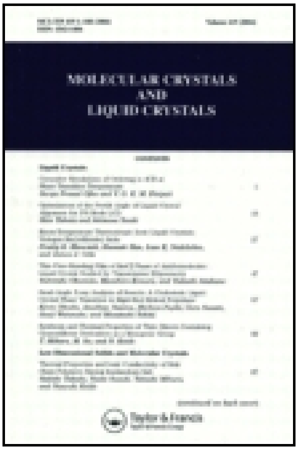

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A New Nematogn-Like Nitroxide Free Radical To Probe The Structure And Dynamics Of Nematic Liquid Crsytals

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A NEW NEMATOGEN-LIKE NITROXIDE FREE RADICAL TO PROBE THE STRUCTURE AND DYNAMICS OF NEMATIC LIQUID CRYSTALS

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The preparation of a new nematogen-like nitroxide spin probe N-(p-methoxybenzylidene)-4-amino-2,2,6,6-tetramethylpiperidino-1-oxyl is described. Initial electron paramagnetic resonance results are reported for this probe introduced into the nematogen MBBA.

INTRODUCTION

The study of liquid crystals by introducing a small amount of a paramagnetic impurity into the mesophase is now a well established technique.[1] From the analysis of the electron paramagnetic resonance (EPR) spectra and under the implicit assumption that the behavior of the paramagnetic probe reflects, in some way, the behavior of the liquid crystal, one obtains information regarding the static and dynamic properties of the liquid crystal itself. That this implicit assumption is not unreasonable has been demonstrated by the fact that rod-like paramagnetic probes have been shown to order in nematic mesophases.[2,3] Nevertheless, an impurity is a perturbation on the system and it is desirable to mimic as nearly as possible the structure of the liquid crystal molecules by the structure of the paramagnetic impurity while still retaining the desirable features of the probe molecule.

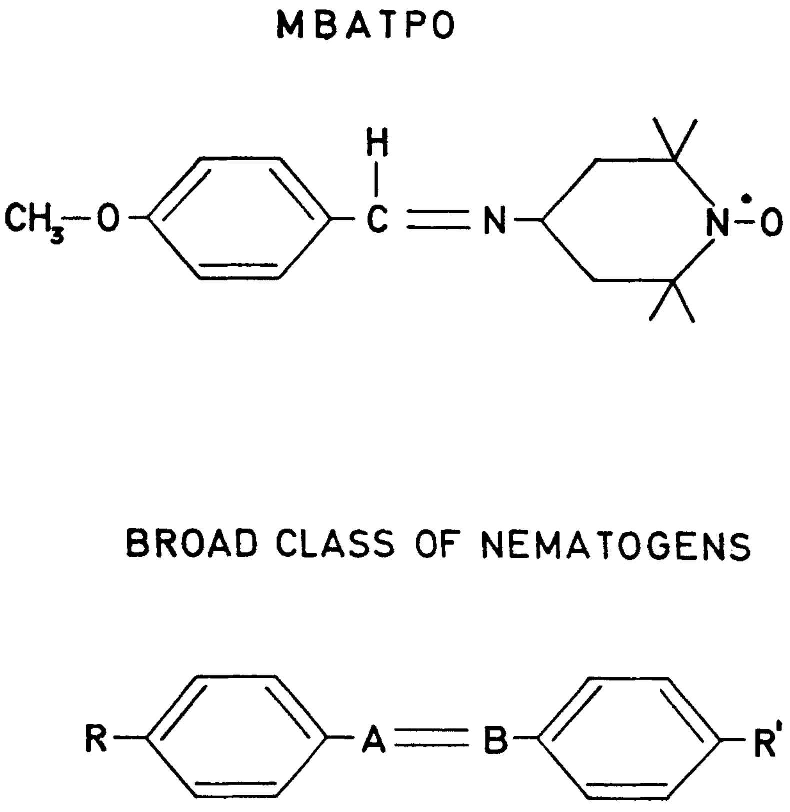
The nitroxide spin probes have proved to have many desirable features: simple spectra, chemical stability,[4] and the ability to probe rotational[5] and translational[6] motion on a time scale of interest in many liquids. Advances in understanding the electron spin relaxation mechanisms of these nitroxide probes in isotropic[7] and ordered fluids over the last several years have provided a rather detailed description of their motion.

The purpose of this letter is to introduce a new nematogen-like spin probe and to report some of its properties. This work has the same basic aim as that of Ferruti *et al.*[2]: to produce a probe suitable for a wide range of studies of certain nematic liquid crystals. However, the label we report has the added advantage that it is *rigid*.

Figure 1 shows the structure of N-(p-methoxybenzylidene)-4-amino-2,2,6,6-tetramethylpiperidino-1-oxyl, which we refer to as MBATPO in the remainder of this letter. The same figure shows the structure of a broad class of organic molecules which have the same general structure, i.e., two *para* substituted aromatic rings rigidly linked by a double bond, which form nematic mesophases.[8]

SYNTHESIS OF THE NEMATOGEN-LIKE SPIN PROBE MBATPO

The synthesis of the probe molecule MBATPO involves the condensation of a carbonyl compound with a nucleophilic reagent. The nitroxide radical 4-amino-2,2,6,6-tetramethylpiperidino-1-oxyl (Eastman lot no. C3X) was dried over P_2O_5 before use. All other materials were used without further purification or preparation. In a round bottom flask, which also served as the pot in a simple distilliation apparatus, the radical was dissolved in enough benzene to allow between 10 and 15 ml of solvent for each gram of the radical.


MBATPO

BROAD CLASS OF NEMATOGENS

Figure 1 The structure of the new nematogen-like spin probe MBATPO and a broad class of nematogens. For MBBA, R is CH_3-O, A is CH, B is N and R' is $(CH_2)_3CH_3$.

To this mixture was then added enough p-anisaldehyde (Eastman lot no. A2F) to provide a slight excess (1.1:1.0 molar ratio) over the radical.

The reaction mixture was heated slowly to boiling at atmospheric pressure. The small amount of water generated in the condensation of the radical and p-anisaldehyde came off as a benzene-water azeotrope (b.p. 68°C), and the remaining benzene was distilled off slowly until the reaction mixture appeared as a dark red oil.

A small column (~10 ml capacity), packed with a slurry of silica gel (60-200 mesh) and diethyl ether, was used to isolate the product radical. The reaction mixture was diluted with just enough ether to allow it to flow easily and run through the column. There appeared a green-brown band that did not elute, and a brown-red band. The red fractions were combined and the ether was evaporated by means of very low heat and a stream of N_2, to leave a red, crystalline solid. This solid was dissolved in hexane at its boiling point and recrystallized at room temperature, yielding deep red plates whose melting range was 93.0-94.5°C.

Analysis: Computed: C, 70.56%; H, 8.72%; N, 9.68%. Found: C, 70.67%; H, 8.64%; N, 9.80%. I. R. absorptions (in $CHCl_3$):6.1μ, 6.25μ, C = N –; 8.0-8.5μ, N – O; 9.75μ, Ar-O-CH.

EPR MEASUREMENTS

EPR spectra at X-band were recorded with either a homebuilt reflection-type spectrometer using 6 kHz magnetic field modulation or a Varian Associates V4502 X-band spectrometer employing 100 kHz modulation. Dual cavity techniques were used with both spectrometers. Di-*tert* butyl nitroxide in benzene (degassed and sealed in a capillary tube) was used as a standard (a_N= 15.45±0.020G and a g-value, $g=2.0061_5 \pm 0.00005$ assumed). The temperature was controlled with a Varian 4557 variable temperature unit to within ±0.5°C or a homebuilt gas-flow cryostat capable of regulating the temperature to within ±0.5°C.

Samples were sealed under approximately 1 atm of nitrogen in 2.0 mm I.D. quartz sample tubes after removal of oxygen by the freeze-pump-thaw technique.

RESULTS AND DISCUSSION

Figure 2 shows EPR spectra of MBATPO in n-butyl alcohol at 22.5°C (Figure 2a), in MBBA at 80°C (Figure 2b), and in MBBA at 22.5°C (Figure 2c). The spectra are presented in first derivative form and show the three familiar hyperfine lines due to the interaction between the unpaired electron and the nitrogen (I=1) nucleus.

The rather dramatic departure of the spectrum in Figure 2c from most nitroxide spectra observed at X-band is due to (1) ordering of the spin probe by the nematic liquid crystal, (2) the fact that the nitroxide moiety is oriented such that the N-O bond is approximately along (within ~10°) the long axis of the molecule, and (3) complicated motional effects that do not allow one to assume that the motion perpendicular to the long axis is either fast or slow compared with the hyperfine and g-tensor anisotropies.[1,9] It is not appropriate to enter into details here, but manifestation of the motional effects discussed by Polnaszek _et al._[1] in liquid crystals is quite prominent for MBATPO in MBBA. In Table 1 we give the results of measurements of EPR parameters for MBATPO in MBBA at 22.5°C (parallel) where it is seen that the hyperfine spacing measured between the center and low field lines is about one Gauss larger than the corresponding spacing between the center and high field lines. Correct treatment of such data requires the simulation of EPR spectra using an appropriate slow motional theory.[1] This work is in progress. Table 1 also gives data corresponding to an orientation of the nematic director perpendicular to the external field. This orientation was achieved by flowing MBBA through a capillary which passed through the microwave cavity. The rate of flow was increased until the EPR line spacing no longer changed. That a high degree of nematic order was obtained

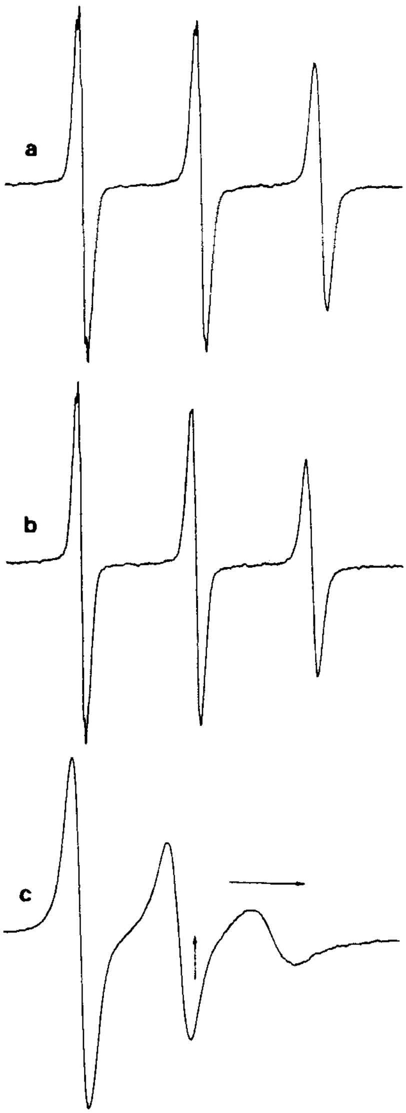


Figure 2 EPR spectra of MBATPO in (a) n-butyl alcohol at 22.5°C, (b) MBBA at 80°C and, (c) MBPA at 22.5°C. The partial resolution of intramolecular proton hyperfine structure is apparent in spectra (a) and (b). The vertical arrow marks g=2.0061 and the horizontal arrow of 10 G length points toward increasing field. In (b) a_{iso} = 15.59 G and g_{iso} = 2.0063_2.

TABLE 1. EPR PARAMETERS FOR MBATPO IN MBBA[a]

Orientation[b]	A_{eff}[c] (Gauss)	$a_{1,0}$[d] (Gauss)	$a_{0,-1}$[e] (Gauss)	g_0[f]	g_{center}[g]
Parallel	12.89	13.32	12.45	2.0074_0	2.0076_7
Perpendicular*	17.13	16.72	17.54	2.0055_9	2.0053_5

[a] Temperature = 22.5°C. *[RADICAL] = $2\mathrm{X}10^{-3}$M, sample <u>not</u> degassed, clearing point 41°C. [b] Orientation of director with respect to static magnetic field. [c] $A_{\mathrm{eff}}=\frac{1}{2}(a_{1,0}+a_{0,-1})$. [d] $a_{1,0}$= separation between low field line and center field line. [e] $a_{0,-1}$= separation between center field line and high field line. [f] g_0 = g-value of center line. [g] g_{center} = g-value of mid-point between the low and high field lines.

by this procedure was demonstrated by preparing a "polycrystalline" liquid crystal sample composed of finely ground glass particles on to which the liquid crystal was introduced. The polycrystalline spectral features which resulted then corresponded to those expected from the values in Table 1. Full experimental details will be published in due time.

We anticipate that MBATPO will prove to be a useful addition to the available spin probes used in liquid crystal research and are currently engaged in electron spin relaxation studies of MBATPO in various liquid crystalline solvents.

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