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Charge transport in columnar stacked triphenylenes: Effects of conformational fluctuations on charge transfer integrals and site energies

K. Senthilkumar, F. C. Grozema, F. M. Bickelhaupt,^{a)} and L. D. A. Siebbeles^{b)}
*Radiation Chemistry Department, Interfaculty Reactor Institute, Delft University of Technology,
Mekelweg 15, NL-2629 JB Delft, The Netherlands*

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Values of charge transfer integrals, spatial overlap integrals and site energies involved in transport of positive charges along columnar stacked triphenylene derivatives are provided. These parameters were calculated directly as the matrix elements of the Kohn–Sham Hamiltonian, defined in terms of the molecular orbitals on individual triphenylene molecules. This was realized by exploiting the unique feature of the Amsterdam density functional theory program that allows one to use molecular orbitals on individual molecules as a basis set in calculations on a system composed of two or more molecules. The charge transfer integrals obtained in this way differ significantly from values estimated from the energy splitting between the highest occupied molecular orbitals in a dimer. The difference is due to the nonzero spatial overlap between the molecular orbitals on adjacent molecules. Calculations were performed on unsubstituted and methoxy- or methylthio-substituted triphenylenes. Charge transfer integrals and site energies were computed as a function of the twist angle, stacking distance and lateral slide distance between adjacent molecules. The variation of the charge transfer integrals and site energies with these conformational degrees of freedom provide a qualitative explanation of the similarities and differences between the experimental charge carrier mobilities in different phases of alkoxy- and alkylthio-substituted triphenylenes. The data obtained from the present work can be used as input in quantitative studies of charge transport in columnar stacked triphenylene derivatives. © 2003 American Institute of Physics.

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I. INTRODUCTION

In discotic liquid crystalline materials disklike aromatic molecules form π -stacked columnar aggregates. The π -orbitals on adjacent molecules overlap yielding a one-dimensional pathway for charge migration. This offers promising possibilities for application of these materials in photocopying, nanoscale molecular electronic devices such as light-emitting diodes and field-effect transistors and photovoltaic cells.^{1–4} Within the class of liquid crystalline discotic materials, the triphenylene derivatives have been studied in great detail, with respect to both structural and physical properties. (See Fig. 1.)

Of particular relevance to their possible use in electronic device applications are charge carrier mobility measurements. Experimental mobility values have been obtained from time-of-flight (TOF) measurements,^{5–13} pulse-radiolysis time-resolved microwave conductivity (PR–TRMC) measurements^{14–20} and frequency dependent AC conductivity measurements on doped samples.^{21–24} The conductivity in triphenylene derivatives is mainly due to transport of positive charges (holes) and for the liquid crystalline phase mobility values in the range 10^{-3} – 10^{-1} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ have been reported. From PR–TRMC measurements mobil-

ity values as high as $0.2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ have been found for the crystalline phase of alkylthio-substituted triphenylenes.¹⁵ For a recent review of the experimental conductivity data see Ref. 25.

Structural studies of liquid crystalline triphenylene derivatives have revealed that the average intracolumnar stacking distance and twist angle are close to 3.5 \AA and 45° , respectively, while structural fluctuations in the form of longitudinal oscillations, twisting motion and lateral slides of the molecules (see Fig. 2) play a prominent role.^{26–31} Structural disorder has a detrimental effect on the charge carrier mobility and gives rise to disperse photocurrent transients and a frequency dependence of the charge carrier mobility.^{18,21–24} The presence of disorder causes stacks of triphenylene molecules to have a non-periodic structure and consequently electronic band structure calculations, which can be used to describe charge transport in molecular crystals,³² are inapplicable. Quantitative insight into the effects of structural disorder on the mobility of charge carriers requires an alternative theoretical treatment of charge transport. Theoretical studies based on incoherent hopping models^{18,33,34} or (partially) coherent motion²⁰ including effects of dynamic or static structural fluctuations have been used to estimate hole mobilities in triphenylene derivatives. The theoretical mobility values presented until now are at least one order of magnitude higher than the experimental values for liquid crystalline triphenylene derivatives. Recently, the mobility of charge carriers in DNA has been cal-

^{a)}Also at: Afdeling Theoretische Chemie, Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands.

^{b)}Author to whom correspondence should be addressed. Electronic mail: siebbeles@iri.tudelft.nl

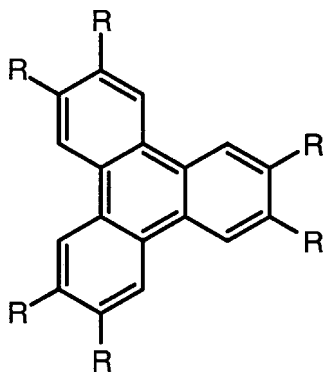


FIG. 1. Chemical structure of the triphenylene derivatives investigated, $R=H$, OCH_3 , or SCH_3 .

culated by using a model based on tight-binding method combined with structural fluctuations of the molecular lattice.³⁵ This model could well serve as a starting point for a theoretical treatment of charge transport in columnar stacked triphenylenes.

The theoretical models for charge transport require accurate values of electronic couplings for charge transfer (also referred to as charge transfer integrals or hopping matrix elements) and site energies (energy of a charge when it is localized at a particular molecule) as a function of the geometric conformation of adjacent molecules. Charge transfer integrals for hole transport have been estimated from band structure calculations³⁴ or from the energetic splitting of the highest-occupied molecular orbitals (HOMOs) in a system consisting of two adjacent molecules.^{20,33} These procedures are only correct in case the spatial overlap between the HOMO orbitals on different molecules is equal to zero and the site energies of the two molecules in a dimer system are identical.³⁶ These conditions are not generally fulfilled in the systems considered here. In addition, information about the fluctuations of the site energies cannot be obtained from the procedures mentioned above. Therefore, an alternative method is applied in which the spatial overlap, charge transfer integrals and site energies are calculated directly without invoking any approximation. The calculations were performed using the Amsterdam density functional (ADF) theory program³⁷ and the quantitative molecular orbital

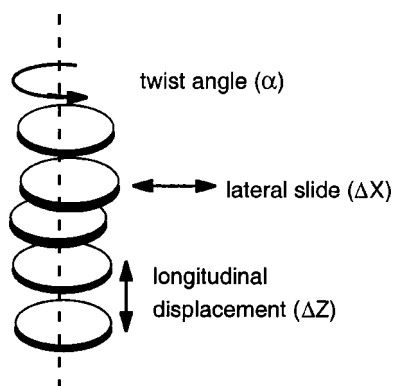


FIG. 2. Schematic representation of columnar stacked triphenylene molecules with disorder in the form of different twist angles (α), stacking distances (ΔZ), and lateral slide motions (ΔX).

(MO) model contained in Kohn–Sham density functional theory (DFT).³⁸ With the ADF program the orbitals of a stack of triphenylene molecules can be expressed in terms of the molecular orbitals on the individual molecules. The spatial overlap integrals belong to the standard output of the ADF program, while the charge transfer integrals and site energies are directly obtained as the off-diagonal and diagonal matrix elements of the Kohn–Sham Hamiltonian. The aim of the present work is to provide values of the charge transfer integrals and site energies involved in hole transport in columnar triphenylene derivatives, which can be used in future calculations of absolute mobility values. The theoretical methodology is described in Sec. II. The results obtained for unsubstituted and alkoxy- or alkylthio-substituted triphenylenes are discussed in Sec. III. The conclusions are presented in Sec. IV.

II. THEORETICAL METHODOLOGY

An excess charge carrier in a molecular system can be described by the tight-binding Hamiltonian³⁹

$$H = \sum_{n,k} \varepsilon_n^k(R(t)) a_{n,k}^+ a_{n,k} + \sum_{\substack{n,k,n',k' \\ n \neq n'}} J_{n,n'}^{k,k'}(R(t)) a_{n,k}^+ a_{n',k'} \quad (1)$$

In Eq. (1) $a_{n,k}^+$ and $a_{n,k}$ are the creation and annihilation operators of a charge at the n th molecule in molecular orbital k , $\varepsilon_n^k(R(t))$ is the site energy of the charge and $J_{n,n'}^{k,k'}(R(t))$ is the charge transfer integral involving orbitals k and k' on the molecules n and n' . Both the site energies and the charge transfer integrals depend on the intramolecular and intermolecular geometric degrees of freedom, which may fluctuate in time and are collectively denoted as $R(t)$. Hence, polaronic effects due to possible coupling of an excess charge carrier to the nuclear degrees of freedom are included in the Hamiltonian in Eq. (1). For a complete description of the dynamics of a charge carrier the kinetic energy due to nuclear motions must be added to Eq. (1), as has been done in a previous study on charge transport in DNA.³⁵ Usually the wave function of an excess positive charge can be written as a linear superposition of the HOMOs of the individual molecules.

A triphenylene molecule belongs to the D_{3h} point group. The highest occupied π -orbitals, φ , are twofold degenerate and belong to the irreducible representation (irrep) E'' .⁴⁰ A columnar stack of triphenylene molecules with the molecular planes perpendicular to the stacking axis and the centers of mass on this axis has C_3 symmetry for any twist angle between the molecules (except zero degrees). Consequently, a HOMO belonging to the E'' irrep on one molecule will have nonzero electronic coupling with both HOMOs on an adjacent molecule. However, if symmetry adapted linear combinations (SALCs) of the HOMOs on the individual molecules are made, such that they belong to the irrep E of the C_3 symmetry group, each orbital on a particular molecule couples only with one orbital on an adjacent molecule.

Therefore, it is convenient to transform the HOMOs to the SALCs belonging to irrep E of the C_3 symmetry group. For the n th molecule the SALCs are given by

$$\psi_n^E = \frac{1}{\sqrt{2}} (\varphi_n^1 + i\varphi_n^2), \quad (2a)$$

$$\psi_n^{E*} = \frac{1}{\sqrt{2}} (\varphi_n^1 - i\varphi_n^2). \quad (2b)$$

In Eq. (2) the degenerate HOMOs φ_n^1 and φ_n^2 belong to the E'' irrep of the D_{3h} symmetry group. In case the C_3 symmetry is broken, e.g., by a lateral slide of a molecule in a direction perpendicular to the columnar axis, each orbital in Eq. (2) will have a nonzero charge transfer integral with both HOMOs on an adjacent molecule.

In what follows the SALCs for C_3 symmetry as defined in Eq. (2) will be used to compute the site energies, charge transfer integrals and spatial overlap matrix elements on adjacent molecules. For the orbitals in Eq. (2) the site energy of the n th molecule is given by

$$\begin{aligned} \varepsilon_n &= \langle \psi_n^E | h_{\text{KS}} | \psi_n^E \rangle = \langle \psi_n^{E*} | h_{\text{KS}} | \psi_n^{E*} \rangle \\ &= \frac{1}{2} \{ \langle \varphi_n^1 | h_{\text{KS}} | \varphi_n^1 \rangle + \langle \varphi_n^2 | h_{\text{KS}} | \varphi_n^2 \rangle \}. \end{aligned} \quad (3)$$

In Eq. (3) h_{KS} is the Kohn–Sham Hamiltonian of the system considered, which may consist of two or more triphenylene molecules. The charge transfer integrals involving orbitals on neighboring molecules are given by

$$\begin{aligned} J_{n,n\pm 1}^{E,E} &= \langle \psi_n^E | h_{\text{KS}} | \psi_{n\pm 1}^E \rangle \\ &= \frac{1}{2} \{ \langle \varphi_n^1 | h_{\text{KS}} | \varphi_{n\pm 1}^1 \rangle + \langle \varphi_n^2 | h_{\text{KS}} | \varphi_{n\pm 1}^2 \rangle \\ &\quad + i \langle \varphi_n^1 | h_{\text{KS}} | \varphi_{n\pm 1}^2 \rangle \\ &\quad - i \langle \varphi_n^2 | h_{\text{KS}} | \varphi_{n\pm 1}^1 \rangle \} \\ &= (J_{n,n\pm 1}^{E*,E*})^*, \end{aligned} \quad (4a)$$

$$\begin{aligned} J_{n,n\pm 1}^{E,E*} &= \langle \psi_n^E | h_{\text{KS}} | \psi_{n\pm 1}^{E*} \rangle \\ &= \frac{1}{2} \{ \langle \varphi_n^1 | h_{\text{KS}} | \varphi_{n\pm 1}^1 \rangle - \langle \varphi_n^2 | h_{\text{KS}} | \varphi_{n\pm 1}^2 \rangle \\ &\quad - i \langle \varphi_n^1 | h_{\text{KS}} | \varphi_{n\pm 1}^2 \rangle - i \langle \varphi_n^2 | h_{\text{KS}} | \varphi_{n\pm 1}^1 \rangle \}. \end{aligned} \quad (4b)$$

When the system has C_3 symmetry

$$\langle \varphi_n^1 | h_{\text{KS}} | \varphi_{n\pm 1}^1 \rangle = \langle \varphi_n^2 | h_{\text{KS}} | \varphi_{n\pm 1}^2 \rangle \quad (5a)$$

and

$$\langle \varphi_n^1 | h_{\text{KS}} | \varphi_{n\pm 1}^2 \rangle = - \langle \varphi_n^2 | h_{\text{KS}} | \varphi_{n\pm 1}^1 \rangle. \quad (5b)$$

The charge transfer integral in Eq. (4a) involves the coupling of one of the SALCs in Eq. (2) with the corresponding SALC on an adjacent molecule. The charge transfer integral in Eq. (4b) refers to the cross coupling of the SALC in Eq. (2a) on one molecule with the SALC in Eq. (2b) on the other molecule. Combination of Eqs. (4) and (5) immediately shows that the matrix element in Eq. (4b) is zero when the system has C_3 symmetry. In the case of a lateral slide of a molecule the C_3 symmetry is broken and consequently the charge transfer integrals in Eqs. (4a) and (4b) are both non-

zero. In this situation the four HOMOs in a triphenylene dimer will interact. The mixing of the HOMOs is then fully described by the two transfer integrals in Eq. (4). The spatial overlap integrals are obtained analogous to Eq. (4) by replacing the Kohn–Sham Hamiltonian, h_{KS} , by the identity operator.

The molecular orbitals, φ_n^i , of an individual triphenylene molecule were obtained from density functional theory (DFT) calculations using the ADF program³⁷ with a basis set consisting of atomic orbitals. The matrix elements in Eqs. (3) and (4) were obtained by using the unique feature of the ADF program that allows one to use the molecular orbitals, φ_n^i (fragment orbitals), as a basis set in a subsequent calculation on a system of two or more triphenylene molecules. The standard output of the ADF program then provides the overlap matrix, \mathbf{S} , the eigenvector matrix, \mathbf{C} , and the diagonal eigenvalue matrix, \mathbf{E} . Note, that the overlap and eigenvector matrix are defined in terms of the molecular orbitals on the individual triphenylene molecules and not the atomic orbitals. The matrix elements of the Kohn–Sham Hamiltonian $\langle \varphi_n^i | h_{\text{KS}} | \varphi_{n'}^j \rangle$, can be readily obtained from \mathbf{S} , \mathbf{C} , and \mathbf{E} , since $\mathbf{h}_{\text{KS}}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}$, and consequently $\mathbf{h}_{\text{KS}} = \mathbf{S}\mathbf{C}\mathbf{E}\mathbf{C}^{-1}$. The matrix elements $\langle \varphi_n^i | h_{\text{KS}} | \varphi_{n'}^j \rangle$ were used to evaluate the site energies and charge transfer integrals involving the SALCs as defined in Eqs. (3) and (4). This procedure provides a direct and exact calculation of site energies and charge transfer integrals. It does not rely on the assumption of zero spatial overlap, which is made in the orbital splitting or Mulliken and Hush treatment to evaluate charge transfer integrals.^{36,41} In addition the present procedure is also applicable in cases where an orbital on one molecule couples with two or more orbitals on another molecule.

It should be noted that the site energies and charge transfer integrals to be discussed below refer to the HOMOs on the triphenylene molecules. Hence, in a calculation of the properties and dynamics of an excess positive charge based on the Hamiltonian in Eq. (1), the sign of these parameters must be reversed.

III. RESULTS AND DISCUSSION

The charge transfer integrals, spatial overlap integrals and site energies were computed for different twist angles, intermolecular distances and magnitudes of a lateral slide of one of the molecules in a dimer system of two stacked triphenylene molecules. The results are collected in Tables I and II. In Sec. III A computational and methodological aspects are discussed on basis of the results for unsubstituted triphenylene molecules. In Sec. III B the results for alkoxy- and alkylthio-substituted triphenylenes are discussed and related to experimental charge carrier mobility values.

A. Unsubstituted triphenylene

In the calculations the geometry of an individual triphenylene molecule was optimized without any constraint. This geometry was used in calculations on stacks consisting of two (or more) molecules to obtain the charge transfer and spatial overlap integrals and the site energies. The results reported below were obtained with an atomic basis set of

TABLE I. Charge transfer integrals (J) and spatial overlap integrals (S) for the triphenylene derivatives investigated. The ratio of the imaginary and real part of J and S are also given. Upper part, dependence on the twist angle, α , at a stacking distance of 3.5 Å. Second part, dependence on stacking distance, ΔZ , for a twist angle of 45°. Third part, effect of lateral slide distance, ΔX , on $J^{E,E}$ defined in Eq. (4a) (first row at each distance in the table) and cross coupling, J^{E,E^*} , defined in Eq. (4b) (second row at each distance in the table).

	R=H				R=OCH ₃				R=SCH ₃			
	J	S	$\frac{\text{Im}(J)}{\text{Re}(J)}$	$\frac{\text{Im}(S)}{\text{Re}(S)}$	J	S	$\frac{\text{Im}(J)}{\text{Re}(J)}$	$\frac{\text{Im}(S)}{\text{Re}(S)}$	J	S	$\frac{\text{Im}(J)}{\text{Re}(J)}$	$\frac{\text{Im}(S)}{\text{Re}(S)}$
α												
0°	0.64	0.062	0	0	0.47	0.049	0	0	0.73	0.074	0	0
15°	0.55	0.053	-0.35	-0.35	0.37	0.039	-0.37	-0.37	0.43	0.041	0.36	0.35
30°	0.33	0.032	-0.83	-0.81	0.30	0.031	-0.90	-0.95	0.31	0.032	1.61	1.47
45°	0.12	0.012	-1.87	-1.78	0.22	0.024	0.20	0.17	0.12	0.012	1.61	1.54
60°	0.03	0.003	-1.72	-1.72	0.16	0.018	-1.74	-1.74	0.11	0.011	1.33	1.34
ΔZ (Å)												
3.0	0.20	0.018	-2.08	-2.00	0.41	0.039	-1.56	-1.46	0.28	0.024	1.62	1.56
3.2	0.16	0.016	-1.99	-1.91	0.32	0.032	-1.82	-1.43	0.20	0.019	1.62	1.55
3.4	0.13	0.013	-1.91	-1.82	0.25	0.026	-1.49	-1.40	0.15	0.014	1.61	1.54
3.5	0.12	0.012	-1.87	-1.78	0.22	0.024	0.20	0.17	0.12	0.012	1.61	1.54
3.6	0.11	0.011	-1.84	-1.88	0.19	0.021	-1.46	-1.37	0.10	0.010	1.61	1.53
3.8	0.08	0.008	-1.77	-1.68	0.15	0.017	-1.43	-1.34	0.07	0.007	1.60	1.51
4.0	0.06	0.007	-1.71	-1.62	0.12	0.014	-1.40	-1.31	0.05	0.005	1.59	1.49
ΔX (Å)												
0.0	0.12	0.012	-1.87	-1.78	0.22	0.024	0.20	0.17	0.12	0.012	1.61	1.51
	0	0			0	0			0	0		
1.0	0.06	0.007	-2.38	-2.11	0.13	0.014	-1.35	-1.27	0.06	0.006	1.48	1.37
	0.16	0.015	-2.58	-2.59	0.07	0.007	-1.21	-1.10	0.08	0.008	-0.16	-0.11
2.0	0.12	0.011	-0.85	-0.84	0.03	0.002	-2.43	-3.52	0.03	0.003	-1.67	-1.74
	0.10	0.010	-2.30	-2.33	0.07	0.008	0.45	0.45	0.08	0.008	0.76	0.80
3.0	0.23	0.021	-0.94	-0.95	0.08	0.008	-1.53	-1.52	0.05	0.006	-1.66	-1.57
	0.05	0.005	1.88	1.96	0.12	0.012	10.09	6.91	0.11	0.001	-12.20	-38.76
4.0	0.09	0.010	-0.91	0.92	0.02	0.002	-20.48	-42.02	0.06	0.006	-0.75	-0.69
	0.09	0.010	1.37	1.46	0.10	0.011	-1.87	-2.07	0.11	0.011	-4.31	-5.35
5.0	0.10	0.009	-1.01	-1.00	0.03	0.004	-0.03	-0.58	0.02	0.002	-0.07	-0.05
	0.07	0.006	0.19	0.27	0.04	0.005	-0.04	-0.26	0.05	0.005	22.31	7.43
6.0	0.14	0.013	-0.97	-0.96	0.04	0.003	0.82	0.72	0.07	0.007	-1.59	-1.90
	0.02	0.002	-2.87	-2.13	0.02	0.002	-0.50	-0.45	0.02	0.003	0.03	0.10
7.0	0.06	0.006	-0.92	0.92	0.03	0.003	-0.20	-0.29	0.11	0.018	-1.64	-1.79
	0.06	0.006	-0.05	-0.07	0.01	0.002	0.77	0.64	0.02	0.003	0.51	-0.34
8.0	0.01	0.001	-1.15	-1.20	0.02	0.002	-9.99	-6.01	0.07	0.007	-2.11	-2.37
	0.08	0.007	-0.34	-0.35	0.02	0.003	0.57	0.51	0.01	0.001	-6.20	-3.43
9.0	0.03	0.003	-1.00	-1.00	0.02	0.002	1.42	1.44	0.02	0.002	6.81	6.33
	0.05	0.005	-0.47	-0.47	0.02	0.002	0.66	0.62	0.02	0.002	1.07	1.09
10.0	0.01	0.001	-0.97	-0.96	0.01	0.001	-0.17	-0.12	0.02	0.002	0.22	0.39
	0.02	0.002	-0.54	-0.54	0.00	0.000	-0.97	-1.32	0.02	0.003	0.74	0.74
11.0	0.01	0.001	-0.94	-0.94	0.01	0.001	-2.37	-2.05	0.01	0.002	0.09	0.18
	0.01	0.001	-0.58	-0.58	0.01	0.001	0.12	0.10	0.02	0.002	0.61	0.64

Slater-type orbitals (STOs) of triple- ζ quality including two sets of polarization functions on each atom (TZ2P basis set in ADF).⁴² Using a triple- ζ STO basis set with only one set of polarization functions on each atom (TZP basis set in ADF) gave similar results, while a smaller basis set of double- ζ quality with only one set of polarization functions on each atom (DZP basis set in ADF) gave charge transfer integrals that were ca. 10% smaller than those obtained with the TZ2P basis set. All calculations are performed using the generalized gradient approximation (GGA) of density functional theory (DFT). This proceeds from the local density approximation (LDA) for the exchange and correlation functional based on the parametrization of the electron gas data given by Vosko, Wilk, and Nusair (VWN).⁴³ The gradient corrections of Becke⁴⁴ (for exchange) were used together

with the correlation part of the Perdew and Wang 91 (PW91) functional.⁴⁵ Using other exchange/correlation functionals gave charge transfer integrals that differ by less than a few percent from the values obtained with the Becke/PW91 functional. The absolute values of the site energies were found to vary by 0.1–0.2 eV for different exchange correlation functionals. In particular, it is pointed out that good agreement was obtained between the present PW91 values for the charge transfer integrals and values obtained with the more recently developed asymptotically corrected SAOP (statistical average of orbital potentials), which has been shown to achieve good agreement between its outer valence Kohn–Sham orbital energies and the corresponding vertical ionization energies (VIE) of various types of molecules.⁴⁶ Furthermore, it is noted that the variation of the site energies with

TABLE II. Site energies for the triphenylene derivatives investigated. Upper part, dependence on the twist angle, α , at a stacking distance of 3.5 Å. Second part, dependence on stacking distance, ΔZ , for a twist angle of 45°. Third part, effect of lateral slide distance, ΔX , at stacking distance 3.5 Å and twist angle 45°.

	Site energies ε (eV)		
	R=H	R=OCH ₃	R=SCH ₃
α			
0°	-5.21	-4.22	-4.46
15°	-5.22	-4.23	-4.49
30°	-5.24	-4.26	-4.54
45°	-5.26	-4.30	-4.60
60°	-5.27	-4.32	-4.65
ΔZ (Å)			
3.0	-5.33	-4.40	-4.75
3.2	-5.29	-4.34	-4.67
3.4	-5.27	-4.31	-4.62
3.5	-5.26	-4.30	-4.60
3.6	-5.26	-4.29	-4.59
3.8	-5.26	-4.28	-4.57
4.0	-5.26	-4.28	-4.55
ΔX (Å)			
0.0	-5.26	-4.30	-4.60
1.0	-5.27	-4.30	-4.60
2.0	-5.29	-4.31	-4.58
3.0	-5.34	-4.32	-4.57
4.0	-5.38	-4.34	-4.59
5.0	-5.42	-4.37	-4.60
6.0	-5.45	-4.41	-4.62
7.0	-5.49	-4.44	-4.64
8.0	-5.52	-4.46	-4.66
9.0	-5.54	-4.49	-4.68
10.0	-5.55	-4.50	-4.70
11.0	-5.55	-4.51	-4.71

the twist angle between two stacked triphenylene molecules was identical for the correlation functionals mentioned above. Since in charge transport calculations based on the Hamiltonian in Eq. (1) only the differences between the site energies on different molecules play a role, the results obtained with the different functionals can be considered equivalent.

In the calculations on systems consisting of two stacked triphenylene molecules the HOMO in the dimer was found to be composed of the HOMOs on the individual molecules by more than 98%. The description of a positive charge carrier in terms of the HOMOs only can thus be considered adequate. The dependence of the absolute value of the charge transfer integral in Eq. (4a) on the twist angle between two unsubstituted triphenylene molecules is presented in Fig. 3 and Table I. Note, that the current system involves no lateral slide of the molecules so that the system has C_3 symmetry and the charge transfer integral in Eq. (4b) is equal to zero. The distance between the molecules was taken equal to 3.5 Å. The periodicity in the values of the charge transfer integral reflects the C_3 symmetry of the system. The charge transfer integral varies strongly from 0.64 eV at zero twist angle to reach a minimum value of 0.03 eV at 60°. The ratio of the imaginary and the real part of the charge transfer integral in Eq. (4a), was found to change from 0 at zero twist

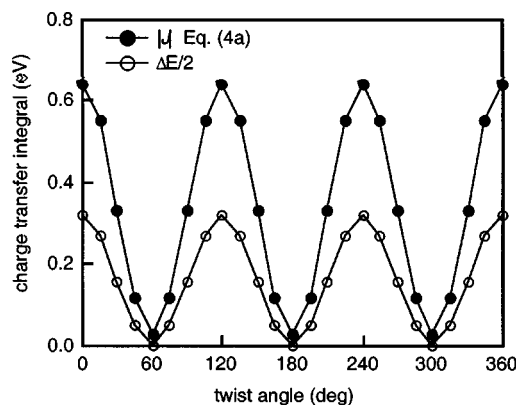


FIG. 3. Variation of the charge transfer integral defined [Eq. (4a)] with the twist angle for unsubstituted triphenylene molecules at 3.5 Å (filled circles) and half of the energetic splitting between the HOMO and HOMO-1 (open circles).

angle to -1.7 for a twist angle of 60°. The magnitude of the imaginary part is determined by the cross coupling between different orbitals with D_{3h} symmetry, see Eqs. (4b) and (5b). This coupling increases with the twist angle since a nonzero twist implies a deviation from D_{3h} symmetry. The spatial overlap was found to vary from 0.062 at zero twist angle to 0.003 at 60°, analogous to the variation of the charge transfer integral. The nearest-neighbor charge transfer integrals computed for a stack of three triphenylene molecules with a mutual twist angle of 45° were identical to those for the dimer system. The charge transfer integrals are thus fully determined by nearest-neighbor interactions. The charge transfer integral involving the next to nearest-neighbor coupling between two triphenylene molecules at a distance of 7 Å was found to be more than an order of magnitude smaller than those for adjacent molecules. Hence, a description of charge transport in terms of next-neighbor electronic couplings only, can be considered adequate.

It is of interest to compare the calculated charge transfer integrals with half of the energetic splitting between the HOMO and HOMO-1 levels. The latter value is often used as an estimation of the charge transfer integral. The charge transfer integral obtained from half the value of the energetic difference between the HOMO and HOMO-1 in a triphenylene dimer is also plotted in Fig. 3 as a function of the twist angle. The charge transfer integrals estimated in this way are significantly smaller than the exact values in Fig. 3. The difference is due to the nonzero spatial overlap integral, S , between the HOMOs on the two triphenylene molecules. The energetic splitting between the HOMO and HOMO-1 can be calculated from the 2×2 secular determinant, which gives

$$\Delta E = \frac{\sqrt{(2 \operatorname{Re}(JS^*) - (\varepsilon_1 + \varepsilon_2))^2 + 4(|J|^2 - \varepsilon_1 \varepsilon_2)(1 - |S|^2)}}{1 - |S|^2} \quad (6a)$$

which for $S=0$ and $\varepsilon_1 = \varepsilon_2$ reduces to

$$\Delta E = 2|J|. \quad (6b)$$

Using the values of J and S together with the site energies obtained from the DFT calculations the energetic splitting

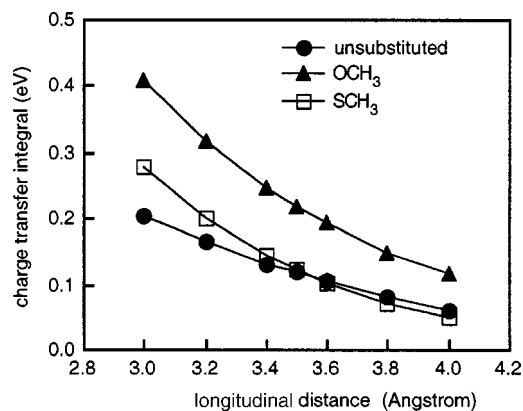


FIG. 4. Distance dependence of the charge transfer integrals in triphenylene derivatives for a twist angle of 45° .

calculated from Eq. (6a) is indeed very close to the difference between the energies of the HOMO and the HOMO-1 in a system consisting of two triphenylene molecules, as expected. Even though in the present case the spatial overlap amounts to $S=0.062$ or less, the use of Eq. (6b) gives inaccurate results for the charge transfer integrals. The reason stems from neglecting the additional terms in Eq. (6a). In case that J and S are real numbers and assuming $1 - S^2 \approx 1$ it can be found from Eq. (6a) that

$$J \approx \frac{1}{2}S(\epsilon_1 + \epsilon_2) + \frac{1}{2}\Delta E. \quad (7)$$

The difference between the value of J and half of the energetic splitting ΔE is thus due to the first term in Eq. (7). The energetic splitting gives an approximation to the generalized charge transfer integral³⁶ $J' = J - \frac{1}{2}S(\epsilon_1 + \epsilon_2) \approx \frac{1}{2}\Delta E$. When the spatial overlap, S , is not taken into account in charge transport calculations based on the Hamiltonian in Eq. (1) the generalized charge transfer integral values may provide a good approximation. However, when the orbitals on a particular molecule in the system couple with more than one other orbital on an adjacent molecule this is no longer appropriate. As discussed above this situation is encountered in stacked triphenylene molecules. For these systems the values of J together with the spatial overlap, S , and the site energies from the present calculations can be used for charge transport calculations.

The dependence of the charge transfer integral on the distance between two triphenylene molecules is shown in Fig. 4 for a twist angle equal to 45° . The charge transfer integral decreases (close to) exponentially with the distance between the molecules; i.e., $J = J(\Delta Z=0)\exp(-\beta\Delta Z)$ with the falloff parameter $\beta = 1.9 \text{ \AA}^{-1}$.

The site energies, as defined by Eq. (3), are given in Table II for different twist angles and longitudinal and lateral displacements between two triphenylene molecules in a dimer system. Increasing the stacking distance, ΔZ , from 3 to 4 Å results in a change of the site energy from -5.33 to -5.26 eV. When increasing the distance further the site energy becomes equal to the HOMO energy of an individual triphenylene molecule, which was found to be -5.53 eV. Hence, the variation of the site energy with the stacking distance exhibits a maximum between short and long stacking

distances. For two molecules at a distance of 3.5 Å and a twist angle of 45° the site energy is -5.26 eV, see Table II. Adding a third triphenylene molecule at a distance of 7 Å from the first molecule increased the site energy on the first molecule further to -5.13 eV. The latter effect on the site energy was also found for two molecules at a distance of 7 Å. Hence, the effect of different molecules on the site energy of a particular molecule is (close to) additive. The site energies are also affected by non-nearest neighbor interactions and consequently the variations of the site energies in Table II with the mutual configuration of the molecules are lower limits to the fluctuations in longer stacks. It was found that the effect of neighboring molecules on the site energy of a particular molecule is mainly due to the Coulomb interaction with the atomic charges on the neighboring molecules, which were calculated by the Voronoi deformation density (VDD) method.^{47,48} Even at a distance of 7 Å the Coulomb energy calculated in this way was found to be approximately 0.1 eV.

Note, that the absolute value of 5.53 eV for the energy of the HOMO of an individual triphenylene molecule differs significantly from the vertical ionization energy, which is 7.9 eV.⁴⁹ This is due, amongst others, to the incorrect (i.e., too fast decaying) asymptotic behavior of the approximate GGA exchange-correlation potentials that cause an upshift of all eigenvalues (i.e., orbital energies) with respect to the exact Kohn-Sham results.⁵⁰ This is in line with the general observation that orbital energies obtained with GGA and hybrid potentials differ from the ionization energies by a close to constant amount for a given molecule.⁵¹ Therefore it is reasonable to assume that the variation of the site energies with the geometrical configuration of the system is accurate. The differences between the values in Table II thus provide a good approximation to the site energy fluctuations as a function of twisting angle and longitudinal or lateral displacements of the triphenylene molecules in a columnar stack.

B. Alkoxy- and alkylthio-substituted triphenylene

The optimized geometry of an individual molecule was found to be such that the substituents on the same phenyl ring are facing away from each other with the carbon atoms in the same plane as the triphenylene core. Figure 4 shows the effect of substituents on the magnitude of the charge transfer integral in Eq. (4a) as a function of distance between two triphenylene molecules with a mutual twist angle of 45° . The distance dependence is stronger when substituents are present. The fall-off parameters are 1.9, 2.3, and 2.1 \AA^{-1} for unsubstituted, methoxy-, and methylthio-substituted triphenylene, respectively. The electronic coupling is largest in methoxy-substituted triphenylene.

The variation of the magnitude of the charge transfer integrals for methoxy- and methylthio-substituted triphenylene with the twist angle is shown in Fig. 5. Comparison of the data for methoxy-substituted triphenylene with those for unsubstituted triphenylene in Fig. 3 shows that the introduction of methoxy-substituents leads to a smaller variation of the charge transfer integral with the twist angle. At zero degrees the charge transfer integral is smaller when methoxy groups are present, while it is larger near 60° . In the case of

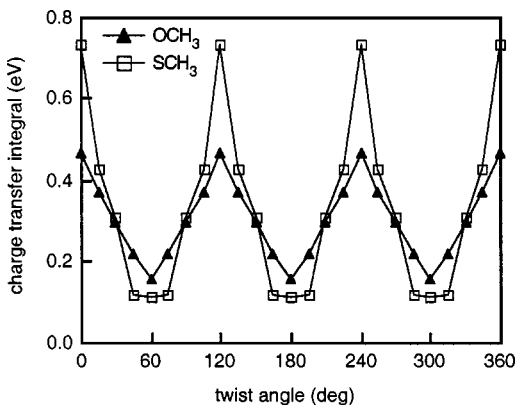


FIG. 5. Variation of the charge transfer integral [Eq. (4a)] with the twist angle for methoxy- and methylthio-substituted triphenylenes with a stacking distance of 3.5 Å.

methylthio-substituents the charge transfer integral has a larger value at zero twist angle, while near 60° it attains a value intermediate between that for the unsubstituted and methoxy-substituted triphenylenes.

The charge transfer integrals for methoxy-substituted triphenylene molecules obtained from the present work are approximately a factor of 5 larger than the values reported in Ref. 34, which were obtained from the valence effective Hamiltonian (VEH) method. The difference is most likely due to the lower level of theory used in Ref. 34. The charge transfer integrals calculated for methylthio-substituted triphenylene from the present work are approximately a factor of 2 larger than those reported in Ref. 33, which were estimated as half the energetic splitting between the HOMO and HOMO-1 in a dimer, calculated at the intermediate neglect of differential overlap (INDO) level of theory. The difference is not surprising, since as is shown by the data in Fig. 3, the estimation of transfer integrals from the energetic splitting gives lower values than the direct calculations.

Figure 6 shows the charge transfer integrals as a function of the lateral slide distance (see Fig. 2) for methoxy- and methylthio-substituted triphenylene. The twist angle was taken equal to 45° and one molecule was displaced in the lateral direction along the C_2 axis of the molecule. Similar results were obtained for a twist angle of 60°. For zero lateral slide distance the charge transfer integral involving different C_3 SALCs on the two molecules, J^{E,E^*} in Eq. (4b), is equal to zero, since in this case the system has C_3 symmetry. As the slide distance increases the charge transfer integral $J^{E,E}$ first decreases, then exhibits local maxima and tends to zero at distances exceeding 8 Å. The charge transfer integral involving different C_3 SALCs on the two molecules, J^{E,E^*} , first increases and then decreases. From the results in Fig. 6 it can be concluded that lateral displacements of ~ 8 Å or more will have a large negative effect on the mobility of charge carriers. The data in Table II shows that lateral displacements affect the site energies most for unsubstituted triphenylene, while the effects are minimum for methylthio-substituted triphenylene.

In triphenylenes fluctuations of the twist angles and intermolecular distance of the order of 50° and 1 Å have been

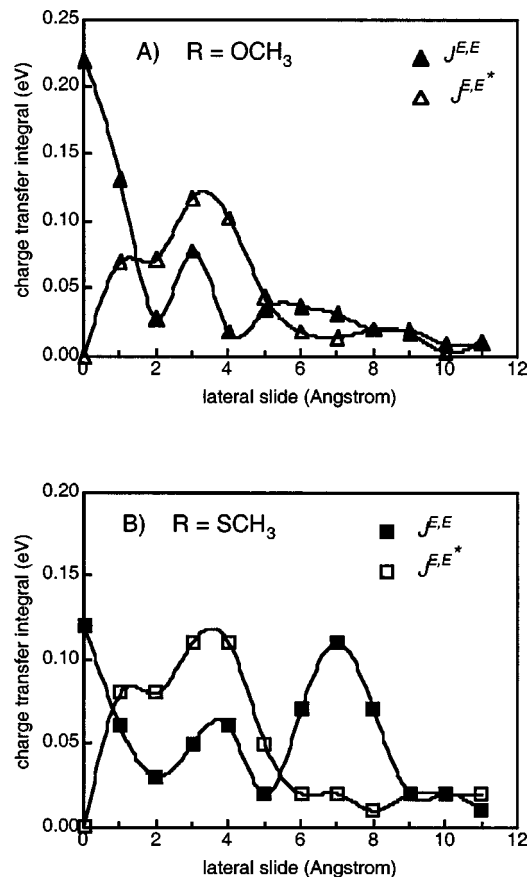


FIG. 6. Dependence of the charge transfer integrals on the lateral slide distance for triphenylene molecules with methoxy- (panel A) or methylthio-substituents (panel B) with a stacking distance of 3.5 Å and a twist angle of 45°.

estimated.³⁴ The data discussed above shows that such fluctuations can lead to variations of the charge transfer integrals and site energies of the order of a few tenths of an eV, see Tables I and II. Site energy fluctuations with a magnitude comparable to or larger than the charge transfer integral will be detrimental to charge transport. In addition the occurrence of large lateral displacements causes the charge transfer integral to become small and will have a strong negative effect on the charge carrier mobility. Improvement of the structural order in triphenylenes is thus expected to have a large positive effect on the charge carrier mobility. In particular a reduction of the average twist from 45° to values near zero degrees, e.g., by using different substituents, will enhance the mobility significantly.

The charge transfer integrals and site energy fluctuations calculated for methoxy- and methylthio-substituted triphenylenes are not very different. This is in agreement with the similar charge carrier mobilities of 0.002 and 0.008 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, as obtained from PR-TRMC measurements on hexyloxy- and hexylthio-substituted triphenylenes, respectively, in the liquid-crystalline D_h phase.¹⁶ In the microwave conductivity measurements charge transport within relatively ordered microdomains is probed, since the charge carriers can follow the oscillating electric field by moving between barriers for charge transport.¹⁸ In contrast, in TOF measurements charge carriers need to traverse the inter-

electrode distance of the order of several μm and the probability that a charge carrier encounters a large structural fluctuation becomes more likely. For instance a large lateral slide of a molecule leads to a relatively small charge transfer integral and consequently a low mobility. The lower mobility values of the order of $0.001 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or less,¹² as found from TOF measurements on alkoxy-substituted triphenylenes, are most likely due to such effects.

The mobility of charge carriers measured for alkylthio-substituted triphenylene in the crystalline *K* phase is about an order of magnitude or more higher than in the liquid crystalline *D_h* phase, depending on the length of the alkylthio-substituent.^{15,25} In the *K* phase the triphenylene cores are tilted by 22° with respect to the columnar axis and the intracolumnar distance between adjacent molecules is 3.45 \AA , which is smaller than the cofacial distance of 3.64 \AA in the liquid crystalline *D_h* phase.²⁷ Using the coordinates of the atoms in the crystalline *K* phase of hexa(hexylthio)triphenylene (HHTT), as obtained from x-ray diffraction,^{27,52} the charge transfer integral was calculated to be 0.19 eV . This value is close to a factor of 2 higher than the charge transfer integral calculated for methylthio-substituted triphenylenes in the equilibrium conformation of the liquid crystalline phase (i.e., a stacking distance of 3.64 \AA and a twist angle of 45°), see Table I. In the presence of dynamic and/or static structural fluctuations the mobility scales approximately with the square of the charge transfer integral.^{20,34} On basis of the calculated charge transfer integrals the mobility of charge carriers in the *K* phase would be approximately a factor of 4 higher than in the liquid crystalline phase. The significantly higher mobility ratio observed experimentally must be due to the fact that the larger structural order in the *K* phase reduces the fluctuations of the site energies, which further enhances the mobility. Interestingly HHTT also exhibits a more ordered liquid crystalline mesophase, in between the *K* phase and the *D_h* phase. In this so-called *H* phase the equilibrium stacking distance and twist angle are similar to the *D_h* phase, while structural fluctuations are less pronounced.²⁷ The mobility in the *K* phase has been found to be a factor three higher than in the *H* phase.¹⁵ This is close to the ratio of the square of the charge transfer integrals computed for the equilibrium conformations of triphenylene molecules in the *K* phase and the liquid crystalline phase.

On basis of the results discussed above a qualitative explanation of the mobilities of charge carriers in different phases of triphenylene derivatives could be provided. A quantitative treatment requires a theoretical model in which the effects of dynamic and static structural fluctuations on the charge transfer integrals and site energies are brought into account in more detail. Information about the structural fluctuations can be obtained from experimental studies and/or molecular modeling. With this information the theoretical model in Ref. 35, which has been applied to describe charge transport through DNA, can serve as an appropriate starting point for the modeling of charge transport in triphenylene derivatives. This will be the subject of a future study.

IV. CONCLUSIONS

The unique feature of the Amsterdam density functional (ADF) theory program to use molecular orbitals as basis functions in electronic structure calculations, was exploited to calculate charge transfer integrals, spatial overlap integrals and site energies involved in hole transport in columnar stacked triphenylene derivatives. These parameters were obtained directly as the matrix elements of the Kohn–Sham Hamiltonian. The charge transfer integrals obtained in this way were found to differ significantly from values estimated from the energetic splitting between the HOMO and HOMO-1 in a dimer. The difference is attributed to the non-zero spatial overlap between the molecular orbitals on adjacent molecules.

Calculations were performed on unsubstituted and methoxy- or methylthio-substituted triphenylenes. The charge transfer integrals were found to vary strongly with the mutual twist angle between adjacent molecules, with the maximum value near 0.5 eV for zero twist and the minimum value of the order of 0.1 eV at a twist angle of 60° . The charge transfer integrals decrease with the distance between the stacked molecules. A lateral slide of one of the molecules causes the charge transfer integrals to first decrease, then to exhibit local maxima and to tend to zero for slide distances above approximately 8 \AA . The variation of the spatial overlap integrals with the mutual conformation of the molecules exhibits a trend similar to that of the charge transfer integrals. The conformational degrees of freedom affect the site energies by an amount of the order of 0.1 eV . These fluctuations are comparable to the magnitude of the charge transfer integrals near the equilibrium conformation of adjacent molecules in a columnar stack and will thus have a significant negative effect on the mobility of charge carriers.

The calculated results provide a qualitative explanation of the similarities and differences between the experimental charge carrier mobilities in different phases of alkoxy- and alkylthio-substituted triphenylenes. The data obtained from the present work can be used in quantitative calculations of charge transport in triphenylene derivatives.

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