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Topology and least motion

A study of the barbaralyl cation

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Summary. A map of the space of conformations of the barbaralyl cation, $C_9H_9^+$, is studied with an angular measure for the distance between equivalent structures and their intermediates, the transition states. The subgroup/coset decomposition of the symmetric group of 9 objects is analysed in order to develop the geometrical picture of the rearrangement space.

Key words: Angular displacement – Barbaralyl – Transition state

Introduction

Determinations of the angular displacements in a hyperspherical formulation are presented for the barbaralyl cations. They are based on the accurate *ab initio* calculations by Cremer et al. [1]. A numerical measure based on the *principle of least motion* is used to form a characterisation of the pathways and to estimate the shape of the potential energy hypersurface.

Intriguing cage structures are exhibited by many hydrocarbons and their ions and the barbaralyl cation with nine CH-groups is a particularly challenging case. It has been examined in detail by experimental [2] and theoretical [3] investigators and a good appreciation of the rearrangement reactions has been obtained. The present effort is directed towards an exploration of the advantages offered by the hyperspherical picture where different conformations correspond to different directions in a multidimensional space and where exchange processes between equivalent atoms and functional groups occur as permutations of particle labels. A given equilibrium conformation of the barbaralyl cation has formally $(9!)^2$ other structures which are of the same geometry since carbon and hydrogen atoms may be renumbered. There are 54 Cartesian coordinates to specify and six of these may be chosen freely as the centre-of-mass position and the angles of orientation of the reference frame. The resulting 48-dimensional subspace might then be partitioned into Voronoi cells associated with each particular structure. It is then of concern to learn about the neighbours of a particular cell in order to apply the *principle of least motion* which enunciates that a chemical reaction proceeds in such a way that the atoms move in the least possible way and that the electronic structure wave function remains similar throughout the rearrangement [4, 5].

Details on the choice of coordinates and the determination of the least distance are offered in the next section of this paper. The third section is devoted to an examination of a particular set of equilibrium structures with six members which are transformed amongst each other under the action of the elements of a subgroup of the full symmetric group. We proceed in the fourth section to explore the neighbours to the previously defined set of structures. Conclusions are presented in the last section.

Coordinates

Particles with masses and positions are described by means of a set $\{(m_j, \boldsymbol{r}_j) \,|\, j = 1, 2, \ldots, N\}$ which are transformed to a mass weighted form,

$$\boldsymbol{x}_j = \boldsymbol{r}_j \sqrt{\frac{m_j}{M}}; \quad j = 1, 2, \ldots, N; \quad M = \sum_{j=1}^{N} m_j$$

and supplied with a constraint

$$\boldsymbol{0} = \sum_{j=1}^{N} m_j \boldsymbol{r}_j = M \sum_{j=1}^{N} \sqrt{\frac{m_j}{M}} \boldsymbol{x}_j$$

which serves to maintain the origin at the centre-of-mass. It is advantageous in this work to employ this constraint instead of a transformation to Jacobi vectors or some other set of independent variables.

The rotational freedom in the choice of coordinates will be exploited through the requirement that each conformation is given in a *principal axes frame* [6] so that for any three-vector $\boldsymbol{a}$ it holds that

$$I(\boldsymbol{a}) = \sum_{j=1}^{N} |\boldsymbol{a} \times \boldsymbol{x}_j|^2 = \sum_{k=1}^{3} I_k a_k^2 .$$

Permutations of labels of equivalent particles leave this form invariant and the sum of the principal values is rotationally invariant and provides a measure of the size of the system. The hyperradius q for a given set of coordinates is defined as the positive root of the equation

$$q^2 = \sum_{j=1}^{N} |\boldsymbol{x}_j|^2 = \tfrac{1}{2} \sum_{k=1}^{3} I_k ,$$

A rotated frame, related to the principal axes frame by the axis of rotation $\boldsymbol{n}$ and the angle of rotation ω, gives the coordinates

$$\boldsymbol{x}_j(\omega; \boldsymbol{n}) \equiv \boldsymbol{x}_j \cos\omega + \boldsymbol{n}(\boldsymbol{n} \cdot \boldsymbol{x}_j) 2 \sin^2 \omega/2 + (\boldsymbol{n} \times \boldsymbol{x}_j) \sin\omega; \quad \forall j$$

and it should be recognised that each rotation gives an identical conformation. Two distinct conformations obtain when no proper rotation can bring them to cover one another perfectly. A rotationally invariant measure for the distance between two structures is given as

$$d_{\alpha\beta}^2 = \min_{\omega; \boldsymbol{n}} \sum_{j=1}^{N} |\boldsymbol{x}_j^{\alpha} - \boldsymbol{x}_j^{\beta}(\omega; \boldsymbol{n})|^2$$

and an angular distance between hyperspherical directions follows as

$$\omega_{\alpha\beta} = \arccos\left[\frac{q_\alpha^2 + q_\beta^2 - d_{\alpha\beta}^2}{2q_\alpha q_\beta}\right].$$

This measure was used with advantage to analyse an anomalous isotopic effect in a rearrangement reaction leading to phenalene [7] and to give a preliminary exploration of the barbaralyl cation dynamics [3].

Equilibrium structures in $C_9H_9^+$

Accurate *ab initio* calculations [1], including perturbation theory adjustments, give an equilibrium, minimum electronic energy structure with the representation given in Fig. 1 as a polyhedron with two different, isosceles triangular and three irregular hexagonal faces. A reflection plane is the only symmetry element, but this shape is slightly distorted from a form with D_{3h} symmetry. The proper rotations of this group, the subgroup D_3, are seen to be isomorphic to the subgroup of the symmetric group S_9 consisting of the substitutions

$$G;\quad \{e, a = (128)(379)(465), a^2, b = (15)(26)(37)(48)(9), ba, ba^2\}$$

with e as the identity, a an element of order three, b an element of order two, and the relation that $ab = ba^2$. Calculations have also identified a structure with the full D_{3h} symmetry [1] as a local electronic energy minimum at some 10 milliHartree (mH) above the absolute minimum.

The optimal D_{3h} structure occurs at an hyperradius of 1.663 bohr and the six minima at 1.706 bohr. These have a common angular distance from the D_{3h} form of 7.92°. Distances between the minima are obtained from the formula

$$\begin{aligned} d^2(g) &= \min_{\omega;\mathbf{n}} \sum_{j=1}^{N} |\mathbf{x}_j^\alpha - \mathbf{x}_{gj}^\beta(\omega;\mathbf{n})|^2 \\ &= \min_{\omega;\mathbf{n}} \sum_{j=1}^{N} |\mathbf{x}_{hj} - \mathbf{x}_{h^{-1}gj}(\omega;\mathbf{n})|^2; \quad \forall\, h, g \in G \subset S_9 . \end{aligned}$$

and correspondingly one finds the angles given by

g	a, a^2	b	ba, ba^2
$\omega(g)$	13.25°	12.74°	10.41°

It is clear that the six structures span a six-dimensional subspace of the reduced space of 48 remaining dimensions. The D_{3h} vector defines a seventh direction which is not contained in the subspace spanned by the six.

Transition state structures

Experimental studies have shown [2] that there is a rapid rearrangement at low temperatures among the six structures which were defined in the previous section. Higher temperatures allow a more extended set of rearrangements showing that

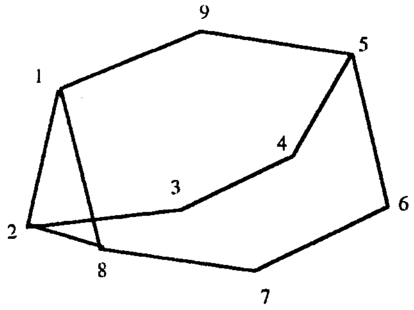

Fig. 1. Skeleton representation of the barbaralyl cation $C_9H_9^+$ with enumeration of groups

there is an equilibration which involves all nine groups. There are transition state structures "between" pairs of equilibrium structures such that they have equal distance to both members of a pair of closest neighbours. Twofold elements of the permutation subgroup correspond to twofold rotations of the "pseudo-D_{3h}" equilibrium form and the transition state geometry exhibits a C_2 axis. Each of the shortest edges in the six vertex simplex of equilibrium forms has a transition structure at a hyperradius of 1.721 bohr and an angular distance from its nearest equilibrium geometries of 6.43°. The second neighbours in the simplex are 13.71° from the transition state and the last pair is 14.65° away. The closest D_{3h} form occurs at 9.59°.

Yet another set of structures is derived from the form termed a bifurcation transition state which can transform to either one of two equivalent sets of six closely located equilibria. The point group symmetry is then C_{2v} and the reflection planes provide for a path to another C_2 form which cannot be generated from the previous one by renumbering the functional groups. An operation is required which both permutes the particle labels and reflects the original coordinate system in a plane. The C_{2v} conformation has the hyperradius 1.738 bohr and the angular distance 4.22° from the nearest C_2 forms. Direct distances from the C_s forms closest to the bifurcation transition state in the two sets are 14.30° and 15.23° and thus somewhat in excess of the distances within each set of six equilibrium structures. Figure 2 and Table 1 give the relevant data.

Each passage way from one set of six forms to another, equivalent, set is connected with a cyclic permutation where a ring of six carbon–hydrogen groups is "rotated" with regard to an edge of three groups. One of the six possibilities may be denoted $p = (195678)(2)(3)(4)$ and the set is then $\{p, apa^2, a^2pa, p^5, ap^5a^2, a^2p^5a\}$. Each member of this set gives a coset, e.g. $\{p, pa, pa^2, pb, pba, pba^2\}$ to the subgroup and a new subgroup, appropriate for the new structure. $\{e, pap^5, pa^2p^5, pbp^5, pbap^5, pba^2p^5\}$. These considerations demonstrate the connectivity between the equivalent structures of the barbaralyl cation as they are illustrated in Ref. [1]. The permutations a and p are sufficient in order to generate the symmetric group S_9 through all possible products and consequently we conclude that there are pathways from any structure to all others through transition states equivalent to those discussed above. The multidimensional nature of the situation does not lend itself to any other graphical representation than the notion of each subset of six structures being surrounded by six nearest neighbours of six structures. The transformations that bring one set into another do not permit a sequence of less than six nearest neighbour steps in order to return to the original set. Accordingly one cannot look upon the geometry as possible to map on the three-dimensional simple cubic lattice with periodic boundary conditions.

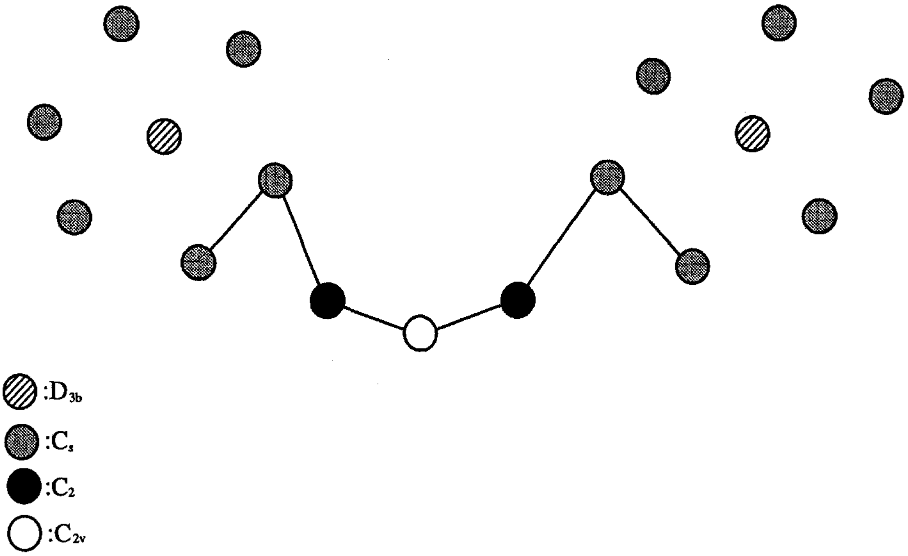

Fig. 2. Illustration of relative positions of two sets of six C_s-equilibrium geometries, each with its nearest D_{3h}-form and a C_2-transition state structure associated with an edge in the equilibrium set, as well as the bifurcation geometry C_{2v} connecting the two sets. The subset of structures require a multidimensional space and the present projection only indicates that neither are any four points in the same plane nor are two sets of six C_s-structures parallel in any sense. Distances reflect only approximately the ones given in Table 1

Table 1. Angular distance between the various structures in Fig. 2

	D_{3h}	C_s	C_s	C_s	C_s	C_s	C_s	C_2	C_{2v}
C_s	7.92°								
C_s	7.92°	10.41°							
C_s	7.92°	10.41°	13.25°						
C_s	7.92°	13.25°	10.41°	12.74°					
C_s	7.92°	12.74°	13.25°	13.25°	10.41°				
C_s	7.92°	13.25°	12.74°	10.41°	13.25°	10.41°			
C_2	9.59°	14.65°	14.65°	13.71°	13.71°	6.43°	6.43°		
C_{2v}	12.93°	17.80°	17.80°	16.36°	16.36°	8.95°	8.95°	4.22°	
C_2	15.93°	20.60°	20.60°	18.71°	18.71°	11.91°	11.91°	8.16°	4.22°
C_s	18.35°	22.20°	23.50°	20.59°	20.82°	14.30°	15.23°	11.91°	8.95°
C_s	18.35°	23.50°	22.20°	20.82°	20.59°	15.23°	14.30°	11.91°	8.95°
C_s	23.72°	27.41°	28.57°	25.19°	25.55°	20.82°	20.59°	18.71°	16.36°
C_s	23.72°	28.57°	27.41°	25.55°	25.19°	20.59°	20.82°	18.71°	16.36°
C_s	26.02°	29.80°	28.66°	28.57°	27.41°	22.20°	23.50°	20.60°	17.80°
C_s	26.02°	28.66°	29.80°	27.41°	28.57°	23.50°	22.20°	20.60°	17.80°
D_{3h}	21.76°	26.02°	26.02°	23.72°	23.72°	18.35°	18.35°	15.93°	12.93°

The sequence below is an example of a six-step cycle which brings a D_{3h}-form around a set of equivalent forms where the middle one represents a simple transposition of two groups on an edge of the structure. This seems to generate structures as close to the starting one as possible, second neighbours at 29.41° and the "opposite" one at 27.44°.

$$\left\{\begin{matrix} 1 & 9 & 5 \\ 2 & 3 & 4 \\ 8 & 7 & 6 \end{matrix}\right\} \Leftrightarrow \left\{\begin{matrix} 9 & 5 & 6 \\ 2 & 3 & 4 \\ 1 & 8 & 7 \end{matrix}\right\} \Leftrightarrow \left\{\begin{matrix} 2 & 9 & 5 \\ 3 & 4 & 6 \\ 1 & 8 & 7 \end{matrix}\right\} \Leftrightarrow \left\{\begin{matrix} 2 & 9 & 5 \\ 1 & 3 & 4 \\ 8 & 7 & 6 \end{matrix}\right\}$$

$$\Leftrightarrow \left\{\begin{matrix} 9 & 5 & 6 \\ 1 & 3 & 4 \\ 2 & 8 & 7 \end{matrix}\right\} \Leftrightarrow \left\{\begin{matrix} 1 & 9 & 5 \\ 3 & 4 & 6 \\ 2 & 8 & 7 \end{matrix}\right\} \Leftrightarrow \left\{\begin{matrix} 1 & 9 & 5 \\ 2 & 3 & 4 \\ 8 & 7 & 6 \end{matrix}\right\}$$

A sequence such as generated by $p, p^2, \ldots, p^5$ brings the structure farther away.

Discussion

Highly degenerate systems, in the sense that many equivalent conformations are accessible, allow for alternative interpretations of the particular rearrangements taking place. The early discussions about the competition between Cope rearrangement, the path through the D_{3h} form for the present ion, and the conclusion about the actual path deduced by Ahlberg and his group [2] illustrates the extensive considerations required in ascertaining a result. The present contribution demonstrates that the principle of least motion, as implemented here in terms of a numerical measure of the distance between conformations, applies. A detailed theory of the rates requires more information on the potential surface and the permutational equivalence between several structures, which implies invariance of the electronic potential energy function under the appropriate symmetric group, becomes an important aspect in the specification. It is realised that one calculation of the total electronic energy for an isolated molecular system defines a manifold of rotationally equivalent geometries. The presence of identical atoms extends such a calculation to a number of these manifolds and it is significant to have means of relating these and to find paths in between. Such questions have been addressed by Mezey [8] in somewhat similar terms as used here.

Actual representations of potential surfaces in many dimensions may be most conveniently effectuated through baricentric coordinates in simplexes. This will circumvent the need to define internal coordinates in terms of bond distances, bond angles and dihedral angles, which often leads to complicated transformations in the dynamical formulation. Our case, the barbaralyl cation, has in the centre-of-mass system 51 dimensions and 48 rotational invariants. A primitive simplex has 49 vertices and it may be tempting to consider these as representing one D_{3h} form, its six close C_s equilibrium structures, six C_2 transition geometries, six C_{2v} bifurcation geometries, another six C_2 transition forms and with these twelve C_s equilibria, as well as twelve more distant vertices. The difficulty with this enumeration is that the distances are computed in a variety of rotated coordinate frames. Pairs of geometries can be defined in the same frame at the shortest distance, but when more forms are introduced, for instance by permutations of particle labels, each pairwise distance requires its own frame. The dynamical consequence of this needs further exploration.

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