

# THE ROLE OF FREE RADICALS AND MOLECULAR SIZE IN MESOPHASE PITCH

I. C. Lewis and C. A. Kovac

Union Carbide Corporation, Carbon Products Division  
Parma Technical Center, Parma, Ohio 44130

## I. Introduction

It is now apparent that the mesophase in pitch can be classified as a nematic liquid crystalline phase.<sup>1,2,3</sup> Most conventional liquid crystals consist of rod-like molecules often containing polar functional groups. Shape factors and polarizability are thought to play a dominant role in liquid crystal formation in such molecules.<sup>4</sup> Since pitch largely contains nonpolar aromatic hydrocarbons and heterocyclics which are flat and disc-shaped, the mechanism for liquid crystal formation in pitch is not understood. Various proposals have been made concerning the liquid crystal interactions in pitch including the involvement of free radicals.<sup>5</sup>

In this paper, we have studied the melting behavior of model compounds which are prototypes of the components of pitch in an attempt to clarify the molecular requirements for mesophase formation.

## II. Experimental Procedure

**A. Aromatic Compounds** - The aromatic compounds, coronene, 1, 2, 8, 9 - dibenzpentalene, decacyclene, 13, 13' - dibenzanthronyl and anthraceno (2',1':1,2) - anthracene were obtained from commercial sources and purified by vacuum sublimation. The hydrocarbon 9,9'-bianthryl was synthesized by the reduction of anthraquinone with Sn and HCl in acetic acid.<sup>6</sup> The compounds 1,14,7,8 - dibenzoperopyrene and terrylene were separated in liquid chromatographic fractions of pitches prepared from pyrene and naphthalene respectively. UV - visible absorption spectroscopy showed that these compounds were the main components of the specific chromatographic fractions.

**B. Stable Aromatic Hydrocarbon Free Radical Precursors** - Benzanthrene and naphthanthrene were synthesized by reduction of benzanthrone and naphthanthrone tosylhydrazones respectively.

**C. Melting Determination** - The melting behavior of the compounds and mixtures were studied using a Kofler micro-hot stage in combination with a Leitz polarizing microscope.

## III. Experimental Results

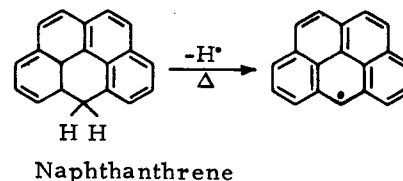
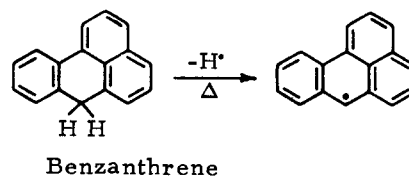
### A. Melting Behavior of Individual Compounds

The individual compounds and their melting points are listed in Table I. Several of the materials melted over a temperature range as a result of the presence of impurities. This was particularly true of the chromatographically separated products, terrylene and dibenzoperopyrene. The most important point,

however, is that in no instance was a liquid crystal transition observed during the melting of any of the compounds in Table I.

### B. Melting Behavior of Terrylene in the Presence of Aromatic Free Radicals

Benzanthrene and naphthanthrene thermally dissociate on melting to form stable free radicals.<sup>7,8</sup>



Examination of these compounds on the hot stage showed that their melting occurred without exhibiting any liquid crystal transition. Mixtures of the hydrocarbon terrylene with approximately equal amounts of the free radical formers were then heated on the hot stage through the melting range and at temperatures up to 400°C. The results are shown in Table II.

Terrylene was found to react rapidly at a low temperature of 350°C to give directly a liquid crystal phase. Mixtures of terrylene with the free radical precursors did not show any liquid crystal transition in the temperature range of free radical formation. In fact, the presence of the free radicals seemed to inhibit the liquid crystal development in terrylene.

## IV. Conclusions

From the results of these studies we conclude that:

1. Large aromatic molecules, even those containing nine condensed rings did not form a liquid crystal phase on melting.
2. Aromatic free radicals do not induce liquid crystal formation for such compounds.
3. Molecular size appears to be a key requirement for development of mesophase from aromatic hydrocarbons.

## References

1. J. D. Brooks and G. H. Taylor, Chemistry and Physics of Carbon, edited by P. L. Walker, Volume 4, p. 243, Dekker, New York, 1968.
2. J. Nehring and A. Saupe, Trans. Far. Soc. II, 11(1972).
3. H. Marsh, Fuel 52, 205 (1973).
4. G. W. Gray, Advances in Liquid Crystals, edited by G. H. Brown, Volume 2, (1976).
5. I. C. Lewis and L. S. Singer, Proceedings of the 12th Biennial Conference on Carbon, p. 265 (1975).
6. F. Bell and D. H. Waring, J. Chem. Soc. 267 (1949).
7. I. C. Lewis and L. S. Singer, Carbon 7, 93 (1969).
8. I. C. Lewis and C. A. Kovac - Unpublished results.

Table II

Melting Behavior of Terrylenes with Free Radical Formers

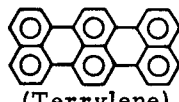
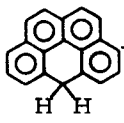
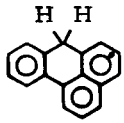

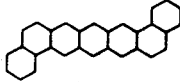
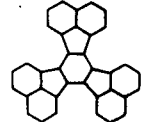
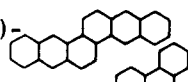
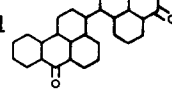
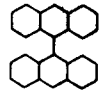
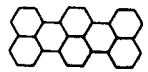
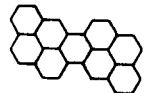
Sample Composition	Melting Range(°C)	Mesophase Formation Temperature (°C)
 (Terrylenes)	155-210	350
 + Terrylenes	100-130	400
 + Terrylenes	80-150	375

Table I

Melting of Aromatic Compounds

Compound	Structure	Melting Range °C (Hot Stage)
Coronene		415-427
1,2,8,9-Dibenzo pentacene		435
Decacycene		391-401
Anthraceno (2',1':1,2)-anthracene		413-421
13,13'-Dibenzanthronyl		355
9,9'-Bianthryl		300
Terrylenes		155-210
1,14,7,8,-Dibenzo peropyrene		400-440