Nonlinear Optical Properties of Some Cholesterol Based Liquid Crystals

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Nonlinear optical (NLO) properties of some azobenzene linked cholesterol derivatives have been described. The presence of donor and acceptor moieties imparts electrooptical and NLO properties to these molecules. Their NLO properties have been studied by electric field poling as well as hyper-Rayleigh scattering techniques. Few of these compounds exhibited NLO activity comparable to that of quartz.

Liquid crystals can be switched by relatively modest electric and magnetic fields and are hence particularly suited for applications in nonlinear optics[1-3] and optical switching[4] devices. The bulk susceptibilities of liquid crystals are related to the orientational order of the non-spherical molecules in the material, which results in anisotropic susceptibilities. Cholesteric liquid crystals are noncentrosymmetric and as such they might be expected to give rise to second harmonic generating (SHG) properties. However studies have shown that the SH signals originate from crystalline particles present in the sample, and the melting of these leads to disappearance of the SH signal.[5] Electric field induced SHG in cholesterics was reported recently by Ozaki *et al.*[1]

In this report, the nonlinear optical properties of some azobenzene-linked cholesterol derivatives (**1a-d**, **2a,b**, Chart 1) studied by electric field poling and hyper-Rayleigh scattering techniques are described. Donor-acceptor substituted azobenzenes are particularly suited for NLO applications because of their large dipole moments, polarizability, ease of chemical functionalization and stability.[6-10] Moreover, azobenzene derivatives have been shown to form dichroic liquid crystal displays and cholesteric dichroic mixtures have better display features.[11] Since photoisomerization of azobenzene is known to bring about transformations in the pitch of cholesteric mixtures such materials can be used in display systems that can be switched on and off using light.[12] The photochemical properties of these materials will be reported separately.[13] Photoinduced ionic conductivity and gelation properties of cholesterol linked azobenzene derivatives have been recently investigated.[14-16]

Cholesteryl derivative of azobenzenes were synthesised by refluxing equimolar amounts of the corresponding hydroxy-substituted azobenzene derivatives, cholesteryl chloroformate and pyridine in toluene. The product was purified by column chromatography over silica gel (100-200 mesh) and recrystallized form suitable solvents in each case. The compounds showed a cholesteric phase on heating. On cooling a focal conic texture of the smectic phase was observed in most cases. These properties are summarised in Table 1.

The bulk NLO coefficient (d_{33}) of these compounds in poled polymer films was carried out as described elsewhere.[17,18] Poly(methyl methacrylate) (n_D^{20}= 1.4900, d = 1.188, mw = 120000) used in the study was purchased from Aldrich Chemical Co. (USA). The polymer was dissolved along with 5 wt % of the compound in spectroscopic grade chloroform and filtered. The resulting solution was spin coated on soda-lime glass and dried at 60 °C for 6h followed by heating at an elevated temperature above the glass transition temperature (Tg) of the polymer for >2h to remove the solvent. Because of the anisotropic nature of liquid crystals, application of electric field generates a torque within the molecule, which can give rise to a reorientation of the director. Polar azo groups present in the molecule also tend to align in the electric field. The electric field poling was performed at a field strength of 3 kV. The d_{33} values of these compounds were obtained relative to a quartz plate (0.5 mm thickness, lc = 20.6 μm, d_{33} = 0.5 pm/V) and are listed in Table 1.

Table 1 also includes the β-values of these compounds estimated by the hyper-Rayleigh scattering technique [19,20] using the vertically polarized beam at 1064 nm from a Nd:YAG laser and the dipole moment values calculated theoretically.[21] There

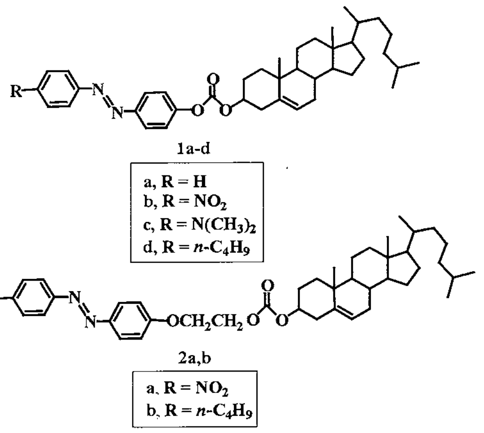

Chart 1

Table 1. Phase transition temperatures and NLO coefficients of the cholesterol derivatives

Compound	DM (azo compd.) (Debye units)	d_{33} (pm/V)	β_{HRS} (x 10^{-30} esu)	Phase transition Temperature[a] (°C)
1a	0.43	3.87	22	K 170 Ch 221 I I 220 (S_A) 120 K
1b	7.05	3.48	86	K 202 Ch 266 I I 242 (S_A) 186 K
1c	2.01	4.84	42	K 196 Ch 231 I
1d	0.20	3.10	36	K 140 Ch 254 I I 248 (S_A) 150 K
2a	7.03	7.74	96	K 216 Ch 264 I I 179 (S_A) 171 K
2b	3.26	1.35	41	K 137 Ch 250 I I 247 (S_A) 163 K

[a] K= crystalline; S_A= monotropic smectic A; Ch = cholesteric; I = isotropic phase

is a good correlation between the experimentally estimated β_{HRS} values with the dipole moment. The dipole moment of the molecules describes the efficacy of the electron donating and accepting properties of the substituents. The azo group is known to contribute more towards the hyperpolarizability of the molecules than the corresponding stilbene groups, making donor-acceptor substituted butadienes highly suitable for designing of NLO materials.[7] The d_{33} value of **2a** (7.74 pm/V) is comparable to that of quartz.

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