Group theory, nuclear spin statistics and tunneling splittings of 1,3,5-triamino-2,4,6-trinitrobenzene

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Received 16 August 2004; in final form 2 September 2004
Available online 28 September 2004

Abstract

The symmetry group of the non-rigid 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is constructed for the internal rotations of the nitro groups that exhibit low rotation barriers of 5 kcal/mole. The permutation group has 48 operations characterized by the wreath product $S_3[S_2]$. The nuclear spin statistical weights for TATB with $^{17}O$, $^{14}N$ and $^1H$ species are computed and the tunneling splitting patterns of the rotational and rovibronic levels of TATB are constructed for the first time. It is shown that the ground rovibronic state of TATB is split into $A_1$, $A_2$, $T_1$ and $T_3$ levels.

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1. Introduction

Spectroscopy of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is becoming the focus of recent studies [1,2]. General interest on TATB is due to its potential as a high-energy material and its stability under thermal, impact or shock initiation conditions [3–20]. The symmetry aspects of TATB have been explored in the context of unusual second harmonic generation of TATB [10,11] due to the centrosymmetric crystal structure of TATB [8,9]. Some possible explanations for the observed SHG of TATB varied from polymorphism [10], non-centro symmetric stacking of molecular layers [11], to the centrosymmetric deformation of the geometry [12]. There is also considerable interest in the development of graph theoretical techniques for the characterization of related polycyclic aromatics [21,22].

Recent temperature-dependent Raman spectra of TATB have revealed [1] that there are more peaks in the spectra than expected or could be attributed to a rigid $D_{3h}$ vibrational mode analysis. As noted by McGrane and Shreve [1], the observed spectra could not be assigned unambiguously due to the presence of more peaks and complex normal modes of the TATB molecule. The temperature dependent spectra of TATB show additional peaks than expected for a rigid TATB. Indeed this appears to be consistent with the group theoretical analysis and predictions in the current work that show splitting of the rovibronic levels of TATB into tunneling levels due to the internal rotation of the nitro groups in TATB.

The recent UV-spectra of TATB demonstrate that radicals of TATB can be generated by exposure to irradiation. Hence there is compelling need to understand the symmetry and rovibronic levels. Manna et al. [17] have shown by extensive ab initio computations that the barrier to internal rotation of the nitro groups is only ~5.6 kcal/mole suggesting that the TATB molecule would exhibit considerable non-rigidity due to torsion of...
the nitro groups. The barrier for the internal rotation to the amino group is considerably larger (~17 kcal/mole) due to a partial C–N double bond of the anilinic group. Thus the TATB molecule is an interesting case of a non-rigid molecule due to the internal rotations of the nitro groups.

The symmetry group of the non-rigid TATB has not been studied up to date. This is especially important for the analysis and assignment of the spectra that exhibit tunneling splittings due to the internal rotation of the nitro groups. Moreover $^{17}$O NMR spectroscopy can be a powerful tool for the study of nitro group internal rotations. Such studies would be benefited by the nuclear spin statistical analysis of $^{17}$O TATB that we provide here. We have developed the symmetry group of the non-rigid TATB, its nuclear spin statistics and the patterns of rovibronic levels splittings due to the internal rotation of the nitro groups.

2. Wreath product group approach to non-rigid TATB

The concept of symmetry group of non-rigid molecules as a permutation-inversion group was formulated first by Longuet-Higgins [23] although there have been earlier works that suggested the need for such a framework. Balasubramanian [24] showed that these groups could be cast into elegant algebraic structures known as wreath product groups. The character theory of wreath product groups has been considered and discussed [25,26]. In particular the development of generators for the characters of wreath product groups has provided a general algorithm for the construction for the character tables of wreath product groups [25]. We show here that the wreath product formalism leads to a permutation group of order 48 for the symmetry group of non-rigid TATB. Other applications of wreath products can be seen in [26–31].

The molecular framework of TATB is shown in Fig. 1. The rigid TATB molecule has $D_3$, $D_{3h}$ and even lower symmetries at various levels of theories. Our recent work shows a $D_3$ to $D_{3h}$ equilibrium structure at higher levels. In the present work the non-rigid group of TATB is formulated by allowing for the internal rotations of the nitro groups. It is assumed here that the amino groups would not exhibit large amplitude motions due to a much larger barrier for this process [17]. We first develop the group of all permutation operations and then introduce the inversion operation since the total group is a direct product of the permutation and inversion groups. Let all the permutations of the rigid framework with $D_3$ symmetry be collected into a group which we call $G$, and as a set of permutations, $G$ is isomorphic to the $S_3$ permutation group in the mathematical literature [32]. In general the $S_n$ group consists of $n!$ permutations of $n$ objects in a set $\Omega$. Thus the permutations of the nuclei of the rigid TATB framework would consist of six permutations isomorphic to both $S_3$ permutation group and the $D_3$ point group. The internal rotations of the nitro group switch the oxygen atoms. Let the permutations of the oxygen atoms of each nitro group be the group $H$, which in this case, is the $S_2$ group of permutations. The overall group of TATB then becomes the wreath product of $G$ with $H$, denoted by $G[H]$. Specifically for TATB the wreath product group becomes $S_3[S_2]$. The group $G[H]$ consists of permutations

$$\{(g; \pi) \mid \pi \text{ mapping of } \Omega \text{ into } H, \ g \in G\},$$

with the composition law

$$(g; \pi)(g'; \pi') = (gg'; \pi \pi'),$$

where

$$\pi_i(i) = \pi(g^{-1}i), \ \forall i \in \Omega,$$
$$\pi^{-1}(i) = \pi(i)\pi'(i), \ \forall i \in \Omega.$$

Since the non-rigidity of TATB arises from the internal rotations of the nitro groups, for simplicity, we can define the set $\Omega$ as the nitrogen nuclei of the nitro groups of TATB. Then all the symmetry operations of non-rigid TATB can be represented as permutations of the oxygen nuclei. The order of the group $G[H]$ is $|G||H|^n$. For the TATB this means the order of the permutation group is

$$|S_3[S_2]| = 3!2!^3 = 48.$$

The conjugacy classes of TATB group are characterized by matrix types defined as follows. Let a permutation $g \in G$ give rise to $a_1$ cycles of length 1, $a_2$ cycles of length 2, \ldots, $a_n$ cycles of length $n$ upon its action on the set $\Omega$. The cycle type of $G$ is then denoted by $T_g = (a_1, a_2, \ldots, a_n)$. To illustrate a permutation $(1)(23)$ of the nitrogen nuclei of all three nitro groups would...
correspond to the cycle type (1,1,0). Let \( C_1, C_2, \ldots, C_s \) be the conjugacy classes of the group H. Since G is a complete \( S_n \) group of \( n! \) permutations, we can cast the cycle type of an element in the wreath product \( G[H] \) by a \( s \times n \) matrix, \( T(g; \pi) \) called the cycle type of \( (g; \pi) \) as defined follows. If \( a_{ik} \) of the cycle products of G belong to the conjugacy class \( C_i \) in the group \( H \), we can define the cycle type of \( (g; \pi) \), which represents the conjugacy class of \( S_n[H] \) as

\[
T(g; \pi) = a_{ik} \quad (1 \leq i \leq s, \ 1 \leq k \leq n).
\]

Table 1 shows all possible matrix types that represent the conjugacy classes of the group \( S_3[S_2] \) of TATB. The number of conjugacy classes and the number of elements in each conjugacy class are obtained using the following technique. Let \( P(m) \) denote the number of partitions of integer \( m \) with the convention that \( P(0) = 1 \). Let \( n \) be partitioned into ordered \( s \)-tuples \( (s = \text{no of conjugacy classes of } H) \), \( (n) = (n_1, n_2, \ldots, n_s) \) such that \( \sum n_i = n \). The number of conjugacy classes of \( S_n[H] \) is given by

\[
\sum_n P(n_1)P(n_2) \cdots P(n_s).
\]

Thus for the TATB’s \( S_3[S_2] \) group the ordered partitions are \((3,0), (0,3), (2,1), (1,2)\) since the \( S_2 \) group has 2 conjugacy classes. By substituting the values of \( P(3) = 3 \), \( P(2) = 2 \), \( P(1) = 1 \) and \( P(0) = 1 \) in the above expression, we obtain the number of conjugacy classes of \( S_3[S_2] \) as \( 3 + 3 + 2 + 2 = 10 \). Ten classes thus obtained are shown in Table 1. The number of elements in each conjugacy class of \( S_n[H] \) is given by

\[
\prod_{i,k} a_{ik} \frac{(k[H] / (C_i)^{m})}{n}.
\]

For example, the order of the fifth conjugacy class in Table 1 is given by

\[
\frac{6.2^5}{1!(1.2/1)1!(2.2)} = 6.
\]

The character table of the \( S_3[S_2] \) group of TATB can be generated using powerful combinatorial generating functions that involve the matrix type manipulations. First the irreducible representations of the \( S_3[S_2] \) group are generated using Clifford’s algebra of induced representations from a smaller group to a larger group [24,32]. The irreducible representations of the \( S_n \) group are well known to be characterized by the partitions of \( n \) [32]. They are denoted by \([n_1, n_2, \ldots, n_m]\), where \( n_1, n_2, \ldots, n_m \) is a partition of the integer \( n \). Thus the irreducible representations of the \( S_2 \) group are \([2]\) and \([1^2]\), while the irreducible representations of the group \( S_3 \) are \([3]\), \([21]\) and \([1^3]\). As reviewed by one of the authors before [24], the irreducible representations of \( S_3[S_2] \) are constructed by first forming the outer tensor (outer direct) products of the representations of \( S_2 \) three times (since there are three nitro groups in TATB) and then finding the inertia factor of each such product, and subsequently inducing the representation from the inertia factor group to the whole group. The unique outer products of for \( S_2 \times S_2 \times S_2 \) are given by

\[
\]


The inertia factor groups of the above products are \( S'_3, S'_3, S'_2 \) and \( S'_3 \), respectively. The overall representations of the \( S_3[S_2] \) groups are obtained by multiplying the above outer products with the irreducible representations of the factor group for each product and then inducing the whole product into \( S_3[S_2] \). That is, the irreducible representations of \( S_3[S_2] \) are given by

\[
A_1 = ([2] \# [2] \# [2]) \circ [3]',
\]

\[
E_1 = ([2] \# [2] \# [2]) \circ [21]',
\]

\[
\]

\[
T_1 = ([2] \# [2] \# [1^2]) \circ [2]' \uparrow S_3[S_2],
\]

\[
T_2 = ([2] \# [2] \# [1^2]) \circ [1^2]' \uparrow S_3[S_2],
\]

\[
T_3 = ([1^3] \# [1^2] \# [2]) \circ [2]' \uparrow S_3[S_2],
\]

\[
T_4 = ([1^2] \# [1^2] \# [2]) \circ [1^2]' \uparrow S_3[S_2],
\]

\[
A_3 = ([1^2] \# [1^2] \# [1^2]) \circ [3]',
\]

\[
E_1 = ([1^2] \# [1^2] \# [1^2]) \circ [21]',
\]

\[
A_4 = ([1^2] \# [1^2] \# [1^2]) \circ [1^3]',
\]

where the \( \uparrow \) stands for the induced representation from the factor group to the whole group [24]. Consequently there are 10 irreducible representations in the \( S_3[S_2] \) wreath product group.

<table>
<thead>
<tr>
<th>No</th>
<th>Matrix</th>
<th>Permutation</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1'</td>
<td>[3 0 0] [0 0 0]</td>
<td>[1^6]</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>[2 0 0] [1 0 0]</td>
<td>[1^2]</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>[1 0 0] [2 0 0]</td>
<td>[1^2]</td>
<td>3</td>
</tr>
<tr>
<td>4'</td>
<td>[0 0 0] [3 0 0]</td>
<td>[2^3]</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>[1 1 0] [0 0 0]</td>
<td>[1^2]</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>[0 1 0] [1 0 0]</td>
<td>[2^3]</td>
<td>6</td>
</tr>
<tr>
<td>7'</td>
<td>[1 0 0] [0 1 0]</td>
<td>[1^4]</td>
<td>6</td>
</tr>
<tr>
<td>8'</td>
<td>[0 0 0] [1 1 0]</td>
<td>24</td>
<td>6</td>
</tr>
<tr>
<td>9'</td>
<td>[0 0 1] [0 0 0]</td>
<td>[3^2]</td>
<td>8</td>
</tr>
<tr>
<td>10'</td>
<td>[0 0 0] [0 0 1]</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>
The character table of the $S_3[S_2]$ group is generated using the generating functions for each of the above 10 irreducible representations. Balasubramanian [25] has developed the generating function algorithm for the characters of the wreath product groups. According to this method let $P_G$ stand for the generalized character cycle index [31] of the irreducible representation $\chi$ of the factor subgroup $G'$ of $G$ as determined by the outer product. $P_G$ is given by

$$P_G^\chi = \frac{1}{|G|} \sum_{g \in G} \chi(g)s_1^{h_1} s_2^{h_2} \cdots s_n^{h_n}.$$ 

Let $T(M)_i$ be the matrix type of the representation of the inertia factor. Then the generating function for the irreducible representation $F^*$ of $S_n[H]$ is obtained by the following replacement:

$$T(G[H])^\chi = P_G^\chi(s_i \rightarrow T(M)_i).$$

In the above expression once every $s_i$ is replaced by the corresponding matrix type $T(M)_i$, algebraic manipulations are done with the cycle type matrices. To differentiate that these are not the usual additions and multiplications of matrices (as they involve cycle types), we have introduced $\oplus$, $\otimes$, $-$ operations for additions, multiplications and subtractions. For example, the following examples illustrate how cycle type matrices are multiplied.

$$\begin{bmatrix} 1 & 0 & 0 \end{bmatrix}^3 \begin{bmatrix} 3 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 3 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

$$\begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix},$$

$$\begin{bmatrix} 1 & 0 & 0 \end{bmatrix}^2 \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 2 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}.$$

As an illustration let us consider two examples. First consider the $A_2$ irreducible representation given by $[2][2][1][1]^3$. Since $[1]^3$ is the factor group irreducible representation, its generalized character cycle index is given by

$$P^{[1]}_{S_3} = \frac{1}{6} \left[ s_3^1 - 3s_1s_2 + 2s_3 \right].$$

The basic matrix types are given as follows for the representation $[2]$ are given by

$$T(M)_1^{[2]} = \frac{1}{2} \left[ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \right],$$

$$T(M)_2^{[2]} = \frac{1}{2} \left[ \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \right],$$

$$T(M)_3^{[2]} = \frac{1}{2} \left[ \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \right].$$

Replacing every $s_i$ by $T(M)_i$ in the expression for $P^{[1]}_{S_3}$ we obtain

$$GF_{A_2} = \frac{1}{6} \left[ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \right]^3$$

$$- 3 \frac{1}{2} \left[ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \right] \times \left[ \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \right]$$

$$+ \frac{1}{2} \left[ \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \right].$$

By using the matrix manipulations indicated above for the cycle types, we can simplify the above expression into

$$GF_{A_2} = \frac{1}{6} \left[ \begin{bmatrix} 3 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + 3 \begin{bmatrix} 2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \right]$$

$$+ 3 \left[ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \right] - 6 \left[ \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \right]$$

$$+ 8 \left[ \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \right].$$

The coefficients in the above expression with the order of the group (48) factored out give the product of the character of a conjugacy class and the number of elements in the corresponding conjugacy class. As seen from Table 1, ten matrix types in the above expression are the conjugacy classes of the group $S_3[S_2]$. The string of coefficients \{1, 3, 3, 1, –6, –6, –6, –6, 8, 8\} in the above expression generates the character \{1, 1, 1, 1, –1, –1, –1, –1, 1, 1\} when the number of elements in each conjugacy class is factored out.

Table 2 shows the entire character table of the group $S_3[S_2]$ thus constructed using the matrix generating function method outlined above. As seen from Table 2, the character table consists of 4 one-dimensional irreducible representations, 2 two-dimensional representations and 4 three-dimensional representations satisfying the condition $4 \cdot 1^2 + 2 \cdot 2^2 + 4 \cdot 4^2 = 48$, the order of the group $S_3[S_2]$. Moreover, using a computer code, we have checked for the orthogonality of every row of the character table with respect to every other row, thus confirming compliance of the great orthogonality theorem. The character table thus generated has all permutations of the non-rigid group of TATB. The inversion operation [23] does not generate any new permutation and it is thus the $E^*$ operation and thus the whole permutation-inversion group is the direct product of the $S_3[S_2]$ group and the inversion group. Thus the character table of PI group of 96 operations is readily generated from Table 2, by replicating blocks of the same table along
the rows and columns and multiplying the last block by –1. This is analogous to how the character table of the rigid planar structure, D_{3h} is generated from the D_{3} group since the inversion operation for the rigid structure also corresponds to E*, and is thus a direct product. Since the inversion operation does not generate any new permutation operations, it suffices to work with the permutation group S_{3}[S_{2}], isomorphic with O_{h}, for all applications.

3. Tunneling splittings of rotational/rovibronic levels and nuclear spin statistics of non-rigid TATB

Table 3 shows the tunneling splitting patterns of the rotational levels of TATB by correlating the D^{(1)} representation into the D_{3} (rigid) and S_{3}[S_{2}] groups using the subduced and induced representation techniques. As seen from Table 3, even in the ground rotational state, non-rigid TATB exhibits tunneling splitting into A_{1} + A_{3} + T_{1} + T_{3} levels. The realistic description involves the direct product of the tunneling, vibrational and electronic irreducible representations. Since the ground electronic state of TATB is a 1A_{1} state the overallrovibronic representation is the product of the tunneling and vibrational irreducible representations. It is thus evident that the coupling of tunneling levels with the vibrational levels can influence the observed spectral splittings as more spectral lines than expected consistent with the recent experimental study [1]. The coupling between tunneling levels and vibrational levels would be larger in the excited vibrational levels due to the break down of Born-Oppenheimer approximation due to non-rigidity of TATB. In order to complete the analysis of the TATB rovibronic levels, we have provided the nuclear spin species and spin statistical weights. The nuclear spin species can also be helpful in analyzing the ^{17}O NMR or ^{17}O multiple quantum NMR spectra of TATB. Since ^{17}O NMR can be a powerful tool to confirm the internal rotations of the nitro groups predicted theoretically [17], we have provided the ^{17}O nuclear spin species data in the S_{3}[S_{2}] group. The spin statistics is obtained using a combinatorial multinomial generating function method [27,28,31] using the character table shown in Table 2. However, the ^{17}O nuclear spin generation was quite challenging in that ^{17}O has a spin 5/2 nucleus and thus exhibits six different spin states per nucleus. Such spin analysis with group theoretical induction and subductions have been done extensively [33,34], and also the character-based cycle indices have been used in many applications [31] including chirality [35]. Let us represent the 6 ms functions of ^{17}O by x_{1}, x_{2}, . . . , x_{6}, where x_{1} represents m_{s} = -5/2, x_{2} represents m_{s} = -3/2, . . . , x_{6} representing m_{s} = 5/2. To illustrate consider the GCCI of the A_{4} representation from Table 2 is given by

\[
P_{G}^{A_{4}} = \frac{1}{48} [6 \cdot 3x_{1}x_{2} + 3x_{1}x_{2}^2 - 3x_{2}^3 - 6x_{1}x_{2}^2 + 6x_{2}^3 + 6x_{1}x_{4}] - 6x_{2}x_{4} + 8x_{2}^2 - 8x_{2}^3].
\]

Table 3
Tunneling splittings of rotational levels non-rigid TATB

<table>
<thead>
<tr>
<th>J</th>
<th>Rigid(D_{3})</th>
<th>Non-rigid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>A_{1}</td>
<td>A_{1} + A_{3} + T_{1} + T_{3}</td>
</tr>
<tr>
<td>1</td>
<td>A_{2} + E</td>
<td>(A_{2} + A_{3} + T_{2} + T_{4}) + (E_{1} + E_{2} + T_{1} + T_{2} + T_{3} + T_{4})</td>
</tr>
<tr>
<td>2</td>
<td>A_{1} + 2E</td>
<td>(A_{1} + A_{2} + T_{1} + T_{3}) + 2(E_{1} + E_{2} + T_{1} + T_{2} + T_{3} + T_{4})</td>
</tr>
<tr>
<td>3</td>
<td>A_{1} + 2A_{2} + 2E</td>
<td>(A_{1} + A_{2} + T_{1} + T_{3}) + 2(A_{2} + A_{4} + T_{2} + T_{4}) + 2(E_{1} + E_{2} + T_{1} + T_{2} + T_{3} + T_{4}) + (A_{1} + A_{3} + T_{1} + T_{3})</td>
</tr>
<tr>
<td>4</td>
<td>2(A_{1} + A_{2} + 2E) + D^{(1)}</td>
<td>2(A_{1} + A_{2} + T_{1} + T_{3}) + 2(A_{2} + A_{4} + T_{2} + T_{4}) + 2(E_{1} + E_{2} + T_{1} + T_{2} + T_{3} + T_{4}) + (A_{1} + A_{3} + T_{1} + T_{3})</td>
</tr>
<tr>
<td>n</td>
<td>2(A_{1} + A_{2} + 2E) + D^{(1)}</td>
<td>2(A_{1} + A_{3} + T_{1} + T_{3}) + 2(A_{2} + A_{4} + T_{2} + T_{4}) + 2(E_{1} + E_{2} + T_{1} + T_{2} + T_{3} + T_{4}) + (A_{1} + A_{3} + T_{1} + T_{3})</td>
</tr>
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Table 2
Character table of the non-rigid group of TATB

<table>
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<tr>
<th>1^6</th>
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<th>1^22</th>
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<th>1^22</th>
<th>2^3</th>
<th>1^4</th>
<th>24</th>
<th>3^2</th>
<th>6</th>
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<tbody>
<tr>
<td>A_{1}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>A_{2}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>–1</td>
<td>–1</td>
<td>–1</td>
<td>–1</td>
<td>1</td>
</tr>
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<td>–1</td>
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<td>–1</td>
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<td>–1</td>
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<td>0</td>
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<td>–2</td>
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<td>–1</td>
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<td>1</td>
<td>–1</td>
<td>1</td>
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The $^{17}$O nuclear spin generator is obtained by replacing every $s_k$ in the above expression by $(a_1^k + d_2^k + \cdots + d_{6}^k)$. Thus the $^{17}$O nuclear spin generator for the $A_4$ representation is given by

$$GF^{A_4} = \frac{1}{48} \left[ (x_1 + x_2 + \cdots + x_6)^6 - 3(x_1 + x_2 + \cdots + x_6)^4 \times (x_1^2 + x_2^2 + \cdots + x_6^2) - 3(x_1 + x_2 + \cdots + x_6)^2 \times (x_1^2 + x_2^2 + \cdots + x_6^2)^2 + 6(x_1 + x_2 + \cdots + x_6)^2(x_1^2 + x_2^2 + \cdots + x_6^2)^3 + 8(x_1^2 + x_2^2 + \cdots + x_6^2)^2 - 8(x_1^6 + x_2^6 + \cdots + x_6^6) \right].$$

The coefficient of a typical term $\sum a_{m}^{17O} \sum a_{n}^{17O} \cdots \sum a_{o}^{17O}$ yields the number of $^{17}$O nuclear spin functions containing $m_1 a_1$ spins, $m_2 a_2$ spins, ..., $m_6 a_6$ spins that transform as the $A_4$ irreducible representation. The irreducible representations for the nuclear spin functions are sorted according to their total $M_F$ nuclear spin quantum numbers, which then enumerate the nuclear spin multiplets for each of the irreducible representations. This involves considerable combinatorics and multinomial expansions and numerous terms that need to be kept track of. Hence a computer code was developed for $^{17}$O nuclear spin generator of TATB. The results are shown in Table 4 together with the $^{14}$N and $^1$H species. The $^{14}$N and $^1$H species are generated in the rigid non-rigid group of TATB. The rovibronic levels and statistics, and thus it would be interesting to look at the $^{17}$O NMR of TATB. The overall nuclear spin statistical weights are obtained as the direct product of $^{17}$O, $^{14}$N and $^1$H species. These weights are shown in Table 5 for all the irreducible representations of the non-rigid TATB. The rovibronic levels and 

### Table 4

<table>
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<th>Symmetry</th>
<th>$^{17}$O Species</th>
<th>$^{14}$N Species</th>
<th>Proton Species</th>
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$^a$ sum of (stat weights $\times$ dimension of reps)$=36 \times 6^6$.

$^b$ sum of (stat weights $\times$ dimension of reps)$=36 \times 6^6$.

D$_3$ group and then induced into the non-rigid group since the amino groups are assumed to be rigid due to a large barrier for internal rotation. As seen from Table 4, TATB exhibits rich non-rigid $^{17}$O nuclear spin statistics, and thus it would be interesting to look at the $^{17}$O NMR of TATB. The overall nuclear spin statistical weights are obtained as the direct product of $^{17}$O, $^{14}$N and $^1$H species. These weights are shown in Table 5 for all the irreducible representations of the non-rigid TATB. The rovibronic levels and
statistical weights of the rigid D$_3$ structure into the non-rigid TATB are correlated by the use of induced representations as follows:

\[ A_1(D_3 : 362867472) \uparrow S_3[S_2] \]
\[ = A_1(72156672) + A_3(26317080) + T_1(154416780) + T_3(110326860), \]

\[ A_2(D_3 : 362727504) \uparrow S_3[S_2] \]
\[ = A_2(71870904) + A_4(26171280) + T_2(154212660) + T_4(110122740), \]

\[ E(D_3 : 725593680) \uparrow S_3[S_2] \]
\[ = E_1(144026820) + E_2(52487820) + T_1(154416780) + T_2(154212660) + T_3(110326860) + T_4(110122740). \]

4. Conclusion

The symmetry group of the non-rigid TATB which exhibits internal rotations of the nitro groups was shown to be the wreath product group $S_3[S_2]$ which contains 48 permutations. The total PI group of TATB is a direct product of this group with the inversion group and contains 96 operations. The character table of the group was obtained using powerful combinatorial generators using matrix type manipulations and was utilized to establish tunneling splittings of the rovibronic levels of TATB. It was shown that even in the ground state of TATB the tunneling splittings of the rovibronic levels of TATB. Our prediction that the tunneling splittings of the signals that do not correspond to the vibrational normal modes alone. Since interaction with crystal environment could also cause such splittings, it would be necessary to obtain the gas-phase spectra to establish the predicted tunneling splittings.

Acknowledgements

The Research at UC Davis was supported by the National Science Foundation under Grant No. CHE-0236434. The work at LLNL was performed in part under the auspices of the US Department of Energy by the University of California, LLNL under contract number W-7405-Eng-48.

References