Extended ab Initio and Theoretical Thermodynamics Studies of the Bergman Reaction and the Energy Splitting of the Singlet *o*-, *m*-, and *p*-Benzynes

Roland Lindh,*,† Timothy J. Lee,‡ Anders Bernhardsson,† B. Joakim Persson,† and Gunnar Karlström†

Contribution from the Department of Theoretical Chemistry, Chemical Centre, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden, and NASA Ames Research Center, Moffett Field, California 94035

Received February 13, 1995®

Abstract: The autoaromatization of (*Z*)-hex-3-ene-1,5-diyne to the singlet biradical *p*-benzyne has been reinvestigated by state of the art *ab initio* methods. Previous CCSD(T)/6-31G(d,p) and CASPT2[0]/ANO[C(5s4p2d1f)/H(3s2p)] calculations estimated the reaction heat at 298 K to be 8–10 and 4.9 ± 3.2 kcal/mol, respectively. Recent NO- and oxygen-dependent trapping experiments and collision-induced dissociation threshold energy experiments estimate the heat of reaction to be 8.5 ± 1.0 kcal/mol at 470 K (corrected to 9.5 ± 1.0 kcal/mol at 298 K) and 8.4 ± 3.0 kcal/mol at 298 K, respectively. New theoretical estimates at 298 K predict the values at the basis set limit for the CCSD(T) and CASPT2[g1] methods to be 12.7 ± 2.0 and 5.4 ± 2.0 kcal/mol, respectively. The experimentally predicted electronic contribution to the heat of activation is 28.6 kcal/mol. This can be compared with 25.5 and 29.8 kcal/mol from the CASPT2[g1] and the CCSD(T) methods, respectively. The new study has a much larger one-particle basis set for the CCSD(T) method as compared to earlier studies. For the CASPT2 investigation the better suited CASPT2[g1] approximation is utilized. The original CASPT2 method, CASPT2[0], systematically favors open-shell systems relative to closed-shell systems. This was previously corrected empirically. The current study shows that the energy difference between CCSD(T) and CASPT2[g1] at the basis set limit is estimated to be 7 ± 2 kcal/mol. The study also demonstrates that the estimated heat of reaction is very sensitive to the quality of the basis set. In particular CCSD(T)/6-31G(d,p) approach underestimates the basis set limit of the enthalpy by approximately 5 kcal/mol. Furthermore, the relative energies of the *p*-, *m*-, and *o*-benzynes are computed at the CASPT2[g1] and CCSD(T) levels of theory. These results help to explain the discrepancy between the two methods in the case of the Bergman reaction. The deficiency of the CASPT2 method is mainly attributed to the approximate way in which the dynamic correlation is included by perturbation theory. A similar sized error is attributed to the CCSD(T) method due to the approximate way in which near degeneracy effects are included. This combined CCSD(T) and CASPT2[g1] study indicates that the most recent experimental value of the *p*-benzyne–*o*-benzyne energy splitting is overestimated.

Introduction

The renewed interest in the Bergman reaction[1] (see Figure 1), in which (*Z*)-hex-3-ene-1,5-diyne (enediyne) is transformed into the singlet coupled biradical *p*-benzyne, was triggered by the discovery in 1987 of the calicheamicin molecule in bacteria living in chalky rocks.[2] The newly discovered molecule demonstrated extremely high potency against cancer cells and became the first naturally abundant substance in a growing new class of anticancer agents.

For this new class of drugs, which will attack and damage the DNA molecule, the principle of the formation of a biradical structure, as in the Bergman reaction, is one of the key steps in their cytotoxic action. The actual full mechanism of the drug action has to a large degree been investigated by Nicolaou *et al.* in an elegant NMR study of the interaction of calicheamicin with duplex DNA.[3] The major step toward the DNA cleavage is a triggering reaction which perturbs the molecular template to which the active part of the drug, the enediyne moiety, is attached. The structural change lowers the heat of activation of the biradical formation. The enediyne moiety being positioned by the complexation of the drug with DNA in the minor grove will now abstract one hydrogen atom (proton and electron) at a time from the opposite phosphodiester strands of the DNA. This will ultimately result in the cleavage of DNA and the subsequent death of the host cell.

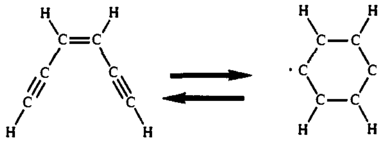

Figure 1. The Bergman reaction in which the (*Z*)-hex-3-ene-1,5-diyne undergoes autoaromatization and forms the singlet *p*-benzyne biradical.

To further improve the understanding of the drug action more precise knowledge of the biradical formation is valuable. The thermodynamics of the Bergman reaction have recently been

---

[†] University of Lund.

[‡] NASA Ames Research Center.

[®] Abstract published in *Advance ACS Abstracts*, May 15, 1995.

(1) (a) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660. (b) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25. (c) Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082. (d) Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4090.

(2) (a) Lee, M. D.; Dunne, T. S.; Siegel, M. M.; Chang, C. C.; Morton, G. O.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3464. (b) Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3466. (c) Lee, M. D.; Dunne, T. S.; Chang, C. C.; Siegel, M. M.; Morton, G. O.; Ellestad, G. A.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 985.

(3) Paloma, L. G.; Smith, J. A.; Chazin, W. J.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1994**, *116*, 3697.

investigated experimentally by Wenthold and Squires[4] in a collision-induced dissociation threshold energy experiment and by Roth and co-workers in a measurement of the NO- and oxygen-dependence of the trapping rate of the *p*-benzyne biradical.[5] They predicted the heat of reaction for the Bergman reaction to be 8.4 ± 3.0 and 8.48 ± 1.0 kcal/mol at 298 and 470 K, respectively. The experiment by Roth and co-workers, in addition to the heat of reaction at 470 K, provides us also with measurements of the heat of activation, 28.23 ± 0.5 kcal/mol, and the relative entropy for the transition state, -10.22 ± 1.0 eu/mol (1 eu mol^{-1} = 1 cal mol^{-1} K^{-1}).

The Bergman reaction has also attracted attention from the theoretical viewpoint. The reaction, which involves the formation of a bond and a biradical wave function as two single, one double, and two triple bonds restructure into an aromatic ring system, includes drastic changes which are difficult to treat in a balanced way by approximate quantum chemical methods. Two methods which possibly could handle this situation in conjunction with a large one-particle basis would be the CCSD(T) method, which for a large number of applications has shown its reliability, and the CASPT2 method. The MRCI approach does not seem practical since a balanced treatment would require a prohibitively large set of configurations in the reference function. The CCSD(T) approach has demonstrated its efficiency in an accurate prediction of difficult problems as in the vibrational spectrum of ozone.[6] In a recent CCSD(T)/6-31G(d,p) study by Kraka and Cremer[7] the heat of reaction at 298 K was computed to 8−10 kcal/mol, the heat of activation at 298 K to be 28.5 kcal/mol, and the entropy change over the reaction at 298 K to be −10.2 eu/mol. The vibrational and temperature corrections in this study were based on MBPT-(2)/6-31G(d,p) harmonic frequencies. At the same time Lindh and Persson[8] published CASPT2[0]/ANO results. In their examination of the Bergman reaction at 298 K, the heat of reaction, heat of activation, and entropy change over the reaction all at 298 K were computed to be 4.9 ± 3.2 kcal/mol, 25.0 ± 3.1 kcal/mol, and −9.64 eu/mol, respectively. In this study the harmonic frequencies were based on CASSCF(12,12)/DZP calculations (12 active electrons in 12 orbitals). Although the theoretical results are consistent with the recent experimental findings, criticism of the two investigations can be put forward. For the CCSD(T) study serious questions arise regarding the stability of the results with respect to improvement of the one-particle space beyond the 6-31G(d,p) basis set. In addition, the *p*-benzyne harmonic frequencies must be evaluated with care. Frequency calculations on the related benzene molecule indicate that treatment beyond the MP2 level of theory is a requirement in order to obtain quantitative agreement with experiment.[9] The CASPT2[0] study, on the order hand, lacks precision due to the empirical correction of the CASPT2[0] energies due to the systematic error which overestimates the electron correlation of unpaired electrons relative to paired electrons. In the study by Lindh and Persson, although a much larger one-particle basis was used as compared to the CCSD(T) study, there are no data presented which will give reliable indications regarding the results at the basis set limit. Hence, to accommodate these weaker points of the earlier studies we have in a combined CCSD(T) and CASPT2 investigation of the energetics of the Bergman reaction utilized a large set of various extended basis sets. Additional points along the reaction path have been included to estimate better the activation energy at the CASPT2 level of theory. The newly developed CASPT2[g1] method[10] rather than the CASPT2[0] method has been employed in order to remove the empirical corrections. This method has recently been able to describe accurately the potential energy surface of Cr_2, *i.e.* predict correct values for bond distance, dissociation energy, and harmonic frequency.[11] Given the great difficulty of this task, no other method can at present accurately solve this problem, this success indicates a great versatility of the CASPT2[g1] method. The thermodynamics for the reactant, the transition state, and the product have been investigated at the CASSCF(12,12)/DZP level of theory.

The collision-induced dissociation experiment by Wenthold and Squires does in addition to the energetics of the Bergman reaction provide us with experimental estimates of the relative energies of the *p*-, *m*-, and *o*-benzyne molecules. This information is critical in making a careful comparison of the CCSD(T) and the CASPT2[g1] methods. These three molecules are very similar apart from the degree of biradical character. In particular we note that *o*- and *m*-benzyne have a smaller biradical contribution to the wave function as compared to *p*-benzyne. Furthermore, *m*- and *p*-benzyne will have quite similar geometrical structures. These conditions offer interesting opportunities in assessing the two methods. Hence, to support the new study with additional valuable information we will perform geometry optimizations of the benzynes at the CASSCF level of theory. Dynamical electron correlation will subsequently be included by the CASPT2[g1] and the CCSD(T) methods.

The rest of the paper will be divided as follows. First, a section on the computational details of the calculations performed in this study is presented. Second, a discussion on the electronic structure of the (*Z*)-hex-3-ene-1,5-diyne and the *p*-benzyne is followed by an analysis of the aspects of the ability of the CCSD(T) and CASPT2 methods to describe these molecules. Here we will also give some brief conclusions regarding errors due to BSSE. Thereafter, an analysis of the results discussed both in the light of the conclusions in the previous subsection and in comparison with the presenlty available experimental findings ends this article.

Computational Details

Geometries were optimized at the complete active space SCF (CASSCF) level of theory[12] (refer to Figure 2 for definitions of the structural parameters). The reaction path was established by complete optimization of the structural parameters for the reactant, transition state, and products. The additional structures were optimized by constraining the distance between the terminal carbons. The active orbital space of the CASSCF calculations for the study of the Bergman reaction included the π orbitals, the orbital pair which will form the radical orbitals, the orbitals which represent the bond formation, and for reasons of a balanced treatment the symmetry partner of the latter. This totals up to twelve electrons in twelve orbitals; the CASSCF calculation used for the Bergman reaction will be denoted CASSCF(12,12) when

---

[4] (a) Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 7414. (b) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401. (c) Squires, R. R. Private communications, using a better estimate of the heat of formation of (*Z*)-hex-3-ene-1,5-diyne and a new reference value for the gas-phase acidity of benzene.

[5] (a) Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1765. (b) Roth, W. R. private communication; the entropy of reaction is mistakenly computed to −7.17 ± 1.84 eu/mol, the correct value should be −13.27 ± 1.84 eu/mol.

[6] Lee, T. J.; Scuseria, G. R. *J. Chem. Phys.* **1990**, *93*, 489.

[7] (a) Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1993**, *216*, 333. (b) Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1994**, *116*, 4936.

[8] Lindh, R.; Persson, B. J. *J. Am. Chem. Soc.* **1994**, *116*, 4963.

[9] Handy, N. C.; Murray, C. W.; Amos, R. D. *J. Phys. Chem.* **1992**, *97*, 4392.

[10] Andersson, K. *Theor. Chim. Acta* **1995**, *91*, 31.

[11] Andersson, K.; Roos, B. O.; Malmqvist, P.-Å.; Widmark, P.-O. *Chem. Phys. Lett.* **1994**, *230*, 391.

[12] (a) Malmqvist, P.-Å.; Rendell, A.; Roos, B. O. *J. Phys. Chem.* **1990**, *94*, 5477. (b) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157. (c) Siegbahn, P. E. M.; Almlöf, J.; Heiberg, J.; Roos, B. O. *J. Chem. Phys.* **1981**, *74*, 2384. (d) Roos, B. O. *Int. J. Quantum Chem. Symp.* **1980**, *14*, 175.

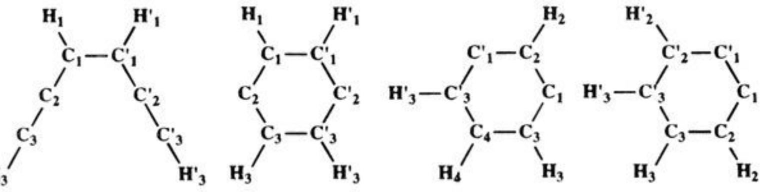

Figure 2. Structural labeling of (*Z*)-hex-3-ene-1,5-diyne and *p*-, *m*-, and *o*-benzyne.

necessary. The reaction path was investigated with the double-ζ plus polarization (DZP),[13] the triple-ζ plus double polarization (TZ2P),[14] and the *averaged* atomic natural orbital (aANO) C[14s9p4d]/(5s4p2d), H[8s4p]/(3s2p) basis sets.[15] The energetics along the reaction path were established by the CASSCF, the original second-order multiconfigurational perturbation theory based on a CASSCF reference function (CASPT2{0}),[16] the newly proposed modified CASPT2{g1},[10] and the singles and doubles coupled-cluster plus a perturbational estimate of the effects of connected triple excitation (CCSD(T))[17] methods. The heat of reaction has for the same methods been computed with the cc-pVDZ,[18] DZP, 6-31G(d,p),[19] TZ2P, aANO C(5s4p2d)/H(3s2p), aANO C(5s4p3d)/H(3s2p), cc-pVTZ,[18] aANO C(5s4p2d1f)/H(3s2p), aANO C(5s4p2d1f)/H(3s2p1d), and aANO C(5s4p3d1f)/H(3s2p) basis sets at the CASSCF/aANO(C(5s4p2d)/H(3s2p)) optimized structures (with the exception of the 6-31G(d,p) basis set where we report the values given by Kraka and Cremer). The thermodynamics for the Bergman reaction were computed by means of statistical mechanics based on a harmonic oscillator model which in turn was based on force constants established at the CASSCF/DZP level of theory. For the study of the energy splitting of the singlet benzynes, the active orbitals in the CASSCF included the π orbitals and the two radical orbitals, in all eight electrons in eight orbitals (CASSCF(8.8)). Here we used only the aANO C(5s4p2d)/H(3s2p) basis set. The energy splitting of the benzynes was subsequently established by CCSD(T) and CASPT2[g1] calculations. In conjunction with these calculations on the benzynes we used a benzene sized basis set for a series of CASPT2[g1] calculations, *i.e.* ghost orbitals on the positions of the missing hydrogens. Additionally, to understand the energetics in the benzene splittings we performed CASSCF(2,2) calculations in which only the two radical orbitals were included in the active orbital space. For these calculations we used the CASSCF(8,8) optimized structures. The core 1s carbon orbitals were frozen in all calculations including dynamic correlation. The one-particle basis was used in the real spherical harmonics representation except for the calculations on the harmonic frequencies.

The calculations were performed with the MOLCAS-2,[20] the MOLCAS-3,[21] and the SIRIUS-ABACUS package[22] using IBM RS6000 and Silicon Graphics Indigo² computers at the University of Lund, and with the SEWARD integral program[23] interfaced to the SWEDEN[24] program suite and the TITAN[25] coupled-cluster programs using the ACSF CRAY C90 at the NASA Ames Research Center.

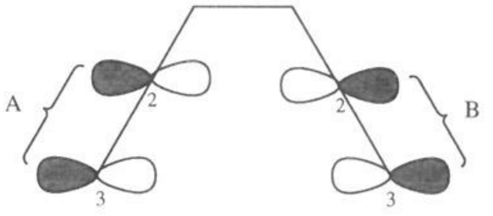

Figure 3. The in-plane p orbitals at the acetylenic terminals in (*Z*)-hex-3-ene-1,5-diyne. They are combined here to a symmetric combination of the π orbitals at terminal A and B.

Electronic Structure

This section is very technical and it is directed at the informed quantum chemist. The section deals with some of the finer details of how the *ab initio* methods we use will behave due to the character of the molecular systems investigated in this paper.

The Bergman reaction involves the transformation of the two doubly occupied in-plane π orbitals of the triple bonds in (*Z*)-hex-3-ene-1,5-diyne to one doubly occupied σ bond and two singlet coupled singly occupied orbitals in *p*-benzyne. The two latter orbitals are the origin of the biradical nature of the *p*-benzyne molecule. The in-plane π-orbitals in (*Z*)-hex-3-ene-1,5-diyne are formed from the symmetric combinations of the in-plane p-orbitals at each acetylenic terminal (here denoted A and B, see Figure 3),

$$\pi_A = (p_2^A + p_3^A)\ \pi_B = (p_2^B + p_3^B)$$

These are now combined to give a symmetric and an antisymmetric combination of the π-orbitals

$$...(\pi_A - \pi_B)^2(\pi_A + \pi_B)^2$$

Here the antisymmetric combination will have the lowest energy due to favorable overlap. The new σ bond which is formed in the *p*-benzyne molecule during the Bergman reaction will be formed from the antisymmetric combination of the terminal in-plane p-orbitals which previously were a part of the triple bonds of (*Z*)-hex-3-ene-1,5-diyne,

$$(p_3^A - p_3^B)^2$$

For the two remaining p-orbitals, p_2^A and p_2^B, we will be able to form two different doubly occupied configurations, namely

$$(p_2^A - p_2^B)^2 \quad \text{and} \quad (p_2^A + p_2^B)^2$$

For a Woodward–Hoffman allowed reaction we expect the latter to dominate due to symmetry conservation. However, in reality we will have, ignoring the other orbitals, a wave function for the *p*-benzyne molecule that can be represented as

$$\alpha(p_3^A - p_3^B)^2(p_2^A + p_2^B)^2 + \beta(p_3^A - p_3^B)^2(p_2^A - p_2^B)^2$$

The Woodward–Hoffman allowed reaction is found for $\beta = 0$ and a perfect biradical wave function is represented by $\beta = -\alpha$. In the latter case the wave function can also be written as

---

(13) Dunning, T. H.; Hay, P. J. *Modern theoretical chemistry*; Plenum: New York, 1976; Chapter 1, p 1.

(14) Exponents: Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. Coefficients: Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716; **1986**, *84*, 6266.

(15) (a) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291. (b) Widmark, P.-O.; Persson, B. J.; Roos, B. O. *Theor. Chim. Acta* **1991**, *79*, 419.

(16) (a) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483. (b) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(17) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(18) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(19) Hariharana, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(20) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. *MOLCAS Version 2 User's Guide*; Department of Theoretical Chemistry, Chemical Center, University of Lund, Lund, 1992.

(21) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. *MOLCAS Version 3 User's Guide*; Department of Theoretical Chemistry, Chemical Center, University of Lund, Lund, 1994.

(22) SIRIUS is an MCSCF program written by H. J. Jensen, H. Ågren, and J. Olsen. ABACUS is an MCSCF energy derivative program written by T. Helgaker, H. J. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor.

(23) Lindh, R.; Ryu, U.; Liu, B. *J. Chem. Phys.* **1991**, *95*, 5889.

(24) SWEDEN is an electronic structure program package written by J. Almlöf, C. W. Bauschlicher, M. R. A. Blomberg, D. P. Chong, A. Heiberg, S. R. Langhoff, P.-Å. Malmqvist, A. P. Rendell, B. O. Roos, P. E. M. Siegbahn, and P. R. Taylor.

(25) TITAN is a set of electronic structure programs written by T. J. Lee, A. P. Rendell, and J. E. Rice.

(26) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1907.

$$(p_3^A - p_3^B)^2(p_2^A \overline{p_2^B} + \overline{p_2^A} p_2^B)$$

The reference of the CCSD(T) method, the SCF wave function, will only be able to describe the Woodward−Hoffman reaction, $\beta = 0$. The second most important configuration of the *p*-benzyne will at the CCSD level of theory be included as a double excitation from the reference configuration, in both the connected and disconnected sense. In this regard, we note that single and double excitations from the second important configuration will be included only in the disconnected sense. On performing the perturbational estimate of the effects of connected triple excitations (T), we will include all of the single excitations, relative to the second configuration, in the connected sense. However, double excitations in the connected sense, relative to the second important configuration, are not directly included at the CCSD(T) level of theory. This would require the direct or perturbational inclusion of the effects of the T_4 operator. The problem of a competing second large configuration does not occur for the enediyne, and therefore CCSD(T) will neglect parts of the correlation energy for *p*-benzyne relative to (*Z*)-hex-3-ene-1,5-diyne. Hence, the CCSD(T) approach should overestimate the heat of reaction for the Bergman reaction, or in other words, it should be an upper bound.

The reference of the CASPT2[g1], the CASSCF, will be able to model wave functions for arbitrary values of α and β. The dynamical correlation energy for the CASPT2 method is included through second-order perturbation theory. Hence, due to the nature of this method all double excitations will be perturbationally included at the same level for all of the configurations included in the CI expansion of the CASSCF. We will also find some triple excitations, *e.g.* a single excitation within the CASSCF space relative to the reference configuration coupled with a double excitation from the inactive/active orbital space. We especially note for the CASPT2 method that the perturbation includes dynamical correlation with respect to all configurations in the CASSCF CI on an equal footing. Thus, the accuracy of the method relies on the premise that the energy contributions from higher orders of perturbation theory are small or cancel out. The size of the perturbation in the CASPT2 approach for a proper CASSCF active space is usually smaller than what is normally found for the MP2 method. Favorable cancellation will take place for small changes of the wave function since the relative difference of the higher order terms will go to zero as the change in the wave function goes to zero. From the analysis above no conclusion is possible regarding the over- or underestimate of the heat of reaction of the Bergman reaction by the CASPT2 method. This depends on the relative degree to which the perturbational scheme over- or underestimates the remaining dynamical electron correlation.

The discussion above also has implications for the difficulties of accurately assessing the energy splitting of the benzynes. Here we note that the *m*- and *p*-benzynes will resemble each other to a large extent. These two structures will have a biradical character with the effect most pronounced in the *p*-benzyne. After the biradical character is resolved we could expect both the static correlation in the π system and the remaining dynamical correlation of the two structures of be of similar size. The situation in *o*-benzyne will, however, be quite different. This molecule will have negligible biradical character since the two electrons in question will form an in-plane π bond. This bond will also drastically change the structure of the *o*-benzyne as compared to the two other benzynes. The new bond will be closer to a triple bond rather than an aromatic carbon−carbon bond. This will change the electron correlation. Hence, any direct assessment of the size of the static and dynamical correlation in *o*-benzyne as compared to the two other benzynes is not simple.

Table 1. Survey of Some Previous Experimental and Theoretical Results for the Bergman Reaction (Enthalpies and Gibbs Free Energy in kcal/mol and Entropies in eu/mol)

property	value	ref	comment
$\Delta H_R(298)$	14	1	group additivity and the Born−Haber cycle
$\Delta H_R(298)$	13 ± 3.0	4b	collision-induced dissociation
$\Delta H_R(298)$	8.4 ± 3.0	4c	collision-induced dissociation
$\Delta H_R(470)$	8.5 ± 1.0	5	*p*-benzyne trapping rates
ΔH_R	22.0[a]	26	MRCI/MIDI
$\Delta H_R(298)$	10.1	27	DFT(B3LYP)/6-31G(d,p)
$\Delta H_R(298)$	9.1	7a	CCSD(T)/6-31G(d,p)
$\Delta H_R(298)$	8−10	7b	CCSD(T)/6-31G(d,p)
$\Delta H_R(298)$	4.9 ± 3.2	8	CASPT2[0]/ANO
ΔH_R	3.42	26	PCI-80
$\Delta S^\ddagger(470)$[b]	−10.22 ± 1.0	5	*p*-benzyne trapping rates
$\Delta S^\ddagger(470)$[c]	3.05 ± 1.5	5	*p*-benzyne trapping rates
$\Delta H^\ddagger(470)$	28.23 ± 0.5	5	*p*-benzyne trapping rates
$\Delta H^\ddagger$	37.8[a]	26	MRCI/MIDI
$\Delta H^\ddagger(298)$	28.5	7a	CCSD(T)/6-31G(d,p)
$\Delta H^\ddagger(298)$	29.5	7b	CCSD(T)/6-31G(d,p)
$\Delta H^\ddagger(298)$	25.0 ± 3.1	8	CASPT2[0]/ANO
$\Delta G^\ddagger(473)$	32.0	1	thermal isomerization reaction

[a] Only electronic contribution. [b] (*Z*)-Hex-3-ene-1,5-diyne → *p*-benzyne. [c] *p*-Benzyne → (*Z*)-hex-3-ene-1,5-diyne.

Table 2. Survey of Some Previous Experimental and Theoretical Results for the Energy Splitting of the Singlet Benzynes (All Values in kcal/mol)

method	ortho−meta	ortho−para	ref
CCSD(T)/6-31G(d,p)	13.7	25.3	7a
CCSD(T)/6-31G(d,p)	13.6	25.4	7b
GVB/4-31G	14.5	23.3	29
CI/6-311G**	15.8	28.4	30
CCCI/pVTZ	18.0	31.0	31
CID	10.0	22.0	4a
CID	15.4	30.7	4b

The BSSE of a reaction like this is difficult to measure in absolute terms. However, if there is an important difference in interatomic distances of the two structures, one should expect the BSSE to favor the structure with the shortest interatomic distance. In the Bergman reaction this will be the case of the terminal carbons which will drastically change their interatomic distance during the course of the reaction. Thus, it is reasonable to expect the BSSE to underestimate the heat of reaction in the Bergman reaction. There are two ways of correcting for the BSSE. The first is to estimate the magnitude of the BSSE and to correct the computed energy difference with this value. The other is to extrapolate the energy difference to the basis set limit, thus avoiding any explicit estimate of the BSSE. In this paper we will adopt the latter approach.

Results and Discussion

Previous Data. We will start this section with a short discussion of the previous experimental and theoretical studies (see Tables 1 and 2). For the heat of reaction we note that the experimental findings are very consistent. However, we also notice that this consistency did not come about until Wenthold and Squires used the same heat of formation of (*Z*)-hex-3-ene-1,5-diyne as Roth *et al.* Hence, the experiments agree on the heat of formation of *p*-benzyne, which they estimate to be 138 ± 1 and 137.9 ± 2.9 kcal/mol, respectively. The consistency of the two experimental results obtained from different experimental methods warrants a high reliability in the estimates. The

Table 3. The CASSCF and CASPT2[0] Relative Energies, and the CASSCF Structural Parameters for Six Structures along the Reaction Path of the Bergman Reaction As Computed with a DZP One-Particle Basis Set (Energies in kcal/mol, Bond Distances in Å, and Angles in deg)

	structures[f]					
	1	**2**[a]	**3**[a]	**4**[a]	**5**[b]	**6**[c]
E_{CASSCF}	0.00[d]	7.43	27.61	35.98	40.40	22.39
$E_{\mathrm{CASPT2[0]}}$	0.00[e]	5.39	19.55	23.10	20.63	−4.22
$R_{C_1H_1}$	1.077	1.076	1.075	1.075	1.075	1.076
$R_{C_1C'_1}$	1.371	1.357	1.388	1.396	1.409	1.449
$R_{C_1C_2}$	1.441	1.441	1.436	1.430	1.419	1.380
$R_{C_2C_3}$	1.216	1.221	1.239	1.255	1.286	1.380
$R_{C_3C'_3}$	4.476	3.175	2.328	2.117	1.923	1.448
$R_{C_3H_3}$	1.059	1.060	1.062	1.065	1.069	1.080
$\phi_{H_1C_1C'_1}$	118.4	121.0	120.4	119.8	118.9	119.1
$\phi_{H_1C_1C_2}$	116.8	119.8	121.5	121.8	122.0	123.1
$\phi_{C_1C_2C_3}$	182.0	160.5	142.4	136.8	131.2	124.4
$\phi_{H_3C_3C_2}$	181.2	171.5	158.6	151.5	141.1	123.1
$\phi_{H_3C_3C'_3}$	125.6	108.2	101.9	103.7	109.3	119.1

[a] Optimized with fixed $R_{C_3C_3'}$. [b] CASSCF transition state optimized with no geometrical constraints. [c] Although the energy is converged with seven significant figures after the decimal point the structure does not fully have the higher symmetry. [d] Total energy, −229.608 224 hartrees. [e] Total energy, −230.162 291 hartrees. [f] Structure **1** is the hexa-3-ene-1,4-diyne molecule and structure **6** is the singlet *p*-benzyne biradical molecule.

Table 4. The CASSCF and CASPT2[0] Relative Energies and the CASSCF Structural Parameters for Six Structures along the Reaction Path of the Bergman Reaction As Computed with a TZ2P One-Particle Basis Set (Energies in kcal/mol, Bond Distances in Å, and Angles in deg)

	structures[e]					
	1	**2**[a]	**3**[a]	**4**[a]	**5**[b]	**6**
E_{CASSCF}	0.00[c]	7.37	28.84	37.89	43.64	27.64
$E_{\mathrm{CASPT2[0]}}$	0.00[d]	5.11	19.46	23.51	21.55	0.42
$R_{C_1H_1}$	1.072	1.071	1.070	1.070	1.070	1.071
$R_{C_1C'_1}$	1.361	1.365	1.378	1.386	1.402	1.442
$R_{C_1C_2}$	1.432	1.431	1.428	1.422	1.409	1.370
$R_{C_2C_3}$	1.204	1.208	1.226	1.241	1.277	1.370
$R_{C_3C'_3}$	4.433	3.175	2.328	2.117	1.896	1.442
$R_{C_3H_3}$	1.053	1.053	1.056	1.058	1.063	1.071
$\phi_{H_1C_1C'_1}$	118.3	120.8	120.5	119.9	118.8	119.1
$\phi_{H_1C_1C_2}$	116.8	120.1	121.6	121.9	122.2	123.2
$\phi_{C_1C_2C_3}$	180.7	160.9	143.2	137.5	131.1	124.6
$\phi_{H_3C_3C_2}$	179.0	172.3	160.5	153.3	141.0	123.2
$\phi_{H_3C_3C'_3}$	125.5	107.6	100.4	102.4	109.1	119.1

[a] Optimized with fixed $R_{C_3C'_3}$. [b] CASSCF transition state optimized with no geometrical constraints. [c] Total energy, −229.651 251 hartrees. [d] Total energy, −230.317 776 hartrees. [e] Structure **1** is the hexa-3-ene-1,4-diyne molecule and structure **6** is the singlet *p*-benzyne biradical molecule.

Table 5. The CASSCF, CASPT2[0], CASPT2[g1], CCSD, and CCSD(T) Relative Energies, and the CASSCF Structural Parameters for Six Structures along the Reaction Path of the Bergman Reaction As Computed with an *Average* ANO C(5s4p2d), H(3s2p) One-Particle Basis Set (Energies in kcal/mol, Bond Distances in Å and Angles in deg)

	structures[h]					
	1	**2**[a]	**3**[a]	**4**[a]	**5**[b]	**6**
E_{CASSCF}	0.00[c]	7.37	28.84	37.84	43.64	27.70
$E_{\mathrm{CASPT2[0]}}$	0.00[d]	5.62	20.71	25.01	23.20	2.34
$E_{\mathrm{CASPT2[g1]}}$	0.00[e]	5.66	20.89	25.31	23.87	3.84
E_{CCSD}	0.00[f]	7.12	26.60	34.29	40.03	31.10
$E_{\mathrm{CCSD(T)}}$	0.00[g]	6.29	22.93	28.52	29.65	10.81
$R_{C_1H_1}$	1.072	1.071	1.070	1.070	1.071	1.071
$R_{C_1C'_1}$	1.362	1.367	1.379	1.388	1.403	1.443
$R_{C_1C_2}$	1.431	1.431	1.428	1.422	1.410	1.371
$R_{C_2C_3}$	1.206	1.209	1.227	1.242	1.278	1.371
$R_{C_3C'_3}$	4.440	3.175	2.328	2.117	1.895	1.443
$R_{C_3H_3}$	1.052	1.052	1.055	1.057	1.063	1.071
$\phi_{H_1C_1C'_1}$	118.3	120.8	120.4	119.9	118.8	119.1
$\phi_{H_1C_1C_2}$	116.8	120.1	121.7	122.0	122.2	123.2
$\phi_{C_1C_2C_3}$	181.7	160.9	143.1	137.5	131.0	124.6
$\phi_{H_3C_3C_2}$	179.1	172.5	160.8	153.5	141.1	123.2
$\phi_{H_3C_3C'_3}$	125.7	107.4	100.2	102.2	109.0	119.1

[a] Optimized with fixed $R_{C_3C'_3}$. [b] CASSCF transition state optimized with no geometrical constraints. [c] Total energy, −229.656 658 hartrees. [d] Total energy, −230.307 183 hartrees. [e] Total energy, −230.306 325 hartrees. [f] Total energy, −230.333 114 hartrees. [g] Total energy, −230.381 177 hartrees. [h] Structure **1** is the hexa-3-ene-1,4-diyne molecule and structure **6** is the singlet *p*-benzyne biradical molecule.

two experimental results are also supported by the CCSD(T)/6-31G(d,p) study of Kraka and Cremer and the CASPT2[0]/ANO study of Lindh and Persson. The MRCI/MIDI study by Koga and Morokuma, however, seems to grossly overestimate the heat of formation. The failure of the MRCI/MIDI study is due to an unbalanced selection of the active orbitals in the CASSCF reference in combination with a poor basis set. Concerns regarding the basis set can also be put forward for the CCSD(T) study of Kraka and Cremer. However, the result is within the error bar of both experimental results. For the entropy we note that no theoretical predictions have been put forward yet. Finally, for the heat of activation we note again the same trends as for the heat of reaction, *i.e.* the experimental result of Roth is supported by the CCSD(T) and the CASPT2[0] results whereas the MRCI study grossly overestimates the value. For the energy splittings of the singlet benzynes, we note that the theoretical results regarding the ortho−meta splitting are more consistent than the estimates of the ortho−para splitting. This is a reflection of the importance of the second configuration in the *p*-benzyne as discussed in the previous section.

The Energetics of the Bergman Reaction. The geometrical parameters and the energetics along the CASSCF(12,12) reaction path for the DZP, TZ2P, and ANO(C(5s4p2d)/H(3s2p)) basis sets are summarized in Tables 3−5. These results are essentially those of the study of Lindh and Persson. Here, however, they have been augmented by one point to facilitate a better estimate of the CASPT2 activation energy. In addition, we have computed CCSD(T) and CASPT2[g1] values for all structures for the ANO basis set. For all structures the CASSCF(12,12) wave function contained 80−82% of the weight of the CASPT2 wave function. Especially, we did not observe any significant differences in the comparison of the weights of the (*Z*)-hex-3-ene-1,5-diyne and *p*-benzyne CASSCF wave function in the first-order CASPT2 wave function. A more detailed discussion regarding the geometrical parameters has already been put forward by Lindh and Persson; we will not reiterate that discussion here. From Table 5 we observe that the CASPT2[g1] energetics essentially are the same as the CASPT2[0] results corrected for the systematic overestimate of the correlation energy for unpaired electrons. As stated by Kraka and Cremer as well as Lindh and Persson the biradical character of the wave functions is well pronounced after the energy barrier has been passed (see Table 6, for example, for the CASSCF(12,12) weights produced in this study).

This can be observed from the fact that the uncorrected CASPT2[0] results are similar to the CASPT2[g1] results for the initial part of the reaction, but differ in the latter part of the reaction, where the biradical character is important. This is as expected since the CASPT2[g1] should treat the latter part of the reaction path differently. A similar trend for the comparison of the CCSD(T) and the CASPT2[g1] is observed. As the importance of the second configuration grows the CCSD(T) and the CASPT2[g1] results deviate more and more. The explana-

Table 6. The Relative Weights (in %) to the Two Configurations in the CASSCF/aANO Wave Function Which Are Due to the Distribution of the Two Radical Electrons in the Two Available Radical Orbitals as They Change along the Reaction Path of the Bergman Reaction

structure[a]	α^2	β^2
1	0.840	0.000
2	0.832	0.000
3	0.811	0.014
4	0.793	0.029
5	0.733	0.088
6	0.566	0.276

[a] The first structure (**1**) is the (*Z*)-hex-3-ene-1,5-diyne molecule. The symbols refer to the definition in the section on the electronic structure where α is the coefficient of the dominant configuration and β the coefficient of the other possible configuration.

Table 7. The Harmonic Frequencies of (*Z*)-Hex-3-ene-1,5-diyne, the CASSCF Transition State of the Bergman Reaction, and *p*-Benzyne Computed at the CASSCF/DZP Level of Theory. Some Numbers for Deuterated Species Are Included (All Values in cm^{-1})

	structures[a]							
	A	B	C	D	E	F	G	H
a_1:								
1	3624	3624	3377	3496	3495	3397	3393	3392
2	3377	2497	2791	3397	2514	2607	3392	1474
3	2225	2223	2102	1685	1684	1630	1422	1402
4	1643	1606	1639	1537	1495	1537	1395	1237
5	1296	962	1294	1245	1020	1243	1240	1185
6	895	855	883	1034	907	1025	1189	1011
7	552	552	429	868	866	654	1006	704
8	385	382	377	631	623	600	993	338
9	97	97	90	780i	780i	776i	646	40
b_1:								
10	3624	3624	3360	3491	3491	3379	3378	3378
11	3360	2475	2792	3379	2491	2611	3378	1731
12	2232	2231	2107	1857	1856	1814	1709	1510
13	1494	1265	1492	1498	1325	1496	1534	1272
14	1060	917	1050	1143	1059	1121	1352	1105
15	721	702	715	1031	923	872	1095	769
16	549	549	426	821	804	737	999	413
17	207	204	198	468	464	454	602	166
b_2:								
18	779	632	778	719	616	711	772	758
19	537	535	416	553	541	425	742	517
20	309	298	300	410	368	407	465	247
a_2:								
21	997	779	997	949	747	948	951	935
22	554	540	539	664	663	592	918	672
23	522	505	415	585	549	521	637	510
24	208	201	198	336	328	305	429	153

[a] A: hex-3-ene-1,5-diyne. B: hex-3-ene-1,5-diyne, deuterated at the vinylic position. C: hex-3-ene-1,5-diyne, deuterated at the acetylenic position. D: transition state. E: transition state, deuterated at the vinylic position. F: transition state, deuterated at the acetylenic position. G: *p*-benzyne. H: *p*-benzyne, two hydrogens deuterated at the same side.

tion for this trend is a combination of the following: (a) as discussed earlier, the CCSD(T) treatment of *p*-benzyne is inferior relative to the CCSD(T) treatment of (*Z*)-hex-3-ene-1,5-diyne and this is more apparent as the second configuration becomes more important; and (b) the approximative nature in which the dynamical correlation energy is included in the CASPT2 method is more apparent as the wave function gradually changes along the reaction path. The heat of activation, estimated with a simple parabolic fit, is for the aANO(C(5s4p2d)/H(3s2p)) basis set estimated to be 25.5 kcal/mol at $R_{C_3C'_3} = 2.06$ Å and 29.8 kcal/mol at $R_{C_3C'_3}$ 1.95 Å for the CASPT2[g1] and the CCSD(T) methods, respectively. The CCSD(T) $R_{C_3C'_3}$ distance for the transition state is a bit shorter than the 1.99-Å result from the CCSD(T)/6-31G(d,p) study of Kraka and Cremer.

Table 8. The Vibrational and Temperature Corrections to the Total Energy for the Bergman Reaction at 0, 298, 372, 472 and 572 K Computed from a Harmonic Oscillator Ensemble Model Based on Force Constants Computed at the CASSCF/DZP Level of Theory (Gibbs Free Energy and the Enthalpy in kcal/mol, and the Entropy in eu/mol)

	states[a]					
temp	A	B	C	D	E	F
0 K						
ΔG	3.42	0.80	3.47	2.74	0.82	0.46
ΔH	3.42	0.80	3.47	2.74	0.82	0.46
ΔS	0.00	0.00	0.00	0.00	0.00	0.00
298 K						
ΔG	4.77	1.97	4.82	4.25	1.99	1.74
ΔH	1.90	−0.41	1.96	1.10	−0.37	−0.79
ΔS	−9.64	−8.00	−9.59	−10.58	−7.94	−8.52
372 K						
ΔG	5.54	2.61	5.59	5.09	2.62	2.41
ΔH	1.40	−0.79	1.47	0.64	−0.74	−1.14
ΔS	−11.14	−9.13	−11.07	−11.98	−9.06	−9.56
472 K						
ΔG	6.72	3.58	6.76	6.35	3.59	3.42
ΔH	0.86	−1.22	0.94	0.17	−1.18	−1.52
ΔS	−12.42	−10.16	−12.35	−13.09	−10.09	−10.48
572 K						
ΔG	8.01	4.63	8.04	7.69	4.63	4.50
ΔH	0.47	−1.57	0.55	−0.13	−1.53	−1.83
ΔS	−13.17	−10.84	−13.10	−13.69	−10.77	−11.07

[a] A: enediyne → benzyne. B: enediyne → transition state. C: enediyne → benzyne, vinylic deuteration. D: enediyne → benzyne, acetylenic deuteration. E: enediyne → transition state, vinylic deturation. F: enediyne → transition state, acetylenic deuterated.

The Thermodynamics of the Bergman Reaction. The vibrational spectrum and the temperature corrections are presented in Table 7 and 8. The temperature correction is here computed from a model of an ensemble of non-interacting harmonic oscillators. For such a model we should expect an underestimate of the actual entropy. At low temperatures as reported in this study, however, the error will be small. This is because the Boltzman distributions at these temperatures will have negligible population of the vibrational states beyond the first excited state. Along the reaction path, the vibrational spectrum is changed such that the lower frequency modes in (*Z*)-hex-3-ene-1,5-diyne become firmer as the molecule is transformed into the more rigid *p*-benzyne structure. Hence, one should expect a zero-point vibrational energy (ZPVE) correction to the electronic heat of reaction and heat of activation to increase these entities. Furthermore, since the vibrational states are more dense for the (*Z*)-hex-3-ene-1,5-diyne structure one should also expect the temperature correction to act in the opposite direction relative to the ZPVE correction. For example, the total vibrational correction to the heat of reaction is computed to be 3.42 and 1.90 kcal/mol at 0 and 298 K, respectively. The entropy of activation at 470 K has experimentally been measured to be −10.22 ± 1.0 and 3.05 ± 1.5 eu/mol for the forward and backward reaction, respectively. The CASSCF/DZP value for the same entities at 472 K is computed to be −10.16 and 2.26 eu/mol, respectively. Considering that the CASSCF transition state is not quite at the right position along the reaction path, as compared to the CCSD(T) and the CASPT2[g1] results, one has to view the findings as being quite reasonable. The entropy of reaction at 298 K is experimentally[5] evaluated to be −13.27 ± 1.84 eu/mol which compares well with the computed value of −12.42 eu/mol. Using the theoretically predicted entropy we estimate that the enthalpy reported by Roth and co-workers at 470 K corresponds to 9.52 ± 1.0 kcal/mol at 298 K. Thus, the first impression that the experimental findings have an excellent agreement has to be reconsidered. In addition, using the vibrational and temperature correction of this paper together

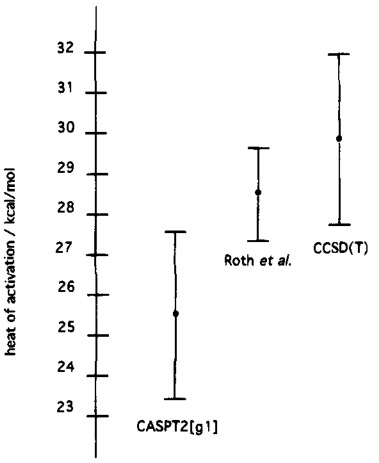

Figure 4. Survey of experimental and theoretical predictions of the electronic contribution to the heat of activation of the Bergman reaction.

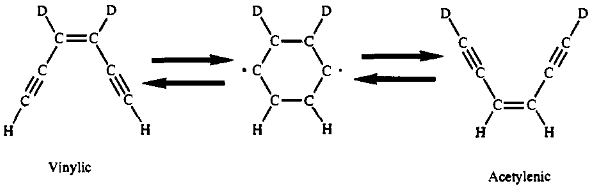

Figure 5. The label exchange in the Bergman reaction.

with the CCSD(T)/6-31G value of Kraka and Cremer we get a heat of reaction at 298 K of 7.4 kcal/mol. This value is a bit lower than the 8−10 kcal/mol reported by Kraka and Cremer. Applying temperature correction to the Gibbs free energy of 32 kcal/mol as reported by Bergman and co-workers we get an electronic contribution of approximately 28 kcal/mol to the activation energy. Similarly, subtracting the vibrational and temperature dependence from the heat of activation of 28.2 kcal/mol as reported by Roth *et al.* we find the electronic contribution to be 28.6 kcal/mol. These two recompiled values compare favorably (see Figure 4) to the 25.5 and 29.8 kcal/mol for the CASPT2[g1] and the CCSD(T) methods, respectively. Here we observe again that CCSD(T) overestimates the energy due to the buildup of the biradical character around the transition state.

At this point we also note that the temperature correction will in the deuterated case (see Figure 5) favor the (*Z*)-hex-3-ene-1,5-diyne species with acetylenic deuteration. This fact will alter the equilibrium constant. It is not clear to us if this fact was considered or had to be considered in the experiment by Jones and Bergman.[1a]

Basis Set Dependency. In Table 9 we list the electronic heats of reaction computed for a number of different basis sets. The entries in Table 9 are ordered with respect to the total CCSD(T) energies, although it should be noted that the C 1s electrons were not frozen for the CCSD(T)/6-31G(d,p) calculations as they have been for all coupled-cluster calculations reported in this study.

First, we note the common trend that the cc-pVDZ, DZP, and 6-31G(d,p) results do not have the same quantitative consistency as the other basis sets. These basis sets should clearly be avoided for future investigations of biradicals. It may be that for some structures, as in this case, they include favorable cancellations of errors. In the case of the CCSD(T)/6-31G(d,p) calculations by Kraka and Cremer the underestimate of correlation energy in the *p*-benzyne is canceled out since the (*Z*)-hex-3-ene-1,5-diyne is more sensitive to the basis set quality. Here the cancellation is of the order of 5 kcal/mol. Second, we also observe that, as expected, the CASPT2[0] consistently underestimates the heat of reaction as compared with the newly developed CASTP2[g1] method. Third, we see that the basis set trends for CCSD(T) and CASPT2[g1] are identical. This is in particular true for the peculiar behavior as the aANO basis set of C(5s3p2d) is extended to C(5s4p3d), C(5s4p2d1f), and C(5s4p3d1f). This basis set dependency is clearly not an artifact of the CASPT2[g1] or CCSD(T) models, but rather a reflection of some real physics. Obviously the (*Z*)-hex-3-ene-1,5-diyne needs both the extra d and f function whereas the *p*-benzyne could do fine with either. From the trend of the values with respect to the basis set limits there is no reason to believe that those should be outside the normal errors associated with these methods. Hence, we report the results from the largest basis sets with an uncertainty, due to basis set incompleteness, of ±2.0 kcal/mol. That is, this uncertainty refers to the value that would be obtained at the basis set limit for that particular method.

From Tables 8 and 9 we derive the theoretical predictions of the heat of formation at 298 K to be 5.38 ± 2.0 and 12.67 ± 2.0 kcal/mol computed with the C(5s4p3d1f)/H(3s2p) basis set at the CASPT2[g1] and CCSD(T) levels of theory, respectively. We emphasize that the uncertainty refers to the basis set limit for the particular method. These results nicely encompass the experimental results (see Figure 6) of 9.5 ± 1.0 and 8.5 ± 3.0 kcal/mol by Roth *et al.* and Wenthold and Squires. In addition to the results of the CCSD(T) and CASPT2[g1] method we note that recent DFT[27] and PCI-80[28] calculations predict the heat of formation at 298 K to be 10.1 and 5.32 kcal/mol, respectively. It is interesting that the multiconfigurational results cluster below the experimental results.

Energy Splitting of the Singlet Benzynes. In this section the *ab initio* energy differences are not corrected for zero-point vibrational energies nor for thermal population of vibrational levels. Due to the similar connectivity of these isomers, and the fact that the zero-point and entropy corrections will cancel to a large extent for the temperatures of interest, it is expected that this approach will have little effect on the computed energy differences. The CASSCF(8,8) optimized structures are collected in Tables 10−12 together with structures from other theoretical investigations. For the *p*-benzyne we note in particular that CCSD(T) and MP2 in comparison with the other methods give a rather long $C_1-C'_1$ bond, 1.426 and 1.420 Å, respectively. This can clearly not be attributed to the one-particle space since the same basis in conjunction with GVB and CASSCF produces a shorter bond distance. Furthermore, on comparing the CASSCF(12,12) and CASSCF(8,8) we note a contraction of the $C_1-C'_1$ bond distance, from 1.443 to 1.409 Å. The rather long distance of the CASSCF(12,12) is attributed to both the σ and π space being included in the active space. This will overestimate the antibonding configurations and result in a too long bond as earlier discussed by Lindh and Persson. For the *m*-benzyne we observe the same trend as in *p*-benzyne, namely the carbon−carbon bonds with both carbons bonding to a hydrogen also are longer as compared to those carbon−

---

(27) Bauschlicher, Jr., C. W. private communication: DFT with the B3LYP correlation functional in conjunction with a 6-31G basis set compute the heat of reaction including the zero-point vibrational energy correction to 11.6 kcal/mol which correspond to a heat of reaction at 298 K of 10.1 kcal/mol.

(28) Siegbahn, P. E. M. private communication, PCI-80: ACPF/DZP with one reference configuration for the (*Z*)-hex-3-ene-1,5-diyne and two reference configurations for the *p*-benzyne yields 3.4 kcal/mol lower energy for the former. The PCI-80 scheme is described in: Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *Chem. Phys. Lett.* **1994**, *223*, 35.

(29) Noell, J. O.; Newton, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 51.

(30) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1993**, *115*, 11951.

(31) Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11958.

Table 9. The Electronic Heat of Reaction of the Bergman Reaction Computed for a Number of Different Energy Functionals and One-Particle Basis Sets. All Calculations Have Been Performed with the CASSCF/aANO(C(5s4p2d)/H(3s2)) Optimized Structures Except for the 6-31G(d,p) Basis Set (All units in kcal/mol)

	basis set[a]									
method	A	B	C	D	E	F	G	H	I	J
SCF	73.35	82.13		77.41	77.32	77.37	78.04	77.76	77.76	77.81
MP2	−15.41	−12.49	−12.31	−11.24	−9.37	10.47	−11.06	−12.10	−12.19	−10.66
CCSD	23.23	27.34	27.21	29.48	31.10	30.37	30.82	29.83	29.77	31.32
CCSD(T)	3.13	4.18	5.5	8.92	10.81	9.94	10.11	9.22	9.10	10.77
CASSCF	23.09	22.39		27.64	27.70	27.80	27.90	28.11		28.19
CASPT2[0]		−4.22		0.42	2.34			−1.77		
CASPT2[g1]	−3.33	−3.11		1.96	3.89	3.00	2.87	2.00		3.48

[a] A: cc-pvdz. B: DZP. C: 6-31G(d,p), energetic according to the paper by Kraka and Cremer. D: TZ2P. E: ANO C(5s4p2d) H(3s2p). F: ANO C(5s4p3d) H(3s2p). G: cc-pvtz. H: ANO C(5s4p2d1f) H(3s2p). I: ANO C(5s4p2d1f) H(3s2p1d). J: ANO C(5s4p3d1f) H(3s2p).

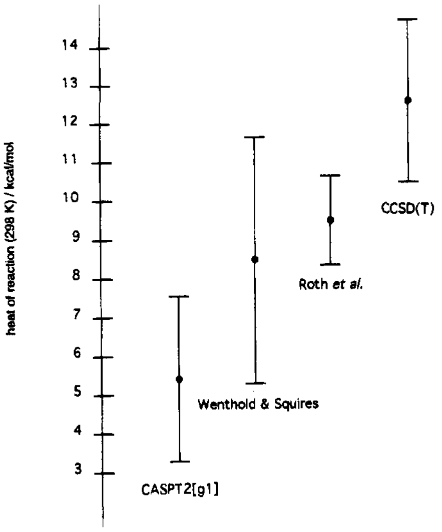

Figure 6. Survey of experimental and theoretical predictions of the heat of reaction at 298 K of the Bergman reaction.

Table 10. Geometrical Parameters for *p*-Benzyne (All Distances in Å)

method	C_1-C_2	$C_1-C'_1$	C_1-H_1
CASSCF(8,8)/DZP	1.387	1.415	1.076
CASSCF(8,8)/(5s4p2d/3s2p)	1.378	1.409	1.071
GVB/4-31G[a]	1.373	1.439	
CCSD(T)/6-31G(d,p)[b]	1.382	1.426	1.082
GVB/6-31G(d,p)[b]	1.370	1.401	1.075
MP2/6-31G(d,p)[b]	1.381	1.420	1.081
CASSCF(2,2)/3-21G[c]	1.369	1.403	
CASSCF(2,2)/6-31G*[c]	1.371	1.401	
CASSCF(2,2)/6-311G**[c]	1.369	1.401	
CASSCF(8,8)/3-21G[c]	1.381	1.415	

[a] Reference 29. [b] Reference 4b. [c] Reference 31.

carbon bonds where one of the carbons carries a radical electron. This can be rationalized as the radical electron participating in C−C bonding through hyperconjugation of the C−H bond. However, the *o*-benzyne structure has a carbon−carbon triple bond. Thus the structure of *o*-benzyne is much more perturbed relative to the benzene structure as compared with the two other benzynes. This difference will also manifest itself as a much smaller biradical character in the *o*-benzyne. The degree of biradical character can be monitored by studying the coefficients of the configurations involving a double occupation of the symmetric and antisymmetric combination of the "radical" orbitals. In *o*-benzyne this corresponds to the in-plane π and π^* orbitals. The weights of these configurations are 0.53 and 0.32, 0.74 and 0.14, and 0.81 and 0.06 in the CASSCF(8,8) model for *p*-, *m*-, and *o*-benzyne, respectively.

The CCSD, CCSD(T), CASSCF(8,8), and CASPT2[g1] energetics are gathered in Table 13. For the closed shell SCF we observe a gross overestimate of the total energies of both *m*- and *p*-benzyne. This is expected since both these moleucles will have a pronounced biradical character as compared to *o*-benzyne. Hence, the SCF treatment of these two structures is not qualitatively correct. At the CASSCF(2,2) level, however, the model is correct with respect to the treatment of the biradical character of the wave function. As anticipated the energy splitting of meta−para at the CASSCF(2,2) level is quantitatively correct. For the *o*-benzyne as compared to the other benzynes, however, we observe a significant discrepancy. This is a manifestation of the structural difference of the *o*-benzyne vs the two other benzynes. The structural difference will change the character of the electron correlation. In particular, the orbital energy distribution of the π-system is not the same. This will result in both an altered correlation within the π-system and the interaction between the π-system and the in-plane π-orbital. At the CASSCF(8,8) level we observe that the major part of the discrepancy at the CASSCF(2,2) level is removed. However, the accuracy of the energy splittings at this level, as compared to experiment, for example, is accidental. One cannot

Table 11. Geometrical Parameters for *m*-Benzyne (All distances in Å)

method	C_1-C_2	C_1-C_3	C_3-C_4	C_2-H_2	C_3-H_3	C_4-H_4
CASSCF(8,8)/DZP	1.384	1.387	1.403	1.072	1.076	1.079
CASSCF(8,8)/ (5s4p2d/3s2p)	1.375	1.378	1.396	1.066	1.072	1.074
GVB/4-31G[a]	1.36	1.389	1.412			
CCSD(T)/6-31G(d,p)[b]	1.377	1.383	1.405	1.078		1.086
GVB/6-31G(d,p)[b]	1.371	1.373	1.389	1.070		1.077
MP2/6-31G(d,p)[b]	1.374	1.377	1.402	1.078		1.086
CASSCF(2,2)/3-21G[c]	1.377	1.373	1.390			
CASSCF(2,2)/6-31G*[c]	1.371	1.373	1.390			
CASSCF(2,2)/6-31G*[c]	1.371	1.373	1.390			
CASSCF(2,2)/ 6-311G**[c]	1.371	1.372	1.389			
CASSCF(8,8)/3-21G[c]	1.388	1.384	1.400			

[a] Reference 29. [b] Reference 4b. [c] Reference 31.

Table 12. Geometrical Parameters for *o*-Benzyne (All Distances in Å)

method	$C_1-C'_1$	C_1-C_2	C_2-C_3	$C_3-C'_3$	C_2-H_2	C_3-H_3
CASSCF(8,8)/DZP	1.262	1.406	1.397	1.426	1.075	1.078
CASSCF(8,8)/ (5s4p2d/3s2p)	1.251	1.399	1.390	1.420	1.070	1.073
GVB/4-31G[a]	1.226	1.389	1.389	1.420		
CCSD(T)/6-31G(d,p)[b]	1.269	1.394	1.411	1.413	1.081	1.084
GVB/6-31G(d,p)[b]	1.260	1.383	1.389	1.404	1.074	1.076
MP2/6-31G(d,p)[b]	1.268	1.389	1.405	1.410	1.080	1.083
CASSCF(2,2)/3-21G[c]	1.261	1.382	1.392	1.403		
CASSCF(2,2)/6-31G*[c]	1.261	1.383	1.389	1.404		
CASSCF(2,2)/ 6-311G**[c]	1.254	1.383	1.388	1.404		
CASSCF(8,8)/3-21G[c]	1.260	1.402	1.396	1.422		

[a] Reference 29. [b] Reference 4b. [c] Reference 31.

Table 13. The Total Energy of Singlet *o*-Benzyne and the Energy Splitting of the Singlet Benzynes Computed for a Variation of Different Methods in Conjugation with an aANO C(5s4p2d)/ H(3s2p) Basis Set. The Most Recent Experimental Results Are Included for Coimparison (Total Energies in hartree and Relative Energies in kcal/mol)

method	total energy	ortho−meta	meta−para	ortho−para
SCF	−229.461 86	32.29	47.41	79.70
CASSCF(2,2)	−229.467 10	−16.20	10.81	−5.39
CASSCF(8,8)	−229.602 31	16.62	10.88	27.50
MP2	−230.340 68	7.16	4.01	11.17
CCSD	−230.351 11	19.84	24.45	44.29
CASPT2[0]	−230.351 82	10.86	12.53	23.39
CASPT2[g1]	−230.350 72	11.41	14.72	26.13
CASPT2[g1][a]	−230.357 03	12.19	14.66	26.85
CCSD(T)	−230.406 52	14.26	12.95	27.21
expt[b]		15.3	15.4	30.7

[a] Benzene sized basis set. [b] Reference 4.

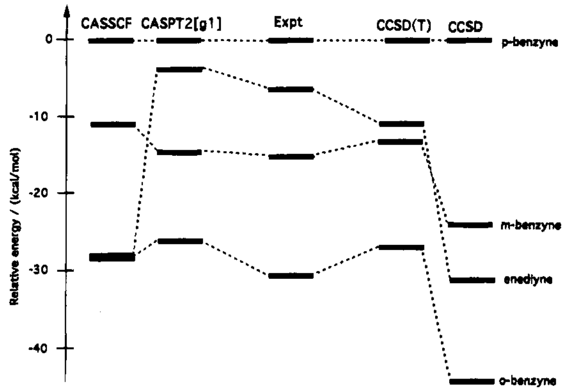

Figure 7. The energy splittings of (*Z*)-hex-3-ene-1,5-diyne and *p*-, *m*-, and *o*-benzyne as computed in this paper compared with recent experimental results. Zero-point and temperature corrections have been excluded.

in advance say that the electron correlation beyond the CASSCF(8,8) should be the same for all three singlet benzynes. For the MP2 method we observe a large overestimate of the correlation for the *m*- and *p*-benzyne as compared with the *o*-benzyne. This is as expected since both the *m*- and *p*-benzyne molecules are biradical. Hence, the reference of these two molecules in the MP2 approximation is in serious error. The poor reference will also create problems in the CCSD calculation. Here, however, this will lead to an underestimate of the correlation for the *m*- and *p*-benzyne as compared to the *o*-benzyne. The error, though, is expected not to be as large as that for the MP2. In particular we note that the energy splitting between the two benzynes with least biradical character is not drastically off from the experiment, the ortho−meta energy splitting being 19.84 and 15.4 kcal/mol for CCSD and the experiment, respectively. The CASPT2 and CCSD(T) levels of theory provide results which are in accordance with experimental findings. However, in line with the earlier discussions on the energy splitting of the reactant and the product in the Bergman reaction, we expect the CCSD(T) result to form an upper bound of the ortho−para energy splitting (27.21 kcal/mol). The 3 kcal/mol difference from the recent CDI result (30.7 kcal/mol) is larger than expected. That is, the present study suggests that the true energy difference lies in the lower part of the range proposed by Wenthold and Squires.[4b] The same arguments would also to some extent hold for the ortho−meta energy splitting. In passing we note that an uncertainty of 1 or 2 kcal/mol in the experimental values may be caused by the fact that the triplet state of *p*-benzyne is only 1 or 2 kcal/mol higher in energy than the singlet and that a slow conversion between the two forms may occur. We also note that of the different CASPT2 results, a better accuracy of the CASPT2[g1] approximation is exhibited as compared to the originally proposed CASPT2[0] approach. This is clearly demonstrated in the ortho−para energy splitting which is underestimated for the CASTP2[0] method since this approach will overestimate the electron correlation of the unpaired electrons in *p*-benzyne. Finally, the CASPT2 results with the somewhat larger benzene basis sets indicate that the size of the basis set centered on the atoms is rather saturated.

Summary

The Bergman Reaction. The Berman reaction has been reinvestigated at the CCSD(T) and CASPT2[g1] levels of theory for a large number of basis sets. The study has in particular evaluated the heats of reaction and activation and the entropy effects. The basis set study shows that the use of small basis sets such as cc-pVDZ, DZP, and 6-31G(d,p) will underestimate the heat of formation by as much as 5 kcal/mol as compared to the basis set limit at the CCSD(T) level. The study exhibits large differences in the heat of formation, 7 kcal/mol, between the CCSD(T) and CASPT2[g1] methods. The difference is significantly smaller, 4 kcal/mol, for the estimated heat of activation. This trend in the difference between the two methods originates from the buildup of a second important configuration as the Bergman reaction proceeds. For both the heat of reaction and the heat of activation, the theoretical results encompass the experimentally deduced values. The CASSCF/DZP derived entropy effects agree with the experimental values derived by Roth *et al.* The experimental heats of formation corrected to the same temperature, 298 K, are found to deviate by about 1 kcal/mol. At present, theory is not able to discriminate between the two experimental numbers.

The Singlet Benzynes. The energy splitting of the singlet benzynes has been studied at the CCSD(T) and CASPT2[g1] levels with a large aANO basis set. The findings demonstrate again the necessity to go beyond CCSD to accomplish an accurate description of biradical molecules. Unlike the energetics of the Bergman reaction, there is no significant difference between the CASPT2 and the CCSD(T) methods. The present *ab initio* results support the latest experimental findings with the proviso that the computed ortho−para energy splitting suggests that the true value lies in the lower end of the experimentally proposed range.

The energy splittings as computed here in this study are graphically displayed in Figure 7 together with the experimental predictions. The figure demonstrates in a nice way the delicate balance which is required in modeling both the static and dynamic parts of the electron correlation by *ab initio* methods.

Acknowledgment. The authors express their gratitude to Prof. B. O. Roos and Dr. P.-Å. Malmqvist for helpful discussions. This study has been supported by a grant from the Swedish Natural Research Council (NFR) and by IBM Sweden under a joint study contract.

JA950504A