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Molecular Design of Novel Discogen Possessing A Semi-Flexible Aryloxytriazine Core

by

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Two compounds have been synthesized which exhibit a discotic mesophase. The molecule includes a semi-flexible tris(benzylidene oxyaniline) triazine core flanked by just one alkyl substituent at the 4' position of each radial ring. An oxygen links the benzylidene aniline groups to the central triazine ring. Calorimetric measurements and polarizing microscopy observations show the existence of discotic mesophases. This appears to be the first example of a semi-flexible core with only minimal alkyl substituents which still produces a discotic liquid crystalline phase.

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MOLECULAR DESIGN OF NOVEL DISCOGEN

POSSESSING A SEMI-FLEXIBLE ARYLOXYTRIAZINE CORE

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Two compounds have been synthesized which exhibit a discotic mesophase. The molecule includes a semi-flexible tris(benzylidene oxyaniline)triazine core flanked by just one alkyl substituent at the 4' position of each radial ring. An oxygen links the benzylidene aniline groups to the central triazine ring. Calorimetric measurements and polarizing microscopy observations show the existence of discotic mesophases. This appears to be the first example of a semi-flexible core with only minimal alkyl substitutions which still produces a discotic liquid crystalline phase.

Introduction

In 1977 the first discotic mesophase was recognized by Chandrasekhar (1,2). It was a hexa-substituted benzene exhibiting a columnar phase deduced from birefringence studies and x-ray work (3,4). Since this time several other examples of discotic liquid crystals have been reported. The molecular geometry needed to obtain this phase has subsequently fallen into two categories. In each case the main desire is to produce a large surface area to thickness ratio which would enhance the probability of obtaining a discotic mesophase. The two categories can be generally broken down into compounds having a large aromatic core with a high number of flexible substituents, such as those derived from triphenylene (5,6), rufigallol (7,8,9) or truxenes (10), or transition metal complexes, such as bis(dithiolene) nickel (11) or bis(beta-diketonato) copper II (12). The latter approach takes advantage of rigid organic compounds which can bind at two sites with the metal. In all cases the objective is to maximize the surface area with both a large rigid core and as many flexible substitutions as possible.

Recently a discotic liquid crystal has been reported by Lattermann having a less rigid core but maintaining a high degree of flexible substitutions (13). The core consisted of 1,3,5-tris(benzoyloxy)benzene. There are a total of nine flexible decyloxy groups bonded, three to each benzoyloxy ring. The total molecule was shown to possess a relatively large surface area when the flexible arms were in the all trans conformation. Intuitively it seems that the core of the molecule would play a greater role in enhancing the discotic behavior than the alkyl or alkoxy substituents. For this reason it was decided to synthesize a molecule having a larger core at the expense of the high number of flexible arms and further a flexible core relative

to examples cited above. The molecular design included here suggests that the discotic phase may be favored due to specific packing requirements even though there would be much empty space within the disc as a result of the flexible central oxygen links and the lack of a multitude of aliphatic substituents. The compounds synthesized were 1,3,5-tris(4-benzylidene oxy-4'-R-aniline)triazines, where R is either hexyl or decyl.

Experimental

All reagents were received from Aldrich Chemical and purified before use. To a 100 ml RBF equipped with magnetic stirrer and condenser was added 50 ml EtOH and 1.1 equivalents of 4-hydroxybenzaldehyde. Next one equivalent of the alkyl aniline was added and a catalytic amount of p-TsOH. This was stirred and refluxed for 4 hours. Upon cooling the product precipitated from solution. The yellow solid was collected by vacuum filtration, washed with cold EtOH then recrystallized with EtOH. The 4-hydroxybenzylidene-4'-alkyl aniline was then reacted with cyanuric chloride.

To a 50 ml RBF equipped with magnetic stirrer and argon purge was added 25 ml dry EtOH followed by 4 equivalents of the 4-hydroxybenzylidene-4'-alkyl aniline and 4 equivalents of sodium hydroxide. Once the solution cleared one euqivalent of cyanuric chloride was added and the solution was stirred at room temperature for 6 hours. The sodium chloride was filtered off and upon neutralization of the solution the product precipitated out. The product was filtered, washed with distilled water, EtOH and ether to remove the remaining starting materials. The product was then recrystallized from acetone producing pale yellow crystals. The purity was checked with thin layer chromatography using tetrahydrofuran and then chloroform as mobile phases.

The thermal properties were evaluated using a Perkin-Elmer DSC-7 at heating and cooling rates of 2°C/min. The onset of each transition is provided, the melting points are uncorrected. The optical properties were

examined using a Nikon Labophot under crossed-polars, magnifications are included with each photograph. A Linkam Scientific TH-600 Hot Stage along with a TMS 90 Controller were used at rates ranging from 5°C/min to 0.5°C/min. The exact rate is included with the photograph.

Results and Discussion

The thermal and optical properties will be assessed for each compound separately. The first compound, hexyl substituent, exhibited three transitions on the first heating as shown in Figure 1. A crystal to crystal transition occurred at 125.0°C having a molar enthalpy of 6.13 kJ/mole. This was followed by a sharp melting point at 153.8°C having an enthalpy of 26.1 kJ/mole. This peak coincides with an optical transition from a sky blue crystalline phase to a yellow mesophase. The material was fluid at this stage. The transition from the discotic phase to isotropic phase occurred at 197.5°C and ΔH=6.50 kJ/mole, corresponding to the loss of all birefringence under the microscope. This compound was thermally well behaved in that the liquid crystalline transitions were readily reversible. Upon cooling the discotic phase was reentered at 199.5°C corresponding to the nucleation of liquid crystalline domains. These domains shown in Figure 3 exhibited classic discotic texture of the columnar phase being very similar to textures reported (5,7,14). The crystalline phase was reentered at 141.5°C. At this point the sky blue texture of the solid phase reappeared as well as a complete textural reorganization. The crystal to crystal transition was not observed while cooling and did not show up on subsequent thermal scans. Upon second heating and cooling the crystal to discotic transition and the discotic to isotropic transition were again observed at temperatures within 0.5°C of the first scan. This thermogram is presented in Figure 4. The thermal properties for this compound were reversible and reproducible.

The second compound was synthesized using 4-decylaniline. The difference in the number of carbons around the perimeter of the disc changed the optical texture which seemed to be due to an increase in viscosity and packing variations. Certain textures could be induced upon shearing which were not observed with the lower molecular weight analog. The first thermal scan is shown in Figure 5. There was no crystal to crystal transition. A crystal to discotic transition was observed at 75.5°C. The molar enthalpy of this transition was 45.2 kJ/mole. This melting point was observed under the microscope but at a slightly different temperature due to sample preparation. The material did not readily flow so that sample was sheared in order to assure its fluid nature and to improve the optical transmittance, the texture is shown in Figure 6. The exact nature of this mesophase is being deduced using x-ray diffraction experiments although it resembled textures reported previously (6). The clearing point was reached at 114.0°C having an enthalpy of 60.5 kJ/mole. Upon cooling the mesophase was obtained as before. This is exemplified by the cooling scan seen in Figure 5 where the discotic phase was reached at 103.5°C, the enthalpy equalling -20.2 kJ/mole. There were multiple peaks observed which may be due to molecular reorganization or slight amounts of impurities. The discotic to crystal transition was bimodal beginning at 81.0°C, ΔH = -9.45 kJ/mole. The second thermal scan of this sample is shown in Figure 7. Here the melting transitions became much broader with the crystal to discotic transition occurring at 74.7°C and the discotic to isotropic transition occurring at 100.1°C. Upon cooling, the sample entered the discotic phase at 100.6°C and interestingly there was only one peak. The bimodal discotic to crystal transition remained with the first transition beginning at 86.4°C and second transition beginning at 82.8°C. This may indicate the existence of another mesophase which will be assessed in the future.

Concluding Remarks

In this study it was found that discotic liquid crystalline phases are exhibited for compounds having a relatively flexible core and only three alkyl substituents. This opens new questions as to the validity of the hypothesis that a rigid core with maximum number of alkyl or alkoxyl substitutents is needed to form such a phase. Further investigations are being undertaken to include the analogs between these two. In this way complete x-ray measurements and spectroscopic studies can be performed and reported. Phase diagrams will be developed to better understand this new set of discotic liquid crystals.

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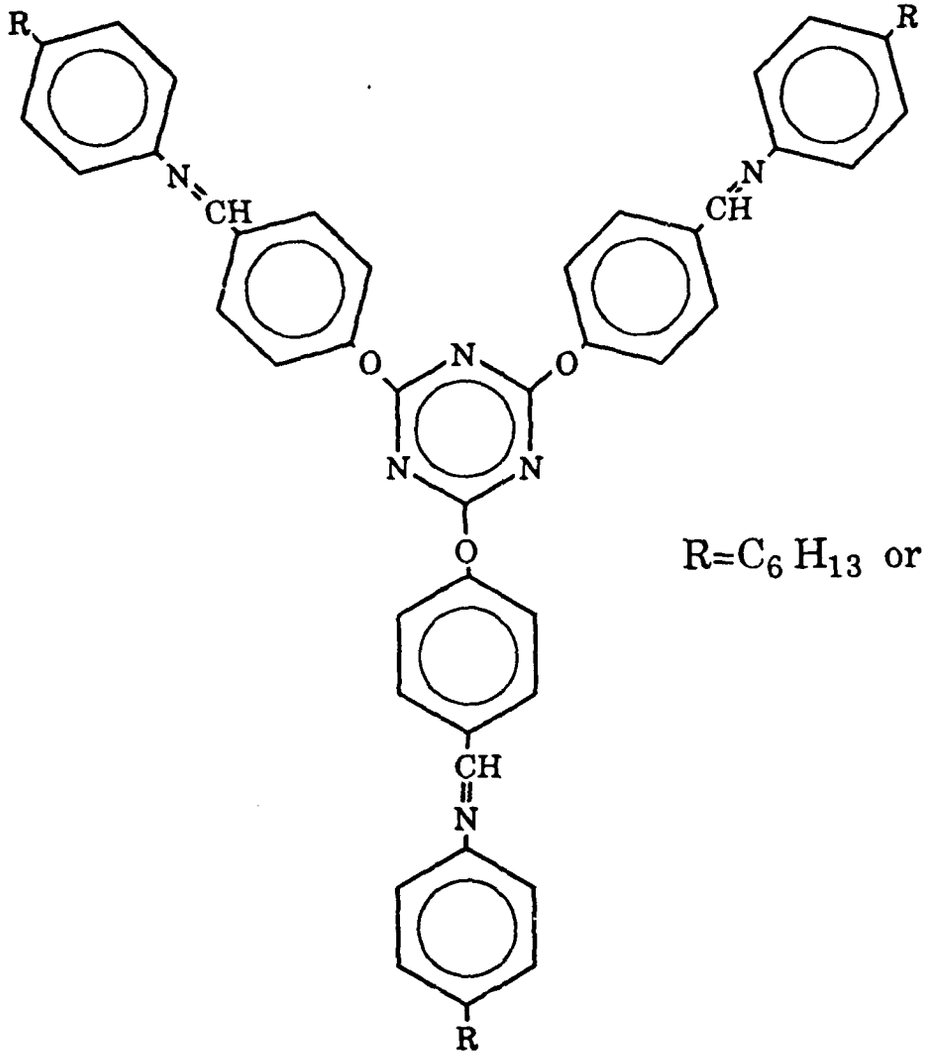

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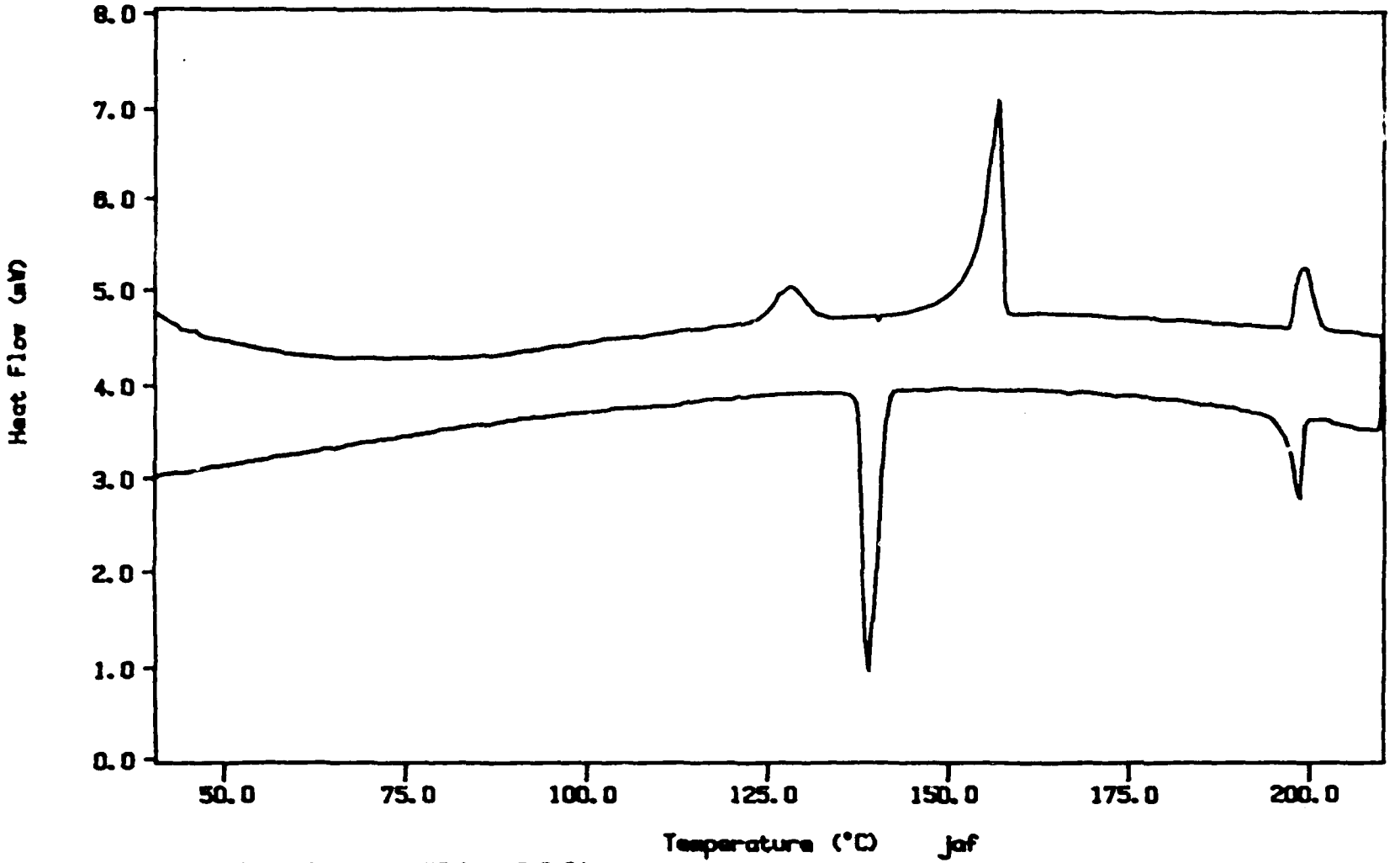

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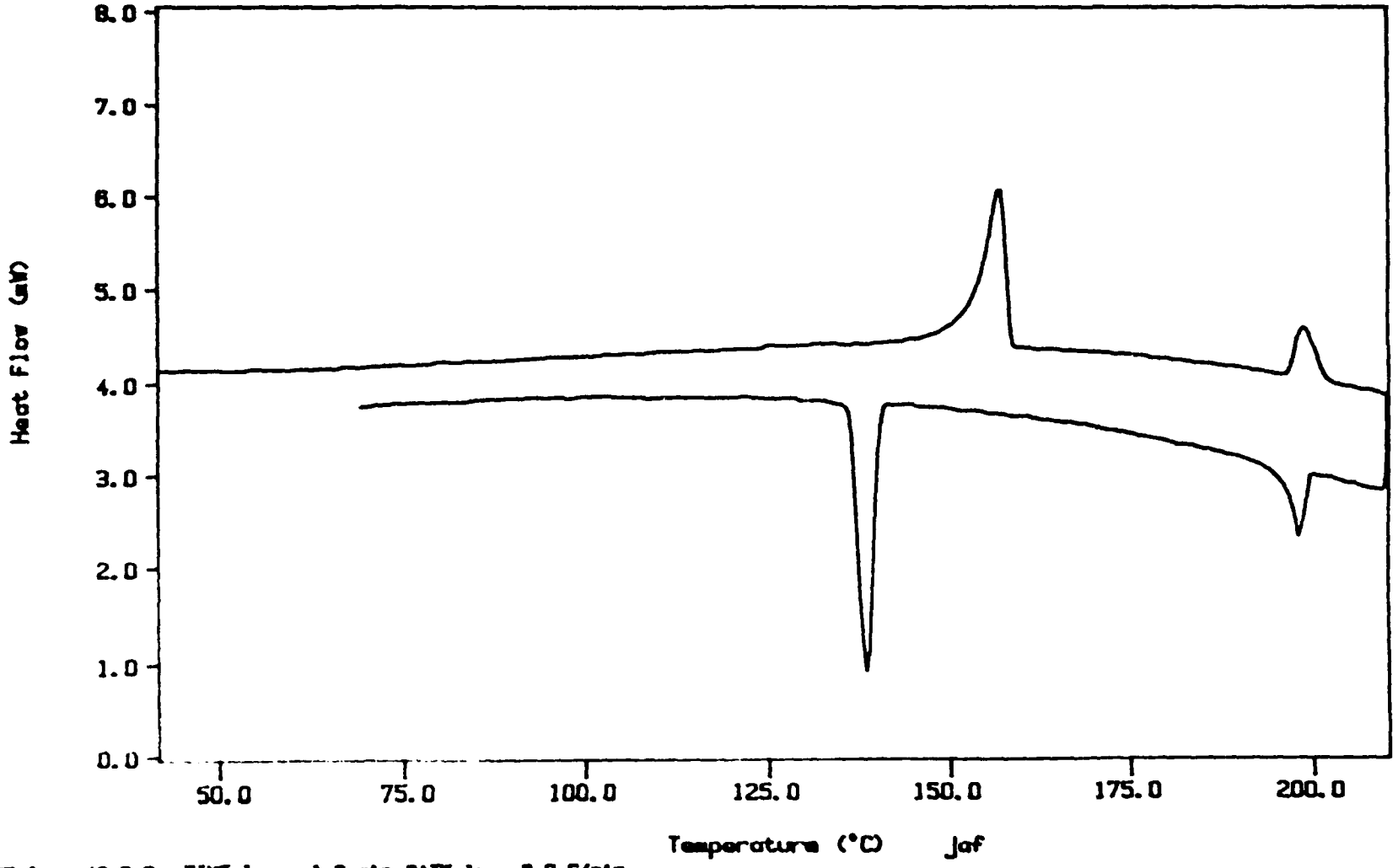

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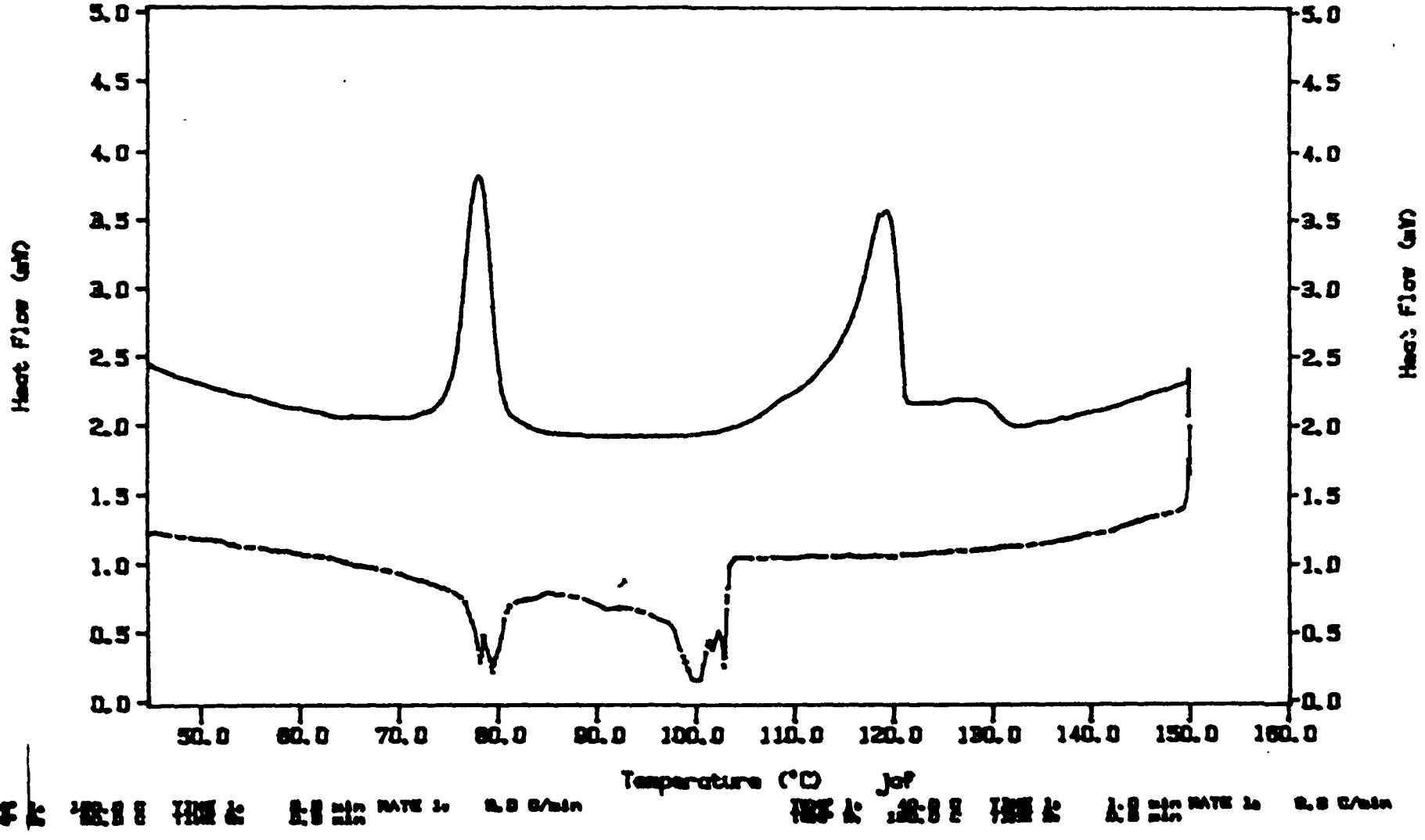

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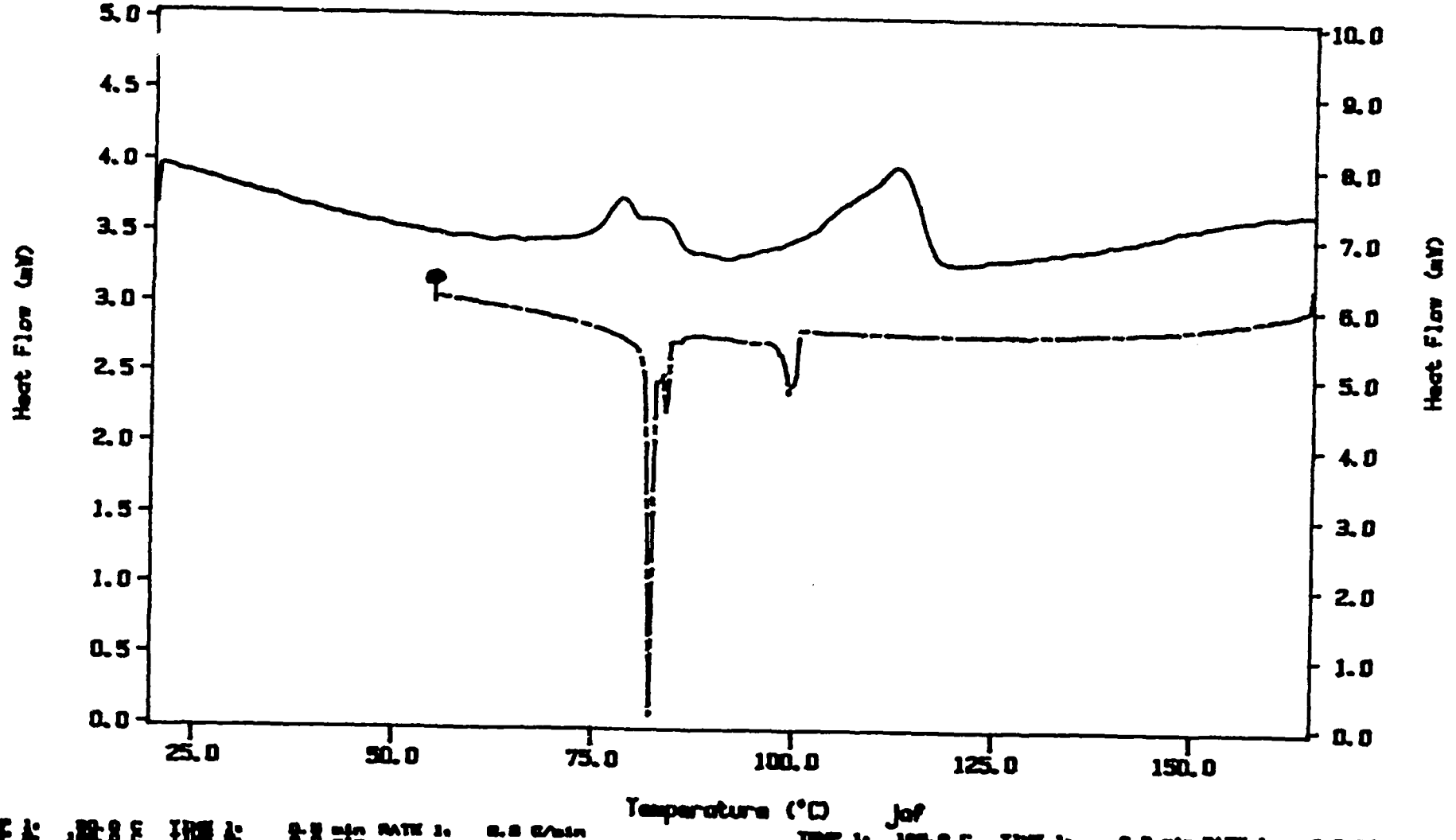

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