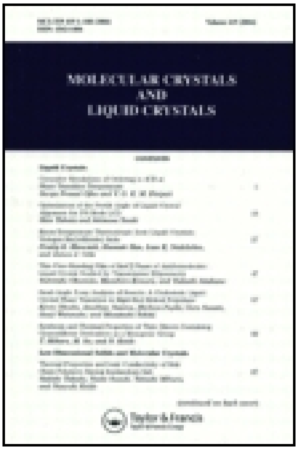

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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V. A. Batyuk [a] , T. I. Shabatina [a] , Yu. N. Morosov [a] & G. B. Sergeev [a]

[a] Moscow State University, Moscow, 119899, USSR

To cite this article: V. A. Batyuk , T. I. Shabatina , Yu. N. Morosov & G. B. Sergeev (1988): Nitroxide Formation in the Solid State of the Liquid Crystal 4-Pentyl-4'-Cyanobiphenyl, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 161:1, 109-117

To link to this article: http://dx.doi.org/10.1080/00268948808070243

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 161, pp. 109–117
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Printed in the United States of America

NITROXIDE FORMATION IN THE SOLID STATE OF THE LIQUID CRYSTAL 4-PENTYL-4'-CYANOBIPHENYL

V.A.BATYUK, T.I.SHABATINA, Yu.N.MOROSOV, G.B. SERGEEV
Moscow State University, Moscow 119899, USSR

Abstract The formation of nitroxides during photolysis of 2-methyl-2-nitrosopropane in nematic liquid crystal 4-pentyl-4'-(5CB) has been studied by ESR at temperatures 183-343K. The kinetics of nitroxide formation is sensitive to the phase state of liquid crystalline systems. In the solid state of 5CB the kinetic manifestation of hysteresis phenomena has been established. In nematic phase 5CB the equalization of rate constants for the tert-butyl radical trapping by nitrosocompounds of different chemical structures has been observed.

At present the chemical reactions in solids are being intensively investigated. It has been shown that the reactivity of organic molecules in crystalline and liquid states significantly differ. Liquid crystals combine the ordered structure of crystals with molecular mobility of liquids. Hence the common interest in them as a medium for conducting chemical reactions. The solid state of liquid crystals and especially of liquid crystalline compositions is characterized by the presence of metastable phase states and structures. Apart from that, the liquid crystalline samples tend to be strongly supercooled. The application of liquid crystalline materials with ever-growing temperature ranges makes the investigation of liquid crystalline compositions and related chemical interactions at low temperatures in the solid and supercooled states extremely interesting.

The chemical processes in the structurally ordered media were studied by ESR spectroscopy of nitroxide radical formation during photolysis of 2-methyl-2-nitrosopropane in a nematic liquid crystal of 4-pentyl-4'-cyanobiphenyl for a wide temperature range of 183-343° K, i.e., including various phase states of the system. Photolysis was conducted in a temperature controlled resonator of an ESR spectrometer.The frozen liquid crystalline samples were cooled from room temperature to the required one. Samples were vacuum treated to eliminate oxygen; the residual pressure in the system did not exceed 10^{-3} torr.

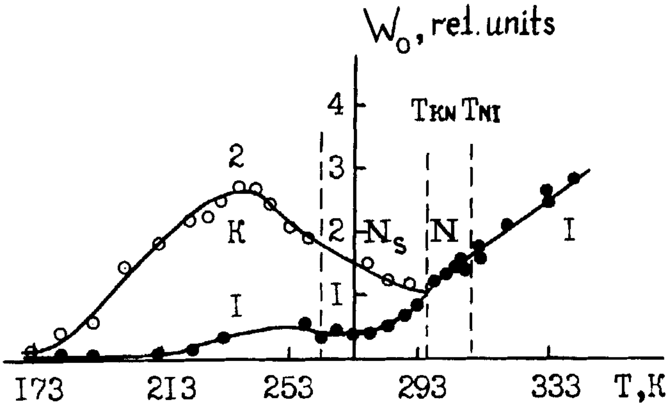
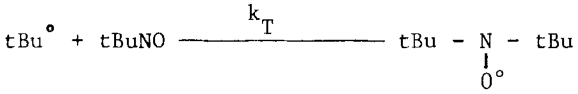


FIGURE 1. The temperature dependence of the initial nitroxide formation rate in liquid crystal 4-pentyl-4'-cyanobiphenyl: 1 - during photolysis in samples cooled from room temperature to the desired one; 2 - in stable crystalline phase produced by warming up samples previously frozen at the liquid nitrogen temperature (with intermediate thermal treatment at 273 for 40 min),
where I = isotropic phase,
N = nematic phase,
N_S= supercooled nematic phase
K = crystalline solid phase,

The interaction of primary tert-butyl radicals with 2-methyl-2nitrosopropane yields stable di-tert-butylnitroxide radicals[1] :



$$tBu^{\circ} + tBuNO \xrightarrow{k_T} tBu - \underset{\substack{| \\ O^{\circ}}}{N} - tBu$$

The initial nitroxide radical formation rates (degree of photolysis of nitroso compounds did not exceed 1%) in a nematic liquid crystal at various temperatures are given in Fig. 1.

The data obtained demonstrate that nitroxide radicals are effectively formed up to 193 K, i.e. considerably below the solid-nematic phase transition temperature (296 K). The given liquid crystalline system was studied using the DTA technique. The cooling of liquid crystalline samples at the rate of 1-2 K/min (conditions of the kinetic experiments) was shown to produce the supercooled nematic phase within a 268-296 K range. In this region the initial rate of the process sharply falls with decreasing temperature (E_a = = 29 kJ/mol) correlating with the reduced tumbling mobility of the internal spin probe of di-tert-butylnitroxide radical in the system (E_r = 30 kJ/mol).

The reaction was also conducted in the stable crystalline phase of 4-pentyl-4'-cyanobiphenyl produced by warming up samples previously frozen at the liquid nitrogen temperature (with intermediate thermal treatment at 273 K for 40 min). The nitroxide formation rate at the same temperatures, in this case, increased by 3-4 times. Thus, on comparison with the above system, we have observed the kinetic manifestation of hysteresis phenomena taking place during cooling-heating of liquid crystalline samples. At these conditions the process rate has a complex dependence on temperature in the range of 296-193 K.

To analyse the process rate in the frozen liquid crystalline samples as a function of temperature, the phase diagram for the system of nitrosocompound (2-methyl-2-nitrosopropane) - liquid crystal (4-pentyl-4'-cyanobiphenyl) was studied. The data obtained indicate the formation of eutectics at 70 mol.% of nitrosocompound and 218 K. At concentrations below 30 mol.% of nitrosocompound, the components form solid solutions. In all ESR experiments the concentration of 2-methyl-2-nitrosopropane did not exceed 1 mol.%. We have previously reported a sharp reduction in nitroxide radical formation rate almost to zero when the components in the system, during freezing, formed a structure of a solid solution type [2]. This can be due to the diffusion, in the matrix, of the primary tert-butyl radical required to form the reaction product, di-tert-butylnitroxide radical. Up to 193 K the process rate in the solid-state system differs from zero and complexly depends on temperature (Fig. 1). The reaction rates can't be extrapolated using the value of activation energy of the process in the isotropic phase of the liquid crystalline system. This testifies in favour of structural and phase inhomogeneity of the frozen liquid crystalline samples and, consequently, to the possibility of the formation of metastable structures.

The nematic mesophase of 4-pentyl-4'-cyanobiphenyl is an intermediate between liquid and solid in its structural and physical properties. The initial formation rate of di-tert-butylnitroxide radicals in it also depends on temperature only slightly.

The interaction of tert-butyl radicals with nitroso compounds of various chemical structure in an orientationally ordered media was studied for the case of photolysis of

2-methyl-2-nitrosopropane in the presence of aromatic nitrosocompounds-nitrosobenzene (NB), 2,4,6-tribromonitrosobenzene (TBNB), 4-methyl-2,6-dib-romonitrosobenzene (MBNB), and 2,4,6-tri-(tert-butyl)nitrosobenzene (BNB) - in the mesophase of a liquid crystal. Orientational ordering takes place in many structured systems, including the solid state of liquid crystals. Unfortunately, the reduced molecular mobility in solids considerably hampers the unambiguous analysis of orientation effects. However, the liquid crystalline mesophase maintains high molecular mobility typical of liquids.

Aromatic nitrosocompounds do not decay in red light and are used as spin traps for alkyl radicals in the system [3]. The interaction of primary tert-butyl radicals with molecules of 2-methyl-2-nitrosopropane and aromatic nitrosocompounds yields two types of nitroxide radicals (aliphatic di-tert-butylnitroxide (R_1) and mixed aryl-aliphatic nitroxide (R_2).

$$\mathrm{tBu}^{\circ} + \mathrm{tBuNO} \xrightarrow{k_T\ (1)} \mathrm{tBu} - \mathrm{N}(\overset{\circ}{\mathrm{O}}) - \mathrm{tBu} \qquad (1)$$

$$\mathrm{tBu}^{\bullet} + \mathrm{ArNO} \xrightarrow{k_T\ (2)} \mathrm{tBu} - \mathrm{N}(\overset{\circ}{\mathrm{O}}) - \mathrm{Ar} \qquad (2)$$

(where Ar = Ph, $C_6H_2Br_3$-, CH_3-$C_6H_2Br_2$-).

The bulky tert-butyl groups in 2,4,6-tri(tert-butyl)-nitrosobenzene create steric hindrance, thus, causing the addition of tert-butyl radicals to the oxygen atoms of nitroso groups[3]. From the experimental spectra, the difference in ESR spectra of R_1 and R_2 enables us to determine the parameters proportional to concentrations of aliphatic and aryl-aliphatic radicals, correspondingly.

The relative spin-trapping constants of tert-butyl radicals (^{k}T) by molecules of nitrosocompounds were determined from the initial accumulation rates of nitroxide radicals W_o (to prevent subsequent processes the degree of photolysis in all cases did not exceed 1%).

$$k_T(2)/k_T(1) = (W_o(2)/\ W_o(1\ ))\ /\ ([M_1])/\ [M_2]) \qquad (3)$$

where $M_{1,2}$ are the monomer concentration of nitrosocompounds actively interacting with alkyl radicals [1]. The monomer concentrations of nitroso compounds were determined by the visible spectrophotometry. The spin-trapping constants were determined to within ±15-20%.

The above aromatic nitrosocompounds noticeably differ in their efficiency of spin-trapping tert-butyl radicals in the isotropic solvent (benzene). The spin-trapping constants of tert-butyl radicals were obtained at 298 K by the competing reaction technique using Eq. (3): k_T (2) = $= 2.3\cdot10^5$ (BNB); $7.9\cdot10^8$ (TBNB); $1.2\cdot10^9$ (MBNB); $2.0\cdot10^9$ (NB), l/mol·s ($k_T(1) = 3.3\cdot10^6$ l/mol·s[4]). k_T (2) value for BNB was previously determined in [4].

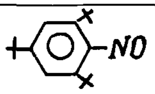
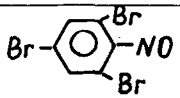
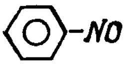
The trapping activation energies for tert-butyl radicals are close to zero[2]. The observed differences in spin-trapping constants and the related differences in pre-exponential factors are mainly caused by steric screening of the active -N=O fragment of the nitrosocompound.

Actually, in 2,4,6-tri(tert-butyl)nitrosobenzene, a high steric effect of tert-butyl substituents screening the active site hinders the addition of tert-butyl radicals. On the other hand, the planar conformation of a nitrosobenzene molecule makes the active site easily accessible; hence the easy addition of tert-butyl radical. The intermediate stage is represented by ortho-Br-substituted aromatic nitrosocompounds. Here the application of the nematic liquid crystal as a medium enables us,by varying temperature, to obtain the orientationally ordered and isotropic states of the system without changing its chemical composition. The subsequent changes in viscosity and dielectric constant of the medium do not exceed 15% [5].

The kinetics of nitroxide radical formation in the nematic liquid crystal 5CB was studied within the temperature range of 298-333 K which includes isotropic and nematic phases.

The relative constants for tert-butyl radical trapping (k_T, rel.units) by nitrosocompound molecules were determined from the initial nitroxide radical formation rates (Eq,(3)) at temperatures remote from T_{NI} in the mesophase of 4-pentyl-4'-cyanobiphenyl at 298 K and in the isotropic phase at 323 K. The obtained results (k_T, rel.units) are listed in Table 1.

TABLE 1 The constants for tert-butyl radical trapping (k_T, rel.units) by aromatic nitrosocompounds in the nematic and isotropic phases of the liquid crystal 5CB

Phase state of the system			
Nematic (orientationally ordered) phase	0.10	9.4	18.9
Isotropic phase	0.14	50.9	215

The constant for tert-butyl radical trapping by 2-methyl-2-nitrosopropane molecules was assumed to be equal to 1.

It follows from Table 1 that the efficiency of tert-butyl radical trapping by nitrosocompounds in the isotropic phase varies by three orders of magnitude. The range of trapping rate constants in the mesophase of the nematic liquid crystal is narrowed by more than an order of magnitude. Thus, in the mesophase of the nematic liquid crystal we observe the levelling of rate constants for the tert-butyl radical trapping by aromatic nitrosocompounds.

Previously, the levelling of reactivities of the chemical compounds belonging to one series was observed only in the solid state of polymeric systems [6-8]. During the system transition liquid to solid-state, the molecular mobility of reactants sharply decreases, thus extremely complicating the study of the observed effects. In our case the levelling effect was observed for the transition isotropic liquid - anisotropic (orientationally ordered) liquid, when the system maintains adequately high molecular mobility. It is therefore possible to conduct a direct experimental study and theoretically interprete the orientation effects in question.

In our opinion, the orientational ordering of nitrosocompounds results in a favourable mutual location of the interacting particles. Hence, the steric conditions for the addition of tert-butyl radical are equalized causing the levelling of reactivities in nitrosocompounds. It may be concluded that the observed effect is primarily steric, entropic, in nature.

It should be noted that the effect of electron structure in nitrosocompounds in this case is not pronounced. For instance, 2,4,6-tribromonitrosobenzene and 4-methyl-2,6-dibromonitrosobenzene differ only in electron-donor force of a substituent in the p-position of the benzene ring. The ratio of their spin-trapping constants $k_T(MBNM)/k_T(TBNB)$ is 0.73 in benzene, 1.11 in the isotropic and 1.19 in the nematic phase of 4-pentyl-4'-cyanobiphenyl, an insignificant change.

The data obtained show that the orientational ordering of the medium can be one of the reasons for the levelling of chemical reactivity of compounds in the structured systems.

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