Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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G. Ionita [a], I. Zarafu [b], A. Paun [b] & P. Ionita [a b]
[a] Institute of Physical Chemistry, Bucharest, Romania
[b] Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, Bucharest, Romania
Version of record first published: 30 Jul 2012.

To cite this article: G. Ionita , I. Zarafu , A. Paun & P. Ionita (2012): EPR Spectra of a Mono- and a Hetero-Diradical in Nematic and Isotropic Phases, Molecular Crystals and Liquid Crystals, 562:1, 141-146

To link to this article: http://dx.doi.org/10.1080/15421406.2012.676834

Mol. Cryst. Liq. Cryst., Vol. 562: pp. 141–146, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.676834

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EPR Spectra of a Mono- and a Hetero-Diradical in Nematic and Isotropic Phases

G. IONITA,[1] I. ZARAFU,[2] A. PAUN,[2] AND P. IONITA[1,2,*]

[1]Institute of Physical Chemistry, Bucharest, Romania
[2]Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, Bucharest, Romania

A hybrid hydrazine–nitroxide monoradical and the corresponding heterohydrazyl–nitroxide diradical were used as probes in 4-cyano-4′-pentylbiphenyl liquid crystal. EPR data (hyperfine constants, rotational time, and anisotropy parameter values) are reported in the range of 25°C–55°C. It was shown by EPR spectrometry that the nitroxide moiety gives an anisotropic triplet line, while the hydrazyl moiety cannot be detected under these conditions.

Keywords Diradical; EPR; hydrazyl; liquid crystal; synthesis

Introduction

Liquid crystals are molecular materials with very high impact in many fields of science; for example, they have anisotropic properties and can be orientated under magnetic or electric fields, making them extremely attractive compounds for different types of applications (most known being the light modulating properties used in displays) [1–4].

Among these materials, 4-cyano-4′-pentylbiphenyl (**5CB**, Fig. 1) is a thermotropic liquid crystal with a nematic phase close to room temperature between 21°C and 35°C [5]. Ordered structures like liquid crystals can be studied by electronic paramagnetic resonance (EPR), if the system contains a paramagnetic probe; thus, the dynamics of stable free radicals in such oriented systems have been reported previously [6–10].

Stable organic mono- and polyradicals have been also used as novel molecule-based organic magnetic materials with multifunctionality; spin systems with magnetic properties depending on external stimuli such as heat and light are also present in literature [9–12]. Di- and polyradicals were studied as well; for example, the EPR of ground state triplets in liquid crystals solutions has been studied since 1960s [12]. Those studies showed that it is possible to align planar molecules with their plans parallel to the magnetic field using a nematic liquid crystals as solvent [1,2,13]. The use of a liquid crystalline spin-probe in diamagnetic liquid crystals is also reported [14,15].

In a previous work, we synthesized a stable hybrid hydrazine–nitroxide monoradical **1** and the corresponding heterohydrazyl–nitroxide diradical **2** and characterized their structure (Fig. 1) [16].

*Address correspondence to P. Ionita, Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, Bucharest 060021, Romania. Fax: +40213121147. E-mail: pionita@icf.ro

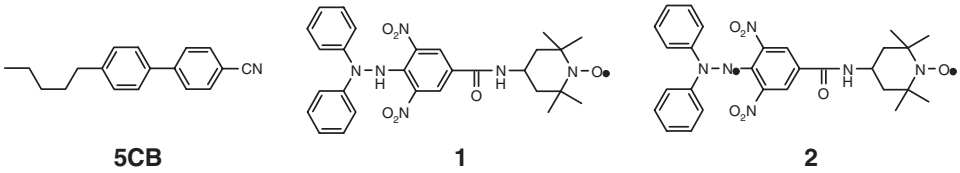

Figure 1. Chemical structure of **5CB**, monoradical **1** and diradical **2**.

This paper deals with the improved synthesis of compounds **1** and **2** and their uses as probes in **5CB**. Variable temperature EPR spectroscopy has been used as main investigation tool.

Results and Discussion

Synthesis

Although the synthesis of the desired compounds **1** and **2** was already reported by us [16], in the present work we have improved the procedure for all steps starting from commercially available materials (Fig. 2).

The reaction of the 1,1-diphenylhydrazine with the activated chloro-derivative 4-chloro-3,5-dinitrobenzoic acid led to the corresponding hydrazine, namely 4-(N′,N′-diphenylhydrazine)-3,5-dinitrobenzoic acid, which is subsequently derivatized with 4-aminotempo in the presence of the coupling agent N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ), yielding the nitroxide monoradical **1** in over 60% yields. In the previous paper [16], the yield of the monoradical **1** in this step, using dicyclohexylcarbodiimide (DCC), reached 40%, while the use of carbonyldiimidazole (CDI) or the acyl chloride led to 25% yield at most.

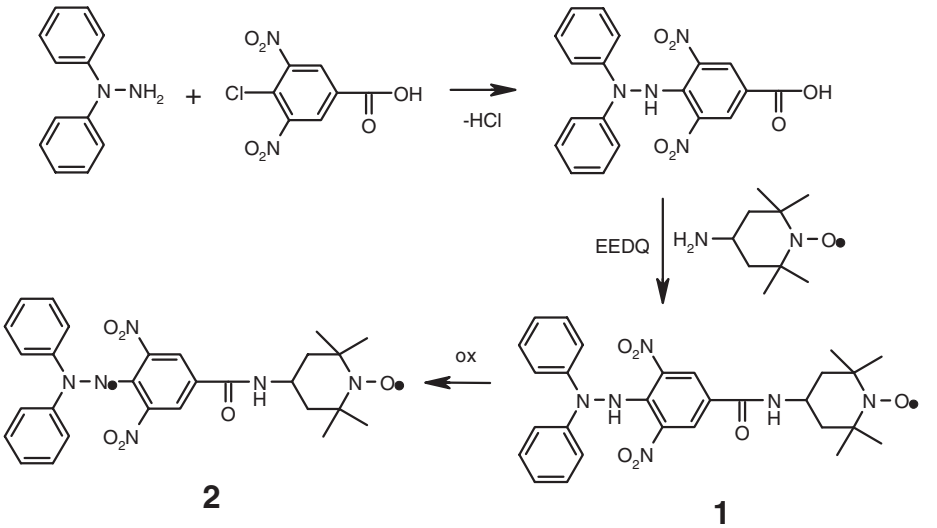

Figure 2. Synthesis of the stable free radicals **1** and **2**.

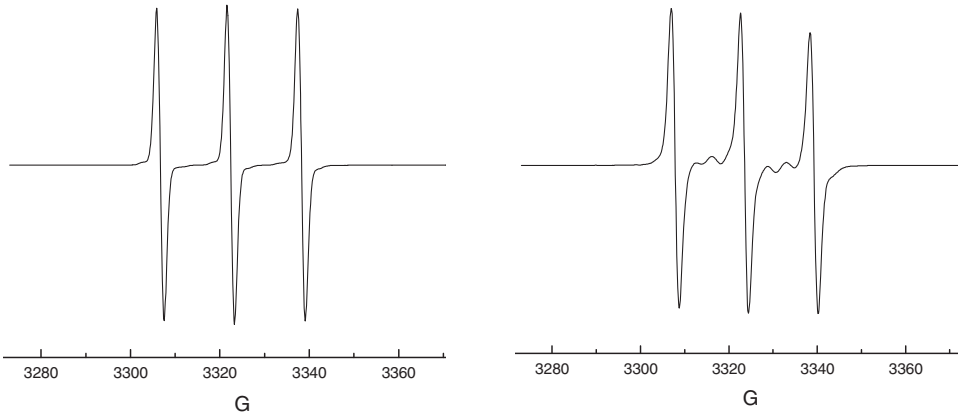

Figure 3. EPR spectra of the monoradical **1** (left) and the diradical **2** (right).

The oxidation of the monoradical **1** to the corresponding diradical **2** (Fig. 2) was achieved in DCM using lead dioxide; the yield is almost quantitative.

EPR Spectroscopy of the Monoradical 1 and the Hetero-diradical 2

EPR spectra of these compounds showed the expected sharp triplet lines of a nitroxide radical (Fig. 3). For the nitroxide **1**, the triplet lines due to the coupling of the free electron with the nitrogen atom have a hyperfine coupling constant (a_N) of 1.6 mT (in DCM), while in the case of the nitroxide–hydrazyl diradical **2**, supplementary broad lines are noticed between the main triplet lines due to the hydrazyl moiety ($a_{N1} = 1.2$ mT; $a_{N2} = 0.5$ mT).

EPR Spectroscopy of the Mono- and Diradical in 5CB

5CB contains a CN group, which is a strong dipolar head and may interact with compounds **1** and **2**, which are aromatic polynitro-derivatives. The well-known bulkiness of the free radical moieties (nitroxide or diphenylhydrazyl), which stabilize the free radicals centers, are detrimental of the mesophase stability [1,2]. Our aim was to study how the **5CB** liquid crystal, used as solvent, affects the shape of the EPR spectra. Variable temperature EPR spectra were recorded in the range of 25°C–55°C.

The motion of a spin label can be characterized quantitatively by the rotational correlation time τ, which is a reciprocal of the frequency of rotation (Eq. 1). In the same way, the relative intensities of the EPR triplet lines can also provide information about the anisotropy of the radical motion. Thus, the values obtained from the EPR spectra were the hyperfine coupling constant of the nitroxide free radical (a_N), the h_{-1}, h_0, and h_{+1} values, represented by the heights of the low field (Fig. 4), middle and high field lines of the ^{14}N hyperfine components, and the anisotropy parameter ε values (Eq. 2) [17]

$$\tau = 6.5\Delta H \left(\sqrt{\frac{h_0}{h_{-1}}} + \sqrt{\frac{h_0}{h_{+1}}} - 2 \right) 10^{-10}, \tag{1}$$

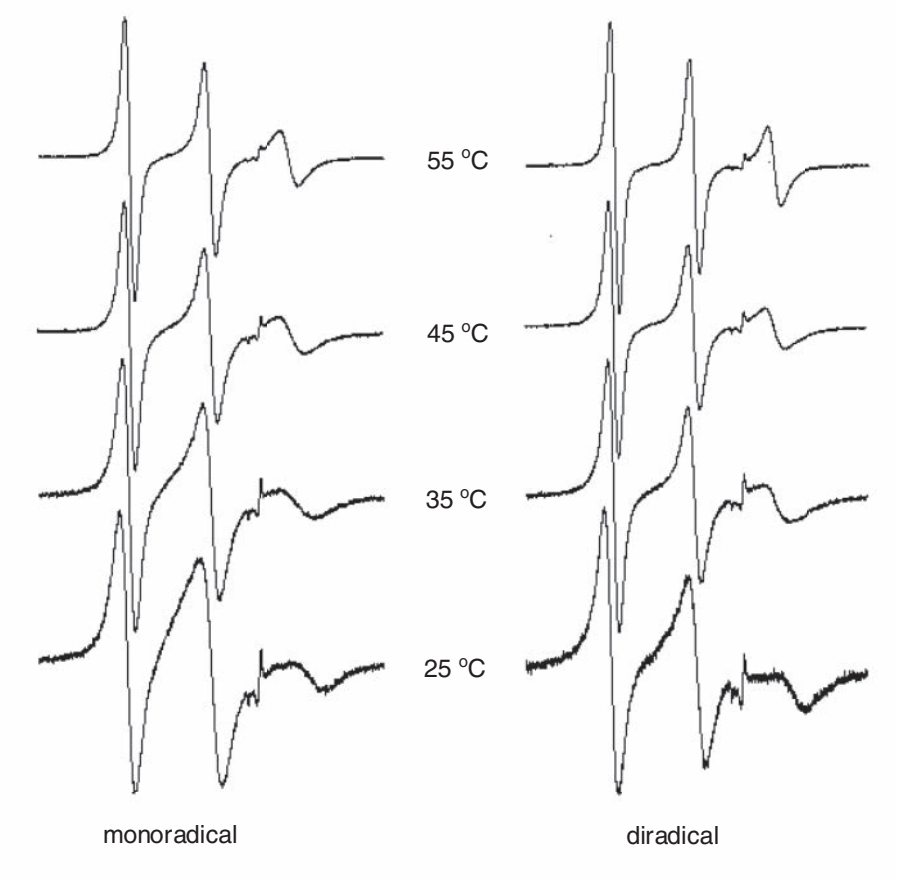

Figure 4. EPR spectra of the monoradical **1** and the diradical **2** in **5CB** at selected temperatures.

$$\varepsilon = \frac{\sqrt{\frac{h_0}{h_{+1}}} - 1}{\sqrt{\frac{h_0}{h_{-1}}} - 1}. \tag{2}$$

At the first sight, both types of spectra look very similar. The first important observation is that the broad lines showed by the diradical **2** in DCM (Fig. 3) are not visible, while the second important observation is that for the EPR spectra of the free radicals **1** and **2** recorded in **5CB** the intensities and the broadness of triplet lines changed dramatically (Fig. 4). These facts are due to the change in the motion of the free radical moiety from fast in DCM to slow in **5CB** (liquid crystal).

Tables 1 and 2 show the earlier enumerated values (hyperfine coupling constant, heights and widths of the triplet lines, τ and ε).

As a general rule, in both cases, the a_N values and the τ values are shrinking with the temperature (with about 1 G for 30°C). These may be explained by the reduced viscosity of the liquid crystal at higher temperature, meaning that the free radical moiety is rotating with a faster frequency. The ε values are always negative, meaning that the line heights are decreasing monotonically with increasing field (easily noticed in Fig. 4). These values

Table 1. EPR parameters at selected temperatures recorded for compound **1** in **5CB**

T (°C)	a_N (G)	h_{-1} (a.u.)	h_0 (a.u.)	h_{+1} (a.u.)	τ (s × 10^{10})	ε
25	16.33	47 (3.36)	36 (4.12)	4 (6.34)	50.21	−16.00
30	16.10	52 (2.75)	40 (3.72)	5 (6.11)	41.22	−14.86
35	16.01	66 (2.53)	50 (3.38)	6 (5.78)	38.57	−14.50
40	15.92	83 (2.43)	61 (2.95)	10 (5.25)	25.44	−10.27
45	15.82	110 (2.33)	75 (2.55)	14 (5.01)	18.88	−7.50
50	15.73	130 (2.20)	100 (2.43)	22 (4.41)	15.93	−9.20
55	15.56	184 (2.05)	122 (2.32)	30 (3.63)	12.53	−5.49

are related to the anisotropy of rotation. Thus, if the long molecular axis is parallel to the N−O bond of the nitroxide radical, ε becomes increasingly negative with the increased anisotropy of rotation [17]. Therefore, for the ε values compiled in Table 1, the variation is easily explained (for the monoradical **1**). A more confusing case noticed in Table 2 (for the diradical **2**), where those values do not follow a pattern. For the diradical **2**, the molecular structure determined by semiempirical calculations indicates a significant torsion angle of 76° (between the dinitrobenzene ring and the N–O bond), suggesting that the benzene ring is nearly coplanar with the nitroxide bond and that the interspin distance is about 1 nm [16].

As a conclusion, it was shown that **5CB** liquid crystal dramatically affects the EPR spectra of a mono- and a diradical, and, moreover, the hydrazyl moiety cannot be detected under these conditions in the EPR spectra.

Experimental

Chemicals and materials were purchased from Sigma-Aldrich. EPR spectra were recorded either on a Jeol JES FA100 (at ambient temperature in DCM) or a Bruker ESP 300 spectrometer (at variable temperature) in **5CB** (concentration about 10^{-4} M).

Synthesis of the stable radicals **1** and **2** was performed by modifying the previously reported procedure [16]; thus, 368 mg 1,1-diphenylhydrazine (2 mmol) were refluxed in chloroform for 2 h with 245 mg 4-chloro-3,5-dinitrobenzoic acid (1 mmol), filtered off, and the solvent removed. Purification of the product was achieved by triturating with hexane. In the next step, 40 mg of the acid (0.1 mmol) dissolved in DCM was reacted with 20 mg 4-aminotempo (0.12 mmol) in the presence 40 mg of EEDQ (0.16 mmol). After

Table 2. EPR parameters at selected temperatures recorded for compound **2** in **5CB**

T (°C)	a_N (G)	h_{-1} (a.u.)	h_0 (a.u.)	h_{+1} (a.u.)	τ (s × 10^{10})	ε
25	16.49	35 (2.86)	25 (3.86)	5 (7.00)	26.97	−7.93
30	16.23	55 (2.55)	36 (3.60)	6 (6.07)	29.46	−7.63
35	15.76	70 (2.31)	52 (2.66)	10 (4.55)	19.74	−8.84
40	15.66	100 (2.11)	70 (2.32)	18 (4.40)	12.18	−5.92
45	15.58	220 (2.00)	112 (2.28)	35 (4.21)	7.42	−2.74
50	15.50	150 (1.97)	115 (2.11)	40 (3.22)	7.81	−5.56
55	15.46	170 (1.82)	143 (2.00)	50 (2.83)	8.65	−9.02

2 days, the mixture was extracted with an aqueous solution of hydrochloric acid (1 M), saturated aqueous sodium hydrogen carbonate, and water. After solvent removal, the solid was purified on preparative TLC plates of silica gel, using ethyl acetate as eluent, yielding the monoradical **1** as pure red–brown solid. Oxidation of **1** in DCM with lead dioxide affords **2** in almost quantitative yields. All analytical data correspond with the literature values [16].

Acknowledgments

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, project number PN-II-ID-PCE-2011-3-0408.

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