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A R T I C L E S

Charge Transport Properties in Discotic Liquid Crystals: A Quantum-Chemical Insight into Structure−Property Relationships

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Abstract: We describe at the quantum-chemical level the main parameters that control charge transport at the molecular scale in discotic liquid crystals. The focus is on stacks made of triphenylene, hexaazatriphenylene, hexaazatrinaphthylene, and hexabenzocoronene molecules and derivatives thereof. It is found that a subtle interplay between the chemical structure of the molecules and their relative positions within the stacks determines the charge transport properties; the molecular features required to promote high charge mobilities in discotic materials are established on the basis of the calculated structure−property relationships. We predict a significant increase in the charge mobility when going from triphenylene to hexaazatrinaphthylene; this finding has been confirmed by measurements carried out with the pulse-radiolysis time-resolved microwave conductivity technique.

1. Introduction

Since the discovery of the first discotic mesogen some 25 years ago,[1] most efforts aimed at understanding the nature of the molecular parameters that favor the formation of such mesophases and control their transition temperatures.[2] It is now well established that molecules forming discotic mesophases are typically made of a central discotic conjugated core substituted by 3−12 saturated chains. The liquid crystallinity results from the microsegregation of the two constituents: the crystalline character is promoted by the interaction between the conjugated cores while the liquid character originates from the melting of the saturated alkyl chains in the mesophase. Discotic molecules organize spontaneously under the form of one-dimensional columns, which can be oriented easily[3] and possess self-healing properties, i.e., the capacity of repairing structural defects in contrast to crystalline materials. The search for such

mesophases is, however, mostly ruled by empirism since subtle changes in the number, size, and nature of the lateral chains can lead to unpredictable evolutions of the thermotropic properties.

More recently, discotic materials have started to be exploited in optoelectronic devices due to their attractive electronic properties, in particular their remarkable charge transport properties; these result from the very efficient drift of charge carriers along the stacking axes of the highly organized columns. Mobility values as high as 0.5 cm^2/(V.s) have been measured by the PR-TRMC (pulse-radiolysis time-resolved microwave conductivity) technique for a liquid crystalline derivative of hexabenzocoronene;[4] this represents an improvement by almost 3−4 orders of magnitude with the respect to the mobility values typically measured in thin films of conjugated materials. This has stimulated the fabrication of organic solar cells mixing liquid crystalline HBC discs and perylene molecules, for which a high power efficiency close to 2% has been reported.[5] The deposition of HBC molecules in the channel of organic transistors coated with alignment layers[6] has been

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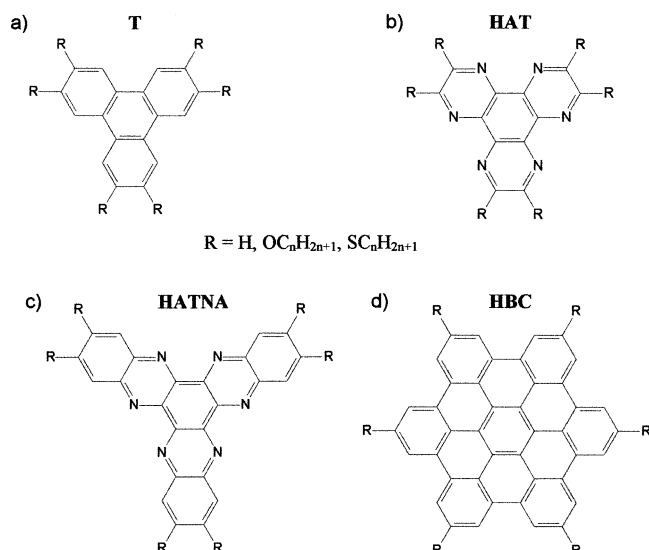

Figure 1. Chemical structure of (a) triphenylene, T, (b) hexaazatriphenylene, HAT, (c) hexaazatrinaphthylene, HATNA, and (d) hexabenzocoronene, HBC. In this work, the discs are unsubstituted (R = H) or substituted by alkylthio (R = SR) or alkoxy (R = OR) groups.

shown to generate micrometer-long columns extending from source to drain, with charge mobilities approaching 10^{-3} cm^2/(V.s) (i.e., sufficiently high to exploit such devices in active-matrix boards[7]). Discotic materials have also been incorporated into light-emitting devices to favor charge transport toward emitting centers.[8]

It is clear that the fabrication of performant optoelectronic devices based on liquid crystalline discotic materials requires a fundamental understanding of the parameters determining the charge transport processes in such mesophases. Our goal is to shed light, with the help of quantum-chemical calculations, on the nature of charge transport at the molecular scale in discotic materials and to establish structure−transport properties relationships. This approach serves to complement macroscopic models for charge transport where the details of the chemical structure of the discotic molecules are not accounted for.[9] We focus here on discotic cores based on triphenylene (T), hexaazatriphenylene (HAT), hexaazatrinaphthylene (HATNA), hexabenzocoronene (HBC), and derivatives thereof; see chemical structures in Figure 1.

The structure of this paper is as follows: We describe in the next section the formalism used to model charge transport in the discotic phases and the way the relevant molecular parameters have been calculated; the PR-TRMC technique used to measure the mobiliy values is also briefly discussed. We focus in section 3 on model systems to characterize the influence on charge transport of the nature of the conjugated core and of the relative positions of the interacting units. The actual organization of the molecules in the columns is also investigated by means of a molecular mechanics approach. The evolution predicted for charge mobility when going from T to HATNA is compared to the results of mobility measurements.
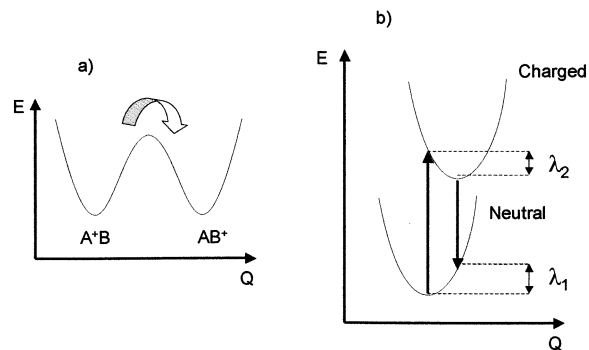
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Figure 2. Schematic representation of (a) a hole transfer from molecule A to molecule B going through a transition state, as assumed in the semiclassical model, and (b) the two energetic terms λ_1 and λ_2 defining the inner reorganization energy.

2. Methods

2.1. Theoretical Methodology. Discotic mesophases do not exhibit perfect order; as a result, charge carriers tend to localize to an extent that depends on the degree of structural disorder. Thus, a coherent bandlike description is inappropriate and a phonon-assisted hopping picture is more suitable as a starting point to describe charge transport.[10] In this case, the charge carriers are localized on single molecules and jump from disc to disc along the stacks. The frequency of charge hopping between two adjacent discs can be estimated to first approximation on the basis of semiclassical Marcus theory; for such a self-exchange electron-transfer process, it is written as[11−14]

$$k_{et} = \left(\frac{4\pi^2}{h}\right) t^2 (4\pi\lambda k_B T)^{-0.5} \exp(-\lambda/4k_B T) \quad (1)$$

Equation 1 indicates that the rate of charge hopping depends on two main parameters: the reorganization energy λ and the intermolecular transfer integral t. High transfer rates, and hence high charge mobilities, require small values for the former and large values for the latter. At this stage, it is worth stressing that a semiclassical approach implies that the system has to go through a transition state, where the two molecules adopt the same geometry, for the charge transfer to occur; see Figure 2a. More advanced vibronic theories introducing tunneling effects across the barrier have been developed, in particular by Jortner and Bixon;[12,15] as expected, such models yield faster transfer rates than the semiclassical approach but provide the same evolutions of the transfer rates when different materials are compared, which is the prime focus of this work. Thus, this justifies the use of semiclassical Marcus theory in our work to comprehend charge transport in discotic materials.

The reorganization energy λ is the sum of two energetic terms: the inner reorganization energy of the molecule (λ_i) and the reorganization energy of the surrounding medium (λ_s).[12] On one hand, λ_i reflects the geometric changes in the molecules when going from the neutral to the ionized state or vice versa; these modifications are significant as a result of the strong electron−vibration coupling characteristic of conjugated materials.[16] The λ_i reorganization energy is the sum of two relaxation energy terms, as sketched in Figure 2b:[17,18] (i) the difference between the energies of the neutral molecule in its equilibrium geometry

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and in the relaxed geometry characteristic of the ion; (ii) the difference between the energies of the radical ion in its equilibrium geometry and in the neutral geometry. The presence of alkyl chains is essential to promote a liquid crystalline character and defines the relative positions of the discs; however, in the calculations, the side chains are simply modeled by hydrogen atoms since they have little impact on the amplitude of the transfer integrals and reorganization energies. As in previous instances,[18,19] we have calculated the reorganization energies at the density functional theory (DFT) level using the UB3LYP functionals and a 6-31G(d,p) basis set[20,21] (note that similar values are obtained when introducing diffuse functions in the basis set); this choice is motivated by the very good agreement obtained in the case of anthracene, tetracene, and pentacene between the UB3LYP reorganization energies and the experimental values extracted from gas-phase ultraviolet photoelectron spectroscopy (UPS) measurements.[18,19] The D_{3h} or higher symmetry of the conjugated discs investigated here leads in most instances to double degeneracy of the frontier electronic levels; the addition or removal of one electron from such degenerate levels leads to a degenerate ionized state which renders the D_{3h} configuration of the charged system unstable. As a consequence, Jahn–Teller and/ or pseudo-Jahn–Teller distortions occur and reduce the symmetry of the system (typically to C_{2v}).[22,23] These Jahn–Teller modes significantly contribute the reorganization energy, as described in the next section.

On the other hand, λ_s describes the change in electronic polarization of the surrounding molecules as well as their possible reorientations around the charge carrier; the latter are expected to be significantly limited in the solid state in contrast to the situation in solution. Expressions have been developed to evaluate λ_s in solution[24,25] but are still lacking for processes taking place in the solid state. However, to first approximation, it can be expected that λ_s depends less on the exact chemical structure of the discs than on their actual packing density, which is similar for all the molecules under study. This is supported by experimental studies showing that the amplitude of the solid-state polarization effects, measured by UPS as the change in HOMO energy when going from the gas phase to the solid state, is very similar for a large number of conjugated molecules.[26,27]

The intermolecular transfer integral t appearing in eq 1 characterizes the strength of the electronic coupling between the molecules; the absolute values can be estimated to a good approximation as half the electronic splitting of the HOMO (LUMO) levels for holes (electrons) in a dimer made of two neutral molecules.[28,29] Unless stated otherwise, the splittings have been computed with the help of the semiempirical intermediate neglect of differential overlap (INDO) Hamiltonian, as developed by Zerner and co-workers,[30] on the basis of geometries of the conjugated cores optimized at the DFT/B3LYP level. In some selected cases, transfer integrals for holes have also been calculated at the DFT level using the Amsterdam density functional (ADF) theory program[31] and the quantitative molecular orbital (MO) model.[32] In ADF, the orbitals of a stack of discotic molecules can be expressed in terms

of symmetry-adapted molecular orbitals of the individual molecules. In dimers conserving the symmetry of the individual molecules, the charge transfer integrals and site energies are thus obtained directly as the off-diagonal and diagonal matrix elements of the Kohn–Sham Hamiltonian, respectively. The calculated transfer integrals are then corrected to account for the overlap among the molecular levels to provide effective values that are relevant for charge transport;[33] we note that such a procedure is not required for the INDO calculations since INDO treats the overlap integrals within the zero differential overlap (ZDO) approximation but takes them implicitly into account through parametrization of the one-electron integrals. These DFT calculations have been carried out at the generalized gradient approximation (GGA) level using the newly developed asymptotically corrected exchange and correlation functional SAOP (statistical average of orbital potentials)[34] and an atomic basis set of Slater-type orbitals (STOs) of triple-ζ quality including two sets of polarization functions on each atom (TZ2P basis set in ADF).[35]

The transfer integrals have been evaluated for model dimers as well as for dimers where the preferred orientation of the two discs has been assessed from molecular mechanics calculations on the basis of the PCFF (polymer consistent force field[36,37]) force field. The latter was successfully exploited in a recent work describing the solid-state packing of polyfluorene backbones substituted by saturated hydrocarbon chains.[38]

The mobility μ of the charge carriers along the stack can be expressed as[39]

$$\mu = \frac{\upsilon}{F} = \frac{\Delta x}{F \Delta t} \qquad (2)$$

with υ the net drift velocity of the charge carriers and F the amplitude of the electric field inducing the charge drift. When considering the case of an ideal discotic column where the interactions between adjacent molecules are all identical and where transport operates by successive uncorrelated jumps, Δx can be set as equal to the interdisc distance and Δt to the hopping time (i.e., the inverse hopping rate). Consideration of static and dynamic disorder along the stack is clearly of high relevance; however it is out of the scope of this paper since our primary aim is to characterize the molecular parameters of charge transport. The ratio of the charge (electron or hole) mobilities obtained for the same electric field for two different discotic stacks with the same intermolecular distance can thus be written as the ratio of the corresponding hopping rates. Assuming that λ_s is also the same for the two stacks, we can thus determine to a very good approximation the mobility ratio for two discotic materials A and B on the basis only of their transfer integrals and internal reorganization energies:

$$\frac{\mu_A}{\mu_B} = \frac{k_{etA}}{k_{etB}} \approx \frac{t_A^2}{t_B^2} \sqrt{\frac{\lambda_{iB}}{\lambda_{iA}}} \exp\left(\frac{\lambda_{iB} - \lambda_{iA}}{4 k_B T}\right) \qquad (3)$$

This equation provides for a simple and direct comparison between the theoretical transfer rates and the experimental mobility values obtained for several discotic molecules.

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Table 1. Reorganization Energies Calculated at the DFT/UB3LYP Level for Positive (P+) and Negative (P−) Polarons in the Compounds under Study

molecule	reorganization energy (eV)	
	P+	P−
T	0.18	0.26
TSH	0.16	0.24
TOH	0.33	0.40
HAT	0.30	0.27
HATSH	0.17	0.32
HATOH	0.38	0.49
HATNA	0.14	0.10
HATNASH	0.10	0.11
HATNAOH	0.22	0.20
HBC	0.10	0.14

2.2. Experimental Details. The triphenylene derivatives were provided by Prof. K. Praefcke (Berlin University of Technology) and used as received. The HATNA derivatives were recently synthesized by some of us.[40]

The charge mobilities were measured using the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique. In the PR-TRMC approach, the material of interest is ionized by a nanosecond pulse of high-energy electrons from a Van de Graaff accelerator. This results in the creation of charge carriers with a uniform and known concentration on the order of 1 ppm. If these charge carriers are mobile, there occurs an increase in the conductivity of the sample which is monitored with nanosecond time resolution as a transient decrease in the power of microwaves propagating through the irradiated medium. The mobility of the charge carriers is determined from the magnitude of the end-of-pulse conductivity. The apparatus used and the method of data analysis as applied to discotic compounds has been described in detail elsewhere.[41] The mobility determined in this way is the sum of the mobilities of the positive and negative charge carriers within organized domains of the solid materials. It is worth stressing that (i) a direct experimental determination of hole versus electron mobility is often impeded by the ease of electron trapping by oxygen or water molecules[42] and (ii) the PR-TRMC technique probes mobilities at the local scale and thus provides values that are only slightly affected by structural defects in contrast to time-of-flight (TOF) measurements; the mobility values measured in the mesophase can thus be readily compared to the theoretical data obtained for defect-free discotic stacks and accounting for geometric fluctuations (vide infra).

3. Results and Discussion

3.1. Internal Reorganization Energy. Table 1 collects the reorganization energies calculated for positive and negative polarons in triphenylene, hexaazatriphenylene, hexaazatrinaphthylene, and their thiol- and hydroxy-substituted derivatives, as well as HBC. The values vary greatly by up to a factor of 5 and range between 0.1 and 0.5 eV. The results point to a significant reduction of the reorganization energy when expanding the size of the disc, i.e., when going from T to HBC or from HAT to HATNA. The reorganization energy of the positive polaron is typically smaller than that of the negative polaron in small discs (T and HAT derivatives) while more similar values are obtained for the larger discs; the same trends have been observed when comparing oligoacenes containing from three to five rings.[18] The smaller reorganization energies obtained for positive polarons in the small discs thus favor hole migration

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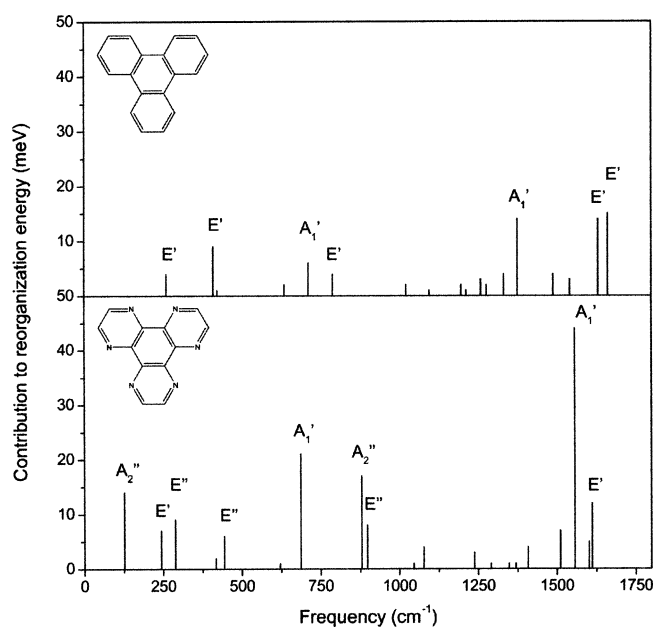(42) Würthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037.

Figure 3. Contribution of the vibrational modes of the triphenylene and hexaazatriphenylene molecules to the reorganization energy associated with the formation of a positive polaron, as calculated at the DFT/UB3LYP level.

along the columns. The introduction of six nitrogen atoms in triphenylene to yield HAT leads to a substantial increase of the reorganization energy for positive polarons while hardly affecting the value obtained for negative polarons.

To get a better insight into the nature of the reorganization processes associated with hole transport in T and HAT, we have analyzed in a detailed way the vibronic interactions in these two systems. The contribution of each vibrational mode to the relaxation energies λ_1 and λ_2 has been obtained by expanding the potential energy of the neutral and radical-cation states in a power series of the normal coordinates (Q_j). In the harmonic approximation, a relaxation energy term λ_{rel} can be written as[12]

$$\lambda_{rel} = \sum_j \lambda_j \quad \lambda_j = \frac{k_j}{2}\Delta Q_j^2 \qquad (4)$$

Here, k_j represents the force constant of the normal mode J while ΔQ_j is the projection of the displacements between the equilibrium geometries of the neutral and radical-cation states on the corresponding normal coordinate Q_j.

The normal-mode analysis has been performed at the UB3LYP/6-31g(d,p) level used to optimize the geometry of the conjugated core. The results, illustrated in Figure 3, indicate that the Jahn−Teller E′ modes provide a significant contribution to the reorganization energy in T. The situation is more complex in HAT: while the interaction with E′ modes remains moderate, there exists a strong additional coupling with A_2'' and E″ modes. This feature is due to significant differences in the electronic spectra of T and HAT. In T, the frontier E″ orbital (which has a π-character) is separated by a large gap (about 0.53 and 1.7 eV) from the next A_1'' and E″ levels; in HAT, the frontier E′ orbital (which has σ-character with significant N lone pair contributions; see Figure 4) is separated only by 0.17 and 0.25 eV from the A_1' and E′ orbitals. These results suggest that in HAT there occurs a strong pseudo Jahn−Teller mixture between the ground $^2E''$ and excited $^2E'$ states due to electron−vibration interactions with A_2'' and E″ modes. Our calculations also reveal

HOMO E'
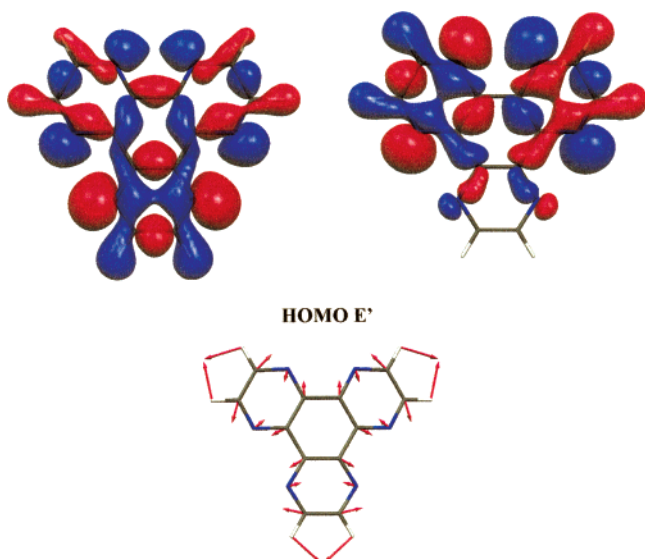
Figure 4. Illustration of the bonding/antibonding pattern of the doubly degenerate HOMO orbitals of hexaazatriphenylene and the atomic displacements associated with the vibrational mode at 1556 cm^{-1}.

Figure 5. INDO-calculated evolution of the HOMO (solid lines) and LUMO (dashed lines) splittings in cofacial dimers made of two triphenylene (squares), hexaazatriphenylene (circles), and HBC (triangles) molecules, as a function of the distance between molecular planes.

Figure 6. INDO-calculated evolution of the HOMO (circles) and LUMO (squares) splittings in a cofacial dimer made of two HATNA molecules as a function of the rotational angle between the discs. The intermolecular distance has been fixed here at 3.5 Å.

a significant increase in vibronic coupling with the totally symmetric A$_1'$ modes in HAT; this is actually the main origin of the overall increase in reorganization energy of the positive polaron in going from T to HAT. The coupling with the A$_1'$ mode (at 1556 cm^{-1}) accounts for nearly 30% of the total reorganization energy in HAT. This is rationalized by the close match between the orientations of the bonding (antibonding) pattern of the HOMO level and the normal-mode vector; see Figure 4.[43]

Since conjugated cores are typically substituted by alkylthio or alkoxy chains to generate liquid crystalline phases, we have also analyzed the impact of these substituents on the reorganization energies. While in most instances alkylthio substitution only slightly affects the reorganization energy, the alkoxy-substituted compounds systematically exhibit much larger values than the unsubstituted cores. This evolution is highly detrimental for charge transport. These results are consistent with the fact that higher mobilities are typically measured for crystalline and liquid-crystalline alkylthio-substituted triphenylene molecules in comparison to the corresponding alkoxy derivatives; this behavior was so far attributed exclusively to changes in molecular packing.[44] Since an increase by 0.2 eV in the reorganization energy reduces the charge mobility by 1 order of magnitude, the design of molecules displaying small reorganization energies is thus a key toward efficient charge transport in discotic liquid crystals.

3.2. Intermolecular Transfer Integral. Here, we investigate for all compounds the impact on the intermolecular transfer integrals of the major types of molecular motion expected within liquid crystalline columns: fluctuations in the intermolecular distance, rotations, and translations of molecules. Figure 5 illustrates the evolution of the HOMO and LUMO splittings in a dimer made of two T, HAT, and HBC molecules, exactly superimposed on top of one another, when varying the intermolecular distance in the range between 3.1 and 4.1 Å. For the three compounds, we observe that (i) the splittings decay
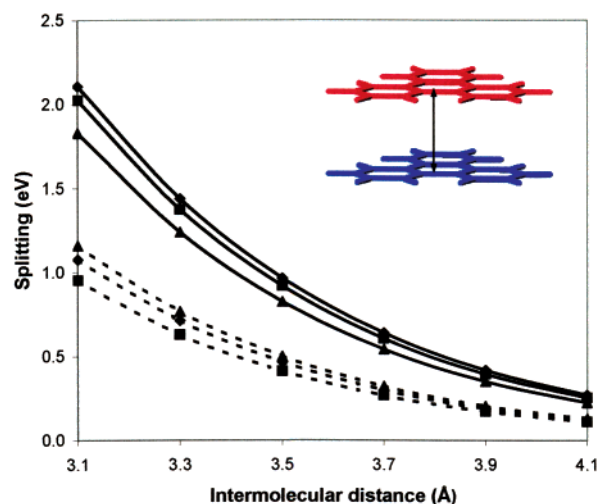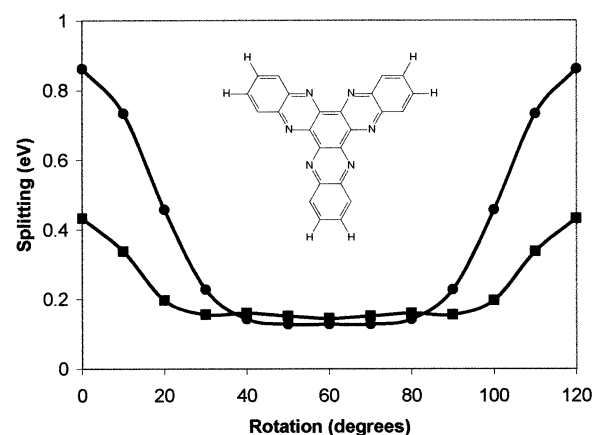
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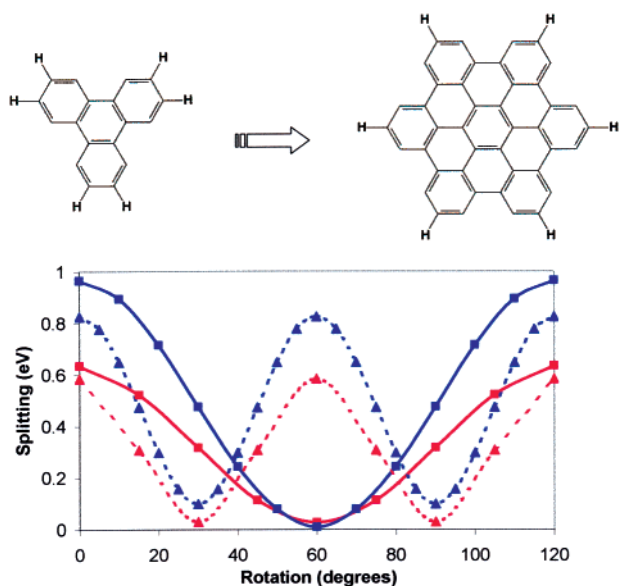(44) van de Craats, A.; Schouten, P. G.; Warman, J. M. *EKISHO* **1998**, *1*, 12.

exponentially with the distance, as a result of the reduction in π-atomic orbital overlap when the two molecules are pulled apart, and (ii) the HOMO splitting is always larger than the LUMO splitting; in such cofacial dimers, this was explained earlier on the basis of the difference in the number of nodes between the two wave functions.[29] Similar trends are observed when introducing nitrogen atoms in the conjugated core or when attaching alkylthio and alkoxy substituents. The main conclusion from these calculations is that for all discs the amplitudes of the transfer integrals are not dramatically affected by small fluctuations of the intermolecular distance; for instance going from 3.5 to 3.6 Å decreases the HOMO and LUMO splittings by at most 20%.

The rotation of one molecule of the dimer around the stacking axis has a much larger impact on the amplitude of the electronic splittings; see Figure 6. In the case of triphenylene, rotating one molecule by 60° leads to a dramatic reduction of the electronic splittings by up to 2 orders of magnitude, with respect to the cofacial configuration (0.01 eV vs 0.97 eV for the HOMO splitting). Thus, any deviation from the cofacial geometry, which is expected in the mesophase to prevent the steric repulsions among lateral chains, is detrimental to the charge transport

Figure 7. Evolution of the HOMO splittings in a dimer formed by two triphenylene (squares) or hexabenzocoronene (triangles) molecules, as a function of the rotational angle, as calculated at the INDO level (blue), and twice the value of the charge-transfer integral calculated at the DFT level (red).

properties; this means that the mobility value around 0.1 cm^2/(V.s) reported for the helical phase of 2,3,6,7,10,11-hexakis-(hexylthio)triphenylene (TSC6) has not reached its limit given that the rotational angle there is of 45.5°.[45,46] The substitution of the triphenylene core by alkylthio or alkoxy chains has no major influence on the calculated electronic splittings.[47] Interestingly, the insertion of nitrogen atoms in the triphenylene core significantly reduces the rotational sensitivity of the HOMO splitting which fluctuates only by a factor of 2 in hexaazatri-phenylene (from 0.92 eV for the cofacial dimer to 0.42 eV for a rotation of 60°); in contrast, the evolution of LUMO splitting is hardly affected by such a derivatization.[47] Importantly, the HATNA molecule emerges as a potential candidate for electron and hole transport since it displays HOMO and LUMO splittings that remain significant, on the order of 0.15 eV, for rotations around 60°; see Figure 6. Thus, the present quantum-chemical calculations prove helpful in designing molecular structures where the transfer integrals remain large for any rotational degree of freedom, a feature of prime interest for device applications. Since the substituents have no major impact on the calculated evolutions, conjugated cores of interest could be made liquid crystalline by tuning the nature of the saturated chains while keeping attractive transport properties.

At first sight, the strong oscillation in transfer integrals for triphenylene and substituted derivatives could be attributed to the presence of voids between the external rings of the conjugated core; this leads to a very small spatial overlap of the electronic wave functions of the two molecules in the dimer for angles around 60°. However, circular-like molecules such as HBC also display a strong evolution of the transfer integrals as a function of rotational angle; see Figure 7. The frequency

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of oscillation is twice larger in HBC than in triphenylene due to the symmetry evolution from D_{6h} to D_{3h}. This result is reproduced at the DFT level, even tough the DFT transfer integrals are found to be systematically smaller than the INDO values by about 30%; however, this has no major consequence when comparing the relative mobilities of different materials, which is the prime focus of our study. To determine which of the DFT or INDO approach is most reliable, detailed calculations of the absolute values of charge carrier mobilities need to be carried out and the results compared to experiments; this will be the subject of future studies.

The present results demonstrate that: (i) an increase in the size of the conjugated core does not necessarily ensure better transport properties since the amplitude of the transfer integrals is strongly dependent on the actual rotational angle in the mesophase; and (ii) the calculated electronic splittings are not governed as much by the shape of the molecule as by a fine balance between intermolecular bonding versus antibonding interactions that are defined by the shape of the electronic wave functions. As a result, the evolutions obtained as a function of rotational angle can hardly be predicted at the simple sight of a molecular structure and point to the relevance of quantum-chemical calculations to understand charge transport at the molecular scale in these materials.

Next, we have analyzed the impact of the lateral displacement of one disc out of the column by calculating the evolution of the electronic splittings in a dimer when the two discs are pulled apart laterally. For symmetry reasons, the degenerate frontier electronic levels of the discs split in a different way in a translated dimer in contrast to the situations encountered when one disc is rotated or the intermolecular distance varied. Moreover, the loss of symmetry does no longer guarantee that the HOMO and LUMO levels of the two molecules have the same energy since each molecule feels in a different way the presence of its neighbor. Such level offsets would increase the apparent calculated splittings;[48] however, they are expected to be small in the case of apolar molecules and have not be taken into account hereafter. Figure 8a illustrates the fast drop of the hole transfer integrals in dimers made of HBC and triphenylene molecules as the degree of translation of one disc along a C_2 axis is gradually increased; similar considerations apply to the electron-transfer integrals. The local maxima along the course of the translation originate from specific geometries promoting a superimposition of several atoms of the two interacting molecules. Significant transfer integrals persist over a much larger distance in HBC since larger discs yield a lower degree of reduction in orbital overlap when translation is applied. It should be noted that in the crystalline phase the molecular cores of alkylthio-substituted triphenylenes are tilted by 22° while the intermolecular distances are about 0.2 Å smaller than in the liquid crystalline phase.[46] According to recent theoretical calculations, this leads to an increase in charge-transfer integral by a factor of about 2,[33] which should result in a higher mobility of charge carriers in the crystalline phase of alkylthio-substituted triphenylene. We stress that the translation of molecules out of the stack is not always detrimental for the charge mobilities. For instance, in a dimer formed by two triphenylene molecules rotated by 60°, the HOMO splitting is estimated to be 0.01 eV in absence of translation and 0.52 eV after a translation of 2.5

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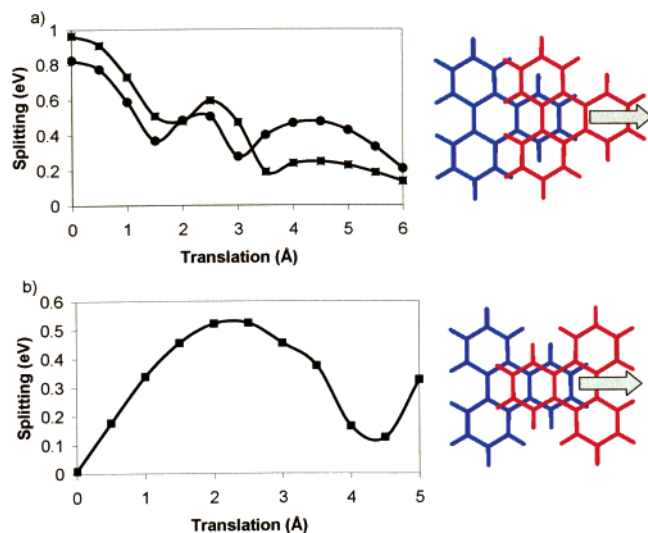
Figure 8. INDO-calculated evolution of the HOMO splittings in (a) dimers formed by two triphenylene (squares) and HBC (circles) molecules in a cofacial configuration (i.e., without rotation between the discs) when translating laterally a molecule along a C_2 axis and in (b) a dimer made of two triphenylene molecules rotated by 60° when translating laterally one molecule along a C_2 axis. Since the degenerate levels split in a different way in such staggered dimers, we refer here only to the largest calculated electronic splittings.

Figure 9. Evolution of the hole mobility (in arbitrary units) in ideal stacks made of triphenylene (squares) and hexaazatriphenylene (circles) molecules as a function of the rotational angle between two discs. The mobilities are calculated as relative values from the ratio of the corresponding charge-transfer rates, taking the hole mobility of triphenylene molecules in their cofacial arrangement equal to one.

Å; see Figure 8b. Thus, subtle effects rule the evolution of charge mobility when going from a crystalline structure, where adjacent discs are typically displaced laterally along a C_2 axis,[49] to a liquid crystalline phase, where the discs are not tilted but just possibly rotated.[50,51]

Despite the fact that the reorganization energies and intra-columnar transfer integrals have so far been addressed separately, these two parameters need to be considered simultaneously to provide a proper description of the charge transport processes. This is illustrated in Figure 9, where we display the evolution of the hole mobility at 300 K (calculated according to eq 1) in stacks made of triphenylene and hexaazatriphenylene molecules, substituted by six thiol groups and separated by 3.5 Å, when rotating every other molecule around the stacking axis. In the cofacial configuration, both the larger transfer integral and smaller reorganization energy calculated for tri-phenylene contribute to a mobility higher (by about 35%) than in hexaazatriphenylene. The steep decay of the HOMO splitting in triphenylene upon disc rotation leads to an opposite situation at 60°; the hole mobility is there approximately 1 order of magnitude higher for hexaazatriphenylene than for triphenylene. Thus, comparing the transport properties of different liquid crystalline discotic materials requires the knowledge of the actual rotational angle in the mesophases and degree of geometric fluctuations induced by thermal effects. This is addressed in the next section with the help of molecular mechanics calculations.

3.3. Organization within the Columns. For all the compounds under study, we have evaluated the rotational angle between two adjacent discs in the stack by optimizing at the PCFF level the geometry of clusters containing up to 4 molecu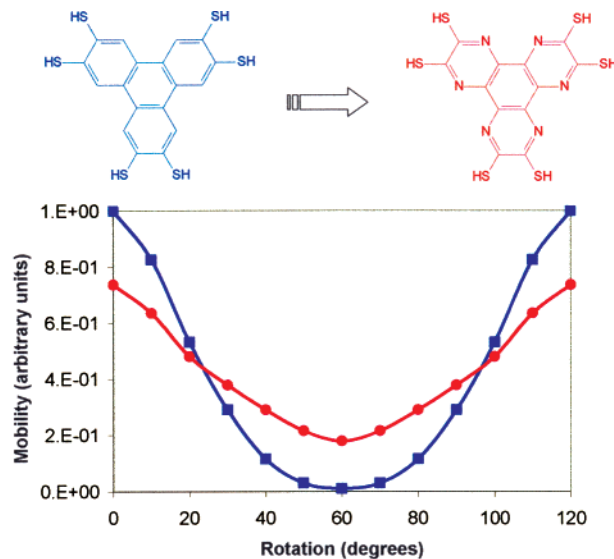les; as the results obtained for dimers are the same as for larger clusters, for the sake of simplicity, we focus here on the dimer results. Since fluctuations in the intermolecular distance only slightly affect the transfer integrals (vide supra), this distance has been systematically fixed at 3.5 Å, as suggested by X-ray diffraction data.[46] Moreover, the conjugated core has been frozen in the geometry optimized at the DFT level to prevent possible distortions when using a classical force field.

When considering fully extended conformations of saturated chains typically encountered in the compounds forming liquid crystalline phases, we calculate in most cases a rotational angle between two adjacent discs on the order of 15°, as a result of strong van der Waals interactions among the lateral chains. However, these extended conformations lead to columnar dimensions that exceed the experimental values.[52] Since our approach does not account for intercolumnar interactions and thus does not reproduce the space filling of the lateral chains around the discotic cores, we have considered an effective size for the lateral chains to reproduce the strength of their van der Waals interactions. It turns out that the reduction of the lateral chains to just two carbon atoms allows us to reproduce the rotational angle of 45.5° measured in the helicoidal phase of TSC6, one of the only compounds for which such an information is available;[45,46] this is illustrated in Figure 10, where the potential energy profile of a dimer made of two triphenylene molecules substituted by six ethylthio groups is displayed as a function of rotational angle. We have therefore adopted the same reduced length of alkyl side chains for all the discs under study. Our methodology is thus unable to describe the subtle influence of the length of the lateral chains on the charge mobilities but rather provides a value representative of a given conjugated core.

Figure 10 also shows the room-temperature distribution of rotamers in dimers made of two triphenylene molecules, as calculated according to a Boltzmann distribution (sampling 13

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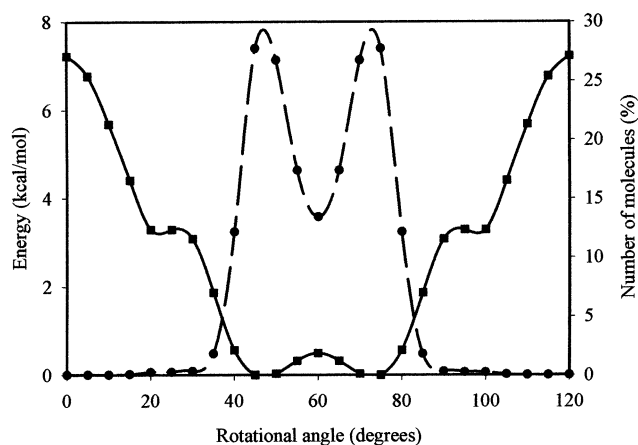
Figure 10. Evolution of the total energy (in kcal/mol) of a dimer made of TSC2 molecules when rotating one disc along the stacking axis, as calculated at the molecular mechnics PCFF level (solid line, left axis). We also illustrate the distribution of the rotamers expected at room temperature from Boltzmann statistics (dashed line, right axis); see eq 5.

angles in the range between 0 and 60°); the latter expresses the percentage n_i of dimers having a rotational angle θ_i as

$$n_i = \frac{\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \tag{5}$$

with E_i the relative energy of the rotamer characterized by an angle θ_i with respect to the global minimum. Since the energy barrier between the equibrium structure and the cofacial geometry is 7 kcal/mol high, this distribution does not encompass configurations with small rotational angles. This indicates that most of the triphenylene molecules cannot fully rotate in the liquid crystalline phase but do oscillate in a limited range of rotational angles around the local minimum, as recently evidenced by quasielastic neutron scattering measurements probing the molecular dynamics at the picosecond time scale.[53] We note that larger displacements of the molecules have also been identified by solid-state NMR spectroscopy on a much longer time scale (around 10^{-8} s) (the hopping process typically occurs on a picosecond time scale);[54] since the number of such defects is expected to be limited along the stacks, they should not affect the mobility values measured at the local scale. However, they should be properly accounted for when describing charge drift over macroscopic distances.

Figure 11 collects the energetic profiles obtained for dimers of TSC2, TOC2, HATSC2, HATOC2, HATNASC2, and HATNAOC2, when rotating one molecule around the stacking axis. The results indicate that the rotational angle associated to the global energy minimum strongly depends on the nature of the discotic core, and this dependence is rather unpredictable. These angles span a range between 15° for the HATNA derivatives to 60° for the triphenylene derivatives; in the latter case, the equilibrium angle lies in the range where the transfer integrals adopt the smallest values. In the order from alkoxy to alkylthio substituents, the optimal angle is reduced in the case of triphenylene, increased in HAT, and stays about the same in HATNA. None of the discs presents a cofacial conformation,
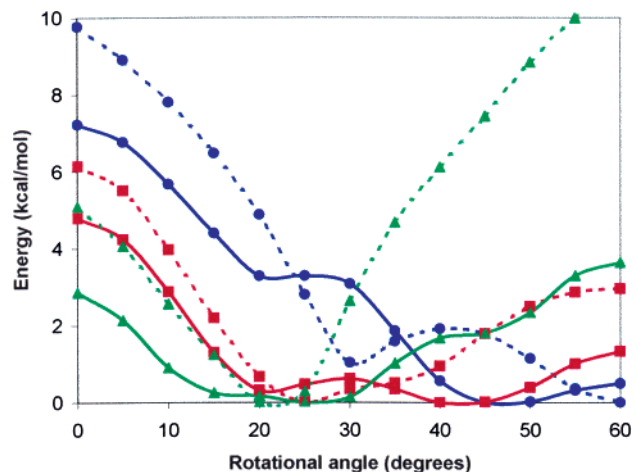
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Figure 11. Evolution of the total energy (in kcal/mol) calculated at the PCFF molecular mechanics level for dimers made of two triphenylene (circles), hexaazatriphenylene (squares), or hexaazatrinaphthylene (triangles) molecules substituted by six SC2 groups (solid lines) or OC2 groups (dashed lines), when rotating one molecule around the stacking axis. The intermolecular distance is fixed at 3.5 Å.

Table 2. Reorganization Energies for Positive (λ_+) and Negative (λ_-) Polarons, Optimal Rotational Angles (in deg), and Thermally Averaged HOMO (t_H) and LUMO (t_L) Splittings for the Various Compounds under Study[a]

molecule	angle	t_H (eV)	λ_+ (eV)	μ_{holes}	t_L (eV)	λ_- (eV)	$\mu_{electrons}$	μ_{total}
TSC2	45	0.09	0.16	1.00	0.02	0.24	0.01	1.01
TOC2	60	0.12	0.33	0.22	0.03	0.40	0.01	0.23
HATSC2	40	0.27	0.17	6.80	0.06	0.32	0.06	6.86
HATOC2	25	0.30	0.38	0.78	0.08	0.49	0.02	0.80
HATNASC2	25	0.21	0.10	10.64	0.10	0.11	2.02	12.66
HATNAOC2	20	0.23	0.22	2.74	0.09	0.20	0.48	3.22

[a] The electron and hole mobilities are calculated as relative values from the ratio of the corresponding charge-transfer rates at room temperature, taking the hole mobility of the alkylthio-substituted triphenylene molecule equal to one.

as a result of Coulomb repulsion between the core and/or high steric repulsion between the peripheral chains; hence, the charge mobilities do not reach their maximal values.

We have finally calculated the relative electron and hole mobilities at room temperature in the various compounds from the ratio of the corresponding transfer rates, taking as reference ($\mu = 1$) the hole mobility in TSC2; see Table 2. To do so, we have used the reorganization energies obtained at the DFT level together with the intermolecular charge transfer integrals associated with the rotational angles provided by the molecular mechanics calculations; the squares of the transfer integrals have been thermally averaged over a Boltzmann distribution to account for the distribution of the rotational angles around the equilibrium value along the stack. The dynamics of the hopping process is so fast compared to the rotational dynamics of the discs that to first approximation we can consider this distribution to be frozen while the charge is drifting along the stack:

$$\langle t^2 \rangle = \frac{\sum_i t_i^2 \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} = \sum_i n_i t_i^2 \tag{6}$$

Note that the averaging in eq 6 is also validated by neutron diffraction experiments indicating that the structural fluctuations are fast compared to the charge carrier hopping rates.[53]

Analysis of Table 2 reveals that the total charge mobility is largely dominated by hole transport, which is consistent with

the fact that the HOMO splitting is systematically larger than the LUMO splitting and the hole reorganization energies are smaller. A significant electron mobility is calculated in the case of the HATNA derivatives, thus making them promising electron transporters, while much lower values are obtained in triphenylene-based compounds. Our results also predict that the hole mobility can be increased by up to 1 order of magnitude when going from triphenylene to HATNA. To check this prediction, we carried out PR-TRMC experiments. The measurements fully confirm the theoretical data as they indicate mobilities of 0.020 cm^2/(V.s) for liquid crystalline triphenylene molecule substituted SC10 chains versus 0.26 cm^2/(V.s) for the liquid crystalline HATNA derivatives substituted by the same lateral chains. Note that (i) this significant increase is not observed for all the lateral chains since mobility values of 0.015 and 0.05 cm^2/(V.s) are obtained for SC8 chains on triphenylene and HATNA, respectively, and (ii) the same trends are provided by the calculations when considering the exact transition temperature of the liquid crystalline phases rather than room temperature.

The significant improvement of the hole mobility in HATNA is mainly attributable to the smaller reorganization energy and rotational angle calculated for the HATNA stacks. The hole mobility is much larger in HAT than in triphenylene and approaches the value obtained for HATNA, as a result of the low rotational sensitivity of the HOMO splitting (vide supra). The calculated mobility values are systematically smaller in the alkoxy-substituted compounds than in the corresponding alkyl-thio derivatives, in agreement with PR-TRMC measurements;[43] this feature originates in the larger reorganization energies calculated for the alkoxy derivatives. All together, the calculations highlight the interplay of several parameters and the need to evaluate all of them to get a reliable description of charge transport in discotic liquid crystals.

4. Conclusions

We have characterized by means of a quantum-chemical approach the main two parameters (i.e., reorganization energies and intermolecular transfer integrals) governing charge transport at the molecular scale in discotic liquid crystals. The transfer integrals have been estimated for model systems as well as for the chain stacking provided by molecular mechanics calculations to allow for a direct comparison between experimental and theoretical data.

We have illustrated that the charge mobilities result from a subtle interplay between the size, nature of the conjugated core and anchoring units, and relative positions of the molecules in the columns. The predicted increase by 1 order of magnitude in hole mobility when going from triphenylene to HATNA derivatives is fully supported by corresponding PR-TRMC measurements.

Since the molecular parameters governing charge transport cannot be assessed at the simple sight of a molecular structure, a theoretical approach such as the one described here can prove useful to design, prior to any chemical synthesis, discotic molecules with potentially high charge carrier mobilities. Additional mobility measurements on discotic molecules are also highly desirable to better validate our theoretical formalism and to help in the selection of the most appropriate quantum-chemical approach to achieve good quantitative agreement.