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Calculation of kinetic energy functions for the ring-twisting and ring-bending vibrations of tetralin and related molecules

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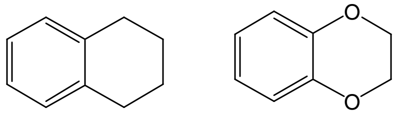
Abstract

Vector methods have been developed for the computation of the kinetic energy (reciprocal reduced mass) expressions for the ring-twisting and ring-bending vibrations of bicyclic molecules in the tetralin family. The definitions of the bond vectors in terms of these coordinates are presented. Both one- and two-dimensional kinetic energy surfaces have been calculated for tetralin and 1,4-benzodioxan and both are significantly coordinate dependent. The results for the S_0 electronic ground states and $S_1(\pi,\pi^*)$ excited states are presented.

Keywords: Kinetic energy functions; Vector methods; Tetralin; Ring-twisting; Ring-bending; 1,4-Benzodioxan

1. Introduction

For many years we have been carrying out determinations of potential energy surfaces utilizing spectroscopic methods [1–5]. These calculations also require the kinetic energy expressions for use in the Schrödinger wave equation. In 1982 we first described how to utilize vector methods for carrying out kinetic energy (reciprocal reduced mass) calculations needed for the determination of potential energy functions for the out-of-plane vibrations of four- and five-membered ring molecules such as cyclobutane and cyclopentene [6,7]. Later we also described similar calculations for a variety of other molecules including asymmetric five-membered ring molecules [8], bicyclic molecules containing benzene rings [1,9–12], 1,4-cyclohexadiene and analogs including 9,10-dihydroanthracene [13], and 1,3-cyclohexadiene and analogs such as 1,2-dihyronaphthalene [14]. The book by Fitts [15] very nicely shows how to make effective use of vectors for studying molecular systems. In the present paper we present the methodology necessary to calculate the kinetic energy expressions for tetralin (TET) and related molecules such as 1,4-benzodioxan (14BZD).



TET 14BZD

2. Calculation methods

Fig. 1 presents for TET the definition of the bond vectors $\vec{\mathbf{u}}_1$ to $\vec{\mathbf{u}}_{22}$ along with the essential geometrical parameters for the bond distances (R_1 to R_6 for the C–C bonds and E_1 to E_4 for the C–H bonds) and bond angles (β_1 and β_2 in the benzene ring, α and γ in the saturated six-membered ring, and T_1 and T_2 for the HCH angles). Additional vectors $\vec{\mathbf{u}}_{23}$, $\vec{\mathbf{u}}_{24}$, and $\vec{\mathbf{u}}_{25}$, which are useful for defining the ring-twisting (τ) and ring-bending (θ) motions, are also shown. $\vec{\mathbf{u}}_{23}$ is the vector connecting atoms 1 and 4 (standard organic nomenclature) in the saturated ring, $\vec{\mathbf{u}}_{24}$ is the same as $\vec{\mathbf{u}}_4$ when the saturated ring is not twisted,

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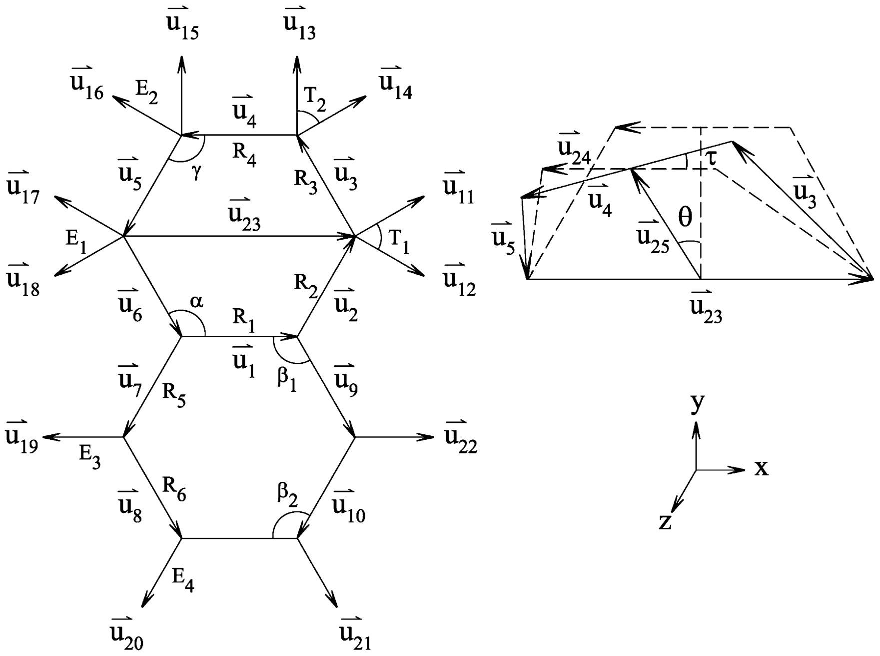

Fig. 1. Vectors for defining the atom positions of tetralin and the definition of the ring-twisting coordinate τ and the ring-bending coordinate θ.

and $\vec{\mathbf{u}}_{25}$ is the vector connecting the midpoints of $\vec{\mathbf{u}}_{23}$ and $\vec{\mathbf{u}}_{24}$.

Table 1 presents the components of each bond vector $\vec{\mathbf{u}}_i = a_i\ \mathbf{i} + b_i\ \mathbf{j} + c_i\ \mathbf{k}$. These vectors can be used not only for TET and 14BZD but also for any molecule with a symmetric saturated six-membered ring attached to a benzene ring. The vectors $\vec{\mathbf{u}}_{23}$, $\vec{\mathbf{u}}_{24}$, and $\vec{\mathbf{u}}_{25}$ can be solved easily, and formulas for these are also shown in Table 1. $\vec{\mathbf{u}}_4$ can be obtained from the following vector equations:

$$|\vec{\mathbf{u}}_4| = R_4, \tag{1}$$

$$\vec{\mathbf{u}}_4 \cdot \vec{\mathbf{u}}_{24} = R_4^2 \cos\tau, \tag{2}$$

$$\vec{\mathbf{u}}_4 \cdot \vec{\mathbf{u}}_{25} = 0, \tag{3}$$

$\vec{\mathbf{u}}_3$ and $\vec{\mathbf{u}}_5$ can be solved from $\vec{\mathbf{u}}_4$, $\vec{\mathbf{u}}_{23}$, and $\vec{\mathbf{u}}_{25}$ using the following vector equations:

$$\vec{\mathbf{u}}_3 + \vec{\mathbf{u}}_4 + \vec{\mathbf{u}}_5 + \vec{\mathbf{u}}_{23} = 0, \tag{4}$$

$$\vec{\mathbf{u}}_3 + \left(-\vec{\mathbf{u}}_5\right) = 2\vec{\mathbf{u}}_{25}, \tag{5}$$

$$|\vec{\mathbf{u}}_3| = |\vec{\mathbf{u}}_5| = R_3. \tag{6}$$

In order to calculate the kinetic energy expressions for the ring-twisting and ring-bending modes, it is necessary to define each of the vectors in Fig. 1 in terms of the θ and τ coordinates so that the derivatives $\delta\vec{\mathbf{r}}_i/\delta\theta$ and $\delta\vec{\mathbf{r}}_i/\delta\tau$ can be calculated by numerical methods. The $\vec{\mathbf{r}}_i$ vector for each atom i is the atom coordinate vector in the center-of-mass system [5–10]. For the calculation it is assumed that all bond distances remain fixed during the vibrations, that the bisector of each CH_2 group remains coincident with the corresponding C–C–C angle bisector, and that each C–H bond lies along the corresponding C–C–C angle bisector of the benzene ring. Once the derivatives have been calculated, they can be used to set up a 4×4 G^{-1} matrix for a one-dimensional problem or a 5×5 G^{-1} matrix for a two-dimensional problem. Inversion of the matrix results in the G matrix containing the g_{44} terms for one-dimensional cases and the g_{44}, g_{45}, and g_{55} terms for two-dimensional cases [5–10]. Note that subscripts 1 to 3 correspond to the molecular rotations.

3. Results

3.1. One-dimensional kinetic energy functions

Whenever a vibrational problem is taken to be one-dimensional, a 4×4 G^{-1} matrix is set up, and, after inversion of the matrix, the resulting g_{44} term is the kinetic energy term (reciprocal reduced mass) for the molecular structure and conformation that was assumed. Typically this varies considerably with the coordinate and a polynomial expression for $g_{44}(x)$ can be written, where x is the vibrational coordinate. These are of the form

$$g_{44}(x) = \sum_{i=0}^{n} g_{44}^{(i)} x^i = \frac{1}{\mu(x)}. \tag{7}$$

The computed $g_{44}(\tau)$ expression for TET in its S_0 ground state was determined to be

$$g_{44}^{S_0}(\tau) = 0.0306595 - 0.00230104\tau^2 - 0.0157768\tau^4 + 0.00458234\tau^6. \tag{8}$$

The bending expansion $g_{44}(\theta)$ is

$$g_{44}^{S_0}(\theta) = 0.0333862 - 0.003280620\theta^2 - 0.003250370\theta^4 + 0.001487040\theta^6. \tag{9}$$

In the $S_1(\pi,\pi^*)$ excited state $g_{44}(\tau)$ for the twisting is