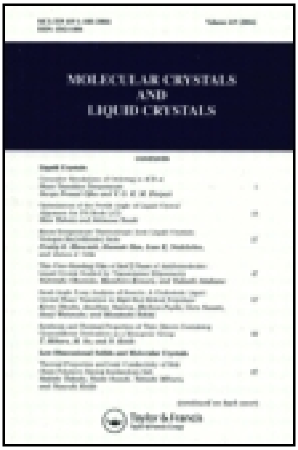

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Mesomorphic Properties of Deuterated 4-n-Pentylphenyl-4′-n-Alkoxythiobenzoates 7S5-d_{26} and 8S5-d_{28}

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Version of record first published: 04 Oct 2006.

To cite this article: K. Lipiński , T. Lipiński , J. Chruściel , A. Suszko-purzycka & A. Rykowski (1994): Synthesis and Mesomorphic Properties of Deuterated 4-n-Pentylphenyl-4′-n-Alkoxythiobenzoates 7S5-d_{26} and 8S5-d_{28} , Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 239:1, 87-93

To link to this article: http://dx.doi.org/10.1080/10587259408047173

Mol. Cryst. Liq. Cryst., 1994, Vol. 239, pp. 87–93
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Printed in the United States of America

Synthesis and Mesomorphic Properties of Deuterated 4-*n*-Pentylphenyl-4′-*n*-Alkoxythiobenzoates $\bar{7}S5\text{-}d_{26}$ and $\bar{8}S5\text{-}d_{28}$

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(Received June 9, 1992; in final form January 7, 1993)

Specifically deuterated liquid crystals, 4-*n*-pentylphenyl-4′-*n*-alkoxythiobenzoates ($\bar{n}S5$) with $n = 7$ ($\bar{7}S5\text{-}d_{26}$) and $n = 8$($\bar{8}S5\text{-}d_{28}$) were synthesized by esterification of the chain perdeuterated 4-*n*-heptyloxy and 4-*n*-octyloxybenzoyl chlorides with the chain perdeuterated 4-*n*-pentylbenzene-thiol. The mesomorphic properties of the deuterated $\bar{7}S5\text{-}d_{26}$ and $\bar{8}S5\text{-}d_{28}$ were determined by DSC. Phase transition temperatures as well as their enthalpy and entropy values were almost always lower than the respective values for the non-deuterated analogues.

Keywords: alkoxythiobenzoates, specifically deuterated liquid crystals

INTRODUCTION

The physical properties of thiol esters belonging to the homologues of 4-*n*-pentylbenzenethio-4′-*n*-alkoxybenzoates ($\bar{n}S5$) have been a subject of systematic studies in recent years. A few experimental methods have been applied: adiabatic[1] and DSC calorimetry,[2] dielectric relaxation[3–7] and quasi elastic neutron scattering experiments (QNS).[8] The last technique plays an important role in the studies of molecular dynamics in mesogenic systems and is particularly useful for the comparison of the properties of non-deuterated versus selectively deuterated liquid crystals. Two members of $\bar{n}S5$ homologous series with $n = 7$($\bar{7}S5$) and $n = 8$($\bar{8}S5$) are especially interesting for such investigations. The substance with $n = 7$ has only the nematic (N) and monotropic smectic C(S_C) phases, whereas the one with $n = 8$ has additionally (S_A) and monotropic (S_C) and (S_Y) phases. The need for specifically deuterated mesogens useful for QNS studies has led us to develop appropriate synthetic methods for preparation of both compounds. This paper is concerned with the synthesis and mesomorphic properties of chain-labelled 4-*n*-pentyl-d_{11}-benzenthio-4′-*n*-heptyl-d_{15}-oxybenzoate $\bar{7}S5\text{-}d_{26}$ (**I**) and 4-*n*-pentyl-d-$_{11}$-benzenethio-4′-*n*-octyl-d_{17}-oxybenzoate $8S5\text{-}d_{28}$ (**II**).

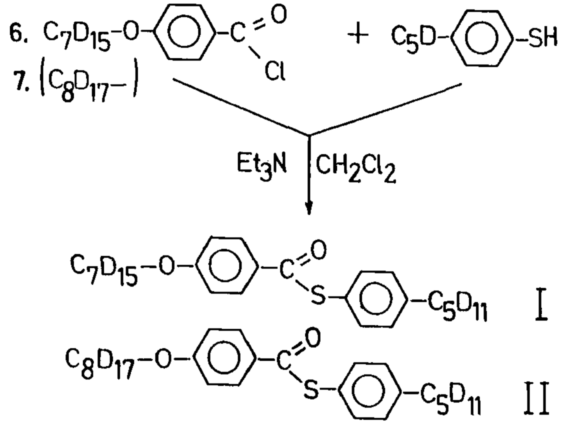
SYNTHESIS OF $\bar{7}$S5-d_{26} (I) AND $\bar{8}$S5-d_{28} (II)

Preparation of non-deuterated $\bar{7}$S5 and $\bar{8}$S5 liquid crystals has normally been based on esterification of corresponding the alkoxybenzoic chlorides with 4-*n*-pentylbenzenethiol.[9,10]

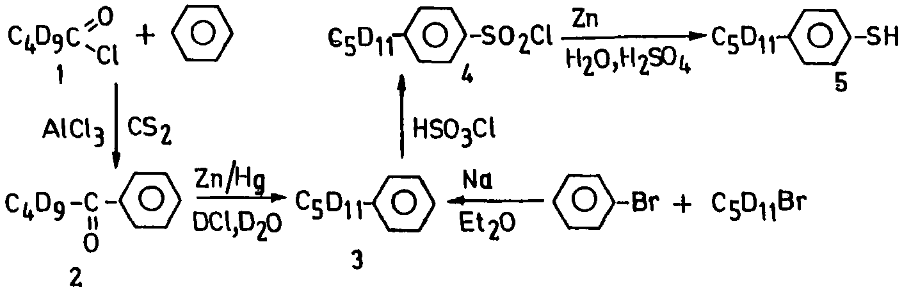
To prepare the specifically deuterated mesogens $\bar{7}$S5-d_{26} (**I**) and $\bar{8}$S5-d_{28} (**II**) being labelled in both the alkyl and alkoxy chains the synthesis of the deuterated intermediates, i.e., 4-*n*-heptyl-d_{15}- and 4-*n*-octyl-d_{17}-oxybenzoyl chlorides (**6**) and (**7**) as well as 4-*n*-pentyl-d_{11}-benzenethiol (**5**) was required.

The route to chain perdeuterated acid chlorides (**6**) and (**7**) was well established by Neubert.[11] The latter involves the synthesis of 4-*n*-heptyl-d_{15}- and 4-*n*-octyl-d_{17}-oxybenzoic acids via reaction of *p*-hydroxybenzoic acid methyl ester with *n*-heptyl-d_{15}-bromide or *n*-octyl-d_{17}-bromide, alkaline hydrolysis of the resulting esters and chlorination with PCl_5. The perdeuterated alkyl bromides, *n*-heptyl-d_{15}-bromide and *n*-octyl-d_{17}-bromide were prepared using iodomethane-d_3 and diethyl malonate.[12]

The second intermediate for the synthesis of $\bar{7}$S5-d_{26} (**I**) and $\bar{8}$S5-d_{28} (**II**), 4-*n*-pentyl-d_{11}-benzenethiol (**5**), was prepared by sulfonation of *n*-pentyl-d_{11}-benzene (**3**) with chlorosulfonic acid, followed by reduction of 4-*n*-pentyl-d_{11}-benzene sul-



SCHEME I



SCHEME II

fonyl chloride (**4**) with zinc in sulfuric acid. Pentyl-d$_{11}$-benzene (**3**) is readily available from bromobenzene and pentyl-d$_{11}$-bromide[12] in a Würtz-Fittig reaction. Pentyl-d$_{11}$-benzene was also prepared in this manner in a 67% yield.

This direct route has the advantage over the Friedel-Crafts route involving acylation of benzene with valeric-d$_9$-chloride (**1**), followed by reduction of *n*-pentanoyl-d$_9$-phenone (**2**) with zinc amalgam. We found that the yield in the reduction step was much lower when deuterated ketone (**2**) was used.

Finally, the specifically deuterated mesogens $\bar{7}$S5-d$_{26}$ (**I**) and $\bar{8}$S5-d$_{28}$ (**II**) were prepared by esterification of the corresponding acid chlorides (**6**) and (**7**) with the thiol (**5**).

Based on MS, ^{1}H NMR and IR spectra of these compounds, the possibility of secondary D → H exchange in the alkyl and alkoxy chains was ruled out under the reaction conditions. The isotopic purities were 96.8% for $\bar{7}$S5-d$_{26}$ (**I**) and 96.5% for $\bar{8}$S5-d$_{28}$ (**II**).

Both compounds have been studied by quasi elastic neutron scattering.[8]

PHASE BEHAVIOUR OF $\bar{7}$S5-d$_{26}$ (I) AND $\bar{8}$S5-d$_{28}$ (II)

The phase behaviour of $\bar{7}$S5-d$_{26}$ (**I**) and $\bar{8}$S5-d$_{28}$ (**II**) compared with that of their hydrogen analogues was studied by means of DSC, using a Perkin-Elmer DSC-2 instrument. Heating and cooling rates were always 5 K/min and the other parameters of the apparatus were also kept constant. Thermograms for both deuterated and non-deuterated materials were carried out with short time intervals between measurements, using sample sizes in the range of 5.00–5.10 mg.

The DSC thermograms were recorded within the temperature range of 250K–400K. For $\bar{7}$S5-d$_{26}$ (**I**) and $\bar{8}$S5-d$_{28}$ (**II**) the phase behaviour of the sample during heating is different from the one measured during cooling of the isotropic phase back to 250 K. On heating a sample of $\bar{7}$S5-d$_{26}$ (**I**) only the following phases were observed: solid Cr nematic N and isotropic I whereas a monotropic smectic C phase appears as well when this sample is colled. When a fresh sample of $\bar{8}$S5-d$_{28}$ (**II**) is heated only four phases were observed: solid Cr, smectic A, nematic and isotropic. During the cooling of $\bar{8}$S5-d$_{28}$ (**II**) seven phases appear: I, N, S$_A$, S$_C$, S$_Y$, CrI and CrII. Reheating this material leads to the same phase sequence as observed in the initial heating Cr-S$_A$-N-I, but the crystalline phase melting to the S$_A$ phase should be CrII. The phase transition CrI-CrII was found for the first time. The same phase transition were also found for the non-deuterated $\bar{7}$S5 and $\bar{8}$S5.

The temperatures, enthalpies and entropies of the phase transitions during the heating and cooling of deuterated and non-deuterated $\bar{7}$S5 and $\bar{8}$S5 are compared in the Table I. The transitions temperatures are about 1–4 deg lower for deuterated than for non-deuterated compounds. These compounds were purified by repeated recrystallization until constant transition temperatures were obtained.

Neubert showed that extensive purification of some deuterated mesogens by high pressure liquid chromatography (HPLC) did not lead to changes in all the transition temperatures.[11] A comparison of the data for $\bar{7}$S5-d$_{15}$ before and after HPLC showed a difference only in the melting temperatures. In this paper, as in our

TABLE I

Comparison of the transition temperatures T, enthalpies ΔH and entropies ΔS phase transition for the deuterated $\overline{7}$S5-d$_{26}$, $\overline{8}$S5-d$_{28}$ and non-deuterated 7S5, 8S5 obtained from DSC

Compound	Transition type	Td/K	T/K	ΔT/K	ΔHd kcal/ mole	ΔH kcal/ mole	ΔSd cal/ mole	ΔS cal/ mole
$\overline{7}$S5	Cr-N	325.9	328.0	−2.1	5.93	6.59	18.19	21.18
	N-I	353.6	355.1	−1.5	0.25	0.29	0.70	0.81
	N-S$_C$	306.6	308.9	−2.3	0.06	0.09	0.20	0.29
	S$_C$-Cr	293.5	296.1	−2.6	4.69	5.08	15.97	17.15
	Cr II-S$_A$	330.0	331.1	−1.1	6.90	7.82	20.90	23.60
	S$_A$-N	333.9	336.3	−2.4	0.02	0.03	0.06	0.08
	N-I	356.1	359.0	−2.9	0.32	0.35	0.89	0.97
$\overline{8}$S5	S$_A$-S$_C$	325.4	326.5	−1.1	0.007	0.008	0.02	0.02
	S$_C$-S$_Y$	300.2	303.0	−2.8	0.69	0.71	2.29	2.34
	S$_Y$-Cr I	284.3	287.6	−3.3	0.92	0.82	3.23	2.85
	Cr I-Cr II	275.3	279.3	−4.0	3.40	4.15	12.35	14.85

Td-transition temperatures of deuterated mesogens, ΔT-transition temperature deuterated mesogen-transition temperature of non-deuterated mesogen, ΔHd-enthalpy of deuterated mesogen, ΔH-enthalpy of non-deuterated mesogen, ΔSd-entropy of deuterated mesogen, ΔS-entropy of non-deuterated mesogen.

previous one[13] we discuss the differences between the thermodynamical values obtained for deuterated and non-deuterated compounds. The maxima corresponding to the phase transitions for all the mesogenes, deuterated and non-deuterated, were narrow (HWHM from 0.1 deg for N-I to 0.5 deg for CrI-CrII). These factors lead us to believe that the effects illustrated in Table I are credible, particularly the values of ΔT which are greater than 1.0 deg. The differences between the deuterated and hydrogen compounds in the transition temperatures are probably due to the difference in the polarizability of the deuterium carbon bond compared with that carbon hydrogen bond[14] or intermolecular interaction differences between the deuterated and non-deuterated liquid crystals.

The transition enthalpies and entropies were also lower for the deuterated compounds except for the S$_Y$-CrI and CrI-CrII transitions (see Table I). The character of the variations of ΔH and ΔS were similar for deuterated and non-deuterated substances. Although deuteration of the alkoxy chains in the 4,4′-dialkoxyazoxybenzenes[13] as well as in the 4-*n*-pentylphenyl-4′-*n*-alkoxythiobenzoates and other liquid crystals leads to a decrease in the transition temperatures between condensed phases, the thorough explanation of this fact requires more studies.

EXPERIMENTAL

All deuterated starting materials were purchased from POLATOM, Poland and had the following isotopic enrichments (min % D) CD_3OD-99.6, D_2O-99.8, NaOD-99.8, LiAID$_4$-99.5. Merck silica gel sheets GF$_{254}$ were used for TLC. Melting points were determined using a calibrated polarizing microscope (VEB Analitic Dresden) and a Perkin-Elmer model 577 was used to obtain routine IR spectra.

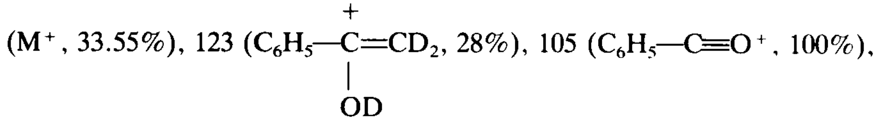
NMR spectra were recorded using a Brücker AM-250 instrument with TMS as an internal standard using CCl_4 as solvent. Mass spectral (MS) data were collected using a LKB-2091 instrument at 70 eV.

Valeric Acid-d_9-chloride (1)

Thionyl chloride (29.4 g, 0.24 mole) was treated dropwise with valeric acid-d_{10} (18 g, 0.16 mole). The whole was refluxed 1 hr, $SOCl_2$ removed by vacuum distillation and the residue distilled at 125°C to give 19.1 g (87.3%) of the desired product (**1**): IR (film) cm^{-1}: 2220, 2120 (med d, C—D), 1795 (str s, C=O) and ^1H NMR showed 1.3% aliphatic protons at 1.1–0.9 δ. (Bromobenzene was used as an external standard.)

n-Pentanoyl-d_9-benzene (2)

A solution of valeric-d_9-chloride (**1**) (17 g, 0.13 mole) in 16 ml of benzene was added dropwise to a stirred solution of $AlCl_3$ (12.5 g, 0.09 mole) in 23 ml CS_2. After the addition was completed, solid $AlCl_3$ (7.5 g, 0.05 mole) was added and the mixture warmed on a steam bath with stirring until evolution of hydrochloric acid ceased. The whole was poured into 100 g of cold 5N HCl, and extracted with three 100 ml portions of Et_2O. The combined ethereal phases were subsequently washed with H_2O, 5% aq KOH and H_2O. The ether layer was dried over anhyd $MgSO_4$ and filtered. When evaporated in vacuo, the filtrate gave the crude liquid *n*-pentanoyl-d_9-benzene, (**2**). Distillation at 241.5°C furnished 21.4 g (93.8%) of the purified material (**2**): IR (film) cm^{-1}: 2220, 2120 (med d, C—D) 1680 (str s, C=O) 1600 with a shoulder at 1570 (Ar); ^1H NMR (CCl_4) δ: 7.81 (m, 2H, ArH ortho to R), 7.34 (m, 3H, Ar meta and para to R). NMR showed 1.4% aliphatic protons at 1.3–0.68 and mass spectrum m/z 171



$$(M^+, 33.55\%),\ 123\ (C_6H_5{-}\underset{\displaystyle OD}{\overset{+}{C}}{=}CD_2,\ 28\%),\ 105\ (C_6H_5{-}C{\equiv}O^+,\ 100\%),$$

77 ($C_6H_5^+$, 29.5%), 50 ($C_3D_7^+$, 55%).

n-Pentyl-d_{11}-benzene (3)

Method A. A mixture of zinc dust (29.7 g, 0.45 g-atom), mercuric chloride (3.2 g, 0.01 mole), 1.8 ml concd DCl and 20 ml D_2O was stirred at RT for 10 min. The liquid was decanted from the solid and the other reagents added to this solid in the following order: 15 ml of D_2O, 22 ml concd DCl and *n*-pentanoyl-d_9-benzene (**2**) (13.5 g, 0.07 mole) in 10 ml CD_3CO_2D. The whole was heated to reflux 24 hr with three 5 ml portions of concd DCl being added at 6 hr intervals. After cooling to RT the reaction mixture was extracted with three 100 ml portions of Et_2O. The combined ether extracts were washed subsequently with H_2O, 10% aq KOH, H_2O and dried over anhyd $MgSO_4$. Concentration of the filtrate to dryness in vacuo gave the crude liquid *n*-pentyl-d_{11}-benzene (**3**). Distillation of this liquid at 199.5°C afforded 5.78 g (48.5%) of the purified material (**3**): IR (film) cm^{-1}: 2220, 2120 (med d, C—D), 1600 with a shoulder at 1570 (Ar); ^1H NMR (CCl_4) δ: 7.06 (s, 5H, Ar). NMR showed 1.7% aliphatic protons at 2.1–1.8 and mass spectrum m/z 159 (M^+, 18.75%), 93 ($C_6H_5—\overset{+}{C}D_2$, 100%), 66 (C_4 D_9^+, 8.2%), 34 ($C_2D_5^+$, 11.43%).

Method B. Sodium (11.1 g, 0.48 g-atom) was added in small pieces to 60 ml of Et_2O at RT with stirring. To this vigorously stirred mixture was added dropwise a solution of pentyl-d_{11}-bromide (27.5 g, 0.17 mole) in bromobenzene (26.7 g, 0.17 mole) while the temperature was kept below 5°C. After the addition was completed, the reaction mixture was stirred at RT for 24 hr. Abs EtOH was added when necessary to decompose any sodium present. The ether layer was washed with H_2O, 5% aq HCl, H_2O, dried over anhyd $MgSO_4$ and filtered. Concentration of the filtrate to dryness in vacuo gave the crude *n*-pentyl-d-$_{11}$-benzene, (**3**) as a liquid. Distillation at 199.5°–200°C afforded 18.3 g (67.8%) of the purified material (**3**).

4-*n*-Pentyl-d_{11}-benzenesulfonyl Chloride (4)

To chlorosulfonic acid (24.07 g, 0.2 mole) was added gradually with vigorous stirring *n*-pentyl-d_{11}-benzene (**3**) (8.3 g, 0.03 mole). The whole was stirred for 2 hr at 60°C and poured into 50 g of ice. The precipitated solid 4-*n*-pentyl-d_{11}-benzenesulfonyl chloride (**4**), was filtered and dried. A sample recrystallized from petroleum ether gave 8.6 g (67.2%) of the purified material (**4**): mp.36.5°C (uncorrected); IR (KBr) cm^{-1}: 2230, 2120 (med d, C—D), 1600 (Ar).

4-*n*-Pentyl-d_{11}-benzenethiol (5)

To a stirred mixture of 57 g ice and concd H_2SO_4 (19.6 g, 0.2 mole) at −5°C was added 4-*n*-pentyl-d_{11}-benzenesulfonyl chloride (**4**) (7.0 g, 0.02 mole) followed immediately by zinc dust (9.6 g, 0.15 g-atom). Stirring was continued for 2 hr at this temperature and then the reaction mixture refluxed for 6 hr. After cooling to RT, the reaction mixture was extracted with three 100 ml portions of Et_2O. The combined ether extracts were washed with H_2O, dried over anhyd $MgSO_4$ and filtered. Removal of the solvent from the filtrate in vacuo gave a liquid which was distilled at 104°C (2 mm Hg) to give 3.03 g (79%) of the desired thiol (**5**): IR (film) cm^{-1}: 2570 (S—H), 2220, 2120 (med d, C—D), 1490(Ar); ^1H NMR (CCl_4) δ: 7.11 (d, 2H, J = 8.5 Hz ortho to R), 6.87 (d, 2H, J = 8.5 Hz ortho to SH) and 3.15 (s, 1, SH). NMR showed 2.3% aliphatic protons at 1.36–0.8 and mass spectrum m/z 191 (M^+, 38.95%), 125 ($D_2\overset{+}{C}—C_6H_4—SH$, 100%), 34 ($C_2D_5^+$, 8.22%).

4-*n*-Pentyl-d_{11}-benzenethio-4′-*n*-heptyl-d_{15}-oxybenzoate (I)

A solution of 4-*n*-pentyl-d_{11}-benzenethiol (**5**) (1.91 g, 0.01 mole) and 4 ml Et_3N in 12.5 ml CH_2Cl_2 was treated dropwise with a soln of 4-*n*-heptyl-d_{17}-oxybenzoyl chloride (**6**) (2.69 g, 0.01 mole). The whole was stirred for 1 hr at RT, washed subsequently with H_2O, 5 aq KOH and H_2O, dried over anhyd $MgSO_4$ and filtered. Concentration of the filtrate in vacuo gave the crude thioester. This material was recrystallized from abs EtOH to give 3.93 g (81.1%) of the purified thioester (**I**):

Transition temperatures 325.9 K (melting point), 353.6 K (clearing point); IR (KBr) cm^{-1}: 2220, 2120 (med d, C—D), 1670 (str s COS) and 1600 with a shoulder at 1570 (Ar); ^1H NMR $(CCl_4)\delta$: 7.89 (d, 2H, $J = 9$ Hz, ArH ortho to COS), 7.29 (d, 2H, $J = 8$ Hz, ArH ortho to alkyl), 7.13 (d, 2H, $J - 8$ Hz, ArH ortho to SCO), 6.82 (d, 2H, $J = 9$ Hz, ArH ortho to RO) and mass spectrum m/z 234 $(D_{15}C_7O—C_6H_4—C^+{\equiv}O$, 38.8%), 122 $(DO—C_6H_4—C^+{\equiv}O$, 100%), 66 $(C_4D_9^+$, 23.8%), 34 $(C_2D_5^+$, 33.4%).

4-*n*-Pentyl-d_{11}-benzenethio-4′-*n*-octyl-d_{17}-oxybenzoate (II)

4-*n*-Pentyl-d_{11}-benzenethio-4′-*n*-octyl-d_{17}-oxybenzoate (**II**) was prepared in the same manner as above in a yield of 79.8% using 4-*n*-pentyl-d_{11}-benzenethiol (**5**) and 4-*n*-octyl-d_{17}-oxybenzoyl chloride (**7**). Transition temperatures 330.0 K (melting point), 356.1 K (clearing point): IR (KBr) cm^{-1}: 2220, 2110 (med d, C—D), 1670 (str s COS) and shoulder at 1575 (Ar); ^1H NMR $(CCl_4)\delta$: 7.88 (d, 2H, $J = 9$Hz, ArH ortho to COS), 7.28 (d, 2H, $J = 8$ Hz, ArH ortho to alkyl), 7.13 (d, 2H, $J = 8$ Hz, ArH ortho to SCO), 6.81 (d, 2H, $J = 9$ Hz, ArH ortho to RO) and mass spectrum m/z 250 $(C_8D_{17}O—C_6H_4—C^+{\equiv}O$, 68.9%), 122 $(DO—C_6H_4—C^+{\equiv}O$, 100%), 66 $(C_4D_9^+$, 53.84%), 34 $(C_2D_5^+$, 29.4%).

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