A new class of three dimensional D–π–A trigonal cryptand derivatives for second-order nonlinear optics†

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Synthesis, crystal structures, linear and nonlinear optical properties of tris D–π–A cryptand derivatives with C3 symmetry are reported. Three fold symmetry inherent in the cryptand molecules has been utilized for designing these molecules. Molecular nonlinearities have been measured by hyper-Rayleigh scattering (HRS) experiments. Among the compounds studied, L1 adopts non-centrosymmetric crystal structure. Compounds L1, L2, L3 and L4 show a measurable SHG powder signal. These molecules are more isotropic and have significantly higher melting points than the classical p-nitroaniline based dipolar NLO compounds, making them useful for further device applications. Besides, different acceptor groups can be attached to the cryptand molecules to modulate their NLO properties.

Introduction

The design and synthesis of organic molecules exhibiting second-order nonlinear optical (NLO) properties have been motivated by their tremendous potential for application in telecommunications, optical computing and data storage.1 Advantages of using organic molecules as NLO materials stem from the fact that they can be designed to optimize the desired NLO property. At the molecular level, compounds likely to exhibit large values of molecular hyperpolarizability, β must have polarizable electrons (e.g., π-electrons) spread over a large distance. It has been shown that extended π systems with terminal donor acceptor substituents exhibit large β values.2 However, a major problem associated with these traditional dipolar chromophores is the nonlinearity–transparency trade-off, such that the desirable increase in second-order polarizability is accompanied by a bathochromic shift3 of the electronic transition, leading to undesirable dispersion, fluorescence as well as re-absorption effects. Although β of a molecule is closely related to the bulk second-order nonlinearity, χ(2) in the solid state, large values of β do not necessarily lead to high χ(2). The large dipole moment in pNA like dipolar donor acceptor molecules make them pack in an anti-parallel fashion leading to centrosymmetry which is detrimental to SHG. Moreover, these 1D molecules, because of their anisotropic structure have small off-diagonal tensor components and produce polarized SH light.

Strategies have been evolved during the past decade to circumvent these drawbacks by extending the charge-transfer dimension from one to two or three.4 The idea is to arrange more symmetrical molecules in isotropic but non-centrosymmetric arrays to achieve large nonlinearity. Investigations on more isotropic molecules belonging to an octupolar group (a multipolar group, in general) such as the D3h group or the tetrahedral cubic group Td or to a quadrupolar group such as the orthorhombic 222 group have been made. For example, 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), the trigonal analogue of the dipolar pNA molecule has generated a lot of interest after it was found that TATB shows5 a powder efficiency of 3 × U in spite of having crystallized in a triclinic P1 centrosymmetric space group. This apparent contradiction was finally resolved when Martin et al.6 reported that structural modulation on the c-axis of the unit cell gives rise to SHG activity in TATB. The two and three-dimensional (2D and 3D) chromophores with D2h, D3h or Td symmetry, termed as octupolar molecules,7 offer several advantages: (i) they can be made more transparent via design, (ii) they can exhibit large second order nonlinearity at no cost to transparency, and (iii) they have greater probability of crystallization in a non-centrosymmetric space group due to the absence of dipolar interactions in the ground state. Several octupolar molecules have been designed and tested for second order NLO response. Noteworthy among them are TATB, crystal violet, tris(4-methoxyphenyl)cyclopropenium bromide8 and triazene derivatives.9

Molecular systems like calixarenes, cryptands and macrocycles form an integral part of supramolecular chemistry and are important for their wide ranging applications in chemistry, biochemistry and materials research. Except for calixarenes,9 however, these molecules remain mostly unexplored in the field of nonlinear optics. Only recently, a cyclophane derivative has been reported10 where sterically constrained π–π stacking has been exploited for fine-tuning linear and NLO properties in the bulk. Besides, these molecules have an added advantage, as they can accommodate cations, anions or neutral molecules in their 3D cavity and thus provide the potential for tuning/switching the NLO property by supramolecular interactions inside the cavity.11

Cryptands having a three-fold symmetry axis passing through the two bridgehead atoms can act as perfect skeletons for designing bulk material for second order NLO. We have recently reported a cryptand in which three π–A chromophores have been attached resulting in a significant bulk second-order NLO response.12 In the present work, we have used two different cryptand molecules L3a and L4m (the subscript o and m corresponds to ortho and meta substituted benzene units

†Electronic supplementary information (ESI) available: 400 MHz 1H NMR spectra, 100 MHz 13C NMR spectra, FAB-MS data of L1–L4, crystal structure packing diagrams for L4. See http://www.rsc.org/suppdata/jm/b2/b202770b/

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present in the three bridges of the cryptands), which are the donor (D) units and derivatized them with three different \( p \)-A units to have D NLO chromophores with three-fold symmetry. The different \( p \)-A units incorporated in the cryptand strands are 2,4-dinitrobenzene, 5-nitropyridine and 4-nitrobenzene. These molecules have been used as efficient \( p \)-A units in important NLO molecules like methyl 2-(2,4-dinitroanilino)-propanoate (MAP), 13 2-(\( N \)-prolinol)-5-nitropyridine (PNP) \(^{14} \) and \( N \)-(4-nitrophenyl)-(L)-prolinol (NPP).\(^ {15} \) We have used two different cryptand cores of varying rigidity in order to see whether this effect gets reciprocated in their molecular and bulk NLO properties. The crystal structures of the compounds have been determined and their nonlinear optical properties at the microscopic as well as at the macroscopic levels explored. Fig. 1 displays the investigated structures. The N atoms in the three bridges of the cryptand act as the donor units. In \( L_1 \), 2,4-dinitrobenzene is the \( p \)-A unit and one such unit is bonded to each nitrogen atom. In \( L_2 \), the \( p \)-A unit has been replaced by 5-nitropyridine and in \( L_3 \) by 4-nitrobenzene. Similarly, in \( L_4 \), \( L_5 \) and \( L_6 \) the \( p \)-A units remain the same except the donor N-atoms are now organized in a different cryptand whose cavity is much more rigid due to the presence of \( \text{meta} \)-substituted benzene units.

**Experimental section**

\( \text{o-N}_2\text{O}_3 \) and \( \text{m-N}_2\text{O}_3 \) were synthesized as reported\(^ {16,17} \) earlier from our laboratory. Reagent grade 2,4-dinitrochlorobenzene (SD Fine Chem., India), 2-chloro-5-nitropyridine (Lancaster) and 1-fluoro-4-nitrobenzene (Fluka) were used without further purification. All the solvents were freshly distilled prior to use and all reactions were carried out under \( \text{N}_2 \) atmosphere.

**Synthesis of the D-\( p \)-A molecules**

The D-\( p \)-A substituted cryptands were synthesised by derivatizing the three secondary nitrogen atoms of the cryptand (Scheme 1). The nitrogen atoms give the cryptand its donor (D) character and the \( p \)-A units were grafted by simple aromatic nucleophilic substitution (ArSN) reactions.\(^ {18} \) We systematically explore the different reaction conditions required for substituting the different \( p \)-A units. 

\( ^1 \text{H} \) NMR and \( ^{13} \text{C} \) NMR spectra were recorded on a JEOL JNM-LA400 FT (400 and 100 MHz respectively) instrument in CDCl\(_3\) with Me\(_4\)Si as the internal standard. FAB mass (positive ion) data were recorded on a JEOL SX 102/DA-6000 mass spectrometer using argon as the FAB gas at 6 kV and 10 mA with an accelerating voltage of 10 kV and the spectra were recorded at 298 K. Melting points were determined with an electrical melting point apparatus by PERFIT, India and were uncorrected. UV-visible spectra were recorded on a JASCO V-570 spectrophotometer in CHCl\(_3\) at 298 K. Analytical data were obtained either from the microanalysis laboratory at IIT Kanpur or from the Central Drug Research Institute, Lucknow, India.

**Synthesis**

**L\(_1\).** To a solution of the \( o \)-cryptand \( L_6 \) (0.56 g, 1 mmol) in dry EtOH (20 mL) was added anhydrous \( \text{K}_2\text{CO}_3 \) (0.44 g, 3.2 mmol) and the reaction mixture was stirred for 10 min. Subsequently, a solution of 2,4-dinitrochlorobenzene (0.65 g, 3.2 mmol) in dry EtOH (20 mL) was added dropwise in 30 minutes and the reaction mixture was allowed to reflux for 6 h. After cooling to RT, the solvent was removed under reduced pressure. The solid product obtained was repeatedly washed with water (6 \( \times \) 200 mL). The tri-substituted product was purified by recrystallization from MeCN to give a yellow crystalline solid. Yield 92\%; mp 215 °C; \( ^1 \text{H} \) NMR: 2.27 (t, \( J \sim 6.2 \text{ Hz} \), 6H), 2.80 (t, \( J \sim 6.2 \text{ Hz} \), 6H), 3.11 (t, \( J \sim 4.3 \text{ Hz} \), 6H), 4.13 (t, \( J \sim 4.3 \text{ Hz} \), 6H), 4.37 (s, 6H), 6.61 (d, \( J \sim 9.6 \text{ Hz} \), 3H), 6.71–6.98 (m, 12H), 7.93 (dd, \( J \sim 9.6 \text{ Hz} \), \( J \sim 2.7 \text{ Hz} \), 3H), 8.51 (s, 3H). \( ^{13} \text{C} \) NMR: 50.44, 51.52, 52.60, 55.34, 66.68, 111.16, 118.09, 121.13, 122.94, 123.44, 129.10, 129.45, 137.01, 137.15, 148.16 and 156.42 ppm. FAB-MS (\( m/z \)) 1058 (100\%); Anal. calcd. for \( \text{C}_5\text{H}_5\text{N}_3\text{O}_{11} \): C, 57.89; H, 4.86; N, 14.56. Found: C, 57.98; H, 4.97; N, 14.49%.

**L\(_2\).** To a solution of \( o \)-cryptand \( L_6 \) (0.56 g, 1 mmol) in dry EtOH (20 mL) of dry \( N \)-methyl-2-pyrrolidone (NMP) was added freshly...
distilled Et3N (0.32 g, 3.2 mmol). Subsequently, a solution of 2-chloro-5-nitropyridine (0.51 g, 3.2 mmol) in dry NMP (20 mL) was added dropwise in 45 minutes and the reaction mixture was allowed to stir at 70 °C for 36 h. It was then poured into cold water (250 mL). The pale yellow solid separated was collected by filtration and washed repeatedly with water (5 × 100 mL). The product was purified by recrystallization from acetone which afforded a brownish-red crystalline solid. Yield 91%; mp 220 °C; 1H NMR: δ 2.87 (s br, 6H), 3.08 (s br, 6H), 3.79 (s br, 6H), 4.28 (s br, 6H), 4.82 (s, 6H), 6.12 (m, 3H), 6.66–7.15 (m, 12H), 7.62 (s br, 3H), 8.82 (s, 3H). 13C NMR: 49.11, 52.66, 56.10, 58.51, 69.25, 114.10, 119.05, 123.30, 127.79, 130.01, 136.78, 138.12, 138.23, 148.28, and 160.11 ppm. FAB-MS (m/z) 1058 (100%); Anal. calcd. for C53H35N11O15: C, 57.89; H, 4.86; N, 14.56. Found: C, 57.84; H, 4.93; N, 14.43%.

L5. A procedure similar to that adopted for L4 was followed using Imn in place of Im. Yield 90%; mp 130 °C; 1H NMR: δ 2.65 (t, J = 6.2 Hz, 6H), 3.02 (t, J = 5.0 Hz, 6H), 3.61 (t, J = 6.2 Hz, 6H), 3.92 (t, J = 5.0 Hz, 6H), 4.67 (s, 6H), 6.32 (d, J = 5.5 Hz, 3H), 8.18 (d, J = 5.5 Hz, 3H), 8.97 (s, 3H). 13C NMR: 47.83, 52.88, 53.33, 56.87, 104.82, 113.29, 114.32, 119.94, 129.94, 132.95, 135.28, 137.98, 146.42, 159.70, and 160.44 ppm. FAB-MS (m/z): 926 (50%); Anal. calcd. for C48H43N11O9: C, 62.65; H, 5.55; N, 16.64. Found: C, 62.40; H, 5.59; N, 16.48%.

X-Ray crystallography. Single crystals could be grown by slow evaporation of the D–π–A cryptands at room temperature in pyridine in the case of L1 and MeCN in the cases of L3 and L4. All our efforts to have single crystals of the remaining compounds suitable for X-ray crystallography remained unsuccessful. In each case, large triangular crystals (up to ~4 mm each side) could be isolated. For the X-ray crystallographic work, a suitable crystal of each compound was mounted at the end of a glass fiber with epoxy cement. Cell parameters and reflection intensities were measured at 298 K on an Enraf–Nonius CAD-4 Mach diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The cell parameters were determined by least-squares fitting of 25 centered reflections in the range, 18 ≤ 2θ ≤ 28. The lattice parameters, data collection method, structure solution and refinement details are listed in Table 1. The structures of L3 and L4 were solved by the direct method using SIR92 and was analyzed using PLATON.

Table 1 Crystallographic data for the D–π–A cryptands L1, L3, and L4

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Weight</th>
<th>Temperature</th>
<th>Wavelength</th>
<th>System</th>
<th>Space group</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Volume (Å³)</th>
<th>Z</th>
<th>Density (calculated)</th>
<th>F(000)</th>
<th>Crystal size (Å)</th>
<th>Independent Reflections</th>
<th>Goodness-of-fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>(C51H51N11O15) 1/3</td>
<td>(C5H5N)</td>
<td>1084.40</td>
<td>293(2) K</td>
<td>0.71073 Å</td>
<td>Trigonal</td>
<td>16.63(5)</td>
<td>16.63(6)</td>
<td>16.00(3)</td>
<td>3832(14) Å³</td>
<td>3</td>
<td>1.431 Mg m⁻³</td>
<td>1704</td>
<td>0.18 × 0.2 × 0.2 mm³</td>
<td>3753</td>
<td>2.321</td>
</tr>
<tr>
<td>L3</td>
<td>(C53H57N9O9)</td>
<td>(C5H5N)</td>
<td>964.08</td>
<td>293(2) K</td>
<td>0.71069 Å</td>
<td>Orthorhombic</td>
<td>12.47(4) Å</td>
<td>21.974(5) Å</td>
<td>36.982(17) Å</td>
<td>10136(6) Å³</td>
<td>8</td>
<td>1.26 Mg m⁻³</td>
<td>4080</td>
<td>0.2 × 0.2 × 0.2 mm³</td>
<td>6604</td>
<td>1.016</td>
</tr>
<tr>
<td>L4</td>
<td>(C53H54N12O15)</td>
<td>(C5H5N)</td>
<td>1099.08</td>
<td>11798(2) Å</td>
<td>11.798(2) Å</td>
<td>Trigonal</td>
<td>11.973(2) Å</td>
<td>12.173(7) Å</td>
<td>19.707(6) Å</td>
<td>2682.0(19) Å³</td>
<td>2</td>
<td>1.361 Mg m⁻³</td>
<td>1152</td>
<td>0.3 × 0.2 × 0.2 mm³</td>
<td>7396</td>
<td>0.935</td>
</tr>
</tbody>
</table>

Photon fluorescence around 532 nm. Fig. 2 displays a plot of 

\[ \frac{I_2}{I_1} \] 

vs. number density of \( L_3 \) as well as ref. pNA. From the ratio of the two slopes in Fig. 2 the value of \( I_2 / I_1 \) was determined by the external reference method. Similarly \( \beta \) for other cryptands was obtained.

The powder SHG measurements were carried out using the Kurtz-Perry method\(^{12}\) utilizing a Q-switched Nd:YAG laser (Spectra Physics, DCR-11, 8 ns) beam. The beam was split into two by a beam splitter and the reflected beam passed through the powder sample. The transmitted beam was focused by a biconvex lens (f.l. 10 cm) to a spot 5 cm away after passing through the glass cell containing the sample. The scattered light in the perpendicular direction was collected by a UV-Visible sensitive photomultiplier tube (PMT). A monochromator (Czerny Turner 0.25 m) was used for wavelength discrimination and no other collection optics were employed. The input power was monitored using a power meter. All data were collected at laser powers \( \leq 24 \text{ mJ pulse}^{-1} \) which is below the threshold for stimulated Raman, self-focusing/self-defocusing, Brillouin scattering and dielectric breakdown. The experimental set-up was first standardized by measuring the \( \beta \) value for pNA in CHCl\(_3\) by the external reference method\(^{22}\) and a value of \( 18 \times 10^{-30} \text{ esu} \) was obtained which was close to the reported value for this compound.\(^{21b}\) The monochromator was scanned at intervals of 2 nm to find if the signal at the second harmonic wavelength has any contribution from two photon fluorescence. The signal then passed through an interference filter (532 nm, 4 nm bandwidth) and was detected by a photodiode. Urea was used for calibrating the SHG signal.

NLO measurements. Second harmonic measurements in solution were carried out by the HRS technique. In HRS experiments, the fundamental (1064 nm) of a Q-switched Nd:YAG laser (Spectra Physics, DCR-3G, 8 ns) beam was focused by a biconvex lens (f.l. 10 cm) to a spot 5 cm away after passing through the glass cell containing the sample. The scattered light in the perpendicular direction was collected by a UV-Visible sensitive photomultiplier tube (PMT). A monochromator (Czerny Turner 0.25 m) was used for wavelength discrimination and no other collection optics were employed. The input power was monitored using a power meter. All data were collected at laser powers \( \leq 24 \text{ mJ pulse}^{-1} \) which is below the threshold for stimulated Raman, self-focusing/self-defocusing, Brillouin scattering and dielectric breakdown. The experimental set-up was first standardized by measuring the \( \beta \) value for pNA in CHCl\(_3\) by the external reference method\(^{22}\) and a value of \( 18 \times 10^{-30} \text{ esu} \) was obtained which was close to the reported value for this compound.\(^{21b}\) The monochromator was scanned at intervals of 2 nm to find if the signal at the second harmonic wavelength has any contribution from two photon fluorescence. The signal then passed through an interference filter (532 nm, 4 nm bandwidth) and was detected by a photodiode. Urea was used for calibrating the SHG signal.

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Results and discussion

Molecular and crystal structures

As the cryptand core inherits a 3-fold axis of symmetry, there arises two possible pathways (Fig. 3) by which these molecules can crystallize: a planar centrosymmetric hexagonal lattice formed by the interactions between identical groups resulting in SHG inactive molecules or a non-centrosymmetric trigonal lattice formed by the interaction between different groups showing SHG activity. Single crystals of \( L_1 \) adopt a trigonal space group while \( L_3 \) and \( L_4 \) crystallize in orthorhombic and triclinic space groups, respectively. All of the three crystal structures maintain the molecular 3-fold axis of symmetry passing through the bridgehead N atoms. Both the \( ^1H \) and \( ^13C \) NMR data are consistent with a 3-fold symmetry of these molecules.

\( L_1 \). This tris \( \pi - \pi \) A cryptand crystallizes\(^{12}\) in a unique non-centrosymmetric trigonal space group \( P3 \). In the asymmetric unit cell, three strands are present and they generate a triad involving A, B and C molecules with the \( C_3 \) symmetry axis passing through the centre of the triad (Fig. 4). The bridgehead nitrogens maintain an endo-endo conformation. The molecule A has a remarkably short distance 4.588(8) \( \text{Å} \) between the bridgehead N atoms, while the same in molecules B and C are...
6.672(12) Å and 6.384(12) Å, respectively. Thus, while in A, the bridgehead nitrogens are pushed inward significantly, they are pushed outward slightly compared to the underivatized cryptand L\textsubscript{0} (6.249 Å).\textsuperscript{24} This shows that the parent cryptand is quite flexible which is not unprecedented for these type of molecules.\textsuperscript{25}

The average distance of the N(amino)–C(benzene) bond is 1.376 Å which is considerably shorter than C–N single bond distance of ~1.45 Å confirming that the amino nitrogen of the cryptand moiety is conjugated with the aromatic ring of the acceptor. The other bond distances and angles in L\textsubscript{1} are within normal literature values.\textsuperscript{13,24} The intramolecular interactions vary in the D–π–A cryptand molecules A, B and C.

Molecule A exhibits two kinds of weak intramolecular H-bonding interactions (Fig. 5a): (i) a C–H···O hydrogen bond involving the C atom (C2a), the H atom (H021a) and the O (O5a) of the phenyl ring with a C–O distance of 3.244 Å. (ii) a C–H···π interaction involving C atom (C13a) of the phenyl ring, H atom (H13a) and the centroid of the dinitro substituted phenyl ring (Ct01) of the symmetry related strand with a C–π distance of 3.850 Å.

Molecule B shows a C–H···π interaction similar to that observed in molecule A (Fig. 5b). It involves the C atom (C13b) of the phenyl ring, H atom (H13b) and the centroid of the dinitro substituted benzene ring (Ct01) of the symmetry related strand with a C–π distance of 3.916 Å.

Molecule C shows an intramolecular C–H···O interaction (Fig. 5c) involving C atom (C2c), H atom (H022c) and O atom (O1c) of the \textit{ortho}-nitro group with a C–O distance of 2.978 Å. The phenyl and the dinitro substituted benzene rings are far apart and thus are not involved in the C–H···π interactions found in molecules A and B.

It is to be noted that only $\frac{1}{3}$ of each molecule A, B and C are in the asymmetric unit. In effect, therefore, the molecule A has six intramolecular (three C–H···O and three C–H···π) interactions, molecule B has three C–H···π interactions, while molecule C shows three intramolecular C–H···O interactions. These interaction distances are collected in Table 2.

Two different kinds of intermolecular H-bonding interactions are present amongst A, B and C leading to the trigonal network. Molecules A and B are held together by one C–H···O interaction involving C atom (C8b) of the dinitro substituted benzene ring, H atom (H08b) of the molecule B and O atom (O3a) of the \textit{ortho}-nitro group of molecule A having a C–O distance of 3.279 Å (Fig. 6). Likewise, molecules B and C interact by forming another C–H···O hydrogen bond involving benzyl carbon (C9b), H atom (H091b) and oxygen atom (O4c) of the \textit{ortho}-nitro group with a C–O distance of 3.285 Å. Molecules B and C also interact in an edge-to-face manner forming a C–H···π bond with a distance of 3.583 Å. These distances for the intermolecular interactions are also given in Table 2.

Table 2 Geometrical parameters for various interactions in the molecules A, B and C of L\textsubscript{1}.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Interaction (Intra)</th>
<th>D/Å</th>
<th>d/Å</th>
<th>θ/deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C(2a)–H(021a)···O(5a)</td>
<td>3.244</td>
<td>2.395</td>
<td>148.57</td>
</tr>
<tr>
<td></td>
<td>C(13a)–H(13a)···Ct01</td>
<td>3.850</td>
<td>3.363</td>
<td>115.02</td>
</tr>
<tr>
<td>B</td>
<td>C(13b)–H(13b)···Ct01</td>
<td>3.916</td>
<td>3.432</td>
<td>114.98</td>
</tr>
<tr>
<td></td>
<td>C(2c)–H(022c)···O(1c)</td>
<td>2.978</td>
<td>2.195</td>
<td>138.97</td>
</tr>
<tr>
<td>A, B and C</td>
<td>C(8b)–H(08b)···O(3a)</td>
<td>3.279</td>
<td>2.540</td>
<td>134.84</td>
</tr>
<tr>
<td></td>
<td>C(9b)–H(091b)···O(4c)</td>
<td>3.285</td>
<td>2.568</td>
<td>132.45</td>
</tr>
<tr>
<td></td>
<td>C(13b)–H(13b)···Ct01</td>
<td>3.583</td>
<td>3.000</td>
<td>122.26</td>
</tr>
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</table>

L\textsubscript{3}. This molecule crystallizes in the orthorhombic space group \textit{Pbca}. A perspective view of the molecule is shown in (Fig. 7). Like in the case of A, B and C molecules in L\textsubscript{1}, this...
A cryptand maintains an endo–endo conformation with a distance of 6.587 Å between the bridgehead N atoms which is slightly longer than that of Lo. All the bond distances and angles are within normal literature values. The intramolecular interactions in this D–p–A cryptand involve two C–H⋯N and one C–H⋯O bond across the 3D cavity of the cryptand (Fig. 7). One of the C–H⋯N hydrogen bonds is formed between the C atom (C9) of the benzylic amino group, H atom (H9b) and amino N atom (N5) with a C–N distance of 3.890 Å. The second C–H⋯N hydrogen bonding interaction involves the atoms C43, H43b, and N2, with a C–N distance of 3.563 Å. The C–H⋯O hydrogen bond is formed between the C atom (C9) of the benzylic amino group, H atom (H9a) and oxygen atom (O9) of the phenyl ring with a distance of 3.871 Å. The intramolecular distances are listed in Table 3.

This molecule does not show any significant intermolecular interactions in the crystal lattice.

The structure of this molecule could be solved in both the triclinic space groups, P1 and P1. However, in the non-centrosymmetric space group P1, the structure did not refine well and many N and O atoms gave negative temperature factors when refined anisotropically. In spite of the fact that this molecule is SHG active, we could refine the structure well in the triclinic centrosymmetric space group. An endo–endo conformation is maintained by this molecule as well with a distance of 8.656(11) Å between the bridgehead N atoms (Fig. 8) which is significantly shorter compared to that in Lm (9.904 Å). All the bond distances and angles are within normal literature values.

### Table 3 Geometrical parameters for various interactions in the structure L3 and L4

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Interaction (Intra)</th>
<th>D/Å</th>
<th>d/Å</th>
<th>θ/deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>L3</td>
<td>C(9)–H(9b)⋯N(5)</td>
<td>3.890</td>
<td>2.929</td>
<td>170.69</td>
</tr>
<tr>
<td></td>
<td>C(43)–H(43b)⋯N(2)</td>
<td>3.563</td>
<td>2.629</td>
<td>161.84</td>
</tr>
<tr>
<td></td>
<td>C(9)–H(9a)⋯O(9)</td>
<td>3.871</td>
<td>2.907</td>
<td>173.15</td>
</tr>
</tbody>
</table>

| L4       | C(26)–H(261)⋯N(1) | 3.165 | 2.419 | 136.89 |
|          | C(26)–H(26a)⋯N(1) | 3.180 | 2.431 | 134.00 |
|          | C(18)–H(182)⋯O(6) | 3.128 | 2.413 | 131.87 |
|          | C(18)–H(18a)⋯O(6) | 3.180 | 2.447 | 132.11 |

| L4       | C(5)–H(05)⋯O(13) | 3.409 | 2.539 | 153.88 |
|          | C(5)–H(5)⋯O(13)  | 3.400 | 2.507 | 161.44 |
|          | C(43)–H(431)⋯O(12) | 3.408 | 2.583 | 148.58 |
|          | C(43)–H(43b)⋯O(12) | 3.430 | 2.572 | 148.18 |

D is the distance between C and the acceptor (O, N, or ring centroid); d is the distance between H and the acceptor (O, N, or ring centroid); θ is the angle at H in C–H⋯A (A=O, N, or ring centroid); Ct is the centroid of the aromatic ring acting as the C–H acceptor; For π⋯π interactions, D is the perpendicular stacking distance.
C5' form two C–H…O hydrogen bonds with the oxygen atoms O13' and O13 respectively with a C–O distance of 3.409 Å. The third C–H…O hydrogen bond is formed by the interaction of the benzylic carbon (C43) and the oxygen of the nitro group (O12') of the neighbouring molecule with a C–O distance of 3.408 Å. These interaction distances are collected in Table 3.

### Linear and nonlinear optical properties

The UV-visible spectral data of compounds L1–L6 were recorded in CHCl3 and are displayed in Fig. 10. All the spectra are characterized by an intense charge-transfer absorption in the near ultraviolet. The molecules L1, L2 and L3 have their charge-transfer band red-shifted by 6–10 nm and are more intense compared to L4, L5 and L6. This can be explained by the increase of the inductive donor effect of the nitroaniline (pNA) molecule, with $\beta_0 = 10 \times 10^{-30}$ esu as measured in CHCl3, whereas, L3 has a slightly higher value (1.2 times) with respect to pNA. The results for the D–π–A meta-cryptand derivatives are interesting in a number of ways. The second order polarizability is greater than that of pNA or ortho-cryptands. In addition, in meta-cryptand L4, the charge-transfer band is blue-shifted compared to the D–π–A ortho-cryptand, L1 leading to a greater transparency. Moreover, the second order polarizability also increases. Similarly, L5 has a higher β compared to the corresponding ortho D–π–A cryptand i.e. L4 and better transparency. L6 has the highest β value in the series and the corresponding static hyperpolarizability value is almost double that of the classical pNA molecule.

The greater transparency as well as hyperpolarizability of the group L4–L6 compared to L1–L3 could be attributed to greater rigidity of the Lm framework compared to that of Ll as seen from the molecular conformation in the solid state. The relatively high β value obtained for L4 while maintaining an excellent transparency in the visible range points out its particular relevance in NLO applications. Thus, a favourable orientation of these chromophores across the cryptand core can be effectively utilized for designing such systems with a large SHG response, although the C1 symmetric chromophore subunits remain unconjugated.

Powder second-harmonic generation (SHG) measurements were carried out on X-ray crystallographically characterized L1–L4 and L6 in order to evaluate their potential as second order NLO materials. Compound L1 exhibited a SHG powder signal which was 0.6 times that of urea in conformity with its acenitic crystallization. Powder samples of L2 also showed a SHG signal of 1.0 times that of urea. These efficiencies are certainly better than those reported for the triaryloxy triazines by Thalladi et al.26 where similar H-bonding and stacking interactions are operational to stabilise the three-dimensional structures.

It is important to note that L4 despite being crystallized in a centrosymmetric space group, shows an SHG powder signal efficiency of 0.05 times that of urea. This points to the presence of some defect sites in the crystal. Although the molecules crystallize in a centrosymmetric space group, there may be regions or zones having defects. In fact, such defects are known in organic molecules and they play a major role in determining the outcome of a photochemical dimerization reaction in the solid state.25 In fact, the X-ray crystallographic data pertaining to the macroscopic ordered region of the crystal say nothing about the molecular packing in the defect region. L5 is stabilized by the H-bonding and stacking interactions in a different fashion compared to the other two cases. This perhaps, would explain why it adopted a centrosymmetric packing. Further experiments are necessary to determine the exact nature of the defects in L5. Compound L4 also shows a SHG powder signal of 0.36 times that of urea although it crystallizes in a centrosymmetric P1 space group. This could be as a result of polymorphism of the crystalline structure or due to a slight difference in the respective molecular orientations within the structural unit cell with respect to a fully centrosymmetric case. This result is not unprecedented and was earlier observed in the case of TATB which also crystallizes in a P1 space group and shows substantial SHG activity.5,6,60 Electron diffraction experiments on TATB indicate60 that the structural modulation on the c-axis gives rise to the resultant SHG value. Similar

| Table 4 Results of hyper-Rayleigh scattering measurements on compounds L1–L6 at 1064 nm |
|------------------|---------|---------|---------|---------|---------|---------|
|                  | pNA     | L1      | L2      | L3      | L4      | L5      | L6      |
| $\lambda_{max}$ | 347     | 370     | 376     | 390     | 364     | 368     | 380     |
| $\beta \times 10^{-30}$ esu | 18.0 | 16.1 | 16.1 | 19.0 | 20 22 27 |
| $\beta_0 \times 10^{-30}$ esu | 10 | 10.6 | 10.5 | 12.2 | 14 15 18 |

Fig. 9 View of the molecules in L4 and various intermolecular interactions present shown by dashed lines. H atoms and solvent molecules have been removed for clarity.

Fig. 10 UV spectra of L1–L6 (1 × 10⁻⁵ M) in CHCl3.
electron diffraction studies on L₄ can throw light on the origin of the observed SHG value but that will be another study.

**Conclusion**

We have shown that bulk second harmonic materials can be built around the three-fold symmetry of cryptand molecules, with strikingly high melting points, exploiting weak molecular forces. However, intermolecular interaction is necessary for a non-centrosymmetric packing in the crystal. The search for an optimal transparency–efficiency trade-off for optically non-linear molecules has led to different approaches via molecular engineering. Cryptand molecules with their inherent three-fold symmetry and three secondary nitrogen atoms are ideal for further derivatization which can provide an easy way to engineer new molecular systems for NLO molecules and materials. Besides, the cavity of a cryptand can be tailored to accept a metal ion which can offer possibilities for tuning/switching capabilities in NLO materials. Research along these lines is in progress in our laboratory.

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**References**