

Self-assembly into liquid crystalline complex through intermolecular hydrogen bonding

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Intermolecular hydrogen bonding by the selective recognition between a binary mixture of non-mesogenic unsymmetrically disubstituted 2-(4-nitrobenzylidene)-6-(4-hydroxybenzylidene) cyclohexanone and derivatives with mesogenic 4-decyloxybenzoic acid, yield novel molecular structures with thermotropic liquid crystalline characteristics.

Almost all the conventional thermotropic liquid crystals are made up of only covalent bonds^{1,2}, with the sole exception of dimers formed through intermolecular hydrogen bonding between carboxylic acids³, or monosaccharides⁴. Brienme reported the formation of liquid crystals through recognition dependent triple hydrogen bonding⁵. Kato reported several studies in which the thermotropic liquid crystalline temperature range was enhanced and new mesophases were induced due to intermolecular hydrogen bonding^{6,11}. A review by poles¹² and Yu reported hydrogen bonding induced ferroelectric liquid crystals¹³. In their studies, only carboxylic acids were used as hydrogen bond donors whereas several pyridine derivatives were tested as proton acceptors. More recently Kago reported the unfolding of thermotropic liquid crystalline phases through intermolecular hydrogen bonding between phenols and 4,4'-bipyridine under conditions wherein neither of the interacting components exhibit liquid crystalline character¹⁴. In this paper we communicate the synthesis of 2-(4-nitrobenzylidene)-6-(4-hydroxybenzylidene) cyclohexanone, a new potentially optical non-linear compound and its supramolecular hydrogen bonded complex with 4-decyloxy benzoic acid which displays enhanced thermotropic liquid crystalline phases.

Experimental Section

The compound, 2-(4-nitrobenzylidene)-6-(4-hydroxybenzylidene)cyclohexanone, was synthesized by the procedures established by us which are pre-

sented below¹⁷⁻¹⁹. 4-Decyloxy benzoic acid was procured from Aldrich Chemical Co., USA.

Preparation of 2-(4-nitrophenyl-1-hydroxymethylene) cyclohexanone

1-Trimethyl silyloxy-1-cyclohexene (4.5g) dissolved in dichloromethane (80 ml), was added dropwise to a mixture of 4-nitrobenzaldehyde (3.2g) and titanium tetrachloride (4.8g) in dry dichloromethane (10mL). The mixture was stirred at -70°C for 1h under inert atmosphere. Distilled water (10 mL) was added and the reactants were kept at ambient temperature for 30 min. The resulting mixture was extracted with dichloromethane and washed with water. The organic layer was dried over anhydrous sodium sulphate. Concentration of the organic layer and column chromatography on silica-gel using 8% acetone in pet. ether gave pure 2-(4-nitrophenyl-1-hydroxymethylene) cyclohexanone, yield: 5.9 g.

Preparation of 2-(4-nitrobenzylidene)-6-(4-hydroxybenzylidene) cyclohexanone

2-(4-Nitrophenyl-1-hydroxy methylene) cyclohexanone (1.5 g) in dry methanol (20 mL) and 4-hydroxybenzaldehyde (0.85 g) were mixed under nitrogen atmosphere. Few drops of boron trifluoride etherate were added and the resulting mixture refluxed for 12 h. Methanol was removed under reduced pressure and the resulting crude product was column chromatographed on silica gel using 12% acetone in pet. ether as eluent to get pure 2-(4-nitrophenyl-1-hydroxy methylene) cyclohexanone, yield:

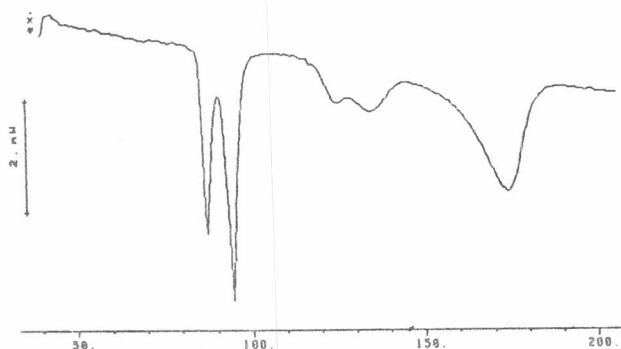
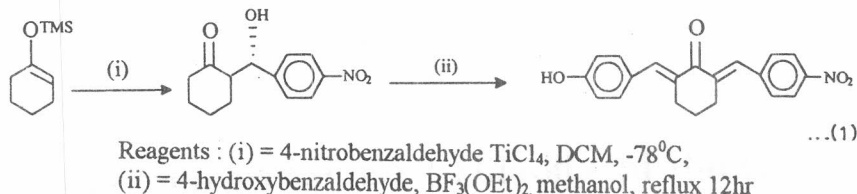


Fig. 1 -- DSC thermogram of hydrogen bonded complex (1:1)

2.1 g. The synthetic scheme is presented in Eq. (1) IR (KBr): 3340, 2928, 1682, 1616, 1592, 1506, 1442, 1412, 1254, 1225, 1188, 988, 834 cm^{-1} ^1H NMR 200 MHz (CDCl_3) 9.9 (s, 1H), 8.25(d,2H), 7.73(d,2H), 7.6(s,1H), 7.55(s,1H), 7.38(d,2H), 6.8(d,2H), 3-2.8(t,t, 4H), 1.75(m,2H); Mass : 335(70%), 334(75%), 318(100%), 306(20%), 288(40%), 278(41%), 260(20%), 232(30%), 215(25%), 202(22%), 185(30%), 165(30%), 157(35%), 145(40%), 131(70%), 115(100%), 107(78%), 103(50%), 89(44%), 77(81%), 65(40%), 55(50%).

Preparation of the binary mixture

2-(4-Nitrobenzylidene)-6-(4-hydroxybenzylidene)cyclohexanone (1mmol) and 4-decyloxy benzoic acid (1mmol) were dissolved in dry pyridine (5 mL) and slowly evaporated under reduced pressure to dryness.

Results and Discussion

The unsymmetrically disubstituted push-pull end functionalised (donor-acceptor), 2-(4-nitrobenzylidene)-6-(4-hydroxybenzylidene)cyclohexanone, do not display liquid crystalline phase [m.p = 203°C]. 4-Decyloxybenzoic acid is present only as a dimer due to hydrogen bonding and this manifests Smectic(S) and Nematic(N) phases [(S-N) 94-117, N-I) 117-143 $^\circ\text{C}$]^{15,16}. The supramolecular hydrogen

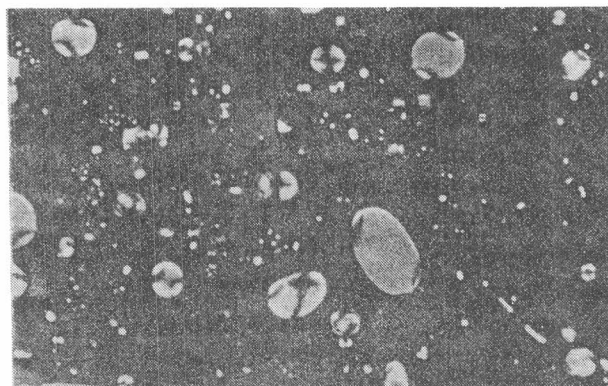
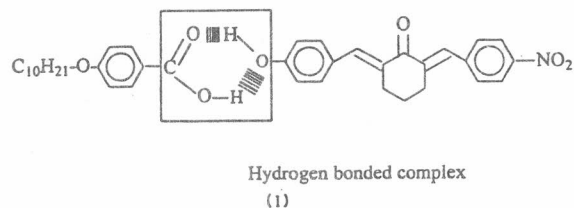


Fig. 2 -- Optical texture of hydrogen bonded complex at 175°C

bonded complex of 2-(4-nitrobenzylidene)-6-(4-hydroxybenzylidene)cyclohexanone and 4-decyloxybenzoic acid exhibits new thermotropic liquid crystalline phases, observed using differential scanning calorimetry and high temperature optical microscopy. Here, both components act as donor and acceptor for hydrogen bonding. The molecular self complementary system formed through intermolecular hydrogen bonds, results in novel liquid crystalline complex(A) (Structure I).



The DSC thermogram of complex A is presented in Fig1. Three first order transitions are noted in the DSC thermogram. All the above transitions observed in DSC in the first heating cycles remained unaltered in second heating cycle. Optical polarizing microscopic observations in this temperature range confirmed the transition temperatures and textural identifications indicated the emergence of a new Smectic A phase along with Smectic C phase. Simultaneously, the nematic range was enhanced (from 147- 175 $^\circ\text{C}$) (Fig.2). High temperature X-ray diffrac-

tion studies to make quantitative estimates and non-linear optical measurements to estimate the second order non-linear optical characteristics of the complex are currently underway.

The results are summarized below. The shift of OH stretching band in the binary mixture by 17 cm^{-1} to lower wavenumber from that in 2-(4-nitrobenzylidene) -6-(4-hydroxybenzylidene) cyclohexanone(phenolic compound), is a further conformation of the hydrogen bonded complexation.

Mesogenic 4-decyloxy benzoic acid (S-N)97-114 (N-I) 114-147 C

Non-mesogenic 2-(4-nitrobenzylidene) -6-(4-hydroxybenzylidene) cyclohexanone (m.p. 203 °C).

1:1 Hydrogen bonded (K-S) 80-90 (S-S) 90-95 (S-N) 96-120 (N-I) 120-175 C complex

K: Crystal, S: Smectic, N: Nematic, I: Isotropic

To conclude, we have demonstrated how hydrogen bonding may be used to assemble non-mesogenic 2-(4-nitrobenzylidene) -6-(4-hydroxybenzylidene) cyclohexanone rigid molecule as core into a well-defined complex, with a stable linear structure, that exhibits liquid crystalline behaviour. It is also visualized that other unsymmetrically disubstituted benzylidene phenols would generate new mesomorphic phases. Finally, we report a new hydrogen bonding system between acids and phenols, both of which can form complementary hydrogen bonding so as to accept as well as donate protons from each other. These supramolecularly hydrogen bonded complexes are being evaluated for NLO properties.

Acknowledgement

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References

- 1 Reintzer F, *Monatsh*, 9, 1988, 421.
- 2 Demus D, Demus H & Zashcke H, *Flussige Kristalle in Tabellen* (VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig), 1974.
- 3 Gray GW & Jones B, *J chem Soc*, 1953, 4179.
- 4 Grodby J W, *Mol Cryst, Liq Cryst*, 110, 1984, 205.
- 5 Brienne M J, Gabard J, Lehn J M & Stibor I, *J chem Soc Chem Commun*, 1989, 1869.
- 6 Kato T & Frechet J M J, *J Am chem Soc*, 111, 1989, 8533.
- 7 Kato T & Frechet J M J, *Macromolecules*, 22, 1989, 3818.
- 8 Kato T, Fujishima A & Frechet J M J, *Chem Lett*, 1990, 919.
- 9 Kato T, Wilson P G, Fugishima A & Frechet J M J, *Chem Lett*, 1990, 2003.
- 10 Kato T, Adachi H, Fugishima A & Frechet J M J, *Chem Lett*, 1992, 265.
- 11 Fukumasa M, Kato T, Urya T & Frechet J M J, *Chem Lett*, 1993, 65.
- 12 Poleos M & Tsiouves Dimitris, *Angew Chem Int Ed*, 34, 1995, 1696.
- 13 Yu L J, *Liquid crystals*, 14, 1993, 1303.
- 14 Kago T *et al*, *Chem Lett*, 1994, 2071.
- 15 Joesten M D & Sheed L J, *Hydrogen bonding* (Marcel Dekker) 1974.
- 16 Gray G W & Goodby J W G (Smectic Liquid Crystals).
- 17 Raju Satya V N & Ponrathnam S (Indian patent filed).
- 18 Raju Satya V N, Rajan C R, Ponrathnam S & Srinivasan K V, *Syn lett*, 3, 1996, 239.
- 19 Raju Satya V N, Sasidharan M, Srinivasan K V, Paul V & Kumar R, *J chem Soc, Chem Commun*, 2, 1996, 129.