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Phase Characterization and Enthalpies of Selected Disubstituted Biphenylcyclohexanes

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PHASE CHARACTERIZATION AND ENTHALPIES OF SELECTED DISUBSTITUTED BIPHENYLCYCLOHEXANES

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ABSTRACT

The data from DSC-thermal analysis of a selected number of disubstituted biphenylcyclohexanes is reported. All nonpolar compounds in the series exhibit smectic B-phases, whereas the polar members with e.g. halogenes or cyano groups either only occur in the nematic phase or nematic and smectic A-phase. The phase behaviour and the enthalpies of transition are discussed.

INTRODUCTION

The synthesis and the transition temperatures of a number of mesogenic compounds, possessing the formula $R-C_6H_{10}-C_6H_4-C_6H_4-X$ (BCH RX) where R and X (numerals stand for number of C-atoms in alkyl group) denote various kinds of terminal groups, had first been reported by Eidenschink et al,[1,2]. Several compounds in this series exhibit smectic properties. X-ray investigations pertaining to the liquid crystalline state, of all the compounds of this series in question, have been reported upon elsewhere [3]. Furthermore this contribution is also concerned with single crystal X-ray data of three members of the same series. As a matter of supplementing the information obtained from the X-ray investigations, the thermodynamic properties of these compounds are now reported on. Further information regarding the susceptibility [4] as well as birefrigence and density [5] have been reported on seperately.

EXPERIMENTAL

The transition temperatures were determined by means of a polarizing microscope Leitz-Orthoplan-Pol in conjunction with a hot stage Mettler FP-52 and control unit FP-5. The transition points were observed with crossed polarizers. The reproducibility of the transition temperatures is within ± 0.1 K. The calorimetric data of each compound was determined with a Du Pont 990 Thermal Analyzer in connection with the appropriate DSC-cell. Additionally the thermal behaviour of all investigated compounds was evaluated with the same apparatus. The heating rate for all thermal and calorimetric investigations was 2 K/min. This permits a reproducibility of ± 0.5 K for transition temperatures determined by means of DSC-analysis. For calibration purposes indium (99.999 %) was utilised. The areas of the endothermic peaks were integrated with a Haff-Planimeter permitting a reproducibility of ± 0.01 in^2. The mass of the samples was determined with a Sartorius micro-balance to within an accuracy of up to ± 0.01 mg.

RESULTS AND DISCUSSION

All mesogenic phase transition temperatures as well as the corresponding enthalpies as determined with the above mentioned apparatus are given in the Table 1.

It should be pointed out that the transition point S_A-N of BCH 7CN could only be determined with the polarizing microscope as practically no signal was obtainable in DSC-analysis even at very high sensitivities.

In addition to this BCH 7CN as well as BCH 5CN showed signs of deterioration when heated up to their clearing points. Subsequent clearing point determinations of the same previously heated samples showed a diminishing intensity and a shift in the transition signal.

All members of this series having a halogen or cyano as terminal substituent were more or less subject to sublimation.

Three of the compounds, namely BCH 50, BCH 52 and BCH 54, exhibit the characteristic mosaic-texture of smectic-B-phases (comparable to the textures of Demus and Richter [6]) when viewed through the polarizing microscope. In contrast to this BCH 30 possess a lancet-type texture with pseudoisotropic regions which is also typical for smectic - B phases. All compounds with halogen or pseudohalogen substituents (in para-position at the phenyl ring) only exhibit nematic phases with the sole exception of BCH 7CN which forms a focal-conic smectic - A phase.

Table 1 Transition temperatures (K) and corresponding enthalpies (kJ/mol) of selected disubstituted biphenylcyclohexanes (BCH RX)

Compound	Smectic phase	T_{C-N} T_{C-S}	ΔH_{C-N} ΔH_{C-S}	T_{S-N}	ΔH_{S-N}	T_{S-I} T_{N-I}	ΔH_{S-I} ΔH_{N-I}
BCH 30	S_B	345.4±0.3	12.0±0.7	-	-	366.1±0.5	8.3±0.6
BCH 50	S_B	331.1±0.3	12.0±0.2	354.8±0.3	4.7±0.2	371.1±0.5	0.4±0.2
BCH 52	S_B	308.0±0.9[a]	18.5±0.6	416.4±0.3	6.8±0.5	430.8±0.8	0.5±0.2
BCH 54	S_B	290.7±0.5	b	432.3±0.4	7.9±0.6	443.8±0.4	0.5±0.2
BCH 5F	-	367.5±0.5[a]	19.7±0.9	-	-	426.0±0.4	0.5±0.2
BCH 5Cl	-	408.8±0.6	19.1±0.5	-	-	458.1±0.4	0.5±0.3
BCH 5Br	-	426.5±0.4	22.3±0.9	-	-	465.8±0.4	0.6±0.2
BCH 5CN	-	367.8±0.4	21.1±0.7	-	-	494.0±0.7	0.7±0.3
BCH 7CN	S_A	350.1±0.6[a]	24.2±0.8	397.9±0.3	c	477.9±0.5	0.7±0.2

[a] These compounds exhibited solid state polymorphism(will be reported on in detail in due course); [b] enthalpies not determined owing to incomplete crystallization

[c] Could not be determined owing to indiscernible signal

An aspect of the mesogenic phase behaviour of the investigated compounds is the presence of a smectic (B) phase in the series BCH 50 - BCH 52 - BCH 54 and the rather conspicuous absence of the same phase when the nonpolar hydrogen atom or alkyl group (in 4'-position at phenyl ring) is exchanged with a polar halogen atom or a pseudohalogen such as the cyano group resulting in the series BCH 5F - BCH 5Cl - BCH 5Br - BCH 5CN. It may thus be concluded that the substitution of nonpolar terminal groups with polar atoms or groups has an inhibitory effect upon the appearence of (higher ordered) smectic phases in compounds with alkyl chains shorter than the heptyl group. With regard to the transition enthalpies as listed in the above Table, one expects and finds the largest values (19-24 kJ/mol) for the crystalline solid-nematic transitions. In comparison with these, the enthalpies of fusion rendering smectic B-phases are generally somewhat lower than the former enthalpy values. A further decrease in the transition enthalpies is to be expected for all smectic B - nematic and smectic B - isotropic transitions. This is duly confirmed by the determined enthalpies of the transitions, which lie between 5 and 8 kJ/mol. The appropriate enthalpy for the transition smectic A - nematic of BCH 7CN has not been listed in the Table for reasons already mentioned above. A comparison of the summation of the transition enthalpies of BCH 50 (17.1 kJ/mol) and all the other members of this series reveals that this compound possess an unexpectedly low value.

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