

Supplementary Material to

Variations on the Bergman Cyclization Theme: Electrocyclizations of Ionic Penta-, Hepta-, and Octadiynes

Dominic A. Sirianni,¹ Xinli Song,² Salmika Wairegi,² Evan B. Wang,² Sebastian A. Mendoza-Gomez,² Adam Luxon,² Maxwell Zimmerly,² Ariana Nussdorf,² Michael Filatov-Gulak,³ Roald Hoffmann,⁴ and Carol A. Parish^{2, a)}

¹⁾*Department of Natural Sciences, Daemen University, Amherst, NY 14226*

²⁾*Department of Chemistry, University of Richmond, Richmond, VA 23173*

³⁾*Department of Chemistry, Kyungpook National University, Daegu 702-701, South Korea*

⁴⁾*Department of Chemistry, Cornell University, Ithaca, NY 14853*

(Dated: 14 March 2023)

Warning: Don't ever print this document — it is long.

^{a)}Electronic mail: cparish@richmond.edu

Contents

I	Theoretical Background	S-3
II	Development of Novel Characterization Approaches	S-5
A	Linear Transit Approach for Transition-State Searching & Qualitative Reaction Profiling	S-5
B	Towards a General Approach for Placing NICS Probes	S-7
III	Supplementary Results & Discussion	S-10
A	Cyclization of the Penta-1,4-diyne Anion	S-10
B	Absolute & Relative Electronic Energies & Enthalpies for All Cyclizations .	S-10
C	Nucleus-Independent Chemical Shift Data	S-10
D	Qualitative Energetic Profiling of Cyclization Processes via Linear Transits .	S-10
E	Methodological Comparison: REKS vs. EOM-SF-CCSD	S-10

List of Figures

S-1	Quantum chemistry on two-level systems	S-4
S-2	Novel scheme for uniquely placing NICS probes	S-8

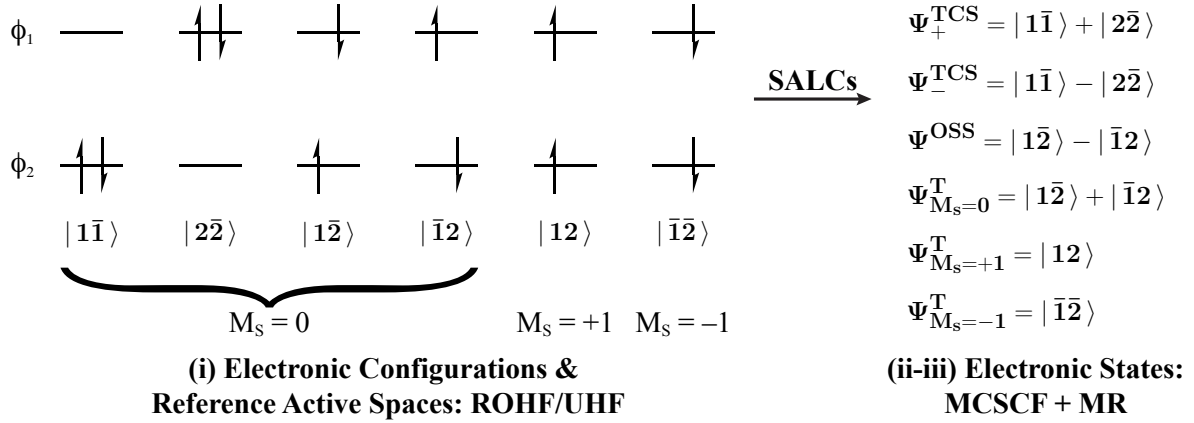
List of Tables

I. Theoretical Background

We are interested in characterizing Bergman-like electrocyclization reactions, in which the reactants are closed-shell, ground state singlets and the products are (presumably) aromatic diradicals. Diradicals are theoretically challenging molecules [10.1021/bk-2015-1209.ch011, 10.1021/acs.chemrev.9b00260] in which two electrons occupy two quasi-degenerate orbitals, the electronic states of which may be approximately described within the context of a two-level system, visualized schematically in Fig. S-1. For sufficiently small orbital energy splitting, the resulting six electronic configurations (Fig. S-1.a.i) combine to produce four symmetry-adapted electronic states: two closed-shell, two-configurational singlets (Ψ_+^{TCS} and Ψ_-^{TCS}), one open-shell singlet (Ψ^{OSS}), and three degenerate components of the triplet ($\Psi_{M_s=-1}^{\text{T}}$, $\Psi_{M_s=0}^{\text{T}}$, and $\Psi_{M_s=+1}^{\text{T}}$), provided in Fig. S-1.a.ii-iii. Aside from the high-spin components of the triplet ($\Psi_{M_s=\pm 1}^{\text{T}}$), each of these electronic states are multiconfigurational, requiring more than one Slater determinant to adequately describe the total wavefunction (referred to as static electron correlation). While a compact, two-configurational self-consistent field (TCSCF) wavefunction would be sufficient to capture the static correlation in this isolated two-level system, real diradicals are not so simple: in addition to the possibility of other quasidegenerate orbitals, whereby a more general, multiconfigurational self-consistent field (MCSCF) wavefunction is required, the contributions of instantaneous, pairwise electron-electron repulsion must also be captured. This dynamical electron correlation necessitates the use of a post-MCSCF, multireference approach, e.g., MR-PT, MR-CI, MR-CC, etc. in order to adequately describe the properties and chemical behavior of these molecules. Determining the reference active space (Fig. S-1.a.i) for molecules such as these is complicated, and MR approaches (Fig. S-1.a.ii-iii; e.g., MR-CC), are computationally intensive for even small systems with only a few heavy (i.e., non-hydrogen) atoms.^{64, 67} Furthermore, if the transition states in these Bergman-like cyclizations are product-like, they too may possess significant diradical character; due to the additional complications inherent to transition-state searches, the application of MR approaches to quantitatively examine diradical-producing reactions has also been limited.

Alternatively, spin-flip (SF) formulations of excited state methods based on single-reference theories like equation-of-motion coupled-cluster (SF-EOM-CC; abbreviated SF-CC)⁵¹⁻⁵⁸ or time-dependent density functional theory (SF-TDDFT)⁴⁹⁻⁵⁰ have been devel-

(a) Multiconfigurational + Multireference Approach



(b) Spin-Flip Approach

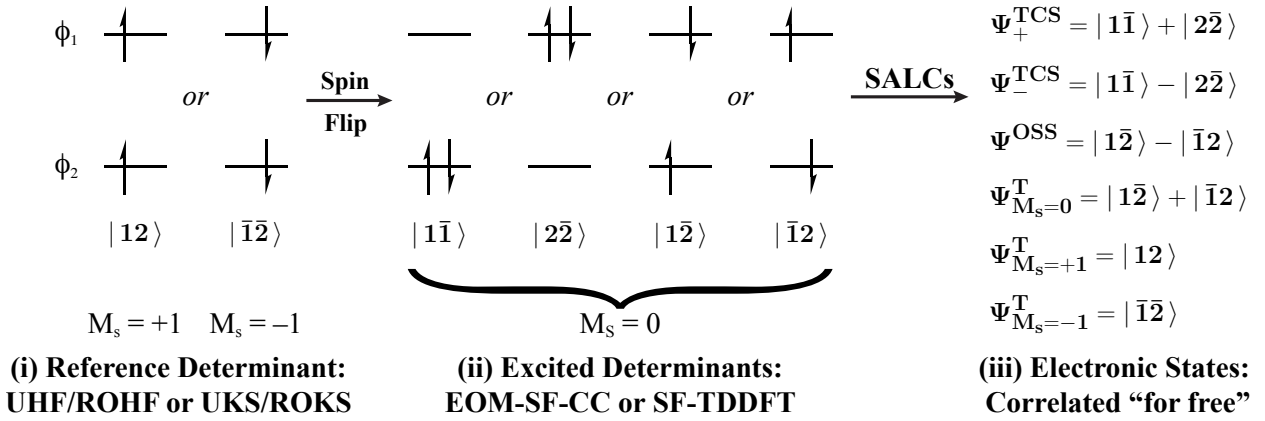


FIG. S-1. Schematic representations of two different approaches to study diradical molecules, within the context of a simple two-level system comprised of two electrons (labeled 1 and 2) in two quasidegenerate orbitals ϕ_1 and ϕ_2 . Permutations of the orbital occupations in this two-level system produces six distinct electronic configurations, represented above as a Slater determinant $|\phi_1(i)\phi_2(j)\rangle \equiv |ij\rangle$ with electron i occupying the spatial orbital ϕ_1 and electron j occupying ϕ_2 and where an overbar denotes an electron has β spin.

oped that approach these systems in a different way, visualized in Fig. S-1.b. In the SF approach, a high-spin ($M_s = \pm 1$) triplet reference is constructed with an open-shell self-consistent field approach using either a restricted or unrestricted reference (UHF/ROHF or UKS/ROKS; Fig. S-1.b.i), before spin-flip excitations being performed to generate all low-spin ($M_s = 0$) excited determinants (Fig. S-1.b.ii). These determinants may then be combined and symmetry-adapted using the squares of the transition amplitudes generating each spin-flipped determinant as expansion coefficients to generate multiconfigurational

states for which both static and dynamical electron correlation is captured (Fig. S-1.b.iii). In this manner, the problem of applying a post-MCSCF multireference approach to capture both the static and dynamical electron correlation in these systems is reduced within the framework of a relatively more straightforward, computationally tractable single-reference theory where dynamical electron correlation is included “for free” (i.e., not requiring a subsequent correlated computation on top of the spin-flip treatment generating the multi-configurational states of interest). Recently, computational investigations of the canonical Bergman cyclization leveraging SF-TDDFT and SF-CCSD have exhibited good agreement with experimental reaction barriers and thermodynamic quantities,^{17,49} the success of which inspires us to apply these approaches in this work.

II. Development of Novel Characterization Approaches

A. Linear Transit Approach for Transition-State Searching & Qualitative Reaction Profiling

In the field of quantum chemistry, where most computational procedures are notoriously ill-conditioned and difficult to perform, the geometric optimization of transition state (TS) structures is among the least well-behaved classes of computations that are still performed routinely. Nevertheless, TS searching is a critical step in the quantitative characterization of chemical reaction kinetics as well as the determination of reaction mechanisms, making them a necessary ingredient in studies such as this work. Like any geometry optimization, the goal of a TS search is to find a stationary point on the nuclear potential energy surface (PES), where the PES for a molecule comprised of N atoms is defined as a function of $3N - 6$ mutually orthogonal, internal degrees of freedom (or $3N - 5$ for linear molecules) mapping the molecular geometry to its potential energy. In this context, a stationary point on the PES is a molecular geometry for which the first derivative of the electronic energy with respect to perturbation in nuclear coordinates (the gradient) is zero.

For conventional (i.e., non-TS) geometry optimizations, the end goal is to find a stationary point which is also a minimum on the PES, where the curvature of the surface — defined as the sign of the second derivative with respect to nuclear perturbation (the Hessian) at a particular set of nuclear coordinates — is positive when evaluated along all internal degrees of

freedom. The procedure for finding such a point on the PES can be understood conceptually as walking “downhill” from an initial guess structure: by first computing the gradient vector at a given geometry and then perturbing the nuclear positions to minimize the energy along that vector, a new structure can be generated whose energy is lower than the previous one. Eventually, by iteratively repeating this procedure to refine the initial structure, an optimal molecular geometry can usually be found. In practice, however, and especially in the case of large molecules, the $3N - 6$ internal degrees of freedom which define the PES makes the brute-force search for an optimal molecular geometry either prohibitively expensive or too ill-conditioned to be realistic. This makes the choice of a “good” initial guess structure of paramount importance to ensure successful completion of the optimization procedure.¹ Fortunately, chemical intuition and the use of classical potentials (force fields) to refine an initial molecular structure can typically generate an initial guess geometry lying close enough on the PES to the optimal one to be able to seed a successful optimization.

Unlike for conventional geometry optimizations, however, TS searches seek to find a stationary point where the curvature is positive in all directions except one; such stationary points are referred to as first-order saddle points, thanks to their resemblance to an equestrian saddle. Furthermore, the specific direction in which the curvature of the PES is negative must “connect” the desired reactant(s) and product(s) structures, i.e., moving the atoms in the direction of negative curvature will transform the reactant(s) to the product(s). Clearly, TS searches are a much more complicated process than simply walking downhill from an initial guess structure, making the choice of an initial transition state structure all the more paramount. Unfortunately, arriving at good initial structures for TS searches is widely held to be more of an art than a science, relying primarily on experience, chemical intuition, and no small amount of luck. During the course of this work, one of us (DAS) ran out of ideas for generating different guess structures according to this artful approach when faced with yet another unsuccessful TS search, leading to the development of a more systematic, although less aesthetically pleasing, approach for generating guess structures from which to begin TS searches, which is described here. We include this discussion not as a scientific novelty — even though we are not aware of this approach being previously published in the literature — but as a service to the community, with the hope of making TS searches more approachable and routinely successful for practitioners in the field.

As described above, the goal of a TS search is to find a saddle point on the poten-

tial energy surface whose one degree of freedom with negative curvature directly connects the reactant(s) and product(s). Confirming the identification of the desired TS therefore requires computing the vibrational frequencies and normal modes of vibration at the identified stationary point; this frequency analysis should reveal exactly one imaginary (may be represented as negative) vibrational frequency, whose associated normal mode of vibration traces a path of atomic displacement connecting reactant and product. It would be intuitive, then, to try to construct a pathway along this vibrational mode to identify the transition state in a reduced search space (optimizing in only one degree of freedom instead of $3N-6$). Indeed, this is exactly the goal of, e.g., the frozen string[?] and intrinsic reaction coordinate (IRC)[?] approaches, which have become major tools aiding in the identification of transition states. These approaches do suffer from their own complexities and numerical instabilities,[?] however, and can therefore be difficult to converge in their own right. To avoid such issues while retaining the spirit of these path-tracing methodologies, our approach connects reactant and product species directly, with no normal mode information, by simply constructing a geometric “displacement vector” from the difference in atomic positions between the two structures. We then scan the potential energy along this displacement vector by incrementing the molecular structure of the reactant with respect to the fractional extent of reaction, ξ (where $\xi = 0$ corresponds to the reactant and $\xi = 1$ to the product).

Finally, transition state searches can be seeded from these interpolated molecular geometries near the maximum of energy computed along the profile.

B. Towards a General Approach for Placing NICS Probes

As discussed in the Methods section of the main text, the standard location for the placement of isotropic single-point NICS probes for planar, symmetric aromatic molecules is in the center of the ring plane [for NICS(0)] and 1 Å above and below the ring plane [for NICS(± 1)], all three of which must be equidistant from all ring atoms. For the highly nonsymmetric and nonplanar cyclic molecules examined here, however, there are two problems with this convention, namely (i) there does not exist a point (or points) which are mutually equidistant from all ring atoms and (ii) the notions of “above” and “below” are ill defined in the absence of a ring plane. While the first concern is easily circumvented by taking inspiration from the literature 3 where the NICS(0) probe location was originally

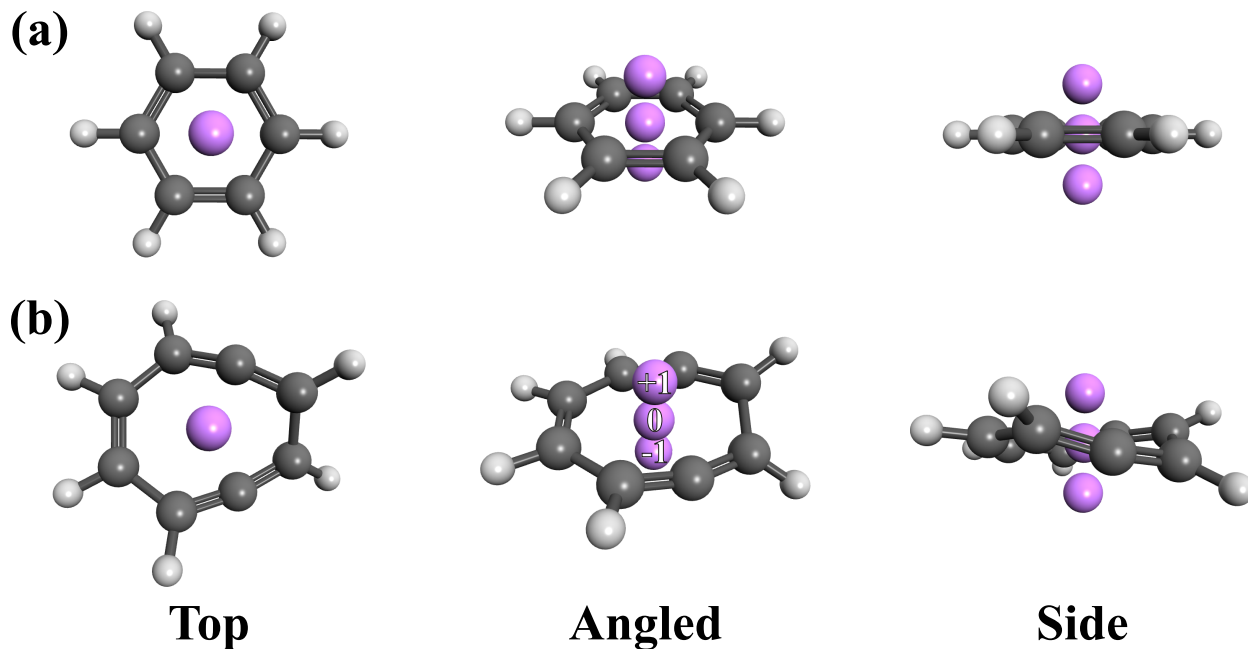


FIG. S-2. NICS(-1, 0, +1) probes (lilac spheres) superimposed on structures for (a) benzene and (b) **8cTL** as viewed from above (left panel), the side (right panel), or an angled perspective (center panel).

defined to coincide with the non-mass-weighted geometric centroid of the ring, the second is still an open question with several conventions existing in the literature for symmetric, non-planar molecules.⁴ Rather than performing a much more involved and costly analysis based on mapping the isotropic NICS values along a grid surrounding our molecules, we have instead determined a system which is capable of unambiguously placing these probes in a manner analogous to NICS(± 1) for our nonsymmetric molecules that will recover previously reported conventions when applied also to symmetric molecules.

To derive where the NICS(± 1) probes should be placed in the more general case of a non-symmetric, nonplanar molecule, it is intuitively sufficient to begin by examining where these probes are placed for the conceptually simplest aromatic molecule: benzene. In benzene, the NICS(0) probe is placed in the center of the ring plane, with NICS(± 1) probes placed 1 Å perfectly above and below the molecular plane (see Fig. S-2.a for visualization). By connecting these points, it is clear that they lie on a line which coincides with the principal axis of rotation (i.e., the C_6 axis of the D_{6h} point group). While not all molecules possess a principal rotation axis defined by their symmetry, all molecules do possess a rotational

reference frame defined by the rotational moments of inertia as originally outlined in the classic text by Wilson, Decius and Cross.⁵ For symmetric molecules, the principal axis of rotation (by symmetry) does coincide with one of the vectors defining this rotational frame, namely the principal moment of inertia. These moments of inertia are defined to be the eigenvectors of the moment of inertia tensor, \underline{I} , a 3×3 matrix with elements given by

$$I_{\alpha\alpha} = \sum_n (\beta_n^2 + \gamma_n^2) \quad (1)$$

$$I_{\alpha\beta} = - \sum_n \alpha_n \beta_n \quad (2)$$

where α_n , β_n , and γ_n are mass-weighted Cartesian coordinates for atom n , within which the origin of the coordinate frame is defined to be the molecular center-of-mass. The three moments of inertia which define the rotational reference frame, $\{|i_n\rangle : n = a, b, c\}$, are the eigenvectors which diagonalize the moment of inertia tensor, \underline{I} :

$$\underline{I}|i_n\rangle = I_n|i_n\rangle \quad (3)$$

It is worth noting that the eigenvalues $\{I_n : n = a, b, c\}$ are related to the conventional (i.e., spectroscopic) rotational constants $N = A, B, C$ according to

$$N = \frac{h}{8\pi^2 I_n}. \quad (4)$$

To place the NICS(\hat{A} 1) probes for a general, non-symmetric and non-planar molecule, we must take several additional considerations into account, namely

1. the atoms being considered in the construction of the moment of inertia tensor are only the ring atoms (i.e., the eight carbon atoms of 8cTL),
2. the origin of the coordinate system should be the non-mass-weighted centroid of the ring atoms, rather than the center-of-mass, and
3. we are only interested in the principal moment of inertia, which coincides with the principal symmetry axis for symmetric molecules.

Therefore, we may simply diagonalize the non-mass-weighted moment of inertia tensor $\tilde{\underline{I}}$, constructed within the non-mass-weighted coordinate frame defined by coordinates $\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}$ and whose origin is placed at the ring centroid according to the eigenequation

$$\tilde{\underline{I}}|\tilde{i}_n\rangle = \tilde{I}_n|\tilde{i}_n\rangle, \quad (5)$$

at which point our NICS(± 1) probes may be placed 1 Å in either direction along the principal moment of inertia in this reference frame, $|\tilde{i}_a\rangle$, as visualized in Fig. S-2.b for species **8cTL**. For the convenience of the reader and as a service to the community, we have provided a script capable of automating this process written in the highly readable Python programming language. See <https://github.com/Parish-Lab/Bergman-Variations-578> for instructions to download, install, and use this script.

III. Supplementary Results & Discussion

- A. Cyclization of the Penta-1,4-diyne Anion
- B. Absolute & Relative Electronic Energies & Enthalpies for All Cyclizations
- C. Nucleus-Independent Chemical Shift Data
- D. Qualitative Energetic Profiling of Cyclization Processes via Linear Transits
- E. Methodological Comparison: REKS vs. EOM-SF-CCSD

References

¹To conceptualize this, imagine standing on the top of a hill and trying to roll a ball down to a friend standing in a depression near the bottom. If you were to drop the ball off the opposite side of the hill to where your friend is standing, the ball is not likely to reach them successfully! So too with geometry optimizations: by starting with a guess structure very different from the optimal one, the optimization procedure will likely either be extremely difficult or entirely unsuccessful.