The Twin-Excited State as a Probe for the Transition State in Concerted Unimolecular Reactions: The Semibullvalene Rearrangement**

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Transition-state (TS) characterization is a central theme in contemporary chemistry, and new experimental methods are constantly being devised to achieve that goal.[1] This paper offers an approach based on the "twin-state" concept,[2] which predicts that the TS of a chemical reaction possesses a twin-excited state[3] that under certain conditions is bound and has a geometry virtually coincident with that of the TS region. Since it is bound, the twin state is, in principle, observable; hence, it is a possible source of information about the TS. This idea is in the spirit of Bersuker's[4] suggestion that every TS should be accompanied by a bound excited state with a similar structure, the properties of which should in principle be measurable by spectroscopic methods and can thus constitute a source of information about the TS. Indeed, extensive discussions in the literature emphasize the ubiquity of the situation in which a transition state is accompanied by an excited-state minimum of similar geometry.[5] We show here that this is a fingerprint of twin states, and demonstrate the idea computationally through the example of the degenerate Cope rearrangement of semibullvalene[6] (henceforth, "the semibullvalene rearrangement"). These ideas, together with the present computational support, provide a physical rationale for the intriguing experimental discovery of Quast et al.[7] that substituted semibullvalenes are colored and thermochromic even though they lack a long-wavelength chromophore.

The twin-state concept, which is based on the valence bond (VB) approach to reactivity,[3, 8] was found[2] to provide a physically lucid explanation for the apparently "anomalous" frequency increase of the b_{2u}[9] mode of benzene and generally in acenes upon excitation of the molecules from the $S_0(1^1A_{1g})$ ground electronic state to the 1^1B_{2u} electronically excited state. This exaltation was shown to be a natural consequence of the fact that the two electronic states can be considered essentially to arise from in-phase and out-of-phase combinations of two Kekulé structures,[2a, c, d] other VB structures being less important.[10] The twin-state concept is depicted in Figure 1 for a degenerate rearrangement reaction of two mirror-image molecules represented by corresponding VB structures that differ only by bonds that have shifted. The

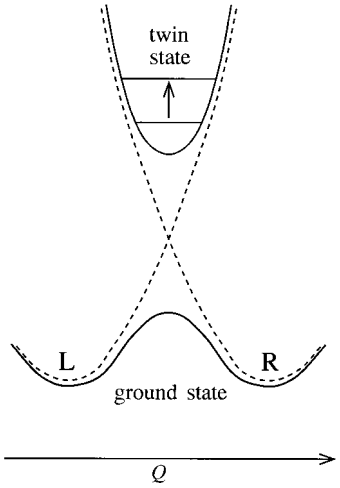
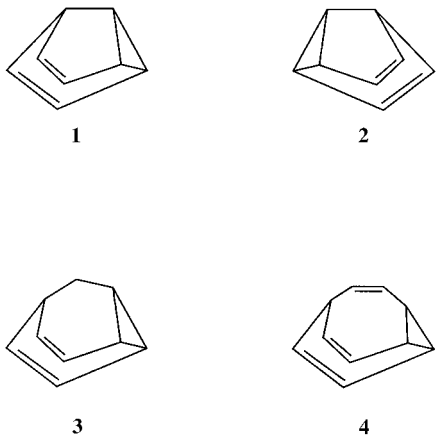


Figure 1. Schematic representation of a degenerate valence isomerization reaction, and the associated energy-level diagram that shows the avoided crossing.

semibullvalene rearrangement is a pertinent example, as evident from the two degenerate mirror-image structures **1** and **2**, but the arguments apply also to other Cope rearrangements and other thermally allowed[11] degenerate rearrangements such as *i*,*j*-hydrogen shifts.[12]



We denote the ground-state wave function of the reactant by $|L\rangle$ and that of the product by $|R\rangle$. As the system moves along the reaction coordinate Q it is assumed that the wave function can be expressed as a linear combination [Equation (1)]. By symmetry, the transition state is located at $Q=0$,

$$\Psi(Q)=c_L(Q)\,|L\rangle+c_R(Q)\,|R\rangle \quad (1)$$

where $|c_L|=|c_R|$. For a case like semibullvalene, in which an odd number of electron pairs[2e] rearrange during the reaction, the ground state electronic wave function transforms as the totally symmetric irreducible representation of the molecular

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point group. Thus, apart from a normalization factor, the ground state may be written as the in-phase combination [Equation (2)].

$$\Psi^{+}(Q=0) = |\mathrm{L}\rangle + |\mathrm{R}\rangle \quad (2)$$

$$\Psi^{-}(Q=0) = |\mathrm{L}\rangle - |\mathrm{R}\rangle \quad (3)$$

The state $\Psi^{-}(Q=0)$ represented by the negative linear combination [Equation (3)] is the excited state that arises from an avoided crossing along the isomerization reaction coordinate (see Figure 1); as such, it is the twin state of $\Psi^{+}(Q=0)$. By construction, the two zero-order VB states $|\mathrm{L}\rangle$ and $|\mathrm{R}\rangle$ are degenerate at $Q=0$, while the avoided crossing leads to the nondegenerate combinations $|\mathrm{L}\rangle + |\mathrm{R}\rangle$ and $|\mathrm{L}\rangle - |\mathrm{R}\rangle$. Thus, based on Figure 1, the TS of the thermal reaction has a twin-excited state that is bound and possesses a geometry virtually coincident with that of the TS region.

At $Q=0$ the system has an additional symmetry element; as a result, the two linear combinations $\Psi^{+}(Q)$ and $\Psi^{-}(Q)$ must have different symmetries. Since $\Psi^{+}(Q)$ transforms as the totally symmetric irreducible representation, the out-of-phase combination $\Psi^{-}(Q)$ must transform as some other irreducible representation of the point group.[2a, 13] By analogy with the case of benzene,[2] the model predicts the following properties for the twin-excited state:

a) The electronic wave function of the twin state belongs to the same irreducible representation as the coordinate that interchanges the L and R structures.

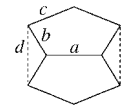
b) Because of the common "parentage" of the two states, the electric dipole transition between states will be small, even if the transition is formally allowed by symmetry.[14]

c) There will be a selective increase in the frequency of one vibrational mode in the excited state relative to the ground state. This mode corresponds to motion along the coordinate that interchanges the two VB structures used to construct the twin pair.

Figure 1 represents an ideal situation; it must be recognized that the minimum of the twin state may collapse[15] as a result of mixing with other states and distortion along the other degrees of freedom. It is therefore essential to ascertain first the conditions for survival of the energy minimum of the twin state. From previous experience, avoidance of situations typified by strong mixing with ionic structures,[2] while conferring some structural rigidity on the system,[15] is likely to lead to survival of the twin-state minimum. This is the reason for our choice of the particular target molecule in question, which seems to meet the basic requirements. Thus, molecules that undergo Cope rearrangements—such as semibullvalene (**1**, **2**), barbaralane (**3**), and bullvalene (**4**)—appear to be natural candidates for this scheme because of their structural rigidity and the fact that reactants and products are properly represented by a single covalent VB structure. In addition, these systems have been extensively studied both experimentally and theoretically. Barriers for the reactions involving **1**/**2**, **3**, and **4** were found experimentally to be rather small (4.8, 8.6, and 12.8 kcal mol^{-1}, respectively).[16] Recent high-level ab initio calculations,[17] as well as experimental evidence,[18] favor a concerted mechanism. If the concerted mechanism applies, the TS and its twin-excited state should both belong to the C_{2v} point group. Based on the twin-state model [Eq. (2) and (3)] the in-phase combination of the two VB structures **1** and **2** corresponds to the TS and transforms as the A_1 representation, while the out-of-phase combination corresponds to the twin (excited) state and should possess B_2 symmetry.

To test the twin-pair concept for the semibullvalene rearrangement we carried out quantum-chemical calculations[19] on the two lowest electronic states. Table 1 summarizes geometries for the transition state and the first excited state, calculated at several levels of theory. The excited state is found to have B_2 symmetry, as predicted by the twin-state model. The geometry of the stable ground state (not listed) reproduces fairly closely the experimentally observed geometry, with C_s symmetry,[20] whereas the TS and the twin-excited states have C_{2v} symmetry. It is apparent from Table 1 that, apart from a slight expansion of the excited state, the two states have very similar geometries. This expansion is analogous to that found both experimentally and computationally for the C–C bonds in the 1^1B_{2u} state of benzene relative to the ground state (1.44 vs. 1.39 Å)[2]. The CISMP2 results were confirmed by more extensive CISD calculations, which, apart from minor changes, reproduce the CISMP2 data. Thus, quantum-chemical calculations support the idea that the twin state has a geometry virtually coincident with that of the TS region.

Table 1. Calculated bond lengths for semibullvalene in the ground state of the TS (1^1A_1) and in the excited twin state (1^1B_2).



	1^1A_1			1^1B_2		
	3-21G	MP2/ 6-31G*	CISD/ 3-21G	CIS/ 3-21G	CIS/MP2/ 6-31G*	UCISD/ 3-21G
a	1.562	1.555	1.572	1.562	1.551	1.554
b	1.506	1.496	1.514	1.504	1.491	1.510
c	1.379	1.392	1.388	1.409	1.409	1.426
d	2.049	2.042	2.064	2.190	2.205	2.240

The calculated energy profile along the reaction coordinate is found to have the form shown in Figure 1. In accord with the qualitative model, the twin-excited state is calculated to have an energy minimum in the TS region, and the calculated oscillator strength for optical transition between the two states is small: 0.0271. The energy gap between the two twin states at $Q=0$ is calculated to be 5.16 eV, while the barrier height for isomerization in the ground state is 13.1 kcal mol^{-1}. Figure 2 depicts the reaction coordinate mode, which has an imaginary frequency for the TS and an exalted real frequency ($8b_2$) in the twin-excited state; both modes are of b_2 symmetry, as is required by the model. (The value obtained for the imaginary frequency, calculated at the harmonic approximation, may be too high, because the transition region is expected to be rather anharmonic.[21]) Calculations thus support the notion that the 1^1B_2 state is the twin state of the

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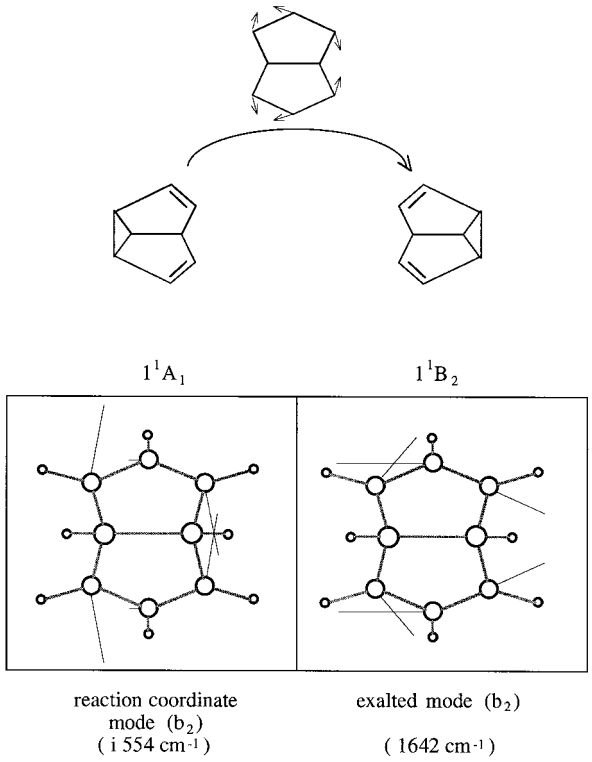

Figure. 2. Vector representation of the calculated b_2 mode that exchanges the two VB structures of semibullvalene. Left: the imaginary vibrational mode at the transition state (ground state 1^1A_1); right, the real vibrational mode of the bound 1^1B_2 state.

transitionstate for the isomerization reaction of semibullvalene, because all three criteria identified above are fulfilled. The two states may be considered to be the in-phase and out-of-phase combinations of **1** and **2**.

An experimental link to the above ideas is found in the work of Quast et al.,[7] who prepared a number of semibullvalene and barbaralane derivatives that are reversibly thermochromic—that is, they become colorless when cooled, and colored when warmed. This phenomenon was interpreted by the authors as being due to the low activation barrier in a system with the energy-level diagram shown in Figure 1. Subsequently, Manz et al.[22] used the same picture and suggested that the semibullvalene rearrangement could be laser-induced, and that the TS population could be monitored simultaneously as a result of the optical transition to the bound excited state. Our twin-state concept, supported by computational results, proves that the excited state does indeed have the deep potential well *assumed* by both Quast et al.[7] and Manz et al.[22] More important, the work provides a clear characterization of the excited state as the twin state of the TS with the properties specified in Equations (1) – (3) above. Thus, consistent with the findings of Quast et al.[7] and as predicted by the twin concept, the molecule is colorless at low temperatures because it resides near the bottom of the ground-state well where levels of the excited state accessible by the Franck – Condon principle are extremely high lying. When warmed, a significant fraction molecules is able to overcome the barrier; the substance thus acquires color, because now some light absorption is due to transitions from vibrationally excited levels of the TS region to the low-lying twin-excited state. We emphasize, however, that the existence of a relatively low-lying bound excited state is not a property of *any* double-well potential system with a low barrier in the ground state, but arises from the fact that this is a twin-state situation.[2, 3]

Our treatment shows that Bersuker's[4] suggestion (that a TS should be accompanied by a bound excited state of a similar structure) is valid for the twin states in the present study. However, the contention that *every* TS must have such a bound excited state cannot be justified in general. Thus, in cases that are not geometrically constrained, or those with high ionicity,[15] the twin-excited state will find alternative geometries in which it is more stable (e.g., H_3, H_3^-, the S_N2 TS[15]). Similarly, it does not apply to conformational interconversion, as we recently verified for the conformational isomerization of cycloheptatriene: An exhaustive search for an excited state with B_1 symmetry and a planar structure did not reveal any bound state.[13]

An experimental verification of the model could be initiated by probing the 1^1B_2 state with two-photon absorption spectroscopy. By analogy with the benzene case, a high-frequency $8b_2$ vibration should be prominent in the spectrum.[9a] Since a transition from the TS to the twin-excited state is weakly allowed by the Franck – Condon principle, the signal itself may be weak, and the actual lifetime of the state could be shortened by a radiationless process that connects it with the ground state, which could smear out the vibrational structure of the transition. If these difficulties were circumvented (e.g., by a proper sequence of IR and visible-laser pulses) then spectral information (excitation and emission) might be transformed ultimately into structural information about the twin state, hence also about the TS region.

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[1] a) J. C. Polanyi, A. H. Zewail, *Acc. Chem. Res.* **1995**, *28*, 119; b) D. M. Neumark, *ibid.* **1993**, *26*, 33; c) P. G. Wenthold, D. A. Hrovat, W. T. Borden, W. C. Lineberger, *Science* **1996**, *272*, 1456; d) T. Bally, S. Chai, M. Neuenschwander, Z. Zhu, *J. Am. Chem. Soc.* **1997**, *119*, 1869; e) C. E. H. Dessent, M. A. Johnson, *ibid.* **1997**, *119*, 5067.
[2] a) S. Shaik, S. Zilberg, Y. Haas, *Acc. Chem. Res.* **1996**, *29*, 211; b) Y. Haas, S. Zilberg, *J. Am. Chem. Soc.* **1995**, *117*, 5387; c) S. Zilberg, Y. Haas, S. Shaik, *J. Phys. Chem.* **1995**, *99*, 16558; d) S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *J. Am. Chem. Soc.* **1996**, *118*, 666; e) S. Zilberg, Y. Haas, *Int. J. Quantum Chem.*, submitted.
[3] S. S. Shaik, *J. Am. Chem. Soc.* **1981**, *103*, 3692.
[4] I. B. Bersuker, *Nouv. J. Chim.* **1980**, *4*, 139.
[5] M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH, Weinheim, **1995**, chap. 4 and 6.
[6] For a recent computational study of semibullvalenes: H. Jiao, R. Nagelkerke, H. A. Kurtz, R. V. Williams, W. T. Borden, P. von R. Schleyer, *J. Am. Chem. Soc.* **1997**, *119*, 5921.
[7] H. Quast, J. Christ, *Angew. Chem.* **1984**, *96*, 606; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 631; H. Quast, K. Knoll, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1993**, *126*, 1047; H. Quast, T. Herkert, A. Witzel, E.-M. Peters, K. Peters, H. G. von Schnering, *ibid.* **1994**, *127*, 921.
[8] S. Shaik, P. C. Hiberty, *Adv. Quantum Chem.* **1995**, *26*, 99.
[9] a) L. Wunsch, F. Metz, H. J. Neusser, E. W. Schlag, *J. Chem. Phys.* **1976**, *66*, 386; b) P. Swiderek, G. Hohlneicher, S. A. Maluendes, M.

  1433-7851/98/3710-1396 $ 17.50+.50/0

Dupuis, *ibid*. **1993**, *98*, 974; c) N. Mikami, M. Ito, *Chem. Phys.* **1977**, *23*, 141; d) J. Wolf, G. Hohlneicher, *ibid.* **1994**, *181*, 185; e) S. Zilberg, U. Samuni, R. Fraenkel, Y. Haas, *ibid*. **1994**, *186*, 303.
[10] E. C. daSilva, J. Gerratt, D. L. Cooper, M. Raimondi, *J. Chem. Phys.* **1994**, *101*, 3866.
[11] R. B. Woodward, R. Hoffmann, *Angew. Chem.* **1969**, *81*, 797; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781.
[12] P. J. Reid, M. K. Lawless, S. D. Wickham, R. A. Mathies, *J. Phys. Chem.* **1994**, *98*, 5597.
[13] S. Zilberg, Y. Haas, unpublished results.
[14] R. P. Feynmann, M. Leighton, M. Sands, *The Feynmann Lectures in Physics*, *Vol. III*, Addison-Wesley, Reading, MA, **1965**, chap. 10.
[15] S. Shaik, A. C. Reddy, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 1631.
[16] For a summary of the experimental data and a review of previous mechanistic interpretations, see M. J. S. Dewar, C. Jie, *Tetrahedron* **1988**, *44*, 1351.
[17] For a review of previous mechanistic interpretations and a high-level ab initio calculation of the mechanism, see D. A. Hrovat, K. Morokuma, W. T. Borden, *J. Am. Chem. Soc.* **1994**, *116*, 1072.
[18] K. A. Owens, J. A. Berson, *J. Am. Chem. Soc.* **1990**, *112*, 5973.
[19] Gaussian 94, Revision D.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.
[20] Y. C. Wang, S. H. Bauer, *J. Am. Chem. Soc.* **1972**, *94*, 5651.
[21] To compare the calculated frequency of the excited state with experiment the former must be scaled by a factor of about 0.9. The resulting value ($\approx 1480\ cm^{-1}$) is 15–20% higher than the frequencies of similar vibrations in the ground state.
[22] M. Dohle, J. Manz, G. K. Paramanov, *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 478; M. Dohle, J. Manz, G. K. Paramanov, H. Quast, *Chem. Phys.* **1995**, *197*, 91.

An Artificial Regulatory System with Coupled Molecular Switches**

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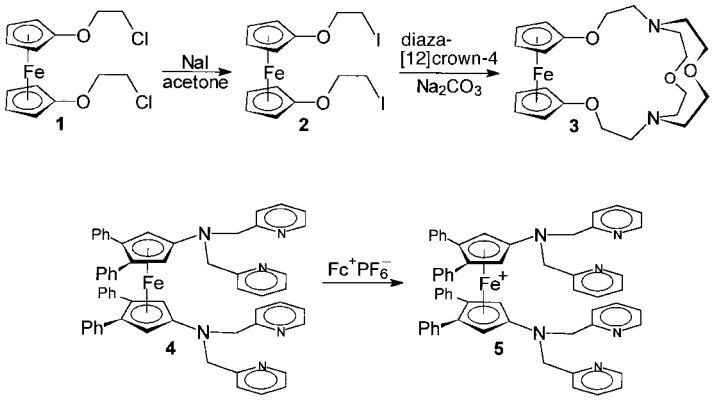
Living organisms rely on an efficient yet complex array of multiply interrelated molecular machines.[1] Recently synthetic chemists have been imitating some of the very basic functions realized in biological systems. This activity has resulted in a number of artificial systems, such as molecular switches,[2–9] sensors,[10] ratchets,[11] wires,[12] artificial enzymes,[13] and self-assembled species[14] to name but a few.[15] We set out to increase the complexity of such systems by designing an artificial regulatory unit in which several molecular components are coupled in a well-adjusted manner.[16, 17] Here, we demonstrate that the interaction of a redox-responsive chelating aminoferrocene, a redox-switchable oxaferrocene cryptand, a Zn^{2+} and a Na^+ salt, and a polyazamacrocycle leads to a system in which the availability of sodium ions can be controlled.

The basic components of the artificial regulatory system described here are two types of redox-active chelating ligands based on ferrocenes. Chelating aminoferrocenes form very stable complexes with soft transition metal ions and respond to the incorporation of metal ions by an anodic shift of the ferrocene redox potential.[18] Complexes of oxaferrocene cryptands with hard alkali and alkaline earth metal ions can become severely destabilized when the ferrocene is oxidized (redox-switching).[19, 20] The efficiency of redox-active ligands in general, crucially depends on the electronic communication between the metal centers involved,[21] and we have recently shown that it is very favorable when donor atoms of a chelating ligand are directly attached to the ferrocene unit.[22]

The construction of an artificial regulatory system based on such ferrocenes requires the careful assembly of several individual components: a redox-responsive ligand (chelating aminoferrocene), a cofactor (Zn^{2+} salt), a redox-switched ligand (oxaferrocene cryptand), a mediator (redox-equivalent), and a deactivator (cyclam = 1,4,8,11-tetraazacyclotetradecane). The individual tasks performed by these subunits are as follows: the redox-responsive ligand binds a cofactor (Zn^{2+}) to become an oxidizing agent, thus generating a redox-equivalent to act as a mediator. This mediator triggers the redox switch and strongly reduces the affinity of the redox-switched ligand for Na^+ ions. The removal of the cofactor by an added deactivator results in the reversal of the switching event and the reactivation of Na^+ binding. In the process as a whole, the availability of Na^+ ions is controlled indirectly by Zn^{2+} ions, by means of electron transfer.

The two types of ferrocenes needed for the artificial regulatory system were synthesized as described in Scheme 1. The dichloride **1** was treated with NaI in acetone to yield the diiodide **2** in 90% yield. The subsequent reaction of **2** with diaza[12]crown-4 generated the oxaferrocene cryptand **3** (Fccrypt) in 80% yield.[23] The simple addition of $NaCF_3SO_3$ to Fccrypt in acetonitrile, followed by evaporation of the



Scheme 1. Syntheses of the redox-active chelating ferrocenes. $Fc^+ = [Fe(C_5H_5)_2]^+$.

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