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SYNTHESIS AND PROPERTIES OF MESOGENIC π-DONORS : PRECURSORS OF MESOMORPHIC ORGANIC CONDUCTORS

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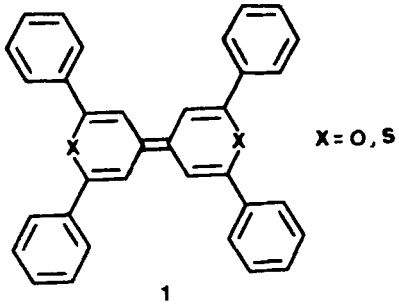
Abstract In sequence with previous work on 4-(2,6 diphenyl 4-H pyran-4 ylidene-2,6 diphenyl) and their sulfur analogs, useful precursors of organic conductors, we now report on the synthesis and properties of parent heterocyclic compounds, 1, in which the phenyls have long chain substituents. Introduction of four alkyl or alkoxy side chains in the para position of phenyl leads to compounds, 2, which exhibit *disk-like mesophases*. All new donors 2 give stables 1:1 charge transfer complexes, 3, with TCNQ. *Disk-like donors lead to mesomorphic conducting complexes*. For example the TCNQ complex of 2b, X = S, R = $C_{12}H_{25}$ exhibits a S_A phase between 120-154°C. The electrical conductivity at room temperature of a single crystal is 0.7 $(\Omega cm)^{-1}$.

The aim of this work is to synthesize organic 1D-conductors having liquid crystal properties. These materials, to the best of our knowledge, have been unknown up to now.

Previous work on the 4-(2,6 diphenyl 4-H pyran-4 ylidene-2,6 diphenyl) molecule and its sulfur analog, 1, demonstrated that these molecules have a quasi-planar structure [1-2] and can be enclosed in a square with sides of 12Å. The compounds 1 are useful precursors of highly conducting charge transfer complexes (C.T.C.)[3] and radical cation salts [4] when X = S.

On the other hand, in the last few years, a new class of liquid crystals, named disk-like, was discovered [5-6]. The originality of this class is its constitution of rigid disk-

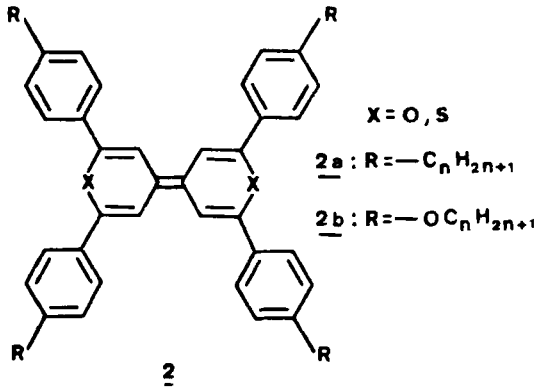
shaped core molecules instead of the elongated ones of the up



1

to now known liquid crystals. However the presence of long aliphatic side chains remains essential for the appearance of the mesophase.

Thus, recently, we have shown that the introduction of four alkyl side chains in the para position of phenyl groups in parent heterocyclic compounds 1 leads to *disk-like mesogenic compounds* [7-8]. The mesophase has been observed for $n \geq 9$ in compounds 2a having alkyl substituents. In the series of alkoxy substituted heterocycles, 2b, a disk-like mesophase appears only when X = S for $n \geq 12$.

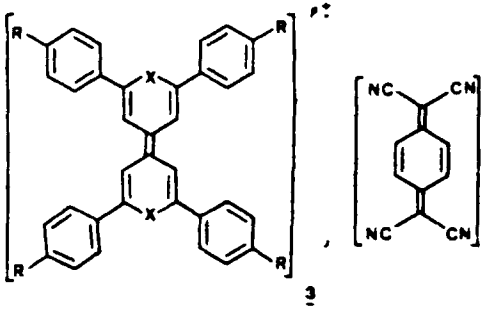


2

After study of redox behavior of 2a, 2b (by cyclic voltammetry) we concluded that they remained powerful π-donors

as are the parent compounds 1. The stability of the formed radical ions ($\log K = E^2_{1/2} - E^1_{1/2}/0.059$) was discussed[8], where $E^1_{1/2}$, $E^2_{1/2}$ are the first and second half-wave ionization potentials.

All compounds 2 form stable 1:1 C.T.C., 3, with TCNQ as an acceptor.



3

ρ : ρ = degree of charge transfer

Among the formed complexes the more interesting one is 3 (X = S, R = $-OC_{12}H_{25}$) which is the first *mesomorphic conducting complex* in our knowledge.

The microscopic observations and preliminary X-ray studies demonstrate a smectic A lamellar phase for this complex between 120° and 154°C which is confirmed by Differential Scanning Calorimetry (D.S.C.).

The room temperature electrical conductivity measured on compressed pellets is $10^{-3}(\Omega cm)^{-1}$ and single crystal measurements gave the value of $0.7(\Omega cm)^{-1}$ [9].

The crystallographic parameters [10] at 25°C are :

a = 18.47 Å		V = 3909 Å^3
b = 9.14 Å	β ≃ 110°	Z = 2
c = 24.64 Å		d_c = 1.22

The obtained complex with the described characteristics allows us to anticipate that the columnar arrangement of the

disk-like donor molecules must be maintained after complexation. In fact it is known that the molecules in the disk-like mesophase form a columnar arrangement with a stacking of the rigid cores of the molecules. The stacking axis can form a variety of angles (for the different species) with the plane of the molecule. The intermolecular distances in the interior of a column are compatible with the found ones for the organic conductors.

The intermolecular forces between adjacent columns are weaker than the intracolumnar ones. This kind of structure allows us to assume that the rigidity of the columnar structure could be preserved after the formation of C.T.C.

So we propose the hypothesis that starting from a mesomorphic *disk-like donor or acceptor we should be able to synthesize mesomorphic charge transfer complexes with non mesomorphic partners*.

It seems to us that the latter hypothesis should be also valid in the case of the radical cation salts. To confirm this we are now trying to synthesize the corresponding compounds.

It must be noted that the analogous efforts failed in the case of tetraaryl substituted tetrathiofulvalene [11-12]. The long chain species [12] in this family are not mesomorphoic.

Recently Saeva and al [13] have published results concerning complexation of 2a (X = O, R =-$C_{12}H_{25}$) with TCNQ and electrochemical oxydation leading to radical cation salts. According to these authors the obtained species exhibit disk-like mesophases. None of the products have a conducting behavior [13] ($\sigma < 10^{-6}(\Omega cm)^{-1}$).

The preparation method for the conducting complex is the

following :

60mg (0.29 mmole) of TCNQ were dissolved in a hot 1:1 mixture of CH_2Cl_2 and CH_3CN(100ml). The donor 2b(X = S, R =-$OC_{12}H_{25}$) 280mg (0.23 mmole) was extracted into this solution. The solution was cooled to room temperature and filtered. This product was washed with ether, pentane and dried. Yield was quantitative.

Single crystals were obtained by the diffusion technique (H-tube) ; solvent CH_2Cl_2-CH_3CN 3:2, molecular concentration 1.2 x 10^{-3}M at 30°C.

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