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MESOMORPHIC BEHAVIOR OF ENAMINE-KETONE COMPOUNDS

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ABSTRACT: Several compounds containing the six-membered hydrogen bonded enamine-ketone ring have been investigated by differential calorimetry. The results show that the enamine-ketone moiety can be used in the synthesis of new liquid crystalline compounds.

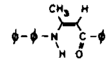
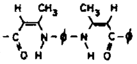
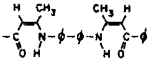
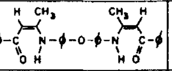
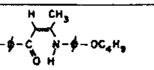
Recently, the melting behavior of some oligomeric para-linked polyphenyls was investigated and the nature of their mesophases was verified.[2,3] The first compound in the series to display a nematic mesophase was p-quinquephenyl. In general, these compounds exhibited relatively high melting temperatures and, in the case of p-sexiphenyl, decomposed at 500°C in the nematic mesophase before forming an isotropic liquid. It was also determined that p-sexiphenyl formed a smectic A mesophase at 434°C which is interesting from the viewpoint of current theories on molecular structure and the formation of smectic phases.

In this study, several compounds analogous to the para-linked polyphenyls were synthesized and studied in which one or more of the phenyl rings has been replaced by a hydrogen bonded enamine-ketone ring. The compounds were synthesized by the condensation of amines with β-ketones to yield, with the removal of water, the desired enamine-ketone compound. The products appeared to be the enamine-ketone form rather than the imine form as indicated by infra-red, carbon 13 and proton NMR spectroscopy. Their melting behavior was determined using a DuPont 990 Thermal Analyzer with a DSC cell in a nitrogen atmosphere at a heating rate of 5°C per minute. This behavior was corroborated by a programmable thermal optical analyzer which also allowed inspection of the materials between crossed polarizers during the heating and cooling cycles.

RESULTS AND DISCUSSION

The structures and melting behavior for the five compounds synthesized in this study are shown in Table I.

TABLE I Melting Behavior Data for Enamine-Ketone Compounds

Compound	Transition	T,°C	ΔH x 10^4, cal/mole	ΔS, cal/mole/°K
1 	K → i	149	1.04	24.6
2 	$K_I \rightarrow K_{II}$ $K_{II} \rightarrow i$	202 225	.022 1.24	.463 24.9
3 	K → n n → i	244 248	1.67 —	32.3 —
4 	K → i	155	—	—
5 	K → i	152	—	—

It should be noted that these structures are quite unusual and do not conform to the generalized structure of a liquid crystalline molecule with a rigid rod center and para-linked flexible aliphatic tails extending from the ends of the rigid core. Four of the five compounds in Table I did not show any liquid crystalline behavior and melted directly from a crystalline solid to an isotropic liquid. Cooling these compounds from the isotropic liquid did not show any evidence of a monotropic mesophase. It is not surprising that compound 4 does not exhibit a mesophase since the introduction of an oxygen linkage produces a bend in the center of the molecule. The synthesis of compound 5 was performed to discover if a single flexible tail extending from the end of the molecule would stabilize a nematic phase. The single compound which exhibited a nematic phase over a 4°C temperature range was bis-4,4'-(2-benzoyl-1-methylvinylamino)biphenyl, 3. The appearance of this phase could be easily missed as the nematic→isotropic transition revealed itself as a barely discernable shoulder on the high temperature side of the solid→nematic transition. It was not possible to determine the nematic→isotropic heat of transition due to the poor resolution of the DTA/DSC trace. The transition temperatures for this compound, quoted in Table I, were taken from the plot of transmitted light intensity versus temperature obtained from the thermal optical analyzer which provided better evidence for the existence of this phase. However, it should be noted that Barrall and Sweeney have found that the major change in anisotropy does not always coincide with the maximum heat consumption as determined by DSC/DTA.[4] A nematic texture was seen on heating and was clearly evident on cooling since the nematic phase supercooled and did not crystallize to a solid until 181°C. A photograph of the nematic texture is shown in Figure 1.

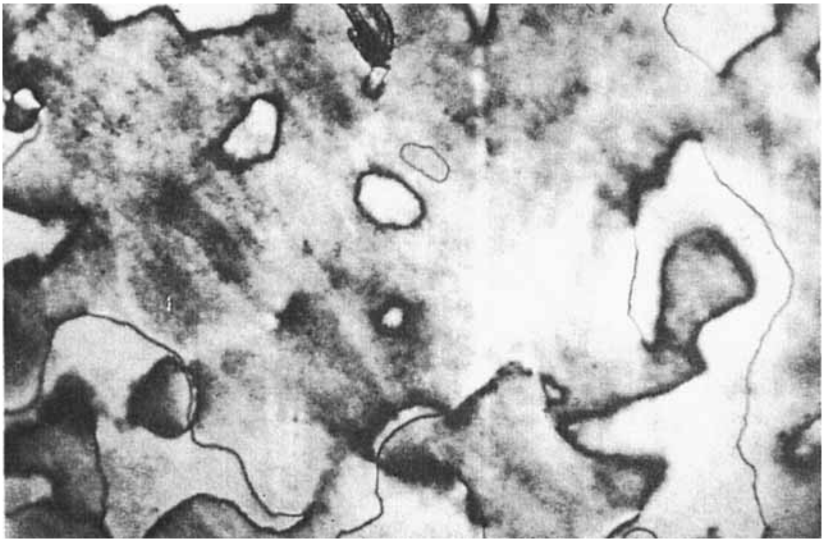


FIGURE 1 Nematic texture of bis-4,4'(2-benzoyl-1-methylvinylamino)biphenyl. Crossed polarizers, cooling cycle, 230°C, X135.

Comparisons of the para-linked oligomeric polyphenyls to the analogous compounds in which one or more of the phenyl rings has been replaced by an enamine-ketone ring demonstrate two main points. Substitution of the enamine-ketone ring for a phenyl ring lowered the melting temperatures in these model compounds. This was achieved while maintaining the liquid crystalline nature in compounds with an unconventional structure.

Secondly, it should be pointed out that the oligomeric polyphenyls are not very soluble. In contrast to this, the enamine-ketone compounds are soluble in chloroform. On the basis of these model compound comparisons, it should be expected that liquid crystalline polymers can be synthesized which exhibit lower melting points and increased solubilities than their phenyl ring analogues. Additional work on enamine-ketone containing liquid crystals is forthcoming.

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