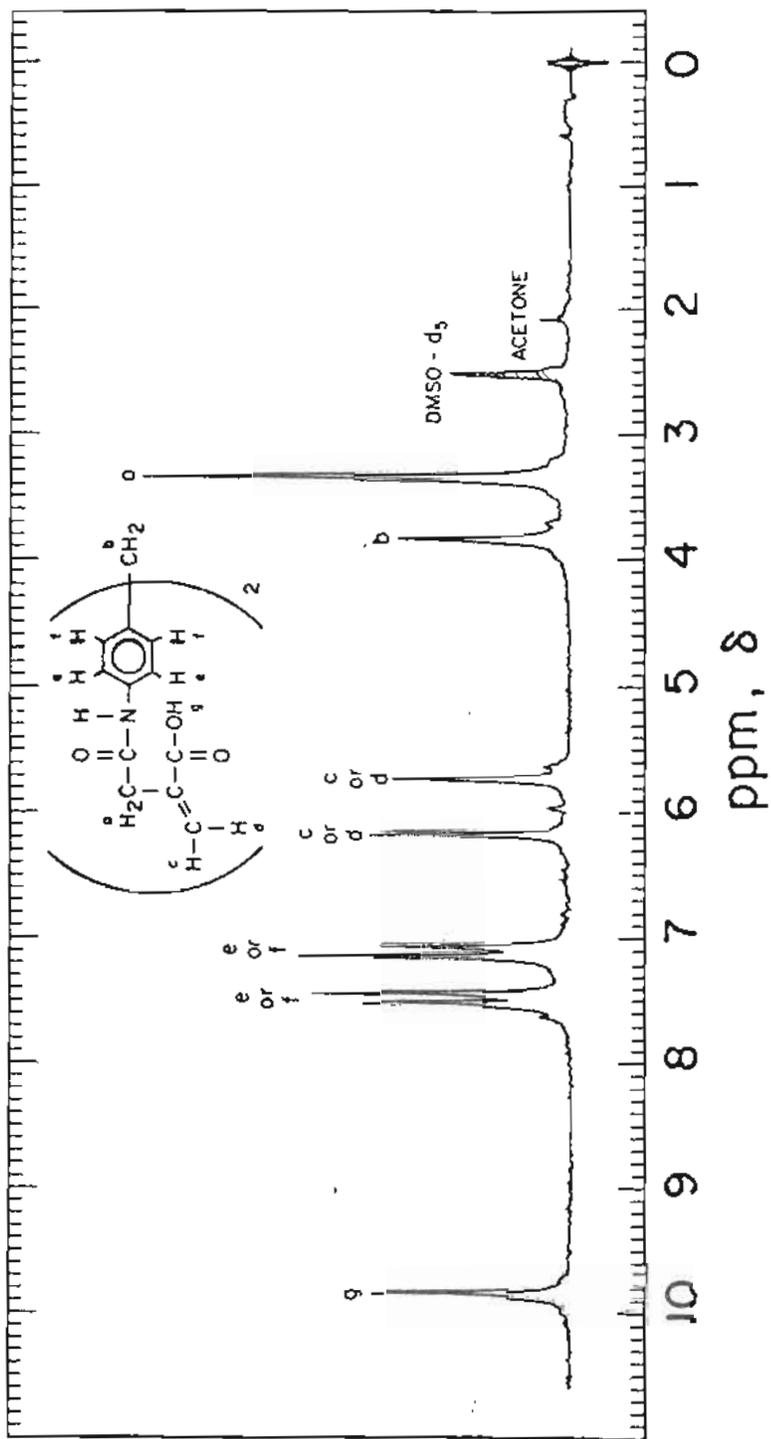


Fig. 1a

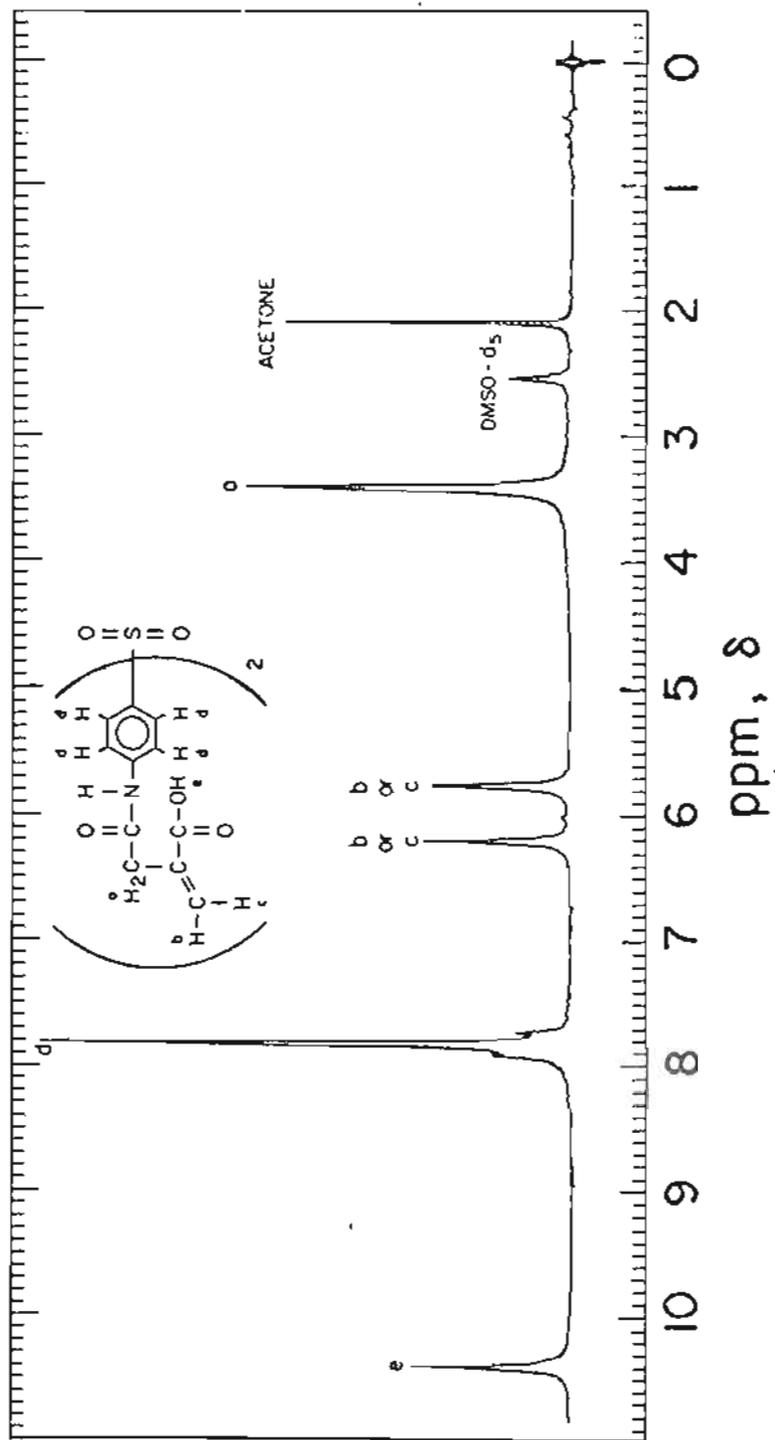


Fig. 1c

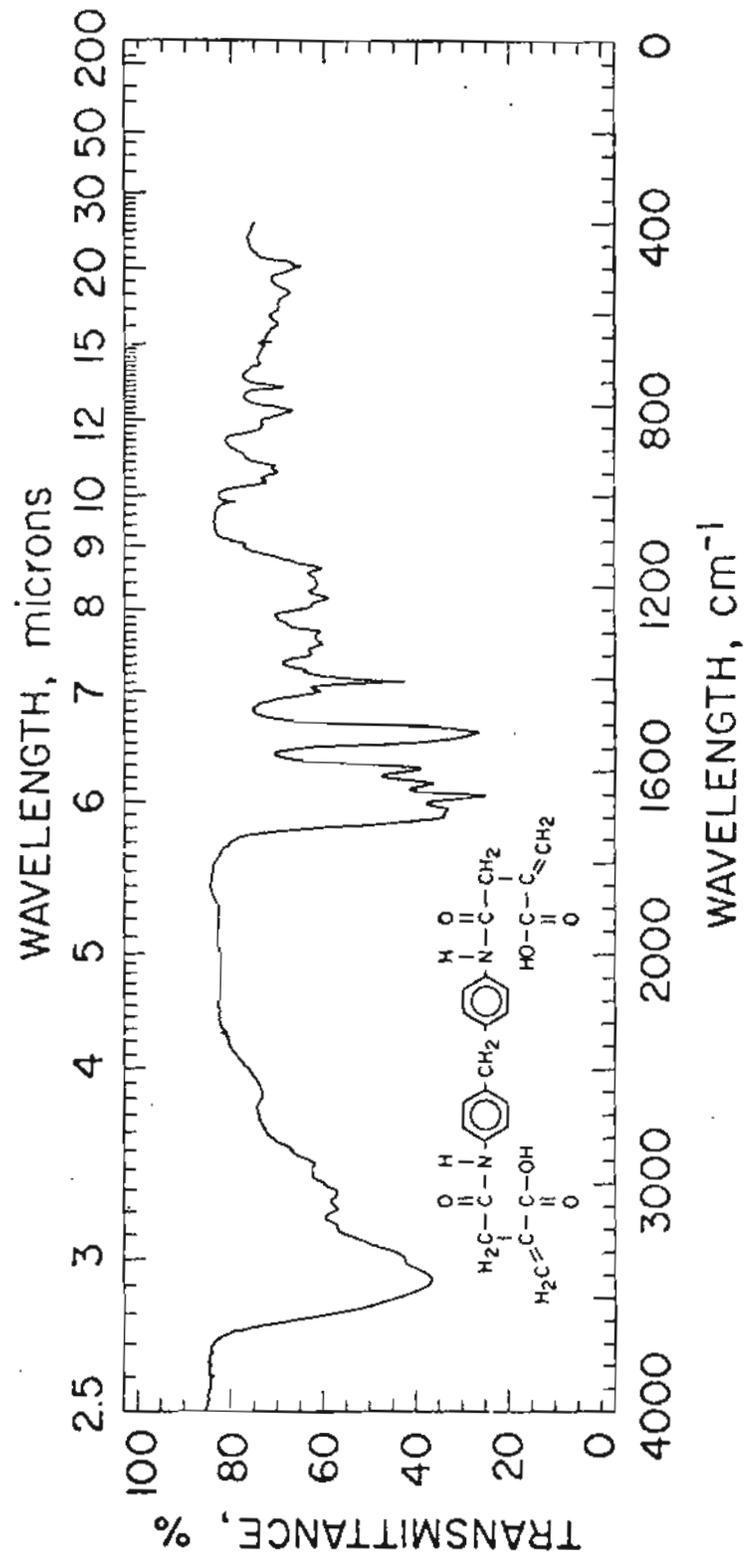


Fig. 2a

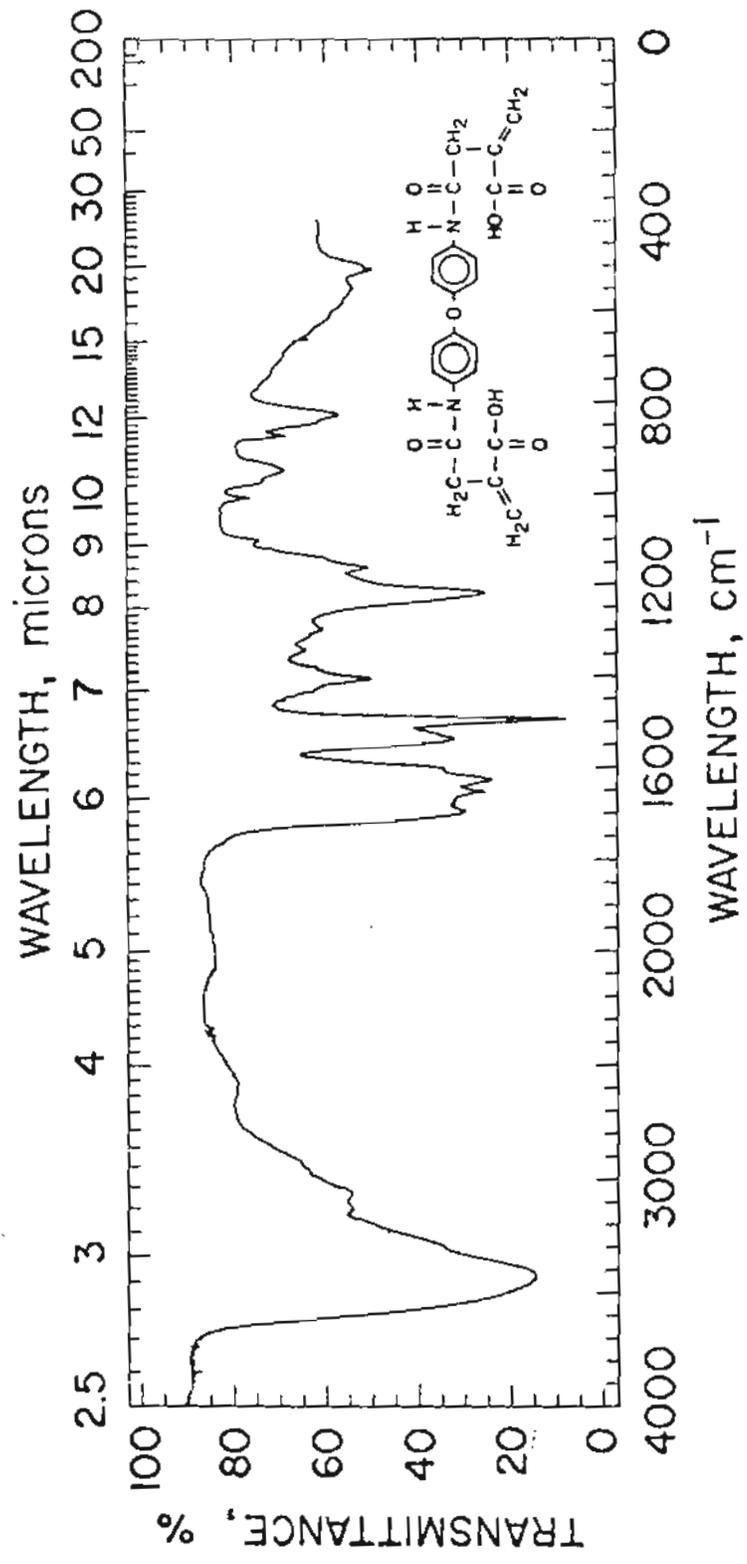


Fig. 2b

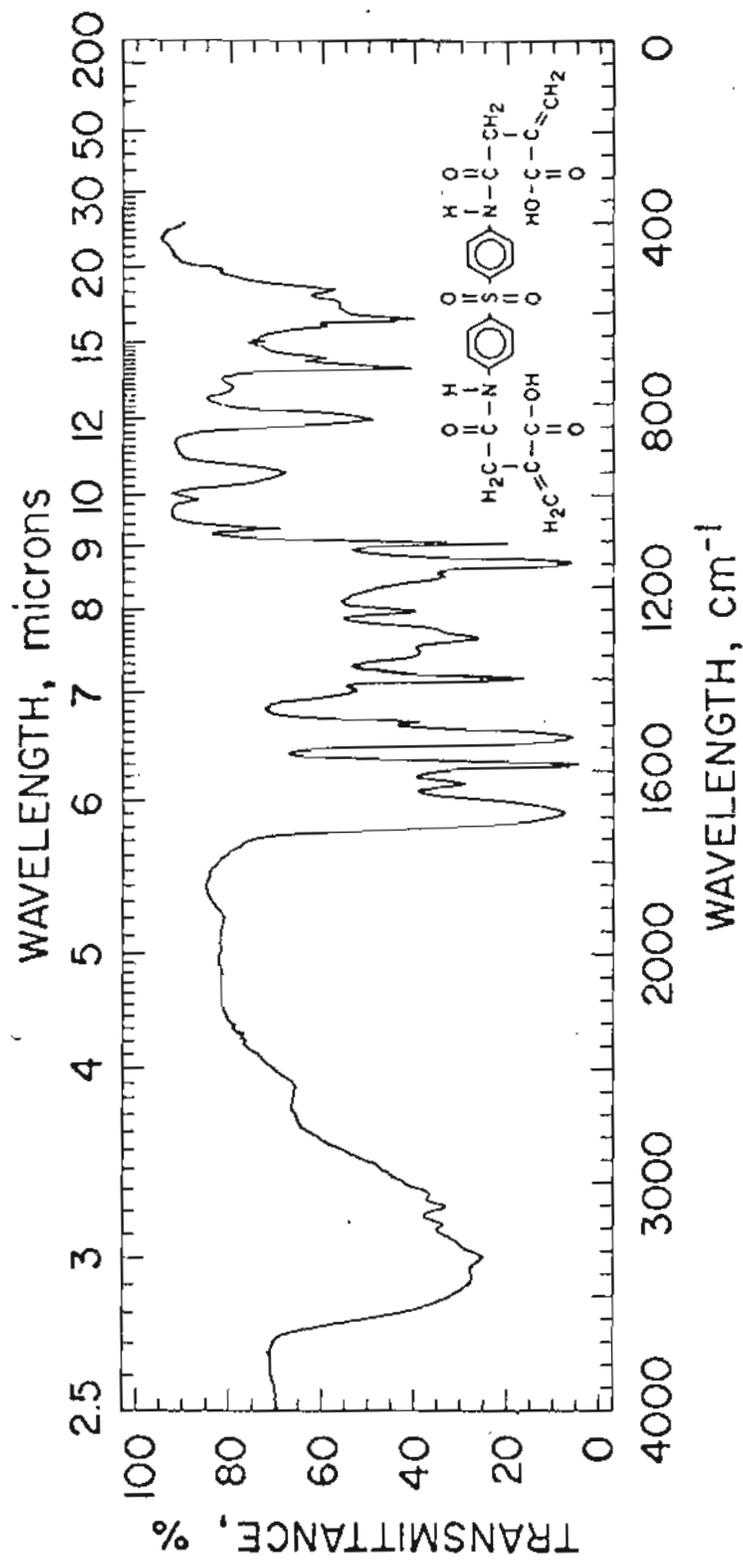


Fig. 2c

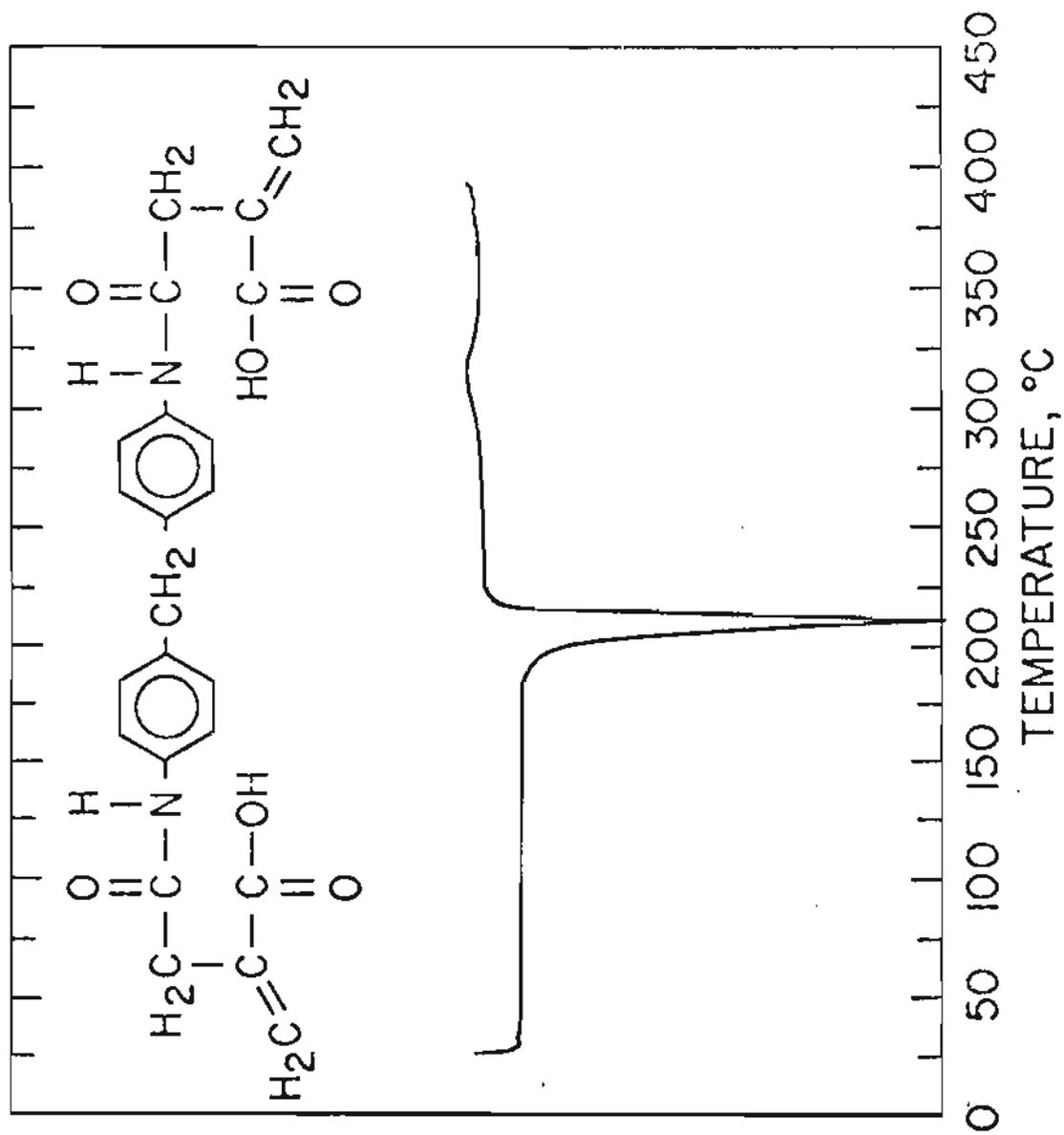


Fig. 3a.

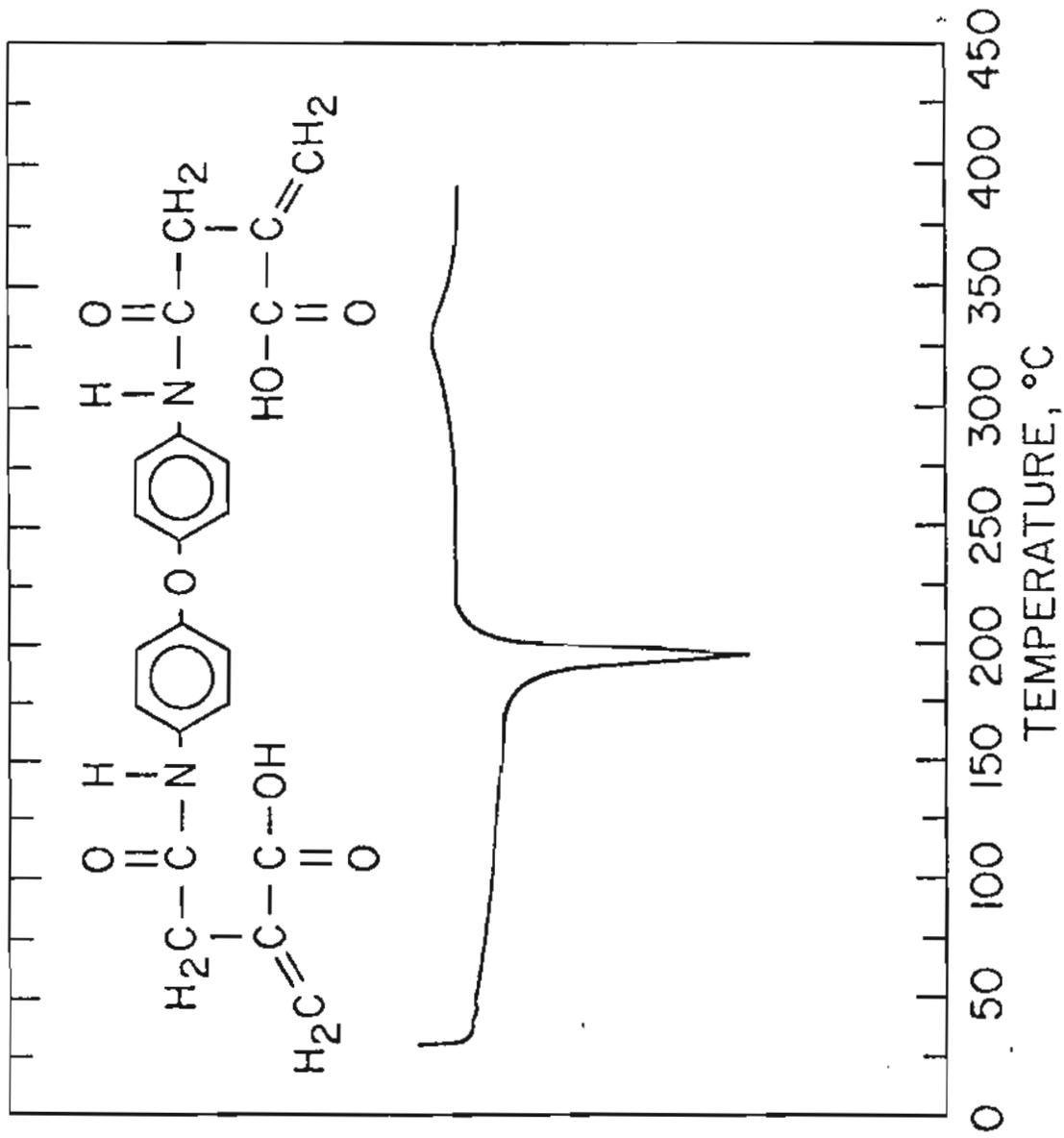


Fig. 3b

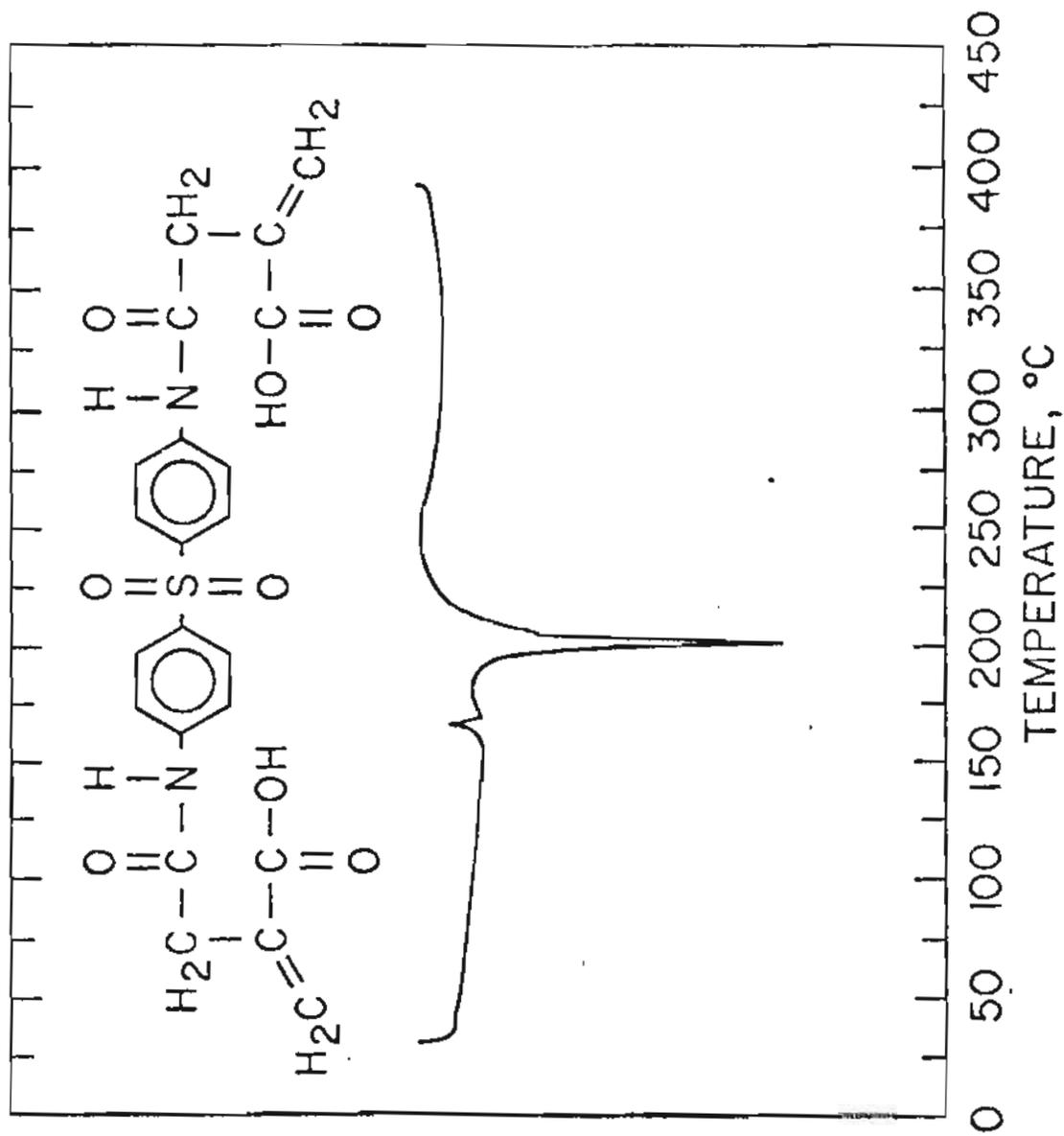


Fig. 3c

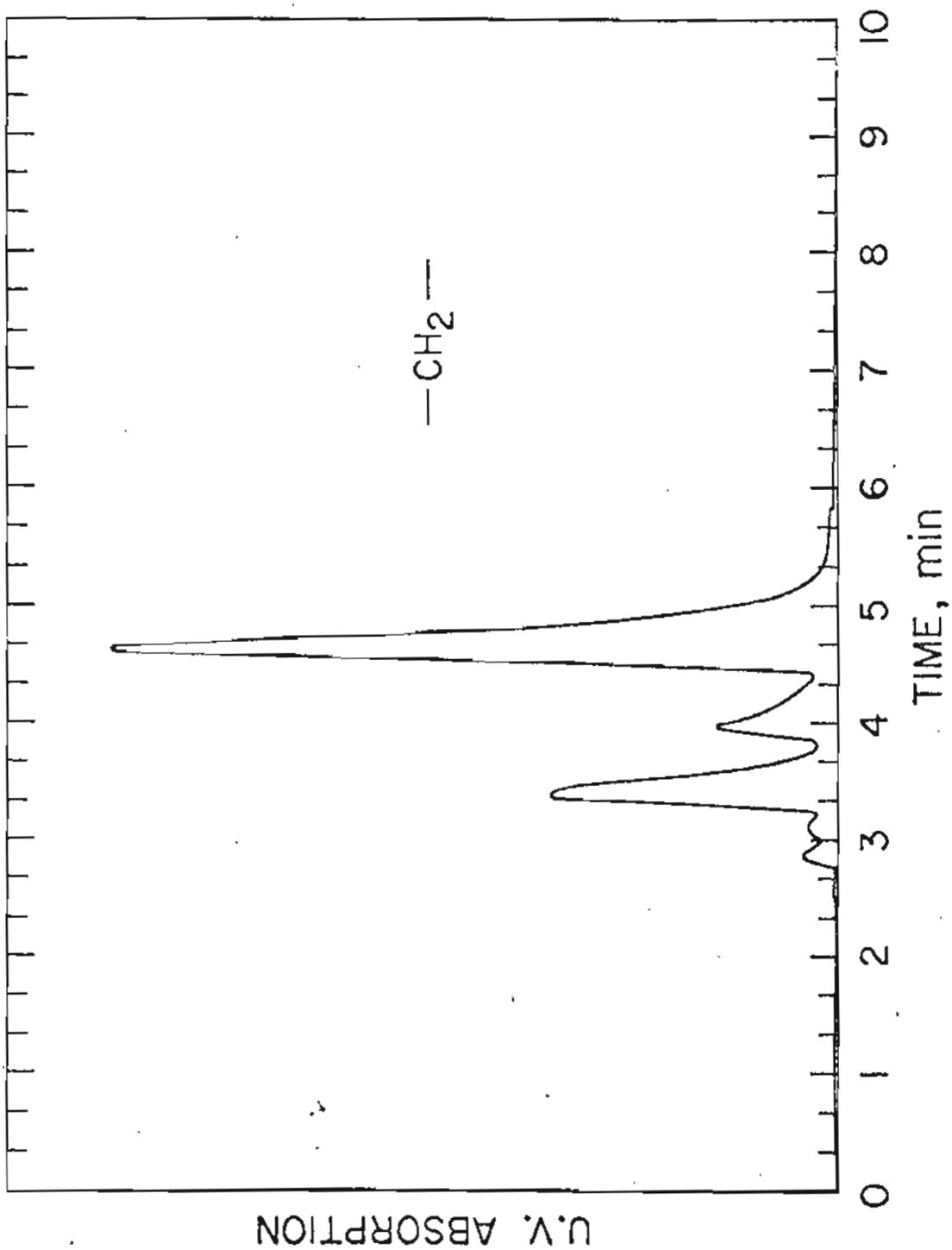


Fig. 4a

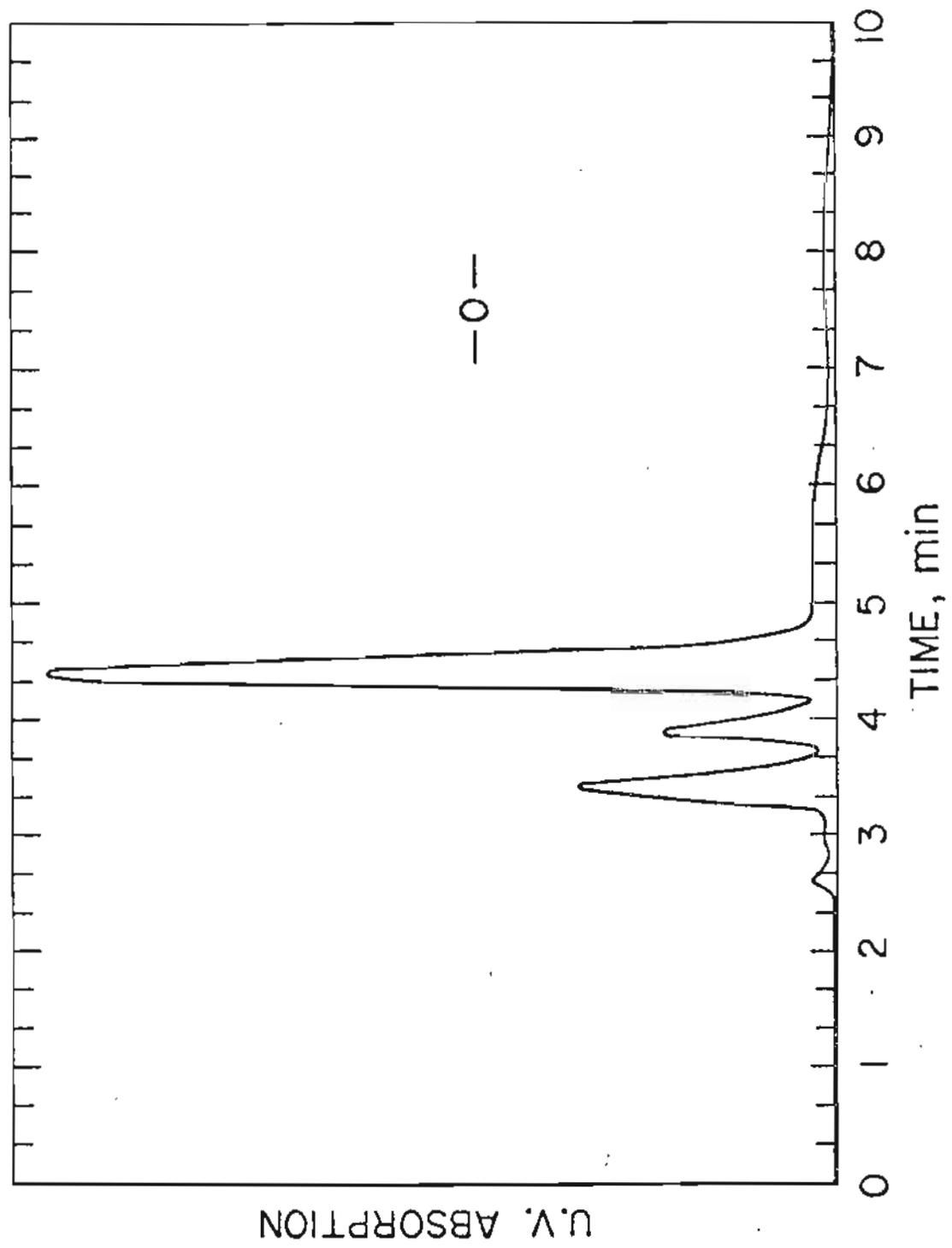


Fig. 4b

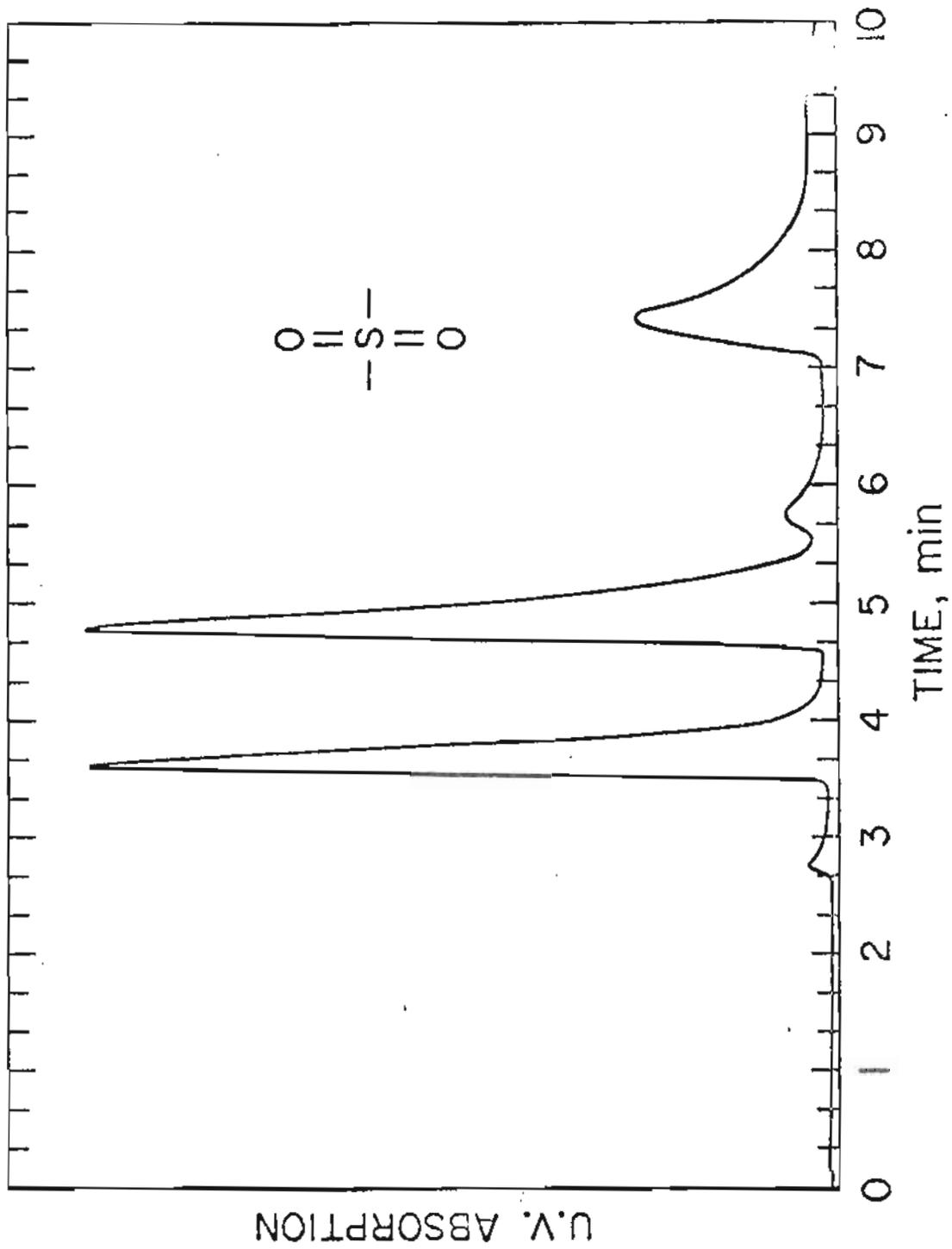


Fig. 4c

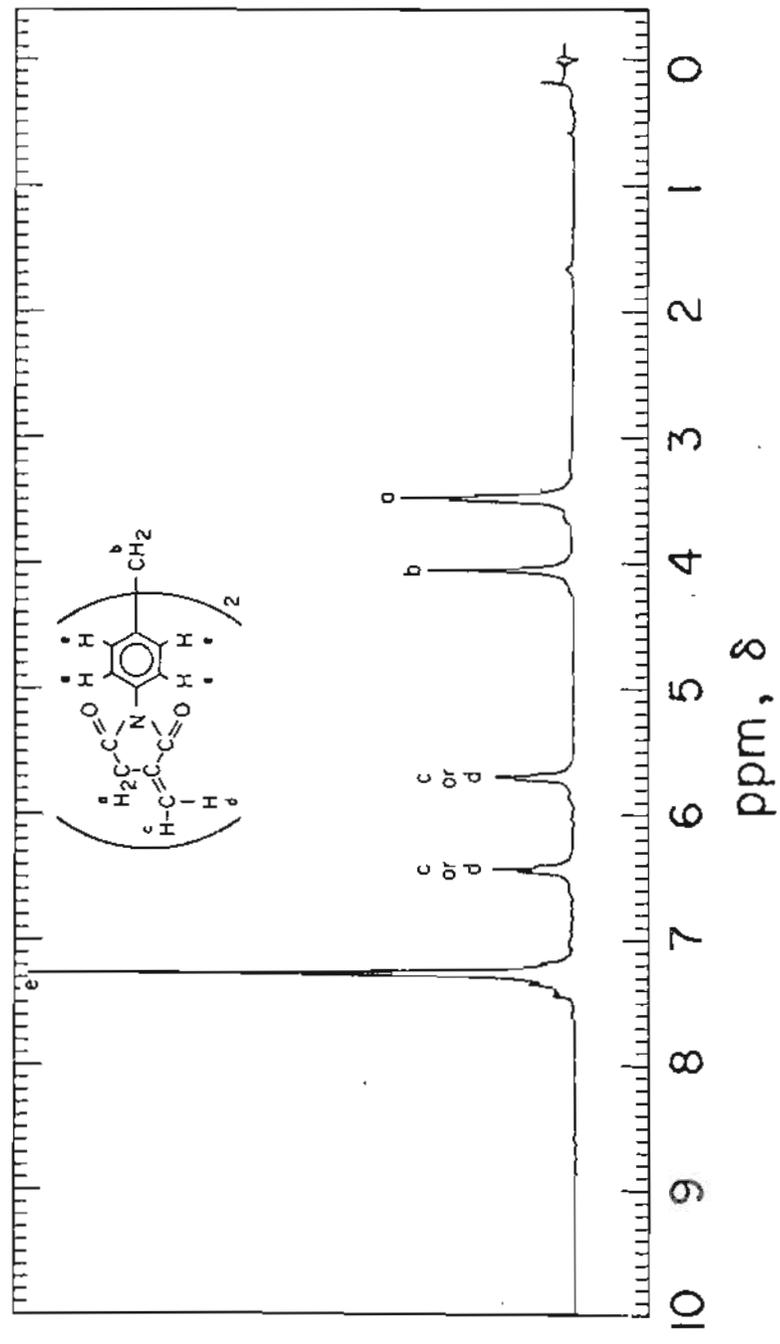


Fig. 5a

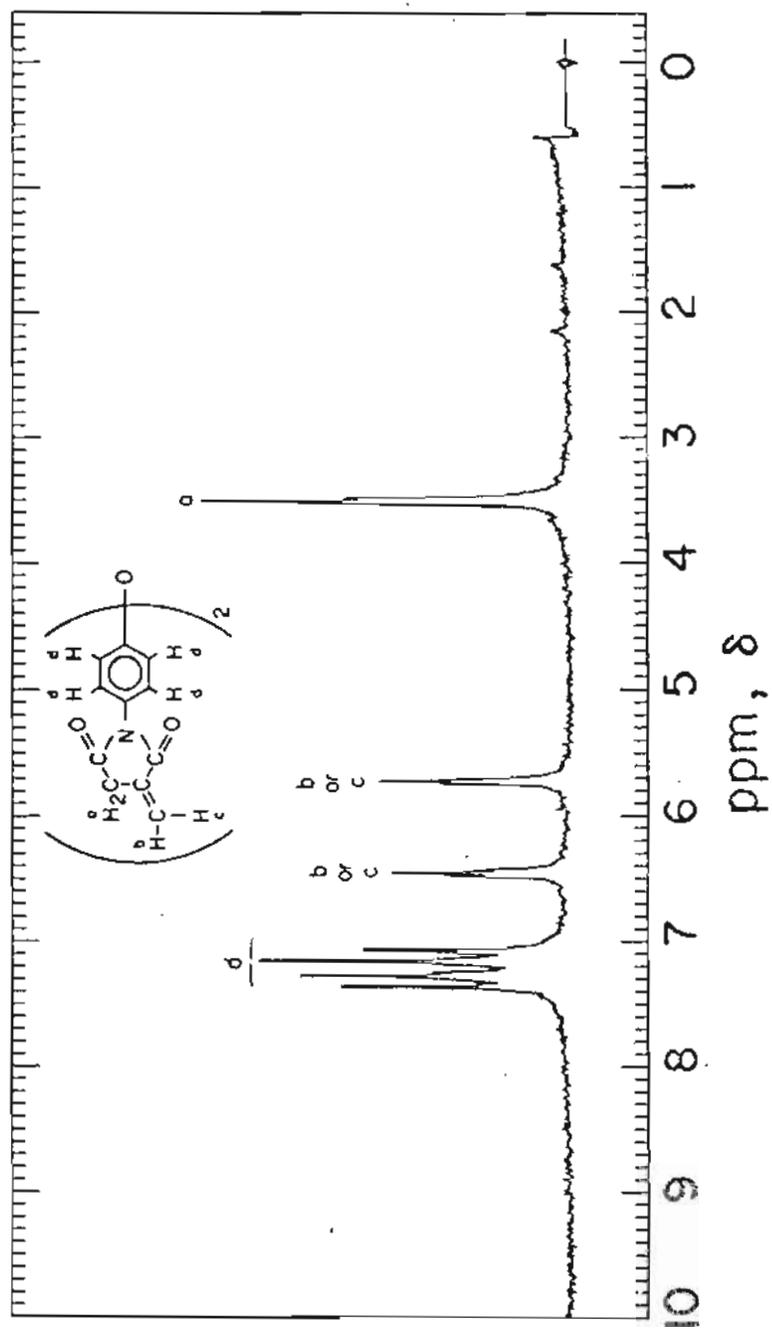


Fig 5b

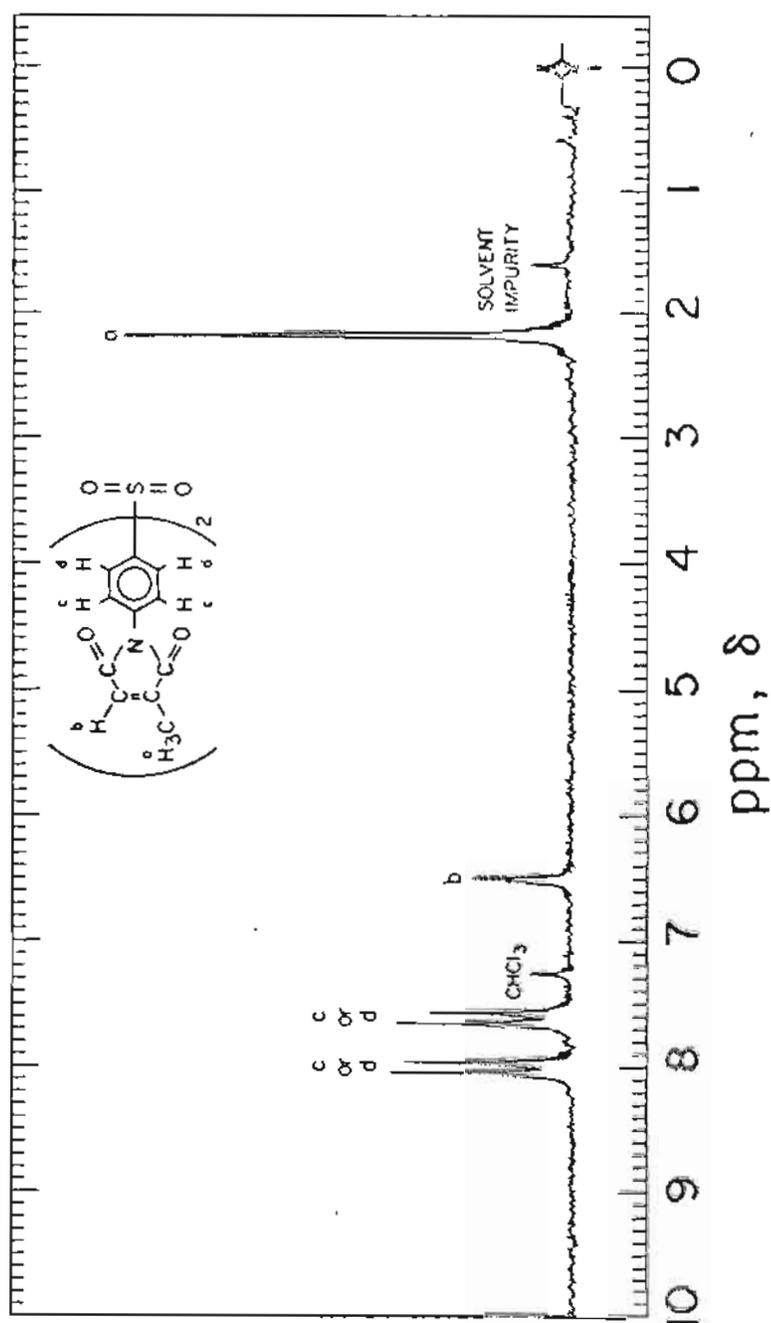


Fig. 5c

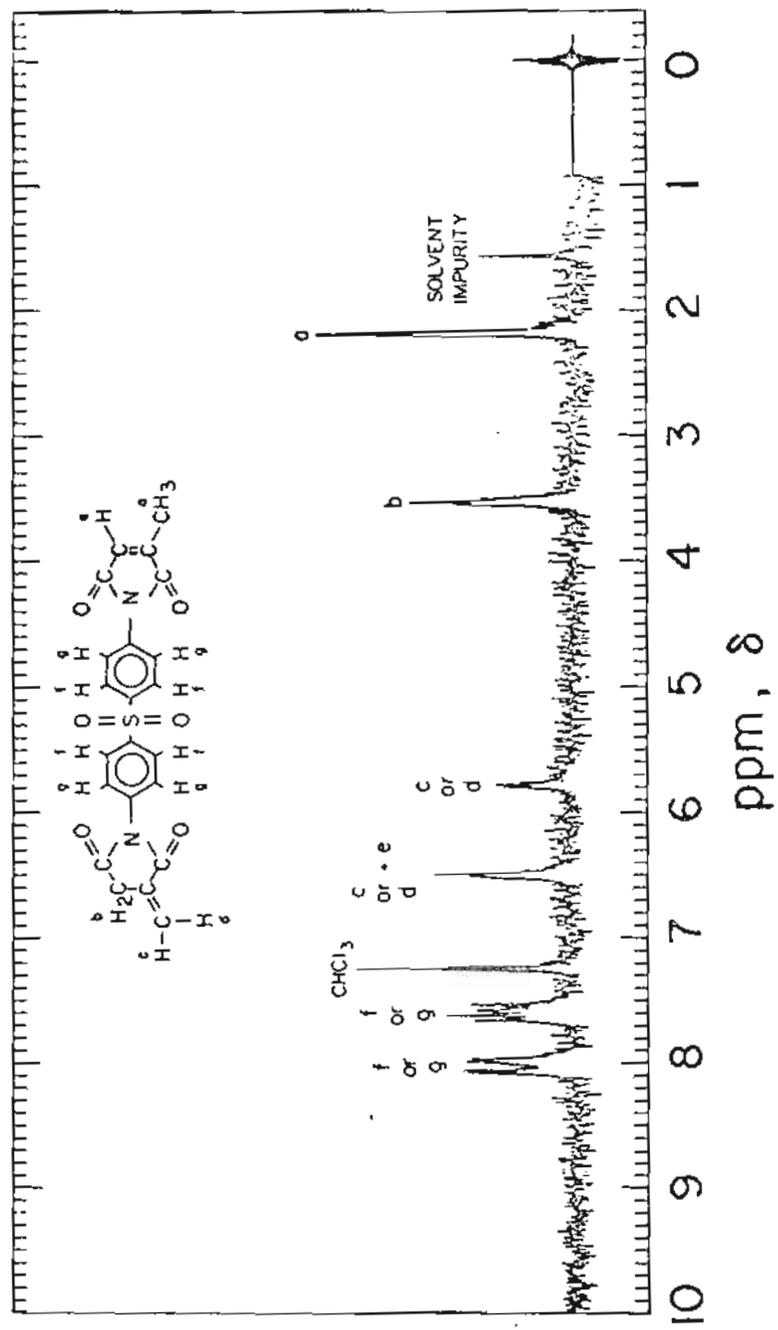


Fig. 5d

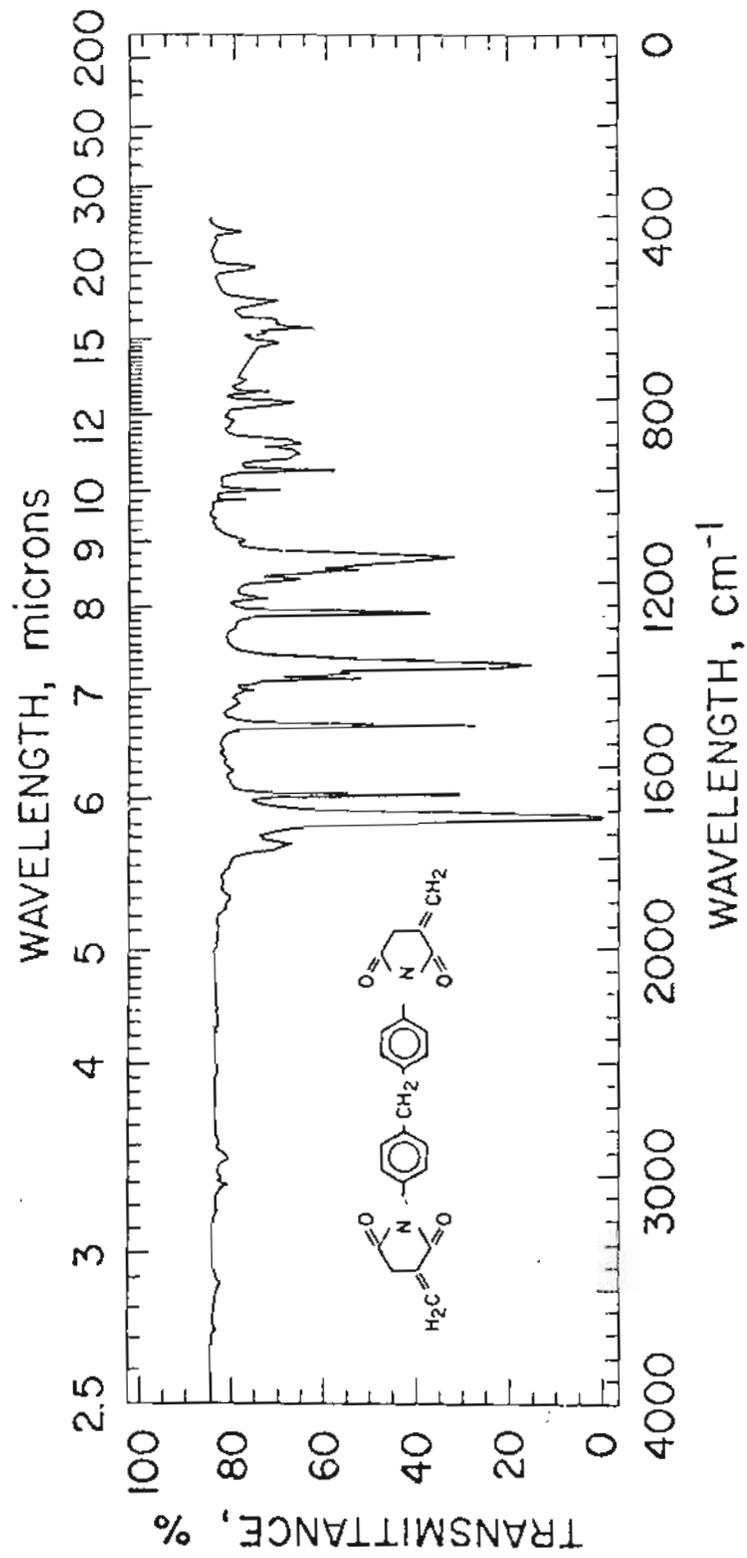


Fig. 6a

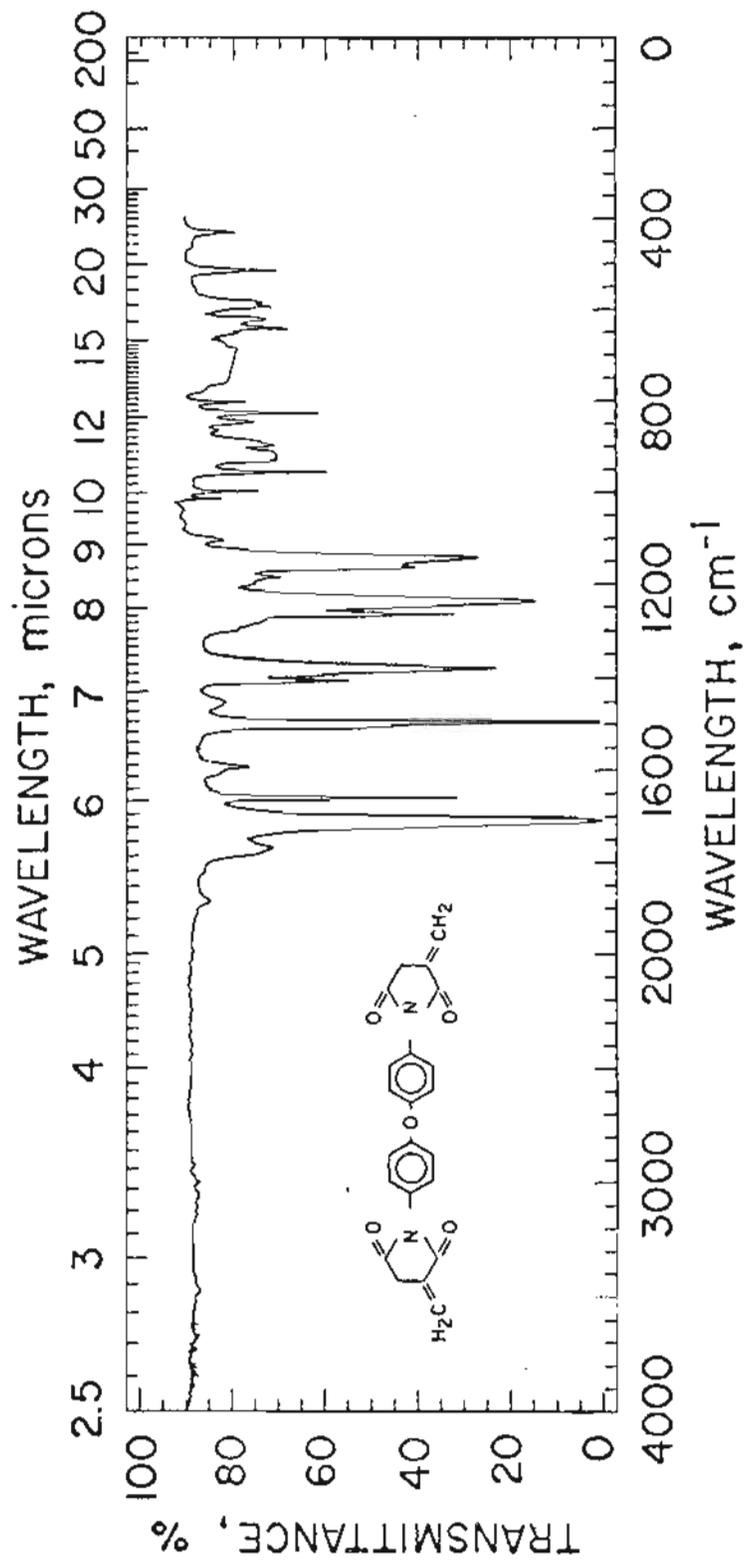


Fig 6b

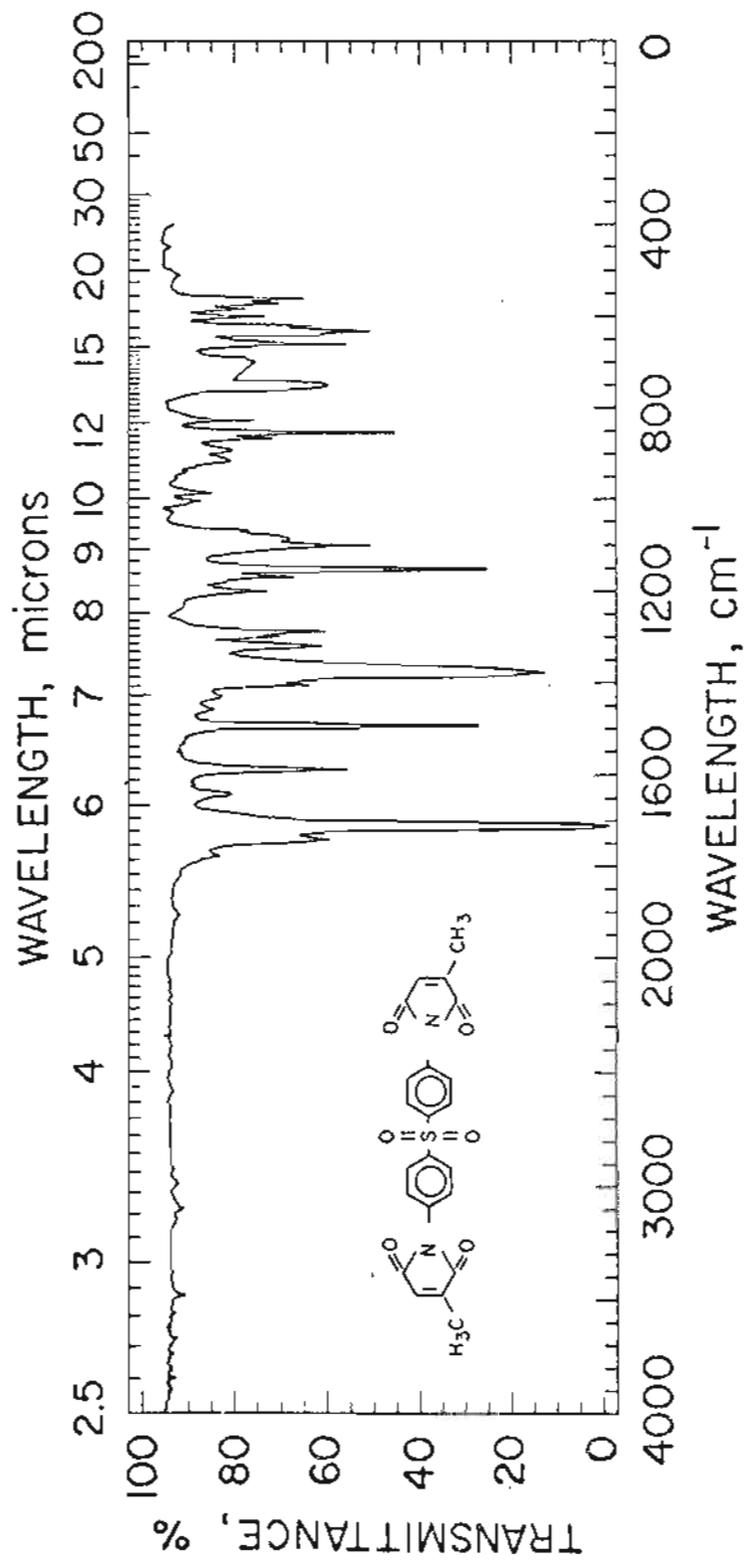


Fig. 6c

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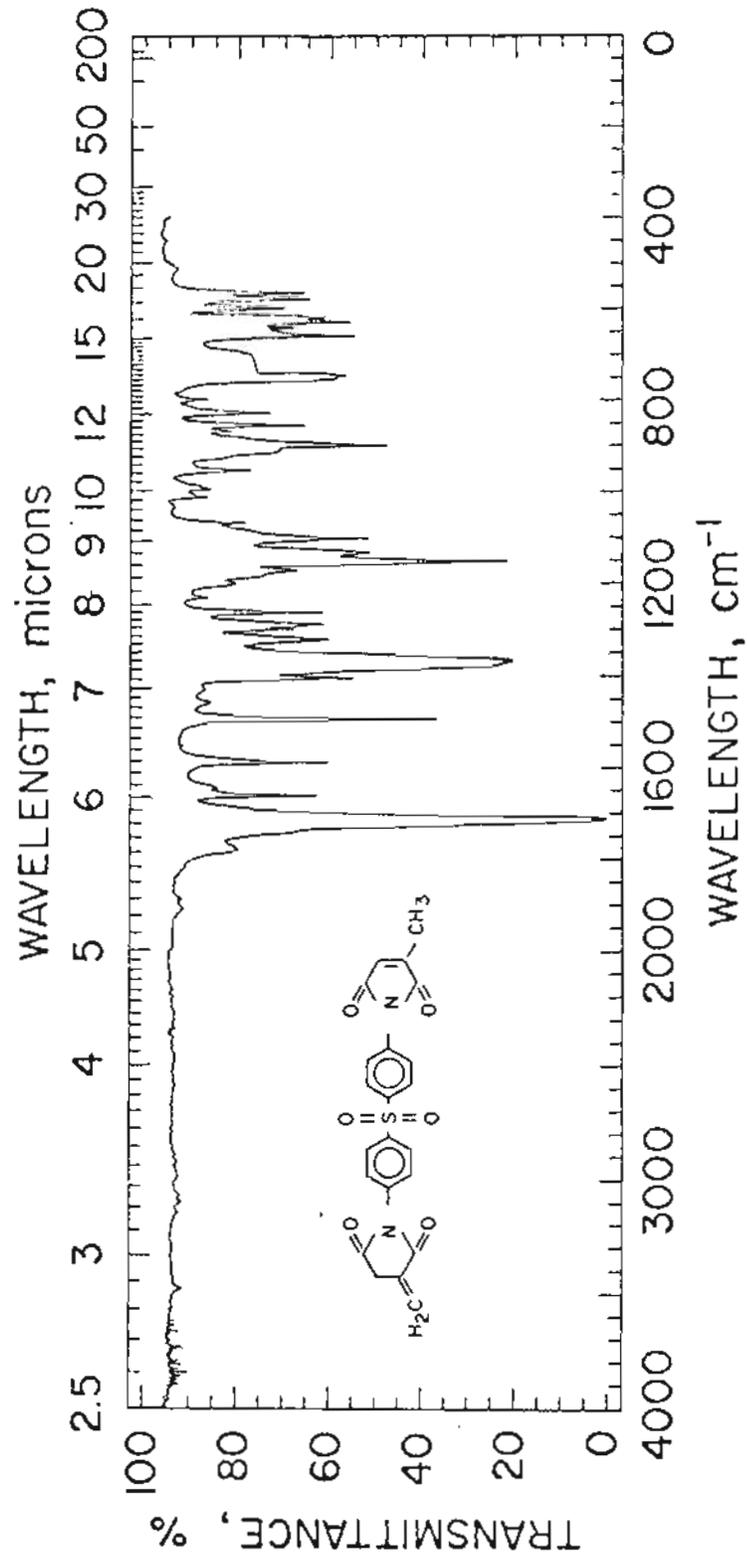


Fig. 6d

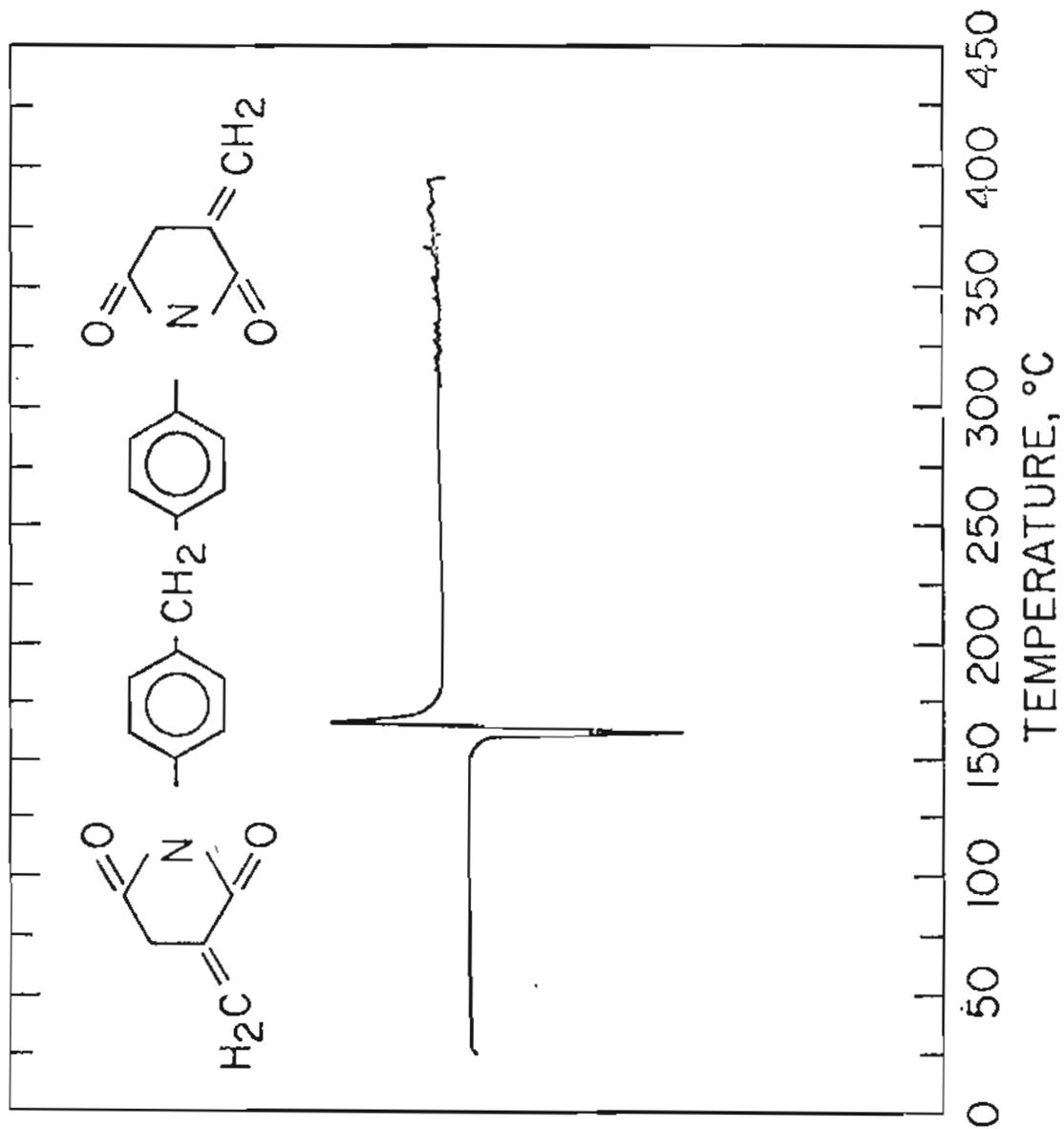


Fig. 7a

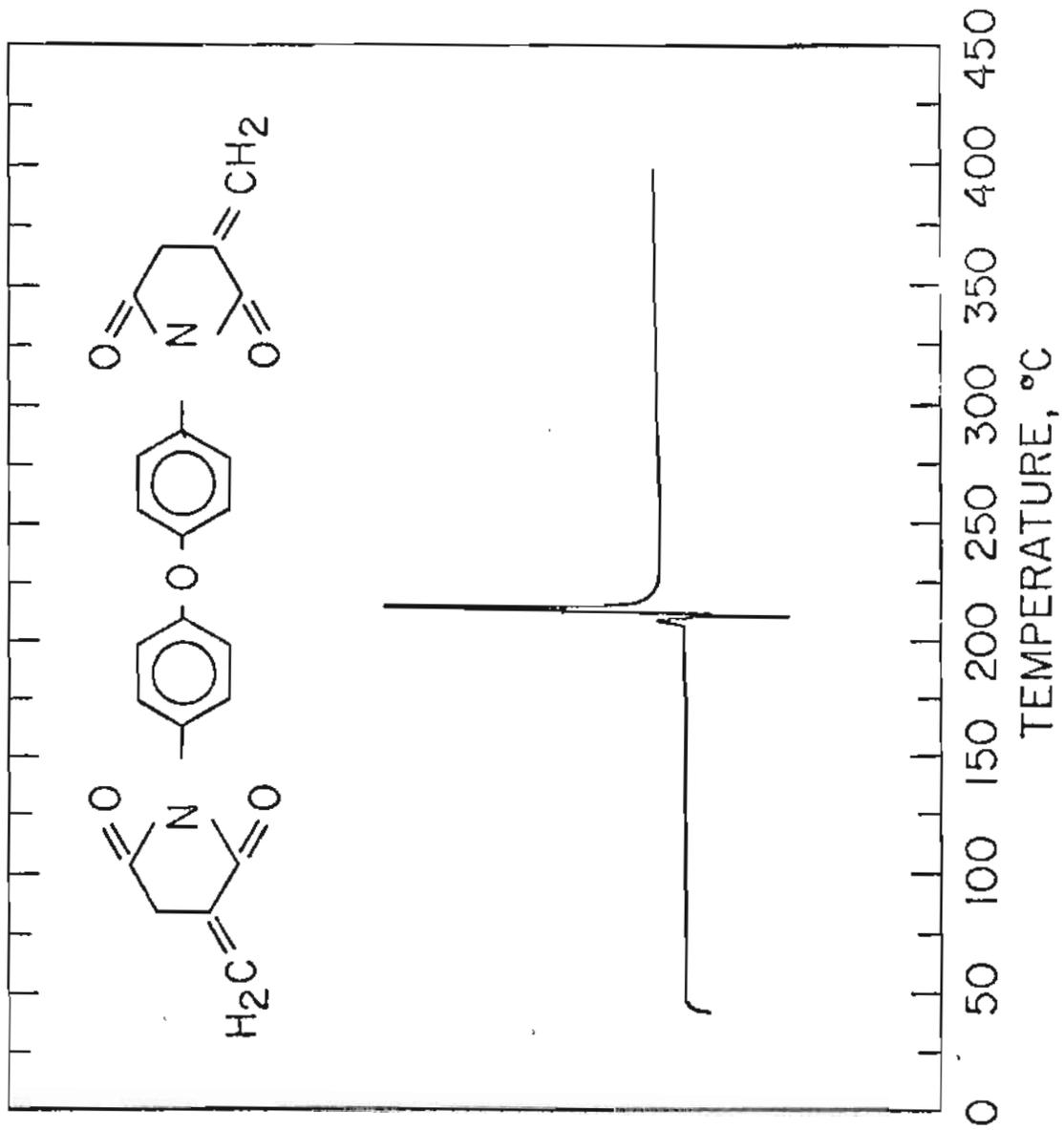


Fig 7b