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Bullvalene: Reaction Graphs for Rearrangements of Heteroatomic and Substituted Positional Isomers

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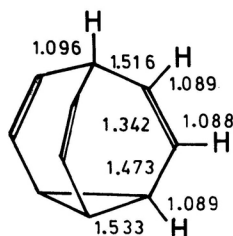
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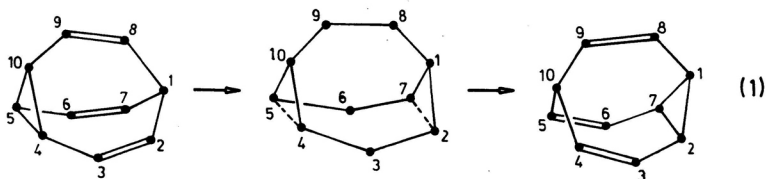
Those of us who have faith in molecular structures are mocked by the fluxional behavior of the bullvalene molecule in which each of the 10 framework atoms is free to move through all possible positions in the structure. Indeed, there are 1,209,600 possible permutational isomers of bullvalene. But the situation simplifies enormously if we replace one or more carbons by heteroatoms or *exo*-hydrogens by other substituents and then consider only positional isomers. For example, bullvalene with a single cage heteroatom or substituent has only four different positional isomers. Rearrangements involving positional isomers can be conveniently represented by a reaction graph in which the vertices correspond to individual isomers and the edges stand for processes that carry one isomer into another. The different energies of the isomers can be estimated by the rule of topological charge stabilization. In this paper, reaction graphs and relative isomer energies are used to rationalize previously reported experimental observations of isomerizations of heteroatomic and substituted bullvalenes.

Bullvalene, $C_{10}H_{10}$, undergoes a fast degenerate Cope rearrangement that permits every carbon atom in the molecule to occupy every possible site in the cage-like frame. Scott and coworkers¹ have commented that the fluxional behavior of bullvalene »seems almost to mock the very concept that molecules have structure.« It was Doering and Roth² who in 1963 proposed bullvalene as a molecule whose structure should exhibit a rapid Cope rearrangement. This prediction was almost immediately verified by Schröder who synthesized bullvalene and studied its rearrangement.^{3,4} The fluxional behavior of bullvalene has been followed by ¹H-, ²H-, and ¹³C- NMR spectroscopy, each of which at room temperature shows a single peak, indicating the equivalence of atoms on the NMR time scale.⁵⁻⁸ The activation energy for rearrangement is ~13 kcal/mol



The structure of bullvalene has been determined by gas-phase electron diffraction,⁹ X-ray crystallography,^{10,11} and single crystal neutron diffraction methods.¹² In the crystal, the molecule is distorted from ideal 3-fold symmetry but microwave and vibrational spectra have been interpreted as being consistent with C_{3v} symmetry for bullvalene.¹³ Despite the fluxional behavior observed in NMR experiments, the precise structural studies reveal three normal and localized carbon-carbon double bonds and a cyclopropane ring of ordinary dimensions. The strain energy of the molecule has been calculated to be 35 kcal/mol.¹⁴ Since the accepted value of the strain energy of cyclopropane 27.5 kcal/mol, most of the strain energy of bullvalene is accounted for in the cyclopropane ring with only about 2.5 kcal/mol for each of the seven-membered rings.¹⁴ Hoffmann and Stohrer have used qualitative MO theory to describe the bonding in bullvalene as an interaction of the Walsh MO's of the cyclopropane ring with the π orbitals of the three $-C=C-$ units arranged around a 3-fold axis.^{15,16}

Eq. (1) illustrates the proposed Cope rearrangement for bullvalene:

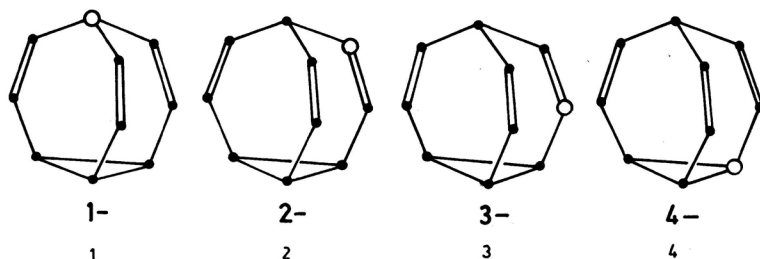


This mechanism is indeed consistent with the observation that each carbon is free to occupy every site in the skeletal frame. Since there are 10 possible sites for the location of the first carbon, 9 for the second, and so on, there are 10! permutations of carbons among the skeletal sites. But the molecule has a 3-fold axis of symmetry and we do not count as distinct permutations those that differ only by rotation in space, so the number of identical but distinguishable (by labeling) permutational isomers of bullvalene is reduced to $10!/3$ or 1,209,600.¹⁸

The permutational isomerization of bullvalene has been discussed from the viewpoint of Muetterties' topological representations.¹⁹ The topological representation for the rearrangement of bullvalene is a mathematical graph in which each vertex represents a permutational isomer and the edges connecting the vertices correspond to rearrangement processes, eq. (1), that convert one isomer into another. Since there are $10!/3$ permutational isomers or graph vertices and each vertex has degree 3 (three edges emanating from it) the resulting graph or topological representation for the complete process is exceedingly complicated and consequently only small portions of it have even been written down.¹⁸

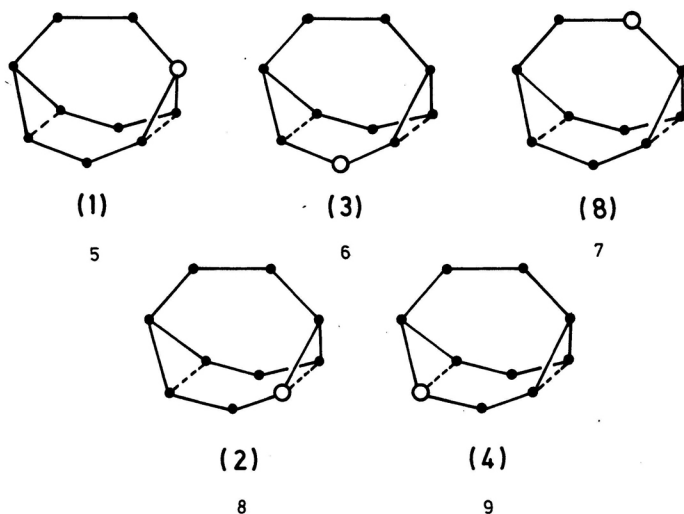
If we abandon the study of permutational isomers and instead consider the rearrangement of positional isomers, specified by the replacement of one or more carbons

by heteroatoms or one or more *exo*-hydrogens by some other kind of substituent, then the situation simplifies enormously. For example, only four different positional isomers can be made by the replacement of a single hydrogen by a bromine or the replacement of C-H by N. These isomers can be specified by the number of the site in the bullvalene framework at which heteroatom replacement or substitution has been made (1-4):

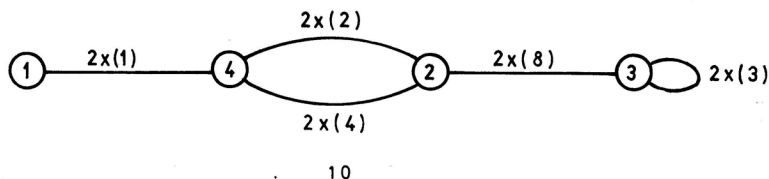


These four positional isomers can be represented by four vertices in a reaction graph in which edges represent connections established by eq. (1). Reaction graphs have been very useful in organizing the observed chemistry of other systems that undergo degenerate rearrangements such as the carboranes and heteroatomic and substituted molecules related to the fluxional ion P_7^{3-} .²⁰⁻²⁷

To generate the reaction graph relating the positional isomers 1-4 start with a single heteroatom or substituent in each of the 10 positions of the starting structure in eq. (1) and determine the resulting isomer on the product side of the equation. Relate both reactant and product isomers to the representative isomers 1-, -4-. For example, if we start with a heteroatom at position 8 on the reactant side (equivalent to 2-) the resulting structure on the product side has a heteroatom at a position equivalent to 3-. This establishes an edge in the reaction graph linking vertices representing isomers 2- and 3-. There are 10 possible starting sites for the heteroatom so there are 10 edges in the reaction graph. The edges traverse five transition state positional isomers 5-9 which can be classified as three unique or achiral isomers (1), (3), and (8) and a pair of enantiomeric structures (2) and (4).

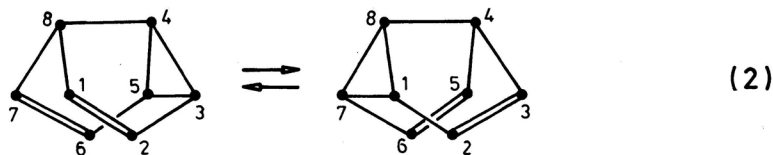


The reaction graph *10* relates the four positional isomers (represented as vertices denoted by index numbers in circles) connected by 10 edges that describes processes involving the five transition state isomers for a monosubstituted or monoheteroatomic bullvalene.



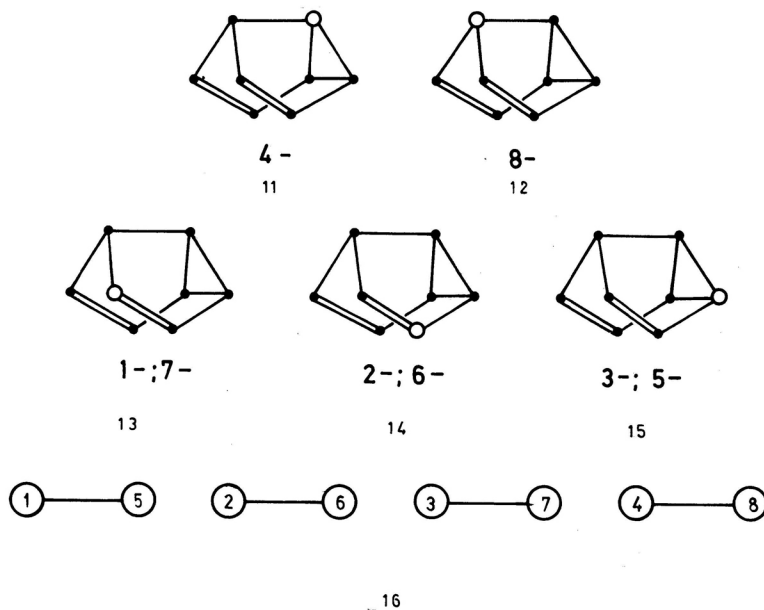
Vertices 1- and 4- are linked by two edges, both of which correspond to processes involving the transition state positional isomer (1) or 5. Vertices 4- and 2- are connected by edges that correspond to interconversions through the enantiomeric transition states (2) and (4). Vertex 3 has two loops: edges that begin and end on the same vertex and which relate to the transition state structure (3). The connectivity in *10* is important; it shows, for example, that bullvalene positional isomers 2- and 3- are directly interconvertible, but to produce 3- from 1-, the reaction must traverse the other two isomers 4- and 2-. Elsewhere, we have pointed out the relationship between point group symmetry of the isomer and the degree of the corresponding vertex in the reaction graph.²⁷ Generally, the higher the symmetry of the isomer, the lower the degree of its vertex in the reaction graph. Isomers of the same point group have vertices of the same degree. In the four bullvalene isomers 1-4, 1 has C_{3v} symmetry while 2-4 are only C_s . The degree of vertex 1 in *10* is 2; vertices 2, 3, and 4 each have degree 6.

That a path exists between any pair of isomers in *10* gives rise to the result that all carbons can move through all possible sites in the bullvalene structure by means of eq. (1). This is not true for other related systems that undergo fast Cope rearrangements. For example, semibullvalene rearranges according to eq. (2).²⁸ If we introduce a single heteroatom or substituent into semibullvalene, we get a total of 8 isomers including two achiral isomers 4- and 8- (11 and 12) and three pairs of enantiomers 1-, 7- (13); 2-, 6- (14); and 3-, 5- (15).



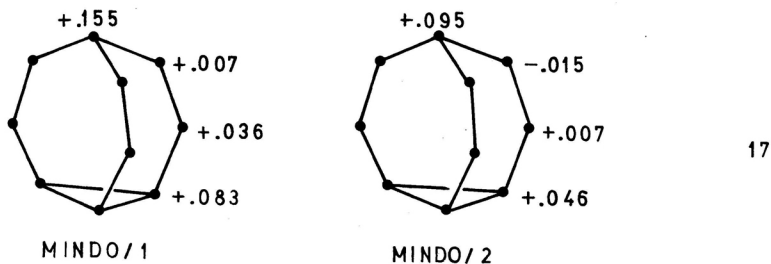
The reaction graph for monosubstituted semibullvalene (16) consists of four disconnected subgraphs. These show, for example, that 1- and 5- interconvert but no edge or process leads from either of these two isomers to any of the other six isomers.

The four positional isomers 1-4 of monosubstituted bullvalene are chemically different and have different energies. We can estimate the relative energies of these isomers using the rule of topological stabilization.²⁹ Although the bullvalene molecule is almost spherical, connectivity of atoms in the structure establishes a non-uniform distribution of atomic charge and the stabilities of heteroatomic or substituted bullvalene positional isomers are determined by how well the electronegativity of the heteroatom or substituent matches the charge already determined for the position by the topology



of bullvalene. The rule has worked well in ordering energies of positional isomers among planar conjugated systems,²⁹ adamantanes,³⁰ carboranes,³¹ and others.^{25,26} Here is how it works for bullvalene.

Iwamura, Morio and Kunii³² have reported MINDO/1 and MINDO/2 calculated net atomic charges for the carbon atoms of bullvalene as shown in 17:



Although the two varieties of calculations yield charges Q_N that are quantitatively quite different, the relative charges show the same trend:

$$Q_2 < Q_3 \ll Q_4 < Q_1$$

A take-home lesson here is that the details of the approximate method of calculation are unimportant; relative charges are determined by molecular topology. The rule of topological charge stabilization predicts that an electronegative heteroatom or an electron-withdrawing substituent would prefer to be located at the cage site that al-

ready has the largest negative charge. Thus, for the bullvalene positional isomers we have the order of relative stability:



Reaction graph 10 serves as a roadmap across the energy surface that relates interconversion of these isomers. If we take the connections established in this graph and assume that the energy of an individual isomer $N-$ is proportional to the site charge Q_N ,^{25,26} we can construct the reaction energy profile shown in Figure 1. In this diagram, we used the MINDO/1 charges for convenience and assumed that the activation barriers separating bullvalene positional isomers are small as is the activation barrier between permutational isomers of bullvalene itself.

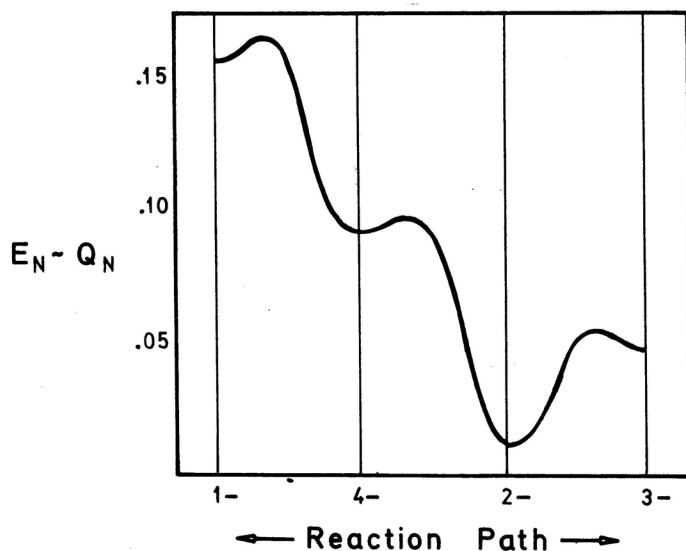
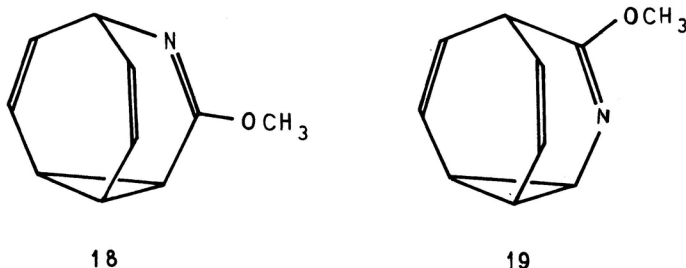


Figure 1. Positional isomer energy $E_N \propto Q_N$ along the reaction path established by reaction graph 10 relating isomers of monosubstituted bullvalene.

From our experience with *ab initio* energies calculated for the boranes and carboranes, isomers based on the position of a heteroatom in the skeletal frame may differ in energy by tens of kcal/mol, while those based on the location of *exo*-substituents may differ by only a kcal/mol or two.²⁴

The energy profile in Figure 1 is in accord with the experimental observations of Schröder and coworkers³³ who studied the relative concentrations of monosubstituted positional isomers of bullvalene: $2- > 3- \gg 4- > 1-$. Paquette and coworkers³⁴ have prepared azabullvalenes and observed interconversion of the isomers 18 and 19 which correspond to 2- and 3-, respectively. They found 18 to be the more stable of the two in agreement with our conclusions.



The proposed mechanism of isomerization, reaction graph, pattern of charge densities, and experimental observations of framework reorganizations combine to form a consistent picture.

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SAŽETAK

Bulvalen: reakcijski grafovi za pregradnju heteroatomskih i supstituiranih pozicijskih izomera

B. M. Gimarc i J. J. Ott

Postoji 1,209.600 permutacijskih izomera bulvalena. No situacija se bitno pojednostavnjuje, ako se jedan ili više atoma ugljika zamijene heteroatomima. Slično vrijedi za zamjenu atoma vodika nekim supstituentima. Pregradnje pozicijskih izomera mogu se prikladno opisati reakcijskim grafovima. Energije izomera mogu se procijeniti s pomoću pravila topološke stabilizacije naboja.