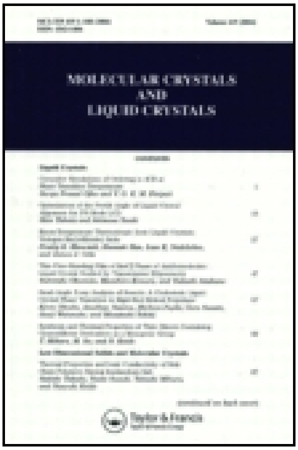

Molecular Crystals and Liquid Crystals

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

The Plastic Crystal State of Ferrocenecarbaldehyde

Jack M. Wilson [a] , Rhonda Harden [a] & Jay Phillips [a]

[a] Department of Physics, Sam Houston State University, Huntsville, Texas, 77340

To cite this article: Jack M. Wilson , Rhonda Harden & Jay Phillips (1976): The Plastic Crystal State of Ferrocenecarbaldehyde, Molecular Crystals and Liquid Crystals, 34:10, 237-240

To link to this article: http://dx.doi.org/10.1080/15421407708083713

Mol. Cryst. Liq. Cryst., Vol. 34 (Letters), pp. 237-240
©1977, Gordon and Breach Science Publishers, Ltd.
Printed in the United States of America

THE PLASTIC CRYSTAL STATE OF FERROCENECARBALDEHYDE*

JACK M. WILSON, RHONDA HARDEN, AND JAY PHILLIPS
Department of Physics
Sam Houston State University
Huntsville, Texas 77340

(Submitted for Publication May 13, 1977)

ABSTRACT

Mössbauer spectroscopy and microscopic observation indicate that the state of ferrocenecarbaldehyde between 43.5°C and 123.5°C is a plastic crystal state and could not be a liquid crystal state. Sudden loss of mössbauer effect and birefringence at the lower transition temperature may be explained in terms of the increased rotational mobility of plastic crystals.

I. INTRODUCTION

The apparent liquid crystalline state of ferrocenecarbaldehyde was first observed by Graham et al[1] and more recently investigated by Verbit and Halbert.[2] Each of these investigators reported that ferrocenecarbaldehyde exhibits a liquid crystalline state between approximately 44°C and 125°C. The transition from solid to liquid crystal is sharp and accompanied by a sudden loss of birefringence, however the resulting state is highly viscous. Verbit and Haller determined more precisely that the melting transition occurred at 43.5°C with an enthalpy of transition of 3.0 k cal/mole and an entropy of 9.5 cal/deg mole, while the clearing point occurred at 123.5°C with enthalpy of 0.6 k cal/mole and entropy of 1.6 cal/deg mole. They suggest an interpretation of the state in terms of plastic crystals[3] or alternatively as an isotropic liquid crystal.

The loss of birefringence prevents the assignment of the phase to one of the standard classifications on the basis of textures observed on microscopic observation between crossed polarizers. The optical isotropy implied by this observation is the unusual and interesting property that distinguishes this compound from other reported liquid crystals.

We have investigated the lattice rigidity of this compound as well as the molecular isotropy of the structure through the observation (or lack of observation) of mössbauer effect in the temperature range of 25°C to 55°C.

II. RESULTS AND DISCUSSION

Observation through a polarizing microscope of a small quantity of ferrocenecarbaldehyde between a cover slip and slide showed the abrupt loss of birefringence near the melting transition temperature reported above. The optical isotropy persisted to room temperature, super cooling, as reported by Verbit and Halbert. The sample would remain in the super cooled state for several hours after reaching room temperature before crystallizing to the birefringent solid. Little change was observed in the appearance of the sample over the entire range of the mesophase including the supercooled range.

A sample of ferrocenecarbaldehyde was mounted in a 2mm thick nylon washer with inside diameter of 1.25 cm. The washer was mounted in a cylindrical brass oven with a concentric 1.25 cm hole along the axis. The oven's temperature was controlled to within 0.5°C, however the accuracy of temperature measurement was ± 1°C. The gamma beam from the mössbauer spectrometer was directed through the oven and sample. A series of spectra was obtained in the temperature range from 25°C to 55°C. Figure 1 shows the percent effect as a function of temperature.

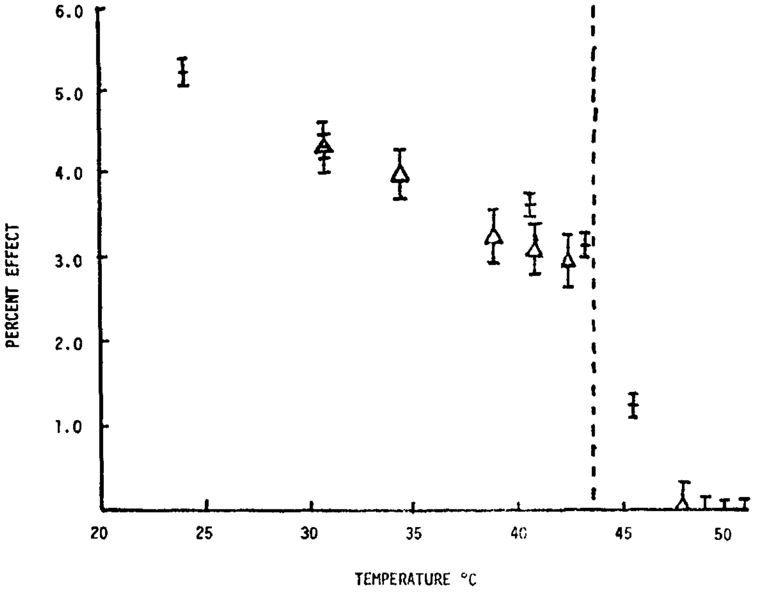

Fig. 1

The percent effect of the thin sample (Δ) was normalized to be the same as the thick sample (+) at 30.5°. The actual percent effect was .79% at 30.5°. Of course the standard deviation of the thin sample data is larger than the thick as shown. For the thick sample the 44.5° run was probably a mixture of solid and mesophase because temperature gradients across the sample may have been large. Otherwise, the abrupt disappearance of the effect coincides with the melting temperature. This is in contrast to liquid crystals in which the disappearance of the mössbauer effect anticipates the phase change.[5,6,7] The disappearance of the effect in the mesophase indicates that the structure is dramatically less rigid than the solid. This is somewhat surprising in view of the high viscosity of the mesophase. It has also been shown[6,7] that the Mössbauer effect would be observable in a very viscous liquid crystal state. We would have seen any effect in the mesophase larger than 0.05 percent.

Because of this loss of Mössbauer effect at the melting point we are forced to conclude that upon melting the molecule gains either translational or rotational mobility. The extremely high viscosity would indicate that any increased mobility must be rotational rather than translational. This would be consistent with the optical isotropy in the mesophase. These properties are inconsistent with the models of liquid crystals in which molecules have substantial translational mobility and minimal rotational mobility. In fact ferrocenecarbaldehyde appears to be best classified as a plastic crystal. Although many known plastic crystals exhibit second order phase transitions, it is well known that the rotational transition becomes first order when the molecular enevelope is an oblate sphere or pear shaped.[3,9] The first order transitions reported by Verbit and Halbert would thus be understandable in terms of the shape of ferrocenecarbaldehyde.

ACKNOWLEDGEMENTS

We are grateful to Dr. L. Verbit of S.U.N.Y. at Binghamton for a gift of chemicals, and to both he and Dr. D. Uhrich of Kent State University for several helpful conversations.

*This work was supported by the Robert A. Welch Foundation of Houston, Texas on grant number X-588.

REFERENCES

1. P. J. Graham et al., J. Amer. Chem. Soc., 79, 3416 (1957).

2. L. Verbit and T. R. Halbert, Mol. Cryst. and Liq. Cryst., 30, 209 (1975).
3. J. G. Aston, in Physics and Chemistry of the Organic Solid State, ed. D. Cox, M. M. Labes and A. Weissberger, Interscience, New York, 1963, Chapter 9.
4. H. Sackman and D. Demus, Mol. Cryst., 2, 81 (1966).
5. D. L. Uhrich, J. M. Wilson, and W. A. Resch, Phys. Rev. Lett, 24, 355 (1970).
6. J. M. Wilson and D. L. Uhrich, Mol. Cryst. and Liq. Cryst. 25, 113 (1975).
7. R. E. Detjen, D. L. Uhrich, and C. F. Sheley, Physics Lett., 42, 522 (1973).
8. D. L. Uhrich, R. E. Detjen, and J. M. Wilson, Möss. Effect Meth., 8, 175 (1972).
9. J. G. Aston, Pure Appl. Chem, 2, 231 (1961).