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SYNTHESIS OF (2-CYANOETHYL)-AMIDES FOR
APPLICATIONS IN GAS CHROMATOGRAPHY

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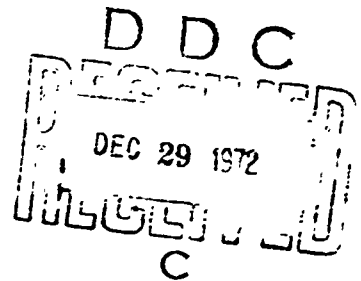
SYNTHESIS OF (2-CYANOETHYL)- AMIDES FOR APPLICATIONS IN GAS CHROMATOGRAPHY

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by

George E. Fodor

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ABSTRACT

Synthesis of several aliphatic and aromatic amides and diamides are described in this report. The compounds' infrared spectra are given. These are candidate compounds as high-temperature liquid phases to be used in gas chromatography for the class separation of aromatic and aliphatic hydrocarbon compounds.

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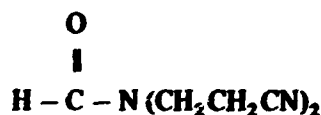
I. INTRODUCTION

Several cyanoethylated compounds have been prepared and their separating capability as liquid phases in gas chromatography studied.⁽¹⁻⁴⁾ Stavinocha and Newman⁽⁵⁾ use N,N-bis-(2-cyanoethyl)-formamide (I) as the precutting liquid phase for the isolation of aromatic hydrocarbons in the GC analysis of gasolines. Usefulness of (I) is limited to operations at or below 125°C for the separation of mixtures that do not contain alcohols, phenols, oxygen, or water. Use of new liquid phases having lower reactivity and volatility than (I) would reduce these limitations. This report describes the synthesis of several candidate compounds for this purpose; however, their GC application will be discussed elsewhere.

II. DISCUSSION

Since the interaction of (I) with aromatic hydrocarbons is not well understood, it was assumed that either the 2-cyanoethyl or the bis-(2-cyanoethyl)-amide groups are involved. It was further assumed that in (I) the formyl group is responsible for its relatively high hydrolytic and oxidative reactivity and should be eliminated.

Bis-(2-cyanoethyl)-amine (II) and tris-(2-cyanoethyl)-amine⁽⁶⁾ (III) were found to have negligible selectivity toward the isolation of aromatic hydrocarbons. Similar results were obtained with the commercially available⁽⁷⁾ p-[N,N-bis-(2-cyanoethyl)-amino]-benzaldehyde (IV) where the amino and formyl groups are separated by a phenylene ring.



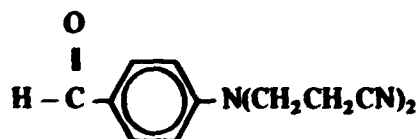
(I)



(II)

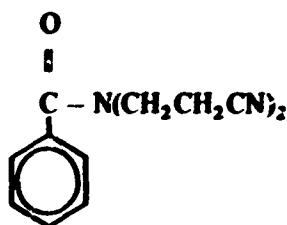


(III)

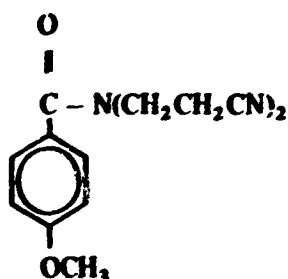


(IV)

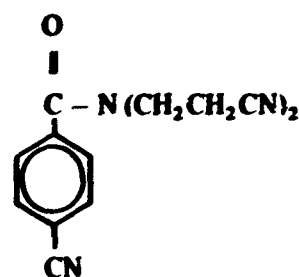
It appeared that the active site in (I) is the bis-(2-cyanoethyl)-amide group. Several mono- and diamides of this series were prepared and their ability to isolate aromatic hydrocarbons at elevated temperatures determined. To illustrate, syntheses of the following compounds are given: N,N-bis-(2-cyanoethyl)-benzoyl amide (V); 4-methoxy-N,N-bis-(2-cyanoethyl)-benzoyl amide (VI); 4-cyano-N,N-bis-(2-cyanoethyl)-benzoyl amide (VII); N,N'-tetra-(2-cyanoethyl)-oxalyl diamide (VIII) and N,N'-tetra-(2-cyanoethyl)-adipyl diamide (IX).



(V)



(VI)



(VII)

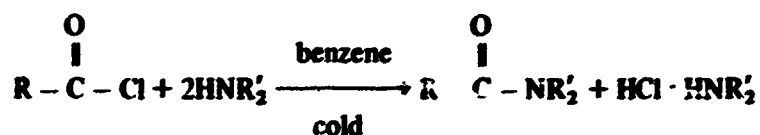


(VIII)



(IX)

Although a number of routes are available for the synthesis of amides⁽⁸⁻¹¹⁾, the most convenient route for this series of compounds was found to be a modified version of the method described by Maxim⁽¹²⁾:



Commercial acid chlorides were used, but usually after purification. Bis-(2-cyanoethyl)-amine was synthesized after Buc.⁽¹³⁾

III. EXPERIMENTAL

Melting points are uncorrected and were determined on a Fisher-Johns apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared absorption spectra were obtained on a Perkin-Elmer 621 in KBr discs containing approximately 2 mg of sample in 300 mg of KBr.

Reactions were carried out in a dry round-bottom three-neck flask, equipped with mechanical stirrer, pressure equalizing addition funnel, and reflux condenser. The system was pressurized to approximately 5 mm Hg with a dried, purified nitrogen atmosphere, and the flask was cooled in an ice-water bath. The acid chloride, dissolved in abs. benzene, was added dropwise to the vigorously stirred solution of bis-(2-cyanoethyl)-amine (II). Enough abs. benzene was used to allow efficient stirring. After the addition of the acid chloride solution, the reaction mixture was stirred for 1 hr and allowed to stand overnight. The solids were filtered on a No. 41 Whatman filter in a Büchner funnel, and purified by the appropriate workup, depending upon the solubility of the products. The amine hydrochloride was recovered from the aqueous washes.

N,N-bis-(2-cyanoethyl)-benzoyl amide (V). Redistilled benzoyl chloride (14.06 g, 0.10 mole) in 50 ml of abs. benzene was added over a 35-min period to 24.66 g (0.20 mole) of (II) in 100 ml of abs. benzene. In workup, the solids were washed with benzene and water, then dried by suction. The washed and dried solids were recrystallized from hot benzene to produce (V), mp. 112-113°C, Figure 1*, in nearly quantitative yield. *Analysis*: Calculated for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.77; N, 18.49. *Found*: C, 68.88; H, 5.91; N, 18.41.

4-methoxy-*N,N*-bis-(2-cyanoethyl)-benzoyl amide (VI). An abs. benzene (100 ml) solution of p-anisoyl chloride (17.06 g, 0.10 mole) was added over a 55-min period into 24.63 g (0.20 mole) of (II) in 200 ml of abs. benzene. The solid product was filtered and washed with water. The water insoluble precipitate was combined with the benzene solution and twice recrystallized from hot benzene to produce 22.59 g (87.8%) of (VI), mp. 107.5-108.5°C, Figure 2. *Analysis*: Calculated for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.88; N, 16.33; *Found*: C, 65.21; H, 5.70; N, 16.16.

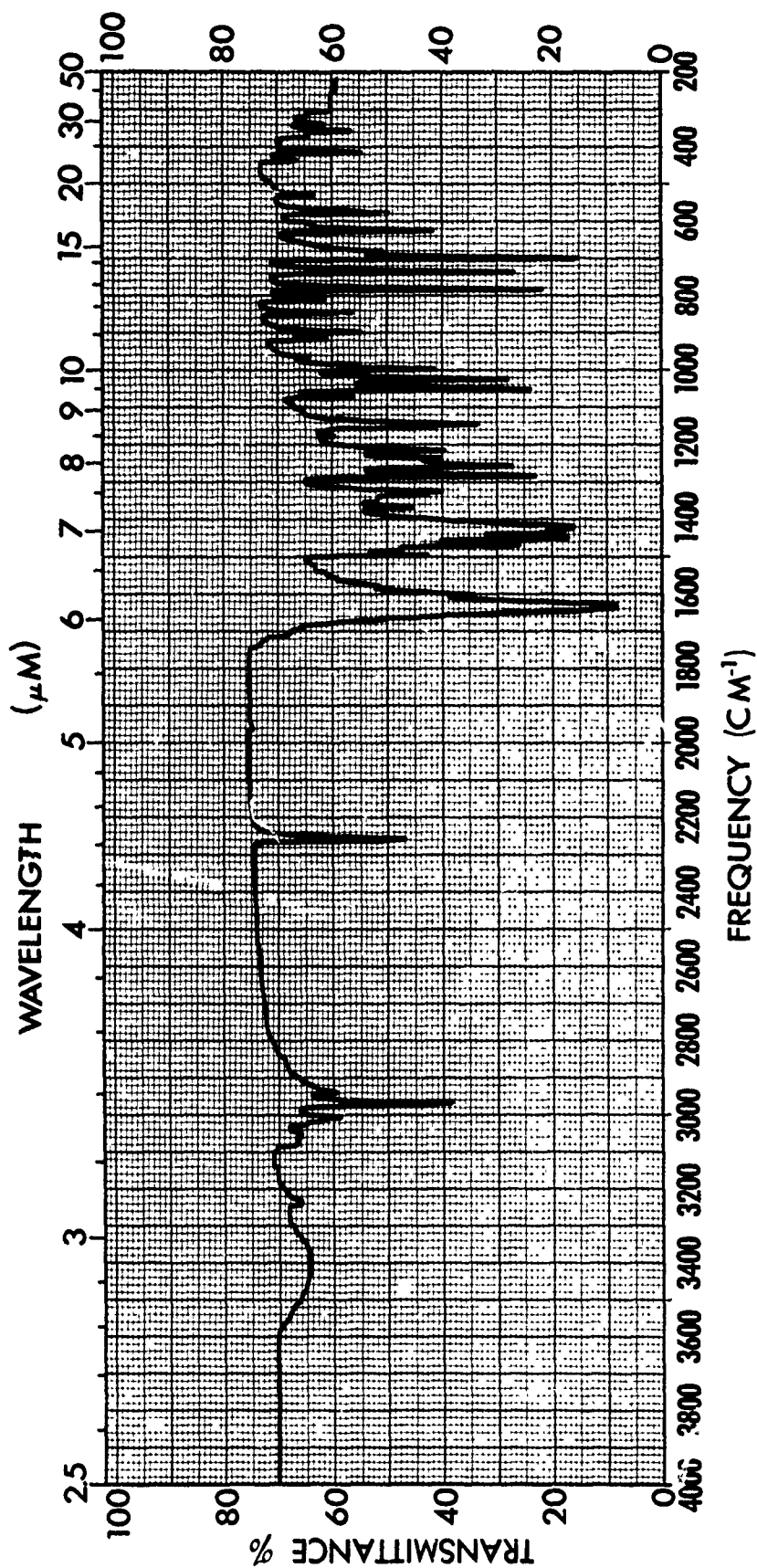
4-cyano-*N,N*-bis-(2-cyanoethyl)-benzoyl amide (VII). A solution of 4-cyanobenzoyl chloride (16.56 g, 0.1 mole) in 200 ml of abs. benzene was added over a period of 30 min into 24.63 g (0.2 mole) of (II) in 200 ml of abs. benzene. The benzene and water-washed precipitate was recrystallized from hot benzene. The product, 21.09 g (83.6%) had a melting point of 124.5-125.5°C, Figure 3. *Analysis*: Calculated for $C_{14}H_{13}N_4O$: C, 66.65; H, 4.80; N, 22.21. *Found*: C, 66.60; H, 4.77; N, 22.15.

N,N'-tetra-(2-cyanoethyl)-oxalyl diamide (VIII). A solution of oxalyl chloride (12.75 g, 0.10 mole) in 125 ml of abs. benzene was added over a 55-min period into 49.37 g

*Figures are located at the end of the text.

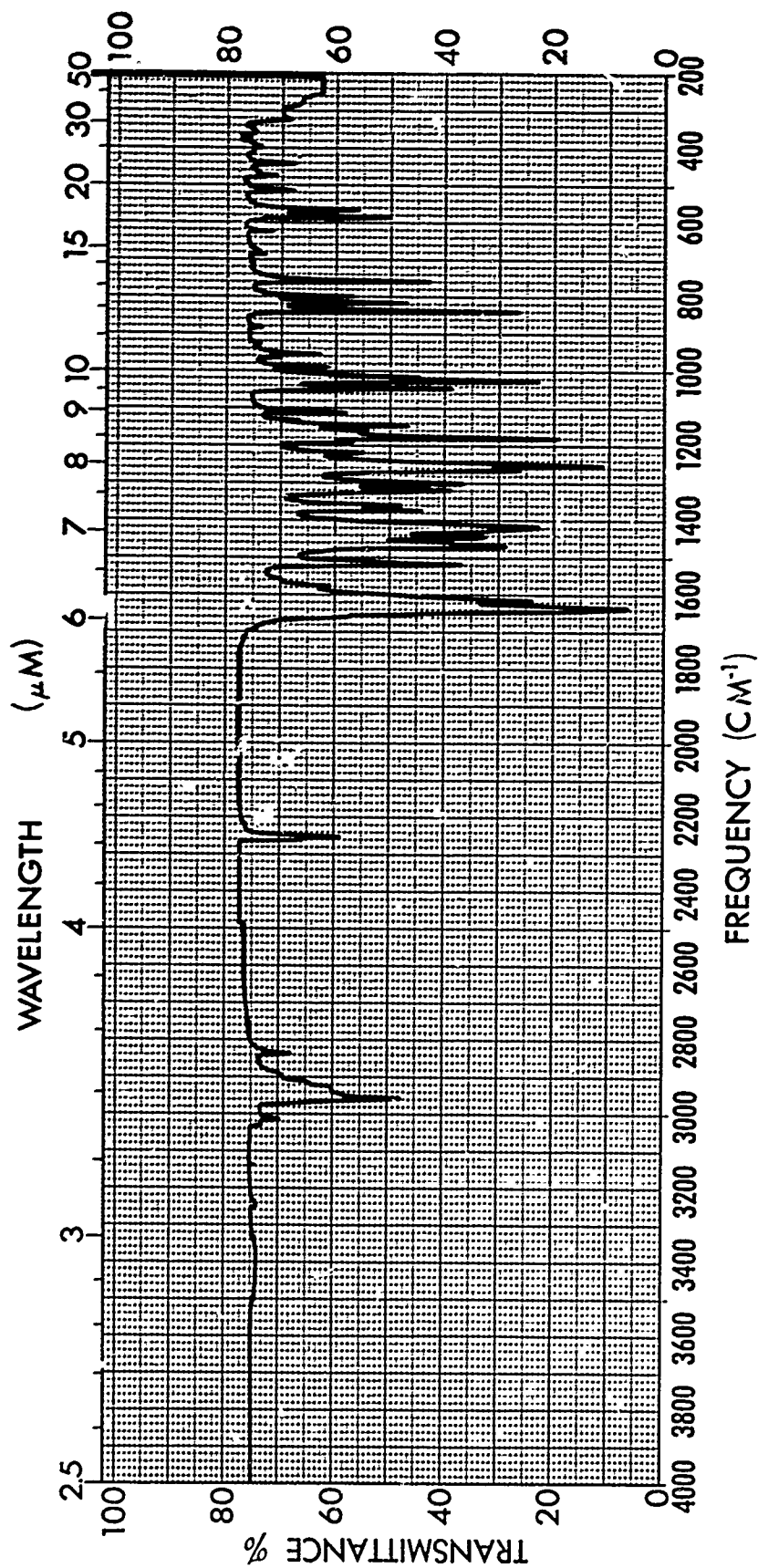
(0.40 mole) of (II) in 400 ml of abs. benzene. The filtered precipitate was washed with benzene and water. This crude product was placed in a large extraction thimble, covered with glass wool, and extracted several times with methanol in a Soxhlet extractor. From the methanolic solutions (VIII) crystallized as long, white needles, 29.42 g (98%), mp. 123-124.5°C. Figure 4. *Analysis*: Calculated for $C_{14}H_{16}N_6O_2$: C, 55.99; H, 5.37; N, 27.98. *Found*: C, 56.07; H, 5.38; N, 27.94.

N,N'-tetra-(2-cyanoethyl)-adipyl diamide (IX). Redistilled adipyl chloride (18.3 g, 0.10 mole) in 100 ml of abs. benzene was added in 100 min into 49.26 g (0.40 mole) of (II) in 400 ml of abs. benzene. The filtered precipitate was successively washed with benzene, water, methanol, and benzene. The crude product (35.4 g) was purified in a Soxhlet extractor (similarly to compound VIII) using methylene chloride as the solvent to give 33.27 g (93.3%) of (IX), mp. 134.5-135.5°C, Figure 5. *Analysis*: Calculated for $C_{18}H_{24}N_6O_2$: C, 60.65; H, 6.79; N, 23.58. *Found*: C, 60.54; H, 6.66; N, 23.40.



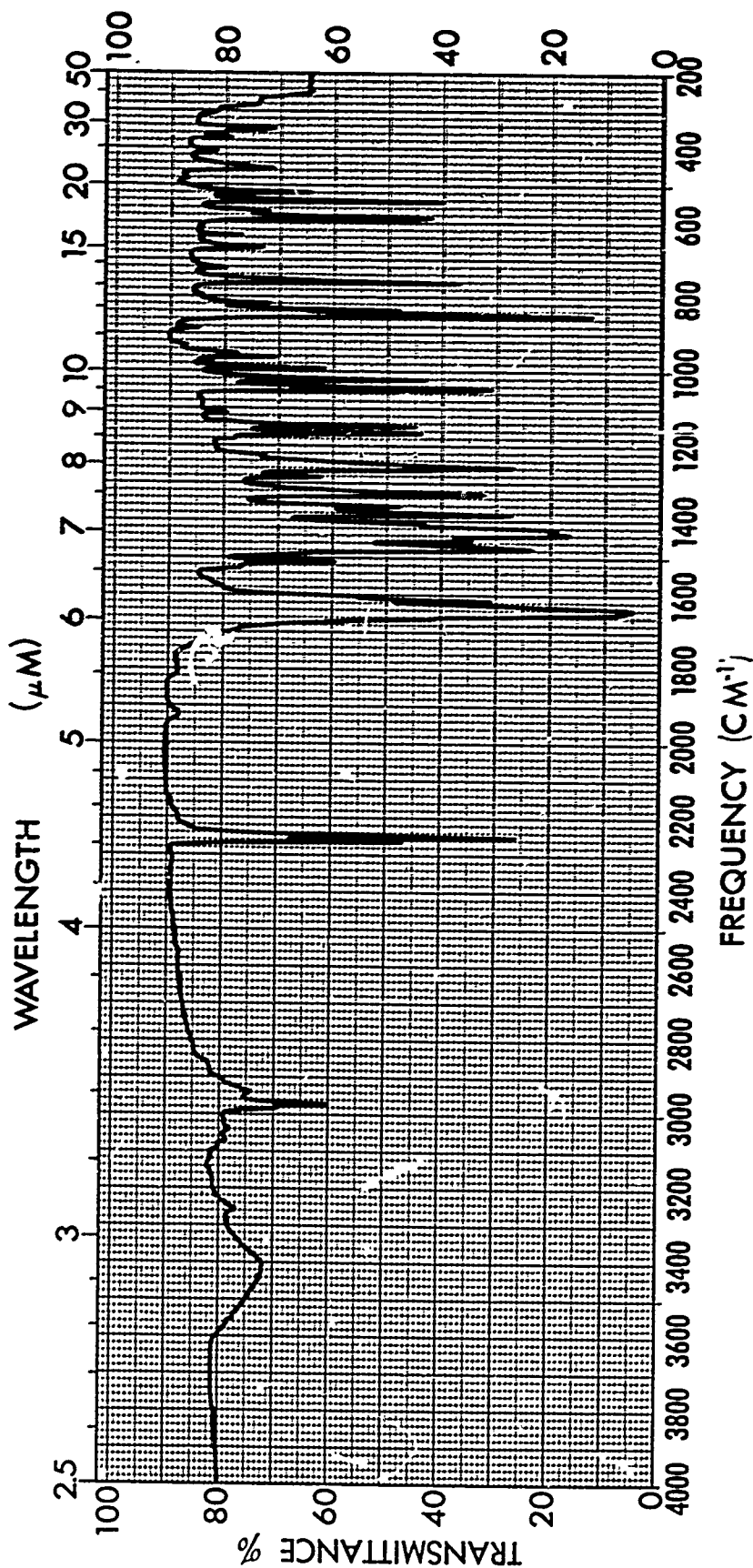
SPECTRUM NC 136.13	ORIGIN	LEGEND	REMARKS
SAMPLE N,N-BIS-		1.	
(2-CYANOETHYL)- BENZOYL	PURITY MP. 112-113°C	2.	<chem>O=C(NCC#N)c1ccccc1NCC#N</chem>
AMIDE	PHASE KBr DISC	DATE NOV. 1972	
	THICKNESS	OPERATOR D.C.B.	

FIGURE NO. 1. N,N-BIS-(2-CYANOETHYL)-BENZOYL AMIDE



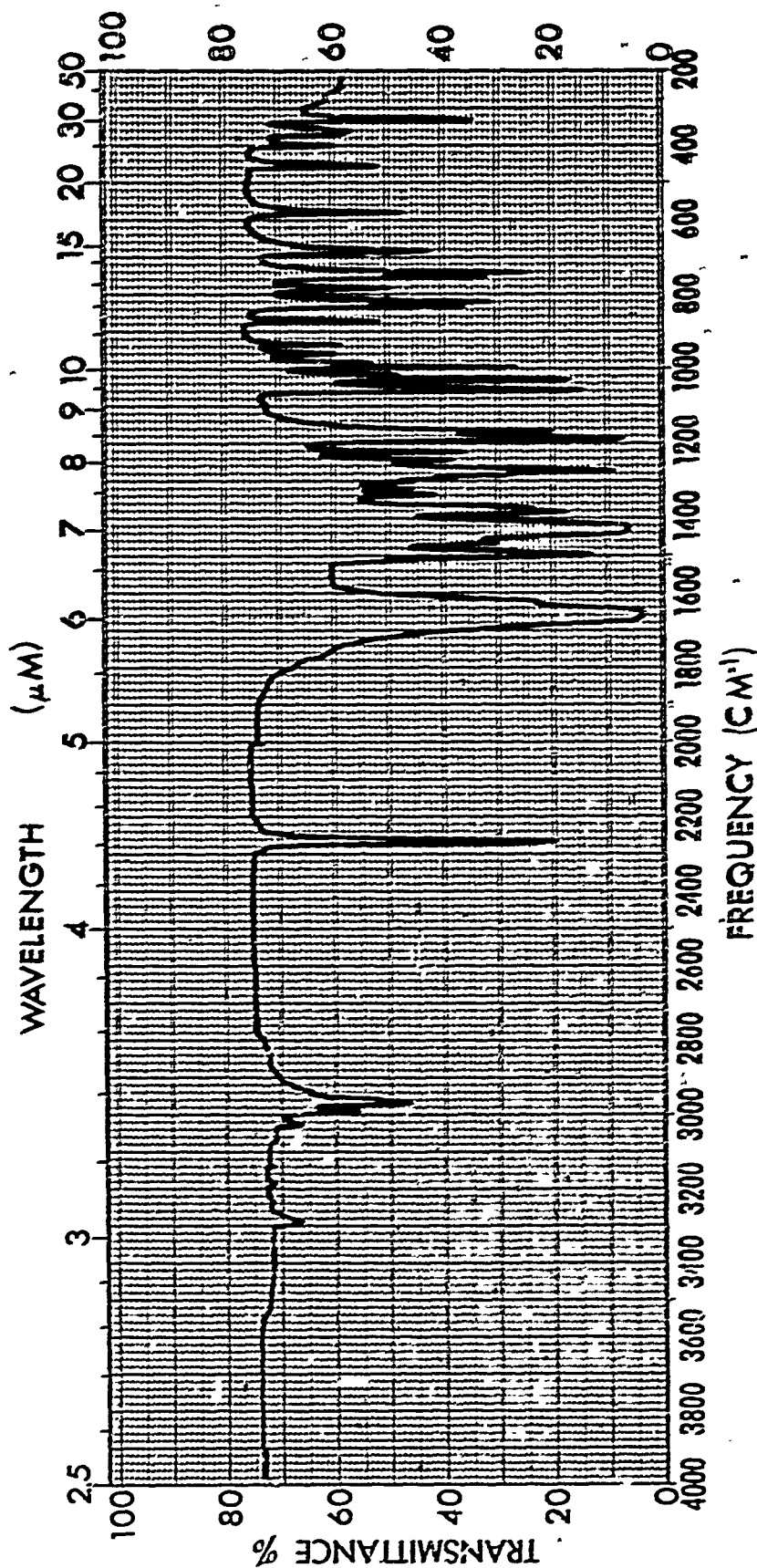
SPECTRUM NO. <u>144-6</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE <u>4-METHOXY-</u>	_____	1. _____	$\begin{array}{c} \text{O} \\ \\ \text{C} - \text{N}(\text{CH}_2\text{CH}_2\text{CN})_2 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{OCH}_3 \end{array}$
<u>N,N-BIS-(2-CYANOETHYL)-</u>	PURITY <u>M.P. 107.5-108.5°C</u>	2. _____	
<u>BENZOYL AMIDE</u>	PHASE <u>KBr DISC</u>	DATE <u>NOV. 1972</u>	_____
_____	THICKNESS _____	OPERATOR <u>D.C.B.</u>	_____

FIGURE NO. 2. 4-METHOXY-N,N-BIS-(2-CYANOETHYL)-BENZOYL AMIDE



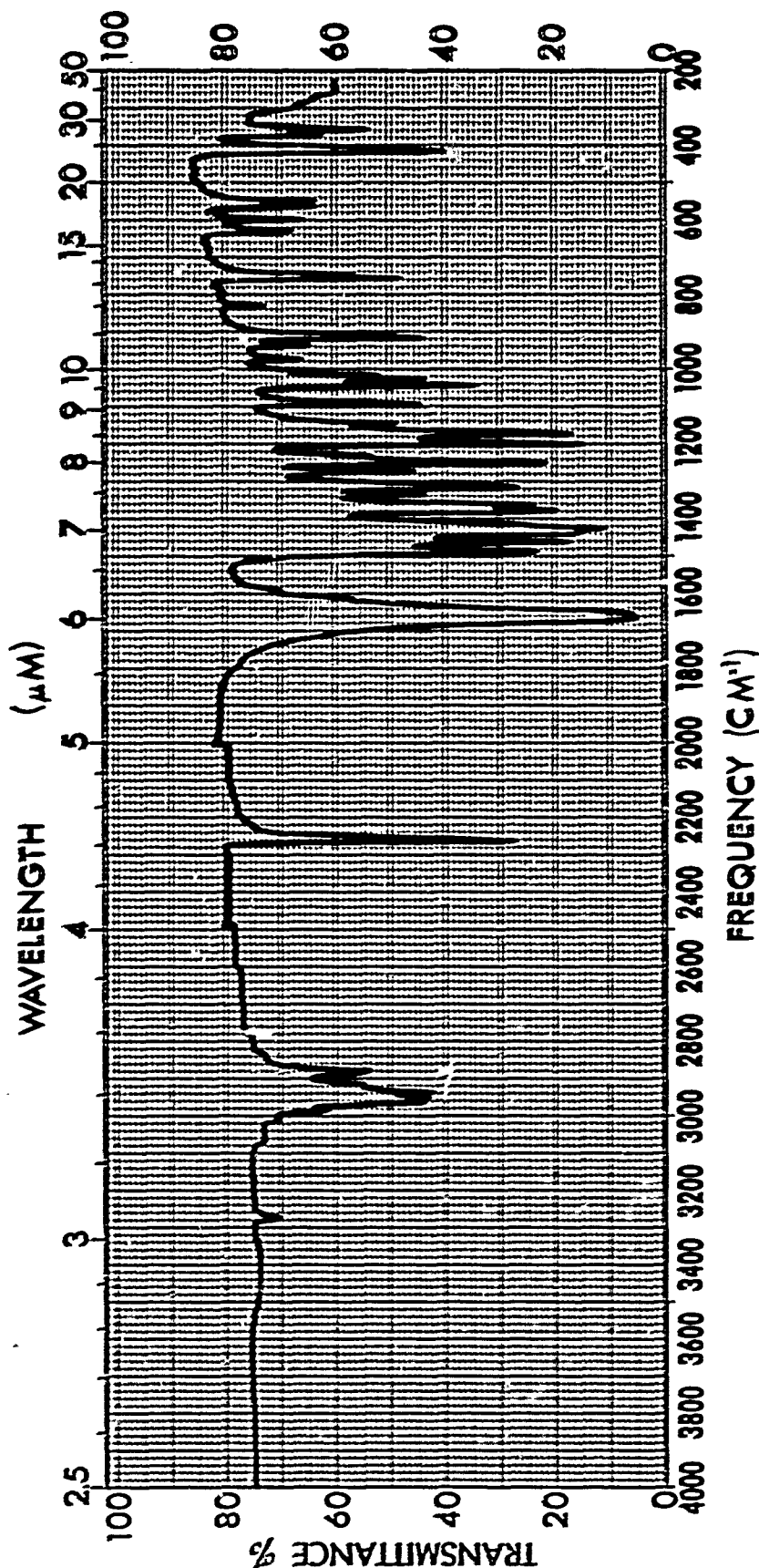
SPECTRUM NO. <u>145-2</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE <u>4-CYANO-</u>	_____	1. _____	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{N}(\text{CH}_2\text{CH}_2\text{CN})_2 \\ \\ \text{C}_6\text{H}_5 \\ \\ \text{CN} \end{array}$
<u>N,N-BIS-(2-CYANOETHYL)-</u>	_____	2. _____	
<u>BENZOYL AMIDE</u>	PURITY <u>M.P. 124.5-125.5°C</u>	DATE <u>NOV. 1972</u>	OPERATOR <u>D.C.B.</u>
	PHASE <u>KBr DISC</u>	THICKNESS _____	

FIGURE NO. 3. 4-CYANO-N,N-BIS-(2-CYANOETHYL)-BENZOYL AMIDE



SPECTRUM NO. 1003	ORIGIN	LEGEND	REMARKS
SAMPLE N.N'-TEL		1.	<chem>O=C(NC(=O)CC#N)CC#N</chem>
(2-CYANOETHYL)-OXALYL	PURITY M.P. 123-124.0°C	2.	<chem>O=C(NC(=O)CC#N)CC#N</chem>
DIAMIDE	PHASE KBr DISC	DATE NOV. 1972	
	THICKNESS	OPERATOR D.G.D.	

FIGURE NO. 4. N,N'-TEL (2-CYANOETHYL)-OXALYL DIAMIDE



SPECTRUM NO. <u>130-4</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE <u>N,N'-TETRA-</u>	_____	1. _____	_____
<u>(2-CYANOETHYL)-ADIPYL</u>	PURITY <u>M.P. 130.5-135.6°C</u>	2. _____	<u>β-NIG(1261126N)2</u>
DIAMIDE	PHASE <u>KBr DISC</u>	DATE <u>NOV. 1972</u>	<u>(6112)4</u>
	THICKNESS _____	OPERATOR <u>P.G.B.</u>	<u>α-NIG(1261126N)2</u>

FIGURE NO. 3, N,N'-TETRA-(2-CYANOETHYL)-ADIPYL DIAMIDE

ACKNOWLEDGMENT

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