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# Synthesis and Mesomorphic Behavior of a Donor−Acceptor-Type Hexaazatriphenylene

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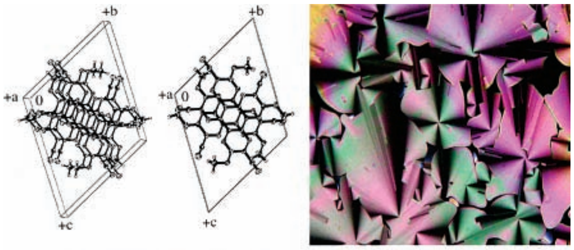
## ABSTRACT



The crystal structure of $HATCNOR_1$ The optical texture of $HATCNOR_6$

**A new donor-acceptor, 1,4,5,8,9,12-hexaazatriphenylene $HATCNOR_n$, is described. The synthesis of $HATCNOR_1$ and $HATCNOR_6$ is achieved by the regioselective displacement of 1,4,5,8,9,12-hexaazatriphenylene hexacarbonitrile (HATCN) with an alkoxy group. The X-ray analysis revealed self-assembly of $HATCNOR_1$ in the solid state. $HATCNOR_6$ is the new difunctionalized hexaazatriphenylene discotic liquid crystal.**

The unique ordered molecular assemblies of the columnar mesophase of compounds containing a disk-shaped molecule that possesses remarkable charge transport properties have led to their exploitation as functional materials for application as light-emitting diodes,[1] photovoltaic cells,[2] and field effect transistors.[3] The discotic mesogens are primarily of two types: electron-rich core or p-type (donor) and electron-deficient core or n-type (acceptor). Among the most widely investigated p-type mesogens are the triphenylene derivatives, and a large number of synthetic methods have been reported.[4] The n-type mesogens are scarce, and acceptor materials with high charge mobility are in demand. Recently, the electron-deficient heterocycles hexaazatriphenylene (**HAT**)[5,6] and hexaazatrinaphthylene (**HATN**)[7−9] have been reported as new n-type mesogens.

In our effort to discover new n-type columnar discotic liquid crystals, we have also become interested in **HATN** and **HAT** as potential columnar mesogens with NLO properties. The main outstanding feature for octopolar molecules to exhibit large molecular hyperpolarizability is the presence of alternating donor-acceptor groups as their

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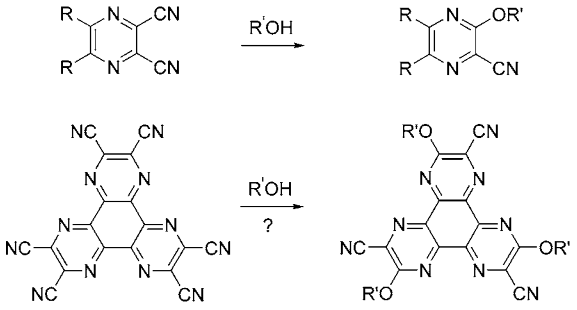
peripheral substituents. However, there has been no report on **HATN** and **HAT** derivatives possessing simultaneously both donor-acceptor substituents, probably because of the lack of practical synthetic methods. Here, in this paper we report an expedient synthesis and mesomorphic behavior of the donor-acceptor 3,7,11-trialkoxy-2,6,10-tricyano-1,4,5,8,9,-12-hexaazatriphenylene (**HATCNOR**$_n$). Further, single-crystal X-ray structural determinations have been possible for the 3,7,11-trimethoxy-2,6,10-tricyano-1,4,5,8,9,12-hexaazatriphenylene (**HATCNOR**$_1$); this shows **HAT**-**HAT** $\pi$-complexation in the solid state.

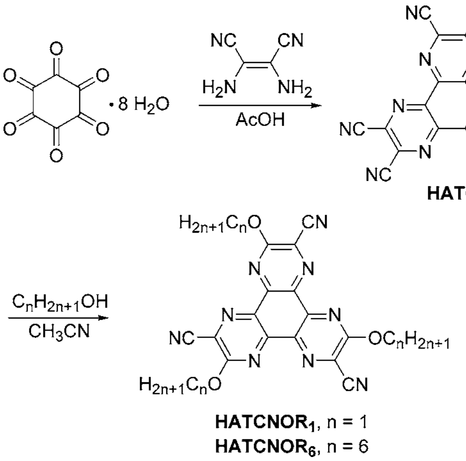
It has been reported that 5,6-disubstituted pyrazine-2,3-carbonitrile undergo selective substitution of only one nitrile group with alcohols, giving 5,6-disubstituted 3-alkoxypyrazine-2-carbonitrile. We thus anticipated that the difunctionalized donor−acceptor (**HATCNOR**$_n$) might be similarly synthesized from the regioselective substitution of the readily available 1,4,5,8,9,12-hexaazatriphenylene hexacarbonitrile, **HATCN**, with alcohols (Scheme 1).[10]

**Scheme 1**



The starting material, **HATCN**, was originally reported as a black solid,[11] and more recently as a yellow orange solid after rigorous purification.[12] We first studied the reaction of the yellowish-orange **HATCN**[12] with methanol in refluxing acetonitrile. The reaction proceeds to give a complex mixture of products that was found difficult to purify. At this point we felt that most of the unwanted compounds from the reaction were obtained from the impurities present in the previously reported yellowish-orange **HATCN**. Therefore, we have attempted to undertake further purification of **HATCN**. Our approach involved dissolving the yellowish-orange **HATCN**[12] in acetonitrile, followed by dropwise addition into water to give a pale-yellowish suspension. **HATCN** as a stable pale-yellowish solid was obtained after centrifuging the suspension. The purified **HATCN** was reacted with methanol in refluxing acetonitrile, and this gave easily separable **HATCNOR**$_1$ in 40% yield (Scheme 2). It was found advantageous to use the freshly purified **HATCN** whereby the reaction proceeded more cleanly. Elemental analysis and $^{13}$C NMR spectrum confirmed the substitution of three methoxy groups in **HATCNOR**$_1$.

**Scheme 2.** Synthesis of **HATCNOR**$_{1,6}$



The single methoxy peak in the $^1$H NMR spectrum corresponded to this symmetrical structure. The high regioselectivity of the substitution reaction could be attributed to the electron-donating nature of the methoxy group that deactivates the adjacent positions toward further nucleophilic addition; hence the nitrile groups at the 3,7,11-positions in **HATCN** were the most readily substituted (Scheme 3). Reaction of **HATCN** with *n*-hexanol under similar conditions gave 3,7,11-trihexyloxy-2,6,10-tricyano-1,4,5,8,9,12-hexaazatriphenylene (**HATCNOR**$_6$). We thus have developed a clean and practical protocol for the synthesis of **HATCNOR**$_n$.

**HATCNOR**$_1$ yielded yellow triclinic crystals from acetonitrile. Interestingly, the X-ray structure of **HATCNOR**$_1$ revealed rigorous stacking and **HAT-HAT** $\pi$-complexation in the solid state. This stands in contrast to the electron-deficient **HAT** derivatives, which like most of the hitherto known electron-deficient aromatic heterocycles[13−17] are predisposed to avoid self-$\pi$-overlap in the solid state. Also, $\pi$-complexation in the solid state has been previously achieved via the interplanar hydrogen bond for **HAT**-hexaamide.[18] The introduction of three methoxy groups in **HATCNOR**$_1$ has dramatic consequences upon the stability of the resulting $\pi$-complexation of these compounds in the solid state. We believe that the presence of methoxy groups in the electron-deficient **HAT** nucleus has over-ridden the avoidance of $\pi$-complexation. The molecules are packed in a staggered ABAB layer arrangement with one of the molecular centers offset from the stacking axis. The mean

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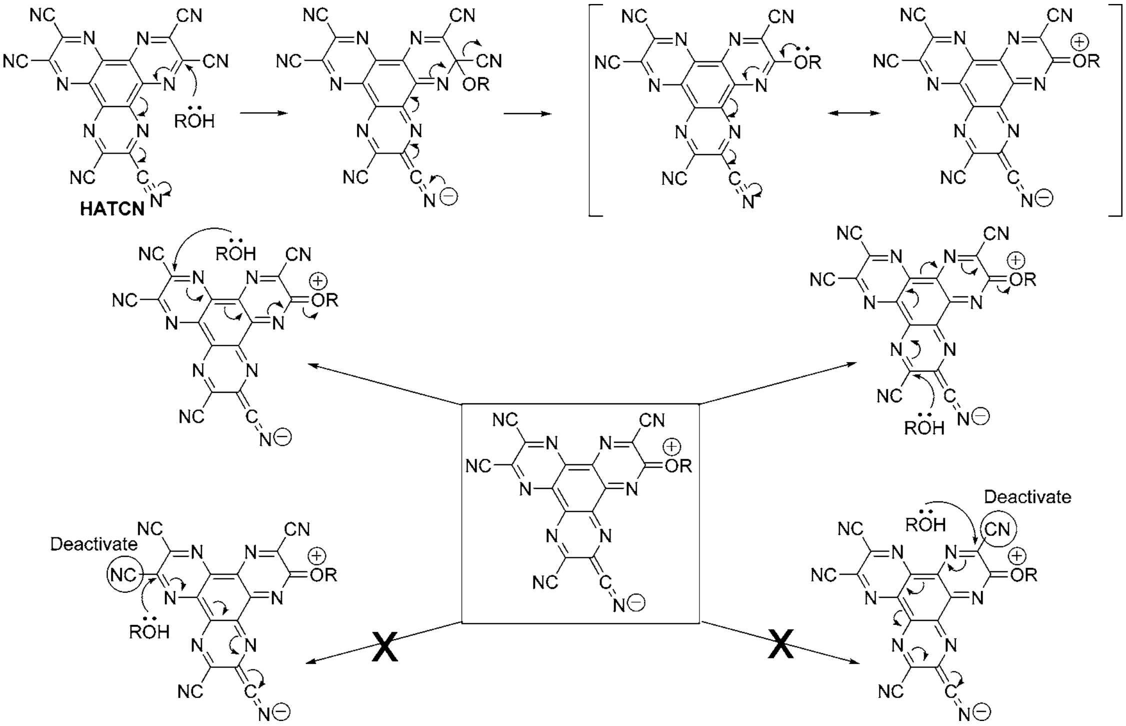
**Scheme 3.** Proposed Regioselective Displacement of 3,7,11-Nitrile Groups



interplanar distance of 3.27 Å between **HAT** rings is smaller than the van der Waals sum of 3.54 Å[19] and is consistent with $\pi$-complexation (Figure 1). **HATCNOR**$_1$ is a truly noncovalent supramolecular assembly for the **HAT** nucleus through $\pi$-complexation in the solid state.

Polarizing optical microscopy (POM) and differential scanning calorimetry were used to check the thermal behavior of **HATCNOR**$_1$ and **HATCNOR**$_6$. Only **HATCNOR**$_6$ exhibited an enantiotropic mesophase. As shown in Figure 2, the melting transition of 141 °C for **HATCNOR**$_6$ is much lower than that of 187 °C for the hexakis(hexyloxy)-**HAT**.[9] This further emphasized the effectiveness of the vertical self-organization of the donor−acceptor **HAT** mesogen. The optical texture shown in Figure 3 is typical of a columnar mesophase. X-ray diffraction studies confirm the ordered hexagonal columnar mesophase assignment. As shown in Figure 3, a sharp small angle peak at 15.85 Å indexed as the (100) reflection was detected and the calculated lattice parameter of 18.30 Å corresponds to the intercolumnar distance. In the wide-angle region, one broader hallo centered at 4.55 Å is typical of the interchain distance and one narrower peak at 3.39 Å corresponds to the intracolumnar stacking period.

It has been reported that higher charge-carrier mobilities[20] along the columns can be obtained with shorter intracolumnar disk-to-disk distances. Hence, a high charge-carrier mobility along the columns can be expected for **HATCNOR**$_6$ since the distance of 3.39 Å is significantly smaller than those (3.50−4.00 Å) of the typical semiconducting columnar mesogens.[21]

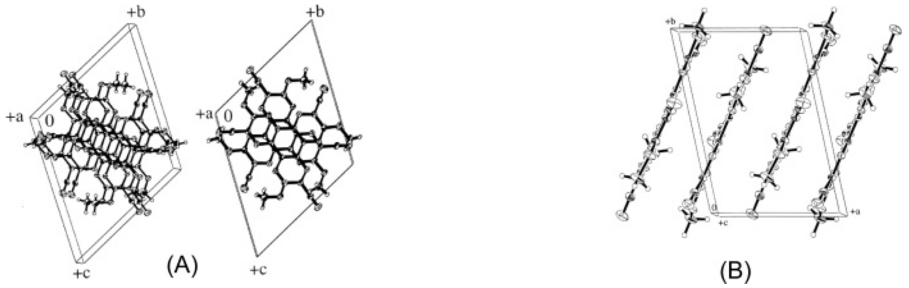


**Figure 1.** (A) Top view of **HATCNOR**$_1$ showing staggered ABAB layer arrangement with an offset of the centroids of the **HATCNOR**$_1$ molecules. (B) Side view of **HATCNOR**$_1$ showing regularly spaced ABAB layers.

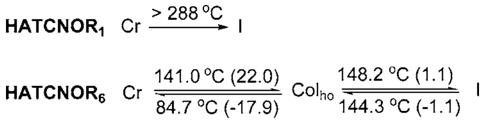


**Figure 2.** Phase Behaviors of **HATCNOR**$_n$. The transition temperatures (°C) and enthalpies (in parentheses/kJ mol$^{-1}$) were determined by DSC at a rate of 10 °C/min. Cr, crystalline phase; Col$_{ho}$, ordered hexagonal columnar; I, isotropic.

The ground-state intramolecular interaction of the donor (-OHex)-acceptor (-CN) group in **HATCNOR**$_6$ is in good agreement with the UV−vis spectroscopic analysis (Figure 4). The UV−vis spectrum of **HATCNOR**$_6$ in acetonitrile is dominated by absorption at 348 and 307 nm, respectively. In comparison, **HATCN** showed $\lambda_{max}$ values at 321 and 281 nm, corresponding to a red shift of 27 and 26 nm, respectively. The observed red shift is in good agreement with the participation of the lone pair at the oxygen atom.

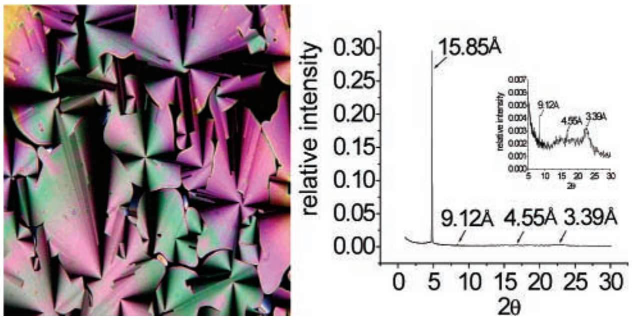


**Figure 3.** Optical texture (magnification ×200) and X-ray diffraction pattern obtained for the columnar phase of **HATCNOR**$_6$ at 143 and 124 °C, respectively.

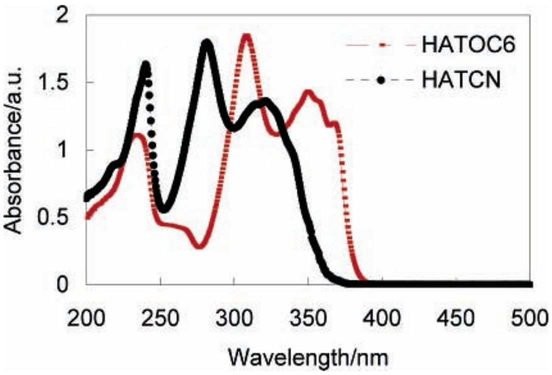


**Figure 4.** UV−vis spectrum of **HATCN** and **HATCNOR**$_6$.

In conclusion, we have shown that difunctionalized hexaazatriphenylene **HATCNOR**$_n$ with alternating substituted donor and acceptor groups can be readily prepared and self-assembles into columnar superstructures in both the solid and liquid crystalline state.

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**Supporting Information Available:** Complete synthetic experimental details and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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