New Way of Describing Static and Dynamic Deformations of the Jahn–Teller Type in Ring Molecules

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ABSTRACT: A new method is presented to describe deformations of an N-membered planar ring (N-ring) molecule in terms of deformation vectors that can be expressed by a set of \(2N - 3\) deformation amplitudes and phase angles. The deformation coordinates are directly derived from the normal vibrational modes of the N-ring and referenced to a regular polygon (N-gon) of unit length. They extend the conceptual approach of the Cremer-Pople puckering coordinates (J. Am. Chem. Soc. 1975, 97, 1354) to the planar ring and make it possible to calculate, e.g., a planar ring of special deformation on a Jahn–Teller surface. It is demonstrated that the \(2N - 3\) deformation parameters are perfectly suited to describe the pseudorotation of a bond through the ring as it is found in cyclic Jahn–Teller systems. In general, an N-membered planar ring can undergo \(N - 2\) different bond pseudorotations provided the energetics of such a process is feasible. The Jahn–Teller distortions observed in ring compounds correspond either directly to the basic pseudorotation modes or to linear combinations of them. Any deformed ring molecule can be characterized in terms of the new ring deformation coordinates, which help to identify specific electronic effects. The usefulness of the ring deformation coordinates is demonstrated by calculating the Jahn–Teller surfaces for bond pseudorotation in the case of the cyclopropyl radical cation and cyclobutadiene as well as the ring deformation surfaces of disulfur dinitride and its dianion employing multireference averaged quadratic coupled cluster (MR-AQCC) theory, equation-of-motion coupled cluster theory in form of EOMIP-CCSD, and single determinant coupled cluster theory in form of CCSD(T).

1. INTRODUCTION

A chemical reaction proceeding along a reaction path can be described in its very first stage via a molecular vibration or a combination of molecular vibrations.\(^1\)\(^-\)\(^3\) A molecular vibration in turn can be formulated in such a way that it is driven by a leading parameter (an internal coordinate, a symmetry coordinate, a puckering coordinate, etc.).\(^4\)\(^-\)\(^8\) Hence, by studying the molecular vibrations of a molecule it is possible to define a reaction coordinate for any change of a molecule or reaction complex. This should provide a possibility of identifying and investigating molecular changes, especially rearrangements, that previously were not known or not well understood.

In this work, we investigate the in-plane vibrations of a planar ring\(^7\)\(^,\)\(^8\) because they initiate in-plane deformations or rearrangements of the ring molecule that conserve planarity and lead to new ring forms or ring-opening and acyclic forms. Such processes can be Jahn–Teller distortions,\(^8\)\(^,\)\(^9\) bond pseudorotation,\(^9\)\(^,\)\(^10\) or the closely related bond shifting in annulenes.\(^11\)\(^-\)\(^16\) Bond pseudorotation has been observed in the case of charged small ring molecules whereas bond shifting is typical of larger annulenes. In both cases, experimental and theoretical descriptions have focused on stationary points of the associated potential energy surfaces (PES) rather than exploring the PES along a deformation or rearrangement path. The basic difficulty of describing such a path stems from the definition of generally applicable reaction coordinates. In this work, we will introduce a new concept for describing intrinsic deformations as well as rearrangements of planar rings. In deriving this concept, we will be guided by the previous work on pseudorotation of puckered rings and the description of this process with the help of ring puckering coordinates.\(^17\)\(^-\)\(^22\)

The new concept is based on a partitioning of the \((3N - 6)\)-dimensional configuration space of an N-membered ring molecule (“N-ring”) into subspaces in which specific ring puckering or ring deformation processes can take place. In view of the fact that ring-puckering can be described in an \((N - 3)\)-dimensional subspace,\(^17\)\(^,\)\(^21\)\(^,\)\(^22\) deformations of a planar N-ring should take place in a \((2N - 3)\)-dimensional subspace spanned for example by N bond lengths and \(N - 3\) bond angles. Because there are \(N\) bond angles in the planar N-ring, the choice of \(N - 3\) bond angles cannot be unique and therefore it is desirable to specify a special set of \(2N - 3\) deformation coordinates that complements in the case of a nonplanar N-ring the \((N - 3)\) puckering coordinates and helps to describe in-plane deformations of the N-ring in a unique way. These ring deformation coordinates (RDCs) can be obtained by analyzing the in-plane vibrational modes and their symmetries for a suitable N-membered reference ring, then utilizing the symmetry information to define RDCs applicable to any N-ring, and finally associating the electronic structure changes of a ring with...
specific ring deformations or dynamic deformation processes such as bond pseudorotation or bond shifting. In this work, it will be shown that RDCs are useful tools for (i) analyzing the geometry of planar ring molecules, (ii) describing static and dynamic ring distortions caused, for example, by a Jahn–Teller effect, and (iii) calculating deformation surfaces for bond pseudorotation, ring inversion, or bond stretch isomerization.

Results of this work are presented in the following sequence. In section 2, we will define the N-membered reference ring, its configurational space, its molecular vibrations, and its symmetry. Utilizing this analysis, we will derive in section 3 RDCs and present their mathematical foundation. In section 4, ring deformations will be characterized with the help of the RDCs and the concept of bond pseudorotation in Jahn–Teller systems will be discussed. Application of the RDCs will be presented in the following section 5.

2. SYMMETRY ANALYSIS OF RING VIBRATIONS

Conformational and deformational changes of an N-ring molecule are described by utilizing, as a suitable reference, the N-membered regular polygon (\(N\)-gon) of \(D_{N_h}\) symmetry, which we locate in a reference plane called the mean plane (following the nomenclature used for the derivation of ring puckering coordinates\(^{7,21,22}\)). The normal of the mean plane is chosen to be the \(z\)-axis and the mean plane to be identical with the \(x,y\)-plane. Furthermore, the geometrical center of the \(N\)-gon is used as the origin of the coordinate system. Atom 1 (vertex 1) of the polygon is located at the 9 o’clock position, which gives the direction of the \(x\)-axis and the atoms of the polygon are sequentially numbered clockwise around the ring (see the example of a 5-gon in Figure 1).

In general, an \(N\)-gon undergoes \(3N\) motions, which can be classified with the help of the \(D_{N_h}\) character tables for \(N\) being even or odd (Tables 1 and 2)\(^{23,24}\). Because of the positioning of the \(N\)-gon in the mean plane and the fixing of the positions of the origin and atom 1, translations and rotations described by the irreducible representations \(\Gamma(\text{translation}) = A_{2u} + E_{1u}\) and \(\Gamma(\text{rotation}) = A_{2g} + E_{1g}\) for \(N\) being even and \(\Gamma(\text{translation}) = A_{2u}'' + E_{1u}'\) and \(\Gamma(\text{rotation}) = A_{2g}'' + E_{1g}'\) for \(N\) being odd, respectively, are frozen (Table 1 and Table 2). There remain \(3N - 6\) vibrational motions for the \(N\)-gon that split into \(N - 3\) (out-of-plane) puckering motions and \(2N - 3\) (in-plane) deformation motions. The puckering vibrations are characterized by the irreducible representations \(\Gamma(N\text{even}) = \sum_{m=\text{odd}} E_{m(u,g)} + B_{m(g)}\) for \(E_{m(u,g)} m\) even, \(u, g\) odd, \(g\) for \(B_{m(g)}\) \(N/2\) even, \(u, g\) even, \(N/2\) odd, and \(g\) and \(\Gamma(N\text{odd}) = \sum_{m=\text{odd}} E_{m(u,g)} (\text{see also Table A1, Supporting Information})\). The \(B_{m(g)}\) representation produces the out-of-plane displacements leading to crown conformations (puckered 4-ring with \(u\) inversion symmetry, chair of 6-ring with \(g\) inversion symmetry, crown forms of 8-, 10-ring, etc.). All other vibrational modes occur in pairs of \(N\)-symmetry. It has been shown\(^{17,21,22}\) that the \(N - 3\) out-of-plane vibrations with

![Figure 1. Definition of ring deformation vectors \(d_k\) (included as arrows in the small 5-gons centered at the vertices) for a 5-gon. Symbols used in the text are indicated.](image-url)

### Table 1. Identification of Ring Motions Using the Character Table for the \(D_{N_h}\) Point Group for \(N\) Being Even

<table>
<thead>
<tr>
<th>(D_{N_h}) ((N) even)</th>
<th>(E)</th>
<th>(2(C_2)^n)</th>
<th>(C_2)</th>
<th>(N/2C_2)</th>
<th>(N/2C_2^n)</th>
<th>0</th>
<th>(2(S_N)^n)</th>
<th>(a_h)</th>
<th>((N/2)a_d)</th>
<th>((N/2)a_d)</th>
<th>ring motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_{1u})</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>
<td>+1</td>
<td>breathing</td>
</tr>
<tr>
<td>(A_{2g})</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>
<td>-1</td>
<td>(R_x)</td>
</tr>
<tr>
<td>(B_{1u})</td>
<td>+1</td>
<td>(-1)</td>
<td>(-1)((N/2))</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>(-1)((N/2))</td>
<td>+1</td>
<td>+1</td>
<td>deformation</td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>+1</td>
<td>(-1)</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>(-1)((N/2))</td>
<td>-1</td>
<td>-1</td>
<td>crown puckering</td>
</tr>
<tr>
<td>(E_{u}g)</td>
<td>+2</td>
<td>2 cos((2m\pi/\tau))</td>
<td>2(-1)</td>
<td>0</td>
<td>0</td>
<td>+2</td>
<td>2 cos[(2m(N/2 - n)\pi] / \tau)</td>
<td>2(-1)m</td>
<td>0</td>
<td>0</td>
<td>(m = 1: R_{x}T_{x}, R_{y})</td>
</tr>
<tr>
<td>(A_{1u})</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>
<td>-1</td>
<td>deformation; puckering</td>
</tr>
<tr>
<td>(A_{2g})</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>
<td>+1</td>
<td>(T_{x})</td>
</tr>
<tr>
<td>(B_{1u})</td>
<td>+1</td>
<td>(1)</td>
<td>(-1)((N/2))</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>(-1)((N/2))</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>+1</td>
<td>(-1)</td>
<td>(-1)((N/2))</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>deformation; crown puckering</td>
</tr>
<tr>
<td>(E_{u}u)</td>
<td>+2</td>
<td>2 cos((2m\pi/\tau))</td>
<td>2(-1)m</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>-2 cos[(2m(N/2 - n)\pi] / \tau)</td>
<td>2(-1)m+1</td>
<td>0</td>
<td>0</td>
<td>(m = 1: T_{u}T_{x}, T_{y}, T_{z}) deformation</td>
</tr>
</tbody>
</table>

\(^a n = 1, \ldots, (N/2) - 1; a_{dx}/a_{nx} = a_{dx}/a_{nx}\) for \(N/2\) being odd and \(a_{dx}/a_{nx}\) for \(N/2\) being even.
symmetries of the $D_{N\text{h}}$ point group, if frozen at finite vibrational displacements, define $N - 3$ basis conformations specified by $N - 3$ puckering parameters, which split up in puckering amplitudes $q_n$ and pseudorotation phase angles $\phi_n$, with $n = m = 2, \ldots, (N - 1)/2$ for $N$ being odd and $n = m = 2, \ldots, (N - 2)/2$ and a single amplitude $q_{N/2}$ for $N$ being even (see Supporting Information, Table A1). In the case of puckering, $n = 0$ and $n = 1$ refer to overall movements of the ring such as translation along the $z$-axis ($n = 0$) or rotation at axes perpendicular to the $z$-axis.

There are $2N - 3$ in-plane vibrations, of which the ring breathing mode leads to a symmetry-conserving deformation of the polygon ($\Gamma(N, \text{even}) = A_1g \Gamma(N, \text{odd}) = A_1g$, Tables 1 and 2) and the remaining $2N - 4$ vibrational modes invoke symmetry-changing deformations of the $N$-gon. All deformation vibrations have to be invariant under the $C_{N/2}$-symmetry operation of the $D_{N\text{h}}$ group. For $N$ being odd, these are the vibrations with $E_{m'}/C_{0}$ symmetry and for $N$ being even, vibrations with $B_{1g}/C_{2n}$ (both for $N/2$ even), $B_{1u}/B_{2u}$ (both for $N/2$ odd), $E_{m''}/C_{N/2}$ for $m$ being even, and $E_{m''}/C_{N/2}$ for $m$ being odd. Deformation vibrations frozen at finite displacements in line with $E$-symmetry define ring deformation pairs, which can be described by $n$ pairs suitable RDCs with $n = 1, \ldots, (N - 2)$. Each ring deformation pair is connected by a dynamic ring deformation process that corresponds to in-plane pseudorotation (see section 4).

In the case of $N$ being odd, there are $(N - 1)/2$ $E_{m''}$ symmetrical deformation pairs ($m = n = 1, \ldots, (N - 1)/2$) leaving $(N - 3)/2$ deformation pairs with $m > (N - 1)/2$, which also have to be of $E'$-symmetry. Because there are no $E_{m''}$ irreducible representation with $m > (N - 1)/2$ in the $D_{N\text{h}}$ group, we define $m' = N - m$ for $m > (N - 1)/2$ and specify the missing deformation vibrations to be $E_{m''}$ symmetrical. This implies that $(N - 3)/2$ ring deformation pairs (and the corresponding ring deformation processes) can mix because they possess the same symmetry $E_{m''} = E_{m''}$ (see section 4).

In the case of $N$ being even, there are $N/2 - 1$ $E_{m(\text{sd})}$ symmetrical ($u$ for $m$ odd, $g$ for $m$ even) deformation modes. One additional deformation mode can be formed after recognizing that $B_{1g}$ and $B_{2g}$ symmetrical vibrations ($N/2$ even) both lead to a lowering of $D_{N\text{h}}$ to $D_{N/2h}$-symmetry and accordingly form a deformation pair for $m = n = N/2$ as do the $B_{1u}$ and $B_{2u}$ symmetrical vibrations for $N/2$ being odd. This leaves $(N - 4)/2$ deformation pairs unspecified, which we determine, in a way similar to that in the case of the odd-numbered rings, by defining $m' = N - m$ for $m > N/2$, i.e., $m = n = N/2 + 1, \ldots, N - 2$. Again, this leads in $(N - 4)/2$ cases to the possibility of a mixing of deformation vibrations with the same symmetry. In the following, we will specify the deformation displacements of the vibrational deformation modes by a suitable set of RDCs reflecting the symmetries of the $D_{N\text{h}}$ group.

### 3. DERIVATION OF RING DEFORMATION COORDINATES

For the purpose of deriving a set of suitable deformation coordinates, the planar $N$-gon is used as a reference for the corresponding $N$-ring and specified by a set of initial coordinates. The standard orientation of the $N$-gon is obtained by choosing the geometrical center of the ring as origin of the coordinate system:

$$\sum_j R_j^{(0)} = 0$$

where $R_j^{(0)}$ denotes the position vector of atom $j$ in the $N$-gon and $j = 1, \ldots, N$. The reference plane is spanned by vectors $R'$ and $R''$ defined in eqs 2 and 3:

$$R' = \sum_j R_j^{(0)} \sin \theta_j$$

$$R'' = \sum_j R_j^{(0)} \cos \theta_j$$

where the angle $\theta_j$ used to rotate position vector $R_j^{(0)}$ into vector $R_j^{(0)}$ is given by

$$\theta_j = \frac{2\pi(j - 1)}{N}$$

The reference plane is taken to be the $xy$-plane in the coordinate system of the ring, which means that the unit vector $u$ defined via the cross product between $R'$ and $R''$

$$u = \frac{R' \times R''}{|R' \times R''|}$$

points into the direction of the $+z$-axis. When atom 1 is positioned on the $-x$-axis, the coordinate system of the “ring standard orientation” is defined and the positioning of the $N$-gon in the $xy$-plane is fixed, thus eliminating any overall rotations and translations (Figure 1).

In the following, it will be useful to set $j - 1 = k$ and renumber all position vectors according to $k = 0, \ldots, N - 1$. The in-plane deformation of the $N$-gon at point $k$ can be given by a deformation vector

$$d_k = d_k^x x_k + d_k^y y_k$$

### Table 2. Identification of Ring Motions Using the Character Table for the $D_{N\text{h}}$ Point Group for $N$ Being Odd

<table>
<thead>
<tr>
<th>$D_{N\text{h}}$ ($N$ odd)</th>
<th>$E$</th>
<th>$2(C_2)^a$</th>
<th>$NC_2'$</th>
<th>$\sigma_h$</th>
<th>$2(S_2)^a$</th>
<th>$N_{2v}$</th>
<th>ring motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1'$</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>breathing</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>$R_e$</td>
</tr>
<tr>
<td>$A_1''$</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>$T_e$</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>$T_z$</td>
</tr>
<tr>
<td>$E_{m'}$</td>
<td>+2</td>
<td>$2 \cos(2mnt\pi/N)$</td>
<td>0</td>
<td>+2</td>
<td>$2 \cos(2mnt\pi/N)$</td>
<td>0</td>
<td>$m = 1$: $T_{1v}, T_{2v}$ deformation</td>
</tr>
<tr>
<td>$E_{m''}$</td>
<td>+2</td>
<td>$2 \cos(2mnt\pi/N)$</td>
<td>0</td>
<td>-2</td>
<td>$-2 \cos(2mnt\pi/N)$</td>
<td>0</td>
<td>$m = 2, \ldots, (N - 1)/2$: puckering</td>
</tr>
</tbody>
</table>

$a = n = 1, \ldots, (N - 1)/2$; $\alpha_{2x}/\alpha_{2y}$ is $\alpha_{\pi}/\alpha_{\sigma}$ for $N/2$ being odd and $\alpha_{\pi}/\alpha_{\sigma}$ for $N/2$ being even.
where $x_k, y_k$ are the local unit vectors at point $k$ and $d_k^x, d_k^y$ are the associated coordinates. Vectors $R_k = R_x^{(n)} + d_k^x, d_k^y$ specify the positions of the atoms of an $N$-gon after deformation (see as an example a 5-gon in Figure 1). The linear space $L_k$ at point $k$ is spanned by vectors $x_k$ and $y_k$. The deformation of the $N$-gon is a vector $d$ of the linear space $L_k$, which is a direct sum of all $L_k$ according to $L = \oplus_{k=1}^{N} L_k$, thus implying that $d = \oplus_{k=1}^{N} d_k$.

The analysis of the deformations of the $N$-gon depends on the choice of a specific basis in $L$. We define $x_k^{(n)}$ and $y_k^{(n)}$ to be the vectors $x_k$ and $y_k$ rotated by the angle $\omega_k^{(n)} = 2\pi(n + 1)/N$, i.e.,

$$x_k^{(n)} = x_k \cos \omega_k^{(n)} - y_k \sin \omega_k^{(n)}$$

$$y_k^{(n)} = x_k \sin \omega_k^{(n)} + y_k \cos \omega_k^{(n)}$$

A set of all vectors $x_k^{(n)}$ and $y_k^{(n)}$ with fixed index $n$ can be regarded as a vector of space $L$, i.e., $x^{(n)} = \oplus_{k=1}^{N} x_k^{(n)}$ and $y^{(n)} = \oplus_{k=1}^{N} y_k^{(n)}$ are the elements of $L$. The set of all $x^{(n)}$ and $y^{(n)}$, $n = 0, ..., N - 1$, form a basis in $L$. Therefore, an arbitrary planar deformation, $d = \oplus_{k=1}^{N} d_k$, of the $N$-gon can be written as a linear combination of $x^{(n)}$ and $y^{(n)}$,

$$d = \sum_{n=0}^{N} A_n x^{(n)} + B_n y^{(n)}$$

The coefficients $A_n$ and $B_n$ are the Fourier transforms of coordinates $d_k^x$ and $d_k^y$. Accordingly, the deformation vector for atom $k$ can be written as

$$d_k = \sum_{n=0}^{N} d_k^{(n)} = \sum_{n=0}^{N} A_n x_k^{(n)} + B_n y_k^{(n)}$$

We shall refer to $d_k^{(n)}$ as the $n$th deformation mode at atom $k$.

One of the advantages of utilizing vectors $x_k^{(n)}$ and $y_k^{(n)}$ as basis vectors is that the coefficients $A_n$ and $B_n$ do not depend on the atom index $k$, and therefore the deformation vectors of the $n$th mode at each atom of the $N$-gon have the same norm and phase. Figure 2a,b gives schematic representations of the deformation modes of a 3-gon and a 6-gon.

For $n = 0$ in eq 10, the breathing mode and the in-plane rotation mode of the $N$-gon are obtained. Similarly, the modes with $n = N - 1$ are always translations in the $x$ and $y$ directions, respectively. Hence, the RDCs introduced separate out rotations and translations of the $N$-gon.

The deformation vectors $x^{(n)}$ and $y^{(n)}$ transform according to 2-dimensional representations $A$ and $B$, respectively, whereas all other pairs $x^{(a)}$ and $y^{(n)}$ transform according to 2-dimensional representations $E$ (compare with Tables 1 and 2 or Figure 2a,b). The symmetry group of the $N$-gon after having encountered the $n$th mode is found as follows. The breathing, rotational, and translational modes leave the symmetry group unchanged. The deformation modes of the $N$-gon reduce its symmetry from $D_{Nh}$ to either $C_{hn}$ or $D_{hn}$ ($C_{hn} \equiv C_{0}, D_{hn} \equiv C_{2h}$), where $l$ is the greatest common divisor of $n$ and $N$. Examples of the symmetry classification are given in Figure 2a,b.

For the purpose of comparing finite deformations in different $N$-gons, it is convenient to represent the $n$th deformation mode in the form

$$d_k^{(n)} = t_n \cos \tau_n \cdot x_k^{(n)} + t_n \sin \tau_n \cdot y_k^{(n)}$$

where $t_n = (A_n^2 + B_n^2)^{1/2}$ is the deformation amplitude and $\tau_n = \arctan(B_n/A_n)$ is the phase angle of the $n$th deformation process. This implies that each deformation vector $d_k^{(n)}$ has the length $t_n$ and that $\sum d_k^{(n)} = 0$ for $n = 1, ..., (N - 2)$ of any $N$-gon. The parameter $T$ determined by

$$T^2 = \sum_{n=1}^{N-2} t_n^2 = \sum_{n=0}^{N-1} A_n^2 + B_n^2$$

$$= \frac{1}{N} \sum (d_k^x)^2 + (d_k^y)^2$$

represents a total planar deformation amplitude ($T \geq 0$). For the case $n = 0$, we specify the radius $R$ of the circumscribed circle of the deformed $N$-gon via the relationship

$$R^2 = A_0^2 + B_0^2$$

It is useful to define a breathing deformation amplitude $t_0 = R - R_0$, which compares the radii of the circumscribed cycles of reference $N$-gon and deformed $N$-gon. In this way, all $2N - 3$ deformation parameters are specified and their contribution to the actual form of the $N$-gon can be studied. Computer programs have been written that (i) determine from the Cartesian or internal coordinates of an $N$-membered ring puckering and deformation coordinates and (ii) build from an input in terms of puckering and deformation coordinates the Cartesian or internal coordinates needed for a quantum chemical calculation.23,26
4. CHARACTERIZATION OF RING DEFORMATION MODES LEADING TO BOND PSEUDOROTATION

One can calculate the Cartesian coordinates of a deformed N-gon for which its RDCs are known via eqs 14 and 15:

\[ x_k = -R \cos \omega_k + \sum_{n=1}^{N-2} t_n \cos(\tau_n - \omega_n) \]  
\[ y_k = R \sin \omega_k + \sum_{n=1}^{N-2} t_n \sin(\tau_n - \omega_n) \]

and all \( z_k = 0 \). In the case of a puckered N-ring, the out-of-plane deviations are given by eqs 16 and 17:

\[ z_k = \sqrt{\frac{2}{N}} \left( \sum_{n=2}^{N/2-1} q_n \cos(\varphi_n + \omega_n) \right) \]  
\[ z_k = \sqrt{\frac{2}{N}} \left( \sum_{n=2}^{N/2} q_n \cos(\varphi_n + \omega_n) \right) + \sqrt{\frac{1}{N}} q_{N/2} (-1)^k \]

where one has to consider that in the case of puckering \( n \) starts with 2 and therefore \( \omega_n = 2\pi nk/N \). The projection of the puckered ring into the mean plane is given by coordinates \( x_k, y_k \) and the associated RDCs of eqs 14 and 15. For the deformed polygons shown in Figures 3 and 4 (see Supporting Information, Figures A1–A4) eqs 14 and 15 have been used directly.

Figures 3 and 4 show the \( N - 2 \) deformation cycles \( n \) of an \( N \)-gon with \( N = 3 \) and 4 where \( \tau_n \) values of 0.3 Å (\( R = 1 \) Å) and specific \( \tau_n \) values have been used. Changing the latter in small steps of 15° between 0 and 360°, as done in the case of the 3-ring, provides an impression of how the ring smoothly deforms along the \( n \)th deformation process. In other cases, \( 2N \) specifically deformed \( N \)-gons of the \( n \)th deformation process have been selected from the infinite number of ring forms generated by increasing \( \tau_n \) from 0 to 360°. Each deformation process can be characterized by two basis forms in a way that a linear combination of these basis forms generates any other planar ring form in the \( \{r_{\text{in}}, r_{\text{out}}\} \)-subspace. For this purpose, the basis deformation vectors \( x_n, y_n \) can be used, which, however, do not lead always to ring forms that can be easily recognized by the chemist (e.g., \( N = 3 \), \( y_1 \) specifies a \( C_3 \)-symmetrical form rather than one of the six, easy recognizable \( C_{3v} \)-symmetrical forms; see Figure 2a for \( n = 1 \)). Instead, we specify as basis forms the high-symmetry forms with \( \tau_n = 0 \) and \( \tau_n = \Delta \tau/N \), where \( \Delta \) is the largest common divisor of \( N \) and \( n \) as specified in section 2. Each of these basis forms appears \( N/l \) times along the deformation cycle in steps of \( \Delta \tau = 2\Delta \tau/N \). Including the reference \( N \)-gon, there are \( 2N - 3 \) basis forms that can be used to generate any deformed \( N \)-gon via a linear combination of properly weighted basis forms.

Inspection of the deformed \( N \)-gons in Figures 3 and 4 as well as those for the larger \( N \) values given in the Supporting Information reveals that the \( n \)th deformation mode changes bond lengths and bond angles of the \( N \)-gon in such a way that the impression of an \( (N - n) \)-membered planar ring is provided. In general, an \( N \)-gon will approach an \( (N - 1) \)-gon if one internal angle \( \Delta \theta \) of the \( N \)-gon approaches 180° or, alternatively, one bond length \( r \) approaches 0. Hence, a systematic search for widening angles \( \Delta \theta \) (yielding an \( n \)-gon) or decreasing bond lengths \( r \) makes it possible to classify a deformation as an \( N - 1, N - 2, etc. \) deformation, i.e., a deformation that gives the impression of reducing the \( N \)-gon to an \( (N - 1) \)-gon, an \( (N - 2) \)-gon, etc. In this connection it has to be considered that (i) meaningful bond angle/bond length changes have to be distinguished from negligible changes (see Supporting Information) and (ii) \( \Delta \theta \) and \( r \) changes occurring at the same \( N \)-gon vertex or at subsequent \( N \)-gon vertices have to be counted only once. In this way, deformation regularities are revealed (see Supporting Information) that specify the \( n \)th deformation of an \( N \)-gon as effecting \( n \) local, disconnected sides of the \( N \)-gon and in this way approximating an \( (N - n) \)-ring, i.e., in the case of \( N = 5 \), mode \( n = 1 \) leads to the approximation of a 4-ring, mode 2 to a 3-ring, and mode 3 to a 2-ring. Because a digon contrary to higher polygons does not exist, the deformation leads actually to a stretched or compressed \( N \)-gon so that, especially in the case of larger \( N \), the impression of a circle (“digon”) deformed (by stretching or compression) to an ellipse results. The analysis of ring deformation is summarized in the Supporting Information.

When the ring deformation mode \( n \) for a \( N \)-gon changes from \( \tau_n = 0 \) to \( \tau_n = 360° \), the ring form changes in a way that can be viewed in different ways as becomes obvious from inspection of Figure 3: (i) one can follow one particular bond (identified by the numbers of the ring atoms bonded) along a deformation cycle: This bond carries out a bond stretching vibration (long—short—long). (ii) Alternatively one can follow a bond of about constant length during ring pseudorotation. This bond (e.g., bond 2—3 in the 3-ring given by the light circles) switches at 60, 180, and 300° its position (Figure 3) so that after a full pseudorotation cycle it has moved through the ring to wind up at the starting position. Hence bond pseudorotation is caused by continuous deformation of the ring and bond switching in steps of \( 2\pi/N \) degrees. Of course, the choice of the reference bond is arbitrary in this connection: Bond 1—2 would have its “rest” positions at 60, 180, and 300° whereas the bond switches would take place at 0, 120, and 240° in the case of the 3-ring. Apart from this it becomes obvious when viewing the deformation cycles of the Supporting Information that for larger \( N \) focusing on a specific bond is...
problematic as all bonds in the ring are shifted. In this situation the following approach simplifies the analysis: Because the deformations traveling through the ring are caused by vibrational modes of specific symmetry (see Tables 1 and 2), it is easier to focus on the high symmetry forms and determine the changes associated with a symmetry element such as a $C_2$ axis passing through atom I for $r_n = 0$. Such an analysis reveals that it is better to speak of in-plane pseudorotation as the process where the maximum in-plane deviation from the $N$-gon is cycling through the ring without leading to any angular momentum. Nevertheless, we will use in this work the term “bond pseudorotations” as it is commonly used in the literature.

If bond pseudorotation takes place in a 2-dimensional deformation subspace and the cause for the internal process is a Jahn–Teller instability, we will speak of the associated PES as a Jahn–Teller surface. In those cases where pseudorotational subspaces are associated with degenerate vibrational modes of the same symmetry it is unlikely that a ring deformation processes is limited to one subspace. Mixing will take place so that a deformation path is defined in a larger deformation space rather than a single subspace. The contributions from the various deformation parameters can be related to special electronic effects that help to understand structural and energetic preferences.

Besides pseudorotation a deformed ring may cross directly the center of the cycle where the $D_{NH}$-symmetrical form is located. Considering that in chemistry any intramolecular rearrangement that leads from the original configuration to the corresponding mirror image is called inversion (inversion of the cyclohexane chair, ammonia inversion, inversion of the configuration at an asymmetrical C atom, etc.), one is tempted to call this processes also an inversion. However, closer inspection of the deformation cycles reveals that the inversion processes proceed between equivalent forms related by a switching of bonds (see, e.g., Figure 3). Therefore, one should correctly describe deformation processes through the $D_{NH}$-symmetrical form as inversions accompanied by bond-switching or “bond-switching inversions”, which for reasons of simplicity we will call in the following just “inversions.”

5. APPLICATION OF THE RING DEFORMATION COORDINATES

For the purpose of demonstrating the usefulness of the RDCs introduced in this work, we will discuss Jahn–Teller and other deformations in 3- and 4-rings. Calculations were carried out with the ab initio program packages COLOGNE2010,26 COFUR,27 and MOLPRO.28 We used restricted and unrestricted coupled cluster theory with all single (S) and double (D) excitations and a perturbative treatment of triple (T) excitations, i.e., CCSD(T) and UHF-CCSD(T)29 where the latter acronym is used to prevent confusion with unitary CC theory.30,31 Multireference problems were treated by using MR-AQCC (multireference averaged quadratic couple cluster)32 and EOMIP-CCSD (equation-of-motion ionization potential coupled cluster theory in the single and double excitations approximation).33–35 All calculations were carried out with the cc-pVTZ basis set.36 Geometry optimizations and frequency calculations were based on the use of RDCs.37

5.1. Cyclopropane Radical Cation (1). Removal of an electron from the degenerate HOMO of cyclopropane (symmetric and antisymmetric Walsh MOs) leads to the Jahn–Teller unstable electron configuration $2\text{E}^\prime$, which can be stabilized by a $e'$-symmetrical distortion to the $C_2v$-symmetrical states $2\text{A}_1$ and $2\text{B}_2$ in the course of a first-order Jahn–Teller effect where the state symmetry results from the fact that either the $a_1$-symmetrical or the $b_2$-symmetrical Walsh MO is singly occupied.9,10 Early work on the problem38–44 was summarized, with specific consideration of bond pseudorotation, in the literature.10 More recent work concerns the description of the ionization process, the resulting PE spectrum, and the dynamics of the Jahn–Teller distortion45 as well as the vibronic spectra and the nonradiative decay dynamics of 1.46

The cyclopropane radical cation is a multireference system, which can no longer be correctly described by single determinant theory such as DFT, HF or MPn with small $n$. UHF-CCSD(T) is included because infinite order excitation effects some nondynamic electron correlation,47,48 and therefore it is able to provide a reasonable description, which, however, has to be verified by true multireference (MR) methods. We used EOMIP-CCSD35–36 because configuration mixing in the radical cation is dominated by determinants that are related to the closed shell configuration of cyclopropane by a removal of one electron. In addition, we employed MR-AQCC with a two-state averaging based on a CASSCF reference function with a 5-electron, 6-orbital active space (MR-AQCC(5,6)) (Table 3).

At all levels of theory, the $A_1$ state of 1 is found as the global minimum of the Jahn–Teller PES. UHF-CCSD(T), MR-

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{Pseudorotation cycles of the 4-gon.}
\end{figure}
The calculated deformation energy surface $V(t_1, t_2)$ of the cyclopropane radical cation is of the general form

$$V_O(t_1, t_2) = V_{00} + V_{22}t_2^2 + V_{44}t_4^4 + (V_{24}t_2 t_4 + V_{42}t_2 t_4)\cos 3t_1$$

The calculated coefficients $V_{nn}$ are listed in Table 4. They are valid in a region $0.07 < t_1 < 0.2$ Å. For smaller values of $t_1$ $(t_1 < 0.07)$, the Jahn–Teller bond pseudorotation potential increases steeply to a value close to 21 kcal/mol (Table 3), which is best described using an exponential function in connection with a switching function:

$$V_I(t_1, t_2) = A + B \exp\{Ct_1 + Dt_2 \cos 3t_1\}$$

so that the total potential function results as

$$V(t_1, t_2) = V_I(t_1, t_2) S_I(t_1) + V_O(t_1, t_2) S_O(t_1)$$

In view of the high barrier for inversion through the 3-gon form (EOMIP-CCSD: 20.26; MR-AQCC(5,6): 21.44; UHF-CCSD(T): 20.92 kcal/mol, Table 3) yielding either the 120°- or

[Table 3. Calculated Ring Deformation Coordinates of 3- and 4-Membered Rings$^{a,b}$]

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<th>sym</th>
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<th>C2C3</th>
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<th>C2H</th>
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$^a$ Relative energies in kcal/mol, breathing radius $R$, amplitudes $t_n$, and bond lengths in Å, phase angle $\tau_n$ and bond angles in degrees. $^b$ The irrep. is B$_1$ if the C3 frame is lying in the xz plane or B$_2$ if the C3 frame is lying in the yz plane.
240°-form (Figures 3 and 5), this process is slow at room temperature and can be excluded at lower temperatures whereas bond pseudorotation is rapid at room temperature. The e'-symmetrical Jahn–Teller deformation leads to an increase of “breathing” amplitude $t_\theta = R - R_0$ from 0 to 0.0156, 0.0179, and 0.0176 Å for EOMIP-CCSD, MR-AQCC(5,6), and UHF-CCSD(T) (Table 3), which reflects the fact that the CC bonds become longer by the value of $t_\theta$ on the average. At the same time the deformation amplitude $t_1$ increases from 0 to 0.14 and 0.15 Å for the $^2A_1$-forms, which indicates the deformation of the cyclopropane framework to a biradicaloid state close to the trimethylene biradical, which, contrary to the latter, possesses still some stabilizing interactions between the separated C atoms. In the literature, some experimental results were discussed in favor of the generation of the trimethylene biradical; however, this could not be confirmed by quantum chemical calculations and it is more likely that $I(2\sigma C_1)$ had been observed, which is known to be the starting point for the formation of the propenyl radical cation. The $^3B_2$ transition state for bond pseudorotation has been considered because of its similarity with a methylene-ethene $\pi$-complex to be a starting point for the dissociation into methylene and the ethene radical cation, which would imply two transition states in sequence.

We note that different electronic factors caused by substituents can stabilize either the minima or the transition states of bond pseudorotation. $\pi$-Donor–$\sigma$-acceptor substituents at C2 and C3 will lower the barrier so that $1$ approaches a free pseudorotator whereas $\pi$-acceptor substituents at C1 lead to a stabilization of the minima forms thus increasing the barrier.

In view of the rapid bond pseudorotation with a barrier of just 2.4 kcal/mol, all measured properties, e.g., hyperfine structure constants, are time-averaged properties, which make it difficult to draw any conclusion with regard to the electronic structure of 1. This problem can be solved with the help of the calculated Jahn–Teller surface shown in Figure 5. By calculating the property in question as a function of the pseudorotation phase angle $\tau_1$, then assuming a Boltzmann statistic, and utilizing the calculated potential of the Jahn–Teller-PES, we can determine time-averaged properties, which can be directly compared with measured data. In this way, it is possible to analyze the corresponding measured data. This is the basis of the DORCO method, which one of us has successfully used to determine from time-averaged NMR spin–spin coupling constants the puckering of a pseudorotating ring. Also the investigation of dynamic processes involving both ground and excited states of $1$ will be simplified by taking advantage of calculated Jahn–Teller surfaces for the different states.

### Table 4. Calculated Ring Deformation Surfaces$^a$

<table>
<thead>
<tr>
<th>C$_4$H$_4^{+*}$, 1</th>
<th>C$_6$H$_6$, 2</th>
<th>N$_2$S$_2$, 3</th>
<th>N$_2$S$_2^{2-}$, 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{10}$</td>
<td>4.352 $V_{10}$</td>
<td>7.497 $V_{10}$</td>
<td>0.169 $V_{10}$</td>
</tr>
<tr>
<td>$V_{20}$</td>
<td>−392.494 $V_{20}$</td>
<td>−450.877 $V_{20}$</td>
<td>1798.550 $V_{20}$</td>
</tr>
<tr>
<td>$V_{40}$</td>
<td>1440.531 $V_{40}$</td>
<td>1376.830 $V_{40}$</td>
<td>−11495.326 $V_{40}$</td>
</tr>
<tr>
<td>$V_{23}$</td>
<td>0.721 $V_{23}$</td>
<td>3134.050 $V_{23}$</td>
<td>−34.884 $V_{23}$</td>
</tr>
<tr>
<td>$V_{43}$</td>
<td>−593.032 $V_{43}$</td>
<td>−365686.575 $V_{43}$</td>
<td>1027.009 $V_{43}$</td>
</tr>
<tr>
<td>$V_{62}$</td>
<td>18533094.659 $V_{62}$</td>
<td>443.555 $V_{62}$</td>
<td>644.052 $V_{62}$</td>
</tr>
</tbody>
</table>

$^a$ Coefficients $V_{nm}$ in (kcal/mol) Å$^{-n}$; $A$ and $B$ in kcal/mol; $C$ and $D$ in (kcal/mol) Å$^{-n}$. For 1, the potential is given in eqs 18 and 19. For all other compounds, the first subscript of $V$ indicates the power of the deformation amplitude $t$ and the second the prefactor $m$ of the deformation phase angle in $\cos mt$.
b$_{1g}$-symmetrical deformation changes the nonbonded rather than the bonded distances in cyclobutadiene, which does not lead to an effective separation of pseudodegenerate states $^1$B$_{1g}$ and $^1$B$_{2g}$ and subsequent stabilization. The potential function increases for increasing $t_2$ in the 0°-to-180° direction of $\tau_2$ where this increase is quadratic, reaching a value of 21 kcal/mol at $t_2 = 0.08$ Å. This is in line with the fact that the square form 2a is a first-order transition state for the bond shift reaction. The $t_2$-deformation of 2b applied for $\tau_2 = 45^\circ$ (parallelogram, Figure 4) leads to an increase in energy of just 5.6 kcal/mol, thus revealing that the parallelogram form is stabilized relative to 2a. This reflects the fact that b$_{1g}$ and b$_{2g}$-symmetrical deformations are equally mixed for $\tau_2 = 45^\circ$ and that b$_{2g}$-symmetrical deformation increases the energy difference between the pseudodegenerate states.

The calculated Jahn–Teller surface of 2 is shown in Figure 6, and the corresponding potential, in Table 4. The MR-AQCC-(4,4) calculations reveal that at normal temperatures larger parts of the Jahn–Teller surface are energetically accessible and that bond shifting can also involve some bond pseudorotation at slightly higher energies than that of 2a. Push–pull substituents can change the surface and make rhombic forms accessible. In recent work, Eckert-Maksic and co-workers$^{51}$ have documented Can change the surface and make rhombic forms accessible. In

![Figure 6](image)

**Figure 6.** Bond pseudorotation (Jahn–Teller) PES of cyclobutadiene calculated at the MR-AQCC(4,4)/cc-pVTZ level of theory. Minima are located at $t_2 = 90$ and 270°. See Figure 2 for further explanations. Compare also with Figure 1, $\eta = 2$.

between the S atoms in line with early suggestions based on more qualitative considerations.$^{70}$ This description has been challenged by Schleyer and co-workers, who have pointed out that a direct confirmation of biradical character in terms of natural orbital occupation numbers has never been given.$^{71}$ These authors find on the basis of the valence space optimized doubles method that 3 is a 2$\pi$-aromatic molecule with a low aromatic stabilization energy of just 6.5 kcal/mol, NS bond orders of 1.25, and some weak biradical character of just 12%. Two of the six $\pi$-electrons are in the bonding MO whereas the remaining $\pi$-electrons occupy nonbonding MOs (see Figure 8).

The CCSD(T) equilibrium geometry of 3 calculated in this work confirms a $D_{2h}$-symmetrical rhombic form ($\tau_2 = 0^\circ$) close to the experimental geometry and the ideal square form 3a. The small deviation from 3a is reflected by the calculated deformation parameters $t_0 = 0.0007$ and $t_2 = 0.0097$ Å. By imposing an incomplete bond pseudorotation to the rectangular form at frozen $t_2$, we obtain only a small increase in energy of 0.43 kcal/mol. The calculated pseudorotation surface shown in Figure 7 is very flat. At room temperature, a heat content of 0.6 kcal/mol will make large parts of the deformation surface accessible for 3, which can carry out ring inversions, bond pseudorotation, librations, and other movements. Our calculations show, however, that these movements will not lead to a major change in the electronic structure of 3, for example by substantially increasing its biradical character.

If two electrons are added, thus leading to the disulfur dinitride dianion 4, an 8$\pi$-electron system is obtained that might be considered as being antiaromatic. However, antiaromaticity is invoked by partial occupancy of a set of degenerate $\pi$-MOs, which is not the case for 4 (Figure 8). Instead, an NS antibonding 2b$_{1u}$-symmetrical $\pi$-MO is doubly occupied (see Figure 8), thus leading to a weakening of the NS bonds that lengthen from 1.664 Å in 3 to 1.820 Å in 4 (Table 3). Apart from this bond weakening, 4 has deformation properties similar to those of the neutral molecule 3, as is reflected by the calculated deformation parameters and the deformation surface (Tables 3 and 4) that hardly differs from that of 3 (Figure 7). The energy differences between

![Figure 7](image)

**Figure 7.** Bond pseudorotation PES of N$_2$S$_2$ calculated at the CCSD(T)/cc-pVTZ level of theory. The minimum is located at $\tau_2 = 0^\circ$, $t_2 = 0.0097$ Å of a flat surface. See Figure 2 for further explanations.
the deformation forms listed in Table 3 differ by a factor of 2, which still makes dianion 4 a floppy molecule with large deformation motions.

5.4. Normal Coordinates and Deformation Coordinates.

Because the RDCs are derived from the normal vibrational modes of a planar ring, the question may arise whether the use of normal rather than deformation coordinates could lead to a similar description of deformed rings. Indeed, such an approach was performed by Liehr and is also described by Bersuker.

There are a number of reasons why RDCs are superior to normal coordinates when deformed ring molecules are described. Normal coordinates depend on the number \(N\) of ring atoms, symmetry, atomic masses, interactions between ring and substituent atoms, and the deviation of the ring molecule from planarity. There is no simple way of deriving normal coordinates of ring molecules from symmetry, atomic masses, interactions between ring and substituent atoms. (i) Analytical first and second energy derivatives in terms of RDCs are easily used to carry out energy, geometry, or vibrational frequency calculations for a given deformation. The RDCs developed do not suffer from these problems: (i) They are defined for any ring irrespective of its size by two simple formulas. Each RDC has a clear mathematical and geometrical meaning. (ii) They do not depend on symmetry, mass, or the interactions of ring atoms and substituent atoms. (iii) Analytical first and second energy derivatives in terms of RDCs are easily determined and have already been used in the geometry optimizations and vibrational frequency calculations presented in this work. (iv) If a given deformation of the ring has to be investigated, this can be easily specified utilizing the RDCs; all remaining independent coordinates are then optimized. Any number of energy points needed for determining the energy dependence of bond pseudorotation or other deformation processes can be specified for a ring molecule (irrespective of \(N\), symmetry, substituents, etc.). (v) Deformations of different rings become comparable via their RDCs, which in turn can be associated with electronic effects. (vi) RDCs quantify the electronic effects of substituents on a ring molecule and facilitate the electronic analysis of deformed rings.

The RDC complement the ring puckering coordinates of Cremer and Pople, which have been extensively used in the literature as they are superior to normal coordinates when the puckering of a ring molecule is described. Any ring molecule can be exclusively described by puckering and deformation coordinates, which is always then of advantage when a conformational process of a ring molecule or a ring form of specified puckers and deformation has to be described.

6. CONCLUSIONS

In this work, we have developed a new way of describing in-plane deformations of planar rings with a set of ring deformation coordinates (RDC):

1. The RDCs are directly derived from the in-plane normal vibrational modes of the ring. For an \(N\)-ring, there are \(2N - 3\) RDCs that are sufficient to describe the geometry of a planar ring without using bond lengths or bond angles. By using the RDCs rather than bond lengths and bond angles, we solve the redundancy problem of ring molecules with \(N\) bond lengths and \(N\) internal ring angles.

2. The RDCs are defined with regard to the \(N\)-gon of unit length as reference ring in a way similar to that of the planar ring itself. The reference for the puckered ring is the planar ring itself, which still makes dianion 4 a floppy molecule with large deformation motions.

3. The pseudorotational subspaces \(n = 1, \ldots, (N - 2)\) define, irrespective of \(N\), ring deformations that are found to change systematically with \(n\). They deform the \(N\)-ring so that the impression of an \(M = N - n\) ring is given. For the largest value of \(n = (N - 2)\), the deformation with \(M = 2\) is obtained, resembling an elliptically deformed circle (2-gon). We note that the deformation vectors and the corresponding RDCs are directly derived from the in-plane vibrational modes, which lead to the same pattern.

4. The two RDCs that span a 2-dimensional deformation space can also be used to define, for each \(n\), two basis forms with high symmetry. All other deformed rings in the 2-dimensional subspace can be viewed as linear combinations of the basis forms.

5. Utilizing the RDCs and the pseudorotational subspaces they span, dynamic deformation processes can be described in a unique way. The investigation of 3- and 4-rings reveals that the double bond shift in 1,3-cyclobutadiene corresponds to a ring inversion of the planar ring involving the square form whereas this process in an odd-membered ring is better described as bond-stretch isomerization via a \(D_{2h}\)-symmetrical form, which can involve more than one bond. Bond pseudorotation turns out to be a constrained bond-stretching followed by a bond-switching for high-symmetry forms.

6. Any complete set of internal or Cartesian coordinates of a planar \(N\)-ring can be transformed into \((2N - 3)\) RDCs. In turn, RDCs can be used to derive the internal or Cartesian coordinates of the ring. Programs that carry out the transformation are provided as free software.

7. The RDCs can be utilized to determine Jahn–Teller surfaces or deformation surfaces in analytical form. This is
possible because any given deformation coordinate can be frozen and the remaining deformation coordinates optimized. In a separate work, we will present the analytical energy gradient and Hessian expressed in deformation coordinates. 37

(8) Application of the RDCs made it possible to calculate the Jahn–Teller or deformation surfaces for the cyclopropyl radical cation, cyclobutadiene, disulfur dinitride, and dianion of the latter thus gaining the following insights: (a) Bond pseudorotation in a 3-ring is best viewed as a combination of bond stretching and bond switching of equally stretched bonds at the transition states of the rearrangement. Bond pseudorotation is only hindered by a barrier of 2 kcal/mol in the cyclopropyl radical cation. It leads to a rearrangement of the ring from biradicaloid minima with some trimethylene character to methylene–ethene cation π-complexes as was already observed by other authors.10 Appropriate substitution will lead to free bond pseudorotation. (b) Cyclobutadiene can undergo besides the well-known bond stretch isomerization via the square form (inversion-process) also bond pseudorotation involving rhombic forms. These rearrangements require in the parent compound some additional energy (slightly above the isomerization barrier of 7.8 kcal/mol) but should become the preferred process in substituted cyclobutadienes of lower than D3h-symmetry. (c) The calculated deformation surfaces of disulfur dinitride and its dianion reveal large deformational flexibility typical of floppy molecules. This, however, does not lead to a specific change of their electronic character: The molecules retain their 2π-aromatic nature without a significant contribution of biradical character.

In conclusion, we see a broad application spectrum of the RDCs developed in this work: (a) For the first time dynamic Jahn–Teller processes can be described on the basis of calculating the corresponding PES. The same set of coordinates can also be used to describe Jahn–Teller deformations in planar acyclic molecules of the type A2n. (b) The RDCs provide also suitable descriptors for opening/closure reactions of planar rings. (c) As previously shown in the case of the puckering coordinates, 21 the deformation amplitudes can be used to express the degree of deformation in percent and then to compare deformations in ring systems of different structure and different size. Processes leading to a crossing from one deformation subspace to another can be described by introducing hyperspherical angles as done in the case of puckering processes. 21(d) Ring substituents lead to a deformation of the ring structure due to the electronic effects they exert on the ring atoms. These deformations can be analyzed in terms of RDCs, then associated with specific deformation modes, and finally used to provide a detailed description of electronic effects induced by the substituents. (e) The concept of the RDCs can be extended to a description of processes such as Berry pseudorotation 73 or deformations in fullerenes caused by ionization, electron attachment, or substitution.

Finally it should be noted that any puckered ring molecules can be completely described by a set of N – 3 puckering coordinates and 2N – 3 deformation coordinates without using a single bond length, bond angle, or dihedral angle. In this way, ring forms of exactly specified pucker and deformation can be investigated. In work under progress, we will demonstrate the advantages of such an approach.

ASSOCIATED CONTENT

Supporting Information. Appendix with additional information on ring deformation and ring puckering coordinates and their relationship to the irreducible representations of the D3h point group (see Table A.1). Pseudorotation cycles of some larger rings (Figures A.1–A.4) that help to visualize the different deformation modes and the eect of the deformations on the ring form. Derived relationship between mode n of the N-ring and its deformations. This material is available free of charge via the Internet at http://pubs.acs.org.

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