CHAPTER 2

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF LIGANDS

2.1 Introduction
2.2 Ligands used in present study (L_{1-10}^{1-10}HH')
2.3 Methods of preparation
2.4 Spectroscopic characterization.
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References
2.1 Introduction

The development of organotin(IV) carboxylate chemistry is highly dependent on a facile synthetic access to the ligands. The ligands used herein are of two types where the carboxylic acid group placed (i) in ortho- position e.g. 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]- and 2-[(E)-4-hydroxy-3-[(E)-4-(aryl)iminomethyl]phenyldiazenyl]- benzoic acids and (ii) in para- position e.g. 4-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]- and 4-[(E)-4-hydroxy-3-[(E)-4-(aryl)iminomethyl]phenyl diazenyl]- benzoic acids. The ligands, 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]- and 4-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]-benzoic acids were prepared by usual diazo-coupling reactions which contain an azo group. The aromatic monoamines react with 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid to form products, such as 2-[(E)-4-hydroxy-3-[(E)-4-(aryl)iminomethyl]phenyl diazenyl] benzoic acid, which contain both azo and Schiff base (i.e. imino) linkages. A similar azo-Schiff base organic compound, namely N-p-methoxybenzylidene-p-phenylazoaniline, is a mesogen and exhibits a nematic liquid-crystal phase; its X-ray structure has also been determined recently [1]. In addition, structures of two similar molecules containing meta azo and imine substituents, also exhibiting liquid crystalline properties, have recently been determined [2,3]. The potential usefulness of such polyaromatic systems has prompted us to investigate the reactivity towards organotin(IV) moiety. However, this family of ligands await characterization as mesogens and the determination of other essential features such as thermotropic, lyotropic and macroscopic (e.g. optical) properties. It should be mentioned here that the condensation products of aromatic monoamines with 4-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid is not possible owing to the insolubility of the later in common organic solvents and water. The ligand frameworks \( (L_1^H\cdot H^\cdot L_2^H) \) were generated \textit{in situ} during the reactions of \( R_SnL^H (R = \text{"Bu or Ph}) \) with the appropriate \( p \)-substituted anilines (refer to Chapter 4).

The ligands used in the present study are described in section 2.2.
2.2 Ligands used in present study ($L^{\text{1-10HH'}}$)

The ligands and their systematic names are given in Table 2.1.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Name</th>
<th>Abbreviation$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>2-[(E)-2-(3-formyl-4-hydroxy-phenyl)-1-diazenyl] benzoic acid</td>
<td>$L^1\text{HH'}$</td>
</tr>
<tr>
<td><img src="image2.png" alt="Image" /></td>
<td>2-[(E)-4-hydroxy-3-[(E)-4-methyl-phenyliminomethyl]phenyldiazenyl]-benzoic acid</td>
<td>$L^2\text{HH'}$</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td>2-[(E)-4-hydroxy-3-[(E)-4-bromo-phenyliminomethyl]phenyldiazenyl]-benzoic acid</td>
<td>$L^3\text{HH'}$</td>
</tr>
<tr>
<td><img src="image4.png" alt="Image" /></td>
<td>2-[(E)-4-hydroxy-3-[(E)-4-chloro-phenyliminomethyl]phenyldiazenyl]-benzoic acid</td>
<td>$L^4\text{HH'}$</td>
</tr>
</tbody>
</table>
(b) Ligands containing a para-carboxylic acid group

<table>
<thead>
<tr>
<th>Ligand Structure</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>2-{(E)-4-hydroxy-3-[(E)-4-methoxyphenyliminomethyl]phenyldiazenyl}-benzoic acid</td>
<td>(L^5_{HH'})</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>2-{(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl}benzoic acid</td>
<td>(L^6_{HH'})</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>4-{(E)-4-hydroxy-3-[(E)-4-methylphenyliminomethyl]phenyldiazenyl}-benzoic acid</td>
<td>(L^7_{HH'})</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>4-{(E)-4-hydroxy-3-[(E)-4-bromo phenyliminomethyl]phenyldiazenyl}-benzoic acid</td>
<td>(L^8_{HH'})</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>4-{(E)-4-hydroxy-3-[(E)-4-chloro phenyliminomethyl]phenyldiazenyl}-benzoic acid</td>
<td>(L^9_{HH'})</td>
</tr>
<tr>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>4-{(E)-4-hydroxy-3-[(E)-4-methoxy phenyliminomethyl]phenyldiazenyl}-benzoic acid</td>
<td>(L^{10}_{HH'})</td>
</tr>
</tbody>
</table>

\(H\) and \(H'\) represent hydroxy and carboxylic acid \(H\) atoms, respectively.

\(The\ ligands, L'_{HH'}-L^{10}_{HH'}\ were generated \textit{in situ} (refer to Chapter 4).\)
2.3 Synthesis of ligands

The 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (L\textsuperscript{1}HH') was prepared by the diazo-coupling reaction between the anthranilic acid and salicylaldehyde in alkaline medium under cold conditions by the method described in our earlier report [4]. The 2-{(E)-4-hydroxy-3-[(E)-4-(aryl)iminomethyl]phenyldiazenyl}benzoic acids (L\textsuperscript{2-5}HH') were prepared by condensation of L\textsuperscript{1}HH' with appropriate p-substituted anilines in anhydrous toluene-ethanol mixture. The 4-{(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (L\textsuperscript{6}HH') was prepared by the diazo-coupling reaction between the p-aminobenzoic acid and salicylaldehyde in an alkaline medium under cold conditions. On the other hand, the 4-{(E)-4-hydroxy-3-[(E)-4-(aryl)iminomethyl]phenyldiazenyl}benzoic acids (L\textsuperscript{7-10}HH') could not be prepared by the condensation of L\textsuperscript{1}HH' with appropriate the substituted anilines owing to the insolubility of the pre-ligand in common organic solvents and water. However, the deprotonated L\textsuperscript{7-10}HH' frameworks were generated during the reactions of R\textsubscript{3}SnL\textsuperscript{6}H (R = "Bu or Ph) with the appropriate p-substituted anilines (refer to Chapter 4). The ligand frameworks are shown in Table 2.1, along with their abbreviations. The details of their synthesis and characterization data are presented in section 2.6 while their spectroscopic data are summarized below.

2.4 Spectroscopic characterization

The IR spectra of the ligands (L\textsuperscript{1}HH'-L\textsuperscript{10}HH') are very complex due to the presence of a large number of vibrational modes due to ring stretch, deformation, in-plane and out-of-plane ring and CH deformations. However, these modes are of little value in the understanding of the structure of the ligands. Valuable information can, however, be obtained from the frequencies of carboxylate stretch, Ar-OH (C-O vibration involving hydroxyl group of salicylaldehyde moiety), the N=N and C=N stretches. Unfortunately, even these modes could not be identified with certainty in all the cases because of the presence of the complex nature of the vibrations in the region where these modes are expected.

The diagnostically important infrared absorption frequencies for the carboxylate antisymmetric \(\nu_{\text{asym}}(\text{OCO})\) stretching vibration for the L\textsuperscript{1}HH' have been detected at 1733 cm\(^{-1}\), around the 1725 cm\(^{-1}\) region for L\textsuperscript{2-5}HH' and 1679 cm\(^{-1}\) for L\textsuperscript{6}HH'. The assignment of the
symmetric $[\nu_{\text{sym}}(\text{OCO})]$ stretching vibration band could not be made owing to the complex pattern of the spectra.

The $^1$H- and $^{13}$C- NMR signals of L$^1$HH' [4] and L$^6$HH' were assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HMQC) and heteronuclear multiple-bond connectivities (HMBC) experiments using gradient coherence selection and also by examining the spin-spin splitting pattern of the signals. The conclusions drawn from the L$^1$HH' assignments were then subsequently extrapolated to the other ligands (L$^2$-L$^5$HH') owing to their data similarity. The $^1$H-NMR integration values were completely consistent with the formulation of the products. The number of $^{13}$C signals corresponds with the proposed formulations of the products. The basic ligand framework is shown in Figs. 2.1-2.3 along with the abbreviations and numbering schemes for spectroscopic analyses. The detailed spectral features are shown below:

Fig. 2.1 Generic structure of the ligand, L$^1$HH'

Fig. 2.2 Generic structure of the ligand, L$^1$HH'-L$^6$HH'

[Abbreviations: L$^2$HH': $X = 4$-CH$_3$; L$^3$HH': 4-Br, L$^4$HH': 4-Cl, L$^5$HH': 4-OCH$_3$]
2.4.1 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (L\(^{1} HH'\)) [4]

IR (cm\(^{-1}\)): 1733 \(\nu(OCO)_{asym}\). \(^{1}\)H-NMR (Pyridine-\(d_5\) / 600 MHz); \(\delta_H\): 7.15 [d, 8.8 Hz, 1H, (A) H5], 7.52 [dt, 1.5, 7.7 Hz, 1H, (B) H5], 7.58 [dt, 1.5, 7.7 Hz, 1H, (B) H4], 7.80 [dd, 1.5, 7.7 Hz, 1H, (B) H6], 8.21 [dd, 1.5, 7.7 Hz, 1H, (B) H3], 8.29 [dd, 2.6, 8.8 Hz, 1H, (A) H6], 8.67 [d, 2.6 Hz, 1H, (A) H2], 10.64 [s, 1H, (A) H3] and 11.51 [bs, 2H, (B) H7 and (A) H4] ppm. \(^{13}\)C-NMR (Pyridine-\(d_5\)/150 MHz); \(\delta_C\): 118.1 [(B) C6], 118.5 [(A) C5], 127.0 [(A) C2], 128.5 [(A) C3], 129.7 [(A) C6], 129.9 [(B) C5], 130.0 [(B) C3] 131.4 [(B) C4], 132.1 [(B) C1], 145.9 [(A) C4], 150.9 [(B) C2], 164.7 [(A) C1], 169.9 [(B) C7] and 191.9 [(A) C7] ppm.

2.4.2 2-[(E)-4-hydroxy-3-[(E)-4-methylphenyliminomethyl]phenyldiazenyl]benzoic acid (L\(^{1} HH'\))

IR (cm\(^{-1}\)): 1725 \(\nu(OCO)_{asym}\). \(^{1}\)H-NMR (DMSO-\(d_6\) / 500.13 MHz); \(\delta_H\): 2.38 [s, 3H, CH\(_3\)], 7.18 [d, 1H, (B) H3], 7.32 [part of AA'BB' system, 2H, (A) H3 & H5], 7.43 [part of AA'BB' system, 2H, (A) H2 & H6], 7.60 [m, 1H, (C) H4], 7.61 [m, 1H, (C) H6], 7.69 [m, 1H, (C) H5], 7.84 [m, 1H, (C) H3], 7.98 [dd, 1H, (B) H4], 8.29 [d, 1H, (B) H6], 9.16 [s, 1H, C(H)=N], 12.91 [bs, 1H, CO\(_2\)H], 14.16 [bs, 1H, OH] ppm. \(^{13}\)C-NMR (DMSO-\(d_6\) / 125.76 MHz); \(\delta_C\): 20.7 [CH\(_3\)], 118.3 [(B) C3], 118.33 [(C) C6], 119.2 [(B) C1], 121.4 [(A) C2 & C6], 126.5 [(B) C4], 129.2[(B) C6], 129.3 [(C) C3], 129.9 [(C) C4], 130.1 [(A) C3 & C5], 130.2 [(C) C2], 131.7 [(C) C5], 137.1 [(A) C4], 144.5 [(A) C1], 144.9 [(B) C5], 150.9 [(C) C1], 161.7 [(H)=N], 164.5 [(B) C2], 168.5 [CO\(_2\)H] ppm.

2.4.3 2-[(E)-4-hydroxy-3-[(E)-4-bromophenyliminomethyl]phenyldiazenyl]benzoic acid (L\(^{1} HH'\))

IR (cm\(^{-1}\)): 1723 \(\nu(OCO)_{asym}\). \(^{1}\)H-NMR (DMSO-\(d_6\) / 500.13 MHz); \(\delta_H\): 7.21 [d, 1H, (B) H3], 7.48 [part of AA'MM' system, 2H, (A) H2 & H6], 7.60 [m, 1H, (C) H6], 7.61 [m, 1H, (C) H4], 7.70 [m, 1H, (C) H5], 7.71 [part of AA'MM' system, 2H, (A) H3 & H5], 7.84 [m, 1H, (C)
H3], 7.99 [dd, 1H, (B) H4], 8.31 [d, 1H, (B) H6], 9.16 [s, 1H, C(H)=N], 12.99 [brs, 1H, CO₂H], 13.57 [brs, 1H, OH] ppm. ¹³C-NMR (DMSO- d₆ / 125.76 MHz); δc: 118.2 [(B) C3], 118.4 [(C) C6], 119.4 [(B) C1], 120.4 [(A) C4], 123.7 [(A) C2 & C6], 126.9 [(B) C4], 128.8 [(B) C6], 129.3 [(C) C3], 129.9 [(C) C4], 130.2 [(C) C2], 131.7 [(C) C5], 132.5 [(A) C3 & C5], 145.1 [(B) C5], 147.0 [(A) C1], 150.9 [(C) C1], 163.1 [C(H)=N], 163.8 [(B) C2], 168.5 [CO₂H] ppm.

2.4.4 2-{(E)-4-hydroxy-3-{(E)-4-chlorophenyliminomethyl}phenyldiazenyl}benzoic acid (L³HH³)

IR (cm⁻¹): 1725 ν(OCO)asym. ¹H-NMR (DMSO- d₆ / 500.13 MHz); δH: 7.21 [d, 1H, (B) H3], 7.53 [part of AA'BB' system, 2H, (A) H3 & H5], 7.57 [part of AA'BB' system, 2H, (A) H2 & H6], 7.60 [m, 1H, (C) H4], 7.61 [m, 1H, (C) H5], 7.69 [m, 1H, (C) H3], 7.99 [dd, 1H, (B) H4], 8.31 [d, 1H, (B) H6], 9.16 [s, 1H, C(H)=N], 12.97 [brs, 1H, CO₂H], 13.59 [brs, 1H, OH] ppm. ¹³C-NMR (DMSO- d₆ / 125.76 MHz); δc: 118.1 [(B) C3], 118.4 [(C) C6], 119.4 [(B) C1], 123.4 [(A) C2 & C6], 126.9 [(B) C4], 128.7 [(B) C6], 129.3 [(C) C3], 129.5 [(A) C3 & C5], 129.9 [(C) C4], 130.2 [(C) C2], 131.6 [(A) C4], 131.7 [(C) C5], 145.1 [(B) C5], 146.6 [(A) C1], 150.9 [(C) C1], 163.1 [C(H)=N], 163.8 [(B) C2], 168.5 [CO₂H] ppm.

2.4.5 2-{(E)-4-hydroxy-3-{(E)-4-methoxyphenyliminomethyl}phenyldiazenyl}benzoic acid (L⁵HH⁵)

IR (cm⁻¹): 1723 ν(OCO)asym. ¹H-NMR (DMSO- d₆ / 500.13 MHz); δH: 3.84 [s, 3H, OCH₃], 7.08 [part of AA'MM' system, 2H, (A) H3 & H5], 7.17 [d, 1H, (B) H3], 7.53 [part of AA'MM' system, 2H, (A) H2 & H6], 7.60 [m, 1H, (C) H4], 7.61 [m, 1H, (C) H6], 7.70 [m, 1H, (C) H5], 7.83 [m, 1H, (C) H3], 7.96 [dd, 1H, (B) H4], 8.26 [d, 1H, (B) H6], 9.16 [s, 1H, C(H)=N], 12.90 [brs, 1H, CO₂H], 14.24 [brs, 1H, OH] ppm. ¹³C-NMR (DMSO- d₆ / 125.76 MHz); δc: 55.5 [OCH₃], 114.8 [(A) C3 & C5], 118.2 [(B) C3], 118.3 [(C) C6], 119.3 [(B) C1], 122.9 [(A) C2 & C6], 126.3 [(B) C4], 128.9 [(B) C6], 129.3 [(C) C3], 129.8 [(C) C4], 130.2 [(C) C2], 131.7 [(C) C5], 139.8 [(A) C1], 144.9 [(B) C5], 150.9 [(C) C1], 158.9 [(A) C4], 160.4 [C(H)=N], 164.3 [(B) C2], 168.5 [CO₂H] ppm.

2.4.6 4-{(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl}benzoic acid (L⁶HH⁶)

IR (cm⁻¹) 1679 ν(OCO)asym. ¹H-NMR (DMSO- d₆ / 500.13 MHz); δH: 7.24 [d, 1H, (A) H5], 7.95 [m (part of AA'BB' system), 2H, (B) H2 & H6], 8.14 [dd, 1H, (A) H6], 8.16 [m (part of AA'BB' system), 2H, (B) H3 & H5], 8.25 [d, 1H, (A) H2], 10.38 [s, 1H, C(H)=O] ppm. Signals
for the phenol and carboxylic acid were exchanged due to the presence of water in the solvent.

$^{13}$C-NMR (DMSO-$d_6$, 125.76 MHz); $\delta$C: 118.7 [(A) C5], 122.4 [(B) C2 & C6], 122.8 [(A) C3], 124.5 [(A) C2], 129.9 [(A) C6], 130.7 [(B) C3 & C5], 132.5 [(B) C4], 144.8 [(A) C1], 154.3 [(B) C1], 164.2 [(A) C4], 166.8 [CO$_2$H], 190.5 [C(H)=O], ppm.

2.5 X-ray crystallography

Crystals of the ligands suitable for an X-ray crystal-structure determination were obtained from toluene (L$^{2}$HH$^{\prime}$ and L$^{3}$HH$^{\prime}$) and chloroform/DMSO mixture (L$^{4}$HH$^{\prime}$) by slow evaporation of the solvent at room temperature. The crystal structures of three of the ligands (L$^{2}$HH$^{\prime}$- L$^{4}$HH$^{\prime}$) have been determined. The data collection and refinement parameters are given in Table 2.2, while selected geometric parameters are collected in Table 2.3.
Table 2.2: Crystallographic data and structure refinement parameters for the ligands (L²HH'-L⁴HH')

<table>
<thead>
<tr>
<th></th>
<th>L²HH'-0.5H₂O</th>
<th>L³HH'-0.5C₇H₈</th>
<th>L⁴HH'-0.5H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₁H₁₇N₃O₂·0.5H₂O</td>
<td>C₂₀H₄₀BrN₆O₃·0.5C₇H₈</td>
<td>C₂₀H₄₁ClN₃O₃·0.5H₂O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>368.39</td>
<td>470.32</td>
<td>388.80</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.10 x 0.2 x 0.20</td>
<td>0.20 x 0.13 x 0.08</td>
<td>0.50 x 0.35 x 0.28</td>
</tr>
<tr>
<td>Crystal shape</td>
<td>Prism</td>
<td>Tablet</td>
<td>Prism</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>160(1)</td>
<td>160(1)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>P̅</td>
<td>C2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>13.0688(4)</td>
<td>8.2708(1)</td>
<td>13.2451(19)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>21.8141(6)</td>
<td>10.7547(3)</td>
<td>21.668(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.5941(4)</td>
<td>12.3929(3)</td>
<td>12.664(2)</td>
</tr>
<tr>
<td>α(°)</td>
<td>90</td>
<td>88.1844(17)</td>
<td>90</td>
</tr>
<tr>
<td>β(°)</td>
<td>92.487(2)</td>
<td>85.3535(16)</td>
<td>91.69(2)</td>
</tr>
<tr>
<td>γ(°)</td>
<td>90</td>
<td>69.6152(13)</td>
<td>90</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>3587.0(2)</td>
<td>1029.91(5)</td>
<td>3632.8(10)</td>
</tr>
<tr>
<td>Z</td>
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<td>2</td>
<td>8</td>
</tr>
<tr>
<td>D₂ (g cm⁻³)</td>
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<td>1.516</td>
<td>1.422</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>0.0948</td>
<td>2.033</td>
<td>2.12</td>
</tr>
<tr>
<td>Transmission factors (min, max)</td>
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<td>0.671, 0.795</td>
<td>0.415, 0.522</td>
</tr>
<tr>
<td>Reflections measured</td>
<td>39399</td>
<td>23736</td>
<td>3534</td>
</tr>
<tr>
<td>Independent reflections (Rint)</td>
<td>4113 (0.079)</td>
<td>4718 (0.0467)</td>
<td>3382 (0.037)</td>
</tr>
<tr>
<td>Reflections with I &gt; 2o(I)</td>
<td>2633</td>
<td>3707</td>
<td>1707</td>
</tr>
<tr>
<td>Number of parameters</td>
<td>263</td>
<td>304</td>
<td>254</td>
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<tr>
<td>R(F) (I &gt; 2o(I) reflns)</td>
<td>0.050</td>
<td>0.0368</td>
<td>0.076</td>
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<tr>
<td>wR² (all data)</td>
<td>0.136</td>
<td>0.0977</td>
<td>0.216</td>
</tr>
<tr>
<td>GOF(F²)</td>
<td>1.02</td>
<td>1.034</td>
<td>1.06</td>
</tr>
<tr>
<td>max, min Δρ (e/Å³)</td>
<td>0.29, -0.19</td>
<td>0.392, -0.541</td>
<td>0.20, -0.25</td>
</tr>
</tbody>
</table>

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Table 2.3: Selected bond lengths (Å) and angles (°) for $L^2\text{HH}^-\cdot 0.5\text{H}_2\text{O}$, $L^3\text{HH}^-\cdot 0.5\text{C}_7\text{H}_8$ and $L^4\text{HH}^-\cdot 0.5\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>$L^2\text{HH}^-\cdot 0.5\text{H}_2\text{O}$</th>
<th>$L^3\text{HH}^-\cdot 0.5\text{C}_7\text{H}_8$</th>
<th>$L^4\text{HH}^-\cdot 0.5\text{H}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(18)-C(21)/ [C(18)-Br]</td>
<td>1.504(2)</td>
<td>1.902(2)</td>
<td>1.730(5)</td>
</tr>
<tr>
<td>O(1)-C(1)/ [O(2)-C(1)]</td>
<td>1.329(2)</td>
<td>1.329(3)</td>
<td>1.311(6)</td>
</tr>
<tr>
<td>O(2)-C(1)/ [O(1)-C(1)]</td>
<td>1.211(2)</td>
<td>1.206(3)</td>
<td>1.207(6)</td>
</tr>
<tr>
<td>O(3)-C(11)</td>
<td>1.303(2)</td>
<td>1.333(2)</td>
<td>1.333(6)</td>
</tr>
<tr>
<td>N(1)-N(2)</td>
<td>1.270(2)</td>
<td>1.262(2)</td>
<td>1.269(5)</td>
</tr>
<tr>
<td>N(2)-N(1)-C(3)/ [N(2)-N(1)-C(7)]</td>
<td>115.0(1)</td>
<td>114.8(2)</td>
<td>114.2(4)</td>
</tr>
<tr>
<td>N(1)-N(2)-C(8)</td>
<td>115.6(1)</td>
<td>115.5(2)</td>
<td>114.3(4)</td>
</tr>
<tr>
<td>C(14)-N(3)-C(15)</td>
<td>125.2(1)</td>
<td>121.7(2)</td>
<td>123.0(4)</td>
</tr>
<tr>
<td>O(2)-C(1)-O(1)</td>
<td>119.6(2)</td>
<td>120.1(2)</td>
<td>118.6(5)</td>
</tr>
<tr>
<td>O(2)-C(1)-C(2)/ [O(1)-C(1)-C(2)]</td>
<td>122.3(2)</td>
<td>121.8(2)</td>
<td>122.1(5)</td>
</tr>
<tr>
<td>O(1)-C(1)-C(2)/ [O(2)-C(1)-C(2)]</td>
<td>118.2(1)</td>
<td>118.1(2)</td>
<td>119.2(5)</td>
</tr>
<tr>
<td>N(1)-C(3)/ [N(1)-C(7)]</td>
<td>1.424(2)</td>
<td>1.429(3)</td>
<td>1.426(6)</td>
</tr>
<tr>
<td>N(2)-C(8)</td>
<td>1.403(2)</td>
<td>1.408(3)</td>
<td>1.411(6)</td>
</tr>
<tr>
<td>N(3)-C(14)</td>
<td>1.295(2)</td>
<td>1.286(3)</td>
<td>1.287(6)</td>
</tr>
<tr>
<td>N(3)-C(15)</td>
<td>1.415(2)</td>
<td>1.416(3)</td>
<td>1.407(6)</td>
</tr>
<tr>
<td>C(4)-C(3)-N(1)/ [C(6)-C(7)-N(1)]</td>
<td>122.2(1)</td>
<td>122.6(2)</td>
<td>122.6(4)</td>
</tr>
<tr>
<td>C(2)-C(3)-N(1)/ [C(2)-C(7)-N(1)]</td>
<td>117.5(1)</td>
<td>117.4(2)</td>
<td>117.1(4)</td>
</tr>
<tr>
<td>C(9)-C(8)-N(2)/ [C(13)-C(8)-N(2)]</td>
<td>115.6(1)</td>
<td>115.1(2)</td>
<td>114.9(4)</td>
</tr>
<tr>
<td>N(3)-C(14)-C(10)/ [N(3)-C(14)-C(12)]</td>
<td>120.5(1)</td>
<td>120.2(2)</td>
<td>120.3(5)</td>
</tr>
<tr>
<td>C(16)-C(15)-N(3)/ [C(20)-C(15)-N(3)]</td>
<td>123.6(1)</td>
<td>123.4(2)</td>
<td>125.5(4)</td>
</tr>
<tr>
<td>C(20)-C(15)-N(3)/ [C(16)-C(15)-N(3)]</td>
<td>117.0(1)</td>
<td>117.0(2)</td>
<td>116.3(4)</td>
</tr>
</tbody>
</table>

Geometric parameters in square brackets with superscript “a” and “b” refer to the $L^3\text{HH}^-\cdot 0.5\text{C}_7\text{H}_8$ (Fig. 2.6) and $L^4\text{HH}^-\cdot 0.5\text{H}_2\text{O}$ (Fig. 2.8), respectively.
The structures of the ligands (L\textsuperscript{2}HH' - L\textsuperscript{4}HH') are discussed in sequel:

2.5.1 Crystal structure of 2-\{(E)-4-hydroxy-3-\{(E)-4-methylphenyliminomethyl\} phenyldiazenyl\}benzoic acid hemihydrate (L\textsuperscript{2}HH'O.5H\textsubscript{2}O)

In the crystal structure of L\textsuperscript{2}HH'O.5H\textsubscript{2}O, the asymmetric unit contains one molecule of the carboxylic acid in a general position plus a water molecule that sits on a C\textsubscript{2}-axis, thereby giving a L\textsuperscript{2}HH':water ratio of 2:1. The three ring system of L\textsuperscript{2}HH' has an extended conformation with both external rings slightly twisted with respect to the central aromatic ring (Fig. 2.4) [5].

Fig. 2.4 View of the molecule of L\textsuperscript{2}HH'O.5H\textsubscript{2}O showing the atom-labelling scheme (50% probability ellipsoids).

The carboxylic acid group is coplanar with its parent phenyl ring [O(1)-C(1)-C(2)-C(7) = 174.8(1)\textdegree]. The carboxylic acid molecule appears to be a zwitterion. The electron density peak associated with the expected phenolic H-atom was found to be closer to the imine N-atom (Table 2.4), although a plotted difference Fourier map of the region suggested that the electron density due to this H-atom is quite smeared out. Plots of difference Fourier maps with the H-atom
position idealized firstly on the O-atom and then on the N-atom showed that neither idealized position fitted the observed electron density optimally, although a better match was obtained when the N-atom was considered to be protonated.

Table 2.4: Hydrogen bonding geometry (Å, °) for \( L^2HH' \cdot 0.5H_2O \)

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>D-H</th>
<th>H···A</th>
<th>D···A</th>
<th>D-H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-H(1)···N(1)</td>
<td>1.00(3)</td>
<td>1.63(3)</td>
<td>2.582(2)</td>
<td>156(2)</td>
</tr>
<tr>
<td>N(3)-H(3)···O(3)</td>
<td>1.17(3)</td>
<td>1.42(3)</td>
<td>2.533(2)</td>
<td>156(2)</td>
</tr>
<tr>
<td>O(22)-H(22)···O(2')</td>
<td>0.99(2)</td>
<td>1.89(3)</td>
<td>2.866(2)</td>
<td>169(2)</td>
</tr>
</tbody>
</table>

Primed atoms refer to the molecule in the symmetry related position: \( \frac{1}{2}-x, y, \frac{1}{2}-z \)

The carboxylic acid hydroxy group in \( L^2HH' \) forms an intramolecular hydrogen bond with the nearest adjacent azo N-atom, while the protonated imine N-H atom forms an intramolecular hydrogen bond with the adjacent deprotonated phenolic hydroxy O-atom. Both of these interactions form six-membered loops with a graph set motif [6] of S(6). In addition, one H-atom of the water molecule forms an intermolecular hydrogen bond with the carbonyl O-atom of the carboxylic acid group of one \( L^2HH' \) molecule. The \( C_2 \)-symmetry of the water molecule means that the second H-atom of the water molecule forms an identical intermolecular hydrogen bond with a second carboxylic group of another \( L^2HH' \) molecule. The net result is the formation of a discrete hydrogen-bonded unit consisting of one water molecule and two molecules of the ligand molecules (Fig. 2.5).

Fig. 2.5 Hydrogen-bonded unit consisting of one water molecule and two molecules of the \( L^2HH' \)
2.5.2 Crystal structure of 2-[(E)-4-hydroxy-3-[(E)-4-bromophenylimino]phenyldiazeny]benzoic acid toluene hemisolvate (L$_3$HH$'$0.5C$_7$H$_8$)

The asymmetric unit in L$_3$HH$'$0.5C$_7$H$_8$ [7] contains one molecule of the carboxylic acid plus half of a toluene molecule that is disordered about a centre of inversion. The three-ring system of L$_3$HH$'$ has an extended and reasonably flat conformation (Fig. 2.6).

The angles between the plane of the central ring and those of the benzoic acid and 4-bromophenyl rings are 6.01(11)$^\circ$ and 27.78(11)$^\circ$, respectively. The carboxylic acid group is coplanar with its parent phenyl ring [O(1)-C(1)-C(2)-C(7) = 179.60(19)$^\circ$]. The molecular conformation and dimensions are very similar to those of the 4-methylphenyl (L$_3$HH$'$) analogue (Table 2.3), with the exception that the L$_3$HH$'$ crystallized in a zwitterionic form where the phenolic H atom had migrated to the imine N atom. In L$_3$HH$'$, this H atom is clearly located on the phenolic O atom. The carboxylic acid H atom forms an intramolecular hydrogen bond with the nearest N atom of the adjacent diazo group, while the phenolic H atom forms an intramolecular hydrogen bond with the adjacent imine N atom. Both of these interactions close six-membered hydrogen-bonded rings.

The molecules pack in a way that facilitates several C-H...O and C-H...Br interactions (Table 2.5). These interactions link the solvent and substrate molecules together into two

![Fig. 2.6 View of the molecule of L$_3$HH$'$0.5C$_7$H$_8$ showing the atom-labelling scheme (50% probability ellipsoids)](image-url)
dimensional networks, which lie parallel to the (101) plane (Fig. 2.7). The C-H–O angles are consistent with the most probable value of 160° for two-centre interactions [8].

Table 2.5: Hydrogen bonding geometry (Å, °) for L\textsuperscript{3}HH'0.5C\textsubscript{7}H\textsubscript{6}

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>D-H</th>
<th>H···A</th>
<th>D···A</th>
<th>D-H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-H(1)···N(1)</td>
<td>0.73(3)</td>
<td>1.92(3)</td>
<td>2.593(2)</td>
<td>154(4)</td>
</tr>
<tr>
<td>O(3)-H(3)···N(3)</td>
<td>0.87(3)</td>
<td>1.76(3)</td>
<td>2.554(2)</td>
<td>151(3)</td>
</tr>
<tr>
<td>C(6)-H(6)···Br(2')</td>
<td>0.95</td>
<td>2.92</td>
<td>3.630(2)</td>
<td>133</td>
</tr>
<tr>
<td>C(12)-H(12)···O(3')</td>
<td>0.95</td>
<td>2.53</td>
<td>3.388(3)</td>
<td>151</td>
</tr>
<tr>
<td>C(17)-H(17)···O(1''')</td>
<td>0.95</td>
<td>2.49</td>
<td>3.419(3)</td>
<td>166</td>
</tr>
<tr>
<td>C(26)-H(26)···O(2'')</td>
<td>0.95</td>
<td>2.50</td>
<td>3.374(6)</td>
<td>153</td>
</tr>
</tbody>
</table>

Primed atoms refer to the molecule in the symmetry related position:
(i) 1+x, 1+y, z-1; (ii) 2-x, -y, -z; (iii) x-1, y, 1+z;
(iv) 2-x, 1-y, -z

Fig. 2.7 The molecular packing of L\textsuperscript{3}HH'0.5C\textsubscript{7}H\textsubscript{6} showing the solvent and substrate molecules forming two dimensional networks

2.5.3 Crystal structure of 2-\{(E)-4-hydroxy-3-\{(E)-4-chlorophenyliminomethyl\}phenyldiazene\}benzoic acid hemihydrate (L\textsuperscript{4}HH'0.5H\textsubscript{2}O)

The crystal structure of L\textsuperscript{4}HH' [9] is similar to that of the L\textsuperscript{3}HH' and crystallizes as L\textsuperscript{4}HH'0.5H\textsubscript{2}O (Fig. 2.8). Interstitial water molecules (one for each two of the L\textsuperscript{3}HH'molecules) are located on four fold axes that pass through the unit cell. The three-ring system assumes an
extended conformation, with both outer rings slightly twisted with respect to the central aromatic ring.

Fig. 2.8 View of the molecule of L^4HH'.0.5H_2O, showing the atom-labelling scheme (50% probability ellipsoids)

These quasi-planar molecules forms sheets, parallel to the (100) plane (see Fig. 2.9), that are linked by weak aromatic C-H...O interactions. Adjacent sheets are linked by strong hydrogen bonds to interstitial water molecules (see Fig 2.10, Table 2.6). Bond lengths and angles within the molecule are unremarkable and similar to those found in 4-methylphenyl and 4-bromophenyl analogues (Table 2.3) and related molecules [2,3].

Table 2.6: Hydrogen bonding geometry (Å, °) for L^4HH'.0.5H_2O

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>D-H</th>
<th>H···A</th>
<th>D···A</th>
<th>D-H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(2)-H(2)O···N(1)</td>
<td>0.82</td>
<td>1.83</td>
<td>2.580(5)</td>
<td>152</td>
</tr>
<tr>
<td>O(3)-H(3)O···N(3)</td>
<td>0.82</td>
<td>1.81</td>
<td>2.544(5)</td>
<td>148</td>
</tr>
<tr>
<td>O(1)W-H(1)W(1)···O(1)</td>
<td>0.852(10)</td>
<td>2.05(3)</td>
<td>2.875(5)</td>
<td>164(8)</td>
</tr>
<tr>
<td>C(5)-H(5)A···O(1')</td>
<td>0.93</td>
<td>2.56</td>
<td>3.457(7)</td>
<td>161</td>
</tr>
<tr>
<td>C(14)-H(14)A···O(1')W</td>
<td>0.93</td>
<td>2.47</td>
<td>3.364(7)</td>
<td>162</td>
</tr>
<tr>
<td>C(19)-H(19)A···O(2&quot;)</td>
<td>0.93</td>
<td>2.59</td>
<td>3.355(6)</td>
<td>140</td>
</tr>
</tbody>
</table>

Primed atoms refer to the molecule in the symmetry related position:

(i)X,1-y, 3/2+z; (ii)x, y, 1+z
Fig. 2.9 The molecular packing of $L^4HH'\cdot 0.5H_2O$, viewed down the $a$ axis, perpendicular to the molecular sheets.

Fig. 2.10 The molecular packing of $L^4HH'\cdot 0.5H_2O$, viewed down the $b$ axis, showing how the atomic sheets are linked by interstitial water molecules.
2.6 Experimental

2.6.1 Synthesis of ligands

2.6.1.1 Preparation of 2-{(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (L'HH')

The ligand, L'HH' was prepared by reacting o-carboxybenzenediazonium chloride with salicylaldehyde in alkaline solution under cold conditions by the method described in our earlier report [4]. The synthetic details are given below:

Anthranilic acid (5.0 g, 36.45 mmol) in a mixture of concentrated HCl solution (5 ml) and water (15 ml) was diazotized with cold NaNO₂ solution (2.75 g, 39.85 mmol, 12 ml). The cold diazonium salt solution was added slowly to salicylaldehyde (4.45 g, 36.44 mmol), previously dissolved in a NaOH solution (3.0 g, mmol, 30 ml) and held at 0-5 °C in an ice-bath, with vigorous stirring. A deep-red colour developed almost immediately and stirring was continued for 1 h. The reaction mixture was kept overnight at 4 °C, followed by 3 h at room temperature and then acidified with acetic acid. The brown-coloured precipitate was filtered, washed with water and dried in vacuo. The crude product was washed thoroughly with hexane, to remove tar-like material and then dissolved in toluene. Several recrystallizations from toluene yielded the product in 50% yield; m.p.: 177-179 °C. Anal. Found. C, 62.20; H, 3.65; N, 10.35.
Calc. for C₁₄H₁₀N₂O₄: C, 62.22; H, 3.70; N, 10.37%.

2.6.1.2 Preparation of 2-{(E)-4-hydroxy-3-{(E)-4-(aryl)iminomethyl]phenyldiazenyl]benzoic acids (L²₅HH')

A typical procedure is described below.

2.6.1.2.1 Preparation of 2-{(E)-4-hydroxy-3-{(E)-4-chlorophenyliminomethyl]phenyldiazenyl]benzoic acid (L₁HH')

An equimolar amount of p-chloroaniline (0.42 g, 3.36 mmol) in hot absolute ethanol solution (15 ml) was added to a hot toluene (30 ml) containing L¹HH' (0.91 g, 3.36 mmol) and the reaction mixture was refluxed for 5 h. The water formed during the reaction was removed using a Dean-Stark apparatus. The reaction mixture was concentrated to half of the initial solvent volume on a hot plate, cooled to room temperature and was kept overnight in a refrigerator whereupon a dark brown solid precipitated. The precipitate was filtered, washed with absolute ethanol (3 x 5 ml) followed by diethyl ether (2 x 5 ml), and then dried in air. The crude product was washed with hexane to remove any tarty materials and recrystallized from ethanol to yield
pure orange crystalline product (0.78 g, 56 %) of L\textsuperscript{4}HH'. M. p.: 225-226 °C. Anal. Found. 63.20; H, 3.65; N, 11.13. Calc. for C\textsubscript{20}H\textsubscript{14}N\textsubscript{3}O\textsubscript{3}Cl: C, 63.24; H, 3.71; N, 11.06 %.

The other 2-\{(E)-4-hydroxy-3-\{(E)-4-(aryl)iminomethyl\}phenyldiazenyl\}benzoic acids, viz., L\textsuperscript{2}HH', L\textsuperscript{3}HH' and L\textsuperscript{5}HH' were prepared analogously by reacting L\textsuperscript{1}HH' and appropriate anilines. The characterization data are presented below.

2.6.1.2.2 Preparation of 2-\{(E)-4-hydroxy-3-\{(E)-4-methylphenyliminomethyl\}phenyldiazenyl\}benzoic acid (L\textsuperscript{2}HH')

Recrystallized from absolute ethanol to give reddish brown precipitate in 70 % yield. m.p.: 199-201 °C. Anal. Found. 69.95; H, 4.65; N, 11.58. Calc. for C\textsubscript{21}H\textsubscript{17}N\textsubscript{3}O\textsubscript{3}: C, 70.20; H, 4.76; N, 11.69 %.

2.6.1.2.3 Preparation of 2-\{(E)-4-hydroxy-3-\{(E)-4-bromophenyliminomethyl\}phenyldiazenyl\}benzoic acid (L\textsuperscript{3}HH')

Recrystallized from absolute ethanol to give orange precipitate in 49 % yield. m.p.: 213-214 °C. Anal. Found. 56.50; H, 3.30; N, 10.01. Calc. for C\textsubscript{20}H\textsubscript{14}N\textsubscript{3}O\textsubscript{3}Br: C, 56.60; H, 3.32; N, 9.90 %.

2.6.1.2.4 Preparation of 2-\{(E)-4-hydroxy-3-\{(E)-4-methoxyphenyliminomethyl\}phenyldiazenyl\}benzoic acid (L\textsuperscript{5}HH')

Recrystallized from absolute ethanol to give dark red precipitate in 54 % yield. m.p.: 174-176 °C. Anal. Found. 67.25; H, 4.60; N, 11.18. Calc. for C\textsubscript{21}H\textsubscript{17}N\textsubscript{3}O\textsubscript{4}: C, 67.21; H, 4.56; N, 11.19 %.

2.6.1.3 Preparation of 4-\{(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl\}benzoic acid (L\textsuperscript{6}HH')

The ligand, L\textsuperscript{6}HH' was prepared by reacting p-carboxybenzenediazonium chloride with salicylaldehyde in an alkaline solution under cold conditions following the method described earlier for the ortho-analogue [4]. The amount of concentrated HCl and water used for the dissolution of the p-aminobenzoic acid was 8 and 32 ml, respectively. The crude L\textsuperscript{6}HH' was obtained after acidification with dil. acetic acid. The light yellow precipitate was filtered, washed with water until the filtrate became neutral and then dried in vacuo. The resultant brown product was then washed thoroughly with hexane to remove any tarry materials and dried. The brown
L'HH' was insoluble in all common organic solvents and water, and consequently could not be recrystallized. The brown precipitate was then re-dissolved in a hot aqueous sodium bicarbonate solution. It was then filtered to remove any undissolved particles and re-precipitated using dil. acetic acid. The precipitate was filtered, washed with water and dried which afforded a bright brown product in 56% yield. m.p.: >275 °C. Anal Found: C, 61.38; H, 3.73; N, 10.26%. Calc. for C_{14}H_{10}N_{2}O_{4}: C, 62.22; H, 3.70; N, 10.37%.

2.6.2 Chemicals used for the preparations

Salicylaldehyde (Lancaster), anthranilic acid (Spectrochem), p-aminobenzoic acid (Sisco) and the substituted anilines (reagent grade) were used without further purification. The solvents used in the reactions/recrystallizations were of AR grade and dried using standard procedures. Toluene was distilled from sodium benzophenone ketyl.

2.6.3 Physical measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin Elmer 2400 series II instrument. IR spectra in the range 4000-400 cm\(^{-1}\) were obtained on a BOMEM DA-8 FT-IR spectrophotometer with samples investigated as KBr discs. The \(^1\)H- and \(^13\)C-NMR spectra of the ligands (L'HH'-L'6HH') were acquired on a Bruker Avance 500 spectrometer operating at 500.13 and 125.76 MHz, respectively. For the ligand L'1HH', the \(^1\)H- and \(^13\)C-NMR spectra were recorded on a Varian Inova 600 spectrometer and measured at 600 and 150 MHz, respectively. The \(^1\)H and \(^13\)C chemical shifts were referred to Me\(_4\)Si set at 0.00 ppm and CDCl\(_3\) set at 77.0 ppm, respectively. Other NMR experiments like correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HMQC) and heteronuclear multiple-bond connectivities (HMBC) were also performed on the same instruments.

2.6.4 X-ray crystallography

Crystals of the ligands suitable for an X-ray crystal-structure determination were obtained from toluene (L'2HH' and L'3HH') and chloroform/ DMSO mixture (L'4HH') by slow evaporation of the solvent at room temperature. The intensity data for L'2HH' and L'3HH' were measured on a Nonius KappaCCD diffractometer using Mo K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å) at 160 K while L'4HH' was measured on a Bruker P4 diffractometer using Cu K\(_\alpha\) radiation (\(\lambda = 1.54178\) Å) at 293 K.

The data reduction for L'1HH' and L'4HH' was performed with HKL Denzo and Scalepack [10] while for L'1HH' was with SHELXTL [11].
The data collection and refinement parameters are given in Table 2.2. Views of the structures are shown in Figs. 2.4 (for $L^3HH'$), 2.6 (for $L^3HH'$) and 2.8 (for $L^4HH'$). The structure of $L^4HH'$ was solved by SHELXTL [11] while the other structures were solved by direct methods by using SIR92 [12].

In $L^2HH'$ and $L^4HH'$, the asymmetric unit contains one molecule of the carboxylic acid in a general position plus a water molecule that sits on a $C_2$-axis. The symmetry-unique H-atom of the water molecule and the carboxylic acid H-atom of $L^1HH'$ and $L^4HH'$ were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. In $L^3HH'$, the asymmetric unit contains one molecule of the carboxylic acid in a general position plus half of a toluene molecule that is disordered about a centre of inversion, with the centre of gravity of the six-membered ring displaced slightly from the inversion centre. The atoms of one entire toluene molecule were defined with the site occupation factors of the atoms set to 0.5. The atoms of the six-membered ring of the toluene molecule were constrained to an ideal hexagon, while neighbouring atoms within each orientation of the disordered toluene molecule were restrained to have similar atomic displacement parameters.

The non-hydrogen atoms were refined anisotropically. All remaining H-atoms in each structure were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent atom ($1.5U_{eq}$ for methyl groups). The refinement of each structure was carried out on $F^2$ using full-matrix least-squares procedures. The calculations were performed using the SHELXL97[13] program for $L^2HH'$ and $L^3HH'$ and SHELXTL [11] program for $L^4HH'$. 

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References