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High Energy Plasticizers (U)

A.L. Rocklin

Shell Development Company
A Division of Shell Oil Company

Sponsoring Agency:
Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards Air Force Base, California
Air Force Systems Command, United States Air Force

Contract No. AF 04(611)-11537

Project No. 3148

Quarterly Report No. 9

April - June 1968

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HIGH ENERGY PLASTICIZERS (U)

Sponsoring Agency: Air Force Rocket Propulsion Laboratory
Research and Technology Division, Edwards, California
Air Force Systems Command, U.S.A.F.

Contract No. AF 04(611)-11537
AFFTC Project No. 3148
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SHELL DEVELOPMENT COMPANY
A Division of Shell Oil Company
Emeryville, California

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FOREWORD

(U) The work described in this report was authorized under AFFTC Project No. 3148, BPSN 623148. The contract project officer is 1 Lt. Curtis McDowell, Air Force Rocket Propulsion Laboratory, RPCS, Edwards, California.

(C) This report is Quarterly Report No. 9 on Contract AF 04(611)-11537 under which Shell Development Company, Emeryville, California, with United Technology Center, Sunnyvale, California as subcontractor will carry out a coordinated program to synthesize, evaluate and develop new energetic plasticizers for the high-energy difluoramino binder, P-BEP, and for nitrocellulose. This report describes the work carried out by Shell Development Company on the synthesis phase during the period April-June 1968.

(U) Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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CONFIDENTIAL ABSTRACT

(C) The energetic plasticizer Shell P722, 2,3-bis(difluoramino)propyl 2,2-dinitropropyl carbonate, shows excellent stability during prolonged heating. As determined by gas evolution, weight loss, and infrared analysis no significant change occurs after heating for 31 days at 90°C.

(C) An improved synthesis of the energetic plasticizer Shell P731, 4,4,4-trinitrobut-1-yl cyanoacetate, is based on the sodium borohydride reduction of trinitrobutyraldehyde to trinitrobutanol (TNBOH) in a water-benzene system followed by direct treatment of the benzene solution with cyanoacetic acid.

(C) Improvements in the synthesis of the energetic plasticizer Shell P831, 2-cyanoethyl 4,4,4-trinitrobut-1-yl carbonate, comprise the preparation of the intermediate trinitrobutyl chloroformate from crude TNBOH, and direct use of the chloroformate without purification.

(C) The new plasticizer candidate 2,3-bis(difluoramino)propyl 4,4,4-trinitrobut-1-yl carbonate was made in fair yield but could not be purified well.

(C) The compound bis(4,4,4-trinitrobut-1-yl) carbonate is a solid melting at 96°C.

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HIGH ENERGY PLASTICIZERS (U)

(C) Summary

(U) Continuation of the work on energetic plasticizers has included stability tests, improved syntheses, and development of new compounds.

(C) The energetic plasticizer Shell P722, 2,3-bis(difluoramino)propyl 2,2-dinitropropyl carbonate, has shown excellent thermal stability during a one-month test at 90°C. Quantitative infrared analysis showed no significant change in the carbonyl and nitro absorptions, nor were any new absorption bands detected. Gas evolution during the whole test period was less than 0.02 ml/g, and weight loss did not exceed 0.25%.

(C) The synthesis of the energetic plasticizer Shell P731, 4,4,4-trinitrobut-1-yl cyanoacetate, has been improved so as to maintain the organic materials in a single solvent, benzene, throughout most of the manipulations. Trinitrobutyraldehyde is reduced to 4,4,4-trinitrobutanol (TNBOH) in benzene phase by treatment with aqueous sodium borohydride solution then, after aqueous washing, the benzene solution of crude TNBOH is treated with cyanoacetic acid to produce high quality Shell P731.

(C) Good quality Shell P831, 2-cyanoethyl 4,4,4-trinitrobut-1-yl carbonate, can be made by converting unpurified TNBOH to the chloroformate followed by direct use of the crude chloroformate without first having to distill it.

(C) The new plasticizer candidate 2,3-bis(difluoramino)propyl 4,4,4-trinitrobut-1-yl carbonate was made in fair yield by N_2F_4 addition to the purified new intermediate allyl 4,4,4-trinitrobut-1-yl carbonate but purification attempts resulted in severe losses. Purity of the recovered material was about 96%.

(C) The new compound bis(4,4,4-trinitrobut-1-yl) carbonate was made in high yield from TNBOH and phosgene but was not suitable as a plasticizer because it is a solid melting at 96°C.

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HIGH ENERGY PLASTICIZERS (U)

(C) Stability Studies of Shell P722 [2,3-Bis(difluoramino)propyl 2,2-Dinitropropyl Carbonate]

(C) In view of the potential application of the energetic compound Shell P722 as a component in a variety of propellant systems a series of tests was conducted to determine its stability on prolonged storage at 90°C. These tests were designed to determine gas evolution, weight loss, and structural changes.

(U) In the gas evolution test a conventional gas sample bulb was sealed to the tip of a 5 ml syringe by a long tube. The apparatus, containing about 2 g of distilled Shell P722 in the syringe section, was lowered into a 90°C oil bath with the syringe in an inverted position and to a depth such that about 1 g of sample was in the heated zone. The hope had been to transfer the evolved gas from the syringe to the gas sample bulb so that it could be analyzed by mass spectroscopy, but after 28 days at 90° only a small bubble of gas had collected. Its volume was estimated as being less than 0.02 ml.

(U) In the weight loss test a 2 g sample of distilled Shell P722 contained in a flask protected by a nitrogen pad was heated in the 90° oil bath and weighed periodically. The weight losses were 0.16% at 5 days, 0.19% at 12 days, 0.25% at 19 days, and no further change at 26 days.

(U) Structural features were checked by infrared analysis. Samples of distilled Shell P722 and of material representative of the 2.5 lb production batch which had been made in the continuous reactor were kept in the 90° oil bath under a nitrogen atmosphere. Samples of each withdrawn periodically and analyzed by quantitative infrared spectroscopy, Figures 1-4, showed that after 31 days at 90°C there were no significant changes in the absorption intensities of the carbonyl and of the nitro absorption bands. Further analyses, Figures 5-8, failed to detect any development of absorption in the hydroxyl and nitrile regions.

(U) On the basis of these tests it is apparent that Shell P722 shows a high inherent stability during prolonged storage at a high temperature. All of the containers used in the tests were made of glass; none of these showed any sign of etching.

(C) Synthesis Studies of Shell P731 (4,4,4-Trinitrobut-1-yl Cyanoacetate)

(C) The nitrile plasticizer Shell P731 is of interest as an effective, energetic coplasticizer having the capacity to increase the compatibility of difluoramino plasticizers with nitrocellulose. It is made by esterifying trinitrobutanol (TNBOH) with cyanoacetic acid. TNBOH is produced in a two-step reaction involving Michael addition of nitroform to acrolein, followed by sodium borohydride reduction of the trinitrobutyraldehyde to the alcohol. This synthesis is now being reexamined so as to consolidate all the steps and to develop a simplified convenient procedure for reliable laboratory preparation of moderate amounts of product.

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(C) The first step was used without change to provide sufficient trinitrobutyraldehyde for the investigation. About 250 g were made in two batches at 70% yield by reaction of nitroform with a 30% excess of freshly distilled acrolein in a mixed methylene chloride-aqueous system.

(C) Several changes were made in the reduction step. Previously this had been done in ethanol solvent but this led to difficulties during the recovery and purification of the TNBOH. Since impurities and byproducts can be removed efficiently by aqueous washing, it was necessary to transfer the product from ethanol to a water-immiscible solvent, preferably one which was lighter than water such as benzene. Stripping off the ethanol was impractical because the solids generated during the reaction produced a slurry that was awkward to handle. Direct dilution of the reaction mixture with water and extraction with benzene did not work well because the ethanol caused poor phase separation. These problems have been avoided and the manipulations simplified by using a two-phase benzene-water system. The reaction is conducted by adding a benzene solution of the aldehyde to a dilute aqueous solution of a 30% excess of sodium borohydride. Since comparable results were obtained at 8° and at 25° it was more convenient to operate without refrigeration at ambient temperature where the mild exotherm could be accommodated by cooling with tap water. By contrast, the ethanol system with its lower heat capacity had required careful cooling to control a strong exotherm. The reaction in the two-phase system is conveniently fast, having gone almost to completion during the one hour addition period, but to make sure that the last traces of aldehyde were reduced the reaction mixture was usually left stirring for an additional hour. Product of improved quality resulted from a second treatment with dilute sodium borohydride solution.

(U) The workup consisted of a series of aqueous washes. At first there were substantial losses because of the appreciable solubility of TNBOH in water but this problem was overcome by washing instead with saturated brine, and by saturating the aqueous phase of the reaction mixture with salt before draining it off. The washed benzene solution can be assayed for TNBOH by stripping off the solvent from an aliquot portion. About 200 g of product were made in several batches, the yields varying from 70% to 75%.

(C) The advantage of this system is that the product stays in the same solvent throughout the whole procedure, and that since benzene is lighter than water all the manipulations from the reduction step through to the final washing can be carried out in a single vessel fitted with a bottom drain. Moreover, the shock-sensitive TNBOH is obtained as a benzene solution in which it can be stored safely and where it is already in the proper solvent for the esterification step of the Shell P731 synthesis. In fact, it is not even necessary to dry the benzene solution before starting the esterification step. The nitrile plasticizer Shell P731 is made in 80% yield by refluxing a benzene solution of TNBOH with a 30% excess of cyanoacetic acid in the presence of Amberlyst 15 ion exchange resin for about 16 hours and collecting the evolved water in a Dean-Stark trap; of course this procedure also removes any water originally present in the benzene solution. The workup involves repeated washing with water to remove most of the impurities, and treatment with dilute aqueous sodium borohydride solution to improve the color. In the final treatment the solvent is stripped off at reduced pressure and the product,

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which is not shock sensitive, heated to about 100° at 20 microns pressure to remove the last traces of solvent and water. Product which was prepared this way, directly from the washed benzene solution obtained from the TNBOH preparation, appeared to be identical with Shell P731 which had been made from carefully distilled TNBOH. A total of 150 g of material has been prepared. The product does not have a detectable melting point but does show a second order glass transition at about -60°C.

(C) Simplified Synthesis of Shell P831 (2-Cyanoethyl 4,4,4-Trinitrobut-1-yl Carbonate)

(C) The energetic nitrile plasticizer Shell P831 is structurally similar to Shell P731, but having a carbonate instead of an ester group. It plasticizes nitrocellulose and, in view of its structural features, would appear to be a potentially efficient coplasticizer for incorporating difluoramino compounds into nitrocellulose-based propellants. It is made in high yield in ethylene dichloride solvent by the pyridine-promoted reaction of 2-cyanoethanol (β -hydroxypropionitrile, hydracrylonitrile with the chloroformate of TNBOH. As in the case of the Shell P731 synthesis described in the previous section, the intention of the present study has been to simplify the synthesis by combining the several steps and eliminating unnecessary operations.

(C) The previous method of preparing trinitrobutyl chloroformate had been to dissolve distilled TNBOH in cold liquid phosgene and then to allow the system to warm slowly so as to expel first HCl and then unreacted phosgene, after which the chloroformate was purified by fractional distillation. The first modification was to avoid using distilled TNBOH. The undiluted alcohol is shock sensitive; since the new procedure (v. supra) provides it as a stable fifteen percent solution in benzene it would be convenient to prepare the chloroformate directly from the benzene solution. This was checked by treating a sample of the solution with phosgene and following the course of the reaction by observing the hydroxyl band strength in the infrared spectrum. Reaction at room temperature was slow but almost complete conversion was achieved by heating the system to about 70°C for sixteen hours, using an ice condenser for phosgene reflux. The yield of distilled trinitrobutyl chloroformate was greater than 95%. It was converted to high quality Shell P831 in over 90% yield.

(C) Since the trinitrobutyl chloroformate was obtained in high yield and left almost no residue on distillation it was probable that the undistilled material was good enough for direct conversion to the carbonate. This was checked in a second preparation where the undistilled chloroformate was used without further treatment after stripping off the benzene solvent. Based on TNBOH, a 94% yield of Shell P831 was obtained which, except for having a darker color, appeared to be of the same quality as material prepared from the distilled chloroformate. Most of the color was removed by treatment with a dilute aqueous solution of sodium borohydride.

(U) The workup, which involved aqueous washing, presented some difficulties because the reaction solvent, ethylene dichloride, is heavier than water.

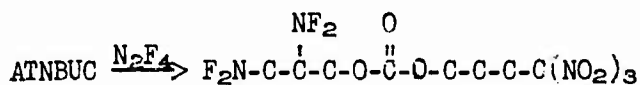
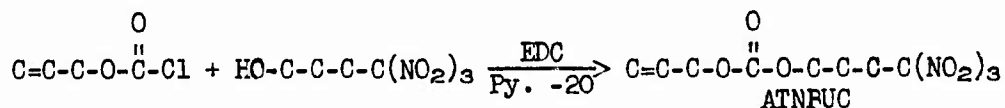
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This was overcome by diluting the organic phase with twice its volume of ether to make it lighter than water. Hexane was not a satisfactory diluent because the product is not soluble in the mixed solvent.

(C) Synthesis of New Plasticizer Candidates

(C) 2,3-Bis(difluoramino)propyl 4,4,4-Trinitrobut-1-yl carbonate

This compound is an analog of Shell P722, in which the dinitropropyl group has been replaced by a trinitrobutyl group in order to achieve a higher molecular weight and a greater energy content. The synthesis paralleled the Shell P722 preparation: an unsaturated intermediate was made by reaction of the nitroalcohol with allyl chloroformate, then converted to the desired product by addition of N_2F_4 to the allyl double bond.



(C) The intermediate was made by adding excess allyl chloroformate to an EDC solution of trinitrobutanol and excess pyridine at $-20^\circ C$. After workup by aqueous washing followed by distillation there was obtained a 71% yield of liquid whose NMR spectrum, Figure 9, was consistent with the expected structure and which indicated a high degree of purity.

(C) This was difluoramined under conditions which had been shown to give complete conversion in the preparation of the analogous compound Shell P722, viz., 2 hours at 100° under 350 psig N_2F_4 in EDC solvent. Partly owing to losses during transfer the crude yield was 75%. Purification attempts increased the losses greatly. The product could not be distilled, and rectification on a silica column with EDC eluent was only partially successful even though this same procedure had worked well with Shell P722. As judged by TLC analysis and refractive index, only about a third of the rectified material was reasonably clean, and even this was shown by proton NMR analysis, Figure 10, to contain about 4% impurities. Repeat chromatographic purification did not improve the product.

(U) In the shock sensitivity test, as measured in a modified Olin-Mathieson closed up tester, there was no perforation of the disc even at 120 kg-cm although the product burned without perforation at 16 kg-cm. The test was negative at 12 kg-cm. The gas evolution during 200 hours at $80^\circ C$, as measured by the Shell syringe test was 0.1 ml/g/100 hrs. Differential thermal analysis in a micro scanning calorimeter at $6^\circ/\text{min}$ showed peaks at 202° and at 227° .

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(C) Bis(4,4,4-trinitrobut-1-yl) Carbonate

(C) In the hope of preparing a highly oxygenated plasticizer by a simple procedure the symmetrical carbonate was made by slow addition of a benzene solution containing a slight excess of phosgene to an EDC solution of TNBOH and a slight excess of pyridine at -20° . Workup gave a 94% yield of a solid product, m.p. $95.3 - 96.6^{\circ}\text{C}$.

(C) Experimental

(U) Infrared Analysis of Shell P722 Samples^{a)}

(U) The samples of Shell P722 which had been heated for 31 days at 90°C were compared with unheated samples by infrared spectroscopy. Each sample was dissolved in carbon tetrachloride to give a solution of known concentration. Spectra of each, Figures 1-4, were obtained on an expanded scale from 5.0 to 7.0 microns using a Beckman LR4 Spectrophotometer. Each spectrum was run using the same cell (0.058 mm) without compensation. Absorbance values for the carbonyl peak at 5.66 microns and for the nitro peak at 6.36 microns were calculated by the usual procedure from the base and peak heights, and the samples compared with each other by dividing the absorbance by the concentration. The data reported in Table 1 show that no detectable change occurs on prolonged heating of distilled material, and that any change occurring on heating the production material is hardly significant.

(U) Table 1. QUANTITATIVE INFRARED ANALYSIS OF SHELL P722 SAMPLES

Material	Conc., g/l	Carbonyl		Nitro	
		A ^{a)}	A/Conc.	A	A/Conc.
Distilled	24.25	0.258	0.106	0.546	0.0225
Distilled, Heated	21.95	0.233	0.106	0.493	0.0225
Production	24.71	0.256	0.104	0.534	0.0216
Production, Heated	27.70	0.284	0.103	0.585	0.0211

a) Absorbance.

(C) Preparation of TNBOH in Two-Phase System

(C) Crude trinitrobutyraldehyde (143 g, 0.691 mole) which had been made by reaction of nitroform and excess acrolein was dissolved in 600 ml benzene and added during one hour at $13-20^{\circ}$ to a well stirred solution of sodium borohydride (15 g, 0.4 mole) in 450 ml water. The system was stirred one more hour then the aqueous phase was saturated with sodium chloride and drawn off. The next day the benzene solution was stirred one hour with a solution of 4 g

a) The analyses were conducted by J.M. Gordon of the Analytical Department.

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sodium borohydride in 200 ml water. The aqueous phase was saturated with salt and drawn off, then the benzene solution was washed four times with 600 ml portions of saturated brine. The last brine wash was colorless. After treatment of the benzene phase with anhydrous $MgSO_4$ and charcoal, there was obtained 632.5 g of yellow solution. When the solvent was stripped from a 9.66 g aliquot portion (to 60° at < 2 mm) there remained 1.558 g TNOBH, $n_D^{25} = 1.4720$, representing a total of 102 g product (71% yield). Benzene extraction of the salt solutions produced another 2.4 g product.

(C) Conversion of Crude TNBOH to the Chloroformate

(C) A 126 g portion of the 16.15% TNBOH in benzene solution, whose preparation was described in the preceding section, was cooled to about 15° while about 25 g phosgene were condensed directly into the liquid, then left for three days under a vented nitrogen atmosphere. Direct infrared analysis showed considerable disappearance of the hydroxyl absorption band. The liquid was heated to reflux at 70° for two eight-hour periods, an ice condenser being used for the phosgene reflux. At the end of this time only a trace of hydroxyl absorption remained. The phosgene and some of the benzene solvent were stripped off through a 10" Vigreux column until the head temperature reached 80° . The benzene solution of the chloroformate was set aside for later conversion to the product, Shell P831 (see below).

(C) Preparation of Shell P831

(C) The solvent was stripped from the trinitrobutyl chloroformate solution described in the preceding section and the residual liquid dissolved in 35 ml ethylene dichloride then added during one hour and 50 minutes to a solution of 8.55 g cyanoethanol and 9.5 g pyridine in 60 ml ethylene dichloride at -20° to $-24^\circ C$. The system was allowed to warm to room temperature. The next day the reaction mixture was diluted with 240 ml ether and stirred with 200 ml portions of wash according to the following schedule: five water, one 0.1 N HCl, two strong $NaHCO_3$, and two water. The solution was dried with anhydrous $MgSO_4$, treated with charcoal, then stripped of solvent to 79° at less than 2 mm pressure. There remained 27.96 g (94% based on 20.3 g TNBOH used for making the chloroformate) yellow liquid, $n_D^{25} = 1.4723$. Dissolution of the product in EDC-ether and treatment with a solution of 0.2 g sodium borohydride followed by the washing and workup procedure described above discharged most of the yellow color but did not change the refractive index.

(C) When the same procedure had been used to prepare Shell P831 from distilled trinitrobutyl chloroformate there was obtained a 92% yield (based on the chloroformate) of almost colorless product, $n_D^{25} = 1.4725$.

(C) Allyl 4,4,4-Trinitrobut-1-yl Carbonate

(C) A solution of allyl chloroformate (6.30 g, 0.0522 mole) in 10 ml EDC was added during a 2 hour period to a solution of distilled TNBOH (10.45 g, 0.05 mole) and pyridine (4.15 g, 0.0525 mole) in 30 ml EDC at $-20^\circ C$. The reaction mixture was kept at -20° for an additional 3 hours then allowed to warm up overnight. After adding 70 ml hexane to make the organic phase lighter

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than water the system was washed three times with 100 ml portions of water, then once with 0.1N HCl, twice with strong NaHCO₃ and twice with water. The organic phase was dried with anhydrous MgSO₄ then stripped of solvent to 65° at < 2 mm. There remained 13.85 g clear yellow liquid. This was distilled through a short path micro still. About 0.6 g of low boiling material was discarded. The main product (10.4 g, 71%) was collected at 110° at 50-60 microns pressure. The structure was confirmed by NMR analysis, Figure 9.

(C) 2,3-Bis(difluoramino)propyl 4,4,4-Trinitrobut-1-yl Carbonate

(C) A solution of 8.76 g allyl 4,4,4-trinitrobut-1-yl carbonate in 40 ml EDC was heated to 100° in a shallow magnetically stirred 80 ml pressure vessel, then N₂F₄ was admitted slowly so that the pressure rose to 350 psig during a 10-minute period. After an hour the system was cooled and vented through a top vent so as to force the unreacted material in the dip tube back into the reaction zone, then the system was brought back to reaction conditions for another hour. At the end of this time the reactor was emptied and the effluent treated immediately with a strong solution of aqueous sodium bicarbonate. After drying with anhydrous MgSO₄ and stripping off solvent there remained 8.78 g (75%) viscous yellow liquid. Some of the product had been lost from the reactor during the venting when excessive foaming forced liquid out through the gas vent line.

(U) Rectification on a 30" x 1.75" silica gel column, using EDC eluent, gave several fractions having varying refractive indexes, as shown below:

Fraction	1	2	3	4	5	6
Weight, g	0.25	2.46	1.70	0.56	0.22	0.28
RI at 25°	1.4470	1.4467	1.4476	1.4496	1.4562	1.4632

Thin layer chromatography (silica, EDC) showed that the first three fractions contained fewer impurities than the later ones. Therefore fractions 1-3 were combined and rectified on a fresh silica column with the results shown below:

Fraction	1	2	3	4	5
Weight, g	0.34	2.57	0.99	0.20	0.06
RI at 25°	1.4471	1.4466	1.4515	1.4678	1.4712

As before, the second fraction was the largest and its refractive index had the lowest value. The proton NMR spectrum of the second fraction, Figure 10, was consistent with the expected structure but the integral showed the purity to be about 96%. DTA analysis, Figure 11, displayed peaks at 201° and at 227°.

(C) Bis(4,4,4-trinitrobut-1-yl) Carbonate

(C) Phosgene was dissolved in 249.04 g EDC and the system weighed periodically. Addition was stopped when the total weight was 282.14 g, the phosgene concentration having reached a value of 11.73%w. A 43.5 g portion of this (containing 0.0515 mole phosgene) was added during 1.75 hours

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to a solution of TNBOH (20.9 g, 0.10 mole) and pyridine (8.4 g, 0.106 mole) in 70 ml EDC at -20°C . The mixture was allowed to warm to 25° during 1.5 hours, then diluted with 220 ml ether and washed three times with 200 ml portions of water, once with 0.1 N HCl, three times with strong sodium bicarbonate solution and twice with water. After being dried with anhydrous MgSO_4 and treated with charcoal the solution was stripped of solvent to 80° at < 2 mm for an hour. There remained 20.8 g (94%) white crystalline solid. A portion recrystallized from benzene-hexane melted $95.3-96.6^{\circ}$.

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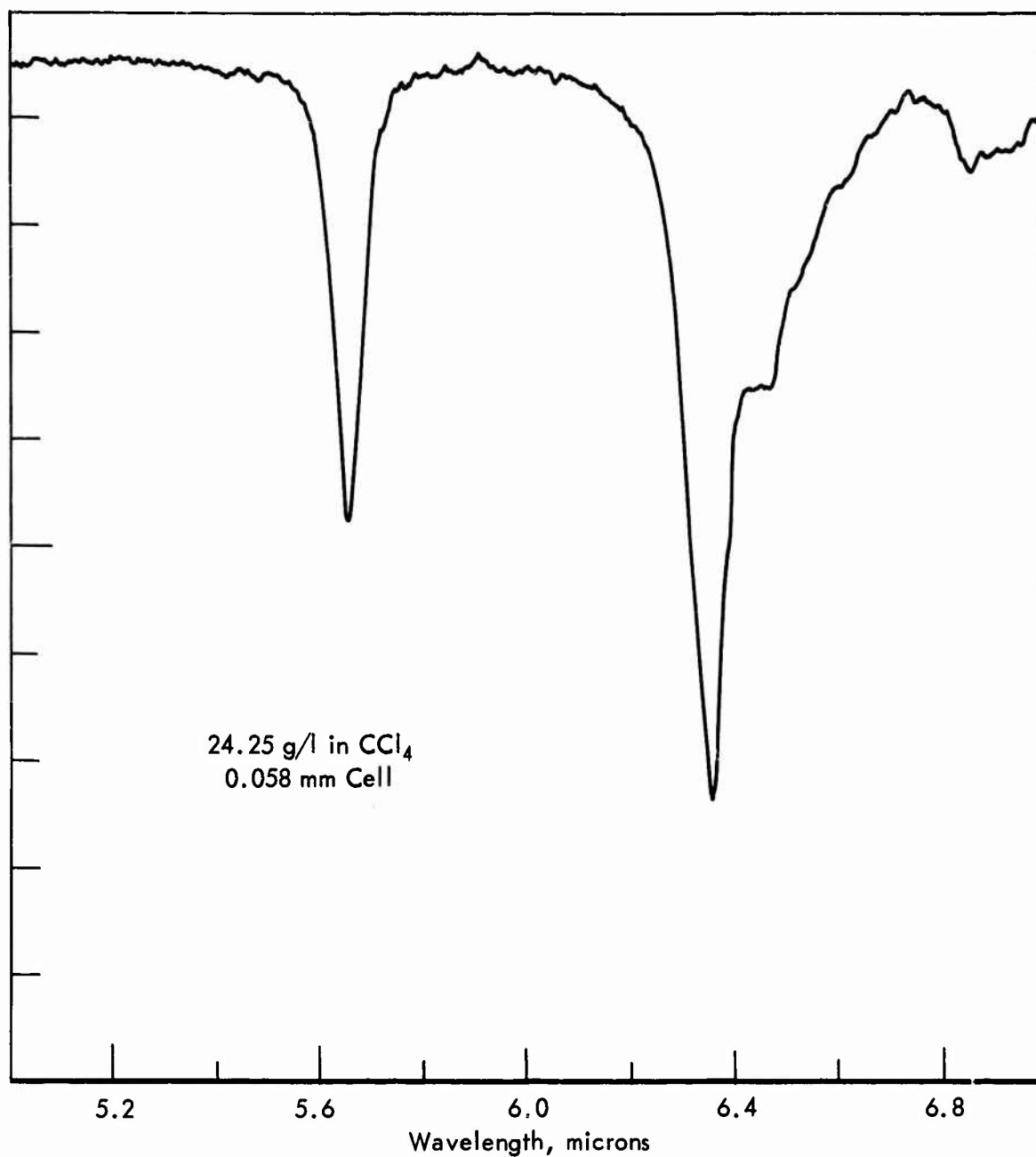


Figure 1. CARBONYL AND NITRO REGION OF INFRARED SPECTRUM
OF DISTILLED SHELL P722,
UNHEATED

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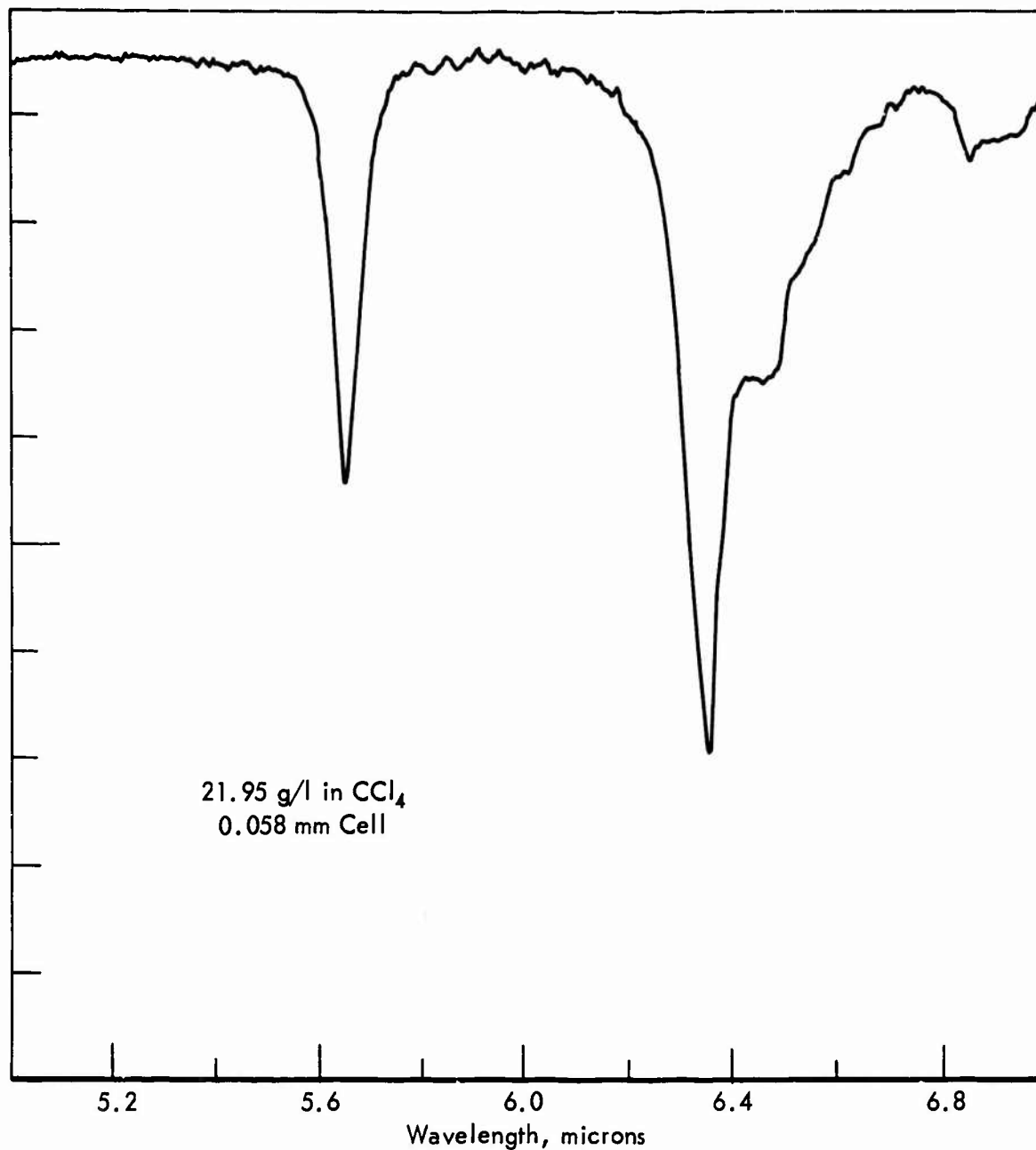


Figure 2. CARBONYL AND NITRO REGION OF INFRARED SPECTRUM
OF DISTILLED SHELL P722,
HEATED 31 DAYS AT 90°C

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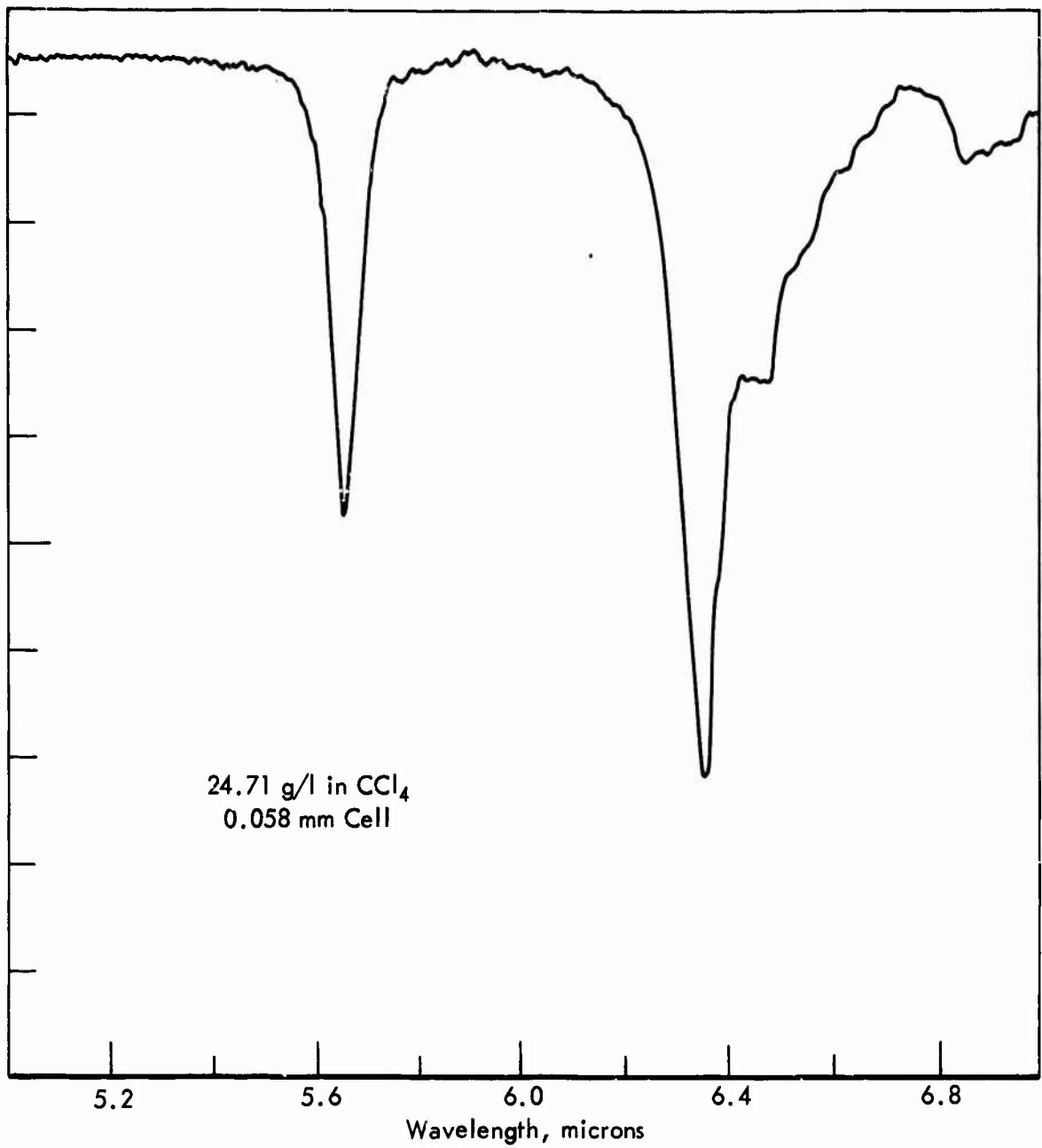


Figure 3. CARBONYL AND NITRO REGION OF INFRARED SPECTRUM
OF PRODUCTION SHELL P722,
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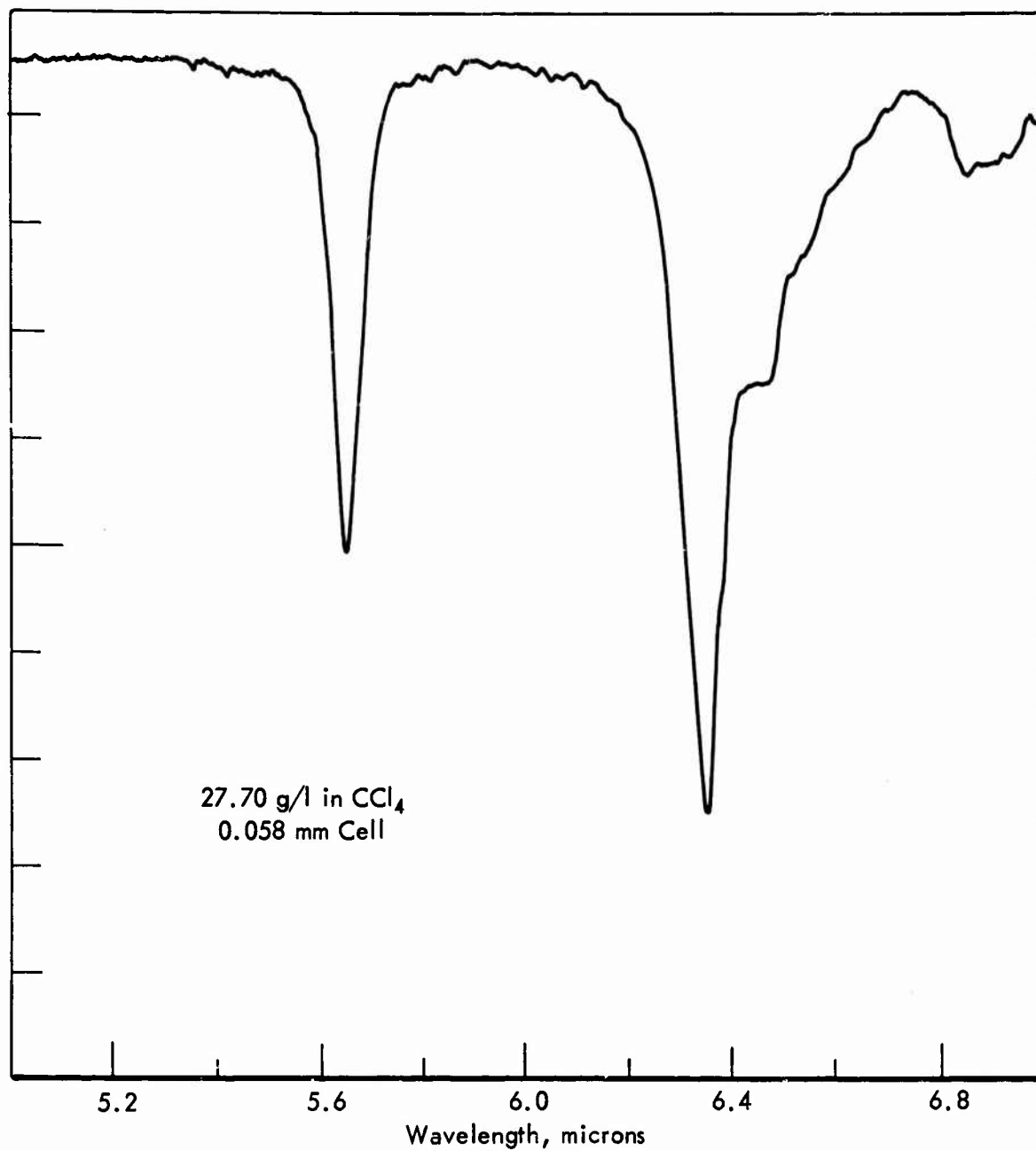


Figure 4. CARBONYL AND NITRO REGION OF INFRARED SPECTRUM
OF PRODUCTION SHELL P722,
HEATED 30 DAYS AT 90°C

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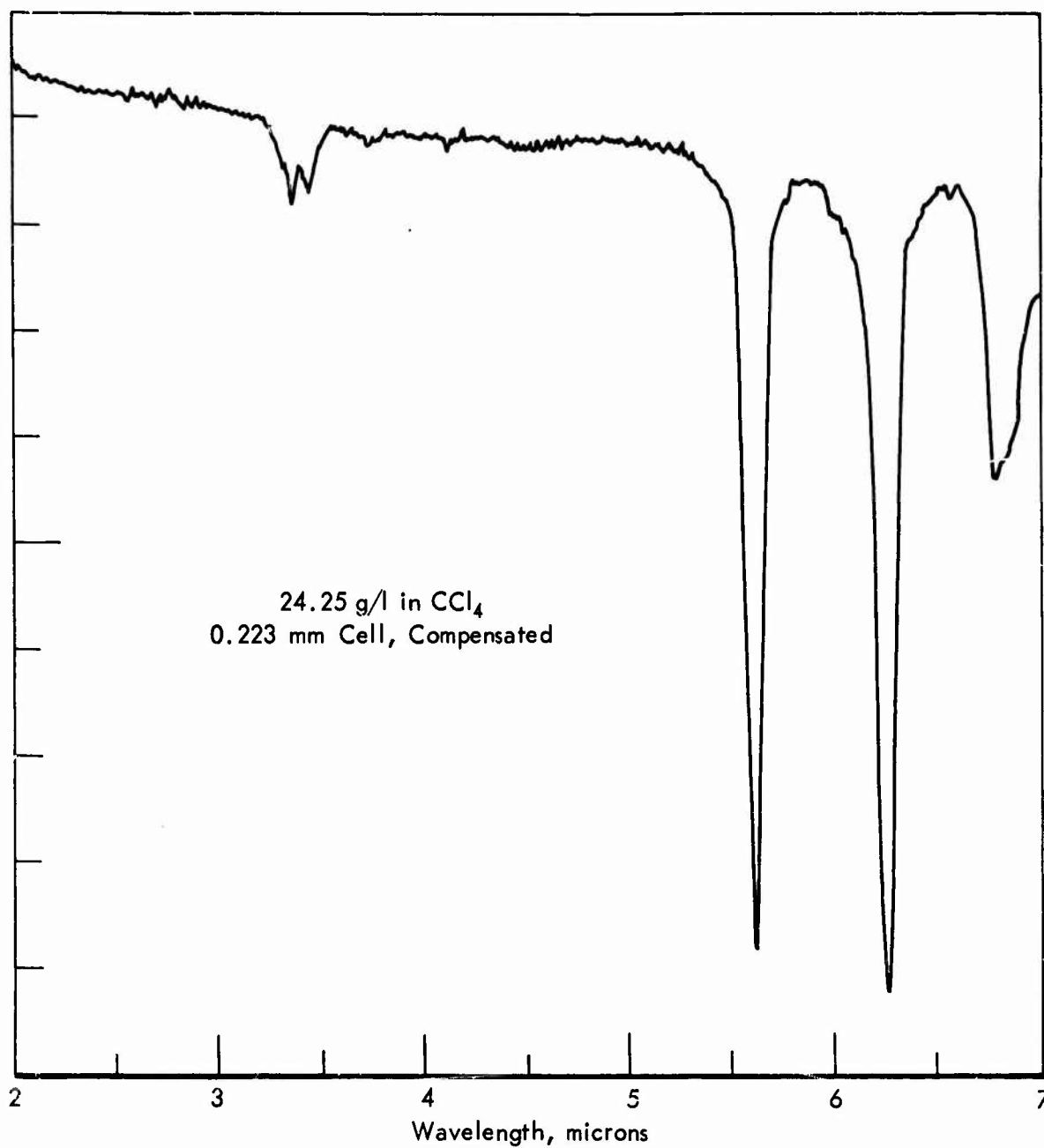


Figure 5. INFRARED SPECTRUM OF DISTILLED SHELL P722,
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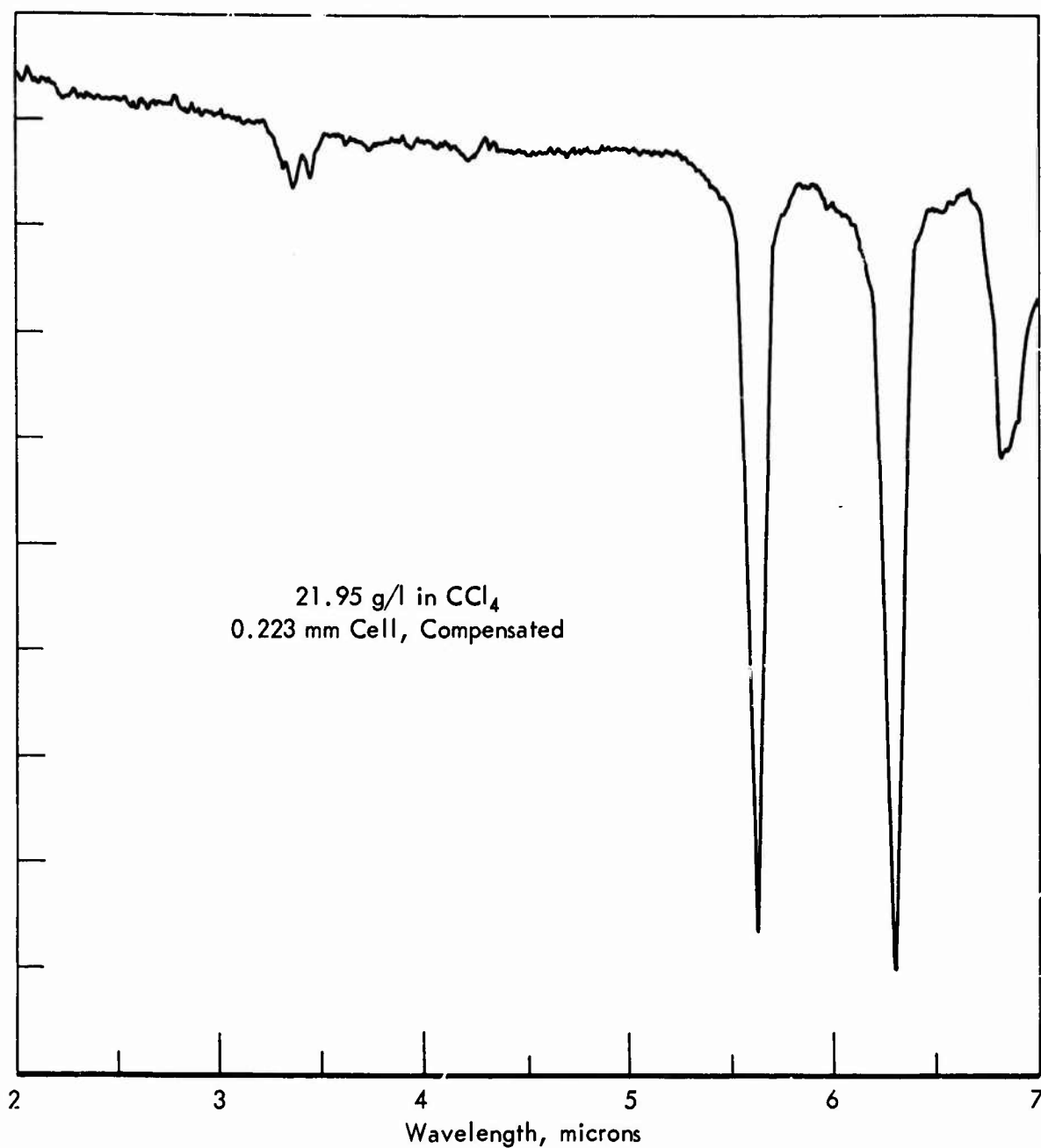


Figure 6. INFRARED SPECTRUM OF DISTILLED SHELL P722,
HEATED 31 DAYS AT 90°C

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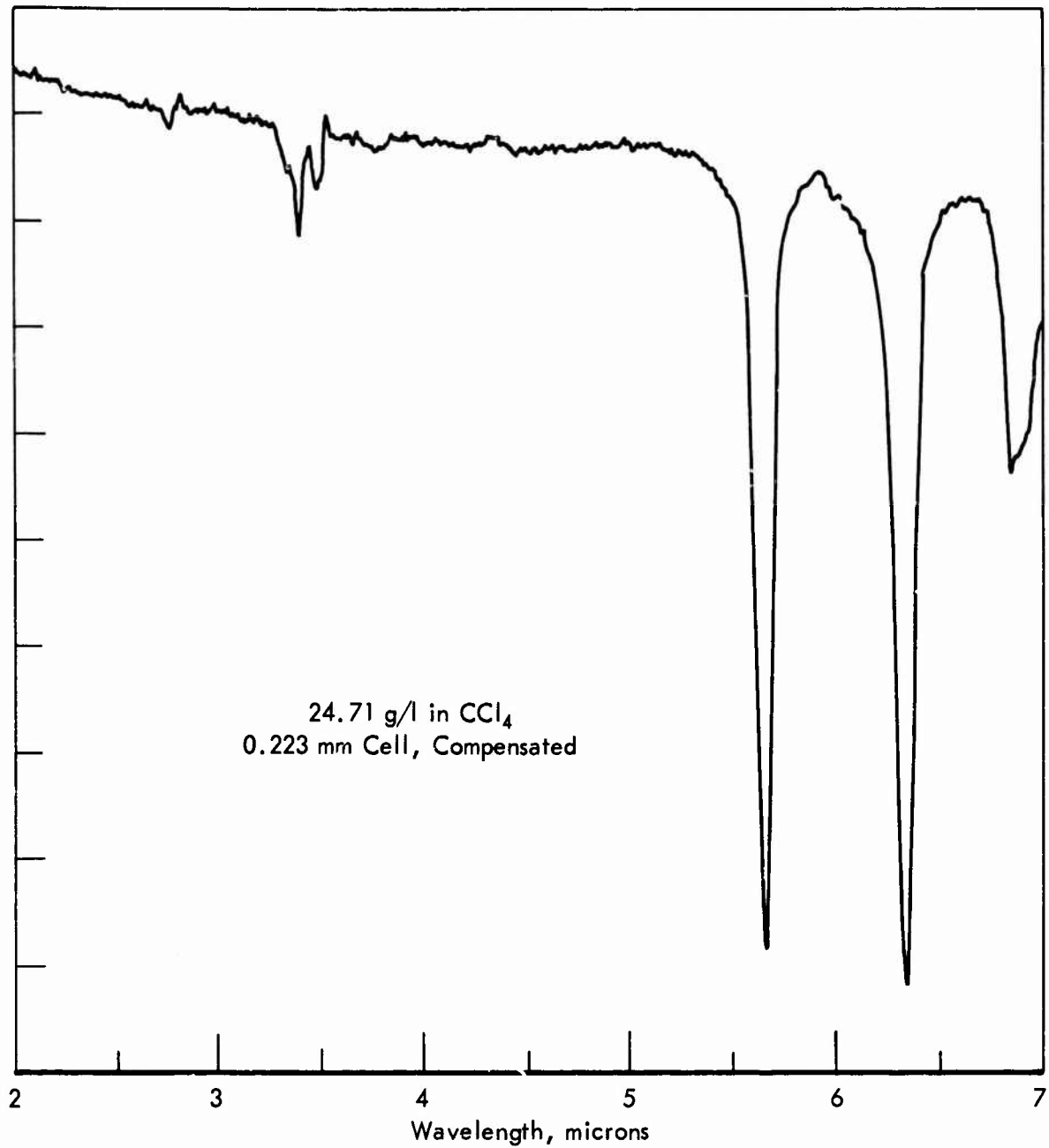


Figure 7. INFRARED SPECTRUM OF PRODUCTION SHELL P722,
UNHEATED

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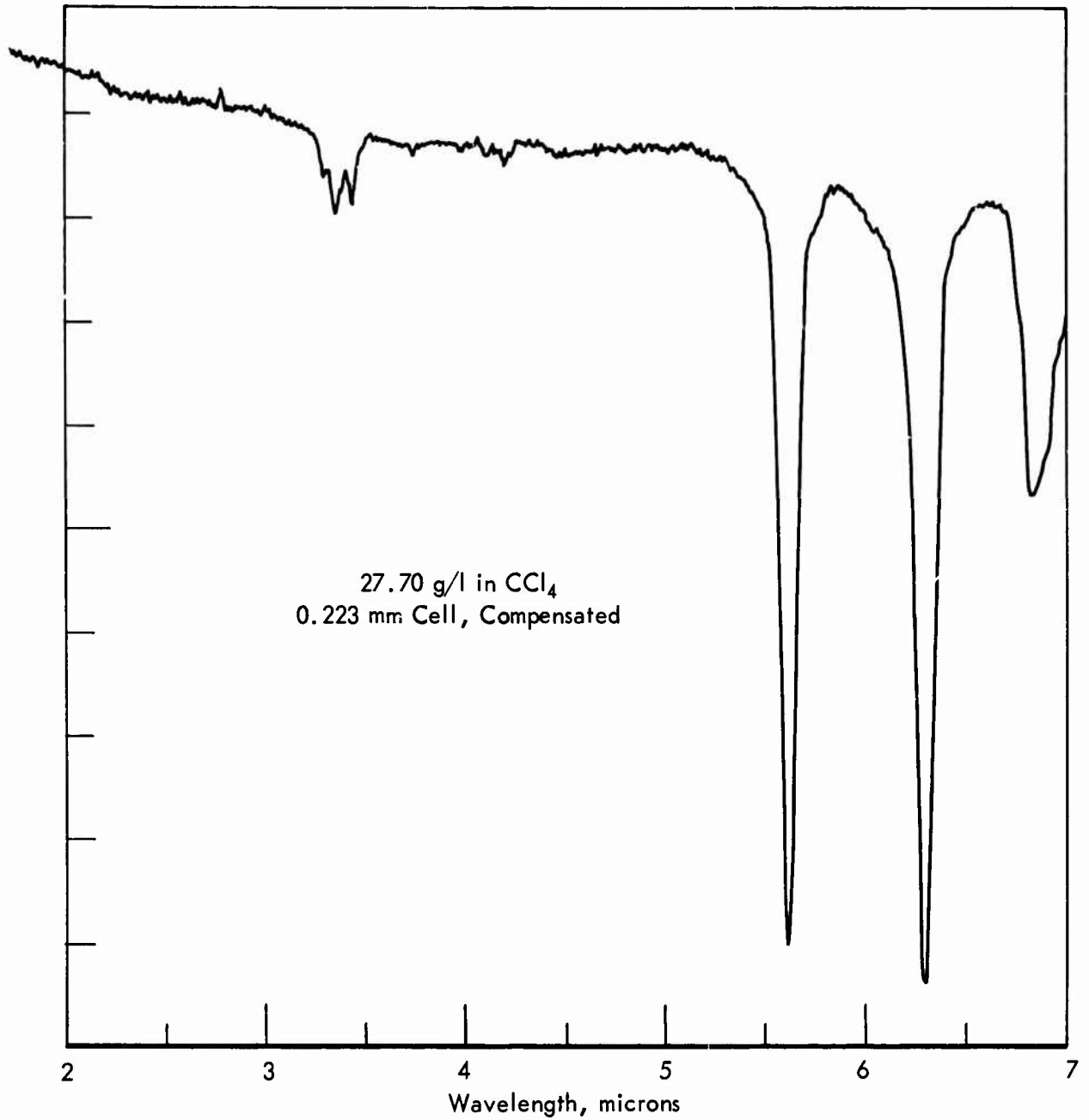


Figure 8. INFRARED SPECTRUM OF PRODUCTION SHELL P722,
HEATED 31 DAYS AT 90°C

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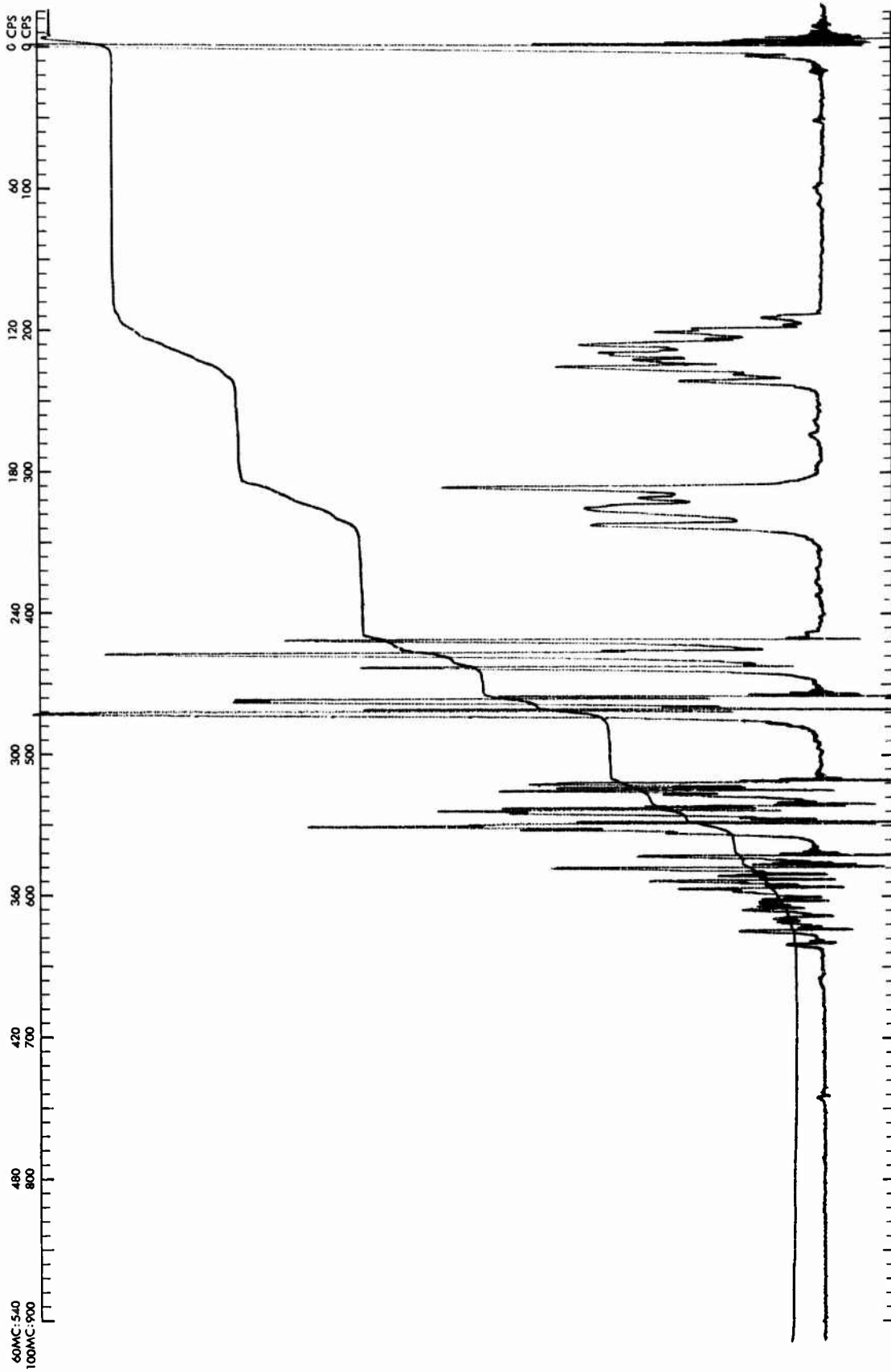


Figure 9. PROTON NMR SPECTRUM OF ALLYL 4,4,4-TRINITROBUT-1-YL CARBONATE

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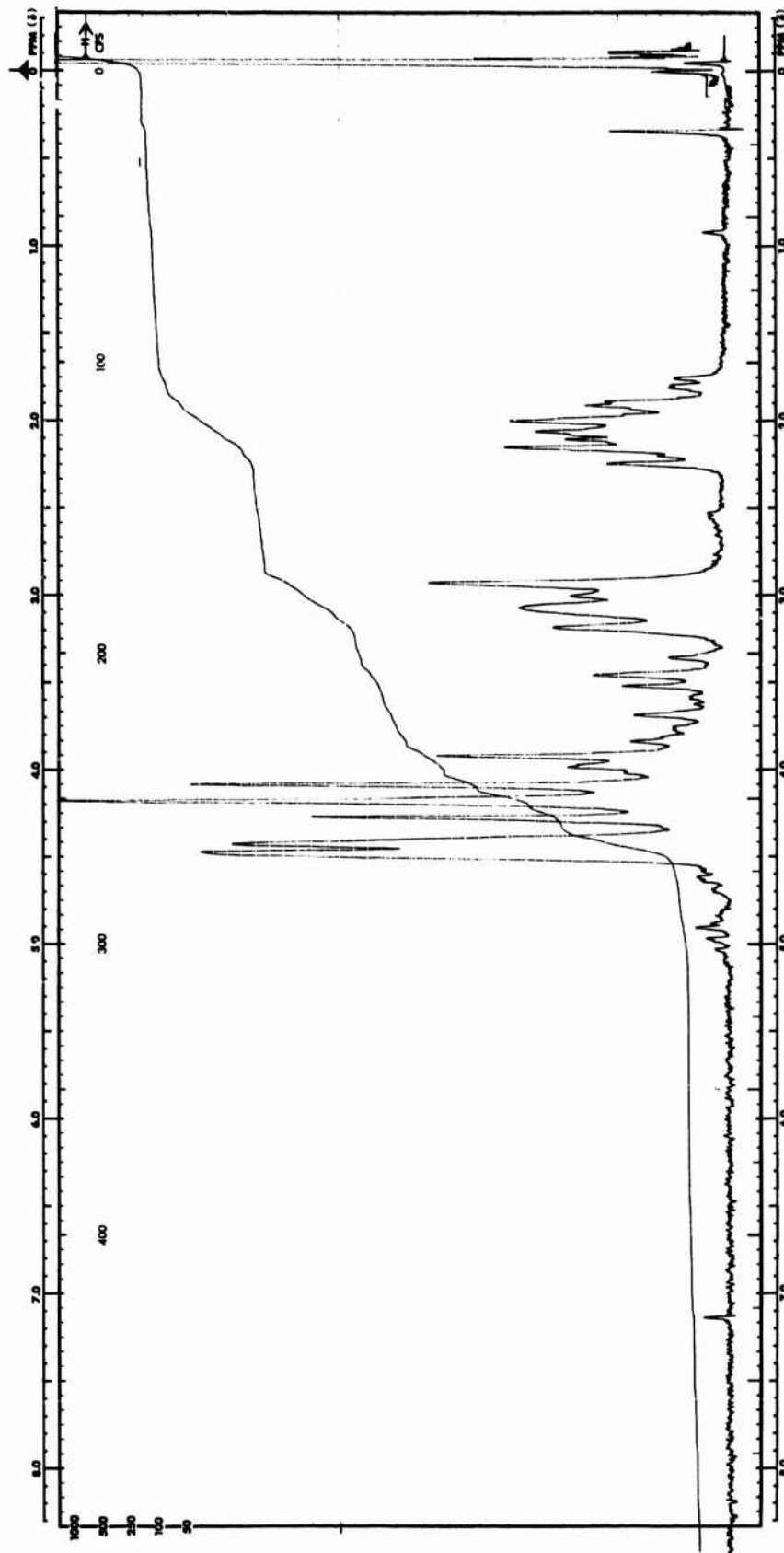


Figure 10. PROTON NMR SPECTRUM OF 2,3-BIS(DIFLUORAMINO) PROPYL
4,4,4-TRINITROBUT-1-YL CARBONATE

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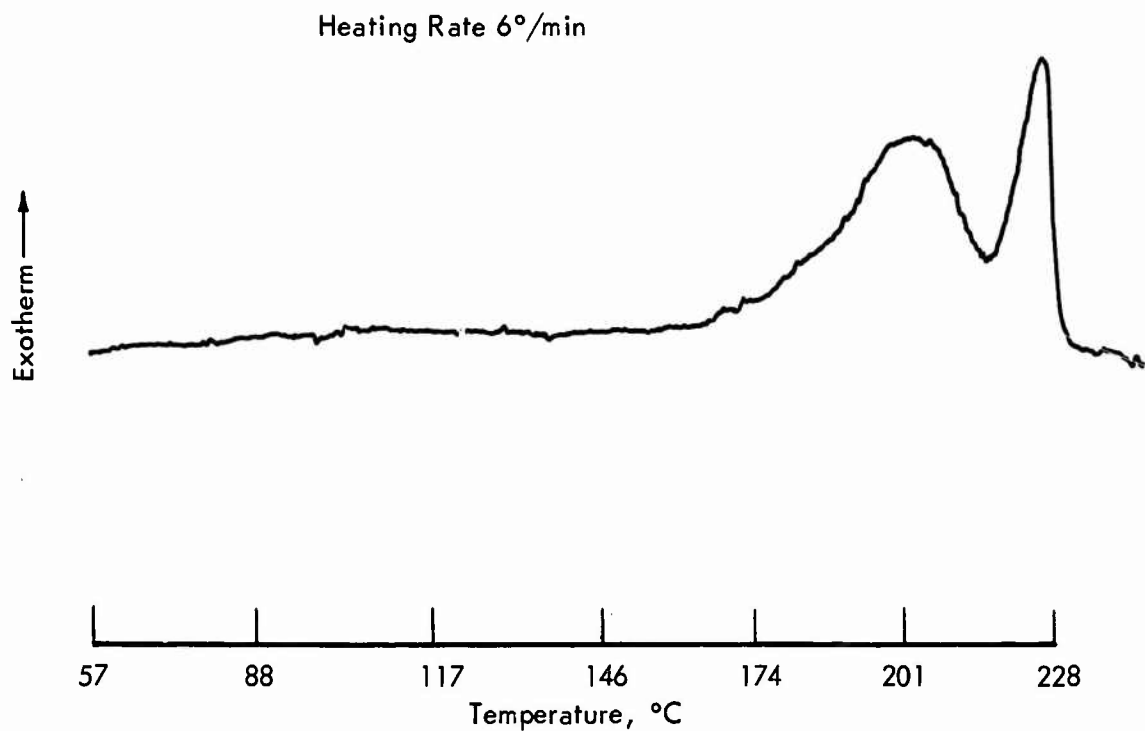


Figure 11. DIFFERENTIAL THERMAL ANALYSIS OF 2,3-BIS(DIFLUORAMINO) PROPYL 4,4,4-TRINITROBUT-1-YL CARBONATE

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13. ABSTRACT (C) The energetic plasticizer Shell P722, 2,3-bis(difluoramino)propyl 2,2-dinitropropyl carbonate, shows excellent stability during prolonged heating. As determined by gas evolution, weight loss, and infrared analysis no significant change occurs after heating for 31 days at 90°C. (C) An improved synthesis of the energetic plasticizer Shell P731, 4,4,4-trinitrobut-1-yl cyanoacetate, is based on the sodium borohydride reduction of trinitrobutyraldehyde to trinitrobutanol (TNBOH) in a water-benzene system followed by direct treatment of the benzene solution with cyanoacetic acid. (C) Improvements in the synthesis of the energetic plasticizer Shell P831, 2-cyanoethyl 4,4,4-trinitrobut-1-yl carbonate, comprise the preparation of the intermediate trinitrobutyl chloroformate from crude TNBOH, and direct use of the chloroformate without purification. (C) The new plasticizer candidate 2,3-bis(difluoramino)propyl 4,4,4-trinitrobut-1-yl carbonate was made in fair yield but could not be purified well. (C) The compound bis(4,4,4-trinitrobut-1-yl) carbonate is a solid melting at 96°C.		

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14. KEY WORDS

High Energy Plasticizers
High Energy Binders
Solid Propellants
PBEP
Nitrocellulose Plasticizers

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