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

NMR Study of the Phase Transitions in Some Derivatives of Cholesterol and B-Nor Cholesterol

Al Nicula [a] , S. Selinger [b] , M. Bogdan [a] & M. Todica [a]
[a] Department of Physics, Babeş-Bolyai University, R-3400, Cluj-Napoca, Romania
[b] Institute for Computer Technique Research, R-3400 Cluj-Napoca, str. Republicii nr. 109., Romania
Version of record first published: 20 Apr 2011.

To cite this article: Al Nicula , S. Selinger , M. Bogdan & M. Todica (1983): NMR Study of the Phase Transitions in Some Derivatives of Cholesterol and B-Nor Cholesterol, Molecular Crystals and Liquid Crystals, 100:1-2, 49-55

To link to this article: http://dx.doi.org/10.1080/00268948308073718

Mol. Cryst. Liq. Cryst., 1983, Vol. 100, pp. 49–55
0026-8941/83/1002–0049/$18.50/0

NMR Study of the Phase Transitions in Some Derivatives of Cholesterol and B-Nor Cholesterol

AL. NICULA[†], S. SELINGER[‡], M. BOGDAN[†], M. TODICA[†]

[†]*Department of Physics, Babeş-Bolyai University, R-3400 Cluj-Napoca, Romania;* [‡]*Institute for Computer Technique Research, R-3400 Cluj-Napoca, str. Republicii nr. 109., Romania*

(Received December 22, 1981; in final form February 28, 1983)

In this paper we analyze by broad line NMR spectroscopy method, the influence of modifying the cholesterol skeleton upon mesomorphic properties and characteristics (phase transition points, mesomorphic ranges, etc.) in some derivatives of cholesterol. From our studies regarding the phase transition points by NMR spectroscopy method, we can assert that derivatives of the B-nor cholesterol have the same behavior as derivatives of the cholesterol.

GENERAL CONSIDERATIONS

It is known that conditions which are necessary and sufficient for the formation of mesophase in cholesterol derivatives depend on their chemical structure. Small modifications in the cholesterol skeleton, apparently not essential, either lead to the appearance or disappearance of the mesomorphic properties.

The influence of modifying the cholesterol skeleton was examined by Wiegand.[1] He concluded that mesophases are formed by cholesterol derivatives only when the substituent is in the 3-position, and when rings A and B are quasi-planar. Certainly, as expected, any modification in the cholesterol skeleton leads to radical changes in behavior, whereas changes in 3- and 17-substituents can be tolerated without loss of cholesteric properties. The 3- and 17-substituents are the terminal substituents.

We have examined the influence of C_6-methylen group upon mesomorphic properties, namely whether its elimination (from B ring of the

cholesterol skeleton, from 6- position and the double bond occurs in the 5,7- position) brings about or not the disappearance of the liquid crystal behavior of the cholesterol or the cholesterol derivatives. The elimination of this group modifies the quasi-planar arrangement of rings A and B. The question is if the changes in the cholesterol skeleton can be tolerated without loss of cholesteric properties or not.

Cholesterol derivatives and B-nor cholesterol derivatives used in our experiments[2] are: cholesterol propionate, B-nor cholesterol propionate, cholesterol caproate, B-nor cholesterol caproate, cholesterol benzoate, B-nor cholesterol benzoate.

The samples were studied through broad line NMR spectroscopy and their absorption spectrum was compared with the absorption spectrum of the B-nor cholesterol derivatives.

The phase structure and molecular mobility of different phases of liquid crystals and the determination of the transition point between liquid crystalline and isotropic phases, have been the object of much research. Especially effective has been the use of the broad line NMR spectroscopy method.[3,4] Many experiments have shown that phase transition are usually accompanied by changes in the line width parameters.

It is known that in the mesophase the resonance signal has two components: a large component due to the cholesterol skeleton and a narrow component due to the terminal substituents. In the isotropic phase there was observed only a single narrow line.

EXPERIMENTAL RESULTS

The experimental apparatus consisted of a model: JNM 3H-60 NMR unit with possibility for heating of samples by means of a hot air blower. Data were collected at 9,2MHz, strength of the magnetic field was 1,4T. Signals were improved with an integrator linked to an X-Y recorder. The temperature controller maintained sample temperatures within ± 1°C by means of a thermocouple located in the sample air cavity. The temperature range was 20–130°C.

Figure 1 shows the absorption spectrum of the cholesterol benzoate obtained at +17°C.

We have observed two signals in the mesomorphic phase characteristic for these samples. The line width is defined as the distance between maximum and minimum slope of the absorption curve, ΔH for the wide component and δh for the narrow one.[5] The cholesterol derivatives must be studied as a powder or polycrystalline sample. The line shape is properly taken to

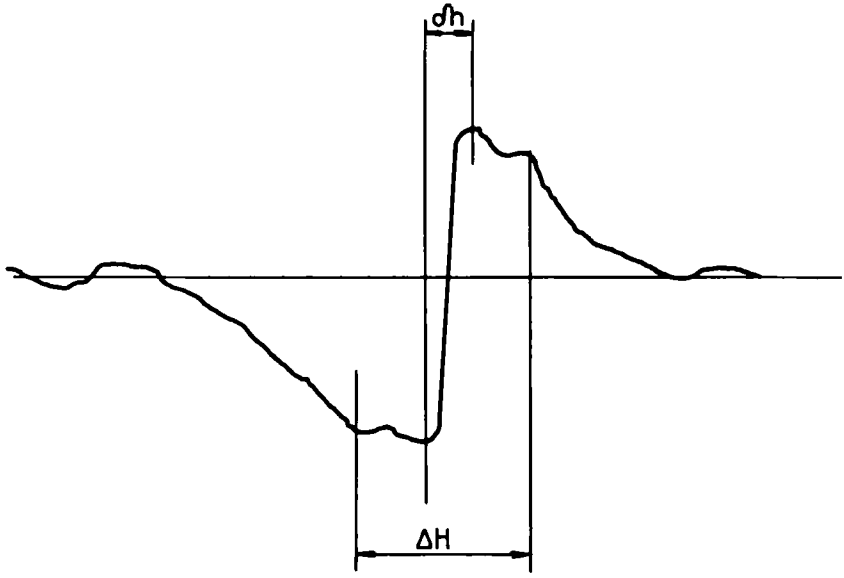

FIGURE 1

be a mixture of Gaussian and Lorentzian, but may be approximated by a Gaussian function.

The study of the temperature dependence of the line width in these samples gives information about the transition points from mesophase to the isotropic liquid phase. Figures 2 and 3 show the line width variation for wide component (ΔH) and narrow component (δh), respectively, in the samples. We have indicated the temperature increases with continuous line while the temperature decreases was indicated with interrupt line.

The phase transition temperatures obtained by this method are in good agreement with some other results, i.e.:

- temperature dependence of the dielectric constants,[6]
- thermoelectrets formed by phase transition in some cholesterol derivatives[7]
- study of the thermal properties.[8]

Although the spectra of the cholesterol and B-nor cholesterol have the same shape as that of their derivatives, they present no phase transition (mesophase–isotropic phase).

In the cases of the cholesterol- and B-nor cholesterol derivatives the wide component ΔH of the line falls slightly with increasing temperature and at a certain temperature it vanishes, indicating the phase transition point. The

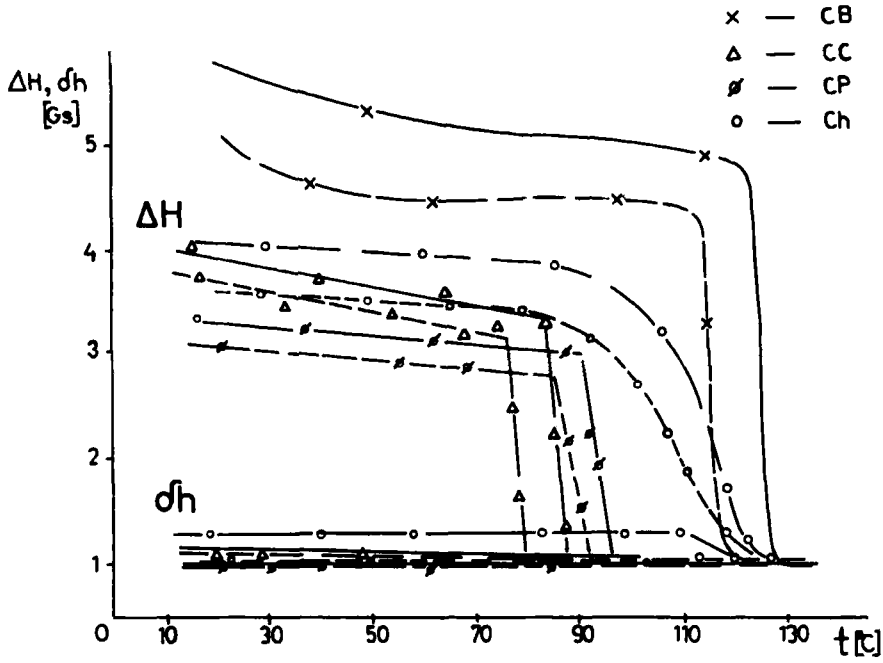

FIGURE 2

narrow component δh has constant width of about 1 gauss and depends not on the temperature.

In the case of the B-nor cholesterol derivatives the shape of the wide line is like that of the cholesterol derivatives and it shows the same temperature dependence but the phase transition point is lower. The narrow component has the same value as at cholesterol derivatives, namely about 1 gauss.

When the temperature decreases, both in cholesterol and B-nor cholesterol derivatives, the wide line appears suddenly but at lower temperature than the transition temperature and has the same width. The result is the hysteresis behavior.

The phase transition temperatures for the samples are presented in Table I.

We have given for every liquid-crystalline substance the melting point and transition temperatures in degrees centigrade.

The compounds 3, 4, 7 and 8 exhibit enantiotropic transition, while the compounds 5 and 6 show a monotropic transition.

The study of the NMR lines slope and width permits the determination of the NMR lines wide and narrow components provenance at the B-nor cholesterol derivatives. Changes in cholesterol skeleton influence only wide line component. Because the cholesterol skeleton is very rigid the

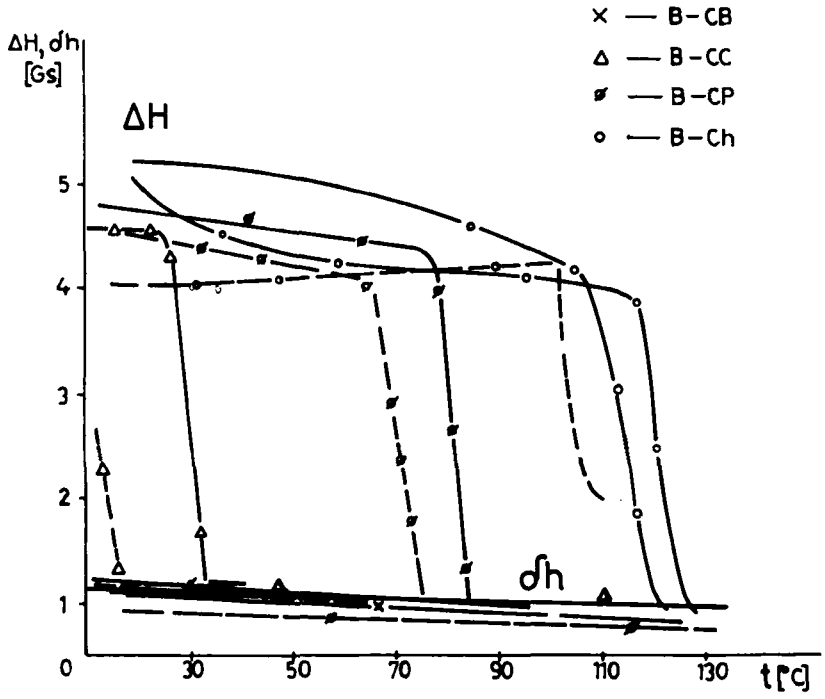

FIGURE 3

dipolar interaction between protons determine a broad NMR signal. The terminal substituents are very mobile and they give a narrow NMR signal. That is why the width of the narrow component did not modify with variation of the temperature, even when the compounds move in to the isotropic phase.

TABLE I

Phase transition temperatures for cholesterol and B-nor cholesterol derivatives

Compounds	*K*	*I*	*CH*	*I*	*CH*
1. cholesterol	Ch	120			
2. B-nor cholesterol	B—Ch	120			
3. cholesterol propionate	CP			99	93
4. B-nor cholesterol propionate	B—CP			80	65
5. cholesterol caproate	CC	91	82		
6. B-nor cholesterol caproate	B—CC	36	18		
7. cholesterol benzoate	CB			129	118
8. B-nor cholesterol benzoate	B—CB			110	

K = solid crystalline state
I = isotropic liquid state
CH = cholesteric modification

The explication regarding the shape of the line is held up by some other authors,[9] who worked liquid crystals replacing the hydrogen of the lateral groups with deuterium. As a result the central line disappeared.

When the temperature increases the proton vibration both in the terminal substituents and the cholesterol skeleton intensifies, and dipolar interaction between protons of the steroid nucleus is mediated. In this case the wide component disappears and compounds move into the isotropic phase.

CONCLUSIONS

Though quite a number of cholesterol derivatives have been synthetized, the existing ideas about the influence of molecular structure upon mesomorphic properties and characteristics (phase transition points, mesomorphic ranges, etc.) can still not serve as a satisfactory guide in the search for new cholesteric mesogens.

Examining conditions for the formation of mesophase with cholesterol derivatives leads us to a model of the molecule of cholesteric mesogen, which consists of a modified cholesterol skeleton.

The new structure of cholesterol skeleton — B-nor cholesterol — influences specifically both the ability of a substance to form a mesophase and its mesomorphic properties. The structure of the steroid part influences mesomorphic properties.

The use of broad line NMR spectroscopy method reveals the same behavior of B-nor cholesterol derivatives and cholesterol derivatives. They presented the same jump at the phase transition between mesophase and isotropic phase and the same hysteresis behavior.

The dipolar interaction seems to dominate. Study of the line shape of the NMR signals enables the determination of the line components provenience. The molecules rigid central part — cholesterol skeleton — gives a broad signal, while the molecules mobile part, terminal substituents, causes a narrow one.

Therefore B-nor cholesterol derivatives have the same behavior as cholesterol derivatives. Moreover, we can say that of eliminating the C_6-methylen group from B ring of the cholesterol skeleton caused no disappearance of mesomorphic properties. Therefore, B-nor cholesterol derivatives form the cholesteric mesogen. The mesomorphic range of these compounds is narrow and phase transition temperatures are lower than those of cholesterol derivatives.

References

1. C. Wiegand and Z. Naturforsch, B4, 249 (1949).
2. S. Selinger, R. Schwartz and A. Juhász (to be published Rev. Roum. Chim.).
3. G. J. T. Tiddy, Phys. Reports, Vol. 57, Nl (1980).
4. G. R. Luckhurst, *Liq. Cryst. and Plastic Cryst.* (New York, 1974), Vol. 2, p. 144.
5. Al. Nicula, Rezonanţa magnetică (Bucureşti, 1980).
6. S. Selinger, F. Puskás, R. Schwartz and A. Juhász, Studia Univ. Babeş-Bolyai, *Phys.*, **26**, 1, 38 (1981).
7. S. Selinger, I. Cuculescu and R. Schwartz, (to be published Phase Trans.).
8. S. Selinger, (to be published Studia Univ. Babeş-Bolyai).
9. P. J. Collings, S. I. Goss and J. R. McColl, *Phys. Rev.*, A11 684 (1975).