Rubicene, an Unusual Contorted Core for Discotic Liquid Crystals

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Abstract: Rubicene, an unusual contorted polycyclic aromatic hydrocarbon, was realized to function as a novel core fragment for discotic liquid crystals. The central π-conjugated motif was prepared from dialkoxyiodobenzene via Sonagashira coupling followed by pentannulation and Scholl cyclodehydrogenation. The synthesized rubicene derivatives were found to be thermally stable and exhibit enantiotropic columnar mesophases. The columnar arrangement of these derivatives has been validated using polarising optical microscopy, differential scanning calorimetry & small-angle X-ray scattering.

Introduction

The chemistry of molecular assemblies known as supramolecular chemistry has been the hot scientific research topic since its discovery.[1] The self-assembly of molecules which is extremely important in materials science results from the interplay of different non-covalent interactions, such as van der Waals forces, ionic interactions, π-π interactions, dipolar and quadrupolar interactions, etc,.[2–4] The supramolecular assembly of organic materials has been the successful pathway for creating ordered nanostructures right from the molecular level to the macroscopic level.[5] Liquid crystalline systems are one of the epitomes of self-assembly phenomena. The liquid crystalline behavior of a molecule is owing to the presence of structural contrast. Vorlander, one of the well-known researcher in this field has proposed the possibility of voltas column like arrangements in plate-like systems.[6] The experimental report from Chandrasekhar and co-workers on the self-organizing benzene hexaesters has shown the light in a new direction of liquid crystal research i.e., discotics. The one-dimensional conductivity of discotic molecules in their columnar organization reflects the anisotropic nature of interactions of molecules within and between the columns.[7–11] The general structure of discogen involves the central core, the peripheral tails, and the linker connecting the above two units.[12] As a result, the qualities of the discogens produced will be a mix of all three elements. The chemistry, self-organization, and applications of discotic liquid crystals have been extensively summarized in many review articles.[13–19] Literature reports suggest that about sixty central cores have been exploited to prepare about 3000 discotic liquid crystals. Most of these are electron-rich (p-type semiconductors) materials. We have reported some of the new discotic liquid crystals, based on decacyclene,[20] tricycloquinazoline,[21] dibenzo[g,p]-chrysene,[22] phenanthro[a]- and phenanthro[b]-phenazines,[23,24] as novel central cores. As described above, the extensive π-π interactions between the cores facilitate the columnar organization. The larger aromatic core may facilitate the enhancement of columnar stability and influence their charge transport properties.[25–28] The literature reports suggest, most of the reported central cores are flat-shaped and exhibit liquid crystalline behavior on functionalization with flexible tails.[29–31] Contorted aromatic molecules have rarely been explored for liquid crystalline properties.

Contorted aromatic cores, which are curved π-conjugated systems have been of great interest due to their structural variety[32–35] and unique optical, electronic,[36] and photophysical properties[37,38] with excellent intermolecular charge transport.[39–42] The literature has reported that the co-assembly involving curved π-fused systems and electron-deficient systems display promising photovoltaic effect[43,44] and OLEDs.[45,46] The contorted π-conjugated molecules have been identified as ideal receptors of molecular recognition.[47] The co-assembled structures of these contorted systems with spherical molecules have been very well documented in the literature.[48] Helicenes are one of the best examples of the contorted core. Thomas J Katz and his colleagues explored the electro-optical characteristics of helicene-based liquid crystals that displayed the columnar hexagonal and discotic nematic mesophases.[49–52] The reports on the liquid crystalline contorted aromatic core are countable.[22,53–61] Rubicene ($C_{26}H_{14}$) is an aromatic polycyclic hydrocarbon consisting of five benzene rings with three linearly fused rings and one benzene ring at each diagonal side.[62,63] It is a planar molecule,[64] but the steric effect of substitution can lead to the contorted structure.[65] It has been extensively studied in the fields of optoelectronics, and organic lasers diodes.[66] Several research groups have synthesized rubicene derivatives[67] and polymers in recent years and shown their immense potential in organic thin-film transistors (OTFTs)[68] and polymers.[69–71] The molecular structure and unique photophysical properties of rubicene prompted us to explore it as a central core to prepare various novel DLCs. Here, we report the

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synthesis of a series of rubicene based discotic liquid crystals by varying the alkoxy chains in the periphery of the rubicene core as shown in Figure 1a. These derivatives self-assemble into columnar hexagonal mesophase. The columnar hexagonal arrangement of these derivatives can be attributed to π-π interactions between the rubicene cores.

Results and Discussion

The synthetic route of all the intermediates and final compounds is shown in Scheme 1. The disubstituted alkynes were prepared from dialkoxyiodobenzene via Sonogashira coupling using the reported literature.[72] The synthesis of prefinal (**6a–c**) and final compounds (**7a–c**) was achieved via palladium-catalyzed pentannulation followed by Scholl cyclodehydrogenation. Pentannulation of 9,10-dibromoanthracene with 1,2-bis(3,4-bis(alkoxy)phenyl) ethyne to give 1, 2, 6, 7-tetrakis(3,4-bis(alkoxy)phenyl) cyclopenta [hi] aceanthrylene. To close the fused aryl groups, we used Scholl cyclodehydrogenation, resulting in a satisfactory yield of 2, 3, 6, 7, 13, 14, 17, 18-octakis(alkoxy)-tetrabenzo [f, h, r, t]-rubicene (70 to 80%). The final compounds show the arrangement of the fused ring system with two [4] helicene-like and two [5] helicene-like fragments that resembled with previous report.[73] The purity and structure of all the compounds were characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF, and elemental analysis, which were in good consent with the molecular structure.

R = $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$
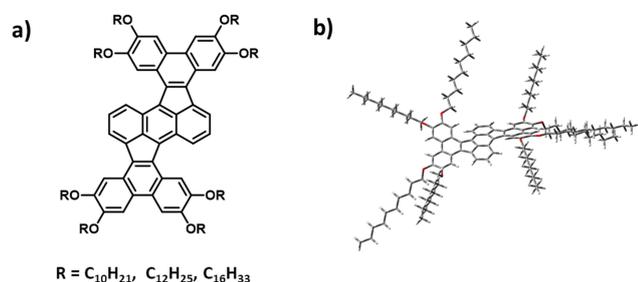
Figure 1. (a) Structure of rubicene derivatives **7a–c** (b) Energy minimized structure of **7a**.
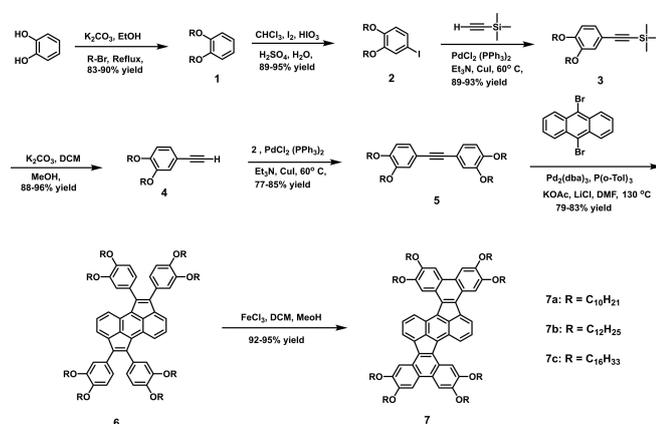
Scheme 1. Synthesis of rubicene derivatives.

We have studied the energy minimized structure of substituted rubicene using density functional theory (DFT) calculations done by GAUSSIAN-09 program at the Becke's three-parameter functional and Lee, Yang, and Parr correlation functional (DFTB3LYP) by using 6-31G (d, p) as basis set. The energy minimized structure is given in Figure 1b. The energy minimized structure had [4] helicene-like and [5] helicene-like fragments, and the splay angles that is, the dihedral angle (a-b-c-d) = A = 5.67, A′ = 3.42, and (e-f-g-h) = B = 41.07, B′ = 42.25 of **7a** were calculated from energy minimized structure. The top view and side view of energy minimized structure are shown in Figure S1. We concluded that the rubicene core has a twisted confirmation based on energy minimized structure deduced from DFT calculations. Further, we have visualized the contour plots of the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) as shown in Figure S2. The energy gap was found to be around 2.23 eV. The optical band gap (Eg) in eV was calculated to be 1.56 (according to the equation Eg = 1240/λ $_{onset}$, where λ $_{onset}$ was resolved as the intersection of the extrapolated tangent of the longest wavelength absorption peak and the x-axis).

The optical properties (absorption coefficient and emission) of **7a–c** recorded in chloroform solution (3×10^{-6} M) are shown in Figure 2. Absorption spectra shows broad absorption peaks extending from 200 nm to 800 nm with prominent absorption features at 263 nm, 295 nm, 360 nm, 400 nm, 545 nm, 676 nm and 739 nm. Emission spectra exhibited a less intense shoulder peaks at 468 nm and two intense vibrationally resolved peaks at 411 nm, and 434 nm for **7a** ($\lambda_{ex} = 360$ nm, $\varepsilon_{360nm} = 1.85 \times 10^4$ M^{-1} cm^{-1}), **7b** ($\lambda_{ex} = 360$ nm, $\varepsilon_{360nm} = 1.96 \times 10^4$ M^{-1} cm^{-1}), and **7c** ($\lambda_{ex} = 360$ nm, $\varepsilon_{360nm} = 2.22 \times 10^4$ M^{-1} cm^{-1}). The Stokes shift of 51 nm was observed between the absorption and emission maxima of **7a, 7b** and **7c**. The epsilon values of 7a-c are higher than that of compound 2b reported in the literature.[73] The detailed explanation for the same is given in the supporting information.

The thermal stability of all liquid crystalline compounds was investigated using thermal gravimetric analysis. All the three compounds were (**7a–c**) placed in a heat scan of 10 °C min^{-1} under a nitrogen atmosphere. Compounds **7a**, **7b**, and **7c** showed no weight loss up to 350 °C and the initial weight loss was observed at 370 °C. The thermal stability was studied till 800 °C, as shown in Figure S3. The decomposition temperature of these DLCs materials is much higher than the isotropic temperatures. It shows that these rubicene derivatives show excellent thermal stability.
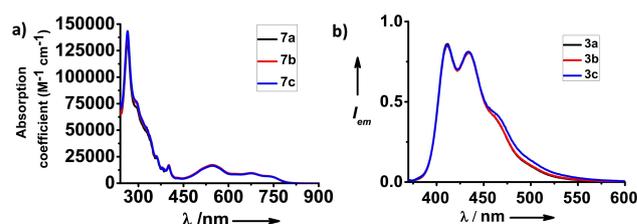
Figure 2. Absorption coefficient (a) and emission (b) spectra of 7a, 7b and 7c.

The monotropic mesomorphic properties of the compounds **6a–c** were determined using a combination of polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Under POM, upon heating, the compounds **6a–c** became isotropic at 81.5 °C, 91.0 °C, and 95.2 °C, respectively. While cooling from the isotropic phase, the mesophase displays typical mosaic textures of a columnar phase. The phase transition temperatures of the liquid crystalline compounds observed under POM were validated using DSC measurements. Upon heating, for compounds **6a** and **6c**, crystal-crystal transitions were observed at 48.2 °C and 53.7 °C and became isotropic at 79.0 °C and 92.0 °C respectively. The isotropic temperature of compound **6b** was found to be 84.8 °C. After cooling from the isotropic phase, the columnar phase transition appears for compounds **6a–c** at 64.9 °C, 61.8, and 51.8 °C, respectively. Compound **6c** crystallizes at 43.8 °C. However, **6a** and **6b** compounds remained in mesophase down to room temperature. The POM images, DSC thermograms, and phase transition temperatures of compounds **6a–c** are given in supporting information (Figure S6, S7, and Table S2).

The mesophase features of synthesized rubicene derivatives were investigated using polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffractometry. All the compounds exhibit enantiotropic mesomorphism with typical mosaic textures of a columnar phase under crossed polarizers upon cooling from the isotropic phase. The POM images of **7a**, **7b**, and **7c** recorded at 150.2 °C, 182 °C, and 120.2 °C, respectively, with the magnifications of 200X are shown in Figure 3. The polarized optical microscopy images revealed that these materials tend to orient columns vertically (homeotropically aligned) to the surface. The homeotropic alignment of the columns is essential for device applications.

The differential scanning calorimetry (DSC) analysis was carried out to validate the phase transitions observed through POM. The compounds **7a**, **7b**, and **7c** exhibited two endothermic phase transitions on heating. At lower temperatures, compound **7a** melts at 100.3 °C, **7b** melts at 77.0 °C and **7c** melts at 41.4 °C, corresponding to the crystal to mesophase transition. At higher temperatures, the isotropic (clearing) transitions were found to be around 207.7 °C, 189.1 °C, and 172.6 °C for **7a**, **7b**, and **7c**, respectively. Upon cooling from the isotropic liquid state to room temperature, compounds **7a**, **7b** and **7c** each exhibited a small exothermic peak at 207.7 °C, 184.7 °C and 170.9 °C, respectively which corresponds to the transitions from the isotropic liquid to the liquid crystalline phase. On further cooling, these materials crystallise at −26.1 °C (**7a**), 0.2 °C (**7b**), and 37.6 °C (**7c**). The DSC thermograms of **7c**

is given in Figure 4(a) and compounds **7a** and **7b** are given in Figure S4. The phase transition temperatures and corresponding enthalpy values of all compounds are shown in Table 1.

Further elucidation of the mesophases of **7a-c** was carried out using X-ray diffraction (XRD) studies. Diffraction patterns of **7a**, **7b** and **7c** compounds at a few temperatures are given in Figure 4(b) and Figure S5. All the compounds are found to exhibit the hexagonal columnar (Col$_h$) phase as evident from the presence of sharp peaks in the small-angle region, whose spacings (d) are in the ratio $1:1/\sqrt{3}:1/2:1/\sqrt{7}$. In the wide-angle region, the diffraction patterns show two broad peaks at d = 4.50 Å and d = 3.61 Å, corresponding to the molten alkyl chains and the core-core separation along the column axis, respectively. The lattice parameter (a) is 31.32 Å, 33.77 Å and 37.35 Å for **7a**, **7b** and **7c**, respectively. From the lattice parameter, the number of molecules spanning each column is estimated to be 1. Observed spacings in the mesophase of the three compounds are given in Table S1. A schematic of the molecular arrangement in columnar hexagonal mesophases deduced from the diffraction data is shown in Figure 5.
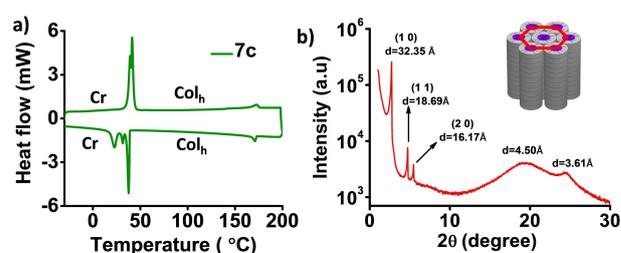
Figure 4. a) DSC thermogram of **7c** b) X-ray diffraction pattern of **7c** at 90 °C.

Table 1. Phase transition temperatures (in °C) and enthalpy changes (J g^{-1}) of **7a**, **7b** and **7c** in the time of heating and cooling.

Compound	Heating	Cooling
7a	Cr 100.3 (55.86) Col$_h$ 207.7 (2.56) I	I 207.7 (2.69) Col$_h$ −26.1 (2.44) Cr
7b	Cr 77.0 (42.40) Col$_h$ 189.1 (1.50) I	I 184.7 (1.44) Col$_h$ 0.2 (17.21) Cr
7c	Cr 41.4 (55.54) Col$_h$ 172.6 (2.94) I	I 170.9 (2.96) Col$_h$ 37.6 (48.70) Cr

Cr–Crystalline phase; Col$_h$–Columnar hexagonal phase; I–Isotropic.
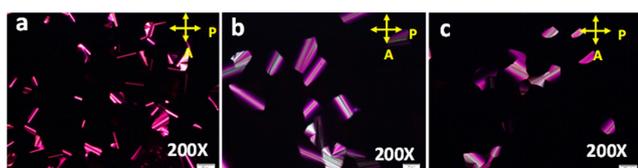
Figure 3. Mosaic textures were observed under POM for a compound a) **7a**; b) **7b**; and c) **7c**.
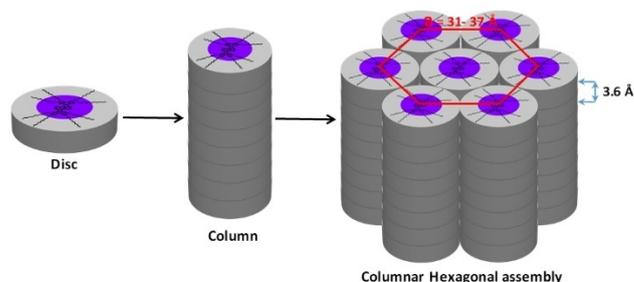
Figure 5. Schematic representation of the self-assembled columnar hexagonal mesophase in rubicene discotic mesogens.

Conclusion

In summary, we discovered that rubicene, a contorted molecule displays liquid crystalline properties upon appropriate peripheral substitution. Three new compounds have been prepared and they all show hexagonal columnar phase with a wide range of temperatures. Here our theoretical studies (Gaussian) suggested that rubicene derivatives employed twist structure where the difference in the splay angles results in a contorted arrangement. All three compounds reveal excellent thermal stability, and POM confirms the formation of the aligned structures. These aligned materials with interesting optical properties are highly attractive for various device applications such as photovoltaic solar cells, light emitting diodes, etc. The device fabrication and studies on the liquid crystalline nature of other rubicene derivatives are in progress.

Experimental Section

Essential Experimental Procedures/Data. ^1H and ^{13}C NMR spectra, DSC thermogram, XRD results, TGA spectra are given in supporting information.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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RESEARCH ARTICLE

A contorted polycyclic aromatic hydrocarbon, rubicene, was found to exhibit unusual self-assembling supramolecular properties, as evidenced from polarising optical microscopy, differential scanning calorimetry and small-angle X-ray scattering.
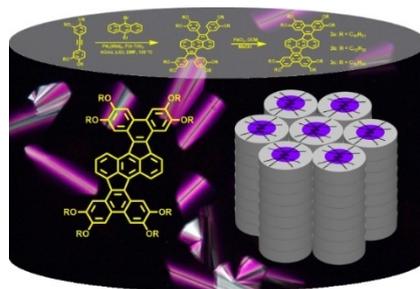
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1 – 6

Rubicene, an Unusual Contorted Core for Discotic Liquid Crystals