

# HUGHES AIRCRAFT COMPANY

CULVER CITY  
CALIFORNIA

## SYNTHESIS OF TEREPHTHALONITRILE

### N,N'-DIOXIDE

(NASA-CR-114705) SYNTHESIS OF  
TEREPHTHALONITRILE N,N-DIOXIDE Final  
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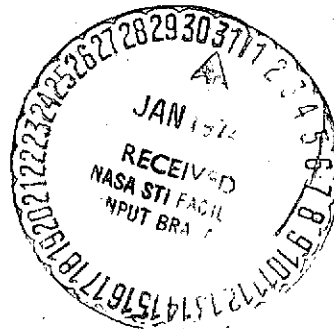
By

K. E. Van Buren

FINAL REPORT

Contract No. NAS 2-7831

December, 1973



National Aeronautics and Space Administration

Moffett Field, California 94035

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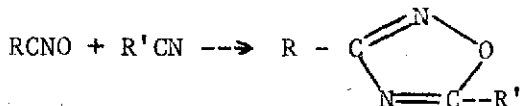
I. FORWARD

This report summarizes work performed under NASA contract NAS 2-7831 and covers the period 11 September 1973 through 31 December 1973. The program entitled, "Synthesis of Terephthalonitrile N,N'-Dioxide," involved the synthesis of 500 g of terephthalonitrile N,N'-dioxide for Dr. Robert Rosser, NASA Chemical Research Projects Office. The TPNO was synthesized by Miss Kathryn E. Van Buren by the method of Dr. Norman Bilow and Dr. A. L. Landis. Assistance was provided by Mr. John Steigleder and Miss Rebecca M. Abrams.

This work was performed in the Materials and Processes Laboratory, which is under the management of Mr. L. B. Keller.

INTRODUCTION

Interest in terephthalonitrile N,N'-dioxide, one of the few relatively stable dinitrile oxides, has increased since it was first synthesized in 1962. The nitrile oxide moiety is capable of undergoing 1,3-dipolar irreversible Diels-Alder type reactions with an acetylene or nitrile electron system to produce a ring structure with very good thermal stability. Nitrile oxides have been coupled with nitriles to yield the 1,2,4-oxadiazole ring.

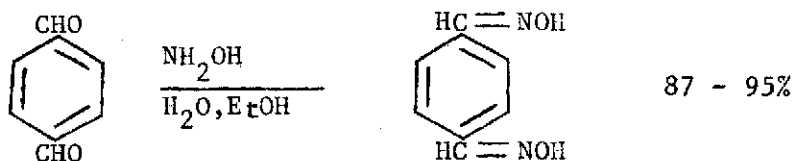


This indicates that a difunctional nitrile oxide can be used in producing under mild conditions polymers with a high degree of thermal stability. Work of this nature has been carried out at Hughes Aircraft Company<sup>1</sup>, as well as by Overberger and Fujimoto<sup>2</sup> and by Akiyama<sup>3</sup>.

Since the potential of TPNO as a crosslinking agent is so great, a patent disclosure (Hughes Patent Disclosure No. PD-72259) has been filed on an improved process developed at Hughes for its synthesis.

WORK PERFORMED UNDER THE CONTRACT

This three-step synthesis of TPNO started with a commercially available dialdehyde, terephthalaldehyde. This was converted to its dioxime.



The dioxime produced was considered pure enough to be used in the next step without being recrystallized.

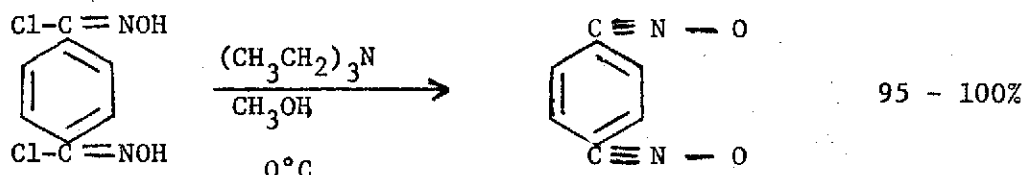
Chlorination of the dioxime to yield the hydroximoyl chloride had previously been carried out at low temperatures in carbon tetrachloride. Substitution of nitrobenzene for carbon tetrachloride increases the yield and produces a relatively pure chloride under room temperature conditions.



The hydroximoyl chloride had to be very well purified before it was dehydrochlorinated to TPNO because of the difficulty of purifying the TPNO. The chloride decomposes in many solvents, but is stable in benzene. Its limited

solubility in benzene requires that it must be recrystallized in very small amounts. This tedious recrystallization must be carried out, however, to yield a high quality product.

TPNO is insoluble in most solvents, and decomposes and dimerizes rapidly when heated. The TPNO must be handled quickly in the cold and contact with solvent avoided. The reaction itself is carried out in dilute solution at 0°C.



#### SYNTHESIS PROCEDURES

##### H1060-02 Terephthaldehyde Dioxime

A solution of 8.15 moles hydroxylamine in water was made by dissolving 570 g hydroxylamine hydrochloride and 320 g sodium hydroxide in 3600 ml distilled water. This was added all at once to 504 g (3.7 moles) terephthalaldehyde in 4000 ml absolute ethanol. The mixture was stirred vigorously. Its temperature reached a maximum of 52°C. The solution pH was maintained at 7 by addition of HCl. After stirring overnight, the mixture was filtered and washed with distilled water, then ethanol. The product was dried and used without further purification. The yield was 531.6 g or 87%.

H1060-08 Terephthalaldehyde Dioxime

An aqueous solution of hydroxylamine was made by dissolving 785 g (11.2 mole) hydroxylamine hydrochloride and 439 g sodium hydroxide in 4000 ml distilled water. It was added all at once to 693 g (5.1 mole) terephthalaldehyde in 5500 ml absolute ethanol. The mixture was allowed to stir without external heating. The maximum temperature was 72°C. After overnight stirring the reaction mixture was filtered. The crude product was washed with distilled water and ethanol, then dried and used without further purification. The yield was 924 g or 106%, indicating that the crystals were still wet.

H1060-03 Terephthalohydroximoyl Chloride

A slurry of 531.6 g (3.24 moles) terephthalaldehyde dioxime was made in 2000 ml nitrobenzene. The slurry was stirred while chlorine gas was bubbled through it. Effluent gases were passed through a sodium hydroxide trap. The mixture was kept near ambient temperature with an ice bath. Chlorination proceeded for a total of 9-1/2 hours, until the product appeared white. The solid was filtered out and washed thoroughly with  $\text{CCl}_4$ , then dried under vacuum. This yielded 549 g, or 70% yield, of unpurified product.

The purification procedure involved recrystallization of small batches of chloride in large amounts of benzene. The proportions ranged from 5 to 20 g chloride per 4000 ml benzene. The addition of charcoal before filtration improved the color and appearance of the product.

H1060-14 Terephthalohydroximoyl Chloride

Terephthalaldehyde dioxime, 423 g (2.58 mole) was slurried with about 2000 ml nitrobenzene. The mixture temperature was kept near 0°C with a dry

ice acetone bath while chlorine gas was bubbled through for 17 hours. No reaction appeared to have occurred. Chlorine gas was passed through for six hours, this time without external cooling. At the end of this time a white solid had formed. The product was filtered and washed with toluene, then dried in a vacuum oven. The toluene was difficult to pull off, so the solid was rewashed with  $\text{CCl}_4$  and redried. It was recrystallized in small batches, using either charcoal or Celite as a purifying agent.

In some cases, a slight impurity in the benzene gave the chloride a pale yellow cast, but infrared analysis showed this chloride to be identical to chloride with no yellow color present.

#### H1060-25 Terephthalonitrile N,N'-Dioxide

Terephthalohydroximoyl chloride (61 g, 0.26 mole) was added all at once to 3100 ml absolute methanol at  $-5^\circ\text{C}$ . Then 68 g, (0.67 mole) triethylamine in 300 ml absolute methanol was added dropwise with stirring over 35 minutes. The mixture was immediately filtered in the cold. The white solid was washed consecutively with methanol, distilled water, and methanol and dried at room temperature for 65 minutes. The yield was 40.0 g, 93%. The product was stored in a freezer.

#### H1060-45 Terephthalonitrile N,N'-Dioxide

Terephthalohydroximoyl chloride (64 g) was dissolved in 3300 ml absolute methanol at  $0^\circ\text{C}$ . Then 71 triethylamine in 300 ml absolute methanol was added dropwise with stirring over 40 minutes. The mixture was filtered and washed consecutively with methanol, distilled water, and methanol. The solid was dried at room temperature under vacuum for two hours. The yield was 45.2g, 100%. The product was stored in a freezer.

H1060-67 Terephthalonitrile N,N'-Dioxide

Terephthalohydroximoyl chloride, 60 g, was dissolved in 3100 ml absolute methanol at  $-10^{\circ}\text{C}$ . To this was added 68 g triethylamine in 300 ml absolute methanol. After 45 minutes addition was finished and the methanol was filtered off. The white product was washed consecutively with methanol, distilled water, and methanol. It was dried at room temperature under vacuum for 45 minutes. The yield was 40.0 g, 97%.

A total of 13 runs was made, accounting for 500 g of TPNO. Every batch of TPNO was milled gently in hydrocarbon oil for infrared analysis. Each spectrum showed the presence only of TPNO, with no starting material impurities or furoxan in evidence. In addition, its activity was monitored by deflagrating a small sample at  $140^{\circ}\text{C}$ . Each sample deflagrated.

Decomposition of the TPNO was prevented by storing it in the freezer and shipping it in dry ice. In this way homopolymerization to furoxan was avoided. Evidence for the absence of furoxan was the absence of an absorption at  $6.3\mu$  in the infrared.

The infrared spectra of terephthalaldehyde dioxime, terephthalohydroximoyl chloride (both water white and pale cream colored), TPNO, and TPNO which had homopolymerized, are included.

Sample Delivery

Five hundred grams of TPNO were shipped to Dr. R. Rosser of the Chemical Research Projects Office on the dates specified below. Also shown is the Hughes Shipper Number.

October 17	Shipper No. 31263	Weight 100 g
November 6	852252	150 g
December 11	852283	110 g
December 18	900107	145 g

REFERENCES

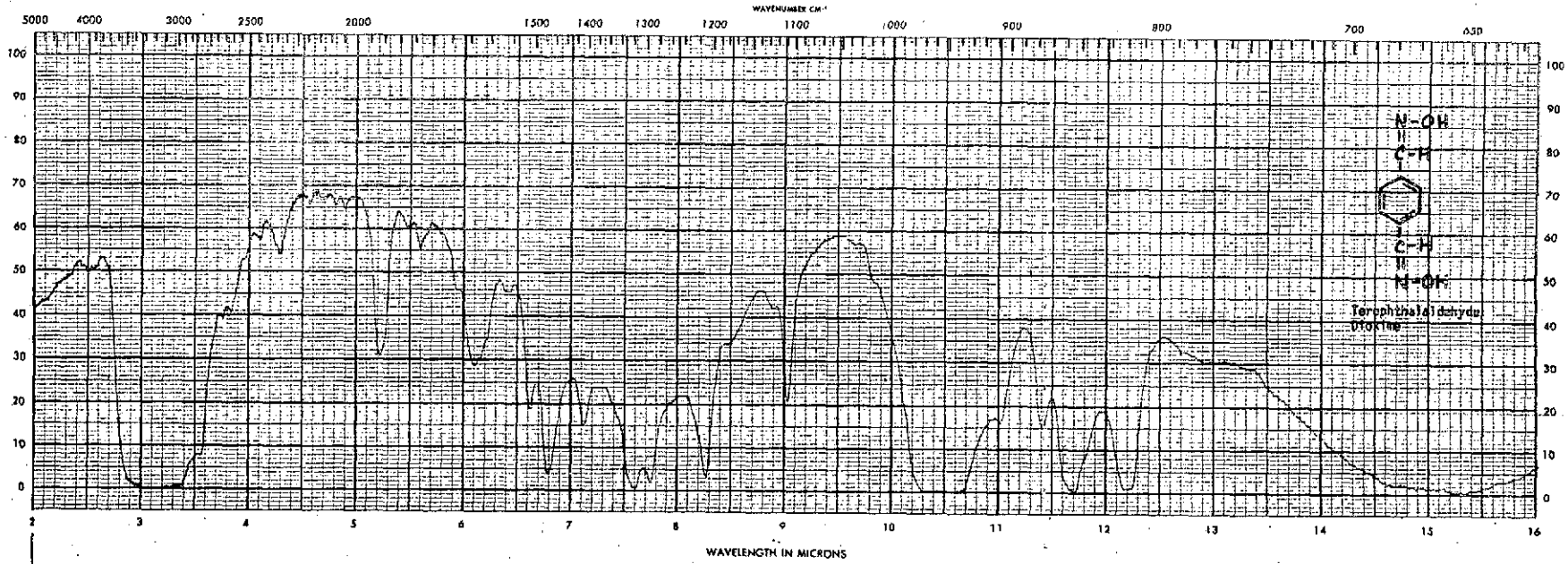
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2. Overberger, C. G., Fujimoto, S., J. Polymer Sci., Pt. B, 3(a), 735 (1965).
3. Akiyama, M., Iwakura, Y., Shiraisi, S., and Imai, Y., Polymer Letters, 4 305 (1966).



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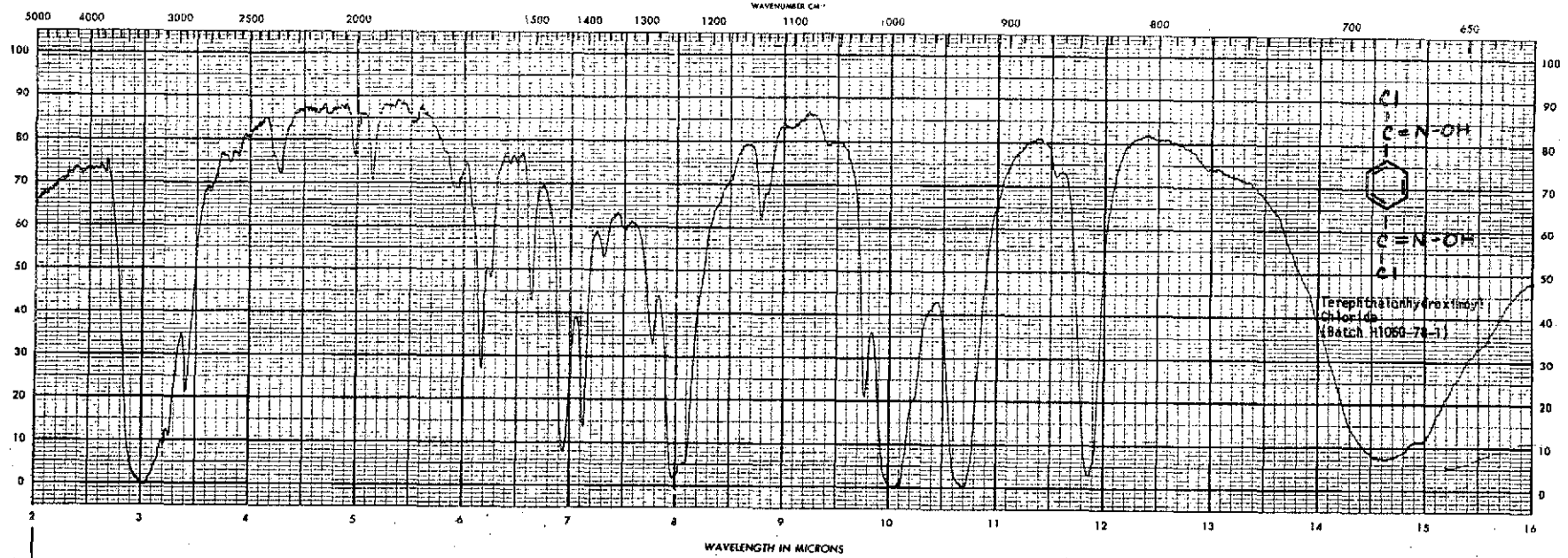


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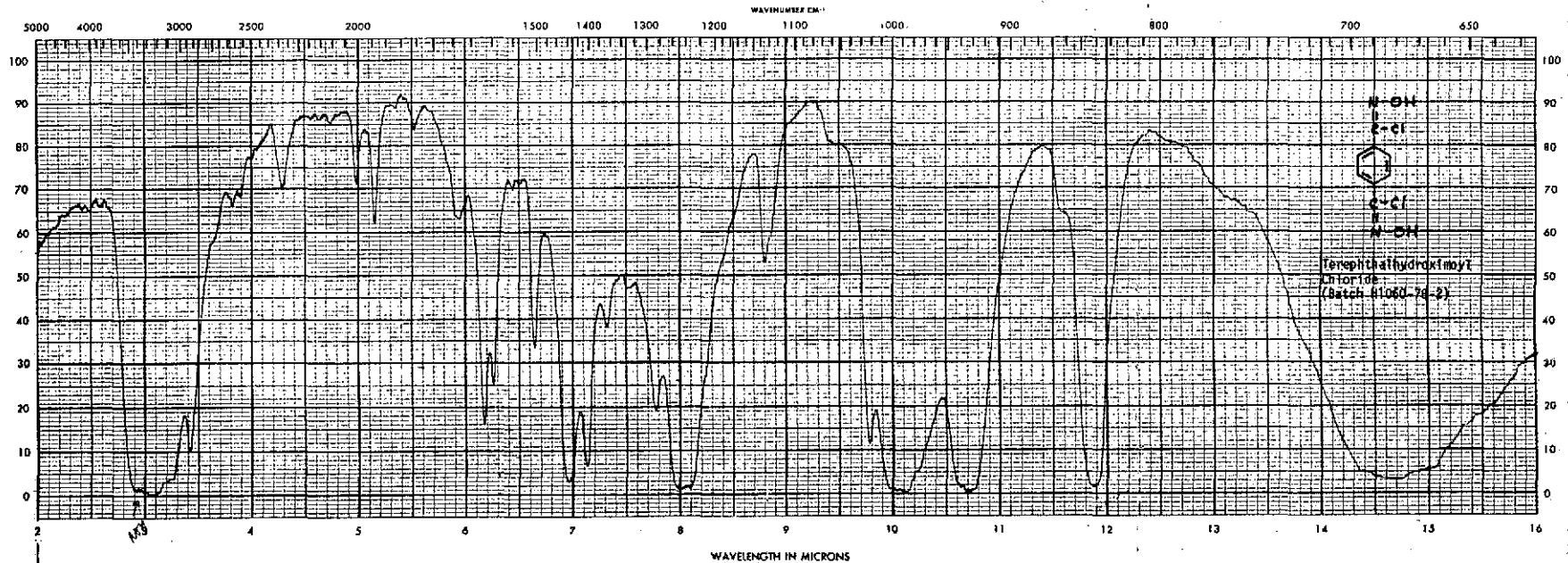
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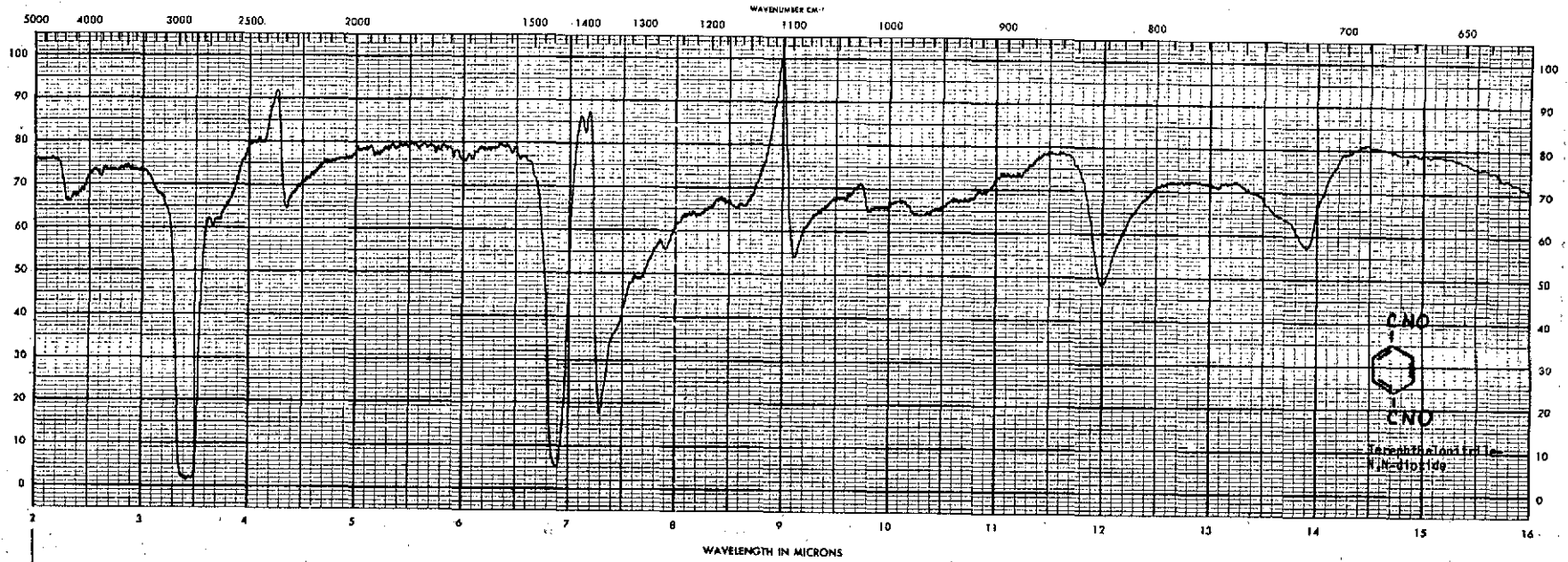
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