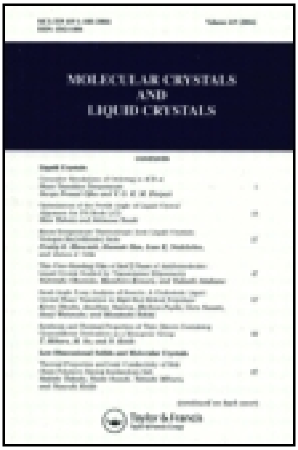

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Synthesis of Polydiacetylene Charge-Transfer Complexes

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Like 1,4-bis(3-quinolyl)buta-1,3-diyne, its structural isomer, 1,4-bis(4-isoquinolyl)buta-1,3-diyne, undergoes both photo- and thermal polymerization. Thermal polymerization of each material leads to more amorphous, less thermally stable polymers than are observed in the respective photopolymerization. The diacetylenes are found to react with certain organoiodines to give N-I charge-transfer complexes. Thermolysis of the complexes evolves the organoiodine species prior to polymerization of the diacetylene. The complexes fail to polymerize upon photolysis.

Keywords: diacetylene; charge-transfer; polymerization; X-ray; crystallography

INTRODUCTION

While it has been known for more than a century that certain diacetylenes undergo a dramatic color change upon storage under ambient conditions, it was not until Wegner's work in the late 1960's that an adequate explanation for the effect was developed.[1] Building on Schmidt's principles of topochemical reactions,[2] Wegner proposed that the C1 and C4 carbons of adjacent molecules couple, leading to polymer chains. These observations have sparked widespread

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* Corresponding author

interest on several fronts. The unique solid-state phenomenon has provided *insights into the polymerization process in general, while the structure of the* highly defect-free crystalline polymers obtained can be analyzed (in some cases) to an unprecedented level. These polymers are the closest thing to a truly one-dimensional system yet devised. They possess remarkable optical and non-linear optical properties, can be made semi-conducting, and can form very interesting supramolecular architectures.[3]

Diacetylene Host-Guest Systems

There have been a number of publications in which co-crystals or host-guest complexes of DA's have been reported. Reasons for investigating such complexes range from potential magnetic materials,[4] to effecting asymmetric synthesis and separations,[5] to selectively controlling supramolecular architecture.[6]

Very recently, we have extended this concept towards the construction of nanoporous solids (Figure **1**). Our general strategy is to prepare diacetylenes with one or two heterocyclic "head groups" (step **a**) which are expected to form charge-transfer complexes with Lewis acids such as I_2 (structure type **2**) *These could be crystallized* (**b**) *and polymerized* (**c**). *Removal of the Lewis acid* guest from the PDA matrix would then lead to well-defined cavities and channels throughout the host polymer (**d**).

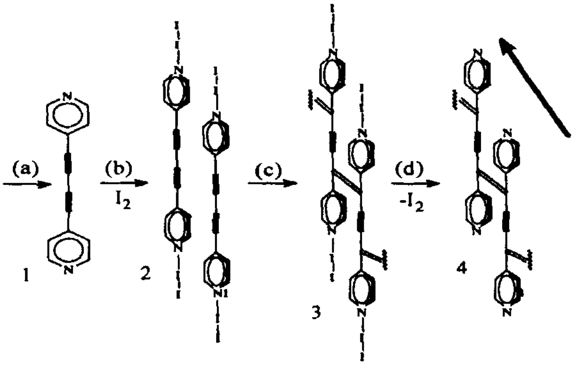


FIGURE 1: Proposed route to nanoporous solids.

Synthetic routes to **1** and derivatives are well known, however, not all 1,3-butadiynes undergo solid-phase polymerization, and the prediction of reactivity from molecular structure is not yet possible. Compounds of structure type **2** have not been previously reported. Our investigations of the N-heterocycle-I_2 interaction have shown this to be a potent tool for crystal engineering,[7] but exposure of diacetylenes to I_2 leads to free radical polymerization of the diacetylene moiety rather than to complexes of type **2**. Recently, we have found that several organoiodines also form charge-transfer complexes with N-heterocycles, and these are far less likely to oxidize sensitive substrates.[8] Here, we will describe the formation of two diacetylene charge-transfer complexes of structure type **2** and discuss our attempts to transform them into polymers of type **3**.

EXPERIMENTAL

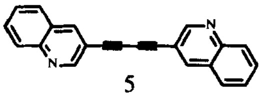
All reagents were purchased from Aldrich and used as received. Solvents were purchased from commercial houses and purified by distillation under argon from appropriate drying agents. The compound 1,4-bis(3-quinolyl)-buta-1,3-diyne, **5**, was prepared according to literature procedures.[9] NMR and IR spectral data were consistent with previous reports. Likewise, 1,4-bis(4-isoquinolyl)buta -1,3-diyne, **6**, was prepared by the same method and gave satisfactory elemental analysis. ^{1}H NMR ($CDCl_3$, δ) 9.22 (s, 2 H), 8.81 (s, 2 H), 8.26 (d, 2 H), 8.01 (d, 2 H), 7.82 (dd, 2 H), 7.64 (dd, 2 H). Charge-transfer complexes **7** and **8** were prepared by dissolving 7 mg of the donor and 1 equivalent of a Lewis acid acceptor in 10 mL of methylene chloride. Crystals were grown by slow evaporation of the solvent. Photopolymerizations were conducted by placing small vials of finely ground compounds or charge-transfer complexes in a Rayonet photoreactor, operating at 254 nm, for 48 hours.

All NMR spectra were acquired on a Varian VXR 300 spectrometer. IR data were acquired on a Perkin-Elmer Paragon 500 FT-IR. Thermal analyses were performed under nitrogen on Perkin Elmer Series 7 TGA and DSC analyzers. All thermal experiments were conducted at a constant heating rate of 10 °C/min; thermal parameters were obtained by standard methods. Thermal microscopy was performed on an optical microscope equipped with a hot stage and electronic data capture system. Single crystal X-ray data for compound **6** were collected on a light-yellow parallelepiped crystal (0.12 x 0.22 x 0.41 mm) at 22±1°C by using a Rigaku AFC7R (18 kW) diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) to $2\theta_{max}$ of 55.0°. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at optimized positions with a group isotropic thermal parameter ($U_H = 0.06(2)$ Å^2).[*]

RESULTS AND DISCUSSION

Synthesis and Thermal Properties of Diacetylenes

Compound **5** and its isomer **6** were prepared from the corresponding bromoquinoline or bromoisoquinoline by the route previously reported for **5**.[9] Compound **5** was isolated in good yield as white needles or thin fibers (depending upon recrystallization solvent) which rapidly turned blue on exposure to light due to photopolymerization of the diacetylene moieties. Conversely, **6** crystallized as yellow parallelepiped crystals, which were stable to ambient light.



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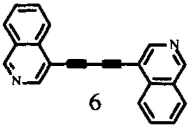

6

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[*] Crystal data for $C_{22}H_{12}N_2{\cdot}C_2I_4$: triclinic, space group *P-1* (No. 2); **a** = 7.362(1), **b** = 19.278(4), **c** = 4.2134(5) Å, $\alpha = 94.07(1)$, $\beta = 98.13(1)$, $\gamma = 97.22(1)$° $V = 584.9(2)$ Å^3 (based on 25 reflections; $21.58 < 2\theta < 26.88°$), $Z = 1$ (TIE molecule centered on inversion center at the origin; bis(isoquinolyl)butadiyne molecule centered on inversion center at (*0.0, -0.5, 0.5*)), *Dcalc* = 2.37 g cm-3, μ(Mo Kα) = 5.34 mm-1, empirical absorption correction, transmission coefficients: 0.57-1.00, 2909 data measured, 2698 unique ($R_{int} = 0.033$), 2242 observed ($I > 2\sigma(I)$), $R(F) = 0.061$, $R_w(F) = 0.093$. Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

Quinoline derivative **5** has been reported to undergo polymerization upon heating or exposure to either UV or gamma radiation. Thermal gravimetric analysis (TGA) shows that after an initial mass loss due to evaporation (onset temperature, *ca.* 240 ° C) it undergoes a transformation to a material which retains most of its mass up to nearly 600 °C (Figure **2** curve **a**). Compound **6** (curve **b**) shows essentially the same behavior. After exposure to UV radiation for 48 hours, photopolymers of **5** and **6** were formed. The photopolymer of **5** was a deep blue color, while that of **6** was a deep brown. These were found to have significantly greater thermal stability than the products of the thermal polymerization. After an initial evaporation of unreacted diacetylene (and a second mass loss for **5** around 400 °C), the materials only slowly degrade; retaining more than 50% of their mass up to 800 °C.

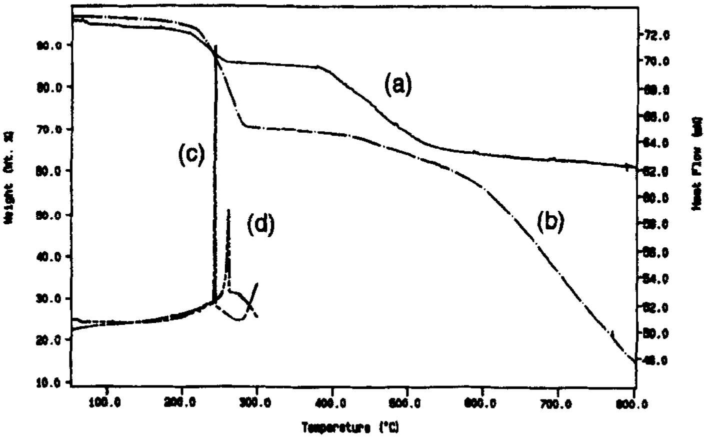


FIGURE 2: TGA and DSC curves for **5** (**b**, **d**) and **6** (**a**, **c**)

Differential scanning calorimetry (DSC) for the two compounds shows that the transformations which halt the mass loss in the TGA experiment are endothermic, with onset temperatures of 242 and 258 °C for **5** and **6**, respectively (Figure **2**, curves **c** and **d**, respectively). These endotherms are not consistent with a solid-state polymerization, but are due to the melting of the diacetylene. Thermal microscopy confirms that the compounds first melt, then polymerize. Interestingly, while the melting/polymerization process of compound **5** is followed by observable crystallization of polymer, the polymerization of **6** results in a completely amorphous material. In each case, the resulting polymers are dark brown, completely unlike the deep blue needles obtained by photopolymerization of **5**.

Charge-Transfer Complexes

In order to explore the potential for nanoporous solid formation by this route, a charge-transfer complex was prepared by slow evaporation of a solution containing equal molar amounts of **6** and tetraiodoethylene (complex **7**). Figure 3 shows the structure and packing diagram of the complex.

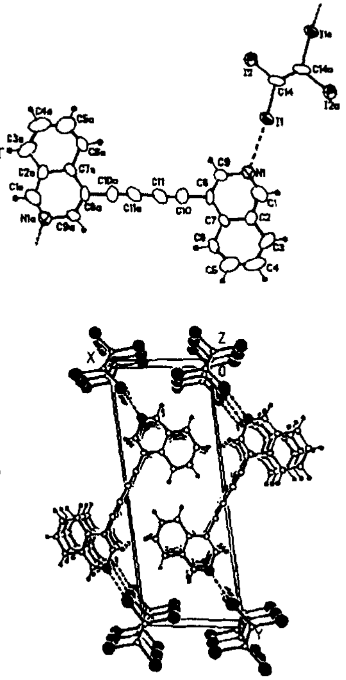
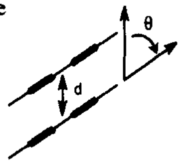


FIGURE 3: X-ray data for **7**.

Both isoquinoline moieties associate with an iodine from the TIE guest. Each TIE interacts with two donor molecules, resulting in infinite chains oriented along the crystallographic y axis. Weak donor·acceptor interactions between iodine atoms (I···I distances of 3.868(3) - 4.148(3) Å), similar to those observed for a variety of related complexes,[8] form loosely associated layers of TIE molecules. These interactions orient the chains such that both the donor and the acceptor molecules stack along the z axis. Each donor·acceptor stack is translationally equivalent. The N-I distance of 2.951(9) Å is similar to those of previously reported TIE charge-transfer complexes.

In order to efficiently undergo topochemical polymerization two critical stacking parameters must fall within certain limits. These are the distance between molecules within the stack (d) and the angle made between the direction of the stack and the long axis of the diacetylene molecule (θ). In complex **7**, the stacking distance (d= 4.25 Å), somewhat shorter than the optimal distance of approximately 5 Å, but similar to that observed in the structure of **5**. The molecular axis, however, is angled at 75° to the stacking direction, significantly different from the desired 45 ° angle. This puts the reacting centers at greater distance and forces greater atomic motion to occur before polymer formation.



Attempted Polymerization of a Charge-Transfer Complex

Our efforts to photopolymerize **7** were, as predicted from the crystal structure, unsuccessful. Since we had previously noted that diacetylene **5** photopolymerizes more efficiently than **6**, we next prepared a charge-transfer complex with this donor. A 1:1 molar solution of **5** and tetrafluorodiiodobenzene (TfDIB) in methylene chloride was prepared and small crystals of the corresponding charge-transfer complex **8** were grown by evaporation. In figure **4**, curve **a** shows the TGA results for TfDIB, while curve **b** shows the results of the CT complex **8**.

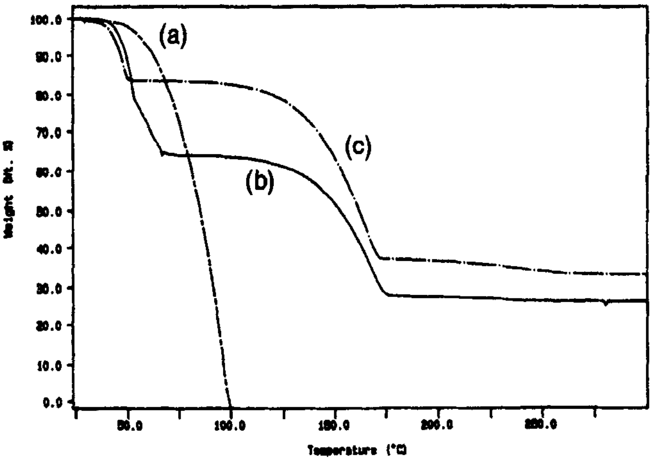


FIGURE 4: Thermal data for complex **8**.

The complex shows two mass losses attributable to TfDIB. The first, with an onset temperature of 50 °C, is due to unreacted acceptor in the solid mixture. The second is due to acceptor loss from the host-guest matrix of the charge-transfer complex. Both losses occur before reaction of the diacetylene.

Photolysis of the grey charge-transfer complex did not result in the formation of the deep blue color seen in the polymerization of **5**. Indeed, the photolyzed material appeared identical to the starting charge-transfer complex. Figure **4**, curve **c** confirms this observation. The photolyzed material shows the same thermal behavior as the starting material (except for some variation in the amount of free TfDIB). Thus, in this case, complex formation disrupts the critical crystal packing parameters required for solid phase polymerization.

Acknowledgments

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