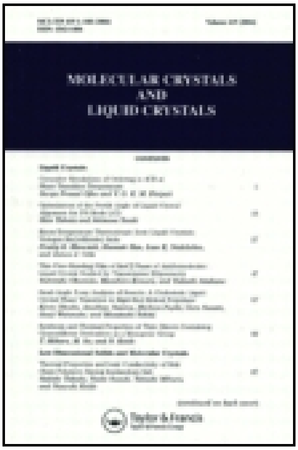

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Investigations of Plastic Crystallinity in a Series of Organo-Substituted Carboranes[†]

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This investigation is concerned with the study of a series of organo-substituted 1,2-dicarba-*closo*-dodecaborane-11 (*o*-carboranes) compounds for plastic crystalline behavior. Differential thermal analysis has shown the existence of low temperature mesophases for six of the series of ten compounds studied. X-ray powder diffraction investigation of the six compounds showing mesophases indicates that in the highest temperature phase three had facecentered cubic lattices and the others orthorhombic lattices. Of the three compounds on which X-ray powder diffraction data at low temperature was obtained, it was shown that all had lattices in all of the lower temperature phases that could be indexed as orthorhombic.

INTRODUCTION

Previous investigations of the physical properties of 1-vinyl-*o*-carborane[1] have established that this compound exhibits characteristics of the plastic crystalline state of matter at ambient temperature. It was shown to be optically isotropic, waxy material the molecules of which occupy a face-centered cubic lattice with subambient phase transitions of large entropy compared to that observed at the isotropic melting point. The present investigation was initiated to establish:

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1.) the existence of other carborane derivatives exhibiting these properties, 2.) the effects of varying the structure of the organic substituent group upon the mesomorphic behavior, and 3. the nature of the lower temperature phases observed by powder X-ray diffraction within the plastic crystalline carborane mesophases.

EXPERIMENTAL

Commercial samples of *o*-carborane and l-vinyl-*o*-carborane (Olin Chemical Co.) were purified by vacuum sublimation and column chromatography on a one meter silica gel column. l-Isopropenyl-*o*-carborane and l-bromomethyl-*o*-carborane (Ventron-Alfa Inorganic Chemicals) were purified by vacuum sublimation and preparative gas chromatography on an eight foot SF-96 column. The l-allyl-*o*-carborane was purified by preparative gas chromatography on a six foot Carbowax-20M column. The l-methyl-*o*-carborane was prepared by the hydrolysis of 1-carboranyl methyl magnesium bromide prepared from 1-bromomethyl-*0*-carborane with magnesium turnings in anydrous ether.[2] The l-*n*-propyl-*o*-carborane and 1,2-dimethyl-*o*-carborane were prepared by reaction of *n*-propylbromide and methyliodide with the lithium salts[3,4] of *o*-carborane and l-methyl-*o*-carborane in anhydrous ether, respectively. The preceeding three carborane derivatives were purified by preparative gas chromatography on the eight foot SF-96 column. The l-phenyl-*o*-carborane was provided by Prof. John N. Little of this department. It was purified by re-crystallization from cyclohexane followed by vacuum sublimation.

The mesomorphic transition temperatures of these carboranes were obtained on a differential thermal analysis apparatus similar to the design of Barrell, Porter and Johnson.[5] A gas cooling loop was added to permit operation down to $-100°C$ and the samples were sealed in evacuated melting point tubes. Linear temperature ramps were provided by a Varian Aerograph model 202 gas chromatograph temperature programmer and ΔT versus time plots[6] were recorded on a Sargent x-t recorder. The transition temperatures were manually recorded using a Honeywell model 2745 potentiometer with an ice point reference.

A specially constructed flat plate powder diffraction camera[7] was utilized in conjunction with a Norelco X-ray generator to record the low temperature X-ray data. Cooling was provided by a low temperature nitrogen gas stream and the sample area was enclosed with mylar film during exposure to prevent moisture condensation on the sample capillary. Sample temperatures were monitored during exposure with a thermocouple placed just below the beam and varied $\pm 1.5°C$ during the experiment. The ambient temperature X-ray data was obtained using a standard powder camera with the Norelco X-ray generator. The powder diffractions lines were indexed as centered orthorhombic lattices utilizing the graphical procedures described by Lipson.[8]

Molecular volumes calculated from the lattice constants were compared with those observed from flotation densities at ambient temperature. Flotation densities[9] of these carboranes were measured in water-isopropanol mixtures for densities less than one and in water-sodium bromide solutions containing a surfactant to wet the carborane surfaces for densities greater than one.

RESULTS

Plastic crystalline behavior has been observed for six carborane derivatives in this study. The parent member of the series, *o*-carborane forms a face-entered cubic lattice at ambient temperature with a single phase transition at +3°C. Since the area of this transition is only 30% of that observed at the isotropic melting point and the carborane is a relatively hard organic-like solid, it can be regraded as a disordered crystalline solid rather than a true plastic crystalline solid. Both l-methyl-*o*-carborane and 1-bromomethyl-*o*-carborane, with densities of 0.969 and 1.30 g/cc, respectively, are too soft to be powdered and form single crystals when cooled from the melt, thus precluding X-ray powder diffraction measurements. Also no phase transitions are observed for either of these compounds below the isotropic melting point, Table 1. In the case of 1-isopropenyl-*o*-carborane, no phase transitions are observed below the isotropic melting point as shown in Table 1. The X-ray powder diffraction data for this compound, Table 2, indicates that in the solid state the lattice is orthorhombic but very

TABLE 1

Mesomorphic transitions of the carboranes

Compound	III	II	I	Melting Point
$H-\theta-H$	---	---	+3°C	+295°C
$CH_3-\theta-H$	none	none	none	+223°C
$BrCH_2-\theta-H$	none	none	none	+31°C
$CH_3-\theta-CH_3$	-24°C	+7°C	+23°C	+266°C
$C_2H_5-\theta-H$	-35°C	-12°C	+7°C	+37°C
$CH_2{=}CH-\theta-H^a$	---	-65°C	+11°C	+79°C
$C_3H_7-\theta-H$	-34°C	-9°C	+26°C	+67°C
$CH_2{=}CHCH_2-\theta-H$	---	-36°C	-16°C	-3°C
$CH_2{=}(CH_3)C-\theta-H$	none	none	none	+45°C
$\phi-\theta-H$	+18°C	+28°C	+36°C	+72°C

ϕ = phenyl group; $\theta = C_2B_{10}H_{10}$ cage group

[a] T.J. Klingen and J.R. Wright, *Mol. Cryst. Liq. Cryst.*, 16, 283, (1972).

TABLE 2

Ambient temperature[a] carborane crystal lattices and molecular volumes

Compound	Structure	*Molecules* Unit Cell	Lattice Constants	Lattice Volume Powder X-ray	Molecule Flotation	Flotation Density
$H-\theta-H$	fcc	4	a = 9.82 A	237 A^3	243 A^3	0.984g/cc
$CH_3-\theta-CH_3$	fcc	4	a = 10.6 A	298 A^3	---	---
$C_2H_5-\theta-H$	fcc	4	a = 10.6 A	298 A^3	304 A^3	0.929g/cc
$CH_2{=}CH-\theta-H$	fcc	4	a = 10.6 A	298 A^3	304 A^3	0.929g/cc
$C_3H_7-\theta-H$	orthorhombic	16	a = 21.0 A b = 16.9 A c = 13.7 A	304 A^3	308 A^3	1.002g/cc
$CH_2{=}(CH_3)C-\theta-H$	orthorhombic	4	a = 11.5 A b = 11.3 A c = 9.9 A	322 A^3	301 A^3	1.015g/cc
$\phi-\theta-H$	orthorhombic	8	a = 18.6 A b = 14.1 A c = 10.5 A	336 A	327 A	1.118g/cc

[a] Ambient temperature 23 to 25°C

θ represents carborane cage $C_2B_{10}H_{10}$; ϕ represents phenyl group C_6H_5.

nearly tetragonal. Thus, this compound, which is hard and brittle, can be considered as a crystalline solid below its isotropic melting point.

The compound, l-vinyl-*o*-carborane, has been previously observed to form plastic crystalline mesophases,[1] and has been tabulated in Table 1 for comparison purposes. The l-ethyl- and the 1,2-dimethyl-*o*-carboranes have been shown to have three mesomorphic transitions as shown in Table 1. The plastic crystalline transitions of 1,2-dimethyl-*o*-carborane are only slightly higher than that observed for the unsymmetrical l-ethyl- and l-vinyl- derivatives of identical carbon number. Although the 1,2-dimethyl-*o*-carborane has a much higher isotropic melting point, Table 4, it has a face-centered cubic lattice with a 10.6Å unit cell edge identical to that observed for the l-ethyl- and l-vinyl-*o*-carboranes.

Both l-*n*-propyl-*o*-carborane and l-allyl-*o*-carborane show mesomorphic behavior as indicated in Table 1. The l-*n*-propyl-*o*-carborane has three transitions below the isotropic melting point with the transition at +26°C being particularly large. Less than 5% of the total area of the endotherms is observed at the isotropic melting point transition. l-Allyl-*o*-carborane is the first liquid member of this class to exhibit mesomorphic behavior below ambient temperature having two low temperature phase transitions as shown in Table 1. The compounds l-*n*-propyl-, l-allyl- and l-phenyl-*o*-carboranes crystallize in nonprimitive orthorhombic lattices, as shown in Tables 2 and 3. Apparently the alkyl side chain is now too large to permit packing into the face-centered cubic system. In the case of l-phenyl-*o*-carborane three mesophases are observed, as shown in Table 1. This carborane derivative contains the largest substituent group of the series with all mesophase transitions occurring above +18°C.

In order to further characterize the low temperature transitions of l-vinyl-, l-ethyl- and l-allyl-*o*-carborane, low temperature X-ray powder diffractions of these compounds were also determined, Table 3. In l-vinyl-*o*-carborane the initial transition below +11°C gives rise to a more dense orthorhombic structure. The transparent ambient temperature phase turns translucent during the low temperature exposure and was previously observed[1] to form a birefringent crystalline material upon cooling. l-Ethyl-*o*-carborane undergoes transitions which distort the face-centered cubic lattice into lower orthorhombic symmetry without appreciable volume contraction until the lowest temperature phase at −50°C is reached. In the low temperature of l-allyl-*o*-carborane, Table 3, no unit cell volume change is observed below successive mesomorphic transitions, but the near tetragonal ordering of the highest temperature is further distorted into more distinct crystal axes at lower temperature.

TABLE 3

Low temperature carborane crystal lattices and molecular volumes

Compound	Temperature	Structure	*Molecules* Unit Cell	Lattice Constant	Lattice Volume/Molecule Powder X-ray
$C_2H_5-\theta-H$	− 5°C	orthorhombic	8	a = 16.0 A b = 13.9 A c = 10.8 A	301 A^3
	−28°C	orthorhombic	16	a = 21.0 A b = 15.6 A c = 14.3 A	293 A^3
	−50°C	orthorhombic	16	a = 17.65 A b = 15.4 A c = 13.8 A	235 A^3
$CH_2{=}CH-\theta-H$	−15°C	orthorhombic	8	a = 14.15 A b = 13.1 A c = 11.2 A	260 A^3
$CH_2{=}CHCH_2-\theta-H$	−10°C	orthorhombic	8	a = 16.9 A b = 12.8 A c = 12.1 A	328 A^3
	−26°C	orthorhombic	8	a = 19.1 A b = 12.3 A c = 11.3 A	332 A^3
	−50°C	orthorhombic	8	a = 18.9 A b = 13.3 A c = 10.6 A	333 A^3

TABLE 4

Isotropic transition temperature of the carboranes[a]

Compound	°C	Compound	°C
$CH_3-\theta-H$	203	$H-\theta H$	295
$CH_3-\theta-I$	126	$CH_3-\theta-CH_3$	260
$CH_3-\theta-CH_2Br$	126	$I-\theta-I$	165
$CH_2BR-\theta-H$	36	$BrCH_2-\theta-CH_2Br$	62
$C_2H_5-\theta-H$	37		
$C_2H_3-\theta-H$	79		
$CH_2=(CH_3)C-\theta-H$	45	$\theta-[-C(CH_3)=CH_2]_2$	82
$C_3H_5-\theta-H$	-3	$\theta-(C_3H_5)_2$	62

[a] R.T. Holzman, Ed., *Production of the Boranes and Related Compounds*, Academic Press, New York, 1967.

DISCUSSION

The experimental results indicate that more than half of the series of organocarborane derivatives with substituents containing two to six total carbons exhibit plastic crystalline behavior near ambient temperature. Of the compounds forming face-centered cubic lattices, the highest temperature plastic crystalline phase, all have cell constants of 10.6 Å whereas the parent compound, *o*-carborane, has a cell constant of only 9.82 Å with all compounds having four molecules per unit cell. Using the cell constants to calculate the total cell volume and the data of Ketelaar[10] to calculate the cell volume occupied by the molecule, an excess free volume of approximately 65 $Å^3$ per unit cell is observed in the case of these substituted carboranes relative to the *o*-carborane unit cell. This volume, approximately 6% of the total cell volume, is "free volume" in which hindered rotation can occur.

Guthrie and McCullough[11] have suggested that for plastic crystalline transitions in simple cubic systems, a method of estimating relative transition temperatures may be obtained by counting available occupancy sites. Substantially more sites should be available for the 1-ethyl- and 1-vinyl-*o*-carboranes in the cubic system since they possess 15 distinct orientations with respect to each cube corner whereas 1,2-dimethyl-*o*-carborane, of indentical lattice constant, has only one unique orientation with respect to each cell edge. Since no great differences are observed for the plastic crystalline transition temperatures of these derivatives, this simple counting procedure overestimates the trends with regard to even-odd substitution, although distinct differences are observed in the isotropic transition temperatures, as shown in Table 4. Hindered rotation about some axes due to the lower symmetry observed in the low temperature forms implies more complicated interactions must be considered in order to estimate the transition temperatures and energy barriers as indicated by the work of Chihara and coworkers[12,13] in simpler systems.

It is interesting to note that in the case of five of the six carborane derivatives showing mesomorphic behavior, X-ray diffraction data can be indexed to an orthorhombic lattice in their low temperature mesophases. Also, the increased size of the substituents in the cases of 1-allyl- and 1-phenyl-*o*-carborane may make their existence in a face-centered cubic lattice, in the high temperature mesophase, highly improbable.

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