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MESOGENIC DITHIOLATES : NEW DISK LIKE Π-ACCEPTORS

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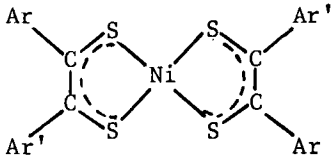
Abstract Starting from p-hydroxyphenylacetic acid we have been able to synthesize mesogenic dithiolates of transition metals with long chain substituents. Introduction of n-alkoxy side chains reduces the electronic affinity of this system, nevertheless those compounds are weak acceptors and can form complexes with π-donors which have a low ionization potential (E_A-I_P < 0.1V).

INTRODUCTION

In line with our previous work on disk like Π-donors [1,2,3] we have attempted to synthesize new Π-acceptors, having mesomorphic properties. It is known that a metal bis-dithiolene system exhibits acceptor properties [4,5]. Thus we expected to obtain mesogenic metal bis-dithiolene planar molecules by introducing long chain substituents. We describe here the synthesis and the properties of Nickel bis-dithiolene in which phenyl groups are substituted in para position by alkoxy OC_nH_{2n+1} substituents.

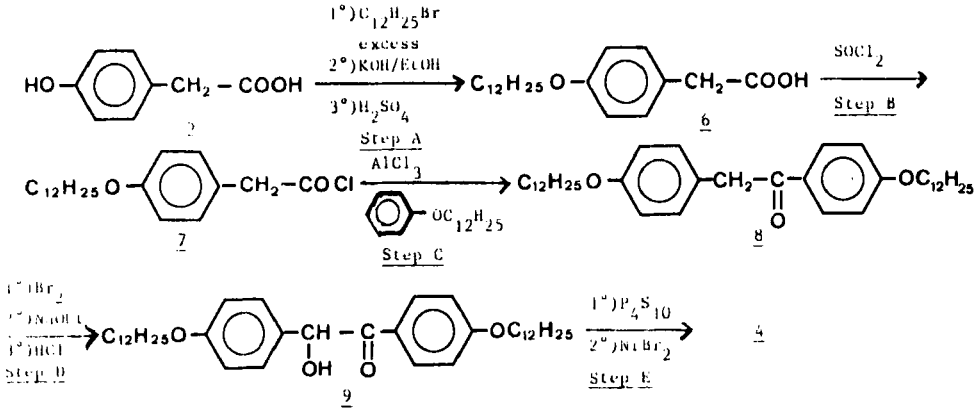


Ar = Ar'	= C_6H_5	1
Ar = Ar'	= $pC_6H_4OCH_3$	2
Ar = H ; Ar'	= $pC_6H_4OC_{12}H_{25}$	3
Ar = Ar'	= $pC_6H_4OC_{12}H_{25}$	4

SYNTHESIS

Nickel bis-dithiolenes with aromatic substituents 1 and 2 have been described by Schrauzer [6]. They are obtained by the

transformation of an α-hydroxyketone (benzoin) into a thiophosphoric ester which is then treated with a divalent salt of transition metal MX_2 (M = Ni, Pt, Pd etc...). We have used this method to prepare compounds 3 and 4. But the classical benzoin synthesis could not be used in the case of long chain alkoxy substituted benzaldehydes. So compound 4 has been prepared according to following reaction sequence.



Starting from phenylacetyl chloride instead of 7 we obtained (step C) the 4-dodecyloxydesoxybenzoin 10, then in step D, the 4-dodecyloxybenzoin 11, and finally 3 (step E).

REDOX PROPERTIES

The electrochemical results for 3 and 4 (cyclic voltammetry are given in TABLE I together with those obtained by us for 1 and 2 in experimental conditions which are different from those used by Schrauzer. As expected introduction of electron donating groups OC_nH_{2n+1} decreases the electron affinity of such systems, compared to the tetraphenyl derivative, 1, described by Schrauzer[6]. However, they are able to form complexes with low ionization potential π-donors.

TABLE I

	$E_1^{1/2}$	$E_2^{1/2}$
1	0.132	-0,677
2	0.052	*
3	0.072	*
4	0.030	*

* The second half wave was poorly resolved so the $E_2^{1/2}$ value could not be given.

The reduction potentials were determined at a concentration of 10^{-3}M in methylene chloride ; 0,1M tetrabutylammonium fluoroborate ; the value is for a platinum electrode ; SCE ; 0.1V/second.

MESOMORPHISM

Microscopic observations allow us to conclude that 3 and 4 are mesomorphic but not isomorphic.

3 $\quad 81°C < M_1 < 116°C$

4 $\quad 124°C < M_2 < 166°C$

The texture of 4, observed in the mesomorphic range, seems to be similar to disk like Π-donors having also binar or tetragonal symmetry [3]. X-Ray diffraction study would permit a more precise identification [8].

COMPLEXATION WITH Π-DONORS

Compounds 3 and 4 although being very weak acceptors (TABLE I) could form complexes with Π-donors of the dipyranylidene series. Results are given in TABLE II. The formation of charge transfer complexes is observed when $E_A - E_D < 0.1$Volt. How-

ever, we must take into account the steric hindrance due to the long chain substituents in both Π-donors and Π-acceptors.

TABLE II

A \ D	DIPϕ_4	DIP(ϕOCH_3)$_4$	DIP(ϕOR)$_4$ R=C_7 p	DIP(ϕOR)$_4$ R=C_9 o	DIP(ϕOR)$_4$ R=C_9 p	DIP(ϕOR)$_4$ R=C_{12} o	DIP(ϕOR)$_4$ R=C_{12} p
1	-0.092 [a]	-	0.097[a]	0.030[b]	0.072[a]	0.050[b]	-0.018[a]
2	-0.172 [b]	0.028[a]	0.017[b]	0.050[b]	-0.008[b]	-	-
3	-	0.046[a]	0.035[a]	-	0.010[a]	-	-

a) obtained CTC

b) no CTC

CONCLUSION

We have shown that Nickel bis-dithiolene compounds with long chain alkoxy substituents have mesomorphic properties. However introduction of electron donor substituents decreases the electron affinity of such compounds which can only be complexed with low ionization potential Π-donors. A study of other planar mesogenic systems with higher electron affinity is in progress.

EXPERIMENTAL

The obtained products were identified by their IR and ^{1}H NMR Spectra. The Nickel complexes were identified by their UV ($CHCl_3$), IR and ^{1}H NMR Spectra.

4-dodecyloxyphenylacetic acid 6 (Step A) was synthesized by alkoylation of commercial (Prolabo) 4-hydroxyphenylacetic acid using the experimental conditions described for alkoxyacetophenones [9]. By this way, we obtained a mixture of

substituted acid and ester, which was hydrolyzed in refluxing alcoholic potassium hydroxide for 5 hours. The salt of the acid was then filtered, dissolved in hot water and acidified with dilute sulfuric acid. 4-dodecyloxylphenylacetic acid soon precipitated on cooling and was then filtered and purified by recrystallisation from toluene.

M_p= 83°C ; yield = 91%

^{1}H NMR : δ(ppm) 7.25(d, 2H, C_6H_4), 6.85(d, 2H, C_6H_4), 4(t, 2H, $\underline{CH}_2O$), 3.6(s, 2H, $\underline{CH}_2CO_2H$), 1.3(m, 18H, $(CH_2)_9$), 0.9(m, 3H, $\underline{CH}_3$)

IR ν(cm^{-1}) : ν(CO_2H) 1710, 1420, 1250, ν(φ) 1600, 1520, ν($OC_{12}H_{25}$) 1265

4-dodecyloxphenylacetic acid chloride 7 (Step B)

A mixture of the acid 6 (18.5mmoles), benzene (15ml) and thionyl chloride (2ml) was refluxed for 10 hours until HCl and SO_2 ceased to evolve. Benzene and excess thionyl chloride were evaporated under reduced pressure and the residue distilled.

Bp 180°C (0,1mm) ; yield =95%

Desoxybenzoins 8 and 10 (Step C)

They were obtained by Friedel-Craft acylation of dodecylphenyl ether in CCl_4. To a cooled mixture (0°C) of the acid chloride 7 (10.5mmoles) and $AlCl_3$ (10.5mmoles) was added dropwise dodecylphenyl ether (9mmoles) dissolved in 5ml CCl_4. The mixture was stirred at 0-10°C for 1 hour and allowed to stand for 10 hours at room temperature. After treatment with HCl, extraction with chloroform and washing with sodium bicarbonate, solvents were distilled off under reduced pressure and desoxybenzoins recrystallised from methanol.

M_p= 105°C ; yield = 90% 8
M_p= 76°C ; yield = 70% 10

Benzoins 9 and 11 (Step D)

They were synthesized by the method described by S.S. Jenkins [10] without isolation of the intermediate bromodesoxybenzoin. Their purity was checked by TLC on silica gel (eluant : pentane/ethylacetate, 95/5).

Yields : 46% 9
63% 11

4,4'-didodecyloxybenzoin 9 :

^{1}H NMR : δ(ppm) 8.1(d, 2H, C_6H_4), 7.55(d, 2H, C_6H_4), 7(d,4H, C_6H_4), 5.6(s, 1H, CHOH), 4.05(m, 4H, O-CH_2), 1.3(m, 40H,CH_2) 0.9(m, 6H, CH_3).

IR(cm^{-1}) : ν(C = O) 1680, 1265, ν(C_6H_4) 1605, 1575, ν($OC_{12}H_{25}$) 1260, 1230.

4-dodecyloxybenzoin 11

^{1}H NMR : δ(ppm) 7.95(d, 2H, C_6H_4), 7.4(s, 5H, C_6H_5), 6.9(d, 2H, C_6H_4), 5.95(s, 1H, CH_2), 0.9(m, 3H, CH_3).

IR(cm^{-1}) : ν(C = O) 1680, 1265, ν(C_6H_5) 1600, 1575, ν($OC_{12}H_{25}$) 1260, 1220, 1075, 1020.

Nickel complexes 1-4 (Step E)

All nickel complexes were prepared according to Schrauzer [6]. The long chain substituted nickel complexes were extracted with heptane, filtered,washed with pentane and re-extracted with diglyme, leading to crystalline complexes as dark needles.

Yields : 47% 1 33% 3
31% 2 24% 4

Compound 3

IR(cm^{-1}) 1600, 1357, 1245, 1136, 880.

UV($CHCl_3$, wave lengths in nm) 780, 625, 307, 285.

Compound 4

IR(cm^{-1}) 1605, 1365, 1260, 1155, 900.

UV($CHCl_3$, wave lengths in nm) : 790, 645, 305, 285.

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