

Bullvalene: Reaction Graphs Relating Polysubstituted Positional Isomers

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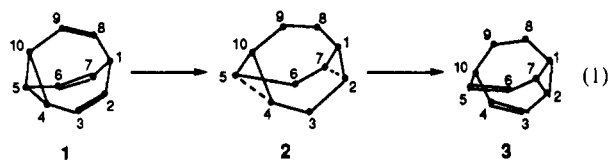
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Bullvalene, $C_{10}H_{10}$, is known to be fluxional as a result of a fast, degenerate Cope rearrangement that can move every carbon atom through all 10 positions in the structural framework. Bullvalene positional isomers, $C_{10}H_{10-n}R_n$, can be made by replacing one or more hydrogens with substituents R. The resulting substitutional isomers are known to undergo rapid isomerization, and over a period of 30 years, Schröder and co-workers have accumulated observations of rearrangements of bullvalenes with $n = 1-6$ identical substituents R. In this paper we present reaction graphs that follow the rearrangements of all possible bullvalene positional isomers for substitution $n = 1-5$. Each vertex in the reaction graph represents an isomer, and each edge stands for a rearrangement process that interconverts the pair of connected isomers. Thus the reaction graph serves as a road map of the energy surface for the substituted bullvalene system. Reaction graphs can be used to interpret the observed isomerization data. We report AM1 calculations of heats of formation of mono- and di-heterosubstituted bullvalene isomers to model relative stability trends of observed substituted isomers.

INTRODUCTION

In 1963 Doering and Roth proposed bullvalene, $C_{10}H_{10}$ (1), as a molecule that should be able to undergo a fast, degenerate Cope rearrangement as described by eq 1.¹



Bullvalene was almost immediately prepared by Schröder,^{2,3} and its fluxional behavior was confirmed by 1H , 2H , and ^{13}C NMR spectroscopy.⁴⁻⁸ The NMR spectra are interpreted as resulting from the complete scrambling of all 10 framework carbons at room temperature. Temperature variations of NMR spectra give an activation barrier of 13 kcal/mol. The detailed structure of 1 has been determined by X-ray^{9,10} and neutron¹¹ diffraction studies and by gas-phase electron diffraction.¹² Microwave and infrared spectra are consistent with an assignment of C_{3v} symmetry for 1.¹³ Neutron and X-ray diffraction experiments on crystalline bullvalene reveal a highly ordered solid.⁹⁻¹¹ The ordered crystal can be reconciled with the fluxional behavior of bullvalene in liquid solution by proposing that in the crystal the Cope rearrangement is followed by a rapid molecular reorientation process.^{8,14} The rates of rearrangement and reorientation in the bullvalene crystal have recently been measured by two-dimensional 2H NMR studies.¹⁵ The structure of the intermediate 2 has been the object of theoretical investigations using semiempirical SCF MO methods.¹⁶

In an earlier paper Gimarc and Ott used a reaction graph to represent the relationship of monosubstituted bullvalene positional isomers to each other at equilibrium.¹⁷ In this paper we extend that study to include reaction graphs for all possible positional isomers for bullvalenes containing n identical substituents R, $C_{10}H_{10-n}R_n$, $n = 1-9$. Reaction graphs have been useful in describing the relationships among positional

isomers of other molecular systems that undergo fast, degenerate cage rearrangements. These include the heteroatomic positional isomers of the *closo*-carboranes and isomers resulting from the replacement of one or more phosphorus atoms by heteroatoms in the P_7^{3-} cage.¹⁸⁻²⁰

PERMUTATIONAL ISOMERS; POSITIONAL ISOMERS

The degenerate rearrangement of 1 gives rise to $10!/3 = 1\,209\,600$ isomers that differ from one another only by the interchange or permutation of the 10 otherwise identical CH groups. All permutational isomers have the same energy. One might consider representing the relationships among these isomers by a mathematical graph in which each isomer is represented by a point or vertex, and processes carrying one isomer into another are shown as edges or arcs connecting different vertices. Because of the enormous number of permutational isomers, only small portions of this reaction graph have ever been written down.^{21,22} If, instead of permutational isomers, we consider the positional isomers that result from substituents attached to the bullvalene carbon cage, a problem of greatly reduced complexity is created. Suppose one hydrogen atom is replaced by a substituent R. The carbon atom to which R is attached can still move to all 10 cage positions, but there are only 4 different sites in the C_{10} cage and therefore rearrangement produces only 4 different positional isomers involving a single substituent R different from hydrogen. We expect the 4 positional isomers to have different energies, although probably not greatly different, and energy barriers separating these isomers should not be much different from the 13 kcal/mol barrier that separates the permutational isomers of unsubstituted bullvalene. We designate the positional isomers as 1, 2, 3, and 4 according to the number of the position at which R is attached to the carbon cage in 1. Schröder and co-workers have used a different labeling system.²³ They used the symbol B to indicate the isomer with substituent R at the bridgehead site 1, C to specify R at one of the cyclopropane sites, 4, 5, or 10, O_b to represent the isomer substituted at the olefin carbon, 2, 7, or 8 next to the bridgehead, and O_c for a substituent at the olefinic carbon, 3, 6, or 9 adjacent to the cyclopropane ring. Although these symbols are very descriptive of substituent location, they become unwieldy for the precise specification of isomers of

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Table 1. Isomer Connections for Monosubstituted Bullvalenes $C_{10}H_9R$ Following the Rearrangement According to eq 1

initial (1)		final (3)	initial (1)		final (3)
1	→	4	6 (=3)	→	3
2	→	4	7 (=2)	→	4
3	→	3	8 (=2)	→	3
4	→	2	9 (=3)	→	2
5 (=4)	→	2	10 (=4)	→	1

**Figure 1.** Reaction graph showing how the four isomers (in circles) of monosubstituted bullvalene are related (by connecting edges) through the mechanism of eq 1. Each edge represents a double connection between a pair of isomers. Thus the reaction graph represents the 10 connections of Table 1.

highly substituted bullvalenes. Therefore we use the numerical designators, but occasionally we resort to B , O_b , O_c , and C for structural descriptions. Where several numerical labels describe the same isomer (such as 4, 5, and 10), we use the label with the lowest numerical value (in this case, 4).

REACTION GRAPHS

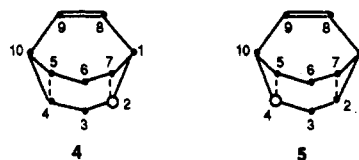
There are 10 possible positions for the location of substituent R in **1** at the start of an isomerization according to eq 1. If R starts out in cyclopropane position 5 (a C position, one equivalent to the 4-isomer), it ends in 3 and an O_b position (equivalent to the 2-isomer). We say that the 4-isomer (the low-number equivalent of 5) rearranges to the 2-isomer. If R starts at 3 (an O_c site) in **1**, it remains as an O_c or 3-isomer in 3. This is a degenerate rearrangement because bonds break and new bonds form to produce an identical isomer. Table 1 collects connections between isomers in **1** and **3** based on the rearrangement mechanism of eq 1. Since there are 10 starting positions in **1**, there are 10 connections or isomerization processes listed in Table 1. Figure 1 is a reaction graph that summarizes and visually displays the connections of Table 1. In Figure 1, a circle encloses each isomer index. Circles are connected by edges, each of which represents a pair of isomerization processes from Table 1. The loop on vertex 3 indicates the degenerate rearrangement of that isomer into itself. Thus, Figure 1 shows how 4 isomers are connected by 10 processes. Each of the double connections linking 4 and

Table 2. Numbers of Isomers and Isomerization Processes for n -Substituted Bullvalenes, $C_{10}H_{10-n}R_n$

n^a	nos. of isomers				total no. of processes
	C_{3v}	C_s	enantiomeric pairs	total	
1	1	3	0	4	10
2	0	9	3	15	45
3	3	13	13	42	120
4	3	19	25	72	210
5	0	24	30	84	252

^a n = no. of substituents.

2 passes through an enantiomeric form (**4** or **5**) of the transition



state **2**. Edges that lie symmetrically on either side of the axis of the graph in Figure 1 indicate processes that pass through enantiomeric transition states. Edges that lie on the axis denote processes that go through achiral transition states. To represent the rearrangement among the four isomers of a monosubstituted bullvalene, Schröder and co-workers have presented diagrams comparable to that in Figure 1.²³⁻²⁷ Balaban has used reaction graphs to describe the equilibrium among substituted bullvalenes, but his approach includes chemically identical permutational isomers and excludes isomers assumed to have high energies.²⁸

For bullvalene containing two identical substituents, $C_{10}H_8R_2$, there are a total of 15 possible isomers including 3 pairs of enantiomers. There are 10 possible sites for the first substituent in **1** and 9 remaining sites for the second. Since we do not distinguish between the order of otherwise identical substituents, there are $10 \times 9 / 2 = 45$ possible rearrangement processes connecting the 15 disubstituted isomers. In general, for a bullvalene with n identical substituents, $C_{10}H_{10-n}R_n$, the number of isomerization processes is given by $10! / [(10 - n) \cdot n!]$. For n -substituted bullvalenes, Table 2 shows the total number of isomers, the numbers of isomers of C_{3v} and C_s symmetry, number of enantiomer pairs, and numbers of isomerization processes for each n .

Figure 2 is the reaction graph for identically disubstituted bullvalenes. The graph is composed with 9 achiral isomers of C_s symmetry on the central axis and the 3 enantiomeric pairs symmetrically disposed on either side of the axis. The 5 loops marked by asterisks are all single connections denoting degenerate isomerizations. All other edges, including the loop on the 24-isomer, are double processes, giving a total of 45 connections represented in Figure 2. Schröder and co-workers give a set of connections between isomer pairs from which a figure related to Figure 2 could be constructed.²⁹ They also show pairwise connections from which a graph can be drawn linking isomers of bullvalene bearing two nonidentical substituents, R and S .³⁰ Nonidentical substituents give rise to many more isomers which lead to much more complicated reaction graphs. We will not mention them further in this paper.

Figures 3-5 present reaction graphs for tri-, tetra-, and penta-substituted bullvalenes. In each case all substituents are assumed to be identical. The arrangement of these graphs follows the pattern of Figure 2. The achiral isomers of C_{3v} and C_s symmetry occupy positions on the central spine of the graph, and enantiomers are paired on either side of the axis.

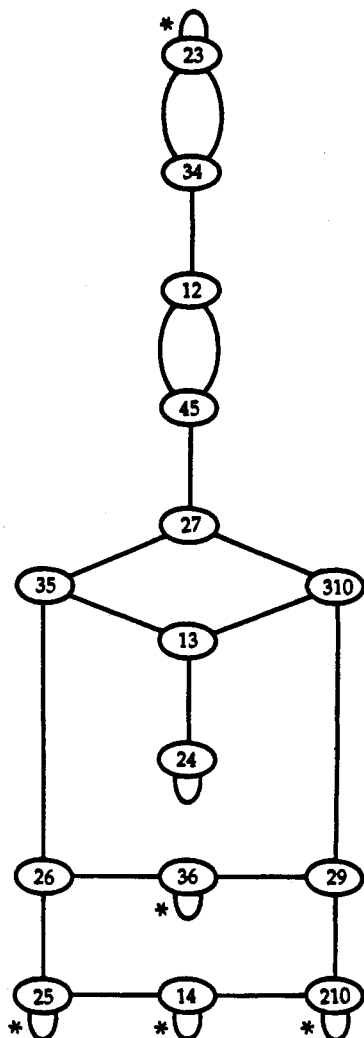


Figure 2. Reaction graph for 45 processes among the 15 isomers of disubstituted bullvalene, $C_{10}H_8R_2$. Isomers on the central axis are achiral isomers of C_s symmetry. Symmetrically located on either side of the axis are the enantiomeric pairs. Five loops denoted by asterisks (*) are single processes. All other lines indicate double processes.

Isomers of C_{3v} symmetry, which occur for $n = 1, 3$, and 4 , have low degrees of connectivity in these graphs and occupy dead-end sites on the central spine. Isomers of lower symmetry, C_s or C_1 , have higher degrees. This says that there are more ways to generate low-symmetry isomers than there are to yield high-symmetry isomers, a plausible result. Reaction graphs for bullvalenes containing 6 or more substituents can be considered to be the reaction graphs relating the isomers as designated by the 4 or fewer positions occupied by hydrogen atoms.

A reaction graph is a road map across the energy surface. Experimentally determined isomer distributions give us insight into the topography of that surface. Observed isomers correspond to minima of relatively low energy on the surface, while undetected isomers must be associated with higher energy minima. We expect all minima to be separated from each other by activation barriers. Bullvalene positional isomers with only a single substituent are probably quite close in energy. In such cases we can expect the energy barrier separating two different isomers to be comparable to the 13 kcal/mol activation barrier for the degenerate rearrangement of unsubstituted bullvalene. Isomer energy differences arise from different inherent preferences of substituents for particular sites on the bullvalene carbon cage. Attachment of an isomer at a preferred site may produce inductive or perturbative

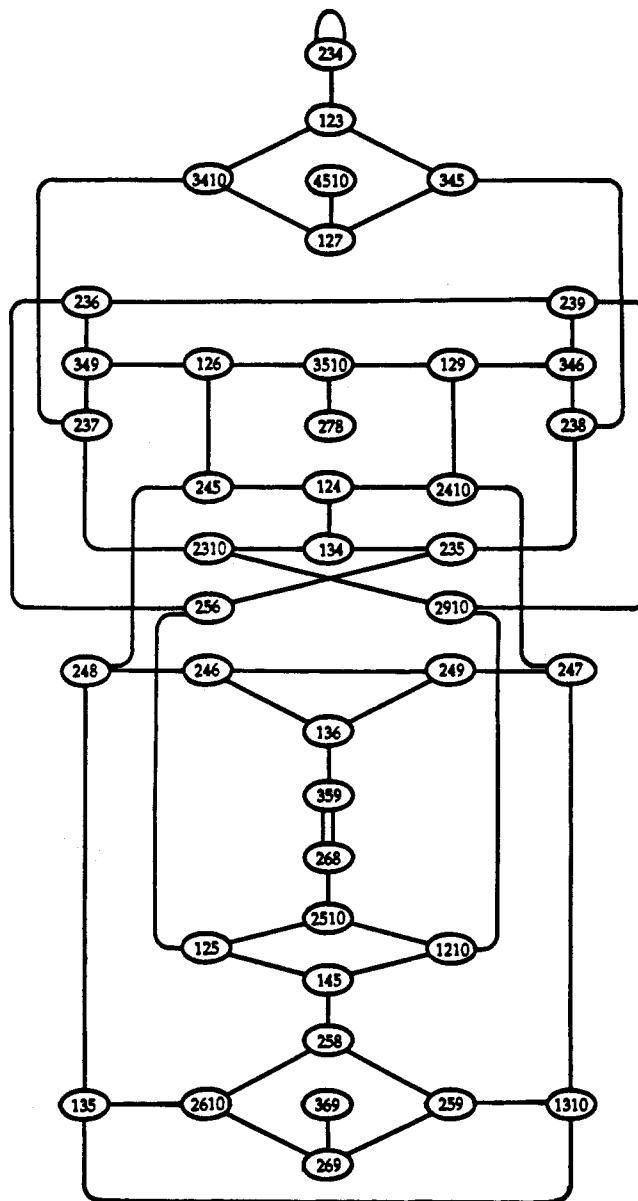


Figure 3. Reaction graph for 120 processes relating 42 isomers of trisubstituted bullvalene, $C_{10}H_7R_3$.

changes in preferences at other sites. As the number of substituents on the carbon frame increases, we might expect to see increases in the range of energy differences among isomers. At some level these energy differences might be as large as the unsubstituted bullvalene activation barrier to rearrangement. High-energy isomers could then act as barriers separating regions of low-energy structures on the map of the reaction graph. Consideration of experimental isomerization data can give us qualitative estimates of barriers separating observed isomers.

INTERPRETATION OF EXPERIMENTAL DATA

Schröder and his co-workers have studied the fluxional behavior of bullvalene and its substituted derivatives for 30 years.^{20-27,29-37} Particularly important for our paper is a series of very recent papers that summarize some of their earlier measurements of isomeric distributions of substituted bullvalenes as well as extend those studies to higher degrees of substitution.³⁵⁻³⁷ Although experiments involving many different kinds of substituents have been reported, we will concentrate on results for phenyl-, bromo-, and methyl-substituted bullvalenes because these involve results for mono-

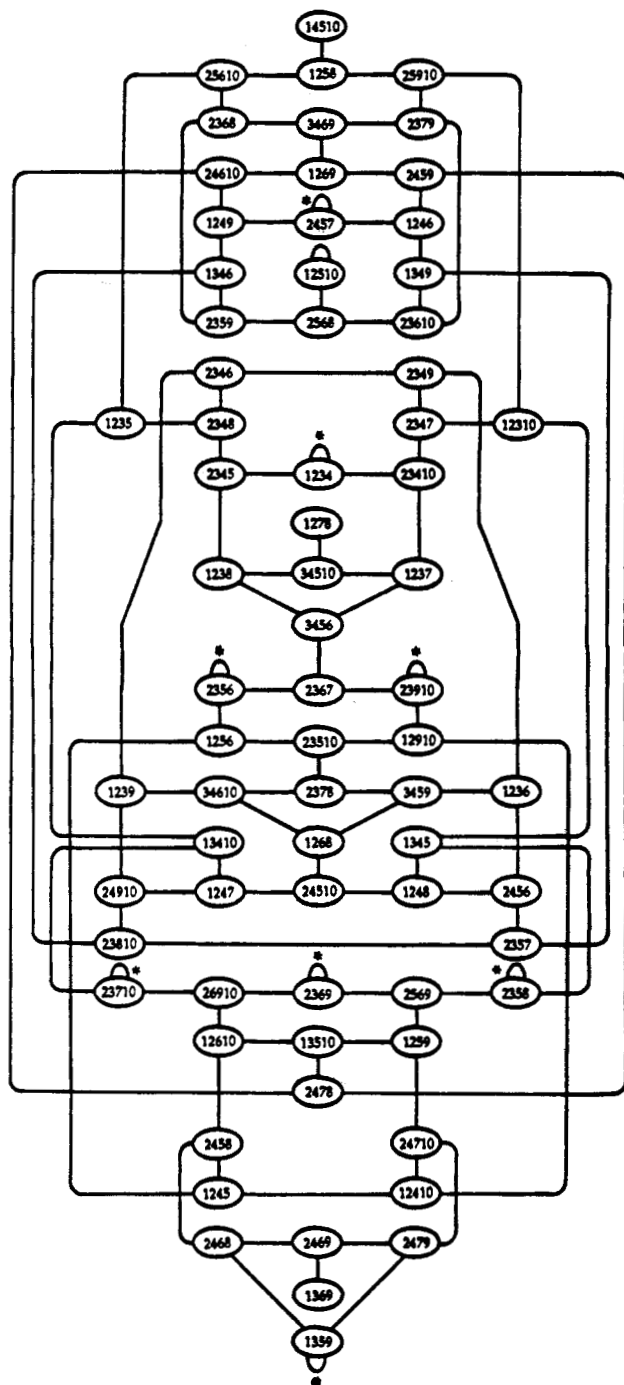


Figure 4. Reaction graph for 210 processes among the 72 isomers of tetrasubstituted bullvalene, $C_{10}H_6R_4$.

through tetra- and even up to hexasubstituted isomers. Table 3 collects the percentages of isomer distributions for phenyl-, bromo-, and methylbullvalenes. From these isomeric percentage distributions one can use the Boltzmann distribution law to show that those isomers that can be identified must be within 1 or at most 2 kcal/mol of each other in energy at room temperature. The unidentified isomers must have higher energies.

In other work, Schröder's group as well as others have described the synthesis and rearrangements of bullvalenes in which external bridging groups are attached to two carbon cage sites.³⁸⁻⁴¹ These are special cases of the disubstituted isomers. We will not consider isomers that result from such bridging in this paper.

The data for monosubstituted isomers in Table 3 show that the 2-position (or O_b in Schröder's notation) is the preferred

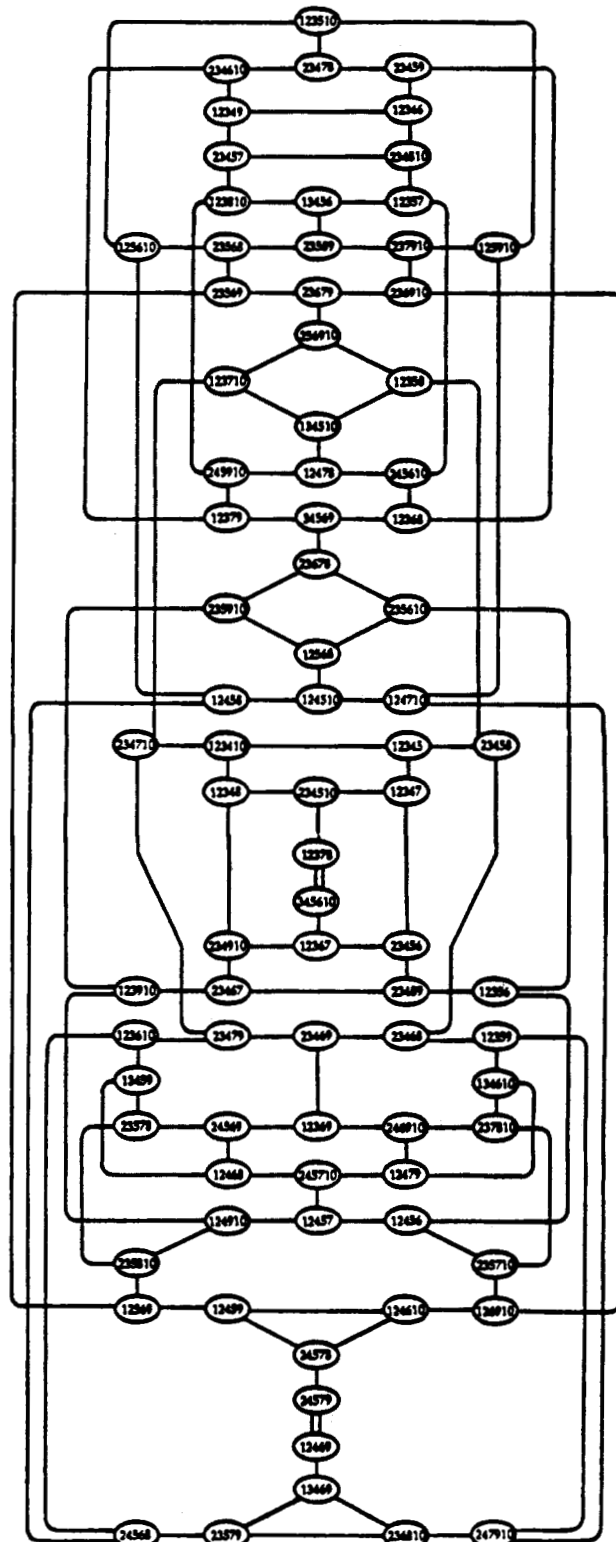
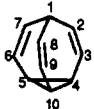


Figure 5. Reaction graph representing 252 processes among the 84 pentasubstituted isomers, $C_{10}H_5R_5$.

site for substitution followed by the 3-position (O_c). The preference for 2-substituted isomers has been rationalized by Hoffmann and Stohrer⁴² who used qualitative MO arguments, and by Gimarc and Ott¹⁷ on the basis of the rule of topological charge stabilization. For more extensive substitution, experimental results in Table 3 show that the 2- and 3-positions are still the preferred sites. Substituents scrupulously avoid the 1- (or B, bridgehead) location; no 1-substituted isomers appear in Table 3. Substitution on the cyclopropane ring (sites 4, 5, and 10, or C) is not common, but examples are

Table 3. Experimentally Determined Isomer Distributions (as Percents in Parentheses) for Polysubstituted Phenyl-, Bromo-, and Methyl-Substituted Bullvalenes, $C_{10}H_{10-n}R_n$ ^a


extent of substitution	substituent		
	phenyl	bromo	methyl
mono	2 (75) 3 (25)	2 > 3 >> 4 > 1	2 (55) 3 (45)
di	27 (53) 26, 29 (40) ^b 36 (7)	27 (14) 26, 29 (59) ^b 36 (27)	27 (35) 26, 29 (50) ^b 36 (15)
tri	278 (25) 268 (49) 269 (26)	278 (10) 268 (33) 269 (66)	278 (10) 268 (40) 269 (35) others (15)
tetra	2478 (38) 2468, 2479 (53) ^b 2469 (9)	2478 (8) 2468, 2479 (49) ^b 2469 (23)	2478 (35) 2468, 2479 (55) ^b 2469 (10)
penta	23578, 237810 (60) ^b 23579, 236810 (40) ^b	23578, 237810 (9) ^b 23579, 236810 (13) ^b 23678 (24) 23679 (54)	
hexa	235789 = 13510 236789 = 14510	235789 = 13510 236789 = 14510	

^a Summarized from refs 35–37. ^b Enantiomeric pair.

known for tetrasubstitution and higher. No identified isomer has more than one substituent on the cyclopropane ring.

Selection of sites for multiple substitution must start with a basic site preference (in order 2 > 3 > 4 > 1) but must also include perturbative or induction effects. Sites 2, 7, and 8 are all O_b positions, and these tend to fill up first or perhaps combinations of 2, 7, or 8 with O_c sites 3, 6, or 9, but in such a way that occupation of adjacent olefinic sites on the same bridge (2, 3; 6, 7; or 8, 9) is avoided or at least postponed to higher substitution. Same-bridge olefinic substituents must be avoided by perturbative effects. For tetrasubstitution, three groups occupy nonadjacent O_b or O_c sites, one on each olefinic bridge. The fourth avoids being adjacent to an occupied O_c substituent and takes up a position on the cyclopropane ring (C or 4, 5, or 10) nonadjacent to any O_c bridge substituent. A fifth substituent would have to go to an olefinic site adjacent to another olefinic substituent or to a cyclopropane site adjacent to another cyclopentane substituent. The data in Table 3 suggest that adjacent olefinic sites (23) are preferred to adjacent cyclopropane sites. A sixth substituent seems to follow the same rule.

CALCULATIONS

In an attempt to study these empirical rules of relative isomer stabilities, we have carried out a series of semiempirical SCF MO calculations for model bullvalene positional isomers. Instead of actually replacing hydrogen by a particular substituent at different positions on the bullvalene carbon framework, we modeled positional isomers by replacing CH units by N. We performed geometry optimized AM1 calculations⁴³ for $C_{10}H_{10}$, C_9NH_9 for 4 positional isomers, and $C_8N_2H_8$ for 12 positional isomers. We used the AM1 routine incorporated in the GAUSSIAN 92 program package.⁴⁴ We included the calculation on unsubstituted $C_{10}H_{10}$ to be certain that our structure and heat of formation agreed with the results of Dewar and Jie¹³ who previously studied bullvalene by AM1 calculations. Table 4 contains our calculated heats of formation for mono- and diheteroatomic

Table 4. Heats of Formation (kcal/mol) of Bullvalene Heteroatomic Positional Isomers, C_9NH_9 and $C_8N_2H_8$, from Geometry Optimized AM1 MO Calculations

	isomer	heat of formation	
		absolute	relative
C_9NH_9	3	80.91	0
	2	84.75	3.84
	4	94.06	13.15
	1	96.76	15.85
$C_8N_2H_8$	36	87.55	0
	26	91.29	3.74
	27	95.79	8.24
	35	100.77	13.22
	23	102.11	14.56
	13	103.22	15.67
	24	104.38	16.83
	25	104.63	17.08
	34	112.20	24.65
	14	116.50	28.95
	12	121.45	33.90
	45	126.09	38.54

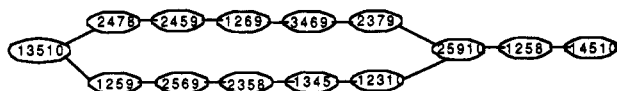
positional isomers. The heats of formation are all positive; the most stable isomer is the one with the lowest heat of formation.

The parent compound $C_{10}H_9N$ of the monoheterosubstituted azabullvalene system has apparently never been prepared although exo-substituted azabullvalenes ($C_{10}H_8NXR$, X = O or S; R = $-CH_3$ or $-CH_2CH_3$) have been studied.^{45–47} In these examples two isomers have been observed in equilibrium with each other. The more stable isomer is the one with nitrogen replacing a CH group at cage position 2 and the XR substituent attached to the carbon at the adjacent position 3. In the less stable isomer the locations of $-N=$ and $-XR$ are just reversed. No isomers with nitrogen or $-XR$ at the 1- or 4-position have been reported. These $C_{10}H_8NXR$ azabullvalenes are examples of systems that contain two non-identical substituents and therefore require a more complicated reaction graph than that featured in Figure 2 for a full description.²⁶ But cage substitution by nitrogen should take precedence over exo-substitution by $-XR$ in determining the relative stabilities of isomers. Therefore, we would expect the lowest energy isomer of the parent compound $C_{10}H_9N$ to have the nitrogen in cage position 2, in agreement with experimental results for exo-substituted isomers. Our calculated heats of formation for monoheteroatomic bullvalenes show a reversal of stabilities for the 2- and 3-isomers compared with experimental results for monosubstituted isomers. Both calculation and experiment agree that the 4- and 1-isomers (C and B positions) are less stable. For diheterosubstitution calculated results show the three isomers of greatest stability, 36, 26, and 27, are the same three as observed, but with different stability orders. The calculated stability order is 36 > 26 > 27. The experimental order varies according to substituent: 27 > 26 > 36 for phenyl substitution, 26 > 36 > 27 for bromo substitution, and 26 > 27 > 36 for methyl substitution. Calculated results agree with observation that O_c and O_b sites are preferred by substituents, as they are in 36, 26, and 27, but they avoid locations adjacent to each other on the same olefinic bridge (as they are in 23). The result that 35 is more stable than 23 implies that with 3 occupied, substitution of a nonadjacent C site (5 or 10) is preferred over substitution at the adjacent site on the olefin bridge. Isomers resulting from substitution at adjacent sites on the cyclopropane ring (45) and at both bridgehead and adjacent olefinic sites (B and O_b or 12) have the highest energies. These conclusions are in general agreement with experimental observations.

REACTION GRAPHS

For monosubstitution all four isomers lie on a connected chain in the reaction graph of Figure 1 with the most stable 2- and 3-substituted isomers adjacent to each other, allowing direct and presumably easy interconversion. Among disubstituted isomers, the 26-, 36-, and 29-isomers are directly linked on a limb that cuts across the axis of the reaction graph of Figure 2. The 26-, 29-enantiomers are separated from 27 by the 35-, 310-enantiomers, respectively. The latter should be relatively low in energy with nonadjacent O_c , C sites occupied. The highest energy isomer might be 14 (or BC). Among 42 trisubstituted isomers, only 3 isomers have been identified experimentally, 278, 268, and 269. These all lie on the central axis of Figure 3. The 278-isomer is at a dead-end position; to isomerize it must pass through 3510 which has two substituents on the cyclopentane rings and then through 126 or 129 which have a substituent at the bridgehead. From there, a number of plausible pathways lead to 268 and 269. Of 72 tetrasubstituted isomers only four have been specifically identified: 2478, 2469, 2468, and 2479. The enantiomeric pair 2468, 2479, and achiral 2469 are directly connected across the main axis of the reaction graph in Figure 4. The 2478-isomer is only a few steps away over a likely path. Observed pentasubstituted isomers are the enantiomeric pairs 23578, 237810 and 23579, 236810. These are separated in Figure 5 by a path of four steps along which the high-energy isomer is probably the 123610, 12359 pair.

We can use Figure 4 to follow the rearrangements of hexasubstituted bullvalenes, identifying vertices by specifying the locations of the 4 hydrogens or unsubstituted sites. The experimentally identified isomers 235789 and 236789 can be described by unsubstituted specifications 13510 and 14510, respectively. Indices that specify hydrogen positions here refer to sites (B and C) that other substituents prefer to avoid. The two observed hexasubstituted isomers are located on the main axis of Figure 4, 14510 at the top and 13510 near the bottom. The shortest paths between the two isomers have 8 steps. There are two such paths:



Along the upper route isomers 2478, 3469, and 2379 force substituents into the least favored positions. The situation along the lower route is not much better; isomers 2569 and 2358 should have high energy also. Observations show that the two identified isomers 236789 and 235789 do not interconvert at room temperature. Perhaps high-energy isomers and the activation barriers between them form an activation barrier that is high enough to prevent equilibration of the identified hexasubstituted isomers.

CONCLUSIONS

For substituted bullvalenes, $C_{10}H_{10-n}R_n$, there are 4 possible monosubstituted isomers, 15 disubstituted isomers, 42 isomers for $n = 3$, 72 isomers for $n = 4$, and 84 isomers for $n = 5$. For $n = 2-5$, enantiomeric isomer pairs are possible. In general there are $10!/([10-n]n!)$ rearrangement processes that interconvert isomers for each n . Isomer counts and numbers of isomerization processes are the same for n and $10-n$.

NMR studies of the equilibrium isomerizations of substituted bullvalenes have been reported for $n = 1-6$, but in each case only a few of the possible isomers are actually observed;

it would be expected that isomers that are even just a few kilocalories per mole higher than the most stable form would occur in percentages too small to be readily observed by NMR. We have presented reaction graphs that visually summarize the reaction processes available to all possible bullvalene positional isomers and use these graphs to interpret the experimental isomerization data. Relatively few observed isomers mean that only small portions of the larger reaction graphs are involved. We have carried out AM1 calculations in an attempt to rationalize the observed trends in relative isomer stabilities.

The reaction graphs themselves have some rather interesting properties. They can be presented in such a way as to readily distinguish between achiral isomers and enantiomers. The less symmetrical isomers (those with C_s symmetry and the enantiomers) have higher degrees of connectivity than do the isomers of highest symmetry (C_{3v}) which always occupy dead-end positions on the central spines of the graphs. The bullvalene reaction graphs join a growing set of reaction network graphs for fluxional systems¹⁸⁻²⁰ that await further study by graph theoretical methods.⁴⁸ These include the evaluation of topological parameters such as topological distance indices that describe the shortest paths between vertices within the graph. Reaction graphs for a number of other fluxional degenerate rearrangements, such as those for hypostrophene,⁴⁹ remain to be written down.

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