Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Phase Characterization, Enthalpies and Entropies of Transition, of Five Substituted N-(1-Biphenylethylidene) Benzylamines

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Version of record first published: 20 Apr 2011.

To cite this article: J. Palacios , C. Alcantara & D. F. M. Rubio (1984): Phase Characterization, Enthalpies and Entropies of Transition, of Five Substituted N-(1-Biphenylethylidene) Benzylamines, Molecular Crystals and Liquid Crystals, 102:8-9, 247-253

To link to this article: http://dx.doi.org/10.1080/01406568408070535

Mol. Cryst. Liq. Cryst. Vol. 102 (Letters), pp. 247-253
0140-6566/84/1028-0247$15.00/0

Printed in the United States of America

PHASE CHARACTERIZATION, ENTHALPIES AND ENTROPIES OF TRANSITION, OF FIVE SUBSTITUTED N-(1-BIPHENYLETHYLIDENE) BENZYLAMINES

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(Received for Publication September 7, 1984)

ABSTRACT.

Five N-(1-biphenylethylidene) benzylamines expressed by the general formula $C_6H_5C_6H_4C(CH_3) = N\text{-}CH_2\text{-}C_6H_4X$ (X = H, m-F, m-Cl, M-Br and p-OCH_3) were synthesized and their thermal behavior studied within the temperature range of -75 to 250°C.
The solid-liquid, liquid-solid transition temperatures were recorded with a DSC analyzer and the thermodynamic parameters ΔH_m and ΔS_m were estimated. A relationship between these parameters and the molecular weigth was found. The compound m-fluoro N-(1-biphenylethylidene) benzylamine showed

an $\ell_i \rightarrow \ell_n$ transition at 341.5°K, which was better observed by cooling the sample at 10°C/min. The liquid crystal behavior was confirmed by cross polarized microscopy.

INTRODUCTION.

The synthesis and primary characertization of five N-(1-biphenylethylidene) benzylamines were first reported by Rubio et al.[1] and their formulae were established as $C_6H_5C_6H_4C(CH_3)$ = $N\text{-}CH_2\text{-}C_6H_4X$ where X = H, m-F, m-Cl, m-Br, p-OCH_3. Since the chemical structure of these compounds suggested the possibility of liquid crystal behavior, we decided to perform the thermal characterization within a broad temperature range, and we calculated some thermodynamic parameters related to the phase transitions. A correlation between molecular weight, size and electronegativity of the substituents and the entropy of fusion is suggested.

EXPERIMENTAL

The five ketimines were synthesized and purified in this laboratory[1]. The purity of these samples was confirmed by chemical and spectroscopical analysis.

In a Perkin Elmer DSC model 1-B calorimeter, temperatures and heat of transition were obtained at five different heating programs (5, 10, 20, 40, 80°C/min.) These samples remained under a

constant flow of nitrogen gas at 30 ml/min during the experiments. The DSC calibration procedure for high and low temperatures and the method of evaluation of results have been described elsewhere[2,3,4].

The melting and solidification temperatures T_m and T_s recorded at several heating programs, were plotted against the square root of the rate of heating $(C_r)^{\frac{1}{2}}$ and extrapolated at $C_r = 0$. Transition temperature data were reproduced to within $\pm$ 0.1°K. Thermodynamic parameters ΔH and ΔS were calculated for phase transitions by integration of endothermic and exothermic peaks[5,6].

RESULTS AND DISCUSSION.

Results were summarized in Table I. The solid-liquid (T_m) and liquid-solid (T_s) temperatures were extrapolated to C_r = 0°C/min. The overcooling effect is responsible for the differences observed in these values. For purposes of comparison, values of T_m and T_s recorded at a heating rate of 10°C/min are shown in the same table.

Whereas the value of T_m increased as the size of the atomic radius of the meta halogen substituent increased, the same phenomenon was not observed for solidification temperatures. The methoxy group in the para position gives a T_m value of 367.6°K, which is 7.8°K lower than the melting point of N-(1-Biphenylethylidene) benzylamine, the compound with the highest melting temperature recorded 375.4°K.

TABLE I.

Substituent X	T_m°K C_r=0	T_s°K C_r=0	T_m°K C_r=10	ΔH_m Kcal/mol	ΔH_s Kcal/mol	ΔS_m cal/mol°K	ΔS_s cal/mol°K
m-H	375.4	368.2	381.0	5.594	-5.427	14.909	-14.741
m-F	353.5	358.1	362.0	10.0101	-10.101	28.317	-28.207
m-Cl	360.6	342.6	369.0	9.306	-7.170	25.106	-20.917
m-Br	373.8	360.8	370.0	5.162	-6.095	13.823	-16.917
p-OCH_3	367.6	356.0	393.0	3.784	-3.311	10.294	- 9.30

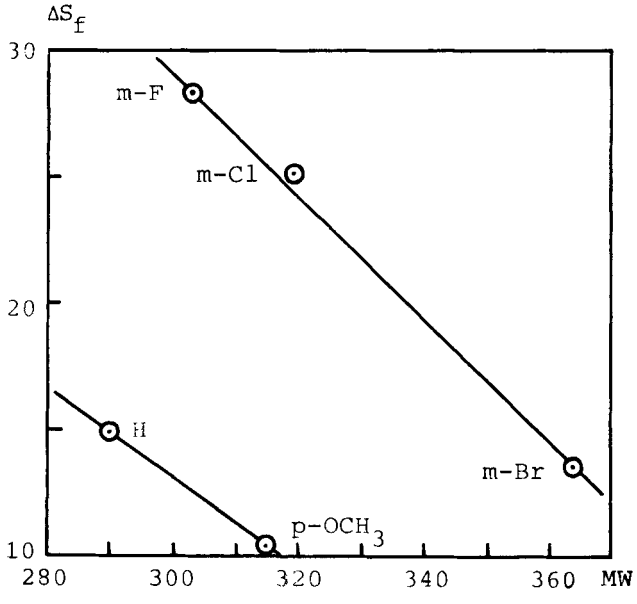

Fig. 1. Transition Entropies ΔS_f vs. Molecular Weight.

When the ΔH_m and ΔS_m values (Table I) were plotted against the molecular weight of the imines, three of them fell on a straight line: the fluoro, chloro and bromo benzylamines. On the other hand, benzylamines with p-methoxy and H, fell on a different line (Fig. 1). It is evident from Table I, that for X = m-F, m-Cl and m-Br, as the molecular weight of substituent X increases, the ΔH_m and ΔS_m values decrease. The size of the substituent has a clear influence on the crystalization behavior of these compounds.

When cooling sample X = m-F at 10°C/min, a

mesophase $\ell_i \rightarrow \ell_n$ transition was recorded at 341.5°K, which was immediately followed by a $\ell_n \rightarrow S$ transition at 339.5°K. The same behavior was not clearly observed during the heating process. On the other hand, a shoulder in the DSC curve appeared very close to the melting temperature (Fig. 2).

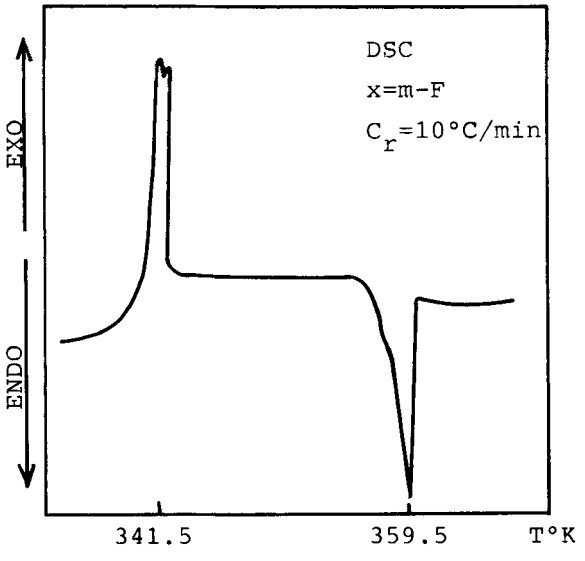

Fig. 2. DSC Trace Sample X = m - F

Correlations between molecular weight, electronegativities, substituent size[7] and values of ΔH_m and ΔS_m were tested. Only those benzilamines with halogen in their structure in meta position followed a straight line.

X-Ray analysis, polarized microscopy and density studies have been started and results will be published soon.

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