CHAPTER 7

CRYSTAL STRUCTURES OF TWO SUBSTITUTED [1,2,4] TRIAZOLE DERIVATIVES

7.1 INTRODUCTION

This chapter describes the crystal structures of two substituted [1,2,4] triazole derivatives TTPN-I and TTPN-II. Both the compounds were synthesized through a rather unusual route (Pathak et al. 1992) and obtained as a rearranged end product of the reaction which is similar to isosteric quinazoline series (Ibrahim et al. 1981 and Ibrahim et al. 1980). These two compounds were tested for pharmacological activities and they were found to be CNS depressant and skeletal muscle relaxant, when evaluated in Swiss albino mice by rota-rod method, as well as photoactometer at the dose level of 5-10 mg/Kg body wt (Pathak personal communication).

7.2 EXPERIMENTAL

The two crystal structures of triazolothienopyrimidine derivatives presented in this chapter are

1) 2-(4-Chlorophenyl)amino-6,7,8,9-tetrahydro-[1]benzothieno[3,2-e][1,2,4]triazolo[1,5-c]pyrimidine, C_{17}H_{14}N_{5}SCl (TTPN-I) and
2) 2-(4-Chlorophenyl)amino-4-methyl-6,7,8,9-tetrahydro-[1]benzo thieno[3,2-e][1,2,4]triazolo[1,5-c]pyrimidine, \( C_{19}H_{16}N_5S Cl \) (TTPN-II)

The schematic molecular diagram of TTPN-I and TTPN-II are shown in Figure 7.1. The details of the crystalisation, data collection, structure solution and structure refinement for both the compounds are given in the following paragraphs.

Colourless, needle shaped crystals of TTPN-I were obtained from ethanol-chloroform mixture. A crystal of 0.62x0.24x0.12mm was chosen up for X-ray studies using polarising microscope. Accurate unit cell parameters were determined from 35 high Bragg’s angle reflections ranging \( 8 < \theta < 25^\circ \) and refined by least-squares method. The intensity data were collected using Siemens P4 diffractometer with graphite monochromator using MoKa radiation. In order to check the intensity decay due to radiation damage and crystal decomposition, three standard reflections were monitored for every 100 reflections and the intensity variation was found to be less than 4%. The data were collected up to \( \theta = 25^\circ \) by \( \theta/2\theta \) scan mode. A total of 2255 reflections were measured, of which 2062 reflections were found to be unique \( [R_{int} = 0.081] \).

Colourless, thin slab crystals of TTPN-II were obtained from chloroform-ethanol mixture. After careful examination under polarising microscope, a crystal of size 0.58x0.38x0.08mm was picked up for data collection. The unit cell parameters were determined from 32 high angle Bragg’s reflections. The same experimental procedure was carried out as in the case of TTPN-I but the data were collected to the \( \theta_{\text{max}} \) of 27.5°. The total number of reflections collected were 5267, of which 3908 reflections were found to be independent \( [R_{int} = 0.024] \).
TTPN-I \( R = H \)
TTPN-II \( R = \text{Me} \)

Figure 7.1 Molecular structures of TTPN-I and TTPN-II.
TTPN-I belongs to orthorhombic space group $P2_12_12_1$, whereas TTPN-II belongs to monoclinic space group $P2_1/c$. In both the cases, the data were treated for Lorentz and polarisation effects but not for absorption. The crystal data and other relevant details of the two compounds are given in the Table 7.1.

7.3 STRUCTURE SOLUTION

The structure solutions of both the compounds TTPN-I and TTPN-II were obtained by direct methods using the program SHELXS86 (Sheldrick 1990).

For TTPN-I, 462 reflections with $|E| > 1.2$ were used for structure solution. The best phase set with CFOM 0.033 gave the expected molecular model with $R_E = 0.290$ for 20 surviving atoms. In the case of TTPN-II, 1054 reflections with high $|E|$ values ($> 1.2$) were used in the phasing process. The resultant molecular model resembled with the expected geometry.

7.4 STRUCTURE REFINEMENT

The trial structures obtained for both the structures TTPN-I and TTPN-II were refined by full matrix least-squares method using SHELXL93 (Sheldrick 1993). The isotropic refinement was carried out initially for all the non-hydrogen atoms; subsequent to it, the anisotropic refinement was carried out. Disorders in the cyclohexane rings were detected during refinement from the large displacement ellipsoids of C3 in TTPN-I and of C3 and C4 in TTPN-II. Hence, those atoms were considered to occupy double positions; the positional and occupancy factors of the alternative sites were refined. The displacement parameters of the alternative sites were set equal during the final stage of the refinement. The population of the major conformers are 94(1) and 92(1)% for TTPN-I and TTPN-II, respectively. The bond lengths associated with the minor component atoms [C3' in TTPN-I,
C3' and C4' in TTPN-II] were made equal to those for the major component atoms using DFIX. All the hydrogen atoms were located from difference Fourier and refined isotropically. The final R factors, R1 is 0.056 for TTPN-I and 0.039 for TTPN-II. The thermal ellipsoid plot for TTPN-I and TTPN-II are given in Figure 7.2 and 7.4 respectively. The plot shows the 50% probability level of thermal ellipsoid with atomic numbering scheme for both the structures.

Fractional atomic co-ordinates and equivalent isotropic temperature factors of the non-hydrogen atoms for TTPN-I and TTPN-II are given in Table 7.2 and Table 7.3 respectively. The anisotropic thermal parameters of the non-hydrogen atoms for TTPN-I and TTPN-II are given in Table 7.4 and 7.5 respectively. The fractional atomic co-ordinates of the hydrogen atoms for TTPN-I and TTPN-II are given in Table 7.6.

7.5 RESULTS AND DISCUSSION

7.5.1 Intramolecular features

The bond lengths involving non-hydrogen atoms for TTPN-I and TTPN-II are given in Table 7.7 whereas the bond angles are given in Table 7.8. The bond lengths and angles involving hydrogen atoms for TTPN-I and TTPN-II are given in Table 7.9. The selected torsion angles involving non-hydrogen atoms are given in Table 7.10. Apart from the geometrical parameters for both the compounds, the deviation of the atoms from the least-squares plane calculations are given in Table 7.11. The ring (cyclohexane) asymmetry parameters for TTPN-I and TTPN-II are given in Table 7.12.

The bond lengths and bond angles observed in both the structures are normal. In TTPN-II, the bond distance C6-C7, 1.434(2)Å is slightly larger than that of C6-C7 (1.413(7)Å) in TTPN-I. This may be due to the higher flexibility of the cyclohexane ring in TTPN-II than TTPN-I. The bond distance N13-C14, 1.352(7)Å in TTPN-I is shorter than TTPN-II (1.372(2)Å) and this may be attributed to the substitution of methyl group (C23) at C14 in TTPN-II.
The part of each molecule comprising of thiene, triazolo and pyrimidine rings is planar with a maximum deviation of $-0.074(4)\text{Å}$ for N15 in TTPN-I and $0.061(2)\text{Å}$ for C1 in TTPN-II. The dihedral angle between this plane and that of the chlorophenyl ring is $1.01(1)^\circ$ in TTPN-I and $4.63(4)^\circ$ in TTPN-II. Thus the molecule as a whole is planar in TTPN-I and TTPN-II but the degree of planarity is somewhat affected by the substitution of methyl group at C14 (TTPN-II).

In both the structures, the cyclohexane ring is disordered adopting two different conformations. In case of TTPN-I, the alternative sites for C3 suggest that the ring has conformation flexibility between half-chair and sofa. In TTPN-II, both C3 and C4 are disordered, where the major conformer is intermediate between half-chair and sofa while the minor conformation is half-chair. In an overall picture, the cyclohexane ring favours more of half-chair conformation than the sofa. Similar disorders in related compounds has been attributed to the presence of energetically similar conformers in the crystal (Kapor et al 1993).

**7.5.2 Intermolecular features**

The molecular packing of TTPN-I in the unit cell viewed down 'a' axis is shown in Figure 7.3 and for TTPN-II viewed down 'b' axis is shown in Figure 7.5. Both the structures are stabilised by intermolecular N-H...N hydrogen bonds, where the lone group (N16-H) is involved with N13 eventhough three possible acceptor atoms are available (N11, N13 and N15). In TTPN-I, the N16-H16...N13$^i$ geometry is N16...N13$^i$, $3.245(6)\text{Å}$, H16...N13$^i$, $2.48(6)\text{Å}$ and N16-H16...N13, $143(5)^\circ$ [symmetry code: (i) $-x+2$, $y+1/2$, $-z+1/2$]. In TTPN-II, N16...N13$^i$, $3.132(2)\text{Å}$, H16...N(13), $2.37(2)\text{Å}$ and N16-H16...N13, $146(2)^\circ$ [symmetry code: (ii) $-x+1$, $-y+1/2$, $+z+1/2$]. In addition to the stability of TTPN-II by hydrogen bonds, there is also the presence of short S...S contact of $3.646(1)\text{Å}$ between the centrosymmetrically related molecules.
Figure 7.2 Thermal ellipsoid (50% probability level) plot of TTPN-I. (The minor conformer of the cyclohexane ring is shown by unfilled bonds.)
Figure 7.3 Packing of TTPN-I molecules viewed down 'a' axis.
Figure 7.4  Thermal ellipsoid (50% probability level) plot of TTPN-II.
Figure 7.5 Packing of TTPN-II molecules viewed down \( b \) axis.
<table>
<thead>
<tr>
<th></th>
<th>TTPN-I</th>
<th>TTPN-II</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular formula</strong></td>
<td>C\textsubscript{17}H\textsubscript{14}ClN\textsubscript{5}S</td>
<td>C\textsubscript{18}H\textsubscript{16}ClN\textsubscript{5}S</td>
</tr>
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<td><strong>Molecular weight</strong></td>
<td>355.84</td>
<td>369.87</td>
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<tr>
<td><strong>Crystal system</strong></td>
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<td>Monoclinic</td>
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<tr>
<td><strong>Space group</strong></td>
<td>P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}</td>
<td>P2\textsubscript{1}/c</td>
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<td><strong>Cell constants</strong></td>
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<tr>
<td>a (Å)</td>
<td>7.354(1)</td>
<td>8.814(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.477(1)</td>
<td>8.718(1)</td>
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<tr>
<td>c (Å)</td>
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<td>22.125(2)</td>
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<td>90.0</td>
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<td>γ (°)</td>
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<td>90.0</td>
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<td><strong>Molecules/Unit cell, Z</strong></td>
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<td>4</td>
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<td>1.445</td>
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<td>0.71073</td>
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<td><strong>Absorption coefficient (mm\textsuperscript{-1})</strong></td>
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<td>0.359</td>
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<td><strong>Crystal size (mm)</strong></td>
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<td>0.80x0.40x0.08</td>
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<td><strong>θ max (°)</strong></td>
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<td>27.50</td>
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<td>-1, -1, -28</td>
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<td>11, 11, 28</td>
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<td>5267</td>
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<td><strong>Independent reflections</strong></td>
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<td>3908</td>
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<td><strong>Parameters refined</strong></td>
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<td>300</td>
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<td><strong>R1</strong></td>
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<td><strong>wR2</strong></td>
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<td>0.1048</td>
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<td>Δρ\textsuperscript{min} (e/Å\textsuperscript{3})</td>
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<td>-0.301</td>
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Table 7.2
Fractional atomic coordinates and equivalent isotropic temperature factors of the non-hydrogen atoms for TTPN-1

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<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}(\text{Å}^2)$</th>
</tr>
</thead>
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<td>1.1903(2)</td>
<td>0.4053(1)</td>
<td>0.053(1)</td>
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<td>S</td>
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<td>0.6361(2)</td>
<td>0.4544(1)</td>
<td>0.044(1)</td>
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<td>C1</td>
<td>0.7554(7)</td>
<td>0.5603(6)</td>
<td>0.4357(2)</td>
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</tr>
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<td>C2</td>
<td>0.6373(8)</td>
<td>0.4731(8)</td>
<td>0.4734(2)</td>
<td>0.050(1)</td>
</tr>
<tr>
<td>C3</td>
<td>0.4409(8)</td>
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<td>0.4543(3)</td>
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</tr>
<tr>
<td>C3'</td>
<td>0.4922(59)</td>
<td>0.3694(54)</td>
<td>0.4481(18)</td>
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<td>C4</td>
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<td>0.4386(8)</td>
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$U_{eq} = (1/3) \sum_i \sum_j a_i^* a_j^* a_i a_j$
Table 7.3
Fractional atomic coordinates and equivalent isotropic temperature factors of the non-hydrogen atoms for TTPN-II

<table>
<thead>
<tr>
<th>Atom</th>
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<th>y</th>
<th>z</th>
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\[ U_{eq} = \frac{1}{3} \sum_i \sum_j \alpha_i \alpha_j a_i \cdot a_j \]
Table 7.4

Anisotropic temperature factors (Å² x 10³) of the non-hydrogen atoms for TTPN-I

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$$T = -2 \Sigma a^2 U_{11} + \ldots + 2hk a^* b^* U_{12}$$
The table below lists the anisotropic temperature factors ($A^2 \times 10^2$) for the non-hydrogen atoms of TTPN-II.

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The formula for the temperature factor $T$ is given by:

$$T = -2 n^2 [ h^2 a^* a U_{11} + \ldots + 2 h k a^* b U_{12} ]$$
Table 7.6

Fractional atomic coordinates and equivalent isotropic temperature factors for TTPN-I and TTPN-II

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Table 7.7
Bond lengths (Å) involving non-hydrogen atoms for TTPN-I and TTPN-II

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Table 7.9
Bond lengths (Å) and Bond angles (°) involving hydrogen atoms for TTPN-I and TTPN-II

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Table 7.10
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Table 7.11

Deviation (Å) of the atoms from least-squares plane calculation for TTPN-I and TTPN-II

* atoms, not included for the plane calculation

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<td>1</td>
<td>0.445(2)x-0.846(1)y-0.294(2)z+4.80(2)</td>
<td>0.3743(6)x-0.8194(5)y-0.4341(5)z+0.165(*) = 0</td>
</tr>
<tr>
<td>2</td>
<td>0.474(1)x-0.807(1)y-0.351(2)z+4.92(2)</td>
<td>0.4072(6)x-0.8000(4)y-0.4406(8)z+0.029(3) = 0</td>
</tr>
<tr>
<td>3</td>
<td>0.493(2)x-0.794(1)y-0.355(2)z+4.73(3)</td>
<td>0.4333(6)x-0.7929(5)y-0.4284(8)z+0.133(6) = 0</td>
</tr>
<tr>
<td>4</td>
<td>0.457(2)x-0.822(1)y-0.340(2)z+5.10(3)</td>
<td>0.3664(7)x-0.7832(5)y-0.5023(7)z-0.359(3) = 0</td>
</tr>
<tr>
<td>5</td>
<td>0.466(1)x-0.8228(5)y-0.3252(4)z+4.88(1)</td>
<td>0.4043(4)x-0.8056(2)y-0.4339(1)z+0.030(2) = 0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plane 1</th>
<th>TTPN-I</th>
<th>TTPN-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-0.010(5)</td>
<td>0.012(2)</td>
</tr>
<tr>
<td>C6</td>
<td>0.005(5)</td>
<td>-0.004(2)</td>
</tr>
<tr>
<td>C7</td>
<td>0.002(4)</td>
<td>-0.009(2)</td>
</tr>
<tr>
<td>C12</td>
<td>-0.006(4)</td>
<td>0.014(2)</td>
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<table>
<thead>
<tr>
<th>Plane 2</th>
<th>TTPN-I</th>
<th>TTPN-II</th>
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</thead>
<tbody>
<tr>
<td>S</td>
<td>0.0001(1)</td>
<td>-0.0010(4)</td>
</tr>
<tr>
<td>N9</td>
<td>-0.004(4)</td>
<td>-0.003(1)</td>
</tr>
<tr>
<td>N13</td>
<td>0.003(4)</td>
<td>-0.004(1)</td>
</tr>
<tr>
<td>C14</td>
<td>-0.002(6)</td>
<td>0.003(2)</td>
</tr>
<tr>
<td>N15</td>
<td>-0.002(4)</td>
<td>0.001(1)</td>
</tr>
<tr>
<td>C23</td>
<td>---</td>
<td>-0.006(3)</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Plane 3</th>
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<th>TTPN-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8</td>
<td>-0.006(4)</td>
<td>0.005(2)</td>
</tr>
<tr>
<td>N9</td>
<td>-0.004(4)</td>
<td>-0.003(1)</td>
</tr>
<tr>
<td>N13</td>
<td>0.003(4)</td>
<td>-0.004(1)</td>
</tr>
<tr>
<td>C14</td>
<td>-0.002(6)</td>
<td>0.003(2)</td>
</tr>
<tr>
<td>N15</td>
<td>-0.002(4)</td>
<td>0.001(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plane 4</th>
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<th>TTPN-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8</td>
<td>-0.006(4)</td>
<td>0.005(2)</td>
</tr>
<tr>
<td>C17</td>
<td>-0.001(4)</td>
<td>0.002(2)</td>
</tr>
<tr>
<td>C18</td>
<td>0.005(5)</td>
<td>0.002(5)</td>
</tr>
<tr>
<td>C20</td>
<td>-0.004(5)</td>
<td>0.002(5)</td>
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<tr>
<td>C21</td>
<td>0.007(5)</td>
<td>-0.004(2)</td>
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<tr>
<th>Plane 5</th>
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<th>TTPN-II</th>
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<tbody>
<tr>
<td>C1</td>
<td>-0.008(1)</td>
<td>-0.0075(4)</td>
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<tr>
<td>C6</td>
<td>0.005(5)</td>
<td>0.056(2)</td>
</tr>
<tr>
<td>C8</td>
<td>0.033(4)</td>
<td>-0.009(2)</td>
</tr>
<tr>
<td>C10</td>
<td>0.000(5)</td>
<td>0.035(2)</td>
</tr>
<tr>
<td>C12</td>
<td>0.056(4)</td>
<td>-0.001(2)</td>
</tr>
<tr>
<td>C14</td>
<td>-0.040(6)</td>
<td>-0.024(2)</td>
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<tr>
<td>C2</td>
<td>-0.160(7)</td>
<td>0.195(2)</td>
</tr>
<tr>
<td>N16</td>
<td>-0.028(4)</td>
<td>0.076(1)</td>
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<table>
<thead>
<tr>
<th>Dihedral angles</th>
<th>plane</th>
<th>TTPN-I</th>
<th>TTPN-II</th>
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<tbody>
<tr>
<td>1 2</td>
<td>4.3(1)</td>
<td>2.22(4)</td>
<td></td>
</tr>
<tr>
<td>1 3</td>
<td>5.4(1)</td>
<td>3.72(5)</td>
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<tr>
<td>1 4</td>
<td>3.1(1)</td>
<td>4.44(5)</td>
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<tr>
<td>2 3</td>
<td>1.4(1)</td>
<td>1.70(5)</td>
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<tr>
<td>2 4</td>
<td>1.4(1)</td>
<td>4.34(5)</td>
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<tr>
<td>3 4</td>
<td>2.7(1)</td>
<td>5.74(5)</td>
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Table 7.12
The ring asymmetry parameters for TTPN-I and TTPN-II

<table>
<thead>
<tr>
<th>Asymmetry parameters for TTPN-I</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS(C1) = 0.175(3)</td>
<td></td>
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<tr>
<td>AC2(C1) = 0.165(2)</td>
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<tr>
<td>ACS(C2) = 0.238(3)</td>
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<tr>
<td>AC2(C2) = 0.138(2)</td>
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<tr>
<td>ACS(C3) = 0.063(3)</td>
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<tr>
<td>AC2(C3) = 0.238(3)</td>
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<tr>
<td>ACS(C3) = 0.190(2)</td>
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<table>
<thead>
<tr>
<th>Asymmetry parameters for TTPN-II</th>
<th>C1</th>
<th>C2</th>
<th>C3’</th>
<th>C4’</th>
<th>C5</th>
<th>C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS(C1) = 0.17(1)</td>
<td></td>
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<tr>
<td>AC2(C1) = 0.058(7)</td>
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<tr>
<td>ACS(C2) = 0.11(1)</td>
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<tr>
<td>AC2(C2) = 0.093(7)</td>
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<tr>
<td>ACS(C3’) = 0.055(8)</td>
<td></td>
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<tr>
<td>AC2(C3’) = 0.110(8)</td>
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</table>