554 J. Am. Chem. Soc. 1986, 108, 554–556

Evidence for the Concerted Mechanism of the Diels–Alder Reaction of Butadiene with Ethylene

K. N. Houk,* Yi-Tsong Lin, and Frank K. Brown

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received August 12, 1985
Revised Manuscript Received November 29, 1985

Diels–Alder reactions of substituted dienes and dienophiles have been found to occur by both concerted and stepwise mechanisms.[1,2] The nature of the mechanism of the prototype Diels–Alder reaction of butadiene with ethylene to form cyclohexene is not only of fundamental interest but has generated fervid fulminations for favorite mechanisms.[1-5] We wish to report new experimental evidence that is compatible only with the concerted mechanism, as well as further theoretical evidence for the synchronicity of this concerted mechanism.[6]

The reactions of 1,1,4,4-tetradeuterio-1,3-butadiene with *cis*- or *trans*-1,2-dideuterioethylene were carried out at 185 °C for 36 h at a pressure of 1800 psi in a stainless steel bomb.[7-10] Infrared spectra of the unreacted dideuterioethylenes indicate that they do not isomerize under the conditions of the reaction. Each cyclohexene product was separated from butadiene dimers by preparative GLC[11] and was then epoxidized with *m*-chloroperbenzoic acid (Figure 1). The NMR spectrum of cyclohexene oxide (Figure 2A) has resonances for the protons at C_4 and C_5 at δ 1.19 and 1.38, corresponding to protons that are cis and trans to the epoxide oxygen.[12] The proton NMR spectra of the epoxides obtained from the reactions of *cis* and *trans*-dideuterioethylenes are clearly different. The DH couplings were partially eliminated by irradiation of the C_3 and C_6 deuteriums to give the spectra shown in Figure 2. The *cis*-dideuterio compound has a singlet resonance at δ 1.19, due to the product with C_4 and C_5 hydrogens cis to the epoxide, and a second singlet at δ 1.38, due to the compound with these hydrogens trans to the epoxide. The epoxide obtained from the reaction of *trans*-dideuterioethylene consists of a racemate with one $C_{4(5)}$ hydrogen cis to the epoxide and one hydrogen trans, coupled by 9 Hz. Although the NMR spectra of both compounds are complicated by the incomplete deuteration of reactants, the small peaks near the base line are not at positions expected for resonances of the "wrong" stereoisomers. These positions are marked with triangles in Figure 2B,C. The areas of the signals in the vicinity of these triangles indicate that there is less than 1% of the cis adduct in the trans product and vice versa.

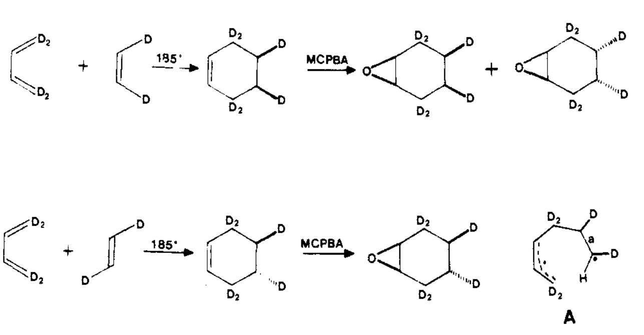

Figure 1. Reactions carried out to establish the stereospecificity of the parent Diels–Alder reaction. A is the potential diradical intermediate in these reactions.

The potential diradical intermediate, A in Figure 1, should have a barrier to rotation about single bond **a** of only 0–0.4 kcal/mol, the experimental and theoretical range of rotational barriers in primary radicals.[13] Extensive scrambling of stereochemistry would occur if this diradical intermediate were formed, even if the barrier to cyclization of the diradical were nearly negligible.[14] Indeed, butane-1,4-diyls labeled with deuterium undergo extensive rotation of the deuterated terminal methylenes before cyclization to cyclobutanes.[10,15] Our results require that the activation energy of the concerted stereospecific reaction is at least 3.7 kcal/mol lower than the activation energy for a stepwise reaction that could scramble stereochemistry. This conclusion is in the range of other estimates (2–10 kcal/mol) of the energy of concert of simple Diels–Alder reactions.[4,16] Our conclusions are in excellent agreement with the early calculations by Salem et al., which predict that the diradical transition state is 2–4 kcal/mol above the concerted.[17] MINDO/3 predicts that the stepwise reaction has a 21 kcal/mol lower activation energy than the synchronous concerted mechanism and that the reaction reported here would give extensive scrambling of stereochemistry in both the recovered ethylene and in the cyclohexane product.[18]

We have also carried out calculations in an attempt to distinguish between synchronous and asynchronous concerted mechanisms.[19] At several theoretical levels,[20] we have located stationary points that have C_s symmetry and have calculated harmonic vibrational frequencies for these stationary points to determine whether they are authentic transition structures.[21,22] Figure 3 summarizes the C_s stationary points obtained by RHF/STO-3G,[23] RHF/3-21G, and UHF/3-21G calculations. Geometries, energies,

---

*Address correspondence to this author at the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024.

(1) For an excellent recent review, see: Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(2) Houk, K. N. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 2, pp 181–271 and references therein.

(3) Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.*, **1984**, *106*, 203. Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

(4) (a) Doering, W. v. E.; Franck-Neumann, M.; Hasselman, D.; Kaye, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 3833. (b) Frey, H. M.; Pottinger, R. *J. Chem. Soc., Faraday Trans 1* **1978**, *74*, 1827.

(5) Stephenson, L. M.; Gemmer, R. V.; Current, S. *J. Am. Chem. Soc.* **1975**, *97*, 5909. Berson, J. A.; Malherbe, R. *J. Am. Chem. Soc.* **1975**, *97*, 5910.

(6) During the course of this work, MCSCF calculations, which predict a synchronous C_s transition structure for the parent Diels–Alder reaction were reported: Bernardi, F.; Bottini, A.; Robb, M. A.; Field, M. J.; Hillier, I. H.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1051.

(7) Tetradeuteriobutadiene was prepared by repeated exchange of the α protons of sulfolene (K_2CO_3, D_2O, 1,4-dioxane), followed by cracking at 130–160 °C and removal of SO_2 by scrubbing the gas with 10% aqueous NaOH (Cope, A. C.; Berchtold, G. A.; Ross, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 3859). NMR and mass spectral analysis indicated that the butadiene was >92% d_4. The *cis*- and *trans*-dideuterioethylenes were prepared by the methods of Nicholas and Carroll.[8] Analysis by infrared spectroscopy[9,10] indicated that the preparations are stereospecific. However, the dideuterioethylenes were contaminated by approximately 5–6% of monodeuterioethylene, as revealed by IR and mass spectral analysis.

(8) Nicholas, P. P.; Carroll, R. T. *J. Org. Chem.* **1968**, *33*, 2345.

(9) Arnett, R. L.; Crawford, B. L., Jr. *J. Chem. Phys.* **1950**, *18*, 118. The IR bands at 724, 842, and 809 cm^{-1} are characteristic of *trans*-1,2-dideuterio-cis-1,2-, and deuterioethylene, respectively.

(10) Dervan, P. B.; Santilli, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 3863.

(11) The separation was complete on a 20% SE-30 on Chromosorb W column at 100 °C. From a 2:1 ethylene/butadiene mixture, cyclohexene, 1,2-*trans*-divinylcyclobutane, 4-vinylcyclohexene, and 1,5-cyclooctadiene were obtained in a 42:2:53:3 ratio.

(12) These (tentative) assignments are made on the basis of the expected anisotropy of the epoxide ring: Paquette, L. A.; Fristad, W. E.; Schuman, C. A.; Beno, M. A.; Christoph, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 4645 and references therein.

(13) Krusic, P. W.; Meakin, P.; Jesson, J. P. *J. Phys. Chem.* **1971**, *75*, 3438. Pacansky, J.; Brown, D. W.; Chang, J. S. *J. Phys. Chem.* **1981**, *85*, 2562. Pacansky, J.; Schubert, W. *J. Chem. Phys.* **1982**, *76*, 1459 and references therein.

(14) For example, even if the activation energy for bond rotation were 0.4 kcal/mol greater than that for closure of the diradical to cyclohexene, the reaction would exhibit only 22% stereospecificity at 185 °C.

(15) Bartlett, P. D.; Cohen, G. M.; Elliott, S. P.; Hummell, K.; Minns, R. A.; Sharts, C. M.; Fukunaga, J. Y. *J. Am. Chem. Soc.* **1972**, *94*, 2099.

(16) Bartlett, P. D.; Schueller, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 6071.

(17) Townshend, R. F.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190.

(18) Dewar, M. J. S.; Griffin, A. C.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 6225. Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650.

(19) Isotope effects measured for the Diels–Alder reactions of anthracene with deuterated ethylenes have been interpreted as supporting a synchronous mechanism: Taagepera, M.; Thorton, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 1168.

0002-7863/86/1508-0554$01.50/0

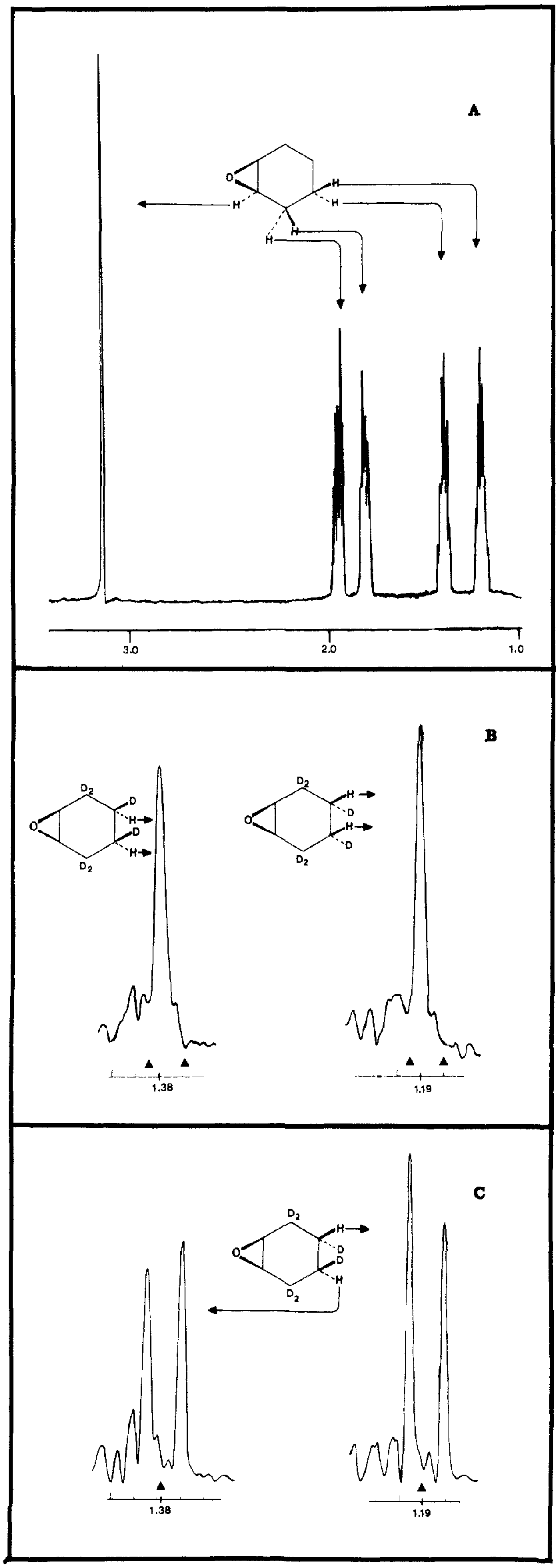

Figure 2. (A) Proton NMR spectrum, 600 MHz, of cyclohexene oxide. (B, C) High-field portions of the 600-MHz NMR spectra of the cyclohexene oxides formed from the epoxidation of the cyclohexene products of the reactions of 1,1,4,4-tetradeuteriobutadiene with (B) *cis*-dideuterioethylene and (C) *trans*-dideuterioethylene. In spectra (B) and (C), the deuteriums at C_3 and C_6 have been decoupled.

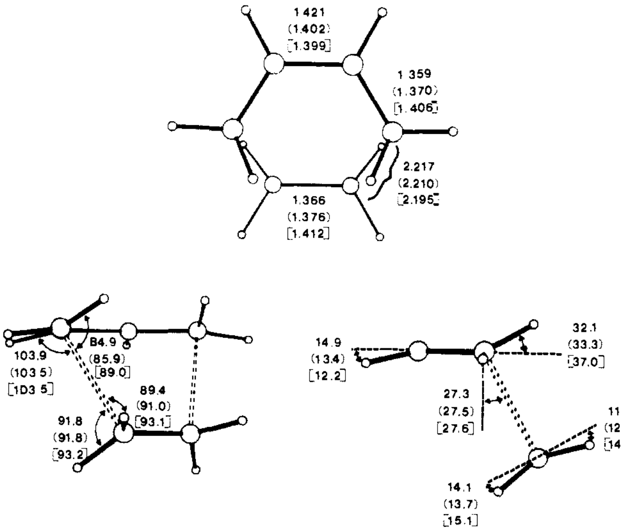

Figure 3. Summary of geometries of C_s stationary points for the butadiene-ethylene reaction. The parameters are (top to bottom) from STO-3G, (RHF/3-21G), and [UHF/3-21G] calculations.

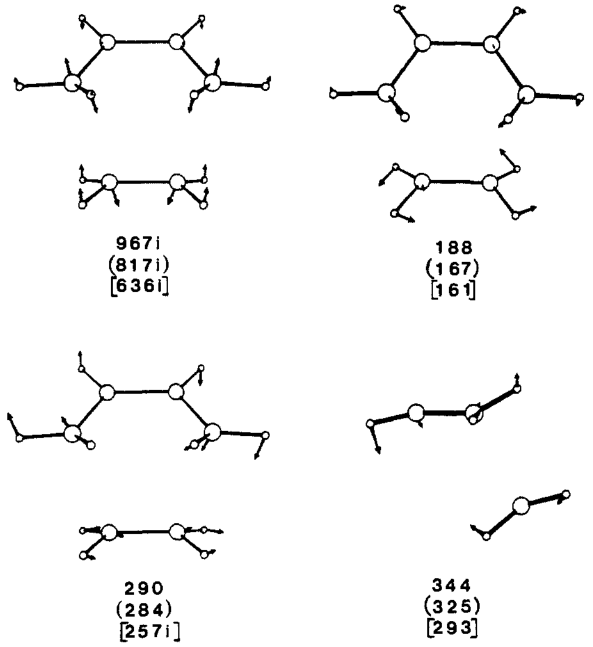

Figure 4. 3-21G transition vectors and low-energy vibrational motions for the C_s stationary points. Calculated frequencies are listed under each drawing.

and entropies are compared to other calculations and experiment in Table I.[24]

Figure 4 shows the transition vector and atomic motions involved in low-energy vibrations. At the RHF levels, there is only one

---

[20] STO-3G: Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. 3-21G: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. 6-31G*: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *20*, 213. MP2: DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229. All calculations were performed with GAUSSIAN82: Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN82, Carnegie-Mellon University, Pittsburgh, PA.

[21] Murrell, J. N.; Laidler, K. J. *Trans. Faraday Soc.* **1968**, *64*, 371.

[22] McIver, J. W., Jr. *Acc. Chem. Res.* **1974**, *7*, 72. In addition to group theory arguments about the possible symmetries of transition states, McIver has presented qualitative arguments which suggest that processes such as the Diels-Alder reaction are asynchronous.

[23] Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 4609.

[24] Additional calculations are reviewed in ref 1 and 6a; see also: Burke, L. A.; Leroy, G.; Sana, M., *Theor. Chim. Acta* **1975**, *40*, 313. Burke, L. A.; Leroy, G. *Ibid.* **1977**, *44*, 219. Jug, K.; Kruger, H.-W. *Theor. Chim. Acta* **1979**, *52*, 19.

Table I. Summary of Calculations on Butadiene–Ethylene C_s Stationary Points[a]

calculation	r_{16}	r_{12}	r_{23}	r_{56}	ΔE[b]	E_a[c]	$\Delta S^\ddagger$ (T)[d]
STO-3G	2.217	1.359	1.421	1.366	36.0	38.6	−42.7
RHF/3-21G	2.210	1.370	1.402	1.376	35.9	38.3	−41.9
4-31G+3×3CI[e]	2.210	1.400	1.360	1.400	42.6		
UHF/3-21G	2.195	1.406	1.399	1.412	27.8	26.9	−42.3
UMINDO/3[f]	*g*					32[h]	−36.9[i]
MINDO/3-CI[j]	2.80, 1.52	1.43, 1.49	1.34	1.45		28.2	
CAS2-STO-3G[k]	2.236	1.394	1.426	1.398			
CAS1-4-31G[l]	2.244	1.389	1.376	1.398			
exptl I[m]						27.5	−30 (760–921 K)
exptl II[n]						32.8–34.3	−41 (800 K)

[a] Bond lengths, r, in Å, energies in kcal/mol, entropies in cal/(deg mol). Absolute energies (au) of the transition structures are −230.03689 (STO-3G), −231.60321 (RHF/3-21G), −231.61621 (UHF/3-21G), −232.87822 (6-31G*//UHF/3-21G), −233.67951 (RMP2/6-31G*//UHF/3-21G), −232.89347 (UHF/6-31G*//UHF/3-21G). [b] Vibrationless energies. [c] The calculated ΔE are for 0 K, and E_a are the calculated ΔE plus zero-point energy and heat capacity corrections for 600 K. Experimental E_a are for the temperature listed in the last column. [d] Since ab initio vibrational frequencies are too large by about 10%, the vibrational frequencies are scaled ($\nu = 0.8929\nu_{\text{calcd}}$). The activation entropies are calculated for 600 K. [e] Reference 17. [f] Reference 18. [g] Not reported. [h] E_a is 9.5 kcal/mol before correction, and 32 kcal/mol after correction.[18] [i] Calculated from the UMINDO/3 entropy of the transition state and the experimental entropies of butadiene and ethylene. [j] Reference 18. [k] MCSCF with the STO-3G basis set and a six-electron CASCF, from ref 6. [l] MCSCF with the 4-31G basis set and a four electron CASCF, from ref 6. [m] Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198. The estimated E_a at 0 K is 25.1 kcal/mol. [n] Calculated from E_a of cyclohexene cycloreversion and the experimental heat of reaction: Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878. Tsang, W. *J. Chem. Phys.* **1965**, *42*, 1805. Tardy, D. C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508.

imaginary frequency, and a C_s synchronous transition structure is predicted. At 185 °C, the temperature at which the reaction occurs, the low-energy vibrations shown would be excited, since RT at 185 °C is 0.9 kcal/mol, or 320 cm^{-1}. As noted in Table I, the activation energies are overestimated by about 8 kcal/mol, a typical error resulting from the neglect of correlation energy in calculations of pericyclic reaction transition structures at the RHF level.[25]

Restricted Hartree–Fock (RHF) calculations require each orbital to be doubly occupied and may be biased in favor of a concerted mechanism.[26] We also located a C_s stationary point with an unrestricted Hartree–Fock (UHF) calculation.[27] The UHF calculated activation energy now agrees quite well with an experimental value. However, the UHF/3-21G C_s stationary point has two imaginary frequencies (Figure 4), so that at this level, there must be a lower energy, unsymmetrical transition structure. However, the UHF calculations are highly biased toward diradical character, since the wavefunction is approximately 50% triplet. A UHF/3-21G optimized hex-2-ene-1,6-diyl singlet diradical with a C_s geometry is calculated to be only 6 kcal/mol higher in energy than butadiene plus ethylene! Thus, UHF drastically overestimates the stability of the diradical as compared to the reactants or the C_s stationary point. MCSCF calculations are necessary to give a balanced description of closed-shell species and diradicals. During the course of this work, Bernardi et al. reported several MCSCF calculations on the butadiene–ethylene reaction. These calculations (Table I) also predict a synchronous transition structure.[6]

These results show that qualitative arguments that claim to prove that Diels–Alder reactions must be asynchronous are fallacious.[28,29] As we suggested earlier,[30] systematic deficiencies in semiempirical techniques lead to erroneous predictions of stepwise mechanisms for concerted cycloadditions. The results reported here suggest that important errors arise in Dewar's calculations[18] due to the use of UHF theory, which guarantees the prediction of a stepwise diradical mechanism. Semiempirical RHF calculations give results similar to ab initio calculations.[31]

Our experiments and calculations are consistent with a synchronous concerted mechanism for the reaction of butadiene with ethylene.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research. We thank Professors William von Eggers Doering, John A. Pople, William L. Jorgensen, and Michael J. S. Dewar and David C. Spellmeyer for helpful discussions. The 600-MHz NMR spectra were obtained at the National Institutes of Health NMR Facility for Biomedical Studies at Carnegie–Mellon University.

Registry No. Butadiene, 106-99-0; ethylene, 74-85-1.

---

(25) Rondan, N. G.; Houk, K. N. *Tetrahedron Lett.* **1984**, *24*, 2519. Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099.

(26) Szabo, A.; Ostlund, N. S. "Modern Quantum Chemistry"; Macmillan Publishing Co.: New York, 1982; pp, 104–107.

(27) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

(28) Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 203. Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

(29) Dewar, M. J. S.; Healy, E. F. *J. Am. Chem. Soc.* **1984**, *106*, 7127.

(30) Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4511. See also: Ortega, M.; Oliva, A.; Lluch, J. M.; Bertran, J. *Chem. Phys. Lett.* **1983**, *102*, 317.

(31) Lee, I.; Han, E. S.; Choi, J. Y. *J. Comput. Chem.* **1984**, *5*, 606. Dewar, M. J. S., unpublished results.