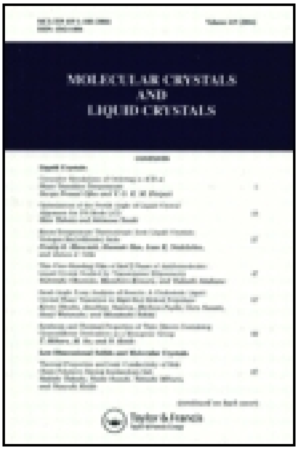

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Bipolar and Monopolar Transport in Diaryldiacetylene Layers

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To cite this article: A. R. Tameev, J. Wright, A. V. Vannikov, A. R. Werninck & G. H. W. Milburn (2001): Bipolar and Monopolar Transport in Diaryldiacetylene Layers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 361:1, 95-100

To link to this article: http://dx.doi.org/10.1080/10587250108025724

Mol. Cryst. and Liq. Cryst., 2001, Vol. 361, pp. 95-100
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Bipolar and Monopolar Transport in Diaryldiacetylene Layers

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Hole and electron transport has been studied by the time-of-flight technique on disubstituted diaryldiacetylene layers prepared by the vacuum deposition method. Basic transport characteristics and their dependence on the electric field, temperature and chemical structure of molecules are determined. The data are fit well into a correlated disorder model. Results of an semiempirical quantum-chemistry calculation (PM3, ZINDO/S) on diaryldiacetylene molecules are in agreement with the experimental data.

Keywords: diaryldiacetylene; time of flight technique; bipolar transport; semiempirical calculations

Although there has been many studies of monopolar (hole or electron) transport in molecular layers, few studies have been conducted on bipolar transport [1-3]. Due to the importance of bipolar transport to single-layer devices [4], this subject is of considerable technological relevance as well. Our earlier investigation demonstrated that the preparation, by the vacuum deposition, of various diaryldiacetylenes (DA) can produce high quality thin layers exhibiting effective hole transport with high values of drift mobility [5]. In this study we have extended our studies to a novel diaryldiacetylene, DA4, which possesses bipolar transport with comparable hole and electron mobilities.

The synthetic preparation and purification of DAs has been described previously [5,6]. Molecular structures of the investigated compounds are illustrated in Fig.1. The DA3 and DA4 molecules have the same DA core structure with different end-groups: R=-O-$C_{12}H_{25}$ (DA3), -CN (DA4).

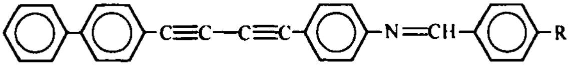

FIGURE 1. Structures of the studied diaryldiacetylenes.

Samples were prepared by thermal sublimation onto a substrate in vacuum of 8×10^{-5} Torr as it has been described previously [5]. Thickness of the DA layers, *d*, was 2.7-6.0 μm. Charge carrier drift mobilities were measured by the conventional time-of-flight technique [5]. The transient currents were measured with a digital oscilloscope Tektronix TDS 340A The transit time was determined from the intersection of the asymptotes to the plateau and the tail of the normal transient. The drift mobility was determined from the conventional expression $\mu = d/(F\cdot t_T)$, where F is the applied field. Optical absorption spectra were recorded on a Beckman DU-7 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 1760-X Fourier Transform Spectrophotometer.

For quantum-chemistry calculations, the geometry of molecules was optimised by the semiempirical MNDO/PM3 using the Polak-Ribiere algorithm [7]. Calculations of the UV-visible spectra for neutral molecules were made by the ZINDO/S [8] with singly-excited configuration interaction (CI) method using 20 both occupied and unoccupied molecular orbitals.

As observed in our previous work [5], the absorption profile of the DA solid layers are in the UV-vis range of 250 to 500 nm and are somewhat broadened with the maxima shifted towards longer wavelengths as compared to the respective DA in chloroform solution. This investigation has revealed that IR spectra of pristine DA3 substance and DA3 deposited layers are fully coincidental. This indicates no changes occurs in the DA3 molecular structure in the course of thermal deposition. Quantum-chemical calculations demonstrated that bands of electronic spectrum for the neutral DA3 molecule in an optimized geometry fall within those seen for deposited layer (Fig.2). As the computed bands are "gas phase" results, we can expect that a solution correction of 0.25-0.30 eV [9] must be applied to these bands.

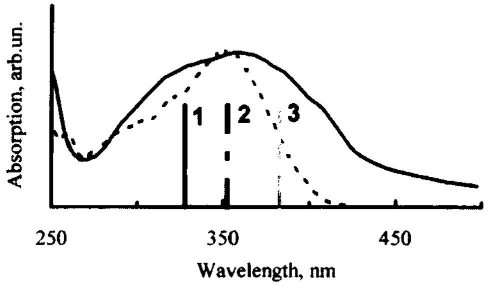

FIGURE 2. UV-visible spectra of the DA3 in chloroform solution (dashed line), evaporated solid layer (solid line) and calculated maxima of absorption spectra for the neutral DA3 molecule in the geometry optimized at neutral state (*1*), cation radical state (*2*), anion radical state (*3*).

Once the correction is taken into account, the agreement between the computed band (*1*) and the DA3 spectrum in solution is seen to be excellent. Furthermore, the absorption bands of the neutral molecules in geometry optimized in cation-radical state (*2*), or, in anion-radical state (*3*), both fall within the band observed for the deposited layer (Fig.2).

This is also the case for DA4 studied. By comparing the observed and calculated DA spectra, one may conclude that the broadening and shifting of the UV band seen in the deposited layers (compared to DA solutions) is caused by a different molecular geometry.

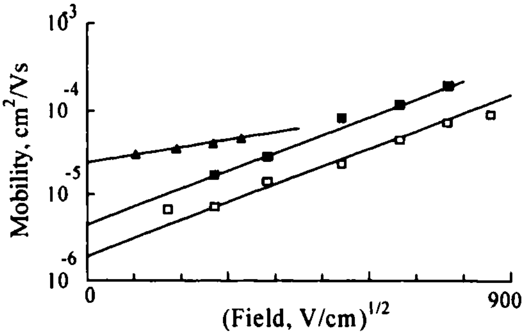

FIGURE 3. Field dependence of hole mobility in DA3 (solid triangles) and DA4 (solid squares) and electron mobility in DA4 (empty squares) at room temperature. Lines were drawn according to Equation 1 in which R=10 A, ε=3.4.

Fig.3 shows the dependence of hole drift mobility for DA3 layers and both hole and electron mobilities for DA4 layers as a function of applied electric field. The field dependence of mobility is linear in coordinates $lg\mu$ - $F^{1/2}$. For DA3 layers, the transit time for electrons was not detected because of the small signal-to-noise ratio. The temperature dependence of both hole and electron mobilities was of an activation type. The activation energy, E_A , decreases as the electric field increases and has a linear dependence when plotted as E_A - $F^{1/2}$ (the plot is not shown). The mobility difference of DA3 and DA4 can not be explain by their geometry as it is the same for both DA3 and DA4 layers.

A number of models that consider the charge carriers transport have been developed. The field and temperature dependences of the drift mobility may be described by the Gill semiempirical expression

$\mu = \mu_0 \exp[E_A(1/T - 1/T_0)/k]$ where μ_0 is the preexponential factor, k is the Boltzmann constant, T_0 is a characteristic temperature, and $E_A = E_A(0) - \beta F^{1/2}$ where $E_A(0)$ is an activation energy at zero field and β is a coefficient. The fact that the activation energy $E_A(0)$ for DA4 (0.30 eV) is higher than that for DA3 (0.18 eV) within the field range used illuminates the cause of the difference in the magnitude of the hole mobility for the DA's studied at room temperature. The Gaussian disordered formalism [10] and the correlated disorder model [11] are the models of sufficient generality. For dipolar systems, the latter leads to the following relationship:

$$\mu = \mu_0 W \exp\left[-\left(\frac{3\sigma_d}{5kT}\right)^2 + C_0\left(\left(\frac{\sigma_d}{kT}\right)^{3/2} - \Gamma\right)\sqrt{\frac{eRF}{\sigma_d}} \right] \qquad (1)$$

where $C_0 = 0.78$, $\Gamma = 2$, W is defined as a part of the transfer integral, R is the distance between transport sites, and $\sigma_d = 2.35ep/\varepsilon R^2$ is the root mean square width of the dipolar energetic disorder (ε is the dielectric constant of the medium). They use the permanent dipole moment p of molecule as a parameter describing a transport molecule. According to our calculation, magnitudes of the dipole moment for DA3 and DA4 are equal to 2.61 and 4.55 Debye respectively. Assuming that R is the same for each DA layer, one can obtain a reasonable agreement between the hole mobility values calculated using both the models and those obtained experimentally for DA3 and DA4. However, the fact that some of the molecules provide the bipolar charge transport (e.g. DA4) whilst another provides only monopolar transport (e.g. DA3) is not explained by any of the models discussed. It is believed that ionization potential (IP) and electron affinity (EA) of molecules are parameters which give an insight into this feature. For DA3, the calculated IP and EA values are equal to 6.9 and 0.6 eV, respectively, for vertical (non-adiabatic) process. For DA4, the IP and EA values are equal to 7.1 and 1.3 eV, correspondingly. The low value of EA for DA3 agrees well with the immobility of electrons in this material.

In summary, the data on mobility are fit well into a correlated disorder model. A molecular geometry of the DA molecules does not seem to be the key factor for the ability of the molecular layers to act as bipolar or monopolar charge transport materials. Electronic properties of these molecules show the best correlation with the results on charge carriers mobility.

Acknowledgments

This work was supported in part by the Russian Foundation for Basic Research (Project 99-03-32111) and the International Science and Technology Centre under Grant N872.

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