

MULTIREFERENCE BRILLOUIN–WIGNER COUPLED CLUSTER SINGLES AND DOUBLES (MRBWCCSD) AND MULTIREFERENCE DOUBLES CONFIGURATION INTERACTION (MRD-CI) CALCULATIONS FOR THE BERGMAN CYCLIZATION REACTION

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Received July 15, 2003

Accepted October 30, 2003

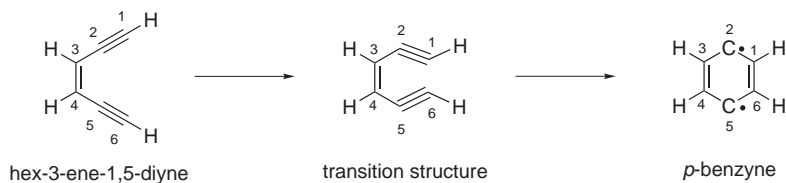
Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday.

We used the Bergman cyclization reaction of hex-3-ene-1,5-diyne to 1,4-didehydrobenzene (*p*-benzyne) as a benchmark system to assess the accuracy of recently developed multi-reference Brillouin–Wigner coupled cluster singles and doubles method (MRBWCCSD) in comparison with the multi-reference doubles configuration interaction (MRD-CI) calculations using the same geometry and basis set. Activation and reaction enthalpies were calculated. We found good agreement between experiment and theory at the MRCI+Q/CCSD(T) level of theory, provided a sufficiently large polarized basis set is used (cc-pVTZ). The MRBWCCSD theory gives results of a somewhat lower accuracy, presumably because of the absence of T_3 clusters in the cluster expansion.

Keywords: Bergman reaction; Ene-dienes; Multi-reference coupled clusters; Multi-reference configuration interaction; *p*-Benzyne; *Ab initio* calculations.

The formation of the 1,4-didehydrobenzene from the hex-3-ene-1,5-diyne (Bergman reaction^{1–3}, cf. Scheme 1 and Fig. 1) has been extensively studied in the last decade, and it has become a useful synthetic reaction^{4–7}. The cyclization reaction yields a diradical structure, which has been demonstrated to be a potent antitumor agent⁸ because of its interaction with DNA strands. 1,4-Didehydrobenzene abstracts hydrogen from a saccharide phosphate backbone to form benzene, which denatures the DNA and ultimately causes cell death.

The enediyne-like structure can be attached to biomolecular templates containing various substituents with different properties. The attachments are responsible for the distribution of the drug inside the organism and/or the initiation of the reaction. In the complex molecule the enediyne-like structure is often strained, which results in a lowering of the reaction energy and energy barrier. The Bergman reaction can therefore be induced both photochemically and thermally^{9,10}, or by changes in the cellular environment, such as pH.



SCHEME 1

Various natural products have been tested successfully, and Nicolaou and co-workers¹¹ have reported the first total synthesis of calicheamicin γ (ref.¹) containing a hex-3-ene-1,5-diyne structure. In these studies structures with different separations of the terminal carbon atoms were used: three bonds for neocarzinostatin¹², four bonds for kedarcidin¹³ or five bonds over the template structure for calicheamicin γ (ref.¹⁴) and esperamicin¹⁵.

To the degree in which thermodynamics and protonation control the reaction, a detailed understanding of its energetics is helpful for the discovery and design of new drugs containing this enediyne structure. However, it is not easy to study this reaction experimentally because of the reactivity of the biradical structure; this is why few data have been reported. Roth and co-workers¹⁶ have characterized the Bergman reaction and its barrier enthalpies by *p*-benzyne trapping rates. They found a reaction enthalpy of

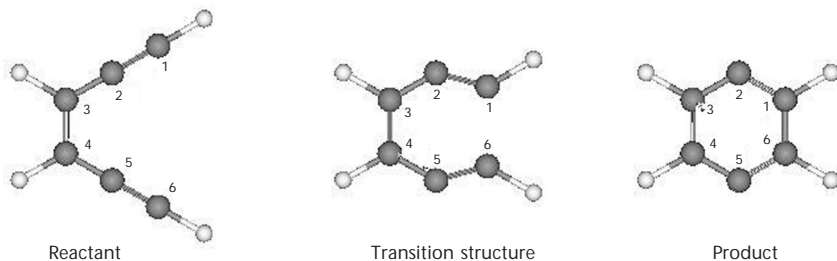


FIG. 1

3D model of the reactant, transition structure and product of the Bergman reaction

8.5 ± 1 kcal/mol at 298 K and the activation enthalpy of 28.2 ± 0.5 at 470 K. Wenthold and Squires¹⁷ have studied the reaction by collision-induced dissociation, and they have found a reaction enthalpy of 13 ± 3 kcal/mol at 298 K. The former value is favored in the literature and we will therefore adopt it as well.

Theoretical studies of the Bergman reaction may be helpful to close this gap. Several papers have been published in the last decade obtaining different results depending on the methodology they use^{18–35}. The diradical structure has also been studied in the context of other templates^{34,36,37}. It has been observed that the multireference character of the diradical structure is caused by a low-lying virtual orbital, which complicates an accurate computational treatment. Standard single-reference methods fail when trying to describe the diradical structure, and only highly sophisticated (and demanding) theoretical methods are expected to solve this problem. As stated by Cramer *et al.*²⁴ enthalpy change for the Bergman reaction cannot be predicted reliably from the difference in absolute enthalpies computed by CASSCF and CASPT2 because of a unbalanced treatment of electron correlation in largely different electronic systems of hex-3-ene-1,5-diyne and *p*-benzyne. We found a similar problem with the multireference configuration interaction (MRCI) calculations³⁵: on extending the basis set from cc-pVDZ to cc-pVTZ, the multireference Davidson correction changed from -1.9 to -0.5 kcal/mol for the energy of activation and from -0.9 to 1.4 kcal/mol for the reaction energy. From the overall experience accumulated in the cited papers, it can be concluded that only CCSD(T) shows a good performance. From this perspective, the multireference Brillouin–Wigner coupled cluster singles doubles (MRBWCCSD) theory^{38–40} seemed to be the method of choice and we considered expedient to apply it to the problem of Bergman cyclization.

COMPUTATIONAL METHODS

The computational methods used have been described already previously and only a brief description is given here. For details on MRBWCCSD, see refs^{38–43} and for MRD-CI refs^{35,44}.

Multireference Brillouin–Wigner Coupled Cluster Singles and Doubles Theory

The correlated ground state wave function is constructed as

$$\Psi_0 = \Omega_0 \Psi_0^P, \quad (1)$$

where Ω_0 is a state-specific wave operator and

$$\Psi_0^P = c_0\Phi_0 + c_1\Phi_1 \quad (2)$$

is the projection of Ψ_0 to the model space.

The set of one-determinantal reference wave functions Φ_j , from which Ψ^P is constructed, has to describe the static correlation in the molecule.

The projected wave function obeys the Schrödinger equation in the model space

$$H^{\text{eff}}\Psi_0^P = \varepsilon_0\Psi_0^P, \quad (3)$$

where H^{eff} is the effective Hamiltonian and subscript 0 denotes the ground state. Eigenvalue ε_0 gives the exact ground state energy. Its computation requires to evaluate H^{eff} matrix elements in the basis of Φ_0 and Φ_1 ,

$$\begin{aligned} H_{00}^{\text{eff}} &= \langle \Phi_0 | H^{\text{eff}} | \Phi_0 \rangle = \langle \Phi_0 | H | \Phi_0 \rangle + \langle \Phi_0 | H_N(0) e^{T(0)} | \Phi_0 \rangle \\ H_{11}^{\text{eff}} &= \langle \Phi_1 | H^{\text{eff}} | \Phi_1 \rangle = \langle \Phi_1 | H | \Phi_1 \rangle + \langle \Phi_1 | H_N(1) e^{T(1)} | \Phi_1 \rangle \\ H_{01}^{\text{eff}} &= \langle \Phi_0 | H_N(1) e^{T(1)} | \Phi_1 \rangle \\ H_{10}^{\text{eff}} &= \langle \Phi_1 | H_N(0) e^{T(0)} | \Phi_0 \rangle, \end{aligned} \quad (4)$$

where $H_N(i)$ is the normally ordered Hamiltonian with respect to the Fermi vacuum Φ_j . The wave operator Ω_0 is assumed in the Jeziorski-Monkhorst form⁴⁵

$$\Omega_0 = e^{T(0)} |\Phi_0\rangle\langle\Phi_0| + e^{T(1)} |\Phi_1\rangle\langle\Phi_1|, \quad (5)$$

where the cluster operators $T(0)$ and $T(1)$ are truncated to singles and doubles.

In the BWCC method, the wave operator Ω_0 is subject to the state-specific analogue of the Bloch equation

$$\Omega_0 = 1 + B_0 V \Omega_0. \quad (6)$$

This is the main difference between the BWCC theory and the usual Hilbert-space MR CCSD theory. In Eq. (6), V is the perturbation as it is defined in the Møller-Plesset partitioning of the Hamiltonian for the single-reference case, and B_0 is the Brillouin-Wigner resolvent

$$B_0 = \sum_{q>1} \frac{|\Phi_q\rangle\langle\Phi_q|}{\varepsilon_0 - E_q}. \quad (7)$$

Substituting Eq. (5) into Eq. (6) yields the equations for the CC amplitudes.

To obtain the ground state energy, one has to solve these equations by an iterative procedure. First, initial guess of the amplitudes is obtained analogous to single reference CCSD. Then the H^{eff} matrix is calculated and diagonalized, which gives ε_0 . Subsequently, ε_0 is used in equations for CC amplitudes, where it enters through the resolvent (7). H^{eff} matrix is constructed from the new amplitudes, and the procedure is repeated until convergence is achieved with the aid of the convergence acceleration (DIIS) procedure. Finally, an additional modified iteration is performed to get approximate size-extensivity correction⁴³.

Multireference Configuration Interaction Theory

For many years the MRCI method has been one of the benchmark tools for accurate calculations of the electronic structure of atoms and molecules. Ever since the development of the direct CI algorithm⁴⁶, which obviates the explicit storage of the CI matrix, highly efficient implementations⁴⁷ have been used for a wide variety of molecules. The generic lack of extensivity of the MRCI method has been at least partially addressed with a number of *a posteriori* corrections^{48,49} and through direct modification of the CI energy-functional⁵⁰⁻⁵⁴. Due to its high computational cost, however, applications of the MRCI method remain limited to relatively small systems. For this reason the configuration-selective version of the MRCI method (MRD-CI), introduced by Buenker and Peyerimhoff⁵³⁻⁵⁵, has arguably become one of its most widely used versions. In this variant only the most important configurations of the interacting space of a given set of primary configurations are chosen for the variational wave function, while the energy contributions of the remaining configurations are estimated on the basis of the second-order Rayleigh-Schrödinger perturbation theory. A configuration is selected for the variational wave function if its perturbative energy contribution or coefficient is above a given threshold λ and the total energy (the sum of the variational and the perturbative contributions) is extrapolated to the limit $\lambda \rightarrow 0$. While this extrapolation is known to fail in isolated instances, it gives a remarkably good resolution of relative energies across the potential energy surface (PES) in the overwhelming majority of applications. Since

the variationally treated subspace of the problem consists of only a fraction of the overall Hilbert space, the determination of eigenstates in the truncated space requires far less computational effort. Indeed, for typical applications the overwhelming majority of the computational effort is concentrated in the expansion loop, where the energy contribution of candidate configurations is computed. Even within this approximation, the cost of MRCI calculations remains rather high. The development of efficient configuration-selecting CI codes is inherently complicated by the sparseness and lack of structure of the selected state vector. In order to further extend the applicability of the method, it is thus desirable to employ the most powerful computational architectures available for such calculations. Our code represents a massively parallel, residue-driven implementation of the MRD-CI method for distributed memory architectures. While efforts to parallelize standard MRSDCI (all single and double excitations) on distributed memory architectures, face significant difficulties rooted in the need to distribute the CI vectors over many nodes⁵⁶⁻⁵⁸, a parallel implementation of MRD-CI can capitalize on the compactness of its state representation. In our implementation the difficulty of the construction of the subset of non-zero matrix elements is overcome by the use of a residue-based representation of the matrix elements, which was originally developed for the distributed memory implementation of MRSDCI^{44,58}. This approach allows to efficiently evaluate the matrix elements both in the expansion loop as well as during the variational improvement of the coefficients of the selected vectors.

CALCULATIONS

MRBWCCSD calculations have been performed with a version of ACES II program⁵⁹ extended for the state-specific MRBWCCSD theory, except vibration frequency jobs, which have been performed using Gaussian 98, Revision A.6 program⁶⁰.

Geometry optimizations have been performed according to the multi-reference character of each system. Since the reactant (hex-3-ene-1,5-diyne) is expected to be a single-reference species we have optimized its geometry at CCSD/cc-pVDZ level of theory. The transition structure (TS) and mainly the product (*p*-benzyne) are expected to have multireference character, thus it would be desirable to optimize their geometries at a multireference level of theory. Unfortunately, analytical gradient geometry optimization at multireference level has not been implemented in the ACES II program version yet, and we have decided to perform this calculation at the single-

reference level. For the transition structure, CCSD/cc-pVDZ calculation did not converge, so we finally obtained it at the CCD/cc-pVDZ level of theory. The product geometry has been optimized at the MRBWCCSD/cc-pVDZ level of theory by a method which does not need gradients. Results are shown in Table I.

The reference space contained two configurations, the Hartree-Fock ground state configuration and the doubly excited one $(\text{HOMO})^2 \rightarrow (\text{LUMO})^2$. We have performed single- and multireference calculations for each structure, with the aim to compare both results and check the effect of the multireference treatment. We have used six basis sets which are summarized in Table II, ranging from 6-31G up to cc-pVTZ.

We have also performed CCSD(T) calculations with the aim to compare these results with MRBWCCSD ones. For this purpose, we have optimized the geometry of both reactant and product at CCSD(T)/cc-pVDZ level of theory. We did not attempt to optimize transition structure geometry using this method because of the problems with CCSD/cc-pVDZ. Subsequently, we have performed single-point calculations of all three species at CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ levels of theory. We have further performed single-point configuration selecting MRD-CI calculations using a recently developed massively parallel implementation of this method^{35,44}.

Finally, in order to obtain the reaction and activation enthalpies, we have performed UCCSD(T)/cc-pVDZ frequency calculations for both reactant and product. Geometry optimizations at this level have been carried out first. From these results we have obtained enthalpy corrections to the previously calculated energy. Enthalpy correction for the transition structure has been calculated at the CCD/cc-pVDZ level of theory. This minor inconsistency was dictated by technical difficulties, but we believe that it has only a very small effect on the calculated enthalpy corrections.

TABLE I
Optimized MRBWCCSD molecular geometries (bond lengths in Å, bond angles in °). For numbering of the carbon atoms *cf.* Scheme 1

System	R_{H1}	R_{12}	R_{23}	R_{34}	$R_{3\text{H}}$	α_{H12}	α_{123}	α_{234}	$\alpha_{23\text{H}}$
Reactant	1.077	1.224	1.442	1.358	1.095	178.8	178.0	124.3	116.9
TS	1.086	1.282	1.413	1.404	1.094	144.4	132.1	118.5	123.2
Product	1.094	1.381	1.381	1.436	1.094	123.5	124.3	117.8	123.5

The single-point MRD-CI calculations on the reactant, transition structure and product were performed in optimized geometries using cc-pVDZ and cc-pVTZ basis sets. The calculations were performed in approximate natural orbitals computed in the Brillouin–Wigner multireference perturbation theory⁶¹. For the calculations we used a unique set of 47 references which lead to Hilbert spaces of up to 24 million configurations for the cc-pVDZ basis set and 160 million configurations for the cc-pVTZ basis set, respectively. Up to 10 million configurations were treated in the variational subspace. The final results were extrapolated to the limit of zero perturbative energy which corresponds to an unselected MRCI(SD) calculation.

RESULTS AND DISCUSSION

Because of the multireference character of the Bergman reaction systems, our first goal was to compute the difference between single- and multi-reference energies for the reactant, transition structure and product. Results in six different basis sets are shown in Table II.

Hex-3-ene-1,5-diyne is believed to be essentially a single-reference system, which explains that inclusion of multireference effects has only a modest (about 2.5 kcal/mol) influence. The product, on the other hand, has a strong multireference character; this system cannot be described at the CCSD level of theory. Energy differences between both treatments are about 20 kcal/mol. Finally, multireference character of the transition structure is halfway between the reactant and product. Multireference calculations lower its energy approximately by 8 kcal/mol, so it should be treated at this level of theory as well. The basis set effect on these energy differences is modest, with the exception of the 6-31G due to the lack of polarization functions.

The results for reaction enthalpy and activation enthalpy are summarized in Table III. Selected most accurate data taken from the literature are also included in Table III for comparison.

First we note that chemical accuracy is achieved at the level of the MRCI+Q/CCSD(T) and CCSD(T) theory using the cc-pVTZ basis set. While the activation energy is already predicted correctly with a smaller cc-pVDZ basis set, the reaction enthalpy is still significantly underestimated in this basis. This points to a lack of differential correlation effects between reactant/transition state and product. This is most likely not a result of omission of nondynamic correlation effects in the latter. Compared with CCSD, MRBWCSD theory lowers the reaction enthalpy approximately by 17.5 kcal/mol and activation enthalpy by 5.25 kcal/mol for all polarized basis sets.

It is clear that the Bergman reaction cannot be explained by CCSD results, which deviate significantly from the experimental values. The MRBWCCSD gives substantially more reliable results. Nevertheless, it still seems to slightly overestimate both enthalpies (mainly TZ results). Since CCSD(T) gives a quantitatively correct agreement with the experimental data, future inclusion of triples in the MRBWCC theory seems to be necessary in order to improve its results. It is well known that a balanced treatment of both dynamic and non-dynamic correlation effects is necessary to quantitatively account for the reaction energetics of the enediynes. Previous calculations^{8,20,22,34,35} have shown that only the CCSD(T) calculations that partially account for triple

TABLE II
Comparison of single-point energies at CCSD and MRBWCCSD levels of theory using different basis sets

System	Basis set ^a	CCSD ^b	MRBWCCSD ^b	ΔE^c
Reactant	6-31G	-229.872744	-229.876808	-2.5
	6-31G**	-230.182209	-230.186620	-2.8
	cc-pVDZ	-230.202387	-230.206568	-2.6
	6-311G**	-230.263146	-230.267289	-2.6
	cc-pVTZ'	-230.316668	-230.320757	-2.6
	cc-pVTZ	-230.395141	-230.399247	-2.6
Transition structure	6-31G	-229.806241	-229.817104	-6.8
	6-31G**	-230.121577	-230.134480	-8.1
	cc-pVDZ	-230.144512	-230.156935	-7.8
	6-311G**	-230.200289	-230.21293	-7.9
	cc-pVTZ'	-230.255565	-230.268102	-7.9
	cc-pVTZ	-230.332692	-230.345533	-8.0
Product	6-31G	-229.824283	-229.847953	-14.8
	6-31G**	-230.140579	-230.172826	-20.2
	cc-pVDZ	-230.161641	-230.193829	-20.2
	6-311G**	-230.215830	-230.247993	-20.2
	cc-pVTZ'	-230.267934	-230.300715	-20.6
	cc-pVTZ	-230.347032	-230.378778	-19.9

^a cc-pVTZ' is a basis set obtained from cc-pVTZ by dropping the highest angular momentum functions (*f*-functions on carbon and *d*-functions on hydrogen). ^b Energies in hartrees. ^c MRBWCCSD - CCSD energy differences in kcal/mol.

excitations and thus non-dynamic correlation effects yield quantitative agreement between theory and experiment. In contrast, pure CCSD calculations fail to quantitatively account for the ring-closure energy of the enediynes.

CONCLUSIONS

We have examined the multireference nature of the Bergman cyclization reaction and found encouraging agreement between MRCI and CCSD(T) calculations. The importance of multireference effects was substantiated by comparison with the recently developed MRBWCCSD method, but triples

TABLE III
Activation and reaction enthalpy of the Bergman reaction at single- and multireference levels of theory^a

Basis set	Method	ΔH_{298}^\ddagger , kcal/mol	ΔH_{298}^0 , kcal/mol
6-31G**	CCSD	37.1	26.2
	MRBWCCSD	31.8	8.7
	MRCI ^b	28.4	3.7
	CCSD(T)	27.0	5.1
cc-pVDZ	CCSD	35.4	25.7
	MRBWCCSD	30.2	8.1
	MRCI ^b	30.1	6.3
	CCSD(T)	26.4	4.4
	BDCC(T) ^c	25.6	7.0
cc-pVTZ	CCSD	38.2	27.5
	MRBWCCSD	32.7	12.9
	MRCI ^b	29.4	10.3
	CCSD(T)	27.6	10.1
6-311+G(3df,3pd)	RB3LYP ^d	29.9	8.5
Experiment ¹⁶		28.7 ± 0.5^e	8.5 ± 1

^a Enthalpy correction at UCCSD(T)/cc-pVDZ level of theory for reactant and product and CCD/cc-pVDZ for the transition structure. ^b Including Davidson correction. ^c This value contains an offset of 0.5 kcal/mol representing a temperature correction²⁸ from 470 to 298 K. ^d Brueckner doubles CC(T) taken from refs^{27,34}. ^e Taken from ref.²⁸; the activation enthalpy was calculated for 470 K and it should be compared with the experimental ΔH^\ddagger of 28.2 kcal/mol.

corrections will have to be incorporated in this method to reach chemical accuracy. With our choice of the reference space, we were able to achieve quantitative agreement between theory and experiment. However, the smaller reference spaces of the MRBWCCSD calculations yielded larger deviations from the experimental results. This indicates that important single excitations are missing in the reference space. The objective of the paper was to provide reliable data on the heat of reaction and enthalpy of activation for the Bergman reaction, which could be used as standards for less sophisticated (and less demanding) calculations, and to show the accuracy attainable by the present state-of-the-art techniques in designing new anti-tumor agents with an enediyne-like structure.

This work was supported by the European Community by a Marie Curie Fellowship IHP under contract No. HPMT-CT-2000-00022. We also acknowledge the support by the COST D23 action (P. Čársky and J. Pittner grant OC D23.001 of the Ministry of Education, Youth and Sports of the Czech Republic) and by the Grant Agency of the Academy of Sciences of the Czech Republic (P. Čársky and J. Pittner grant No. A4040108). W. Wenzel acknowledges the use of the computational resources at the von-Neumann Institute for Computing and the HLRZ Karlsruhe. We wish to thank Prof. D. Cremer for drawing our attention to the problem of Bergman reaction.

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