# Photoconductive Liquid-Crystalline Derivatives of 6-Oxoverdazyl

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**Ⓢ** *Supporting Information*

**ABSTRACT:** 1,3,5-Triphenyl-6-oxoverdazyl radicals **1[n]**, in which each phenyl group is substituted with three alkylsulfanyl groups (n = 6, 8, 10), exhibit a monotropic columnar rectangular (Col$_r$) phase below 60 °C. Detailed analysis of **1[n]** revealed a broad absorption band in the visible region with maxima at 540 and 610 nm and redox potentials $E_{1/2}^{0/+1} = +0.99$ V and $E_{1/2}^{0/-1} = -0.45$ V vs SCE. Photovoltaic studies of **1[8]** demonstrated a hole mobility of $1.52 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ in the mesophase with an activation energy of $0.06 \pm 0.01$ eV. Magnetization studies of **1[8]** revealed nearly ideal paramagnetic behavior in either the solid or fluid phase above 200 K and weak antiferromagnetic interactions at low temperatures.

O ne-dimensional charge transport[1] along the self-assembled columns in discotic liquid crystals[2] has been recognized as a desirable property for applications in photovoltaic cells,[3,4] light-emitting diodes,[5] and field-effect transistors.[6] Therefore, a number of discotics, including those based on triphenylene,[7] pyrene,[8] carbazole,[8] phthalocyanine,[9] hexabenzocoronene,[10] and other polycyclic aromatics have been investigated for their photophysical properties.[11]

More facile generation of an electron−hole pair and higher current is expected in neutral π-radicals than in closed-shell aromatics because of their relatively high lying singly occupied molecular orbital (SOMO) and low ionization potential.[12] In this context, a number of thiazyl and thiazinyl derivatives have been synthesized and investigated as unidimensional semiconductors.[13] Attempts to generate liquid-crystalline π-delocalized stable radicals were unsuccessful[14] until recently. In 2009, Valesco and co-workers[15] reported a carbazole derivative of triphenylmethyl radical that exhibits two columnar phases, quasi-reversible redox pairs with an electrochemical window of 1.5 V, a broad absorption spectrum in the visible region, and phase-dependent magnetic interactions between the cores. This very exciting discovery provided new impetus for the development of other materials of this type in which magnetic properties can be coupled with anisotropic charge transport, dielectric switching, chirality, and photoalignment.

Verdazyls,[16] including 6-oxoverdazyls, are among a handful of π-delocalized radicals that are stable under ambient conditions. They exhibit broad absorption bands in the visible part of the

spectrum and an electrochemical window of ~1.5 V,[17] both controllable by judicious choice of substituents. Some verdazyl derivatives have been investigated as components of paramagnetic semiconductors[18] and in photoexcited molecular systems[19] intended for photomagnetic devices.[20] Here we report the first examples of discotic derivatives of verdazyl **1[n]** (Chart 1) and investigate their liquid-crystalline, electrochemical, magnetic, and photovoltaic properties.

**Chart 1**



**1[n]**   n = 6, R = C$_6$H$_{13}$
n = 8, R = C$_8$H$_{17}$
n = 10, R = C$_{10}$H$_{21}$
n = 12, R = C$_{12}$H$_{25}$
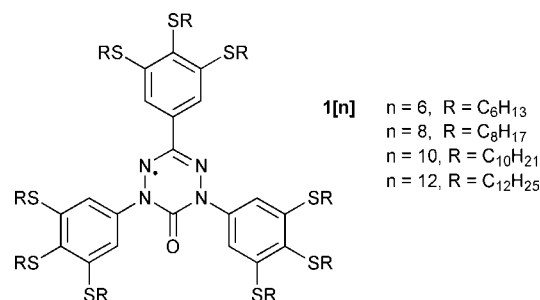
Radicals **1[n]** were obtained from hydrazines **2[n]**[21] and benzaldehydes **3[n]**[22] according to the Milcent method[23] (Scheme 1). Crude hydrazines were converted to hydrazones **4[n]**, which were reacted with triphosgene to give carbonyl chlorides **5[n]**. After isolation and purification, the chlorides were reacted with hydrazine **2[n]** in benzene.[24] The resulting tetrazanes **6[n]** were partially purified and oxidized with K$_3$Fe(CN)$_6$ under phase-transfer catalysis conditions to give radicals **1[n]** in ~20% overall yield. For magnetization and differential scanning calorimetry (DSC) studies, radicals **1[n]** were obtained in comparable yields by oxidation of **6[n]** with PbO$_2$.

All four radicals exhibited low-intensity absorption bands in the visible range (maxima at 540 and 610 nm; Figure 1) that according to time-dependent density functional theory results are due to several electronic transitions originating mainly from the four highest occupied MOs, which are localized on the benzene rings, to the LUMO, which is localized on the verdazyl

**Scheme 1. Synthesis of 1[n][a]**
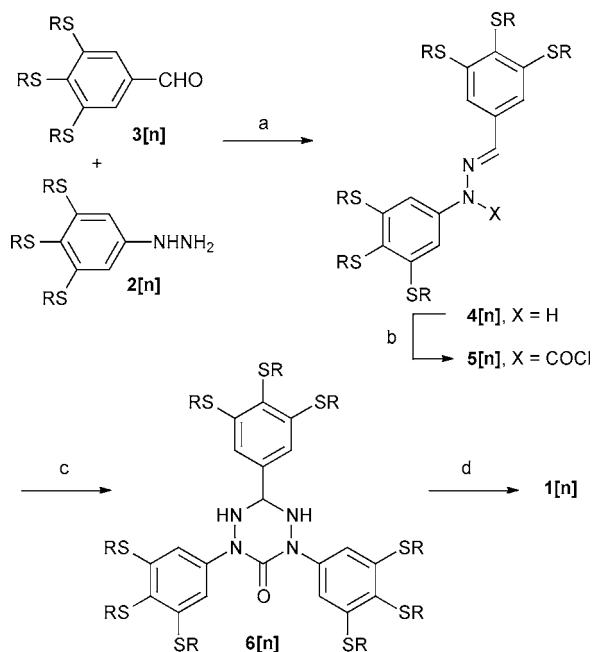


[a]Reagents and conditions: (a) cat. AcOH, EtOH, reflux, ~80%; (b) $CO(OCCl_3)_2$, pyridine, $CH_2Cl_2$, rt, ~65%; (c) 2[n], $Et_3N$, benzene, 50 °C, ~45%; (d) $K_3Fe(CN)_6$, $Na_2CO_3$ 0.5 M, cat. $[Bu_4N]^+Br^-$, $CH_2Cl_2$, rt or $PbO_2$, $K_2CO_3$, toluene/MeCN, rt, ~80%.
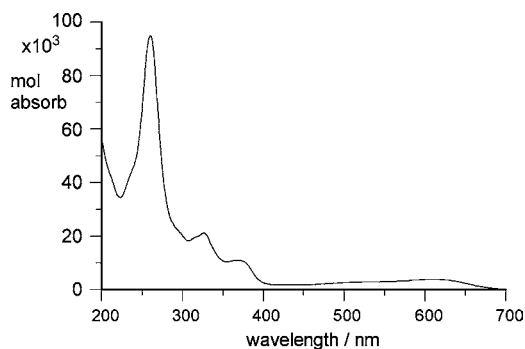


**Figure 1.** Electronic absorption spectrum of 1[8] in hexane.

unit.[25] The excitation involving the SOMO-to-LUMO transition was calculated to occur at 529 nm ($f = 0.03$).

Thermal analysis of a sample of 1[8] freshly crystallized from AcOEt/MeCN revealed a melting transition with a peak at 65 °C (Table 1 and the black line in Figure 2). Upon cooling (blue

**Table 1. Transition Temperatures (°C) and Enthalpies (kJ/mol, in Italics) for 1[n][a]**

| n | |
|---|---|
| 6 | Cr 39 (54.2) Col_r 50 (7.9) I |
| 8 | Cr 62 (108) [Col_r 60 (15.1)] I |
| 10 | Cr 62 (125.6) [Col_r 55 (14.0)] I |
| 12 | Cr 63 (116.6) I |

[a]Determined by DSC (5 K min$^{-1}$) in the heating mode as onset. Cr = crystalline; Col_r = columnar rectangular; I = isotropic.

line), the sample underwent a transition at 56 °C with a relatively small enthalpy (12.1 kJ/mol) to a phase that could be supercooled to −40 °C. The monotropic (M) phase underwent
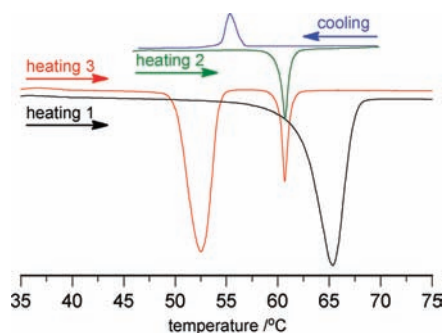


**Figure 2.** DSC traces for 1[8]. The heating and cooling rates were 5 K min$^{-1}$. For a description, see the text.

a transition to an isotropic (I) phase at 60 °C upon heating (green line) with an enthalpy comparable to that recorded on cooling. The crystalline polymorph of 1[8] obtained from the melt was different from that obtained from solutions. It melted with a peak at 52 °C (red line), forming an enantiotropic phase with a transition to the I phase at 60 °C (Figure 2). The position of the I → M transition peak was cooling-rate-dependent.

Optical microscopy revealed that slow cooling of the sample from the isotropic liquid resulted in the growth of crystallites (Figure 3a), while quenching the sample at a temperature
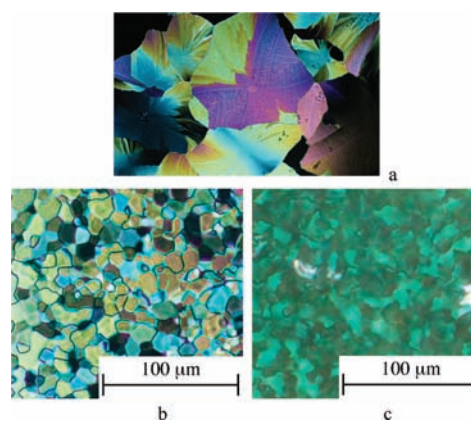


**Figure 3.** Optical textures of 1[8] obtained upon (a) slow cooling, (b) fast cooling, and (c) after 2 h at 30 °C [8× longer exposure than in (b)].

below 50 °C led to the formation of a mosaic texture typical of discotic phases (Figure 3b). The phase slowly lost birefringence (Figure 3c) and the ability to diffract (see below).

Similar mesogenic behavior was observed for the 1[6] and 1[10] homologues (Table 1), but compound 1[12] did not exhibit mesomorphic properties. Thus, 1[12] showed only melting at 63 °C and crystallization at 52 °C, both characterized by large enthalpy changes. Fast cooling of an isotropic sample of 1[12] did not give a birefringent phase such as that in Figure 3b but instead led to the formation of a dark phase similar to that in Figure 3c.

Powder X-ray diffraction (XRD) analysis of the three lower homologues of 1[n] revealed formation of a columnar rectangular (Col_r) phase. The fast-cooled samples gave XRD patterns with two sharp diffraction signals in the small-angle region that can be indexed as (11) and (02) and a typical broad halo at 4.2 Å in the wide-angle region (Figure 4 and Table 2).
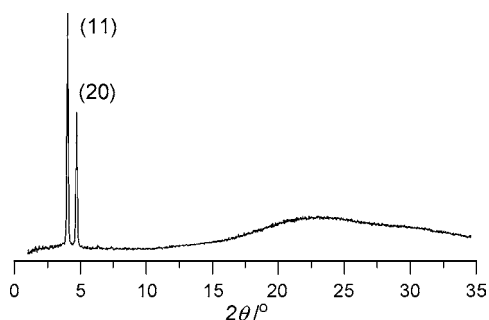
**Figure 4.** XRD pattern for **1**[8] obtained at 25 °C. The second broad halo at 30° (3.0 Å) is due to diffraction on the glass substrate.

**Table 2. XRD Data for the Col$_r$ Phase of 1[$n$] at 30 °C**

| $n$ | Miller indices $hk$ | $d$ spacing (Å) | lattice parameters (Å) |
|---|---|---|---|
| 6 | 11 | 19.7 | $a$ = 24.1 |
| | 02 | 17.1 | $b$ = 34.2 |
| 8 | 11 | 21.9 | $a$ = 26.9 |
| | 02 | 18.8 | $b$ = 37.6 |
| 10 | 11 | 23.5 | $a$ = 29.4 |
| | 02 | 19.6 | $b$ = 39.2 |

The signal positions were almost temperature-independent. Further cooling led to sample crystallization (Figure 3c), which manifested itself in significant changes in the XRD patterns: the sharp signals disappeared, and pronounced small-angle scattering of the X-ray beam was observed instead. This indicates that the crystalline phase grew in the form of nanometer-sized grains. Larger crystallites (or another crystalline polymorph), however, could be observed for slowly cooled samples; in this case, the diffraction patterns exhibited features similar to those of the fast-cooled sample in the Col$_r$ phase, with additional low-intensity sharp reflections over the entire range of the diffractogram. In contrast, all of the patterns obtained for **1**[12] showed only small-angle X-ray scattering but not the Bragg reflections, regardless of the sample cooling rate.

Molecular modeling revealed that **1**[8], in which the octyl groups are in all-trans conformations, can be inscribed into a circle with a diameter of 31 Å, while the unit cell parameters of **1**[8] calculated from the (11) and (02) reflections are $a$ = 26.9 Å and $b$ = 37.6 Å (Table 2). This indicates significant reshaping of the molecule in the Col$_r$ phase, which likely involves a number of gauche conformations of the alkyl chain and/or interdigitation of the chains between neighboring columns.

Magnetization studies at 200 Oe revealed paramagnetic behavior of **1**[8] in both the crystalline and fluid phases (Figure 5). The effective magnetic moment ($\mu_{eff}$) in the crystalline phase was found to be 1.620 ± 0.03 over the temperature range 310−345 K, which is close to the value of 1.732 for an ideal paramagnet and corresponds to 87 ± 3% of the spins. The number of spins increased to 95 ± 2% at ~65 °C, which coincides with the Cr → I transition. No abrupt changes of magnetization were observed at the phase transitions upon cooling (I → Col$_r$) or heating (Col$_r$ → I), and the number of spins remained approximately constant at 95 ± 2%. Cooling of the sample from the I phase to 2 K at 200 Oe showed that the molar susceptibility $\chi_m$ is well-described by the Curie law down to 200 K. At lower temperatures, antiferromagnetic interactions gradually diminished the observed magnetization (Figure 5 inset). Thus, the results indicate that the alkylsulfanyl groups
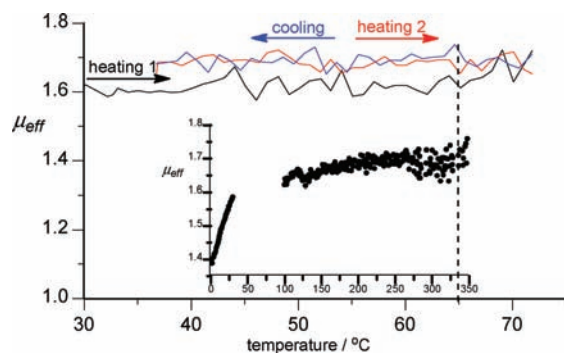


**Figure 5.** Plot of $\mu_{eff}$ vs $T$ obtained for **1**[8] at 200 Oe (rate of 1 K min$^{-1}$). The vertical line represents the melting transition. The inset shows $\mu_{eff}$ vs $T$ for a sample cooled from the I phase to 2 K.

prevent effective intermolecular close $\pi-\pi$ contacts, and the unpaired electrons remain largely isolated in both the solid and fluid phases.

Time-of-flight (TOF) measurements[8,26] found the positive charge carrier (hole) mobility ($\mu_h$) in a fast-cooled, unaligned, multidomain sample of **1**[8] to be 1.52 × 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ at 40 °C (Figure 6), which is in the range of typical values (10$^{-4}$–
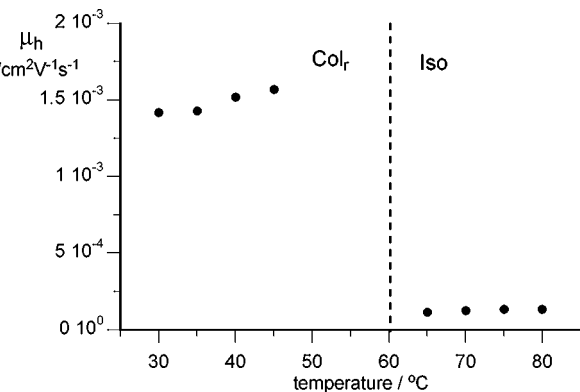


**Figure 6.** Temperature dependence of the positive carrier mobility for **1**[8] obtained by the TOF method at 337 nm. The electric field strength was 40 kV cm$^{-1}$.

10$^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$) and attractive for device applications.[11] The observed value is consistent with a relatively low disproportionation energy[27] calculated for **1**[1] (rigid, 106.6 kcal mol$^{-1}$; relaxed, 97.0 kcal mol$^{-1}$).[25] Arrhenius analysis of $\mu_h$ at several temperatures gave an activation energy of $E_a$ = 0.06 ± 0.01 eV, consistent with a hopping transport mechanism.[28] In the I phase, the charge mobility was lower by a factor of 10 (e.g., $\mu_h$ = 1.25 × 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ at 70 °C), which is typical for other discotics.[11]

Electrochemical analysis of **1**[6] in CH$_2$Cl$_2$ (10$^{-3}$ M) revealed two quasi-reversible redox pairs. The measured potentials, $E_{1/2}^{0/+1}$ = +0.99 V vs SCE and $E_{1/2}^{0/-1}$ = −0.45 V vs SCE, and the cell potential, $E_{cell}$ = 1.44 V, are comparable to those reported for the parent 1,3,5-triphenyl derivative in MeCN.[16b]

In conclusion, the first series of liquid-crystalline derivatives of the verdazyl radical has been synthesized. These compounds, in which the unpaired electron is delocalized in the center of the disk-like molecule, exhibit a monotropic rectangular columnar mesophase above ambient temperature. For the first time, we have demonstrated charge photogeneration and

its transport in a liquid-crystalline radical. The properties of these radicals, such as a broad absorption spectrum and mobility of the photogenerated charge, are desirable for applications in photovoltaic devices and warrant further studies of this class of materials. It is expected that the molecular and bulk properties of these radicals, such as thermal behavior, alignment, disproportionation energy, and charge transport, can be controlled by the judicious choice of substituents and dissymmetrization of the molecule using the synthetic method shown in Scheme 1. This work is currently in progress in our laboratory.

## ■ ASSOCIATED CONTENT

### ⓢ Supporting Information

Full experimental details and data for photoconductivity, magnetization, electrochemical, UV, XRD and thermal analyses; molecular modeling and computations; and synthetic procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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