

REARRANGEMENT REACTIONS IN THE BARBARALYL CATION

Karl Anker JØRGENSEN, Jan LINDERBERG and Peter SWANSTRØM

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

Received November 16th, 1987

Accepted November 20th, 1987

Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

Hyperspherical coordinates are used to define reaction paths for rearrangements of the $C_9H_9^+$ barbaralyl cation and energy profiles are obtained from Gaussian 82 calculations using an STO-3G basis. A formula for the reaction rate is derived from the current autocorrelation function in the WKB approximation.

Contributions to the discussion about the 9-barbaralyl cation and its rapid transitions between equivalent conformations are presented here. We base the description on a hyperspherical specification of the reaction coordinate as a rotation angle. This seems particularly adequate for isomeric transitions¹ like the ones studied by Ahlberg and associates²⁻⁴ for the $C_9H_9^+$ species. Hoffmann and collaborators⁵ suggested that the ion assumed a conformation with a three-fold symmetry axis and that this form was the transition state for a Cope rearrangement. These results were reached on the basis of Hoffmann's extended Hückel scheme⁶ and supported calculations⁷ within the Complete Neglect of Differential Overlap model put forth by Pople and Segal⁸. Detailed investigations²⁻⁴ have questioned the role of the Cope rearrangement in this species and there are suggestions of an alternative route. Calculations of the relative positions on the energy scale of the various conformations were performed by Huang et al.⁹ and the symmetric form was judged to be less favorable than the earlier studies indicated.

The present effort offers extensions of the earlier calculations. We have used the Gaussian 82 program system¹⁰ to optimize geometry parameters in a molecular orbital study using the minimal basis set where Slater type orbitals are expressed in terms of three Gaussian type orbitals (STO-3G). The program system was further used to obtain electronic ground state energies at geometries intermediate between the equivalent minimum energy conformations. A description of the relevant geometries in terms of hyperspherical coordinates is given in the second part of this paper and a reaction coordinate is defined. The third section offers a derivation of a reaction rate formula for the case of a potential well between two barriers. Results for the energy profile and rates are presented in the fourth chapter and the paper

concludes with a discussion of the insufficiencies of the uncorrelated electronic structure calculations to account for the height of the energy barrier.

Hyperspherical Coordinates

Fano¹¹ argues for the adaptation of a hyperspherical picture in the description of scattering processes and in particular for rearrangements. Different associations of the particles in the systems, be they atoms, molecules, ions or functional groups, are mapped on distinct directions in a multidimensional space where the distance from the origin is a measure of the size of the system. Unimolecular reactions among isomeric forms correspond to rotations in this space. Presently we limit our analysis to a system of nuclei, the motion of which is governed by a potential energy function. Masses and coordinates for the nuclei are denoted m_j and \mathbf{r}_j respectively for $j = 1, 2, \dots, N$. The potential energy function may have several equivalent or non-equivalent minima and it is our concern to characterize a part of configuration space that encompasses a few of these. The position coordinates $\{\mathbf{r}_j \mid j = 1, \dots, N\}$ define points in the space R^{3N} . We assume that the system is invariant to translations and rotations and use the center of gravity as origin of a three dimensional reference frame. It holds then that

$$\sum_j m_j \mathbf{r}_j = 0. \quad (1)$$

A theorem by Weyl¹² assures us that internal coordinates can be defined that are expressible in rotational invariants such as scalar products $\mathbf{r}_j \cdot \mathbf{r}_k$ or triple products $\mathbf{r}_j \cdot (\mathbf{r}_k \wedge \mathbf{r}_l)$.

There are needed $3N - 6$ internal coordinates in order to describe the conformation of an N particle system. They specify a set of points in R^{3N} when the condition (1) is accounted for. Two points in this set are related through a rotation of the reference frame. We wish to define a measure for the distance between two distinct conformations, each specified by a set of points and choose a mass weighted formula. The two conformations are defined with coordinates

$$\mathbf{r}_{jA} = \mathbf{e}_x a_{jx} + \mathbf{e}_y a_{jy} + \mathbf{e}_z a_{jz}, \quad j = 1, 2, \dots, N \quad (2)$$

and

$$\mathbf{r}_{jB} = \mathbf{e}'_x b_{jx} + \mathbf{e}'_y b_{jy} + \mathbf{e}'_z b_{jz}, \quad j = 1, 2, \dots, N. \quad (3)$$

The sets $\{(a_{jx}, a_{jy}, a_{jz})\}$ and $\{(b_{jk}, b_{jy}, b_{jz})\}$ are position coordinates for the nuclei in some suitably oriented frame and $(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z)$ as well as $(\mathbf{e}'_x, \mathbf{e}'_y, \mathbf{e}'_z)$ denote basis vectors of rotated frames. A distance measure, q_{AB} , which is independent of the

choice of reference frames obtains from the expression

$$\begin{aligned}
 q_{AB}^2 \sum_j m_j &= \min \sum_j m_j |\mathbf{r}_{jA} - \mathbf{r}_{jB}|^2 = \\
 &= \sum_j m_j (a_{jk}^2 + a_{jy}^2 + a_{jz}^2) + \sum_j m_j (b_{jx}^2 + b_{jy}^2 + b_{jz}^2) - \\
 &- 2 \max \sum_j m_j (a_{jk} a_{jy} a_{jz}) \begin{pmatrix} \mathbf{e}_x \cdot \mathbf{e}'_x & \mathbf{e}_x \cdot \mathbf{e}'_y & \mathbf{e}_x \cdot \mathbf{e}'_z \\ \mathbf{e}_y \cdot \mathbf{e}'_x & \mathbf{e}_y \cdot \mathbf{e}'_y & \mathbf{e}_y \cdot \mathbf{e}'_z \\ \mathbf{e}_z \cdot \mathbf{e}'_x & \mathbf{e}_z \cdot \mathbf{e}'_y & \mathbf{e}_z \cdot \mathbf{e}'_z \end{pmatrix} \begin{pmatrix} b_{jx} \\ b_{jy} \\ b_{jz} \end{pmatrix},
 \end{aligned} \quad (4)$$

where the extremes should be sought in the parameter domain of the group of three dimensional proper rotation matrices, $SO(3)$.

Conformations such as A and B above are associated with hyperspherical radii¹³, q_A and q_B , from formula

$$q_A^2 \sum_j m_j = \sum_j m_j (a_{jx}^2 + a_{jy}^2 + a_{jz}^2) \quad (5)$$

and the distance between two conformations is given by an angular measure ω_{AB} according to the relation

$$q_{AB}^2 = q_A^2 + q_B^2 - 2q_A q_B \cos \omega_{AB}. \quad (6)$$

Many isomeric transformations leave the hyperspherical radius essentially unchanged, that is the trace of the tensor of moments of inertia does not vary, and a reaction can be interpreted as a transition along an angular reaction coordinate. This view is a quantification of the principle of least motion.¹⁴

An electronic energy minimum is found for the barbaralyl cation for a cage conformation which is somewhat distorted from D_{3h} symmetry. Fig. 1 exhibits the geometrical parameters found in our calculations.

It is seen from the figure that a set of permutations of the nuclear labels will generate equivalent conformations and in particular that the topology of the graph is invariant under a set of six permutations forming a subgroup which is isomorphic with S_3 . The operations are similar to the rotations forming D_3 , and when we consider the conformation of exact D_{3h} symmetry there is no distance between the relabeled conformations.

Angular distances between the six equivalent conformations generated by the permutations are listed in the diagram of Fig. 2. The vertices of the diagram are projections of the six linearly independent conformation vectors in R^{48} . They separate in two subsets as the atoms in an alternant hydrocarbon such that the nearest neighbors to a point in one set belong to the other set. All of the conformations have an angular distance from the geometry optimized D_{3h} structure of $8 \cdot 1^0$ while

the hyperspherical radius is $1.713479a_0$ compared to $1.668424a_0$ for the symmetric structure.

A reaction path between two conformations A and B will be parametrized such that

$$\mathbf{r}_j = \lambda_a \mathbf{a}_j + \lambda_b \mathbf{b}_j \quad (7)$$

and if the path should stay on the hypersphere, that is

$$q^2 = \sum_j m_j \mathbf{r}_j^2 / \sum_j m_j = q_A^2 = q_B^2, \quad (8)$$

it holds that

$$\lambda_a = \sin(\omega_{AB} - \omega) / \sin \omega_{AB}, \quad (9)$$

and

$$\lambda_b = \sin \omega / \sin \omega_{AB}. \quad (10)$$

It will be assumed in the following that the variable ω can serve as the essential coordinate for a rearrangement in the sense detailed by Lax.¹⁵

A Reaction Rate Formula

Basic expressions for the reaction rate are derived by Miller, Schwartz, and Tromp.¹⁶ One is in the form of a time integral of a flux-flux autocorrelation function,^{17,18}

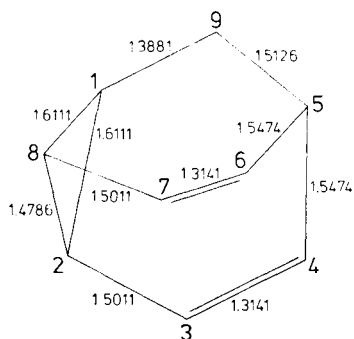


FIG. 1

Carbon-carbon bond lengths for the optimized geometry of the barbaralyl cation $C_9H_9^+$ in Ångströms ($1 \text{ \AA} = 10^{-10} \text{ m}$)

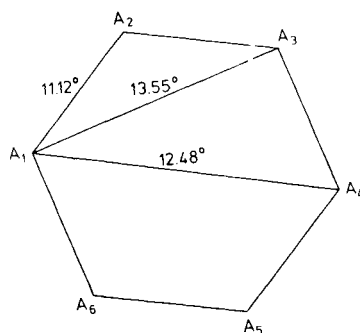


FIG. 2

Hyperspherical arc lengths for reaction paths between equivalent conformations of the barbaralyl cation

while another utilizes the associated spectral density function to define the microcanonical cumulative reaction probability.¹⁹

The derivation of the rate formula follows closely the presentation by Miller and collaborators.¹⁶ We consider the system as one-dimensional with a dimensionless reaction coordinate ω , a reaction path potential energy $V(\omega)$, and the relevant Schrödinger equation

$$[E - V(\omega)] \psi(\omega) + \psi''(\omega) = 0, \quad (11)$$

where the unit of energy is the "rotational constant" $\hbar^2/(8\pi^2 q_A^2 \sum_j m_j)$. It will be assumed that the values of ω can be extended to $\pm\infty$, while $\psi(\omega)$ remains finite, without consequence for the subsequent calculation. The associated propagator or Green function satisfies

$$[E - V(\omega)] G(\omega, \omega'; E) + d^2 G(\omega, \omega'; E)/d\omega^2 = \delta(\omega - \omega') \quad (12)$$

and provides the spectral density function²⁰

$$A(\omega, \omega', \varepsilon) = \lim_{\eta \rightarrow +0} (i/2\pi) [G(\omega, \omega'; \varepsilon + i\eta) - G(\omega, \omega'; \varepsilon - i\eta)]. \quad (13)$$

It enters the definition

$$N(\varepsilon) = \left. \begin{array}{cc} \pi A & \pi \partial A / \partial \omega \\ \pi \partial A / \partial \omega' & \pi \partial^2 A / \partial \omega \partial \omega' \end{array} \right|_{\omega = \omega' = 0} \quad (14)$$

for the microcanonical cumulative reaction probability.¹⁶

We use a Wentzel-Kramers-Brillouin expansion for the Green function²¹ and consider a symmetric potential, $V(\omega) = V(-\omega)$, with a well around $\omega = 0$ surrounded by barriers. The asymptotic regions are allowed for all energies above the bottom of the well. Two phase integrals appear in the formula for the allowed region in the well

$$\varphi = \int_{-\alpha}^{\alpha} [V(\omega) - E]^{1/2} d\omega, \quad V(\alpha) = E. \quad (15)$$

and for the barrier

$$\kappa = \int_{\alpha}^{\beta} [V(\omega) - E]^{1/2} d\omega, \quad V(\beta) = E. \quad (16)$$

The result is

$$N(\varepsilon) = 1/[1 + B^2 \cos^2 \varphi], \quad (17)$$

with

$$B = 2(e^{2\kappa} + 1)/(2 + e^{-2\kappa}). \quad (18)$$

It follows that the maximum probability occurs where $\varphi = (n + \frac{1}{2})\pi$, that is at the near quantized levels of the well. This is pronounced when κ is large, that is near the bottom.

The density of states in the well is

$$\rho(\varepsilon) = \int_{-\alpha}^{\alpha} d\omega A(\omega, \omega; \varepsilon) = \frac{1}{\pi} \frac{\partial \varphi}{\partial \varepsilon} \frac{C - B \sin \varphi \cos \varphi}{1 + B^2 \cos^2 \varphi}, \quad (19)$$

for

$$C = (2e^{2\kappa} + 2 + e^{-2\kappa}) / (2 + e^{-2\kappa}), \quad (20)$$

TABLE I

Values of energies and rates relating to near stationary levels in the barbaralyl cation rearrangement schemes. Energies are given in mH (1 mH = 2.6255 kJ mol⁻¹) and rates k in s⁻¹. Rates $x(n)$ means $x \cdot 10^n$

State	ε	$d\varepsilon/d\varphi$	$\kappa(\varepsilon)$	k
0	2.77	1.70	21.39	9.3 (-6)
1	7.89	1.56	16.59	1.3 (-1)
2	12.62	1.45	12.67	3.0 (2)
3	16.99	1.34	9.30	2.3 (5)
4	21.02	1.22	6.37	7.4 (7)
5	24.66	1.09	3.82	1.1 (10)

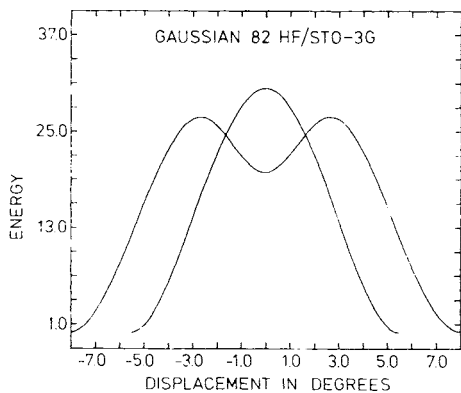


FIG. 3

Energy barrier profiles (in 10⁻³ Hartree) for reaction paths between equivalent conformations of the barbaralyl cation. The narrow barrier corresponds to the shortest arc of Fig. 2, while the other describes a path via the high symmetry D_{3h} structure

and we may define a "decay" rate for the levels ε_n as

$$k_n = 1/[(\hbar C/\pi) \partial\varphi/\partial\varepsilon] \quad (21)$$

$$\varphi(\varepsilon_n) = (n + \frac{1}{2}) \pi. \quad (22)$$

The derivative $\partial\varphi/\partial\varepsilon$, C , and κ should be calculated at $\varepsilon = \varepsilon_n$. These relations should be compared to the analysis by Child²² for the transmission coefficient and by Miller¹⁹ for rates.

Applying the rate expression to the problem of the barbaralyl cation we consider a reaction path consisting of hyperangular segments between the equivalent conformations, similar to the hexagon in Fig. 2. The edges are the shortest route between the conformations and have the lowest barrier for a direct route. The reaction path that goes through the D_{3h} conformation requires a displacement of $2 \times 8.1^\circ = 16.2^\circ$ albeit a somewhat lower barrier.

Energy Profiles and Rates

Our calculations of the electronic energy involved an optimisation of the structure in Fig. 1 at the STO-3G level of the GAUSSIAN 82 package.¹⁰ There are changes of a few picometers in the carbon-carbon bond lengths as compared to the MNDO structure used by Huang et al.⁹ and they result in an energy decrease to -341.607277 Hartree.* The barrier between two equivalent minima was mapped out along a path parametrized according to Eq. (7) and gives the height 0.030407 Hartree = 79.8 kJ/mol, ($A_1 - A_2$), is shown in Fig. 3. Two other paths marked in Fig. 2 were also investigated and gave barriers of 208 kJ/mol ($A_1 - A_3$) and 214 kJ/mol ($A_1 - A_4$). An energy profile for a direct path $A_j - 'D'_{3h}$ was computed as well and is given in Fig. 3 with the $'D'_{3h}$ position at the center and another path joining ($'D'_{3h} - A_k$). The barriers reach 70.4 kJ/mol and the D_{3h} minimum is 52.1 kJ/mol above the other minima.

Rate calculations were performed with the formula from the previous chapter. The double barrier potential was formed by joining two identical barriers at their minimum, creating a potential well. Phase integrals φ and κ were calculated and the energy ε and κ were fitted by cubic splines as functions of φ so that ε , $d\varepsilon/d\varphi$, and κ could be evaluated at $\varphi = (n + \frac{1}{2}) \pi$. The results are listed in Table I for the narrow barrier of Fig. 2. It is seen that no thermal averaging can bring the reaction rate into the observed range.² This is a consequence of the barrier height which is about four times that estimated from experiments.

* 1 Hartree = 2.6255 kJ mol⁻¹.

CONCLUSION

A hyperspherical description of the conformational geometry offers a quantification of the principle of least motion¹⁴ and it has been demonstrated here that the rearrangement reactions in the barbaralyl cation adhere to the notion that the nuclear displacements should be minimal. Estimates of the energy barrier along the reaction path from a minimal basis molecular orbital treatment are inadequate and demonstrate the need for a more detailed description of the electronic structure of this species. Our theoretical analyses give qualitative support to the picture offered by Ahlberg's group for the six-fold rearrangements and rule out the role of the high symmetry D_{3h} structure as an intermediate or transition state conformation.

Rudolf Zahradnik has provided continuing inspiration for more than a quarter of a century to Jan Linderberg, who got an indelible impression of the scope and depth of Zahradnik's mind during some lectures at Uppsala in the early 1960's. He presented the extensive investigations on hydrocarbons, which resulted in his well known book with Pančíř.²³ It has been satisfying to connect with this work through the present study of a hydrocarbon cation, dedicated to Rudolf Zahradnik on the occasion of his 60th year.

Stimulation has been forthcoming from Per Ahlberg to complete this effort.

REFERENCES

1. Linderberg J. in: *Intramolecular Dynamics* (J. Jortner and B. Pullman, Eds), p. 325. Reidel, Dordrecht 1982.
2. Ahlberg P., Harris D. L., Winstein S.: *J. Am. Chem. Soc.* **92**, 4454 (1970).
3. Ahlberg P., Jonsäll G., Engdahl C.: *Adv. Phys. Org. Chem.* **19**, 223 (1982).
4. Engdahl C., Jonsäll G., Ahlberg P.: *J. Am. Chem. Soc.* **105**, 891 (1983).
5. Hoffmann R., Stohren W.-D., Goldstein M. J.: *Bull. Chem. Soc. Jpn.* **45**, 2513 (1972).
6. Hoffmann R.: *J. Chem. Phys.* **39**, 1397 (1963).
7. Yoneda S., Winstein S., Yoshida Z.: *Bull. Chem. Soc. Jpn.* **45**, 2510 (1972).
8. Pople J. A., Segal G. A.: *J. Chem. Phys.* **44**, 3289 (1966).
9. Huang M. B., Goscinski O., Jonsäll G., Ahlberg P.: *J. Chem. Soc., Perkin Trans. 2*, **1983**, 305.
10. Binkley J. S., Frisch M. J., Raghavachari K., Whiteside R. A., Schlegel H. B., Fluder E. M., Pople J. A.: *Gaussian 82* (Revision H, 1984). Carnegie-Mellon University, Pittsburgh 1984.
11. Fano U.: *Phys. Rev., A* **24**, 2402 (1981).
12. Weyl H.: *The Classical Groups*, p. 53. Princeton Univ. Press, Princeton 1964. Cited according to Biedenharn L. C., Louck J. D.: *Angular Momentum in Quantum Physics*, p. 543. Addison-Wesley, Reading 1981.
13. Smith F. T.: *Phys. Rev.* **120**, 1058 (1960).
14. Rice F. O., Teller E.: *J. Chem. Phys.* **6**, 489 (1938).
15. Lax M.: *J. Chem. Phys.* **20**, 1752 (1952).
16. Miller W. H., Schwartz S. D., Tromp J. W.: *J. Chem. Phys.* **79**, 4889 (1983).
17. Yamamoto T.: *J. Chem. Phys.* **33**, 281 (1960).
18. Zubarev D. N.: *Nonequilibrium Statistical Thermodynamics*, p. 386. Consultants Bureau, New York 1974.

19. Miller W. H.: *J. Chem. Phys.* *65*, 2216 (1976).
20. Linderberg J., Öhrn Y.: *Propagators in Quantum Chemistry*, p. 13. Academic Press, London 1973.
21. Linderberg J.: *Int. J. Quantum Chem. S15*, 559 (1981).
22. Child M. S.: *Mol. Phys.* *12*, 401 (1967).
23. Zahradník R., Pancíř J.: *HMO Energy Characteristics*, Plenum Press, New York 1970.