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

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To cite this article: T. J. Klingen & J. R. Wright (1972): Further Evidence for the Plastic Crystalline Nature of l-Vinyl-o-Carborane, Molecular Crystals and Liquid Crystals, 16:4, 283-289

To link to this article: http://dx.doi.org/10.1080/15421407208082791

Molecular Crystals and Liquid Crystals. 1972. Vol. 16, pp. 283–289

Printed in Great Britain

Further Evidence for the Plastic Crystalline Nature of 1-Vinyl-o-Carborane†

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Received June 15, 1971; *in revised form August* 13, 1971

Abstract—In the course of this investigation it has been shown that 1-vinyl-*o*-carborane has two phases between the crystalline solid below −65 °C and the isotropic liquid above +79 °C. In phase I between +11 and +79 °C, this waxy material has been shown to be isotropic with a face-centered cubic structure. In this phase the NMR resonance line width was a function of temperature and found to be of the order of 0.01 gauss, which is consistent with spherical rotation and diffusional motion of the molecular centers of gravity. The evidence presented here together with that previously reported provides convincing evidence of the plastic crystalline nature of phase I. In the range of −65 to +11 °C, phase II, 1-vinyl-*o*-carborane has been shown to be birefringent and more crystalline like in nature.

1. Introduction

It has been previously reported that in the γ-ray radiolysis of 1-vinyl-1,2-dicarba-*closo*-dodecaborane-(11),1-vinyl-*o*-carborane, a high yield of polymer was formed in the waxy phase which exists between +11 °C and the capillary melting point.(1) Since the initial report, evidence was found strongly indicating that this condensed state of 1-vinyl-*o*-carborane was mesomorphic, most probably plastic crystalline in nature.(2) It is the purpose of this work to provide further evidence for the plastic crystalline nature of 1-vinyl-*o*-carborane, which in many respects can be shown to be analogous to substances such as *d*-camphor, a representative example of this dynamic state of matter.

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† This research was supported by the U.S. Atomic Energy Commission under Contract Number AT-(40-1)-3781.

‡ Taken in part from the Ph.D. dissertation of J. R. Wright at The University of Mississippi, August, 1971.

2. Experimental

The 1-vinyl-*o*-carborane used in these studies was obtained from Alfa Inorganics, Inc. This material was purified in either of two ways: the first technique used was vacuum sublimation in a manner described previously;(2) the second method involved the use of preparative GLC(3) on a carbowax-20M column which gave baseline resolution for variously substituted carboranes. Both of these techniques yielded products which were indistinguishable. Methods for discerning the purity of carboranes have been described,(2) and the material described here, according to those criteria, was pure.

A Nikon AFM polarizing microscope was employed for optical examinations; DTA recordings were made with a Columbia Scientific Industries model 202 instrument; a Norelco–Phillips generator and Debye–Sherrer powder camera were used in the X-ray diffraction study; and NMR linewidth data were obtained from absorption spectra using a Varian Associates A-60-A NMR spectrometer.

3. Results

A. DIFFERENTIAL THERMAL ANALYSIS (DTA)

In the previous paper(2) the DTA of 1-vinyl-*o*-carborane was reported in the temperature range between + 5 °C and + 100 °C. In the present study the range was extended to − 150 °C. As is shown in Fig. 1, another endotherm was found to occur at − 65 °C. This DTA recording is at least similar to that of other plastic crystals,(4) indicating the existence of two phases between the crystalline state below − 65 °C and the liquid state above + 79 °C.

B. BIREFRINGENCE

1-vinyl-*o*-carborane sublimed onto a slide which was kept at 0 °C was both crystalline and birefringent. When this material was warmed very carefully to room temperature there resulted an almost total loss of birefringence. The isotropic wax could be obtained by melting this material and allowing it to cool to ambient under a cover slip, or merely by applying mechanical stress to it.

It appears that in the phase immediately below + 11 °C (phase II), 1-vinyl-*o*-carborane occupied a lattice of other than cubic symmetry.

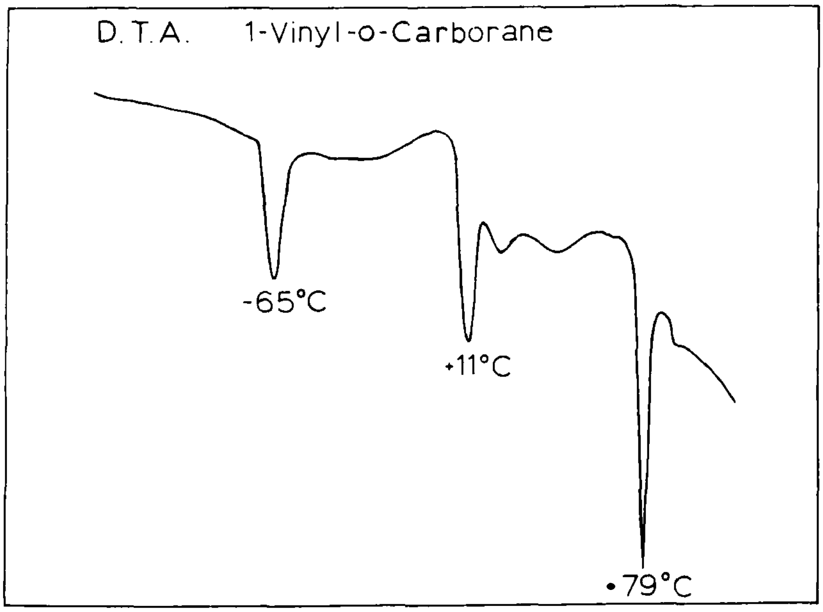

Figure 1. Differential thermal analysis of 1-vinyl-*o*-carborane between −150 and +100 °C using Al_2O_3 as a reference material.

The weak birefringence observed when this material was warmed to room temperature is believed to be due to a superheating phenomenon (i.e., a metastable state was formed).(5)

C. X-RAY DIFFRACTION

The X-ray diffraction phenomena of plastic crystals have been reviewed by Aston.(6) In the limited number of representative examples studied thus far it is observed that the intensities of the diffracted rays fall off sharply with increasing Bragg angle, resulting from a motion and distribution in the lattice such that inphase scattering is confined to electron distributions nearest the molecular centers of gravity, while out of phase scattering produces a heavy background. Also, the approximately spherical symmetry of molecules in almost free rotation leads to lattices of high symmetry,(7) commonly of the cubic type.

We have previously reported(2) that diffractometer scans of 1-vinyl-*o*-carborane wax (25 °C) yielded only two glancing angles and that these corresponded to *d*-spacings at 6.06 Å and 5.27 Å. The geometrical relationship between these two spacings is $2/\sqrt{3}$ and thus consistent with reflections from the 111 and 200 planes of a cubic system. We have since determined these spacings more accurately as 6.12 Å and 5.29 Å and observed additional weak reflections using powder photographs exposed for periods ranging up to 24 hours. *d*-spacing ratios and absences as given in Table 1 are characteristic of a face-centered cubic structure. Data regarding the relative intensity of these lines has not been interpreted.

TABLE 1 X-ray Diffraction Data on 1-Vinyl-*o*-Carborane†

2 ϴ degrees	Rel. intensity	$d_{\text{obs.}}$ Å	$d_{\text{calc.}}$ Å	(hkl)
14.45	very strong	6.12	6.12	111
16.75	strong	5.29	5.29	200
23.75	weak	3.74	3.74	220
27.93	weak	3.19	3.19	311
29.13	weak	3.06	3.06	222

† A Debye–Sherrer powder camera was used to obtain the spectra at 25 °C in a five hour exposure to copper K_α radiation.

A heavy background due to incoherent scattering was evident on these photographs; also, the lines were spotty, indicating a finite number of crystallites within the capillary sample holder. This finding is consistent with the microscopically observed morphology of the wax. These results yielded a lattice constant equal to 10.6 Å at 25 °C and a density of 0.950 gm/cm³.

D. NUCLEAR MAGNETIC RESONANCE

The NMR linewidths immediately below the capillary melting point were narrow enough to be observed with a high resolution spectrometer. Figure 2 presents a succession of scans (cooling) obtained between +46 °C and +96 °C. The complex multiplet downfield ($\delta \sim 6$ ppm) is due to the vinyl group, while the broad singlet upfield ($\delta \sim 4$ ppm) is characteristic of the C–H exopolyhedral; $B_{10}H_{10}$ group protons are buried beneath these resonances unless the spectra are recorded at high amplitude.

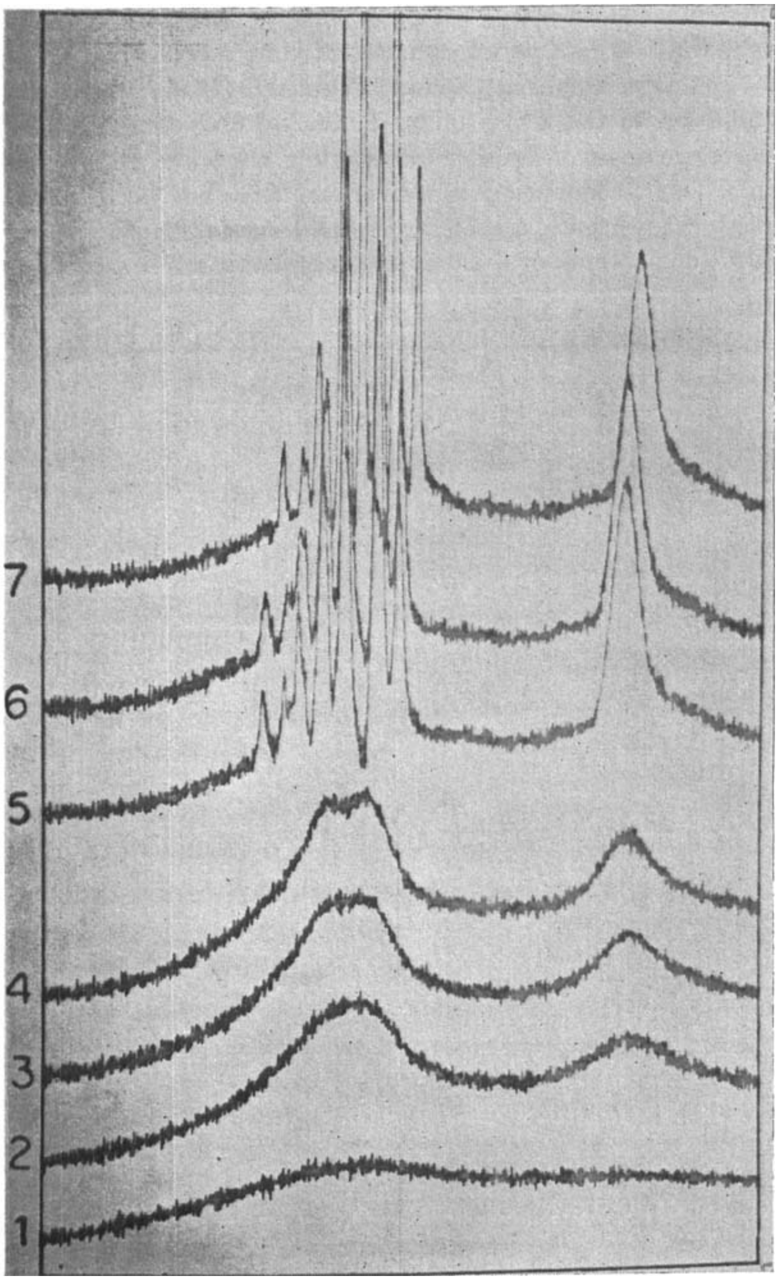

Figure 2. Proton NMR spectra of pure 1-vinyl-*o*-carborane: 1, 46 °C; 2, 66 °C; 3, 71 °C; 4, 76 °C; 5, 81 °C; 6, 86 °C; and 7, 96 °C.

Figure 3 shows a plot of linewidth versus temperature and is based on the width at half peak height observed for the vinyl group alone. This method is admittedly somewhat arbitrary, but it does indicate, in addition to the discontinuity at the capillary melting point, a progressive onset of disorder immediately below the +79 °C transition. This phenomenon is similar to what has been noted for cholesteryl benzoate, a cholesteric liquid crystal.[8] Measurements below + 35 °C were not feasible with a high resolution instrument.

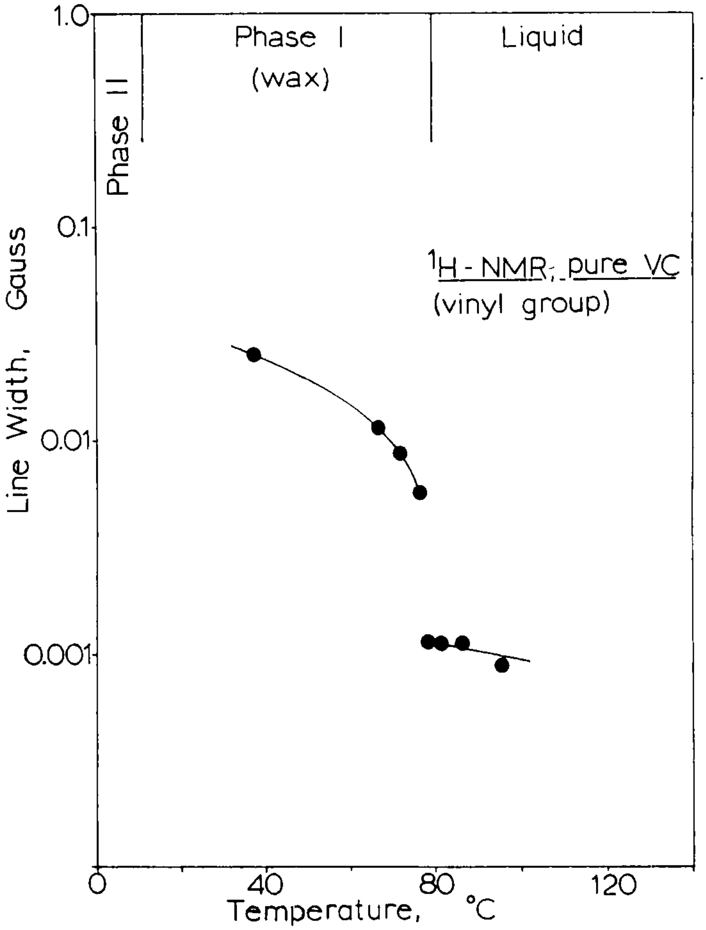

Figure 3. NMR line width of the vinyl resonance of 1-vinyl-o-carborane as a function of temperature.

These narrow linewidths observed in the wax, phase I, of about 0.01 Gauss or less, are consistent with spherical rotation and diffusional motion of the molecular centers of gravity.(6)

4. Discussion

The NMR evidence presented above is a good indication of liquid-like rotation well below the capillary melting point, while the observance of a cubic close packed structure and its resultant optical isotropy establishes a strong relationship between 1-vinyl-*o*-carborane and the other known plastic crystals.(6) Phase II of 1-vinyl-*o*-carborane may involve rotational orientation of almost-spherical *o*-carboranyl polyhedron, or perhaps rotation or libration about a molecular axis, although this question cannot be resolved at the moment.

Acknowledgements

The authors wish to thank Professor W. O. J. Boo for running the X-ray diffraction spectra and Columbia Scientific Industries for running the low temperature differential thermal analysis. One of us (J.R.W.) wishes to thank the U.S. Atomic Energy Commission for fellowship support during the course of this investigation.

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