A Novel Conducting Charge-transfer Complex Containing an Ylide as Donor

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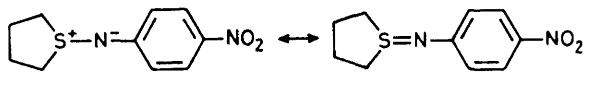
Novel conducting organic solids containing the ylide (**1**) as donor and tetracyanoquinodimethane as acceptor have been synthesized and their properties examined by i.r., e.s.r., and electrical conductivity measurements.

Many charge-transfer complexes composed of various organic donors and acceptors have been studied extensively, particularly those containing TCNQ (tetracyanoquinodimethane) which is a good acceptor. We are interested in organic solids



(1)

involving TCNQ because of recent studies on quasi-one-dimensional systems displaying anisotropic physical properties; some TCNQ–donor complexes exhibit high conductivity owing to their particular structural features.[1] We recently reported the electronic structure of ylides, showing unusual valency properties.[2] Ylides have two main canonical structures: $X^+–Y^-$ and $X=Y$,[3] whose relative contributions depend on the nature of the heteroatom and substituents, which therefore determine both the donor strength and the site from which donation occurs (double bond or Y^- lone pair).

We now report the preparation and properties of a conducting ylide–TCNQ complex. The *N*-aryl sulphilimine (**1**) used was prepared by the published methods,[4] and TCNQ was sublimed several times. Equimolar acetonitrile solutions of (**1**) and TCNQ were mixed under argon and an equimolar amount of 18-crown-6 ether was added. The presence of the crown ether is essential, since in its absence amorphous products were obtained. In the experiments the crown ether was added to improve the solubility of the reaction mixture. The visible spectrum of the solution containing only the ylide and crown ether showed a strong interaction between the ylide and crown ether. This solution and the solution of TCNQ were mixed and stirred under argon at room temperature for two weeks. Some solvent was evaporated off and the remaining solution was kept in a refrigerator for a week, when large black crystals were isolated, thus providing a novel technique for making large crystals. The technique is successful probably owing to a decrease in the rate of complexation due to association: as the sulphilimine (**1**) interacts with the crown ether, the concentration of (**1**) available to react with TCNQ decreases. The concentration of (**1**) also decreases as the complexation proceeds, so that the (**1**)–crown ether complex dissociates and reacts with TCNQ. Thus, the interaction between the sulphilimine (**1**) and crown ether controls the reaction rate. The rod-like crystalline complexes obtained were dried *in vacuo* for 24 h.

The visible spectrum of the complex in acetonitrile showed the existence of typical TCNQ radicals (three main maxima: 679, 741, and 841 nm). Its mass spectrum showed parent peaks (*m/z*, 224 and 204) corresponding to (**1**) and TCNQ, respectively, together with peaks arising from fragmentation of each compound. This indicates a molecular complex of the sulphilimine (**1**) and TCNQ. The molar ratio of ylide (**1**) to TCNQ was determined by elemental analyses as 1:2, *i.e.* (ylide)-$(TCNQ)_2$.

The solid-state i.r. spectrum of the complex (4000—650 cm^{-1}) is not a superposition of the spectra of the constituent neutral molecules, as expected for a strong π-complex; all the bands are broadened compared with those of the constituent molecules and there are changes in the frequencies and intensities. The CN stretching band is broad, at 2180 cm^{-1}, with a shoulder at 2200 cm^{-1}. These values are in the region where the CN stretching modes of the $TCNQ^{\cdot -}$ anion radical typically appear (2200—2180 cm^{-1}).[5] The magnetic properties of the complex were studied by e.s.r. spectroscopy at room temperature, and a typical spectrum of a freshly prepared complex is shown in Figure 1. It shows a three-line absorption of overall width 1.4 G (G = 10^{-4} T).

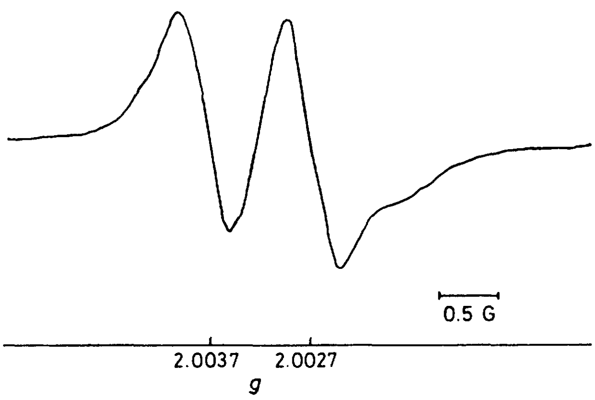


Figure 1. E.s.r. spectrum of the complex (**1**)–TCNQ.

It is known that biradicals show several peaks due to the *g*-factor anisotropy,[6] but the width of the spectrum in Figure 1 is smaller than that of other examples of biradicals[6] and its structure changes with time, probably owing to the effect of atmospheric oxygen and water. The middle peak in particular fades. The *g*-value for the fresh sample (Figure 1) is very different from that of the component TCNQ radical (Li^+-$TCNQ^{\cdot -}$, 2.0025 ± 0.0001).[7] Thus, we suppose that this e.s.r. spectrum, which has an asymmetric multi-structure is a result of the strong interaction between the two radicals. The electrical conductivity of the complex in the form of a small compressed pellet was *ca.* $2 \times 10^{-4}\ \Omega^{-1} cm^{-1}$ at room temperature. An *X*-ray crystal structure determination is in progress.

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