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PHOTOCHEMISTRY OF TNT: INVESTIGATION OF THE
"PINK WATER" PROBLEM. PART II

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White Oak Laboratory, Silver Spring, Maryland

21 November 1975

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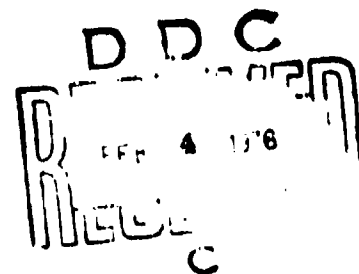
WHITE OAK LABORATORY

PHOTOCHEMISTRY OF TNT: INVESTIGATION OF THE "PINK WATER" PROBLEM,
PART II

21 NOVEMBER 1975

NAVAL SURFACE WEAPONS CENTER
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photo-sensitive (i.e., 2,4,6-trinitrobenzyl alcohol and 2,4,6-trinitrobenzaldehyde). Evidence is also presented on the nature of the primary photolytic process based on deuterium exchange studies, measurements of the photo-decomposition rate at various acidities, and experiments where the photochemical intermediate [TNT⁻] has been trapped.

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21 November 1975

PHOTOCHEMISTRY OF TNT: INVESTIGATION OF THE "PINK WATER" PROBLEM -
PART II

"Pink Water" is the visible evidence of the pollution of streams by contaminated waste water from TNT plants. The coloration is formed by the action of sunlight on dissolved TNT. This report identifies the major photo-decomposition products of TNT and presents evidence on the photochemical mechanism involved in their formation. Such information is necessary to assess the hazard of such pollution and to devise means to counteract its. The work was funded by the Army Medical R & D Command.

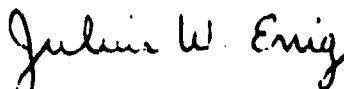
JULIUS W. ENIG
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SEPARATION AND IDENTIFICATION OF TNT PHOTOPRODUCTS

A. Introduction

"Pink water," produced by the photolysis of aqueous solutions containing mainly TNT and lesser amounts of other aromatic nitro-bodies, is undoubtedly a complex mixture. Due to the potential pollution problem posed by waste water containing TNT, and its photochemical decomposition products, the toxicity of "pink water" is being investigated¹. To aid these toxicity studies, the separation and identification of the components of this mixture is required. In order to simplify the characterization of "pink water," we have initially attempted to determine the composition of photolyzed aqueous solutions of TNT, as well as the reaction mechanisms for the formation of these photoproducts. Data from the mechanism studies have greatly assisted in the identification of a number of the "pink water" components. This work is the subject of this report. In the interest of completeness we have included data from our previous report² which deals with the identification of some of the benzene soluble photoproducts. Techniques for the continuous preparation of "pink water" have been described previously².

B. Separation Scheme

Aqueous TNT solutions, after irradiation with a 450 watt Hanovia medium pressure mercury lamp, fitted with a pyrex filter, were extracted and separated according to the scheme outlined in Figure 1. Relatively non-polar single ring compounds were extracted into benzene, polar one and two ring compounds were found in the ether extract (Ether I) and moderately to strongly acidic components were extracted into ether after acidification of the aqueous phase (Ether II). No attempt was made to prevent a small amount of carryover of compounds from one fraction to another as this was to be a rough separation with the final separation and assay coming from the results of chromatographic analysis.

1. "Mammalian Toxicological Evaluations of TNT Waste water," at Stanford Research Institute, Contract No. DAMD-17-74-C-4115.
2. N. E. Burlinson, L. A. Kaplan, and C. Adams, "Photochemistry of TNT: Investigation of the Pink Water Problem," NOLTR 73-172, 3 Oct 1973.

SEPARATION SCHEME

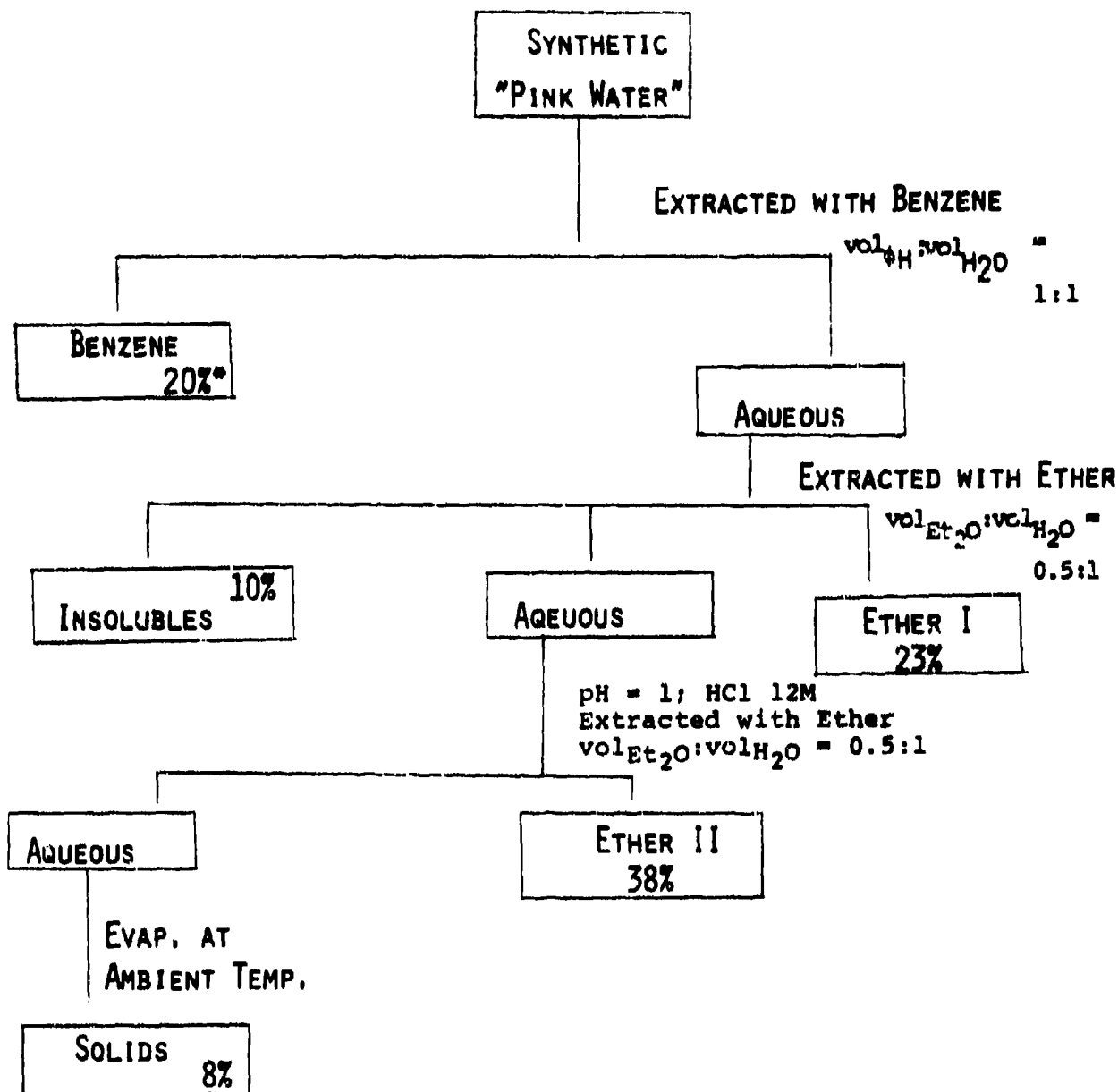


FIGURE 1

* % = PHOTODECOMPOSITION PRODUCTS BY WEIGHT OF TNT IN "PINK WATER"

Separation of "pink water" components was carried out using column chromatography (Silica Gel-60 support) and thin layer chromatography, (TLC). The TLC plates were prepared with Brinkman Silica gel HF 254 Type 60 according to the method described by Hoffsommer³. This grade of silica gel contains a fluorescent indicator that enables one to locate the spots on the developed plate with 254 nm light. A more instructive visualization (Figure 2) is accomplished by spraying the developed TLC plate with ethylene diamine - dimethyl sulfoxide (EDA/DMSO) (1:5 by volume)^{1,4}. Preparative layer chromatographic plates (1/4" thickness) were prepared with Brinkman Silica gel 254 with calcium sulfate binder. The TLC developing solvents were benzene, for the benzene soluble fraction, and benzene:ether:ethanol = 50:30:20 for the Ether I and Ether II fractions.

C. Identification Techniques

The compounds listed in the following tables were identified in a variety of ways. After separation by column, and/or preparative layer chromatography, characterization of the compounds generally was achieved with the aid of NMR, mass spectral, and infrared analysis. Confirmation of the structures, when possible, was done by comparison with authentic compounds, prepared by literature methods. Derivatization of the acidic components in the Ether I and Ether II fractions prior to their separation, greatly facilitated their separation and identification. Carboxylic acids were converted to their methyl esters either by reaction with diazomethane or via treatment of their acid chlorides with methanol.

Assays of the various components present in a given fraction, (i. e. benzene, Ether I, etc.), were obtained by comparing the area of the spot for a given component in a TLC of the fraction with the areas of the spots from known concentrations of the same component concurrently developed on the same plate as the fraction. For those compounds for which authentic samples could not be obtained by other synthetic methods, the compound was first isolated from its "pink water" fraction by preparative chromatography and subsequently used as the standard for assaying the percentage of the compound present in the fraction.

D. Analysis of the Benzene Soluble Fraction

Table 1 lists the "pink water" components of the benzene soluble fraction (20% by weight of the total photoproduct) that have been identified. With the exception of one component just above the origin (Figure 2) and the origin material, the benzene fraction has been completely characterized. These two unknowns represent <2% of the total photoproduct.

3. J. C. Hoffsommer and J. F. McCullough, J. Chromatog., 38,508 (1968).

4. D. J. Glover and E. Kayser, Anal. Chem. 40, 2055 (1968).

TLC OF BENZENE EXTRACT OF PINK WATER

B

2,4,6-trinitrotoluen-

1,3,5-trinitrobenzene

4,6-dinitroisoanthr-
anil

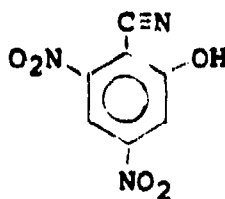
4,6-dinitroanthranil

2,4,6-trinitrobenz-
aldehyde2,4,6-trinitrobenzo -
nitrile2,4,6-trinitrobenz-
aldoxime2,4,6-trinitrobenzyl
alcohol

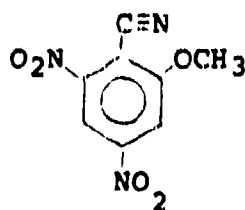
3,5-dinitrophenol

The separation and identification of TNT, TNB, 4,6-dinitroanthranil 2,4,6-trinitrobenzaldehyde and 2,4,6-trinitrobenzonitrile were outlined in our previous report².

A previously unidentified component, I, in the benzene soluble fraction, appeared just below TNB on the TLC plate. It gave a pink color when visualized with EDA/DMSO reagent but quickly faded to yellow. Initial attempts to isolate it pure, from TLC plates, failed due to its instability with respect to the formation of a yellow acidic compound, II, which chromatographed as a single spot in more polar solvents. The NMR spectrum of II exhibited only a pair of meta-coupled aromatic doublets at 824 Hz, and 848 Hz. In the infrared, absorption maxima at 3525 cm^{-1} and 2250 cm^{-1} indicated -OH and -C≡N functionality, respectively. The mass spectrum had a parent ion at $m/e = 209$. Treating II with diazomethane gave III, which was now chromatographable with benzene. In addition to the meta-coupled doublets, now at 858 Hz and 840 Hz, the NMR of III had a singlet for three protons at 430 Hz. The position and intensity of this line was in agreement with a methoxyl group. The mass spectrum of III has a parent ion at $m/e = 223$. The above data permitted the tentative assignment of the following structures to II and III. Confirmation



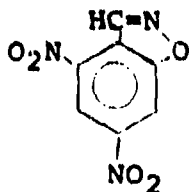
II



III

of their assigned structures came from a comparison with authentic samples prepared from reaction of 2,4,6-trinitrobenzonitrile with sodium methoxide in methanol (see experimental).

A pure sample of I could only be isolated from preparative TLC plates when anhydrous solvents were used for both chromatography and extraction. The mass spectrum was identical to that of II ($m/e = 209$) but its NMR spectrum was not. However, the NMR spectrum was similar to that of the previously isolated 4,6-dinitroanthranil, except that the peaks were at slightly different chemical shifts (see spectra #NMR-1 and #NMR-2). This evidence strongly suggested a 4,6-dinitro-[1,2]benzisoxazole ("isoanthranil") structure for I. Confirmation of



I

TABLE I

COMPOSITION OF BENZENE FRACTION^a

<u>Compound</u>	<u>Estimated Yield</u>
2,4,6-Trinitrotoluene (TNT)	
1,3,5-Trinitrobenzene (TNB)	0.5-1.0%
4,6-Dinitroisoanthranil (4,6-Dinitro[2,1]benzoxazole) (I)	1.0-2.0%
4,6-Dinitroanthranil (4,6-Dinitro[1,2]benzoxazole)	3-4%
2,4,6-Trinitrobenzaldehyde	8-10%
2,4,6-Trinitrobenzonitrile	3-4%
syn-2,4,6-Trinitrobenzaldoxime (IV)	~1%
2,4,6-Trinitrobenzyl Alcohol (VI)	<1%
3,5-Dinitrophenol (VII)	~1%
Unknown	<1%
Origin Material	~1-2%

^a Compounds are listed in order of appearance on TLC plate after developing with benzene.

this assignment was attained from the reported chemistry of substituted benzisoxazoles⁵. Under hydrolytic conditions the isoxazole ring cleaves to yield the corresponding ortho-cyanophenol.

Another component, IV, just below 2,4,6-trinitrobenzonitrile (PicN), at $R_f = 0.2$, was isolated from the TLC plate with an ether extraction. Rechromatographing the isolated material showed that it was decomposing to form 4,6-dinitroisoanthranil (I), PicN and a third compound, (V), coming just below IV on the TLC. The spot for IV turned red-brown when sprayed with EDA/DMSO whereas V gave the same pink to yellow color change as I. A second isolation of IV from TLC with a non-polar solvent in the absence of light gave undecomposed IV (checked by TLC) as a white solid. The presence of PicN suggested the oxime of 2,4,6-trinitrobenzaldehyde, since oximes are known to dehydrate to nitriles. The known oxime was synthesized from 2,4,6-trinitrobenzaldehyde with hydroxylamine in a bicarbonate buffer. The TLC data (i.e., the R_f value and color) matched that of the unknown IV. Likewise, the mass spectra of IV and of the known oxime were identical.

Attempted isolation of V (see above) from the TLC plate resulted in its transformation to the isoanthranil (I) and PicN. Irradiation of a benzene solution of IV in sunlight gave approximately a 1:1 equilibrium mixture of IV and V. Evaporation of the benzene left a white solid. The infrared spectrum (KBr) of this mixture was virtually identical to that of the starting oxime, IV, with the exception of a new broad band at 3250 cm^{-1} . This data suggested that IV and V were perhaps isomers, with V containing a hydrogen bonded OH group. The NMR data for the mixture and for IV is shown in Table II.

TABLE II
NMR CHEMICAL SHIFTS FOR IV AND V^a

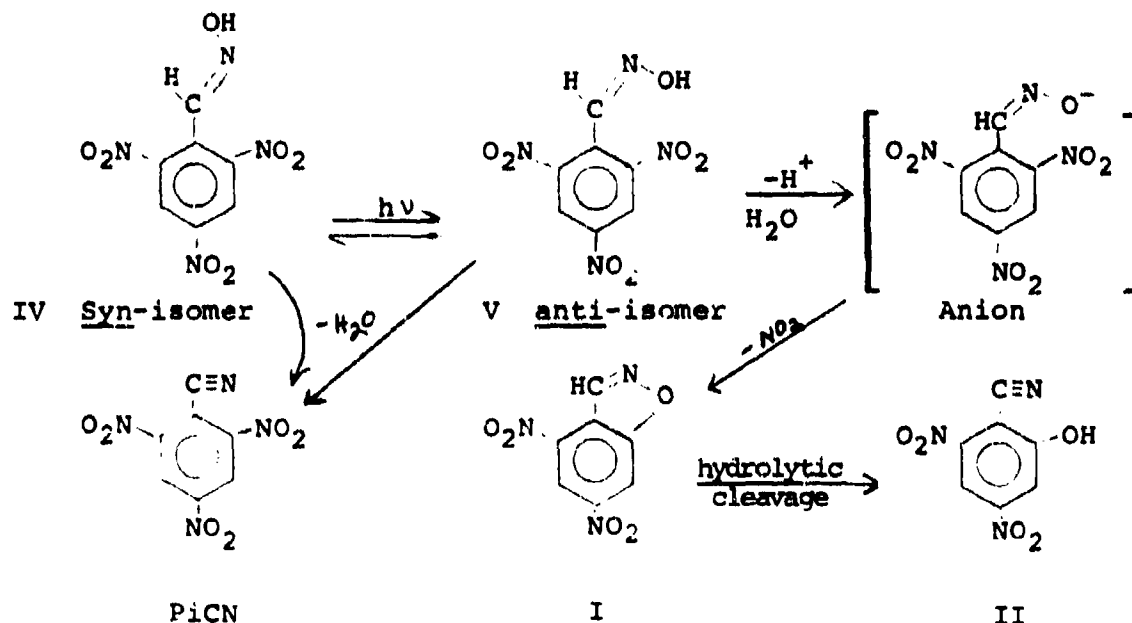
Compound IV	Mixture IV and V
792 (s,1H) ^b	792 (s,1H)
778 (s,2H)	778 (s,2H)
690 (s,1H)	738 (s,1H)
	800 (s,2H)

- a) values reported in Hz downfield from TMS in d_6 - benzene.
b) data in parentheses correspond to multiplicity and integrated area, respectively.

5. K. V. Auwers, Ber., 57B, 461 (1924).
H. Lindemann and H. Thiele, Ann., 449, 63 (1926).
H. Lindemann, H. Konitika, and S. Romanoff, Ann., 456, 284 (1927).
O. L. Brady and G. Bishop, J. Chem. Soc., 127, 1357 (1925).

The NMR resonances for IV at 792 Hz and 778 Hz were assigned to the methinyl and picryl protons, respectively, and the resonance at 690 Hz to the hydroxyl proton. The spectrum of the mixture did not contain resonances for hydroxyl protons⁶, but did show a similar set of peaks for V for methinyl and picryl type protons.

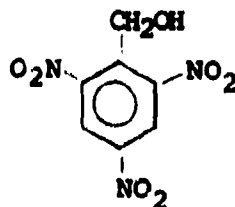
The above evidence suggests a photochemical isomerization for conversion of IV to V, followed by loss of nitrous acid from V to give I. Brady and Bishop⁷ and others⁸ have shown that ring closure can occur with anti-benzaldoximes to give benzisoxazoles. Photo-induced isomerization of oximes is also documented^{9,10}. PicN apparently forms as a dehydration product from IV or V or both. The following scheme is therefore proposed for the chemistry of syn-2,4,6-trinitrobenzaldoxime (IV) in "pink water."



6. The resonance at 690 Hz, present in the oxime IV was not present in the mixture. This would be expected if the exchange of the -OH protons between IV and V was occurring.
7. O.L. Brady and G. Bishop, J. Chem. Soc., 127, 1357 (1925).
8. A. H. Blatt, J. Org. Chem., 20, 591 (1955).
9. L. Fieser and M. Fieser, "Advanced Organic Chemistry," pg 438 Reinhold Publ., 1961.
10. J. P. Vermees and R. Beugelmans, Tetrahedron Lett., 25, 2091, (1969).

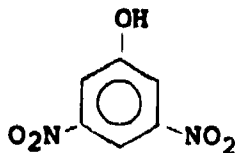
Treatment of IV with aqueous bicarbonate generated the cyanophenol (II) in good yield. This observation agreed with that of Brady and Bishop and our previous observation that I was unstable with respect to formation of II.

Just below the oxime IV TLC spot is another component (VI) in the "pink water" benzene fraction. The spot turned brown with EDA/DMSO and its mass spectrum was identical with authentic 2,4,6-trinitrobenzyl alcohol¹¹. The alcohol VI was found to be very photosensitive and preliminary results of its photochemistry are discussed in Section III.



VI

The last component, VII, to be identified in the benzene fraction was a yellow spot on the TLC at $R_f = 0.08$. This compound appeared to be a dinitrobenzene derivative since spraying it with EDA/DMSO only slightly enhanced the yellow color¹². A solution of VII in water generated a pH~2, indicating the presence of acidic functionality. Its mass spectrum had a parent ion at $m/e = 184$. These data suggested a dinitrophenol. Independently synthesized¹³ 3,5-dinitrophenol had an R_f value and mass spectrum identical with that of VII.



VII

11. K. G. Shipp, J. Org. Chem., 29 2620, (1964).
12. This is a fairly consistent test of the number of nitro groups on a ring - trinitrobenzenes generally give intense colors but dinitrobenzenes show up only pale yellow in color when sprayed with EDA/DMSO (1:5). A greater variety of color is generated, if instead neat EDA is used as the spray reagent.
13. Prepared from 1,3,5-trinitrobenzene with sodium methoxide in methanol followed by heating the resulting 3,5-dinitroanisole with sulfuric acid - (A. Hantzsch, Ber., 40, 341 (1907)).

E. Analysis of the Ether I Fraction

This fraction accounted for 23% by weight of the total photo-product. TLC analysis of this fraction indicated that only trace amounts (<2% of the total weight of the photo-products) of four of the components present in the benzene soluble fraction were carried over into the ether I fraction. These data are summarized in Table III.

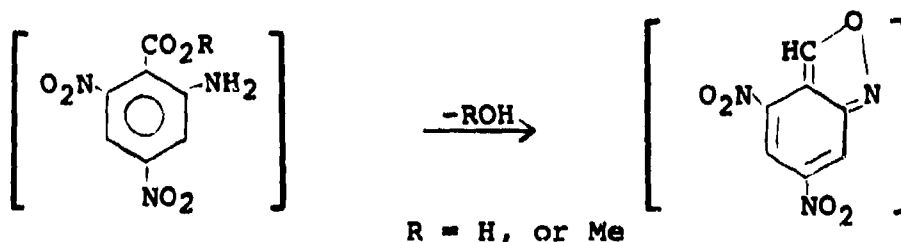
TABLE III

Compounds Identified in the Ether I Fraction

<u>Compound</u>	<u>Estimated Yield</u>
2,4,6-Trinitrotoluene	trace
2,4,6-Trinitrobenzaldehyde	trace
4,6-Dinitroanthranil	trace
2-Amino-4,6-dinitrobenzoic acid	5-6%
3,5-Dinitrophenol	trace

One other compound, representing 5-6% of the total weight of the photo product, was separated from this fraction and identified. Separation of this acidic material was made more facile by first reacting this fraction with diazomethane and subsequently chromatographing and isolating this photo-product as the methyl ester. The free acid was also isolated by a more tedious combination of TLC and recrystallization procedures.

The structure, 2-amino-4,6-dinitrobenzoic acid, was assigned to this compound on the basis of the following evidence. Its mass spectrum exhibited a parent ion at $m/e = 227$ with the base peak coming at $m/e = 209$ (P-18) and another major peak at $m/e 183$ (P-44). The P-44 line is consistent with the loss of CO_2 . The P-18 line is consistent with the loss of water to form the quite stable 4,6-dinitroanthranil ion VIII¹⁴.



14. The base peak, at $m/e = 209$ also appears as the base peak for 2,4,6-trinitrobenzaldehyde and for 2,4,6-trinitrobenzyl alcohol.

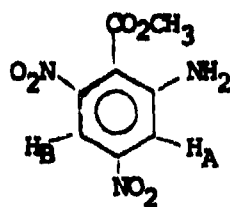
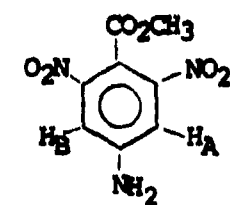
An analogous reaction took place in the mass spectrometer when the spectrum of the methyl ester of 2-amino-4,6-dinitrobenzoic acid was measured. A line at $m/e = 241$ was observed for the parent ion of the ester and, in addition, an intense line was again observed at $m/e = 209$ (P-32). This is consistent with the above reaction $R = Me$.

By contrast, the methyl ester of 4-amino-2,6-dinitrobenzoic acid¹⁵ exhibited a parent ion at $m/e = 241$, but rather than a line at $m/e = 209$, the 4-amino isomer had a line at $m/e = 210$ (P-31). This is consistent with the loss of a methyl group rather than methanol and is reasonable in light of the fact that there is no intramolecular pathway for the loss of the elements of methanol from the 4-amino isomer.

Corroborative evidence for the assignment of the structure to the 2-amino isomer comes from NMR data which are summarized in Table IV.

TABLE IV

NMR Chemical Shifts for Methyl Aminodinitrobenzoate^a

	H _A	H _B	NH ₂	CH ₃
	771 (1) ^b	778 (1) ^b	590 (2)	380 (3)
	761 (2)	————	631 (2)	382 (3)

(a) In acetone - d_6 , shift values in Hz downfield from internal TMS, relative line areas in parentheses.

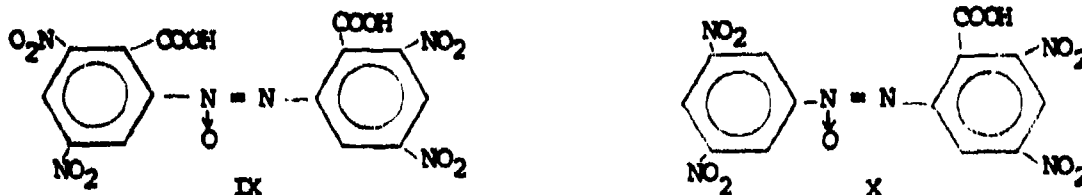
(b) doublets, $J = 1.5$ Hz.

F. Analysis of the Ether II Fraction

This fraction contains 38% of the total photo-product. TLC separation of this fraction was complicated by considerable tailing even when the relatively polar developer benzene:ether:ethanol = 5:3:2, was used. In spite of this difficulty it was possible to

15. G. O. Parks and A. C. Farthing, J. Chem. Soc., 1275 (1948).

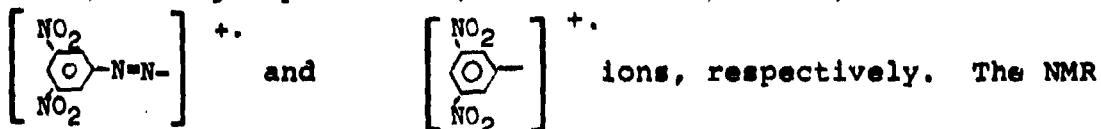
separate and identify six compounds, comprising almost one-half of the weight of the fraction. The compounds found in the Ether II fraction are given in Table V. The compounds referred to as "white compound" (IX) and "monocarboxy white compound" (X) were identified by comparing their R_f values and color with EDA/DMSO on TLC with those of the authentic compounds^{18a,b}. Their existence in the Ether II fraction was suggested by a previous experiment² where photolysis of aqueous 2,4,6-trinitrobenzaldehyde formed "white compound," known^{18b} to decarboxylate to X. It is interesting to note that only one of two possible isomers for X is formed and mass spectrometry evidence suggests the structure below¹⁷



Confirmation of these assignments were obtained from spiking experiments in which known amounts of IX and X were added to separate aliquots of the Ether II fraction and these were chromatographed alongside the unspiked aliquots. The increase in the spot intensity of the spiked, as contrasted with the unspiked aliquot, confirmed the initial assignments.

The major component in the Ether II fraction 2,2'-dicarboxy-3,3',5,5'-tetranitroazobenzene (XI) ("desoxy white compound") was identified by spectroscopic investigation on a chromatographically pure sample isolated from the Ether II fraction. The mass spectrum of "desoxy white compound" showed no parent ion at $m/e = 450$ but had a small peak at $m/e = 406$ and a relatively large one at $m/e = 362$ which would correspond to mono- and didecarboxylation (probably

thermal) . Major peaks at $m/e = 195$ and $m/e = 167$, are attributed to



spectrum shows only a pair of meta-coupled doublets at 926 Hz and

- 16a. S. A. Joshi and W. D. Patwardhan, *Current Science*, 8, 239, (1953).
- 16b. M. Kamlet, H. Adolph, and I. Dunstan, *Nitro Compounds*, *Proc. Intern. Symp. Warsaw 1963* pg 431-44 (Eng.) Cf. C.A. 59, 8625e, C.A. 63, 17956, (1965).
17. Unpublished results from this Center.

TABLE V

Compounds Identified in Ether II Fraction^a

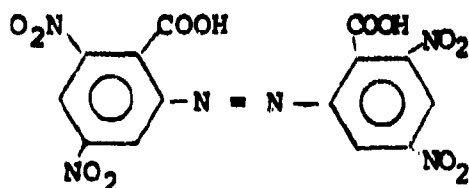
<u>Compound</u>	<u>Estimated Yield</u>	<u>Color^b</u>
1) 2,2'-Dicarboxy-3,3',5,5'- tetranitroazoxybenzene ("white compound") IX	trace	blue-purple
2) 2,2'-Dicarboxy-3,3',5,5'- tetranitroazobenzene ("desoxy white compound") XI	7%	orange-brown
3) 2-Carboxy-3,3',5,5'- tetranitroazoxybenzene ("monocarboxy white compound") X	2%	lavender
4) 2,4,6-Trinitrobenzoic Acid	1%	orange
5) N-(2-carboxy-3,5-dinitrophenyl)- 2,4,6-trinitrobenzamide XIII	1%	red-brown
6) 2-Amino-4,6-dinitrobenzoic acid	4-5%	yellow

a) compounds are listed in order of appearance on TLC plate using benzene:ether:ethanol = 50:30:20 as the developing solvent.

b) color produced by spraying TLC plate with EDA/DMSO (1/5).

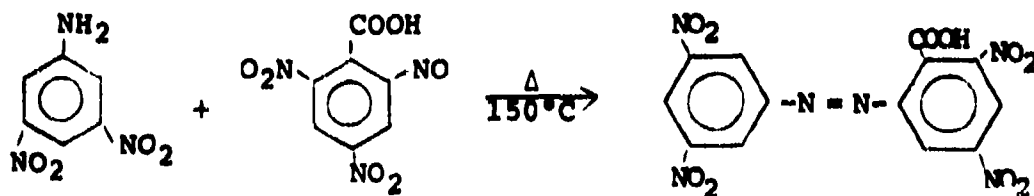
880 Hz (in acetone - d_6) (see spectrum #3) consistent with the assigned structure and eliminating the possibility of azoxy type linkage in favor of a more symmetrical structure. The infrared spectrum of XI showed a broad peak at 3400 cm^{-1} and a strong sharp one at 1725 cm^{-1} indicating a carboxylic acid with the usual numerous aromatic nitro frequencies between 1400 and 1600 cm^{-1} (see spectrum # IR-1). The synthesis of XI could not be achieved but its monocarboxy analog 2-carboxy-3,3',5,5'-tetranitroazobenzene (XII), was independently made by allowing 3,5-dinitroaniline to react with 2-nitroso-4,6-dinitrobenzoic acid (see experimental). Since the NMR spectrum of XI suggested a dicarboxylic acid but its mass spectrum indicated only the monocarboxylic structure, the mass spectrum of XII was expected to be identical to that of XI and indeed it was. However, treatment of XI with phosphorous pentachloride in benzene followed by the addition of methanol gave a dimethyl ester, the mass spectrum of which had a parent ion at $m/e = 478$ and major peaks at

$m/e = 253$ and $m/e = 225$ corresponding to the $\left[\begin{array}{c} \text{NO}_2 \text{---} \text{COOCH}_3 \\ | \\ \text{C}_6\text{H}_3\text{---} \text{N=N} \\ | \\ \text{NO}_2 \end{array} \right]^+$ and the $\left[\begin{array}{c} \text{O}_2\text{N} \text{---} \text{COOCH}_3 \\ | \\ \text{C}_6\text{H}_3\text{---} \text{N=N} \\ | \\ \text{O}_2\text{N} \end{array} \right]^+$ ions, respectively.



XI

"Desoxy White Compound"



XII

A fourth component in the Ether II fraction, 2,4,6-trinitrobenzoic acid (see Table V), was identified by comparison of its TLC- R_f value and its color with EDA/DMSO with that of the known compound¹⁸. Attempts to isolate either the "pink water" component or the authentic acid from a TLC plate resulted in decarboxylation to 1,3,5-trinitrobenzene.

Compound XIII was the next spot isolated from the Ether II fraction (Table V). It was similar to the other components in this fraction in that it was an acidic polynitroaromatic compound (red-brown color with EDA/DMSO). A mass spectrum of XIII showed a small parent ion at $m/e = 466$ and a major P-44 peak at $m/e = 422$ suggesting that monodecarboxylation was occurring. Treatment of XIII with phosphorous pentachloride/methanol gave an apparent methyl ester derivative whose mass spectrum now had a parent ion at $m/e = 480$. This result suggested that only one carboxyl group is present in XIII. The NMR data in Table VI for XIII and its methyl ester confirmed the presence of one carbonyl function in XIII and the possible presence of a picryl-ring (935 Hz) coupled to an unsymmetrically substituted dinitroaromatic ring (920 Hz and 880 Hz). The infrared spectrum

TABLE VI

NMR CHEMICAL SHIFTS FOR XIII AND ITS METHYL ESTER^a

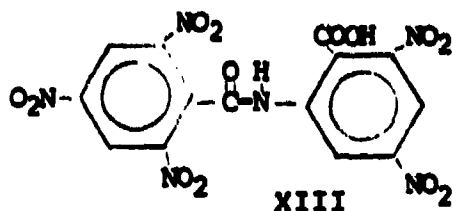
<u>XIII^b</u>	<u>Methyl Ester of XIII</u>
1050 (bs, 1H)	935 (s, 2H)
940 (m, 3H)	920 (d, 1H)
880 (d, 1H)	880 (d, 1H)
655 (bs, 2-3H)	395 (s, 3H)

- a) Shifts are in Hz downfield from TMS and notation in parentheses refer to line multiplicity and integrated area, respectively. The solvent is acetone - d_6 .
- b) The NH and COOH protons are assigned to the broad singlets at 1050 Hz and 655 Hz, respectively, in XIII. However, the 1050 Hz line is not present in the ester and is assumed to be exchanging.

(see spectrum #IR 2) of XIII had absorption maxima at 3580 cm^{-1} and 3510 cm^{-1} indicating free and bonded N-H stretching, at 3200 cm^{-1} attributed to carboxyl OH and a broadened absorption at 1700 cm^{-1} for carbonyl. However, the infrared spectrum of the methyl ester

18. H. T. Clarke and W. W. Hartman, Org. Syn., Coll. Vol. 1, 543 (1941).

derivative (see spectrum #IR-3) showed the carbonyl region now split into two peaks at 1670 cm^{-1} (amide- $\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$ -stretch)¹⁹ and at 1730 cm^{-1} (ester- $\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$ -stretch)¹⁹. With this evidence in hand, structure XIII was



assigned for this "pink water" compound.

The remaining major peaks in the mass spectrum of XIII at $m/e = 240, 210,$ and 194 and also of the methyl ester of XIII at $m/e = 421, 240, 210$ and 194 also agree with this proposed structure.

It is interesting to note that XIII was also found as a minor product in the reported^{16b} synthesis of "white compound" (IX) (see experimental).

The final compound, 2-amino-4,6-dinitrobenzoic acid, identified in the Ether II fraction was also in the Ether I fraction. Its structure proof was discussed in the previous section.

G. Analysis of the Insoluble Fraction

Some physical and chemical characteristics of the insoluble portion of the pink water have been determined. These are outlined in Sec. IV, B.

19. L. J. Bellamy, "Infra-red Spectra of Complex Molecules," Wiley, 1966 pg 179 and 203.

EXPERIMENTAL²⁰

"Pink water" samples, referred to in this report, were prepared by irradiation of aqueous TNT solutions using a 450 watt Hanovia mercury arc with a #7740 pyrex filter. Other information on the preparation and analysis of the TNT solutions and the "pink water" produced is outlined in our previous report².

NMR spectra were obtained with a Varian HA-100 spectrometer, infra-red spectra with Perkin Elmer "Infracord", and mass spectra with a Varian MAT-111 spectrometer.

The TNT used in this study was military grade TNT twice recrystallized from 30% chloroform in carbon tetrachloride. Its purity was estimated to be better than 99.9% by TLC.

A. Preparation of 2-cyano-3,5-dinitroanisole III.

Sodium metal (0.6 g) was dissolved in 15 ml of methanol. A 5.5 ml aliquot of this solution was added dropwise, with stirring, to a boiling solution of 3.0 g (0.0125 mole) of 2,4,6-trinitrobenzonitrile²¹ in 30 ml of methanol. TLC (in benzene) of this reaction mixture exhibited, under UV light, a trace of starting material (at $R_f \sim 0.5$), a major spot (III) at $R_f \sim 0.35$, a second major spot (XIV) at $R_f \sim 0.3$, a minor component (XV) at $R_f \sim 0.25$ and a yellow compound (II) at the origin. The red reaction mixture was allowed to cool and evaporate to half its original volume. Crystals formed and were isolated and recrystallized from benzene. TLC indicated they were mainly compounds III and XIV. They were separated by column chromatography on silica gel-60 using benzene/hexane (1:1) at the start and gradually changing to benzene/hexane, 3:1. Complete separation of III and XIV was accomplished to give 0.75 g (27% yield) of III and 0.50 g (18% yield) of XIV. Recrystallization of III from benzene gave a white solid, M.P. = 120-121°C, after drying 5 hrs at 65°C. NMR spectrum (acetone - d_6), 430 (S,3), 858 (d,1), 840 (d,1). Mass spectrum parent ion at $m/e = 223$. Analysis: Calc. for $C_8H_5N_3O_5$: C, 43.06; H, 2.26; N, 18.83. Found: C, 42.92; H, 2.21; N, 18.74.

B. Preparation of 4-cyano-3,5-dinitroanisole, XIV

Compound XIV, isolated from the fractions from the above chromatography (Sec. A) was recrystallized from benzene and dried 5 hrs at 65°C to give a white solid, M.P. 133-4°C. The mass spectrum had a parent ion at $m/e = 223$, and the NMR spectrum (acetone - d_6) showed peaks at 412 (S,3H) and 810 (S,2H). Analysis: calc. for $C_8H_5N_3O_5$: C, 43.06; H, 2.26; N, 18.83. Found: C, 43.00; H, 2.21; N, 18.76.

20. All NMR chemical shifts are reported in Hz downfield from TMS. The letters and numbers in parentheses refer to line multiplicity and integrated area, respectively.

21. J. Konarski and A. Graczyk, *Roczniki Chemii*, **46**, 745 (1972).

C. Preparation of 2,4-dimethoxy-6-nitrobenzonitrile, XV

The minor component (at $R_f \sim 0.25$), compound XV above, was produced in larger yield when excess sodium methoxide was added to the above trinitrobenzonitrile/methanol solution for preparation of III. On concentration of the reaction mixture, XV crystallized. It was recrystallized twice from methanol and once from benzene to give yellow needles, M.P. 142-3°C. The mass spectrum shows a parent ion at $m/e = 208$ and its NMR spectrum (acetone - d_6) had peaks at 396 (s, 3H), 401 (s, 3H), 732 (d, 1H) and 707 (d, 1H). Analysis: Calc. for $C_9H_8N_2O_4$: C, 51.93; H, 3.87; N, 13.46. Found: C, 51.88; H, 3.88; N, 13.34.

D. Preparation of 2-Hydroxy-4,6-dinitrobenzonitrile, II

The original methanol filtrate from the above preparation of 2-cyano-4,6-dinitroanisole (III) contained III, XIV, and the potassium salt of II. To remove III and XIV from the residue left behind after the filtrate was evaporated, the residue was digested with hot benzene and the remaining insoluble material removed by filtration. The insoluble portion was then stirred with acetone and the remaining insoluble material removed. The acetone filtrate was concentrated and benzene added to the hot solution until it became cloudy. Very fine orange-red crystals formed overnight. These crystals were dissolved in water and precipitated by addition of conc. HCl to give a white solid weighing 0.35 g (~10% yield). A wide range for its melting point and TLC evidence indicated some of the 4-hydroxy isomer may be present. Treatment of a small portion of the white solid with diazomethane in ether followed by TLC analysis of the reaction mixture gave mainly III, but a small amount of XIV was also present. Therefore, the remaining solid was recrystallized (Darco) from ether/chloroform until a sample of pure II was isolated.

After drying at 90°C under vacuum for 5 hrs., it melted at 183-185°C. NMR spectrum (in acetone - d_6) 824 (d, 1H), 848 (d, 1H), OH not present (see spectrum #NMR-4). Analysis: Calc. for $C_7H_3N_2O_5$: C, 40.20; H, 1.45; N, 20.09. Found: C, 40.15; H, 1.47; N, 19.93. The mass spectrum of II had a parent ion at $m/e = 209$ and its IR spectrum (see #IR-4) was also consistent with the assigned structure.

E. General Method for Preparation of Ester Derivatives of the Acidic Components of "Pink Water."

The methyl esters of "white compound," (IX), "desoxy white compound" (XI), "monocarboxy white compound" (X), and the benzamide acid (XIII) were prepared by the following general procedure.

The acid was slurried in benzene, excess phosphorous pentachloride added and the mixture heated to boiling for ten minutes. The solution was then concentrated, cooled, and hexane added slowly until crystals formed. The acid chloride was removed by filtration and added to methanol. In general, the pure methyl ester derivatives

were isolated from a thin layer or preparative layer chromatographic plate for NMR and mass spectral analysis. With the exception of the benzamide ester derivative, which was developed with benzene - EtOAc (85:15), the TLC's of the remaining derivatives were developed with benzene.

F. Preparation of 2-carboxy-3,3',5,5'-tetranitroazobenzene, XII

One and a half grams of 2-nitroso-4,6-dinitrobenzoic acid¹⁸ was added to 2.1 g of 3,5-dinitroaniline, mixed well, and the reaction vial placed in a hot oil bath at 150°C for one minute. Then one milliliter of xylene was added and heating continued for five more minutes. The cooled melt was then extracted with 250 ml of boiling ether. The residue was dissolved in 3 ml of acetone and 75 ml of ether added. A precipitate formed which was removed and discarded. The two ether filtrates were combined and extracted with aqueous bicarbonate. The bicarbonate phase was extracted once with ether then acidified with concentrated hydrochloric acid to give an orange precipitate. TLC analysis showed a trace of "white compound" was still present. Digesting the orange solid in 100 ml of hot water and removing by filtration eliminated the "white compound" impurity. The orange solid (XII) was recrystallized from acetone-water, washed once with water, dried in a vacuum oven for 5 hrs. at 90-95°C to give 0.39 g (15% yield) of yellow-orange crystals, M.P. 255°C (dec.). The mass spectrum showed a parent ion at $m/e = 406$. The NMR spectrum (acetone - d_6) had peaks at 914 (m, 2H); 909 (d, 2H), 901 (d, 1H), 506 (s, 1H) (see spectrum #NMR-5). Analysis: Calc. for $C_{13}H_6N_6O_{10}$: C, 38.44; H, 1.49; N, 20.69. Found: C, 38.61; H, 1.43; N, 20.57.

G. Preparation of N-(2-carboxy-3,5-dinitrophenyl)-2,4,6-trinitrobenzamide, XIII

Five grams of 2,4,6-trinitrobenzaldehyde were heated with 30 ml of concentrated sulfuric acid as previously described¹⁸ for the preparation of "white compound." After removing the insoluble "white compound" by filtration, the filtrate is poured over ice. The white precipitate which forms is removed by filtration, washed with water, stirred with 30 ml of ether and filtered. Digestion of the remaining solid in 25 ml of boiling water, filtering, and repeating the digestion procedure, removed most of the "white compound" impurity. The insoluble product was dissolved in hot acetone, water added to the cloud point and then cooled. The yellow crystals obtained were removed by filtration and dried 1 hr at 180°C to give a M.P. of 277°C. Analysis: Calc. for $C_{14}H_6N_6O_{13}$: C, 36.06; H, 1.30; N, 18.03. Found: C, 35.20, 35.00; H, 1.52, 1.50; N, 17.20, 17.11.

The mass spectrum showed a small parent ion at $m/e = 466$ and a (P-44) peak attributed to the loss of CO_2 . The major peak at $m/e = 240$ is attributed to $[P(C=O)]^+$, which then loses one or two nitro groups to give $m/e = 194$ and $m/e = 148$, respectively. The mass spectrum of the methyl ester derivative (see Section E) gave a

parent ion at $m/e = 480$. The NMR spectrum (acetone - d_6) of the free acid has peaks at 1050 (broad singlet, 1H), 940 (m, 3H), 880 (d, 1H), 655 (broad singlet, H_2O and $COOH$ resonances), (see spectrum #NMR-6). The infrared spectrum of the acid had NH, OH, and broad carbonyl absorption. However, the infrared spectrum of the ester derivative showed both amide $c=O$ and ester $c=O$ absorptions (see spectra #IR-2 and #IR-3).

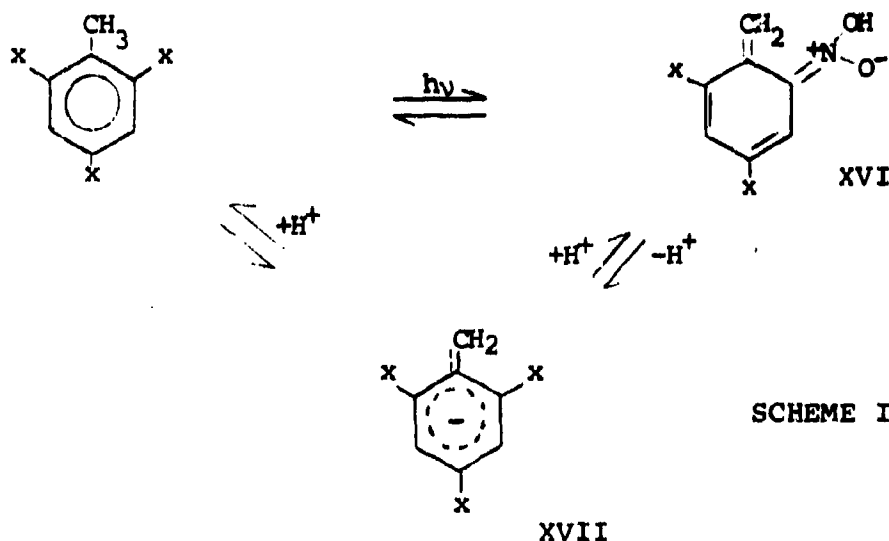
H. Preparation of 1,3,7,9-tetranitroindazolo[2,1a]indazol-6-ol-12-one.
(A photo-dimer of 4,6-dinitroanthranil).

An aqueous solution of 4,6-dinitroanthranil²² ($4.8 \times 10^{-4}M$) was irradiated with a pyrex filter, 450w medium pressure Hg-arc, in a 500 ml Ace Reactor for 1 hr. During the photolysis, an orange solid separated (~50%). Recrystallization of the solid from benzene gave dark orange crystals which changed color to tan at 140°C and decomposed with gas evolution at 170°C. Analysis for C, H, N, and O showed that each dimer was solvated with one molecule of benzene. Its mass spectrum had a parent ion at $m/e = 418$. The structure of the photo-dimer was finally elucidated by single crystal x-ray spectroscopy to be the named compound. The NMR in acetone - d_6 showed peaks at 891 (d, 1H), 878 (dd, 2H), 846 (d, 1H) and 770 (s, 1H) (see spectrum #NMR-7). Analysis: calc. for photo-dimer benzene solvate ($C_{14}H_6N_6O_{10} \cdot C_6H_6$) C, 48.43; H, 2.43; N, 16.94. Found: C, 49.14; H, 2.51; N, 16.94.

22. M. Calvin and J. S. Splitter, J. Org. Chem., 20, 1086 (1965).

MECHANISTIC CONSIDERATIONS OF THE PHOTOCHEMISTRY OF TNT

Flash photolysis studies on TNT²³ and 2,6-dinitrotoluene²⁴ suggest the following mechanism (Scheme I) for the primary photochemical step in the photodecomposition of TNT. Irradiation of TNT produces



SCHEME I

an excited state TNT molecule which intramolecularly abstracts hydrogen to form aci-TNT, XVI. Subsequent ionization of XVI produces the TNT anion, XVII, which can reprotonate to TNT.

To test the possibility of a labile hydrogen being transferred in the primary photo-step, a D₂O solution of TNT was photolyzed for one hour. The undecomposed TNT was isolated by TLC and analyzed by mass spectrometry and NMR. The mass spectrum showed an increase in the m/e = 211, 212, and 213 peaks indicating the presence of -CH₂D, -CHD₂, and -CD₃ isomers. The NMR spectrum showed a decrease of 30% in the methyl signal relative to the aromatic proton signal. A sample of TNT in D₂O, kept in the dark for 24 hours, showed no sign of deuterium incorporation. The deuterated TNT from the photolyzed sample was oxidized with Na₂Cr₂O₇/H₂SO₄ to trinitrobenzene and its mass spectrum confirmed that no deuterium was incorporated into the trinitrophenyl ring.

23. K. Suryanarayanan and C. Capellos, *Inter. J. of Chem. Kinetics*, **6**, 89 (1974).

24. G. Wettermark, M. E. Langmuir, L. Doglotti, E. D. Black, *JACS*, **91**, 2204 (1969).

In order to determine whether TNT decomposition was occurring from the aci or the anion form, three solutions of TNT/D₂O were adjusted to three different acidities using D₂SO₄ (Table VII). The solutions were irradiated for 60 minutes in pyrex tubes then the remaining [TNT] was determined by GC analysis and finally isolated and analyzed for deuterium content.

TABLE VII

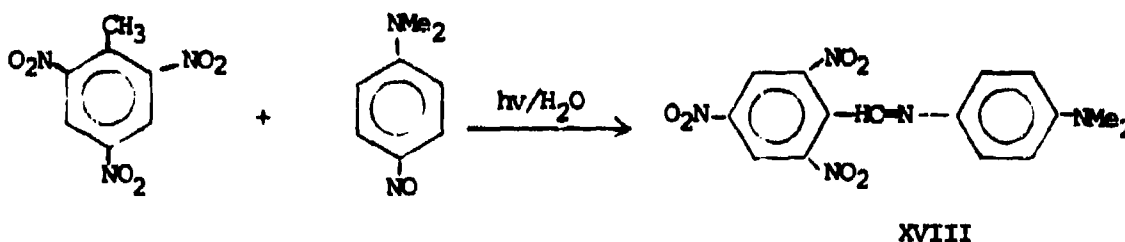
PERCENT PHOTODECOMPOSITION OF TNT VS [D₃O⁺]

	pD ^a = 1.5	pD = 4.0	pD = 7.0
[TNT] ₀	4.01 x 10 ⁻⁴ M	4.01 x 10 ⁻⁴ M	4.01 x 10 ⁻⁴ M
[TNT] _{60 min}	3.31 x 10 ⁻⁴ M	2.82 x 10 ⁻⁴ M	1.85 x 10 ⁻⁴ M
% Decomposition TNT	17.5	29.6	53.8
% Deuterium in TNT	53	47	30

a) pD = pH + 0.4 (R. Bates, "Determination of pH, p.219, J. Wiley & Sons, publ., (1964)).

The data show an inverse relationship between [D₃O⁺] and percent decomposition, indicating that the major pathway for photodecomposition of TNT requires the intermediacy of the TNT anion (XVII). The anion, XVII, is obviously photo-generated since in the dark, no deuterium uptake was observed even at 120°C in 98% D₂SO₄. Other evidence, suggesting the intermediacy of TNT anion in the photodecomposition, is based on the fact that alkaline decomposition of TNT²⁵ gives rise to many of the same products also observed in "pink water," namely, 2,4,6-trinitrobenzaldehyde, 1,3,5-trinitrobenzene, 4,6-dinitroanthranil and 2,4,6-trinitrobenzyl alcohol.

Additional evidence for XVII as an intermediate in the photodecomposition comes from the results of experiments in which the anion was trapped with p-nitroso-N,N-dimethylaniline to form the Schiff base XVIII. In the presence of pyrex filtered light from a medium



25. Unpublished results from this Center.

pressure Hg-arc, an aqueous solution of $4.4 \times 10^{-4}M$ TNT and $4.4 \times 10^{-3}M$ p-nitroso-N,N-dimethylaniline afforded an 80% yield of XVIII after irradiation for only 45 min²⁶. No XVIII could be detected in a dark control reaction after the same time interval. However, in the absence of light, under alkaline conditions known to favor the formation of TNT anion, substantial amounts of XVIII, in addition to the other alkaline degradation products, were formed.

26. p-Nitroso-N,N-dimethylaniline is stable under these photo-conditions.

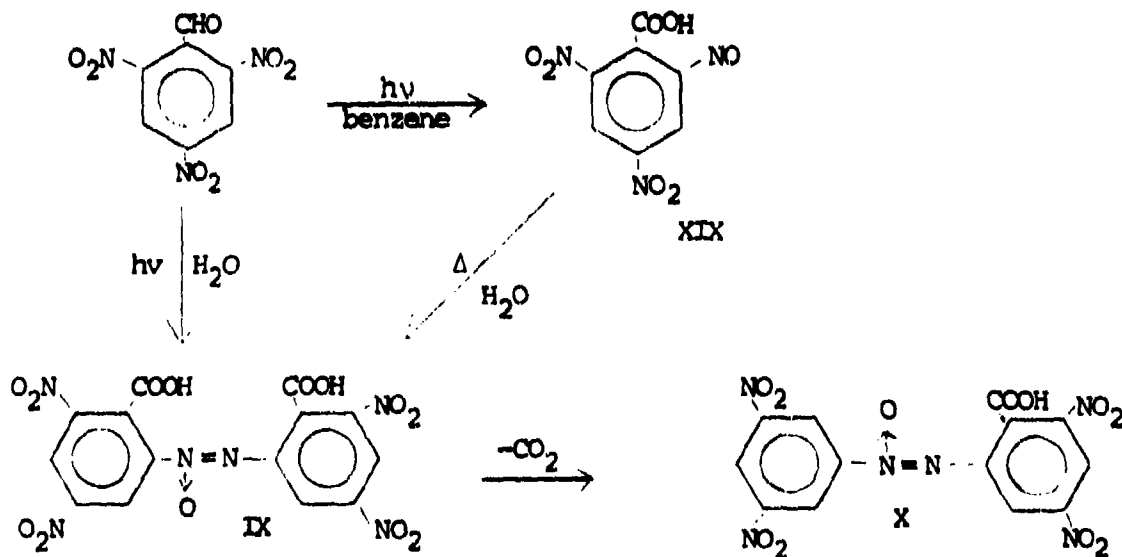
PHOTOLYSIS OF "PINK WATER" PRODUCTS

In our earlier report², we mentioned the observed photosensitive nature of some of the isolated products from "pink water." Studies of their individual photochemistry have greatly aided in identification of a number of other "pink water" products.

It is to be expected that any aromatic nitro groups ortho to a carbon bearing a hydrogen i.e., $\text{C-H} \text{---} \text{NO}_2$ will have a propensity for intramolecular photochemical reaction. This required ortho orientation was recognized as early as 1904 by Sachs and Hilpert²⁷ and there are numerous photochemical reactions in the recent literature²⁸ that demonstrate this fact.

A. Photolysis of 2,4,6-Trinitrobenzaldehyde.

Joshi¹⁶ found that photolysis of 2,4,6-trinitrobenzaldehyde in benzene affords good yields of 2-nitroso-4,6-dinitrobenzoic acid, XIX. However, warming XIX in water formed the azoxy derivative^{18, 29}, "white compound," IX. Upon photolysis of the aldehyde in water, "white compound" is isolated as the major product. Both "white compound" and its monodecarboxylation product X (Table V) were found to be present in small amounts in the Ether II fraction of "pink water".



27. F. Sachs and S. Hilpert, Chem. Ber., 37, 3425 (1904).

28. H. A. Morrison, Chp 4 "Photochemistry of the Nitro and Nitroso Group" Pg 165 in "The Chemistry of Nitro and Nitroso Groups," Part I, H. Feuer, Editor, Interscience (1969) and refs. cited therein.

29. Aromatic nitroso compounds are known to disproportionate to form azoxy compounds: P.A.S. Smith, "Open-Chain Nitrogen Compounds" Vol 2, Cnp. 13, Benjamin Inc. (1966).

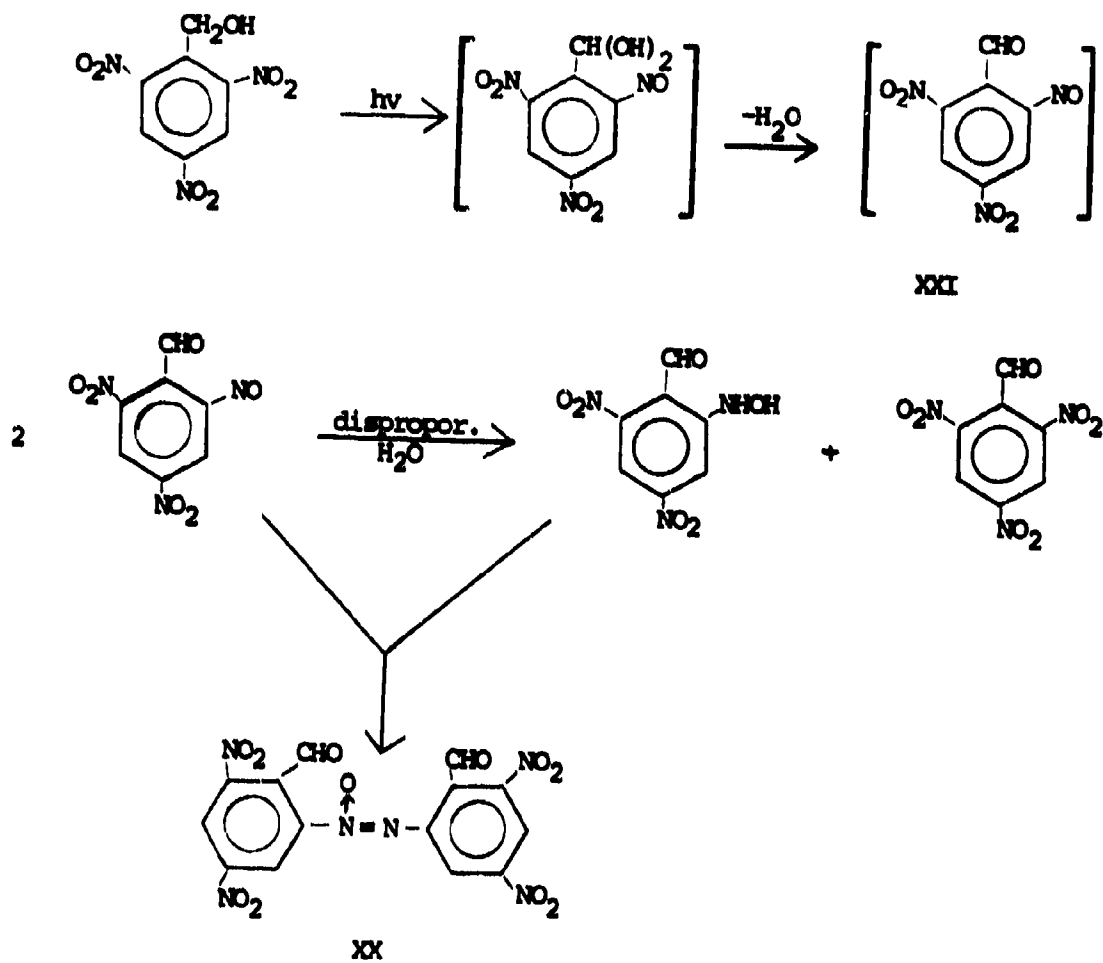
B. Photolysis of 2,4,6-Trinitrobenzyl Alcohol, VI

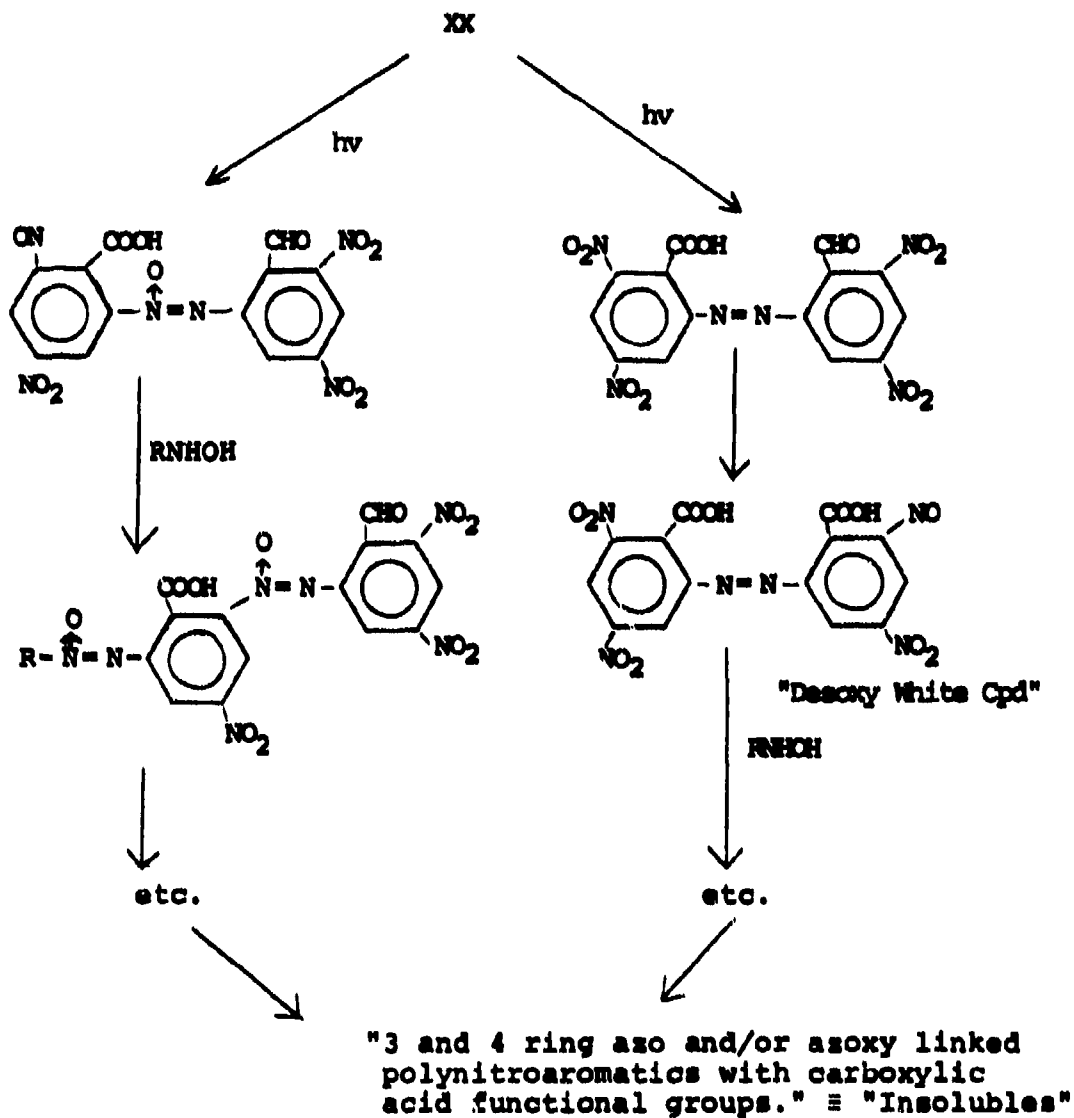
Irradiation of an aqueous solution of 2,4,6-trinitrobenzyl alcohol with pyrex filtered sunlight (1 hr) resulted in rapid formation of an "off white" precipitate XX as the major product. TLC analysis of this solid showed a single spot at $R_f = 0.25$ (in benzene) which turned purple with EDA/DMSO indicating a tetranitroazoxy type compound². NMR analysis of XX (DMSO - d_6) showed peaks at 1060 (s, 1H), 1043 (s, 1H), 930 (d, 1H), 918 (d, 1H), 913 (d, 1H) and 895 (d, 1H). The four sets of meta-coupled doublets ($J = 1.5$ Hz) were consistent with a tetranitroazoxy structure and the two singlets downfield suggested non-equivalent methinyl protons. An infrared spectrum (KBr) of XX had two sharp carbonyl peaks at 1690 cm^{-1} and 1700 cm^{-1} for non-equivalent aldehyde groups. A dialdehyde was further suggested by the formation of both a mono- and bis-2,4-dinitrophenylhydrazone derivative. Based on this data, and a C,H,N, and O analysis, the structure, 2,2-diformyl-3,3',5,5'-tetranitroazoxybenzene is proposed for XX.

Extraction of the remaining aqueous photolysate from XX with ether followed by TLC (in benzene) showed a second major spot for 2,4,6-trinitrobenzaldehyde, two minor spots at $R_f = 0.25$ and 0.20 corresponding to XX and the starting alcohol, respectively, as well as origin material. Thin layer chromatography of the origin material in more polar solvents showed several spots, which turned purple when sprayed with EDA/DMSO. This was indicative of azo- and azoxy-polynitroaromatic acids similar to those compounds listed in Table V, (p. 15). These polar compounds are still to be characterized.

These observations are of interest in light of the fact that 2,4,6-trinitrobenzyl alcohol is found in "pink water." It is only present in about 1% but after considering its observed rapid photodecomposition, the alcohol may be a major photo-intermediate derived from TNT. The major photoproduct from the alcohol, XX, is also photosensitive and upon irradiation gives rise to a red brown precipitate similar in characteristics to the "insolubles" isolated from "pink water." (Figure 1).

These observations lead us to suggest one of the many possible pathways for formation of the "insoluble" components which have so far defied separation:





This proposed pathway includes intramolecular oxygen insertion to the hydrated nitroso aldehyde which in turn dehydrates to XXI followed by disproportionation of XXI to hydroxylaminodinitrobenzaldehyde and trinitrobenzaldehyde. The hydroxylamino-aldehyde and XXI then couple to form the observed azoxydialdehyde XX. Comparison of the final products in this pathway with the general chemical and physical properties of the "pink water" insolubles fraction, listed in Table VIII, shows a rather close similarity.

TABLE VIII

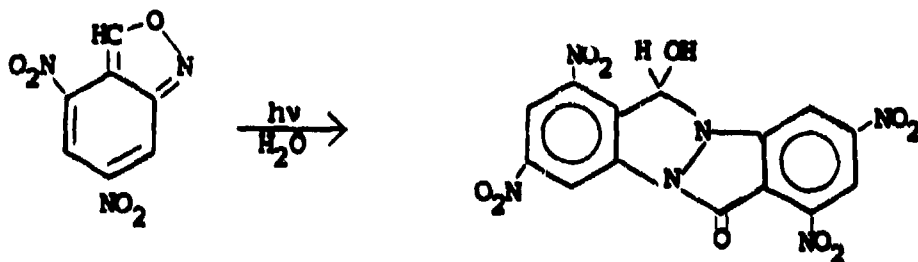
PROPERTIES OF THE INSOLUBLE FRACTION OF "PINK WATER"

- 1) red brown solid
- 2) insoluble in water, benzene, and ether
- 3) soluble in acetone or aqueous bicarbonate
- 4) can be reprecipitated from the aqueous bicarbonate solution
- 5) TLC in polar solvents gave no separations
- 6) spraying the TLC tails with EDA/DMSO enhances the color (dark brown) indicating that dinitroaromatics are still present
- 7) osmometry measurements indicate an average molecular weight of 1500 or higher

Further investigation of the photochemistry of 2,4,6-trinitrobenzyl alcohol is planned.

C. Photolysis of 4,6-Dinitroanthranil.

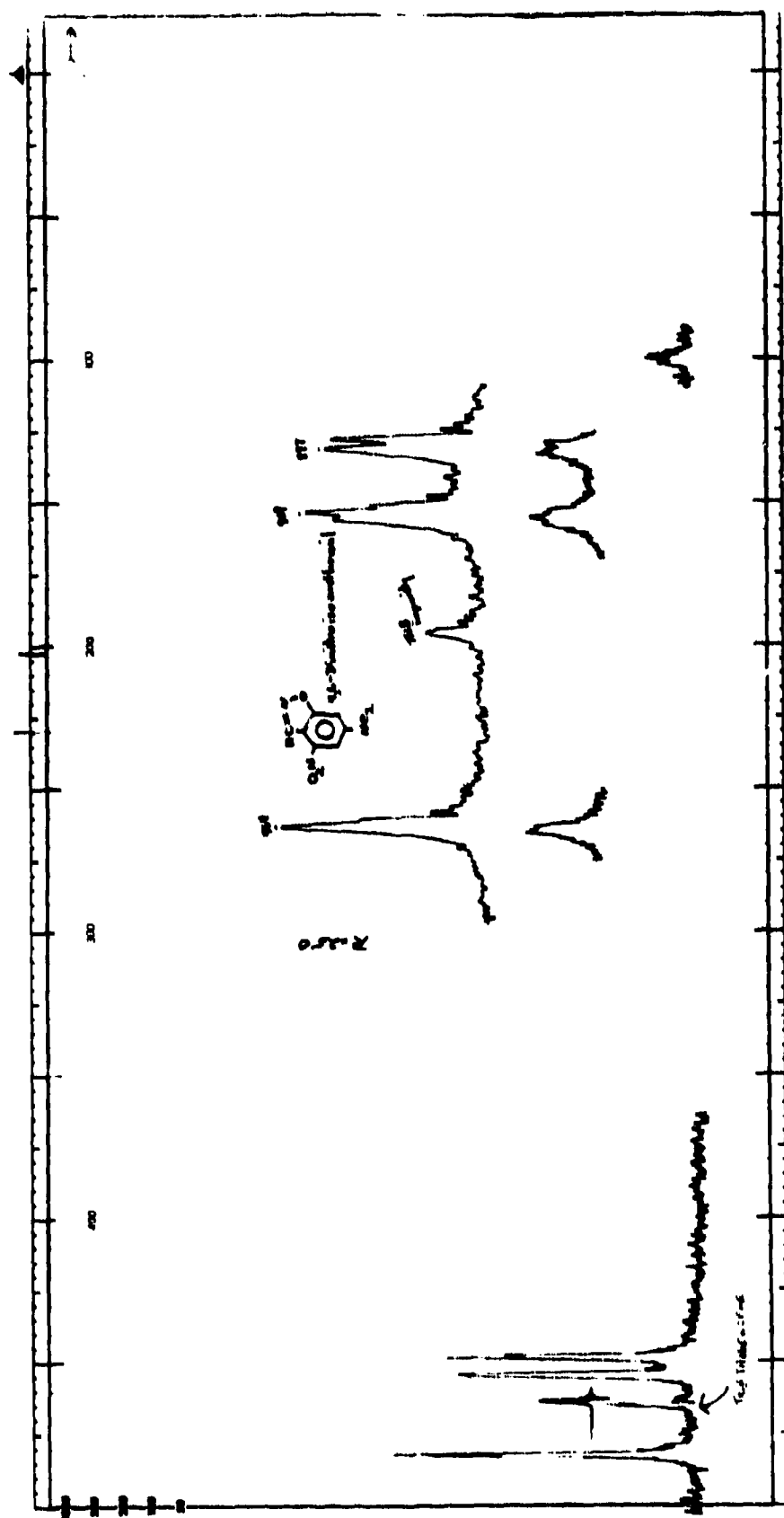
Irradiation of an aqueous solution of 4,6-dinitroanthranil with pyrex filtered light from a medium pressure Hg arc lamp gave about a 50% yield of an orange solid which separated out during the photolysis. The solid was recrystallized from benzene (see experimental) and identified by single crystal x-ray diffraction spectrometry to be 1,3,7,9-tetranitroindazolo[2,1-a]indazol-6-ol-12-one (a photo-dimer of the anil).

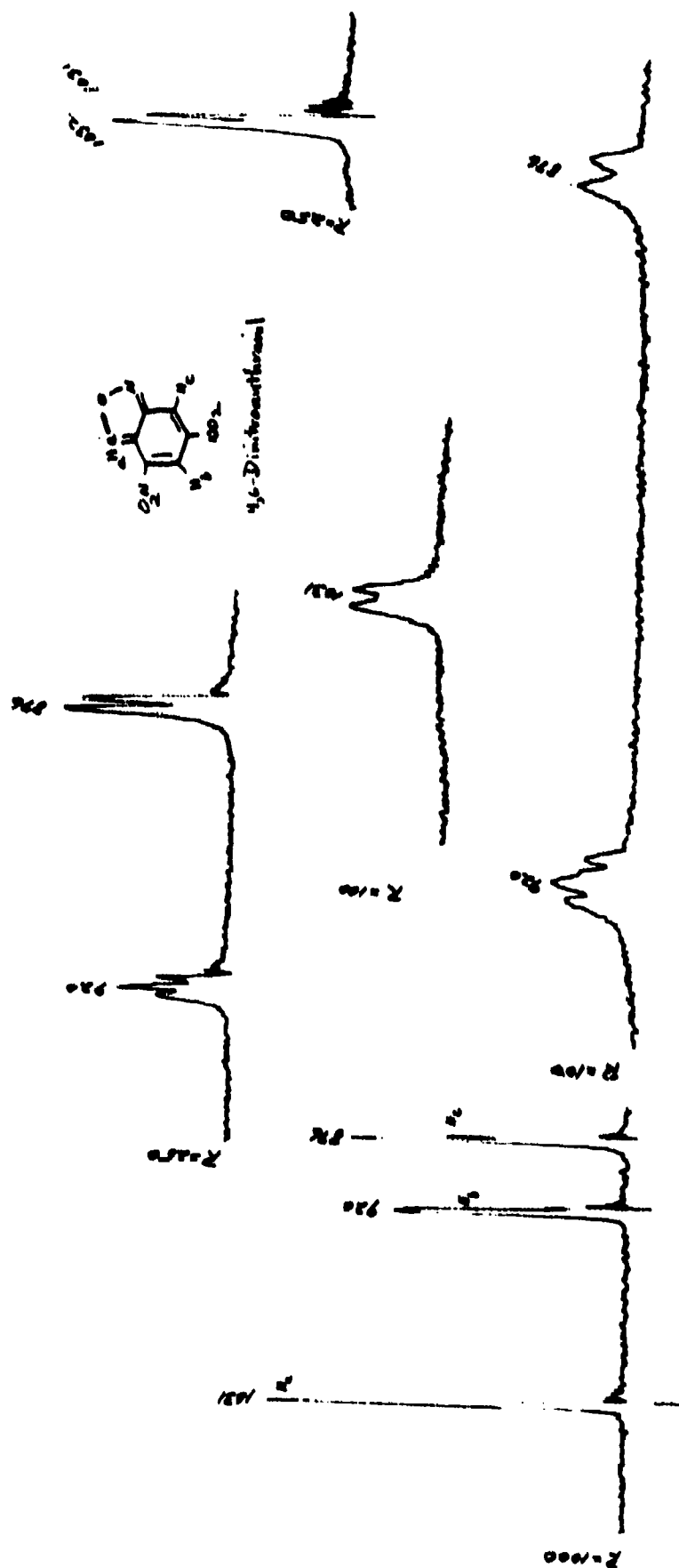


"Anil Photo Dimer"

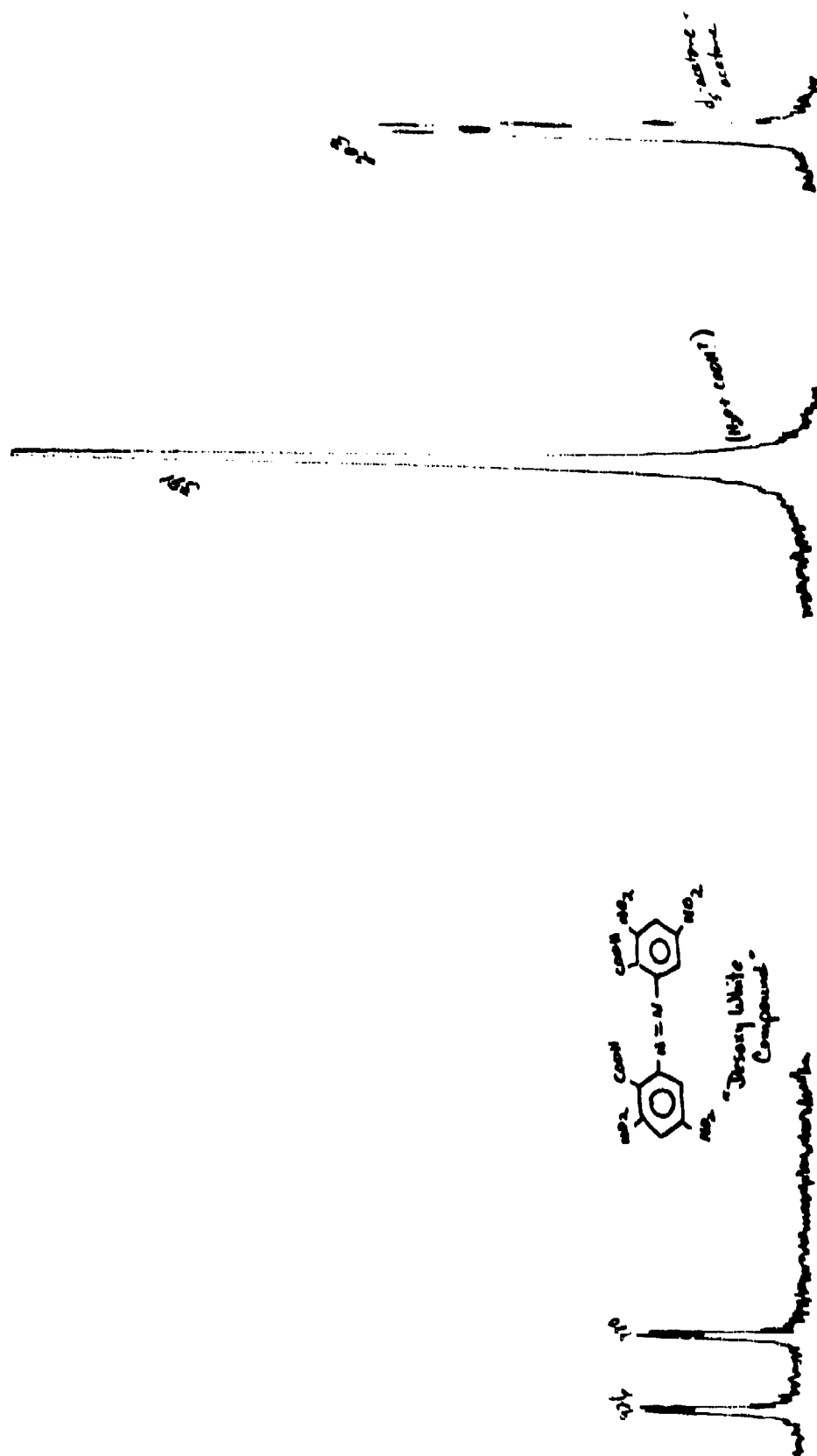
However, facile as this photo-dimerization appears, no dimer has been detected in "pink water."

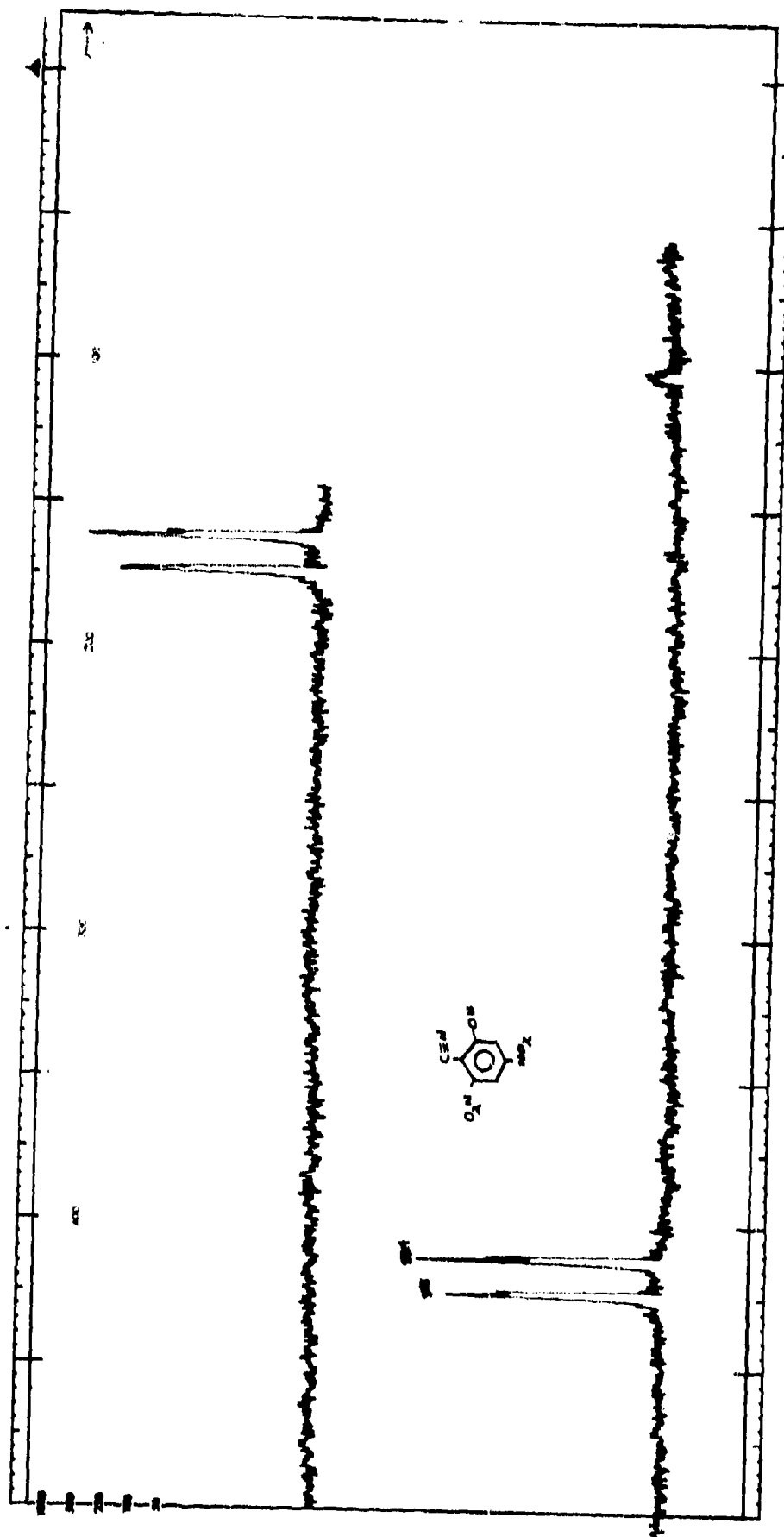
30. E. Bamberger, Chem. Ber., 51, 606 (1918).

NMR #1: 4,6-Dinitroisoanthranil in d_6 - acetone

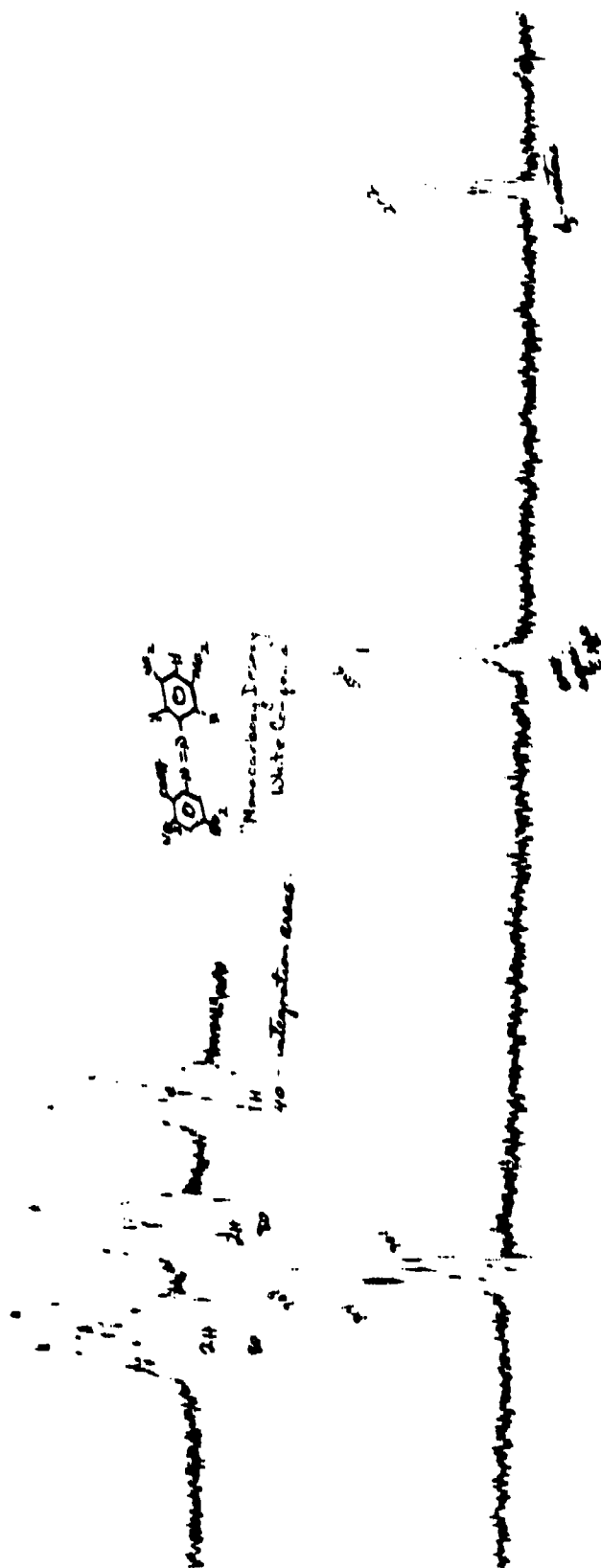
NMR #2: 4,6-Dinitroanthranil in d_6 - acetone

NMR #3: "Desoxy White Compound" in d_6 - acetone

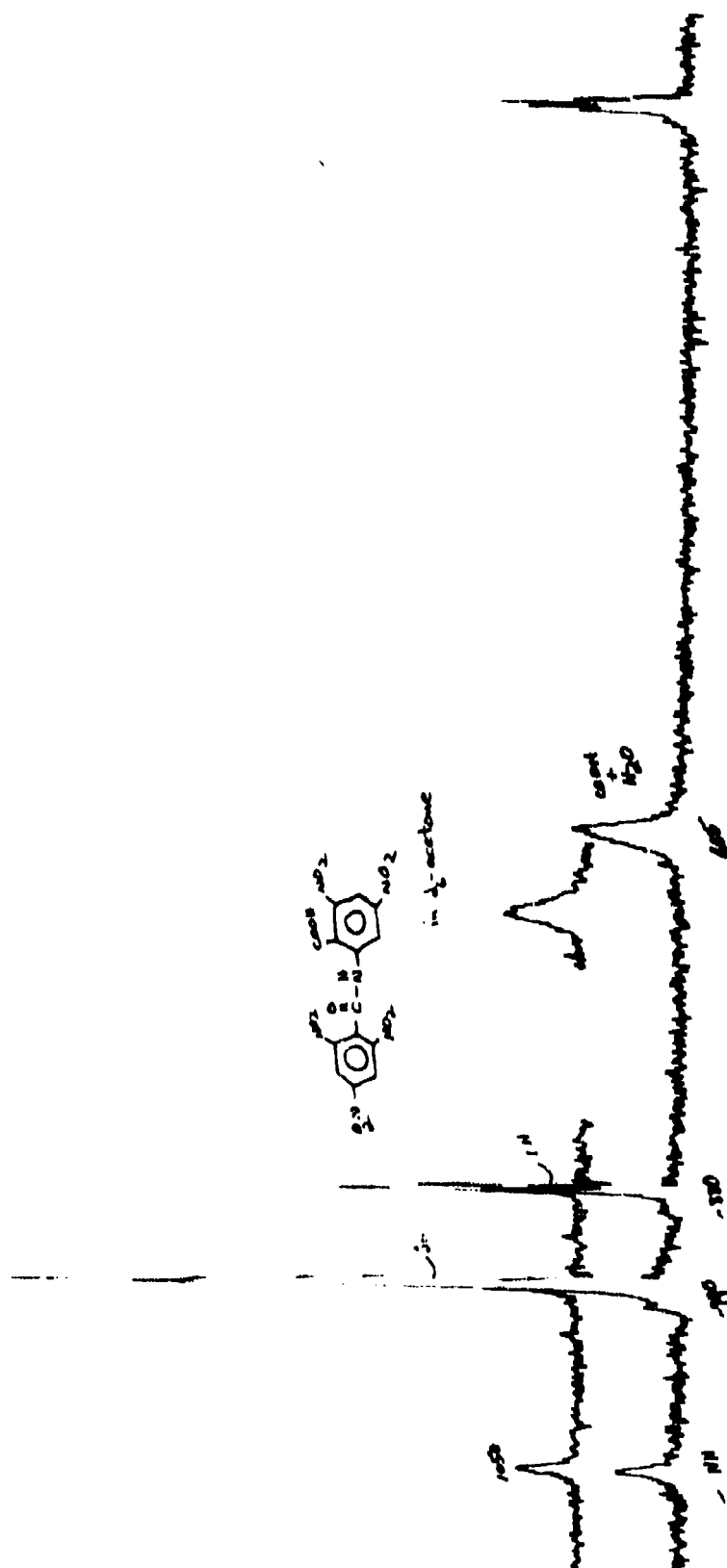


NMR #4: 2-hydroxy-4,6-dinitrobenzonitrile II in d_6 - acetone

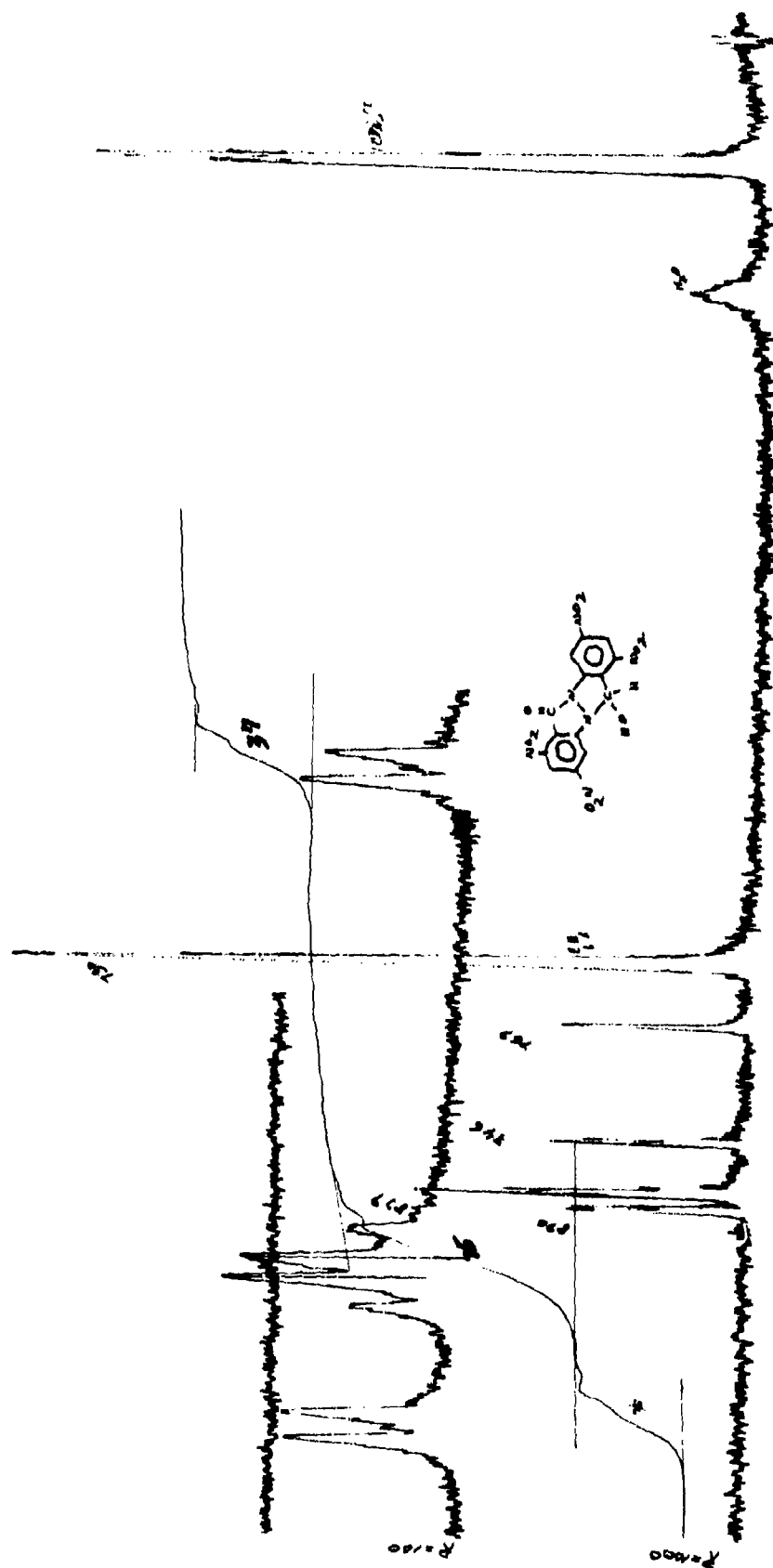
NMR #5: "Monocarboxy Desoxy White Compound" in d_6 - acetone



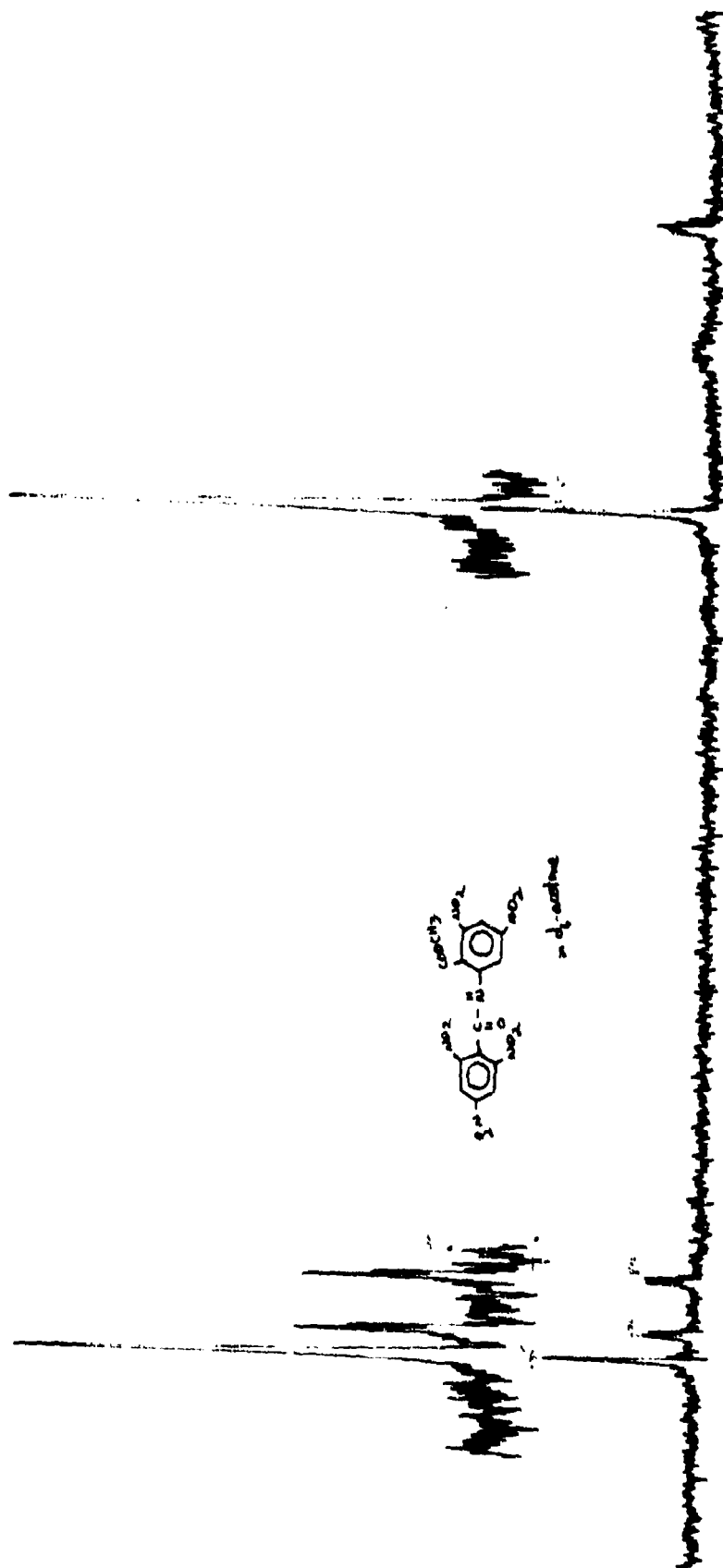
NMR #6: N-(2-carboxy-3,5-dinitrophenyl)-2,4,6-trinitrobenzamide XIII

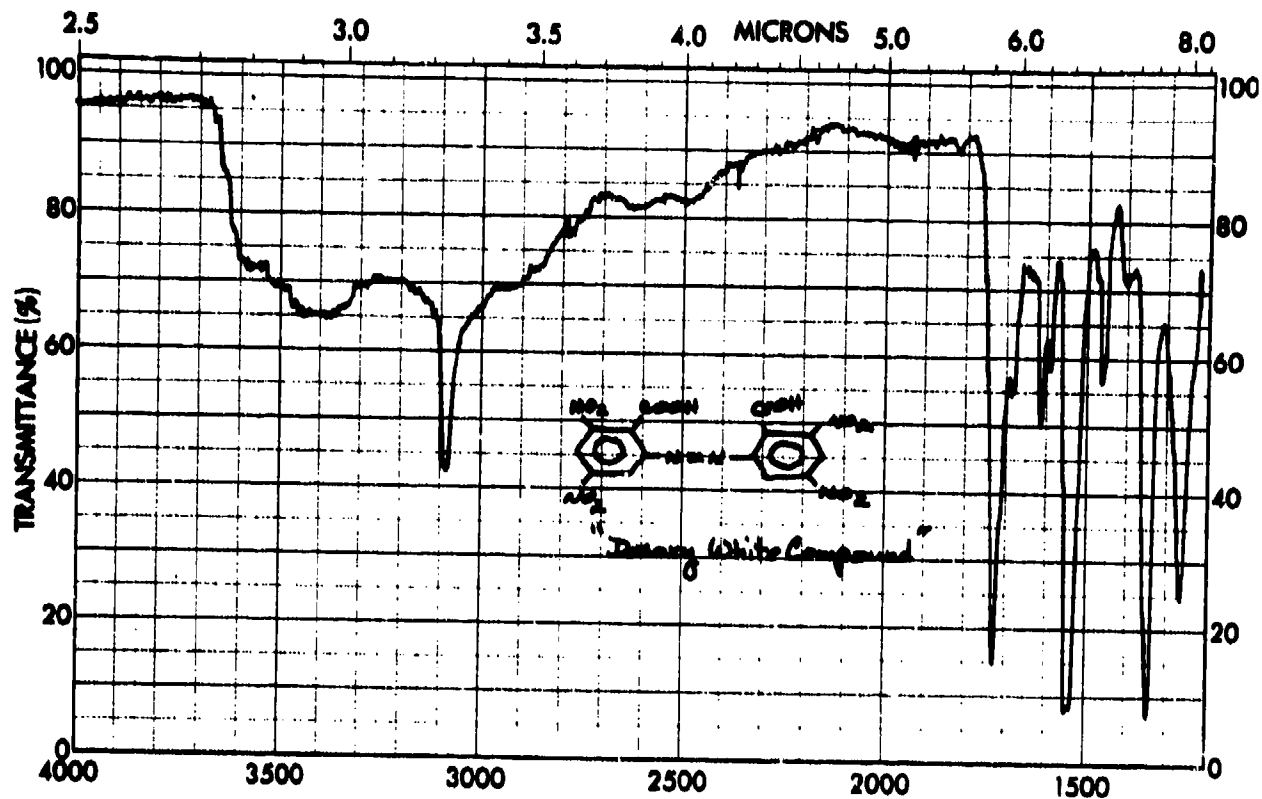


NMR #7: 1,3,7,9-tetranitorindazolo[2,1-a]indazol-6-ol-12-one (photodimer of anil)

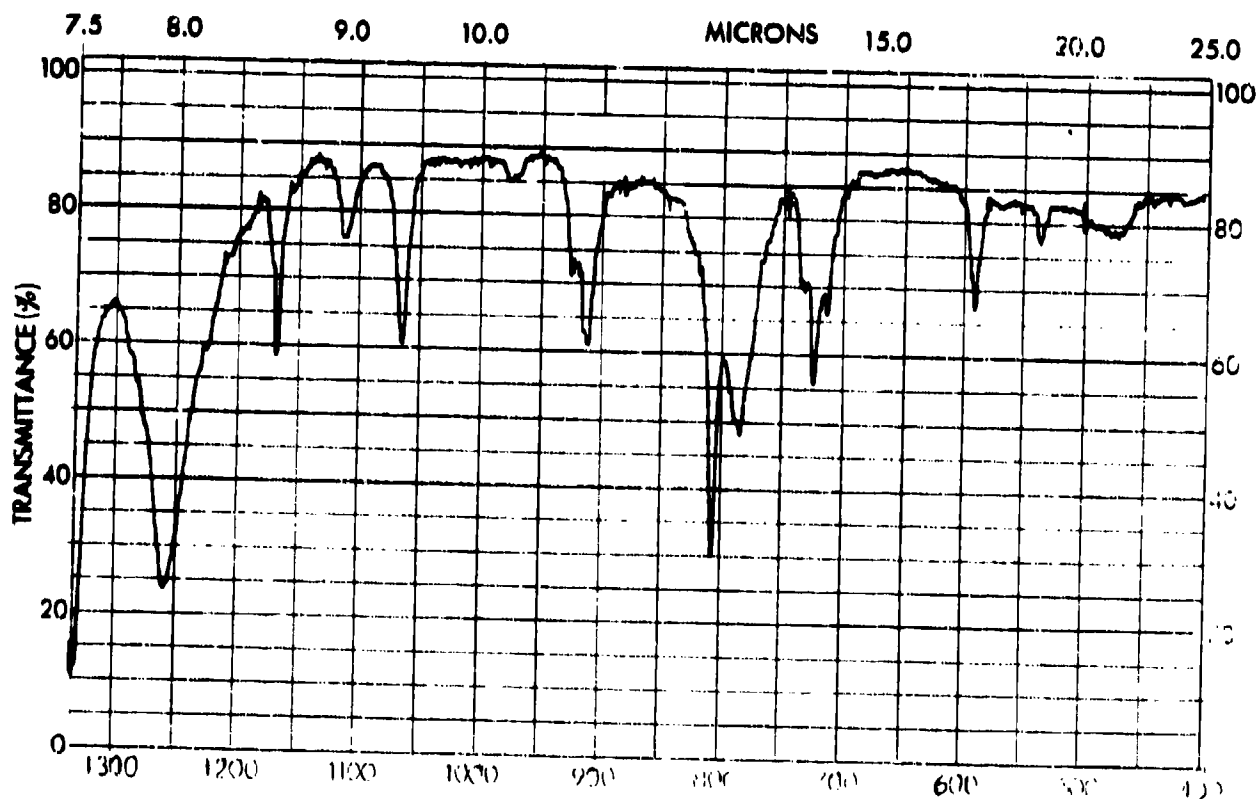


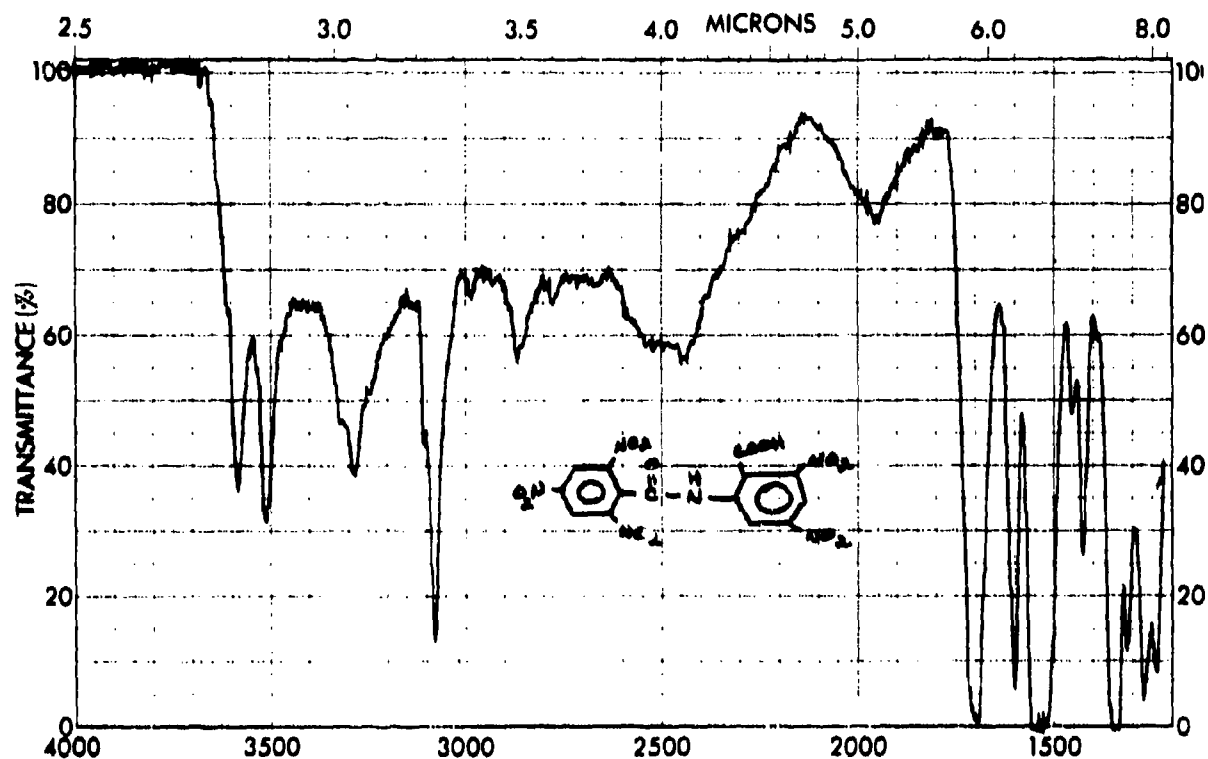
NMR #8: N-(2-carbomethoxy-3,5-dinitrophenyl)-2,4,6-trinitrobenzamide



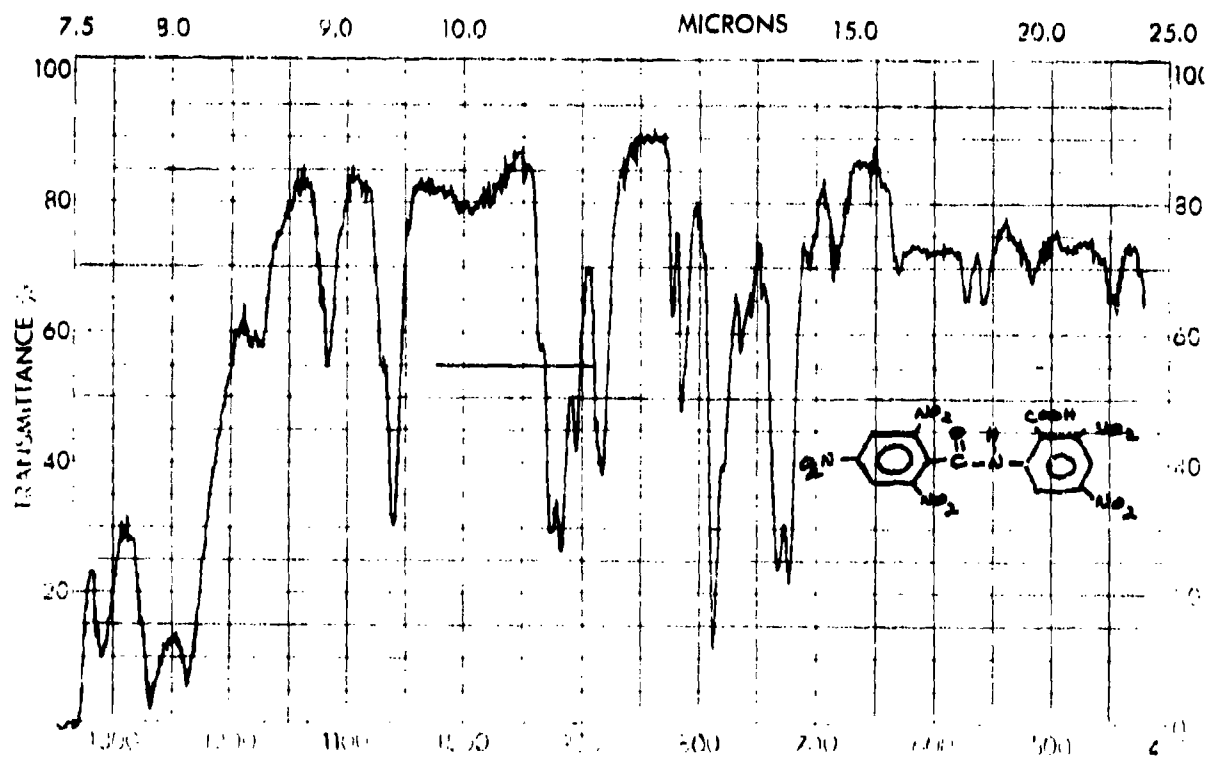


IR #1: "Desoxy White Compound" XI

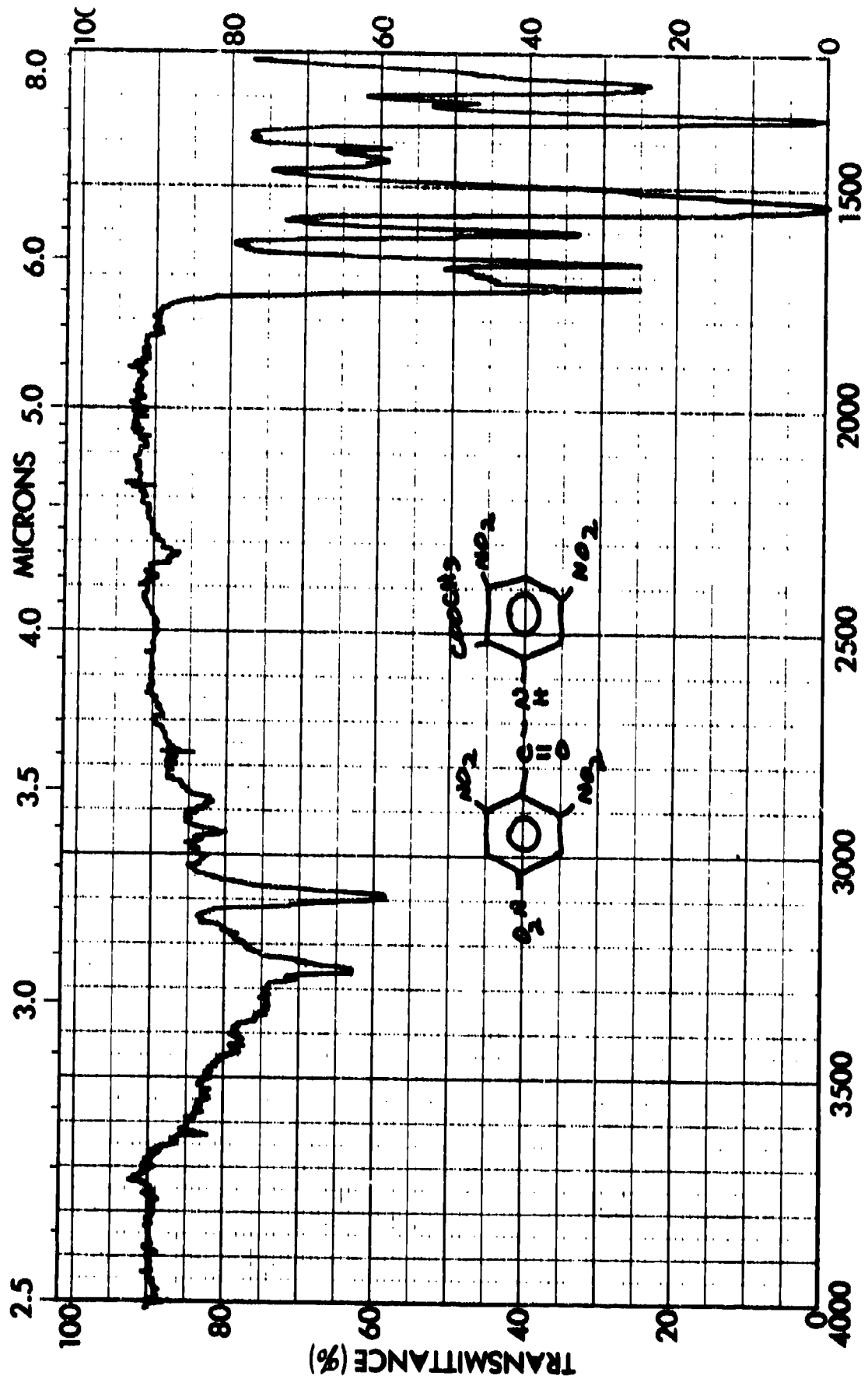


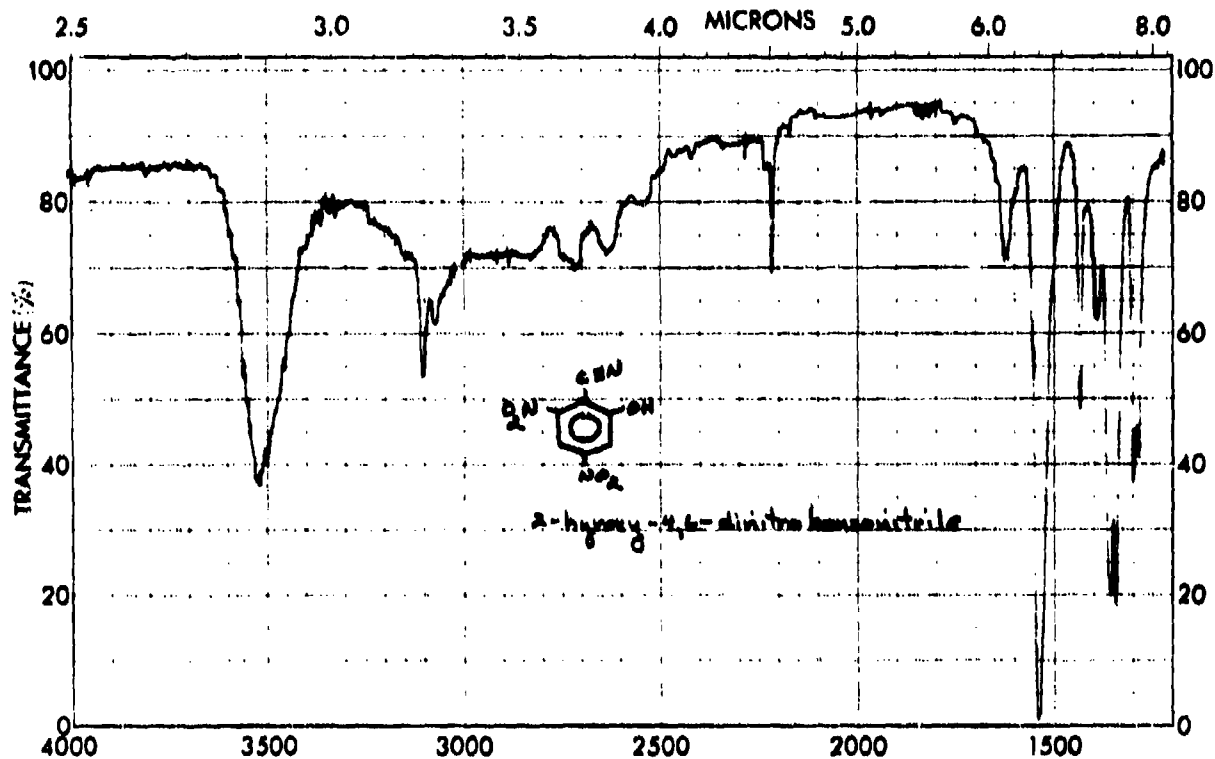


IR #2: N-(2-carboxy-3,5-dinitrophenyl)-2,4,6-trinitrobenzamide,
XIII



IR #3: N-(2-carbomethoxy-3,5-dinitrophenyl)-2,4,6-trinitrobenzamide





IR #4: 2-hydroxy-4,6-Dinitrobenzonitrile II

