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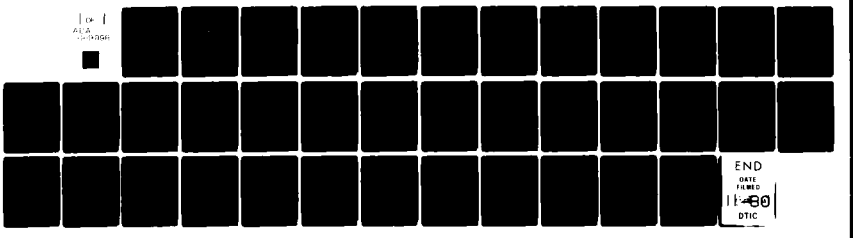

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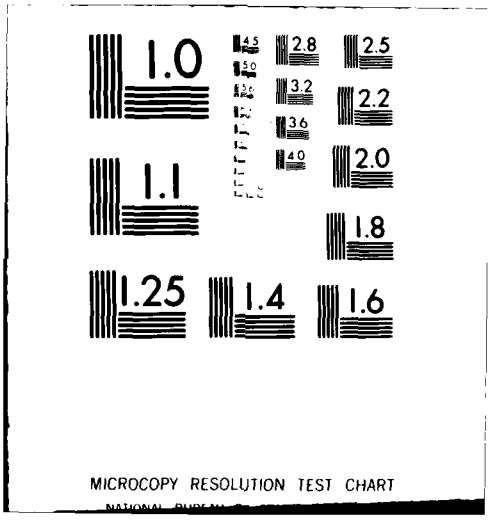
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Dithiene complexes are promising candidates for dye "Q" switches functioning as saturable absorbers operating at two microns. Although these compounds are not commercially available, similar compounds have been prepared. The purpose of this contract was to investigate the synthesis of several dithienes of interest to the Army. The number of dithienes (16), the complexity of the syntheses required to obtain them and the limited funding available was such that the scope

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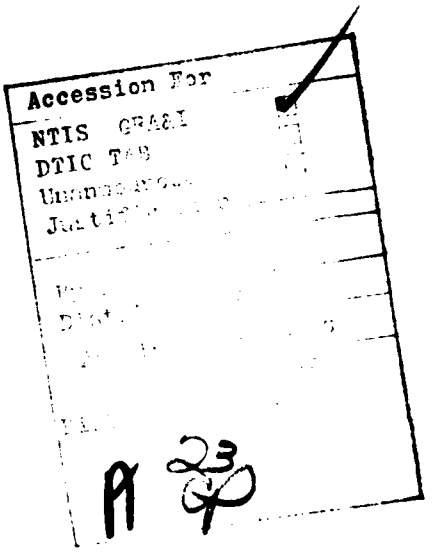
of the program was narrowed by the project monitor setting priorities with regard to which dithiene should be selected for synthesis. 6,7-Dithioquinoxaline was given first priority.



SYNTHESIS SUPPORT FOR THE DEVELOPMENT OF A SATURABLE ABSORBER OPERATING AT TWO MICRONS

Final Technical Report covering period 29 September through 29 February 1980

KEITH B. BAUCOM
CALVIN D. PADGETT

August 1980

U. S. ARMY RESEARCH OFFICE

PCR, INC.
Gainesville, Florida 32602

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Synthesis Support For The Development Of A Saturable Absorber Operating At Two Microns

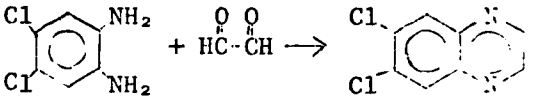
A. Introduction

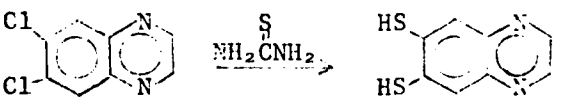
Dithiene complexes are promising candidates for dye "Q" switches functioning as saturable absorbers operating at two microns. Although these compounds are not commercially available, similar compounds have been prepared.[1,2]

The purpose of this contract was to investigate the synthesis of several dithienes of interest to the Army. The number of dithienes (16), the complexity of the syntheses required to obtain them and the limited funding available was such that the scope of the program was narrowed by the project monitor setting priorities with regard to which dithiene should be selected for synthesis. 6,7-Dithioquinoxaline was given first priority.

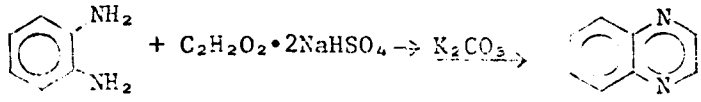
B. Results and Discussion

The synthesis of 6,7-dithioquinoxaline was pursued by the following approach.

1. 

2. 

Although 6,7-dichloroquinoxaline has not been reported, the parent compound, quinoxaline, is prepared in 85-90% yield as follows.[3]

3. 

A first attempt was made to carry out reaction (1) following the procedure reported for reaction (3).

An Erlenmeyer flask containing a stirring bar was charged with 400 ml of water and 25 g (0.141 mole) of 4,5-dichloro-o-phenylenediamine, DOPD. In a second flask 43.0 g (0.151 mole) of $[-CH(OH)SO_3Na]_2 \cdot H_2O$ was dissolved in 250 ml of water. The DOPD/water mixture was stirred and heated at 70° (dissolution did not occur) while the heated (70°) glyoxal solution was added. Stirring was continued for 15 minutes at 70° before the mixture was allowed to cool. When the temperature of the reaction mixture reached ~ 40°, 56.5 g (0.41 mole) of potassium carbonate was added and stirring was continued for one hour.

The mixture was filtered, and both filtrate and filter cake were extracted with several portions of ethyl ether. The combined ether extracts were dried over sodium sulfate, filtered, and evaporated to dryness to leave 7.9 g of solid which was identified as the starting material, DOPD. This was the only product isolated from the reaction.

It was assumed that the reason for the lack of reaction was probably due to the fact that the DOPD was insoluble in water. It was found that the diamine recovered from the above reaction could be dissolved in ethanol and that it would remain in solution when the ethanol was later diluted with an equal volume of water. Consequently, a second reaction was attempted using ethanol as a solvent for the diamine.

The DOPD recovered from the first reaction (7.9 g, 0.0446 mole) was dissolved in 125 ml of ethanol and the solution was heated to 70°. In a second flask 13.0 g (0.0457 mole) of $[-CH(OH)SO_3Na]_2 \cdot H_2O$ was dissolved in 100 ml of 70° water. The hot, aqueous solution of $[-CH(OH)SO_3Na]_2 \cdot H_2O$ was poured into the hot ethanolic solution of DOPD and solids were immediately formed. Stirring was continued for 15 minutes at 70° before the mixture was allowed to cool. When the temperature of the reaction mixture reached 40°, 33 g (0.24 mole) of potassium carbonate was added, and stirring was continued for one hour.

The mixture was filtered, and the filter cake was extracted with ethyl ether. The ethanol was removed from the filtrate on a rotary evaporator to leave a mixture of solids and water. This mixture was extracted with ethyl ether, and these extracts were combined with the ether extracts of the filter cake. These combined extracts were dried, filtered, and evaporated to dryness to leave 3.8 g of a brown solid labelled 1449-55-2.1. This material was found

to melt at 113-118° as compared to a reported melting point of 159-162° for DOPD. However, comparative TLC's (Fig 1) of sample 1449-55-2.1 and DOPD indicated that the product was ~ 50% DOPD.

An attempt was made to isolate the proposed 6,7-dichloroquinoxaline from DOPD by column chromatography. A 1" diameter column was made using 38 g of Silica Gel in hexane. When sample 1449-55-2.1 was added to ethyl ether only a portion of the sample dissolved. This solution was used to put the sample on the column where it began to separate into a yellow front followed by an amber colored material. It was found that the elution could be speeded up by the use of ethyl acetate as a solvent, but this caused decrease in the separation of the components.

The first component was eluted from the column as a yellow solution which was evaporated to dryness to leave a very small amount of material, labelled 1449-55-2.1.1. This was dissolved in ethyl ether so that an infrared spectrum (Fig 2) could be made. In a similar manner the second component was isolated and found to weigh 1.0 g. It was labelled 1449-55-2.1.2. A portion of this material was dissolved in ethyl ether so that an infrared spectrum (Fig 3) could be made. When compared to an infrared spectrum (Fig 4) of DOPD it was obvious that sample 1449-55-2.1.2 was mostly DOPD.

The remainder of sample 1449-55-2.1 was dissolved in ethyl ether and chromatographed on a new column made with 30 g of Silica Gel. Ethyl ether (~300 ml) was the only eluent used in this second chromatographic separation. When the solvent was removed from the eluted solution the remaining product was a bright, orange-brown solid weighing 1.4 g. Because of the low yield and apparent poor quality of product, efforts were directed toward improving the reaction rather than continuing with the isolation and identification of this particular product.

The above reaction was repeated with care being taken to exclude oxygen throughout the course of the reaction and the work-up of product. This was accomplished by the constant use of a nitrogen purge. The reaction was continuously monitored by TLC (Fig 5,6, and 7), and a small amount of product was again isolated by a combination of extractions, chromatographic separations, and steam distillation. Again, the major portion of the product was shown by TLC (1449-55-3.13 in Fig 7) to be DOPD (Fig 5).

The lack of success in preparing the proposed 6,7-dichloroquinoxaline prompted a model reaction for the synthesis of quinoxaline. This was carried out as reported in the literature and as described at the beginning of this report for the first attempted synthesis of 6,7-dichloroquinoxaline.

An Erlenmeyer flask containing a stirring bar was charged with o-phenylenediamine 40.0 g (0.370 mole) and 400 ml of water. In a separate flask 115.6 g (0.407 mole) of $[-HC(OH)NaSO_3]_2 \cdot H_2O$ was dissolved in 1,000 ml of water. Both solutions were heated to 70° and the glyoxal solution was poured into the o-phenylenediamine solution. After stirring an additional 15 minutes at 70° the mixture was allowed to cool to ~ 40°. At this point 138 g (1.0 mole) of K_2CO_3 was added, and stirring was continued until the mixture reached ambient temperature. The mixture was filtered and the filtrate was extracted with several portions of ethyl ether. Evaporation of these extracts produced 39.0 g (82% yield) of an off-white, crystalline product identified as quinoxaline: found, mp = 28-30°; reported mp = 29-30°.

The above series of reactions indicated that the synthesis of 6,7-dichloroquinoxaline required additional modifications.

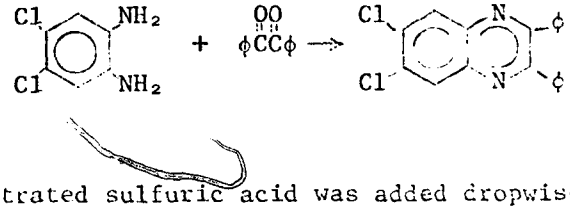
Two attempts were made to prepare 6,7-dichloroquinoxaline using glacial acetic acid as a solvent. In the first reaction 25 g (0.14 mole) of DOPD was dissolved in 400 ml of glacial acetic acid heated at 70°. To this stirred solution solid glyoxal bisulfite (40.2 g, 0.14 mole)

was added in increments during a twenty minute period. After this addition was completed, stirring was continued while the mixture slowly cooled to ambient temperature. The mixture was filtered, and the filter cake was extracted with ethyl ether. The combined filtrate and ether extracts were evaporated to dryness to leave 19.4 g of brown solid which was identified by its infrared spectrum as DOPD.

A second reaction was carried out in acetic acid on a small scale. In this reaction a slight modification was made in that the glyoxal bisulfite was dissolved in water before being added to the solution of DOPD in acetic acid.

An Erlenmeyer flask containing a stirring bar was charged with 2.5 g (0.014 mole) of DOPD and 40 ml of glacial acetic acid. This solution was stirred and heated to 70°. In a separate flask 4.0 g (0.014 mole) of $[-HC(OH)NaSO_3]_2.H_2O$ was dissolved in 40 ml of water and heated to 70°. This solution was slowly poured into the DOPD/ acetic acid solution. It was noted that solids formed immediately. After the addition was completed the mixture was stirred for five hours as it cooled to ambient temperature. It was then filtered to give a small amount of brown solid. This material was sublimed at ~160° under full vacuum to produce a very small quantity of yellow sublimate.

After this last attempt to prepare 6,7-dichloroquinoxaline another model reaction was investigated. Benzil was reacted with DOPD to yield 2,3-diphenyl-6,7-dichloroquinoxaline as described below

4. 

Concentrated sulfuric acid was added dropwise to a stirred solution of DOPD (2.2 g, 12.4 mmole) and benzil (2.6 g, 12.4 mmole) in ethanol (50 ml). When the solution tested acid to pH paper it was heated to a temperature of 65-70°. At this point a crystalline mass formed, but it partially redissolved with further heating. After fifteen minutes at 70° the mixture was cooled to ambient temperature and filtered. The filtrate was diluted with an equal volume of water, and the solids which formed were again removed by filtration. The solid products were combined and recrystallized twice from a solution of 150 ml ethanol/50 ml water.

The final product, a pink solid labelled 1449-82-1.2, was air dried and found to weigh 1.9 g. This represents a 44% yield of 2,3-diphenyl-6,7-dichloroquinoxaline. Analysis for chlorine gave the following:

	%Cl
Found	19.73
Theory for 2,3-diphenyl-6,7-dichloroquinoxaline	20.19
Theory for 4,5-dichloro-o-phenylenediamine	41.47

Another attempt was made to prepare 6,7-dichloroquinoxaline. This time, the procedure described above for the synthesis of 2,3-diphenyl-6,7-dichloroquinoxaline was used.

A three-necked flask containing a stirring bar was charged with DOPD (1.8 g, 10.2 mmole), $[-HC(OH)NaSO_3]_2.H_2O$ (3.0 g, 10.6 mmole), ethanol (50 ml), and water (50 ml). This mixture was stirred and heated to reflux. At this point a clear solution resulted. While maintaining the reflux, concentrated sulfuric acid was added dropwise until the solution became acidic. Reflux was continued for one-half hour followed by cooling to ambient temperature. The mixture was poured into a separatory funnel, diluted with an equal volume of water, and extracted with ethyl ether. The ether extracts were washed with water, dried over sodium sulfate, filtered, and evaporated to dryness to leave a small amount of a brown solid labelled 1449-81-1.1. A nujol mull of this material (Fig 8) established that it was not recovered DOPD (Fig 4).

Sample 1449-81-1.1 was sublimed at 150°/0.05mm to produce 0.15 g of yellow sublimate labelled 1449-81-1.2. Continued sublimation produced an additional 0.08 g of sublimate labelled 1449-81-1.3. Several observations were made from TLC's (Fig 9) of these sublimates. First, the two sublimates were, as expected, the same material. Second, an eluent composed of 80% hexane, 15% toluene, and 5% ethyl acetate indicated that the sublimates were composed of one

major component which moved only slightly from the origin and one minor impurity which was readily eluted. A third observation was that when tetrahydrofuran was added to the developer the major product was readily eluted.

Based on the above observations samples 1449-81-1.2 and 1449-81-1.3 were combined and dissolved in xylene. This solution was chromatographed on a 2.0 g Silica Gel column using a solution of 80% hexane/15% toluene/5% ethyl acetate as eluent until 40 ml of solution was collected. Then, tetrahydrofuran was substituted as the eluent until an additional 50 ml of solution was collected. This solution was evaporated to dryness to leave 1.0 g of the proposed 6,7-dichloroquinoxaline as a solid product, 1449-81-1.5. A TLC (Fig 10) of this material indicated that it was a pure compound. Elemental analysis gave the following:

	%C	%H	%Cl	%N
Found	50.13	2.80	33.82	13.06
Theory for 6,7-Dichloroquinoxaline	48.28	2.02	35.62	14.07

It is observed that the chlorine and nitrogen analyses are 93 and 95% of theory, respectively. This indicates that sample 1449-81-1.5 is probably the desired 6,7-dichloroquinoxaline containing a small amount of solvent which does not exhibit a TLC spot. For example, if the sample still contained 6% tetrahydrofuran the analysis would read as follows:

	%C	%H	%Cl	%N
Found	50.13	2.80	33.82	13.06
Theory	49.37	2.57	33.49	13.22

Sample 1449-81-1.5 was later sublimed to give 0.23 g (11.3% yield) of the proposed 6,7-dichloroquinoxaline.

Reactions similar to Reaction 2 of this report are known to produce thiols from alkyl halides.[4] An attempt was made to use 2,3-diphenyl-6,7-dichloroquinoxaline in a model reaction for the preparation of a dithiol.

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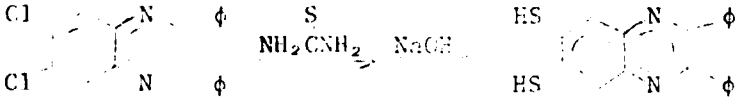

One gram (2.85 mmole) of sample 1449-82-1.2, 0.45 g (5.92 mmole) of thiourea, and 25 ml of dimethylformamide were put into a flask and heated at 100°. Samples withdrawn after 20 and 44 hours were analyzed by TLC (Fig 11). When compared to a TLC of sample 1449-82-1.2 it appeared that all of the starting material had reacted after 20 hours of heating time.

The reaction mixture was cooled to ambient temperature and a solution of 4 g of sodium hydroxide in 10 ml of water was added. This caused the immediate formation of a pink precipitate. This solid was isolated, washed with water, recrystallized from ethanol, and dried under vacuum to leave 1.0 g of solid product labelled 1449-86-1.2. A TLC (Fig 11A) now indicated that the product, 1449-86-1.2, was the starting material, 1449-82-1.2.

Elemental analysis confirmed that the product was not the expected dithiol, but rather the unreacted starting material.

	%C	%H	%N	%S	%Cl
Found for 1449-86-1.2	68.21	3.47	7.78	0	20.54*
Theory for 2,3-diphenyl-6,7-dichloroquinoxaline	68.39	3.46	7.97	0	20.19

*(Note: Chlorine by difference - not analyzed)

It was also observed that the u.v. spectra (Fig 12 and 13) were identical for samples 1449-82-1.2 and 1449-86-1.2.

Reaction 4. was repeated with 10.0 g of DCPD and 11.9 g of benzil in 250 ml of ethanol. The reaction was carried out as described earlier in the report, and the product was again recrystallized from ethanol/water. A quantitative yield of the product, 2,3-diphenyl-6,7-dichloroquinoxaline, was obtained. This material was labelled 1475-51-1.1.

An attempt was made to react 2,3-diphenyl-6,7-dichloroquinoxaline with sodium hydrosulfide to produce the corresponding dithiol. A flask was charged with 3.5 g (0.01 mole) of sample 1475-51-1.1, 2.0 g (0.025 mole) of 70% $NaSH \cdot XH_2O$, and 75 ml of DMF. This mixture was heated at $\sim 75°$ and samples were taken at various intervals, beginning after 16 hours, for examination by TLC. Even after several days of heating the only spot exhibited on the TLC plate was the single spot corresponding to the starting material.

Reaction 1. was repeated twice more for the synthesis of 6,7-dichloroquinoxaline. In both reactions sulfuric acid was used to effect reaction. Final products in both reactions were purified by sublimation. One

reaction produced 1.7 g of product from 25.9 g of DOPD (5.8% yield), and the other reaction produced 2.5 g of product from 22.4 g of DOPD (9.9% yield). Figures 14 and 15 show a comparison of the u.v. spectrum of one of the products, sample 1475-49-1.2, with the u.v. spectrum of a sample which was confirmed by elemental analysis to be 6,7-dichloroquinoxaline.

C. Conclusion.

Reaction conditions have been found which give 2,3-diphenyl-6,7-dichloroquinoxaline quantitatively and quinoxaline in 85% yield. Neither of these reaction conditions have been found to give good yields of 6,7-dichloroquinoxaline. Representative yields of this compound have been 5.8 and 9.9%. The displacement of chlorine from the 6,7 positions of quinoxaline by either sodium hydrogen sulfide or thiourea have been found ineffective. In fact, quantitative recovery of starting material demonstrates this approach to 6,7-dithioquinoxaline to be ill conceived.

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ILLUSTRATIONS

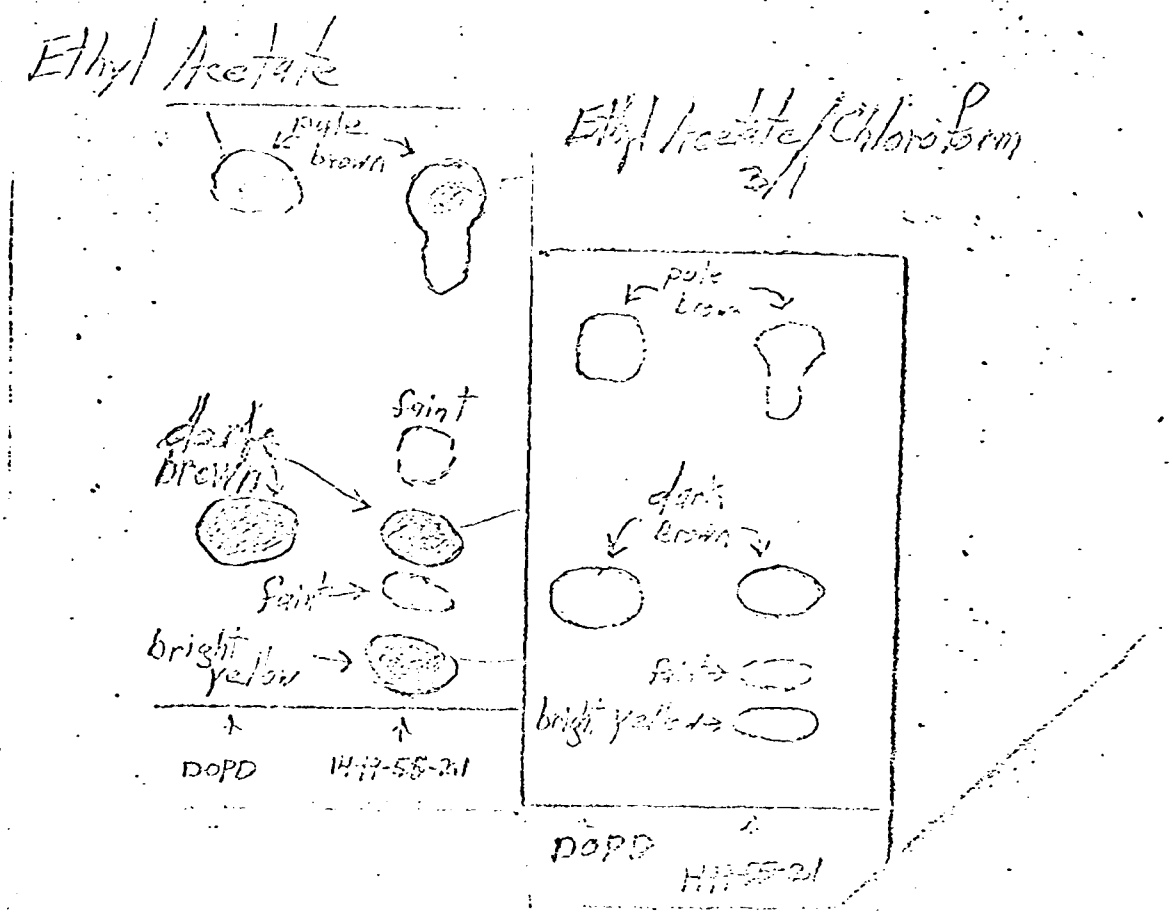


Figure 1

TLC's of 1449-55-2.1 and 4,5-Dichloro-o-phenylenediamine, DOPD

Figure 2

Infrared Spectrum of Sample 1449-55-2,1,1

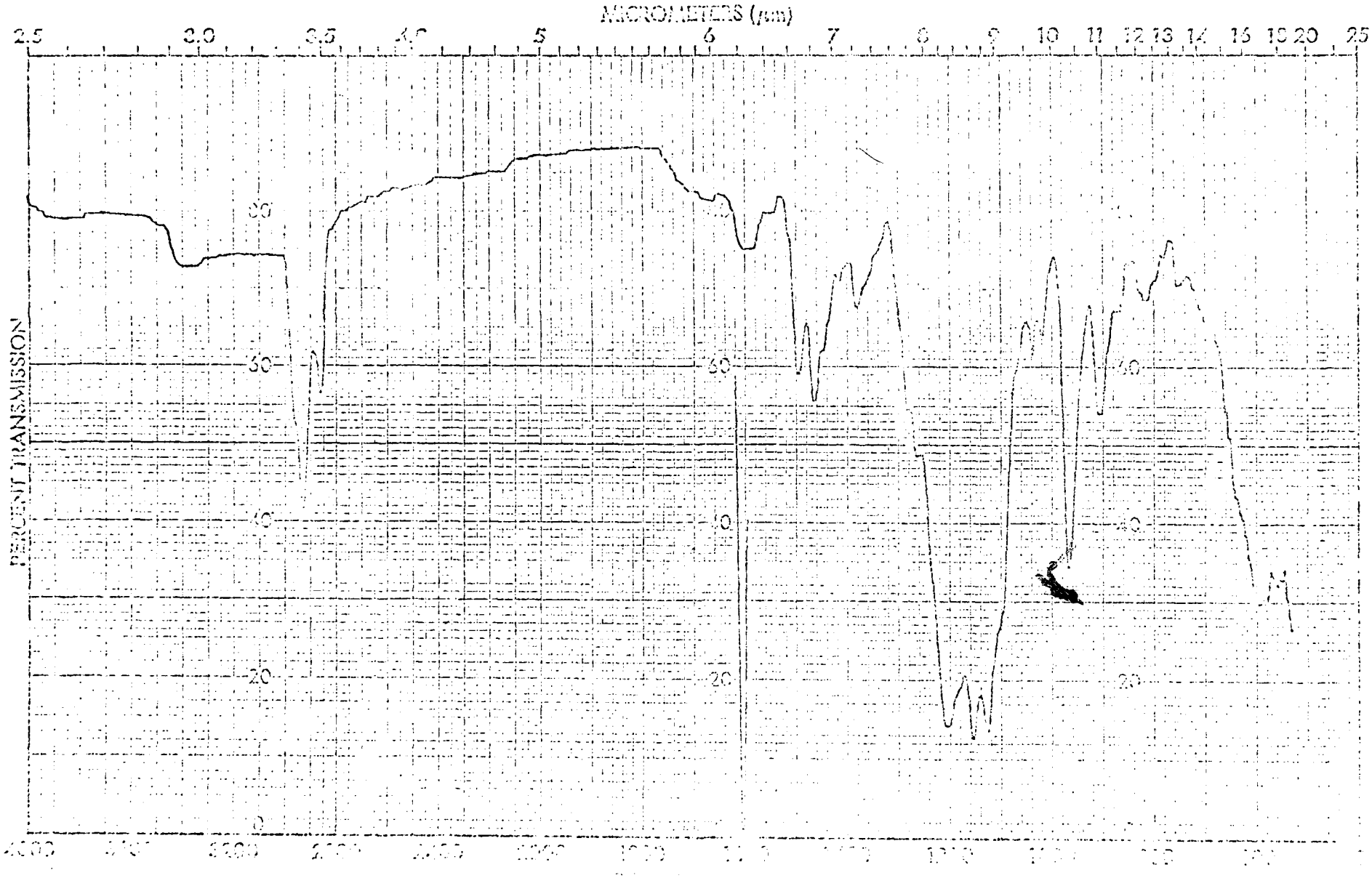


Figure 3

Infrared Spectrum of Sample 1449-55-2.1.2

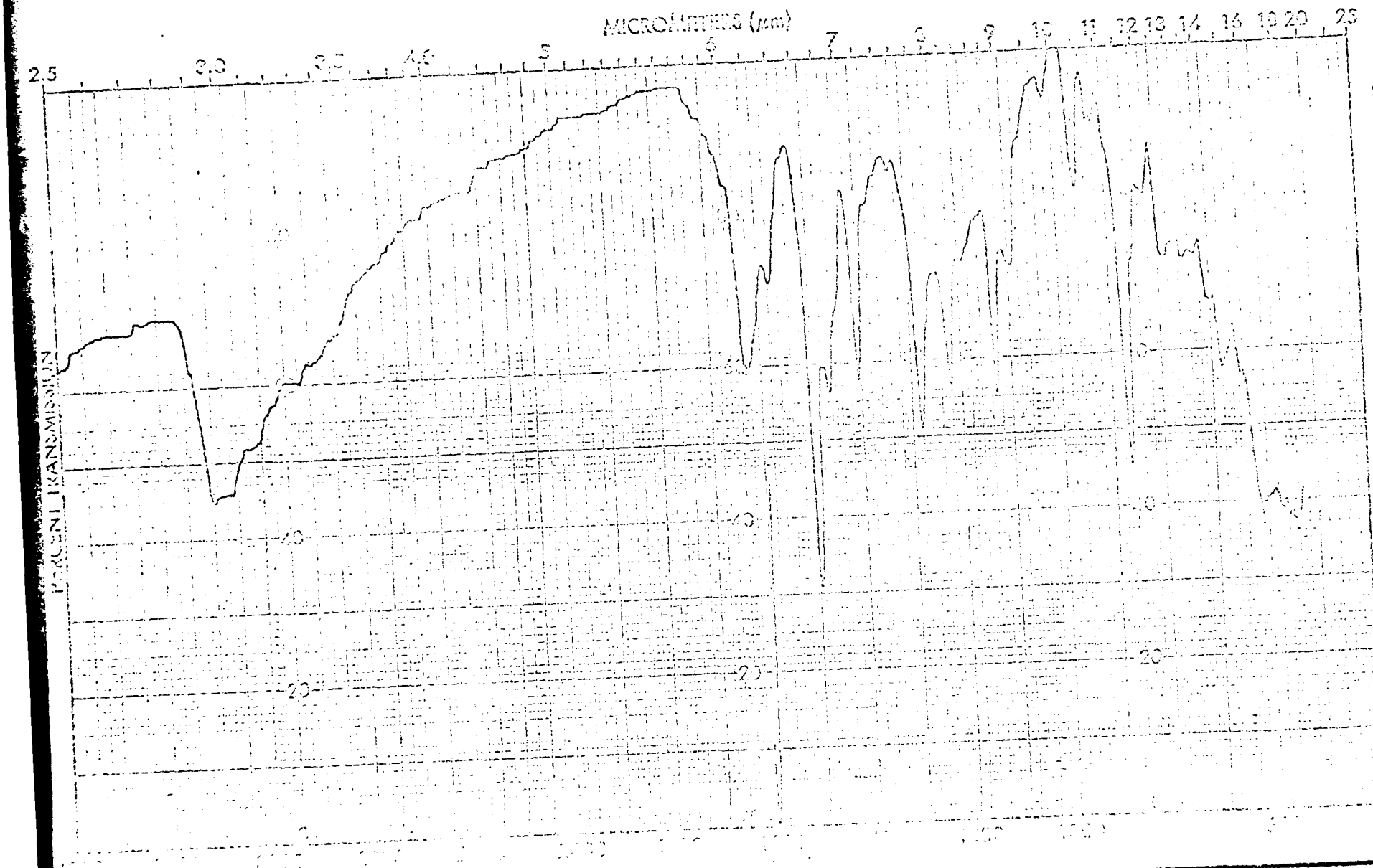
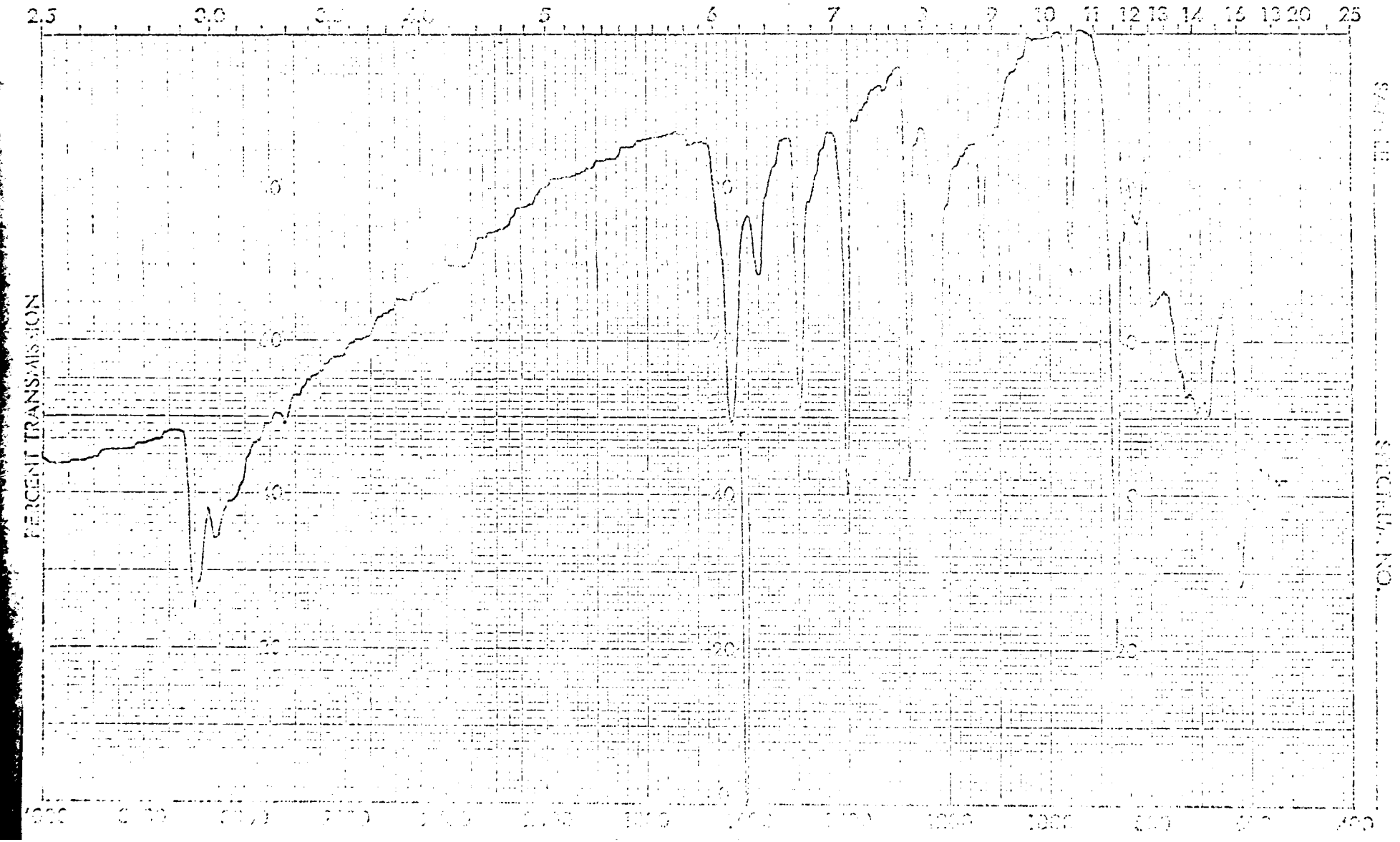


Figure 4

Infrared Spectrum of 4,5-Dichloro-o-Phenylenediamine (DODP)



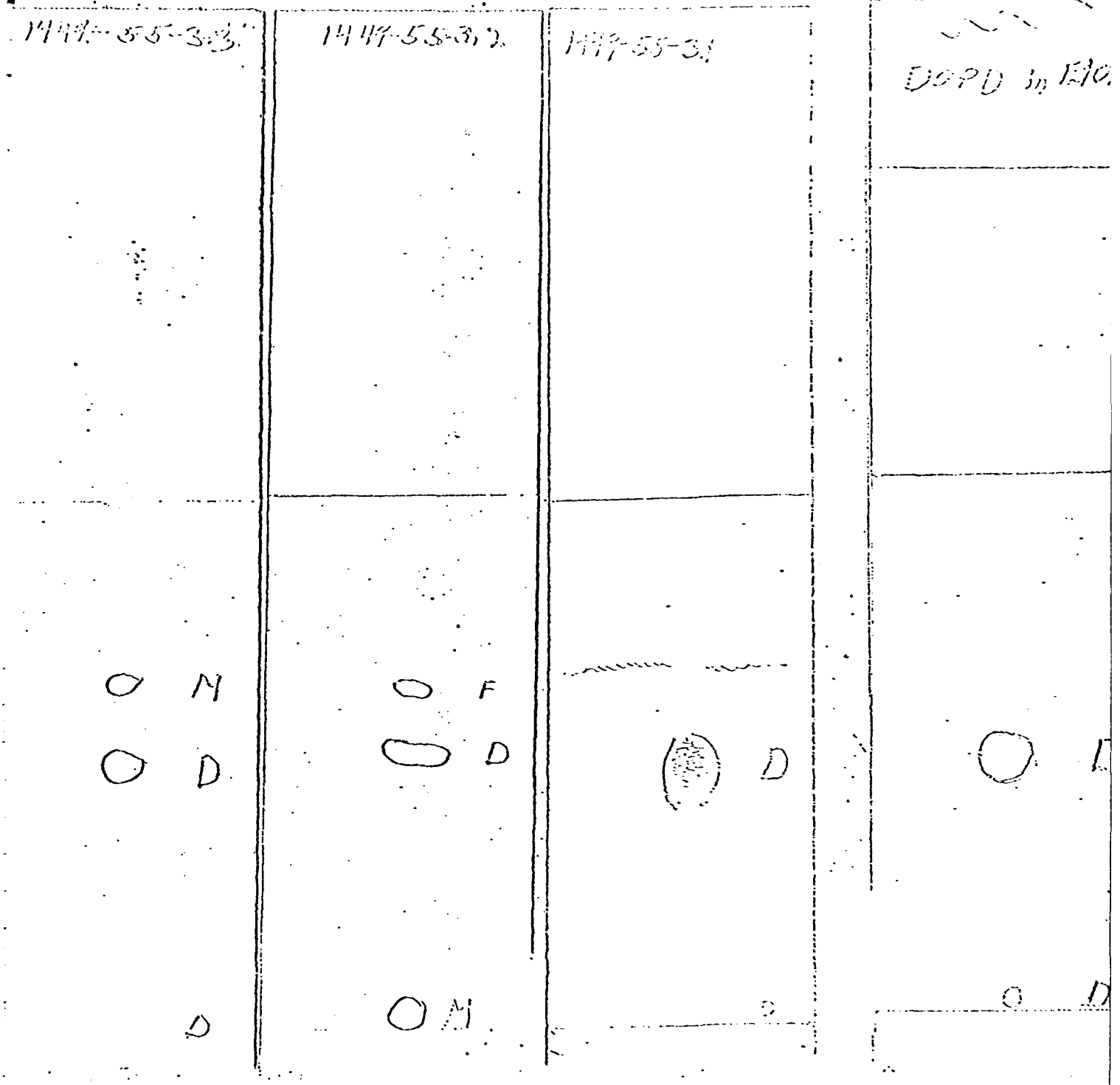


Figure 5

TLC's Monitoring Third Attempted Synthesis of

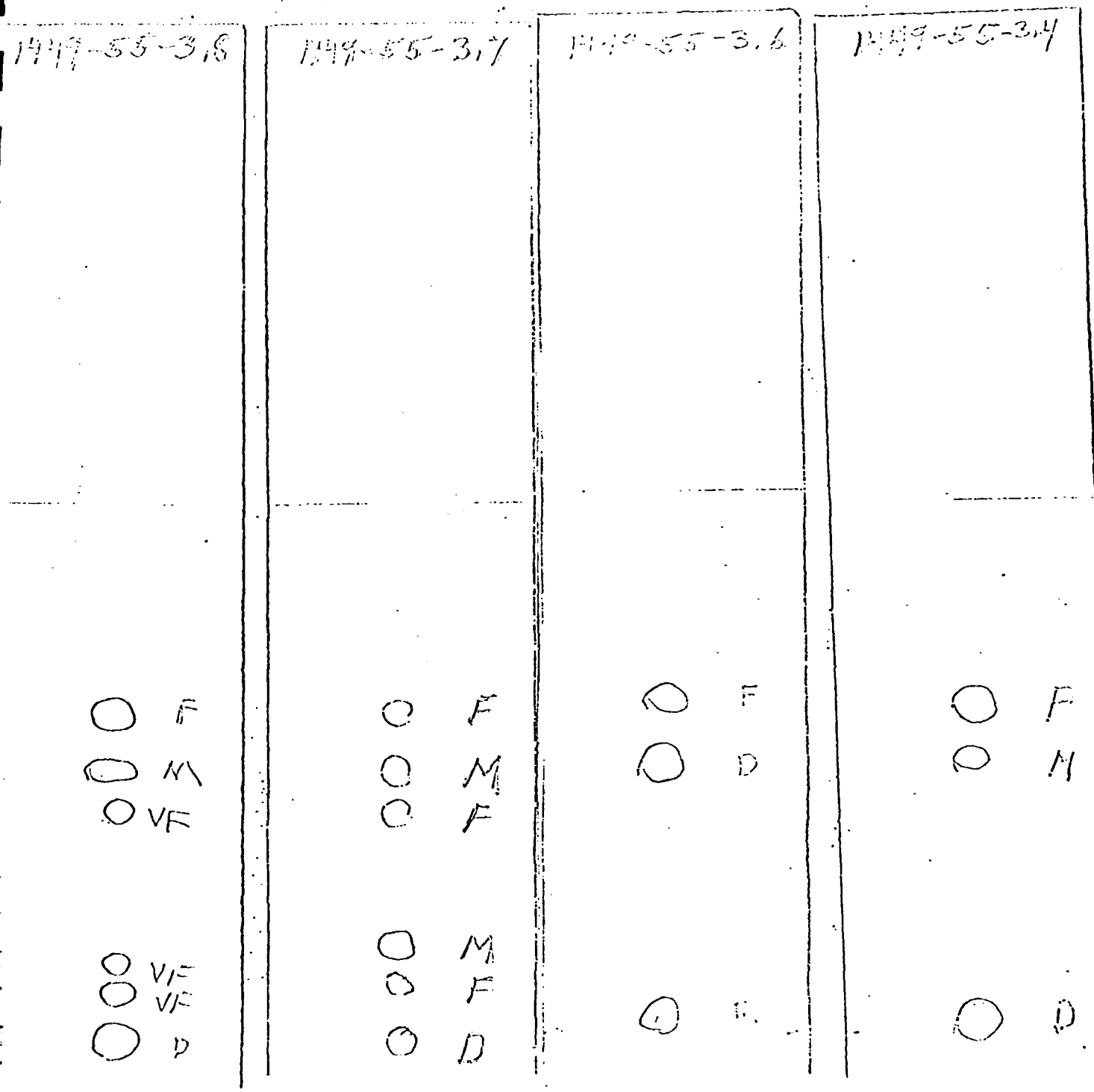


Figure 6

Continuation of Figure 5

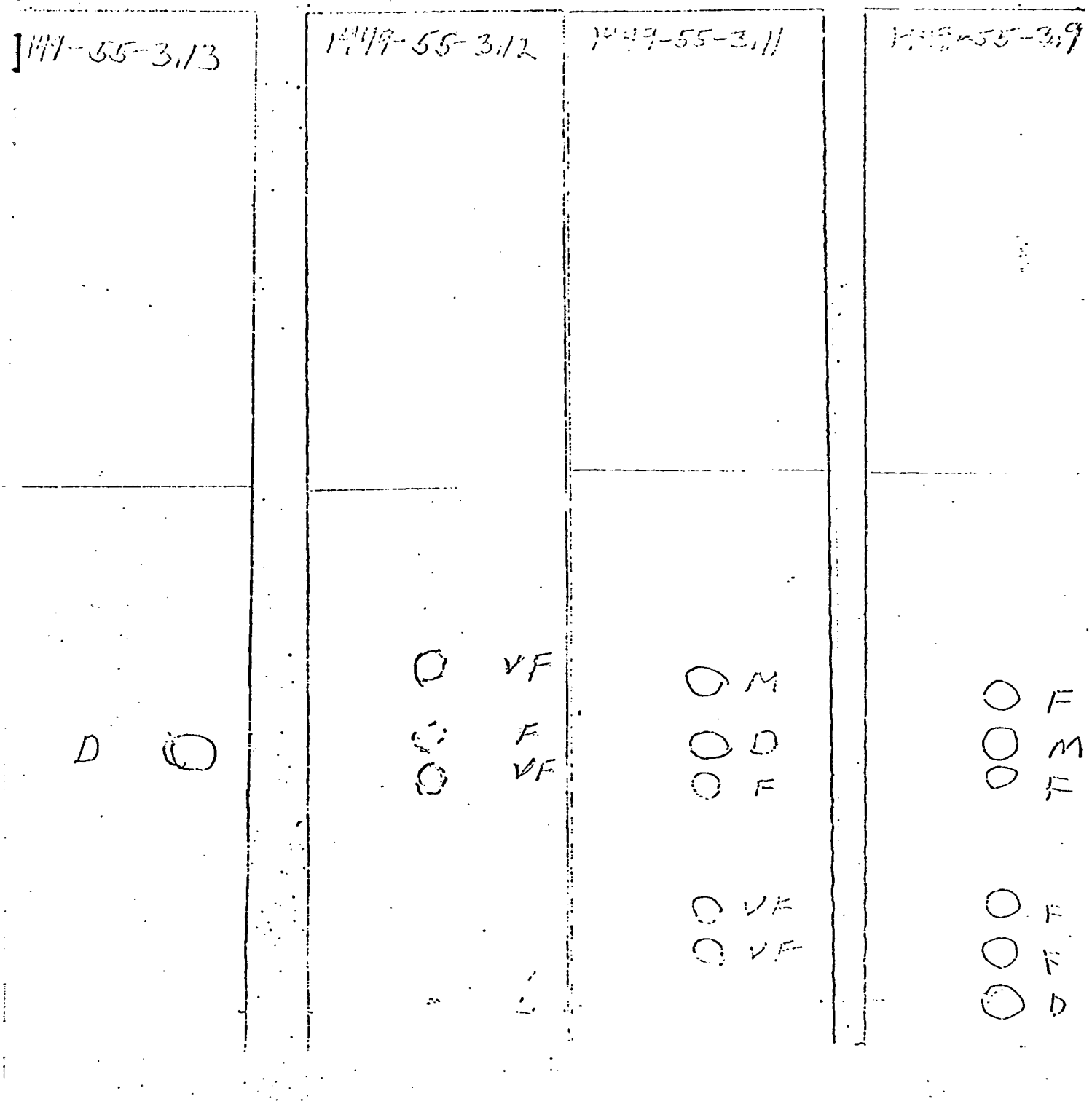
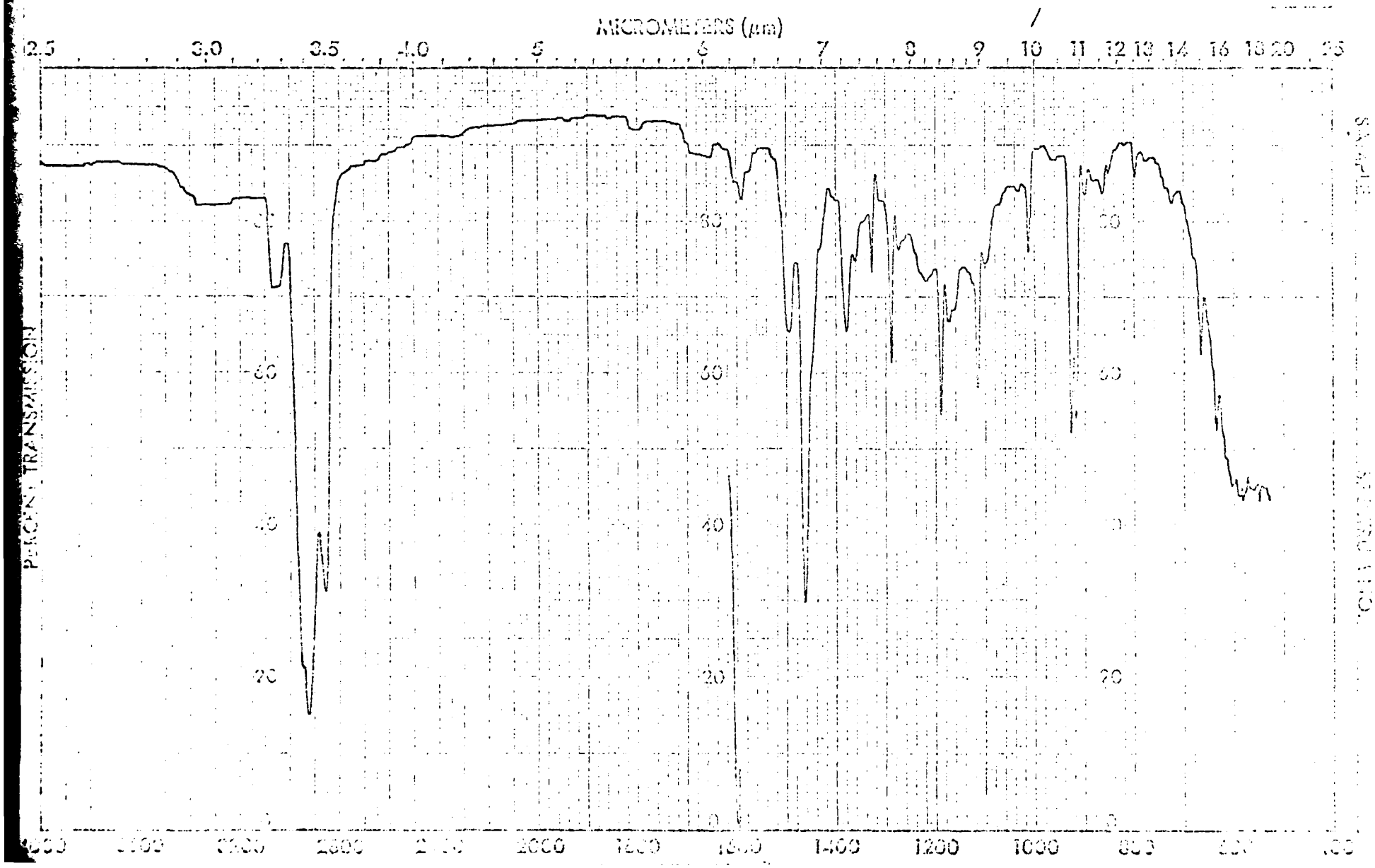


Figure 7

Continuation of Figure 6

Figure 8

Nujol Mull of 1449-81-1.1



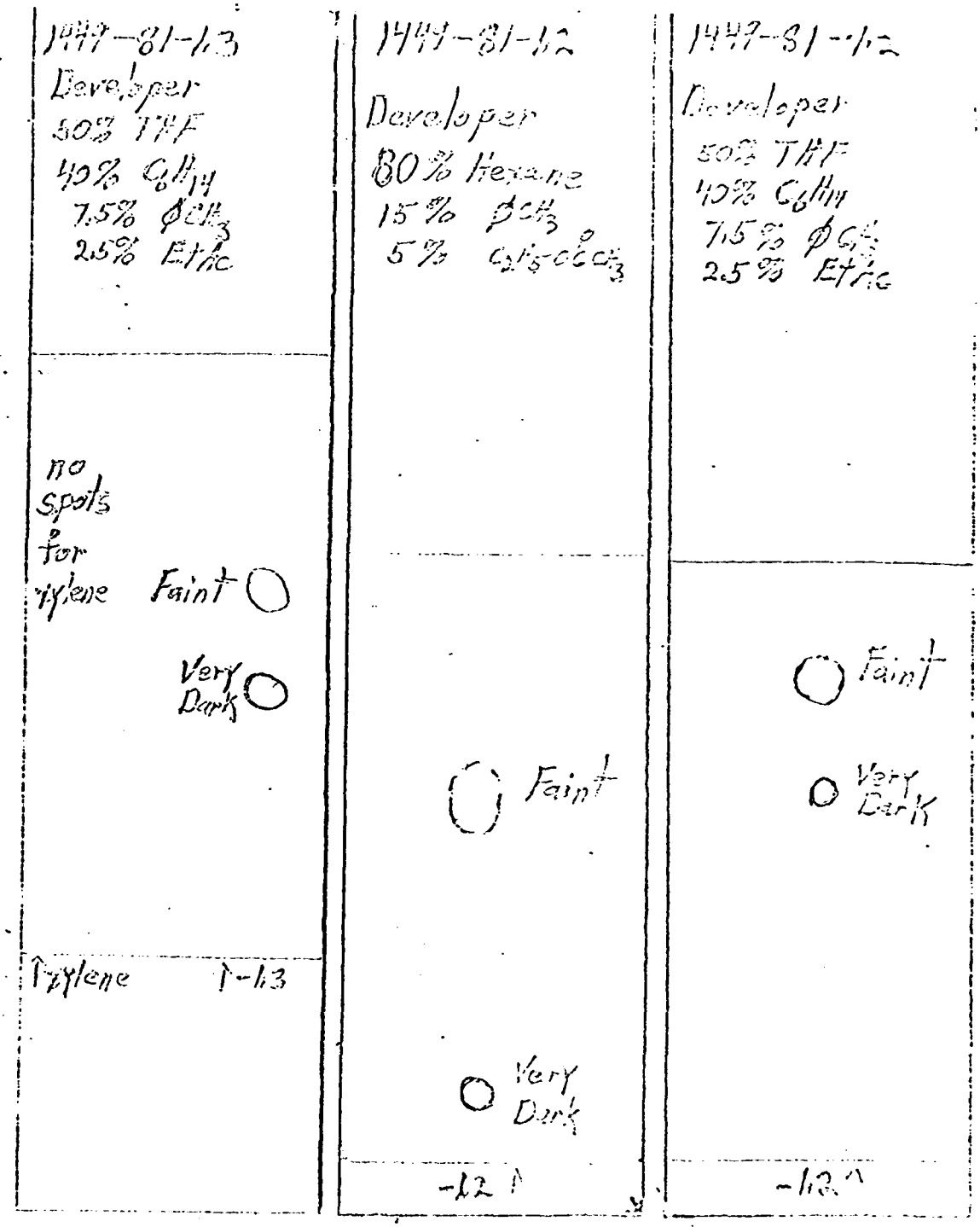


Figure 9

TLC's of Samples 1449-S1-1.2 and 1449-S1-1.3

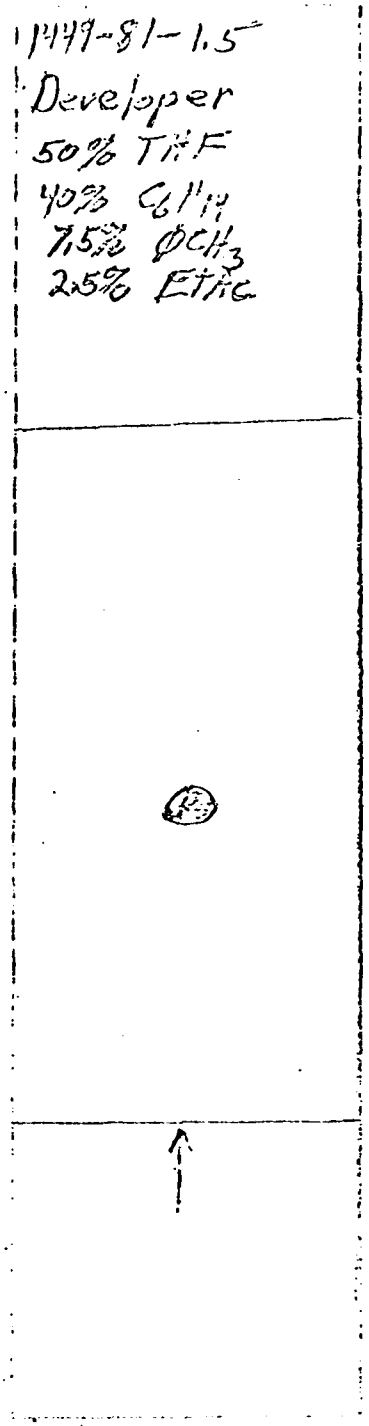


Figure 10

TLC of Sample 1449-81-1.5 (Proposed 6,7-Dichloroquinoxaline)

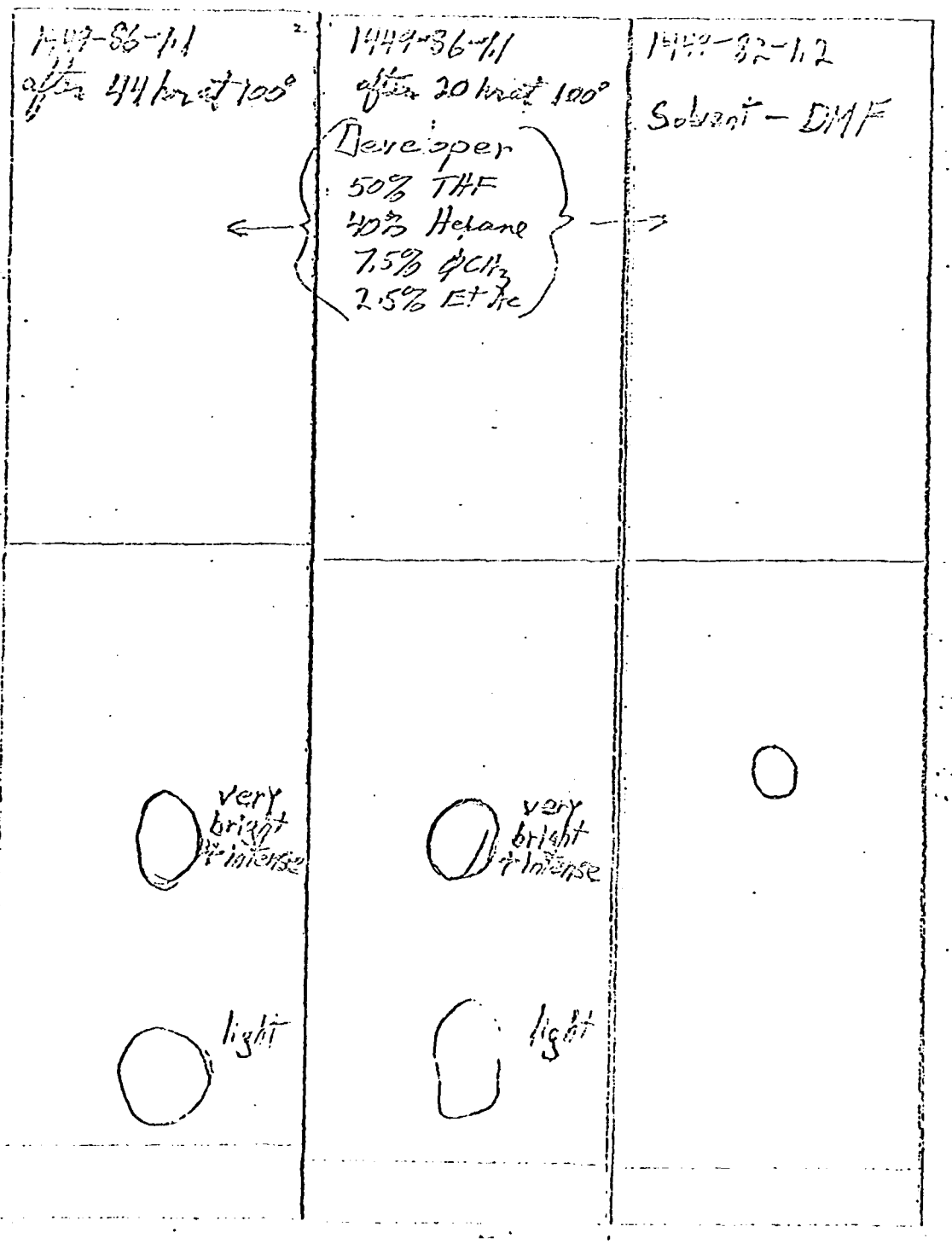


Figure 11

TLC's of Sample 1449-82-1.2 and Products of Reaction with Thiourea

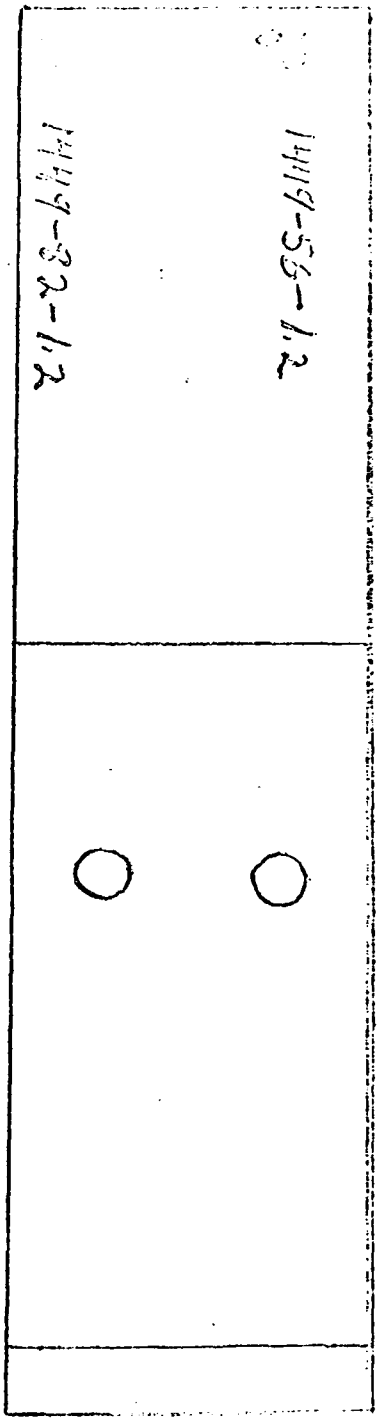


Figure 11A

TLC of Samples 1449-82-1.2 and 1449-86-1.2

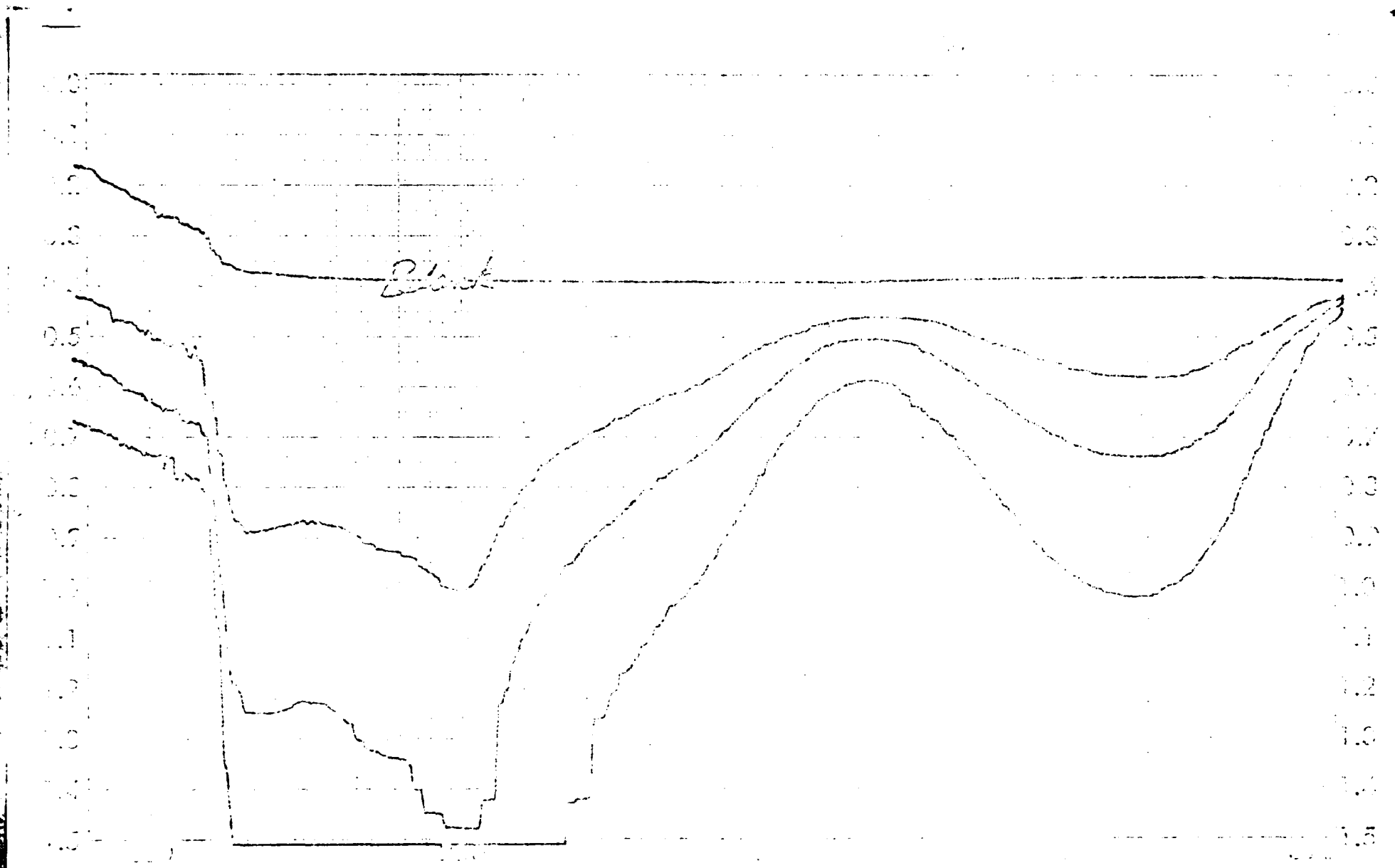


Figure 12

U.V. Spectrum of Sample 1449-82-1.2, 2,3-Diphenyl-6,7-Dichloroquinoxaline

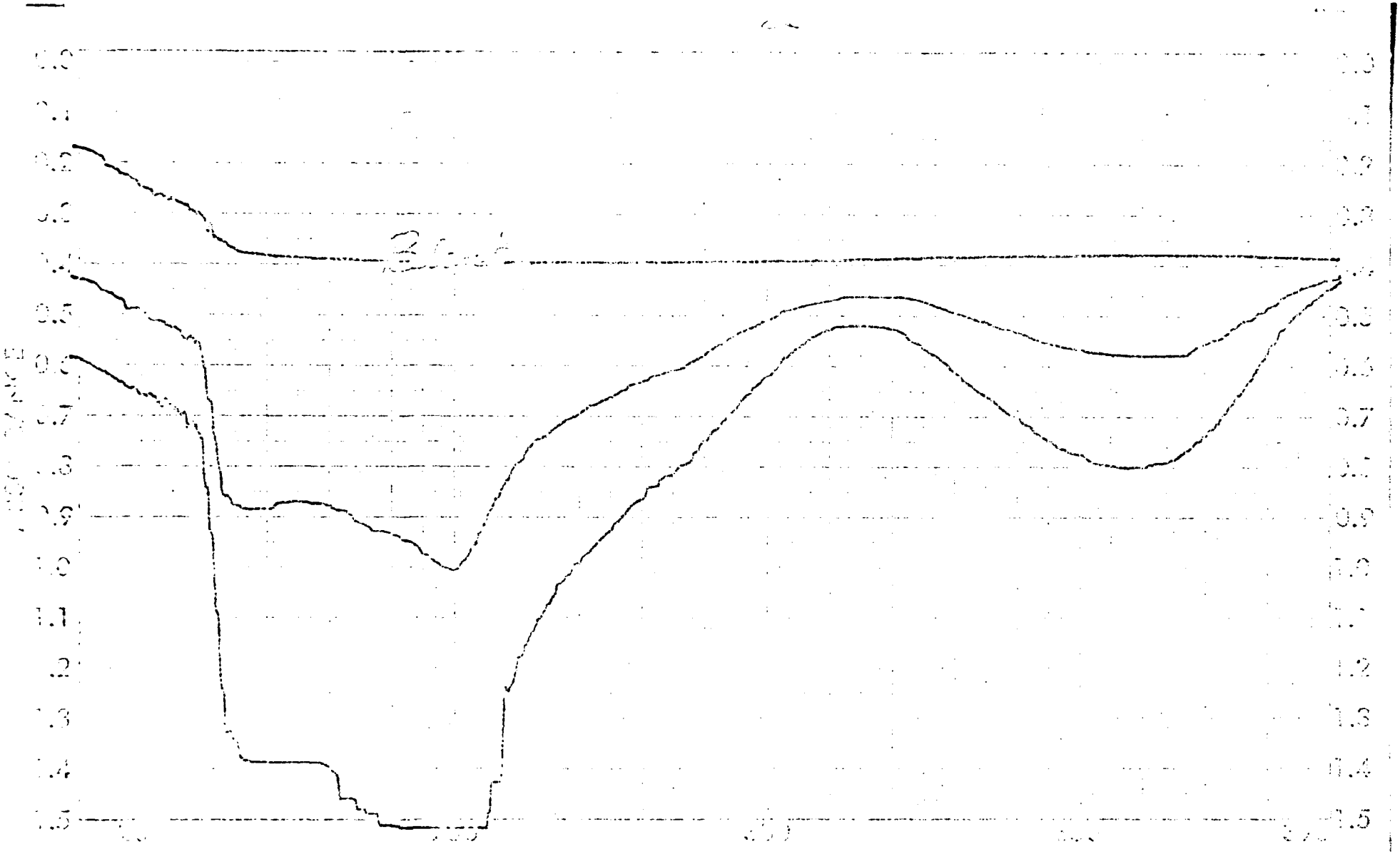


Figure 13

U.V. Spectrum of Sample 1449-86-1.2

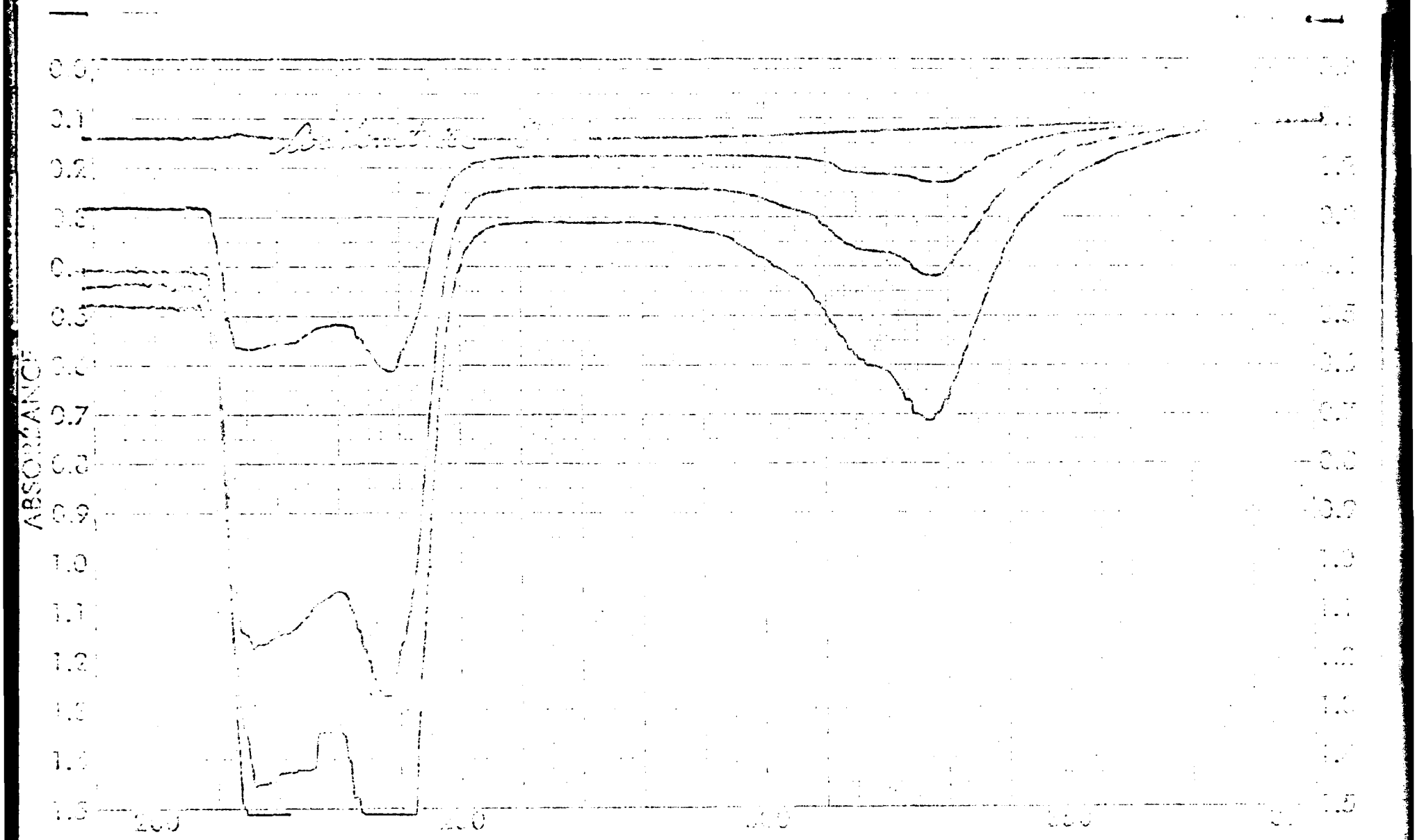


Figure 14

U.V. Spectrum of Sample 1475-49-1.2

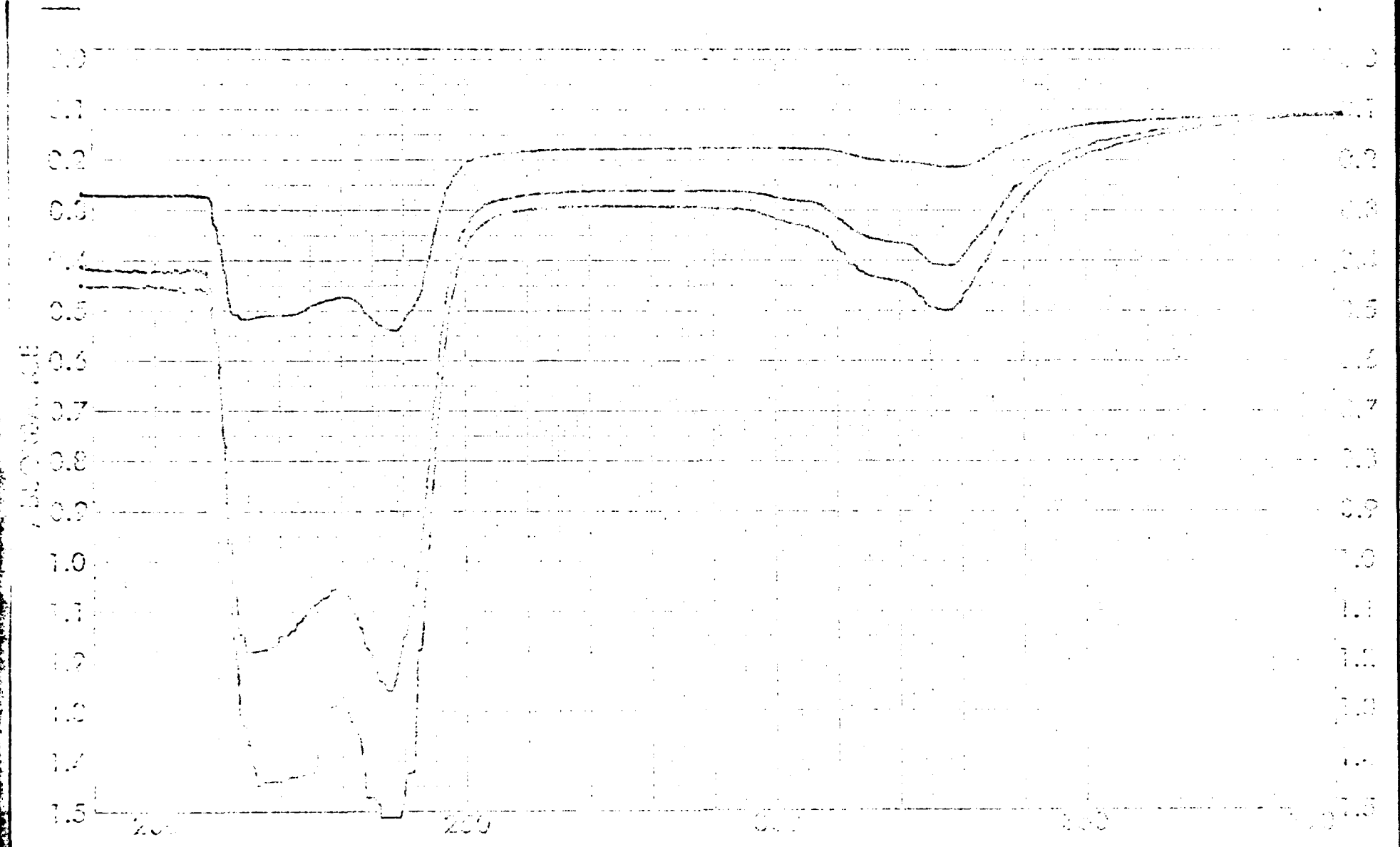


Figure 15

U.V. Spectrum of Sample 1449-81-1.5, 6,7-Dichloroquinoxaline