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An *Ab Initio* SCF-MO Study of Conformational Properties of Cyclodeca-1,2,3-triene

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ABSTRACT

Ab initio calculation at HF/6-31G* level of theory for geometry optimization and MP2/6-31G*//HF/6-31G* for a single point total energy calculation are reported for the important energy-minimum conformations and transition-state geometries of of cyclodeca-1,2,3-triene (**1**). The most favorable conformation of **1** is a unsymmetrical twist-chair (**1-TC**) structure. Degenerate interconversion of **1-TC** with itself can take place *via* C_S symmetric half-chair (**1-HC,** C_S). The calculated energy barrier for this processes is 30.3 kJ mol^{-1}, respectively. The twist (**1-Twist**) conformation of the **1**, with C_2 symmetry, is calculated to be more unstable than the twist-chair (**1-TC,** C_1) geometry by 12.4 kJ mol^{-1}. Interconversion between **1-TC** and **1-Twist** conformations takes place *via* the unsymmetrical transition state, which is 50.3 kJ mol^{-1} above **1-TC** form. The boat (C_1) geometry of **1** is higher in energy by 19.1 kJ mol^{-1}, respectively. Ring inversion in twist-chair and boat conformations takes place *via* C_2 symmetric **1-TB** (**1-HC,** C_2) form and requires 65.6 kJ mol^{-1}.

Keywords. Cyclic cumulenes; Strained molecules; Conformational analysis; Molecular modelling.

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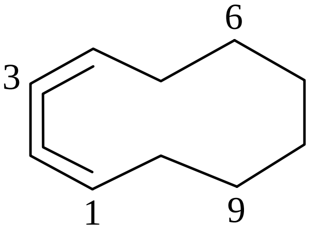
INTRODUCTION

Cyclic structures which contain (*Z*) double bonds are stable in any ring size [1]. For cyclic allenes [2], small rings engender considerable deformation from a linear geometry in which π orthogonality is maintained. Thus, the smallest kinetically stable cyclic allene is cyclonona-1,2-diene [3]. In contrast to cyclic allenes, little is know about the structure of cyclic buta-1,2,3-trienes. The smallest isolable cyclic butatriene reported to date is cyclonona-1,2,3-triene [4]. Elegant experiments have been described for generation and trapping of the smaller cyclic butatrienes [5-7]. One of the most fascinating aspects of these compounds is their smooth transition from shelf-stable compounds to reactive intermediates as ring size diminishes. Cyclic butatrienes comprise a fascinating and fundamental collection of molecules, for which very little data are presently available. The only quantitative estimates of strain energies and geometries in compounds five-to-ten membered originates from aa series of semiempirical (MNDO) calculations [4]. Recently we reported the structural optimization and conformational interconversion pathways of the strained cyclic butatrienes with five-to-nine membered rings by *ab initio* calculations [8].

This study was undertaken to investigate the structural optimization and conformational interconversion pathways of the strained cyclic butatriene **1** by comparing the geometries (HF/6-31G*) and conformational energies (MP2/6-31G*//HF/6-31G*). The results from MP2/6-31G*//HF/6-31G* calculations are used in the discussions below.



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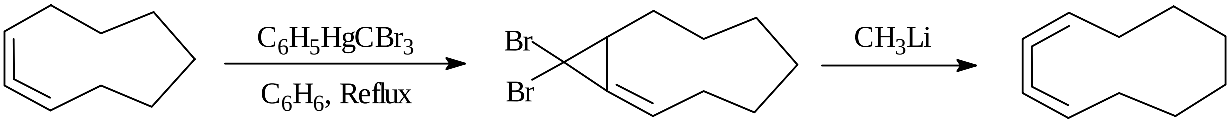
The first known cyclic butatriene was 1,2,3-cyclodecatriene (**1**) reported in 1967 [9]. Although minimally strained, this compound shares the reactivity of most butatrienes and readily polymerizes upon exposure to oxygen. Treatment of 1,2-cyclononadiene (**2**) with one equivalent of phenyl(tribromomethyl)mercury in refluxing benzene followed by removal of phenylmercuric bromide and the solvent gives 10,10-dibromobicyclo[7.1.0]decene (**3**) in nearly quantitative yield [10] (see Scheme 1). Treatment of (**3**) with methyl lithum in ether at -80° followed by warming to 0° and hydrolytic work-up leads to **1**.

Results and Discussion

Conceptually, **1** may be regarded to be constructed by inserting two *sp*-hybridized carbon atoms in the carbon-carbon double bond of (*Z*)-cyclooctene [11]. Therefore, it can potentially exist in twist-chair, twist, boat, chair and twist-boat conformations (see Figure 1). Cyclic butatriene **1** is a fascinating molecule, for which little data are presently available.

The results of *ab initio* calculations for structure optimization and conformational interconversion pathways of **1** are shown in Figure 1 and Table 1. Eight geometries (four energy minima and four transition



2 **3** **1**

Scheme 1

states) were found to be important in description of the conformational properties of **1**. The most stable conformation of **1** is the unsymmetrical twist-chair (**1-TC**) form (see Figure 2 and Table 1).

The calculated energy for the second energy-minimum conformation, *viz*, the C_2 symmetric twist (**1-Twist**) is only 12.4 kJ mol^{-1} above that of **1-TC** (see Figure 2 and Table 1). As the unsymmetrical local C_2 (**1-Local C_2**) form is 12.7 kJ mol^{-1} higher than **1-TC** conformation (see Table 1). The calculated energy for the unsymmetrical boat (**1-Boat**) form is 19.1 kJ mol^{-1} higher than that of **1-TC** conformation. A chiral unsymmetrical energy minimum conformation, such as twist-chair form (**1-TC**), and a C_S symmetric transition state (**4-Chair**) can be envisaged for this cyclic triene (see Figure 2 and Table 1). The energy barrier for conformational enantiomerization of **1-TC** is 30.3 kJ mol^{-1}. Ring inversion of **1-TC** takes place *via* the C_2 symmetric twist-boat (**1-TB**) conformation (Figure 1). The energy barrier for ring inversion of **1-TC** is 65.6 kJ mol^{-1}.

Selected structural data for various geometries of **1** are given in Table 1. The comparison of bond lengths showed fairly small differences. However, the bond angles are expanded in transition-state geometries.

In conclusion, compound **1** can exist as twist-chair (C_1) conformation. Conformational racemization of this chiral form requires 30.3 kJ mol^{-1}. Ring inversion in twist-chair conformation takes place *via* C_2 symmetric twist-boat conformation. It would be valuable, of course, to have direct structural data on **1** for comparison with the results of the *ab initio* calculations.

Computational details

Semiempirical calculations were carried out using the AM1 method [12] with the MOPAC 6.0 program package [13]. Energy minimum geometries were located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints. The geometries of the transition states for conformational interconversion of the equilibrium structures were obtained using the optimized geometries of the equilibrium structures according to procedure of Dewar *et al.* [14] (Keyword SADDLE).

The AM1 results were used as input for the *ab initio* molecular orbital calculations, which were carried out using the GAUSSIAN 98 [15] program. Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints [16]. The restricted Hartree-Fock calculations with the split-valence 6-31G* basis set which include a set of d-type polarization functions on all non-hydrogen atoms were used in these calculations [17]. Single point energy calculations at MP2/6-31G*//HF/6-31G* level were used to evaluate the electron correlation effect in the energies and order of stability of conformers.

Vibrational frequencies were calculated at the 6-31G* level for all minimum energies and transition states, which were confirmed to have zero and one imaginary frequency, respectively. The frequencies were scaled by a factor of 0.91 [18] and used to compute the zero-point vibrational energies.

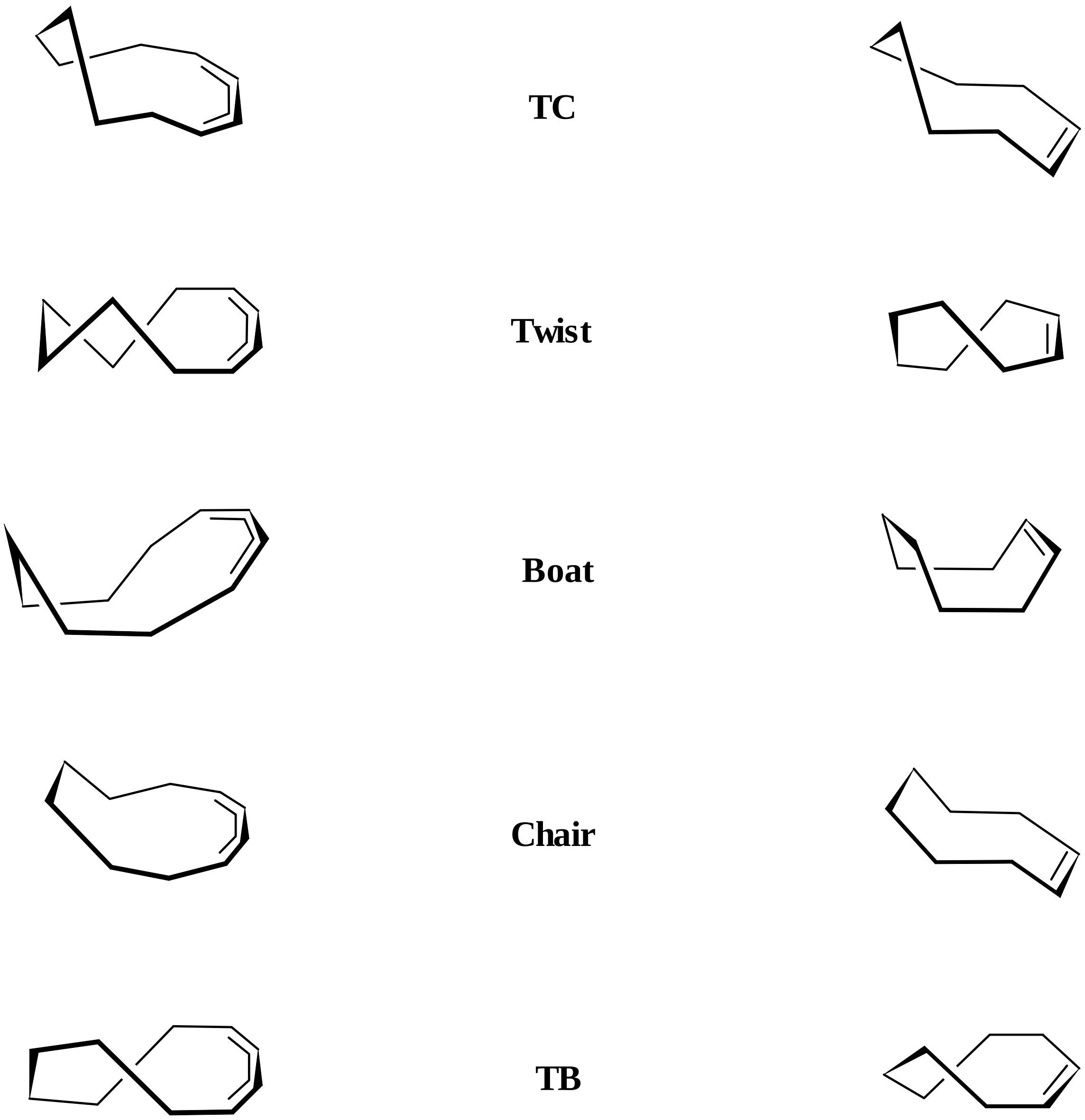


Figure 1. Important conformations of **1** and (*Z*)-cyclooctene.

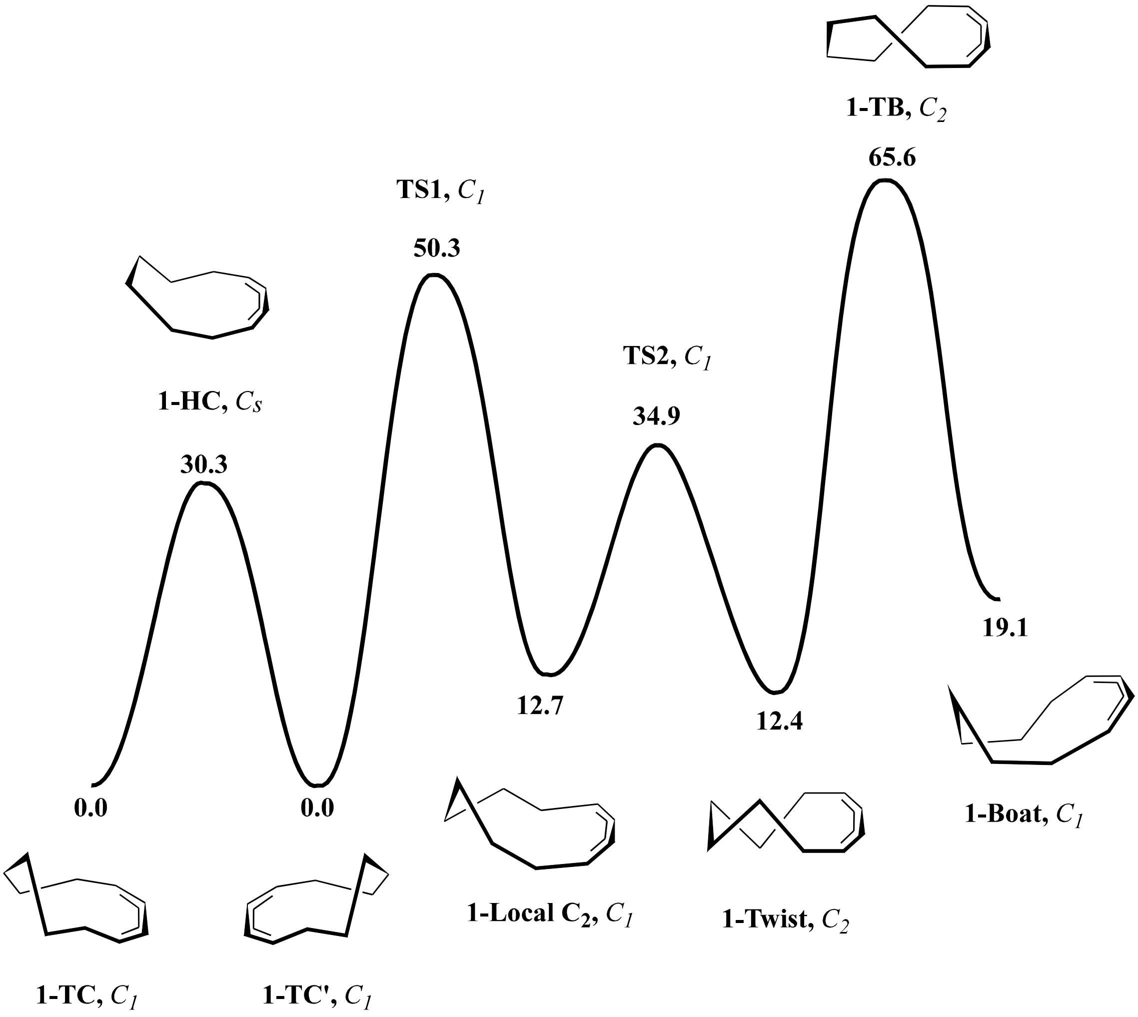


Figure 2. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ mol^{-1}) profile for conformational interconversion of various geometries of **1**.

Table 1. Calculated total and zero-point vibrational (zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations) energies (hartree), relative energy (including zero-point energy, kJ.mol^{-1}) for different geometries of cyclodeca-1,2,3-triene (1)

Structure	**1-TC,** C_1	**TS1,** C_1	**1-Local C$_2$,** C_1	**TS2,** C_1	**1-Twist,** C_2	**1-TB,** C_2	**1-Boat,** C_1	**1-HC,** C_s
HF/6-31G*// HF/6-31G*	-386.7286	-386.7089	-386.7223	-386.7155	-386.7241	-386.6999	-386.7199	-386.7172
MP2/6-31G*// HF/6-31G*	-388.0131	-387.9939	-388.0084	-387.9997	-388.0084	-387.9880	-388.0057	-388.0016
ZPE	0.2295	0.2294	0.2296	0.2293	0.2295	0.229	0.2294	0.2295
$E_{\mathrm{rel}}{}^{a}$	0.0	51.61	16.72	34.03	11.92	74.60	22.55	29.94
$E_{\mathrm{rel}}{}^{b}$	0.0	50.31	12.66	34.91	12.43	65.63	19.09	30.30
r_{12}	1.304	1.304	1.305	1.304	1.305	1.305	1.304	1.304
r_{23}	1.263	1.262	1.263	1.262	1.263	1.263	1.262	1.263
r_{34}	1.303	1.304	1.305	1.303	1.305	1.305	1.302	1.304
r_{45}	1.516	1.523	1.521	1.518	1.516	1.528	1.517	1.514
r_{56}	1.542	1.541	1.546	1.563	1.536	1.553	1.543	1.534
r_{67}	1.542	1.565	1.536	1.538	1.549	1.540	1.543	1.551
r_{78}	1.536	1.553	1.539	1.540	1.545	1.565	1.544	1.568
r_{89}	1.542	1.549	1.550	1.550	1.549	1.540	1.542	1.551
r_{910}	1.533	1.537	1.542	1.537	1.536	1.553	1.542	1.534
r_{1011}	1.516	1.520	1.522	1.518	1.516	1.528	1.520	1.514
θ_{123}	167.9	168.0	171.1	171.5	174.7	161.6	164.9	172.6
θ_{234}	172.3	171.1	167.2	174.9	174.7	161.6	166.6	172.6
θ_{345}	124.3	123.1	120.1	126.9	124.7	117.6	121.3	122.7
θ_{456}	117.9	117.9	115.2	122.1	116.3	113.8	116.7	114.9
θ_{567}	118.5	121.6	117.0	120.3	115.0	116.9	117.5	114.0
θ_{678}	118.9	120.9	116.3	115.1	114.4	120.3	121.3	121.5
θ_{789}	114.1	112.7	113.6	113.3	114.4	120.3	118.0	121.5
θ_{8910}	115.1	116.7	116.6	116.3	115.0	116.9	119.5	114.0
θ_{91011}	114.3	113.7	117.0	116.2	116.3	113.8	114.1	114.9
θ_{10111}	121.8	121.3	122.7	123.3	124.7	117.6	118.5	122.7
ϕ_{1234}	-7.3	12.5	7.0	-2.1	-1.4	6.6	-1.9	0.0
ϕ_{2345}	35.0	-19.8	18.7	-1.6	1.1	-3.9	19.5	-11.8
ϕ_{3456}	17.8	-61.1	-68.7	-26.6	20.7	44.9	5.5	0.7
ϕ_{4567}	-88.2	76.3	51.6	-1.2	-64.2	-138.4	-89.6	69.1
ϕ_{5678}	74.5	1.1	60.3	87.2	121.3	77.9	69.4	-123.2
ϕ_{6789}	64.5	-124.1	-161.9	-162.8	-147.5	-2.8	87.1	0.0
ϕ_{78910}	-155.1	146.9	107.7	119.5	121.3	77.9	-69.5	123.2
ϕ_{891011}	69.3	-75.8	-65.1	-63.3	-64.2	-138.4	-59.1	-69.1
ϕ_{910111}	-5.7	30.1	48.6	30.6	20.7	44.9	71.6	-0.7
ϕ_{101112}	-26.4	13.7	-26.2	6.8	1.1	-3.9	-15.9	11.8

[a] Relative energy with respect to the most stable conformation from HF/6-31G*// HF/6-31G* calculations.

[b] Relative energy with respect to the most stable conformation from MP2/6-31G*// HF/6- 31G* calculations.

References

1. K. B. Wiberg, *Angew. Chem. Int. Ed. Engl.*, **25** (1986) 312; A. Greenberg and J. F. Liebman, *Strained Organic Molecules*; Academic Press: New York (1978); G. Kobrich, *Angew. Chem. Int. Ed. Engl.*, **12** (1973) 464
2. R. P. Johnson, Chem. Rev., **89** (1989) 1111; S. R. Landor, Ed *The Chemistry of the Allenes*; Academic Press: New York, Vol. 1-3 (1982).
3. A. T. Blomquist, Jr R. E. Burger, L. H. Liu, J. C. Boher, A. C. Sucsy, and J. Kleis, *J. Am. Chem. Soc.*, **73** (1951) 5510; L. Skattebol, *Tetrahedron Lett*., **9** (1961) 167; L. Skattebol and S. Solomon, *Org. Synth.*, **49** (1969) 35
4. R. O. Angus Jr and R. P. Johnson, *J. Org. Chem*., **49** (1984) 2880
5. H. G. Zoch, G. Szeimies, R. Romer, and R. Schmitt, *Angew. Chem. Int. Ed. Engl.,* **20** (1981) 877
6. H. G Zoch, G. Szeimies, R. Romer, G. Germain, and J. P. Declercq, *Chem. Ber*., **116** (1983) 2285
7. R. S. Macomber and T. C. Hemling, *J. Am. Chem. Soc*., **108** (1986) 343
8. I. Yavari, H. Kabiri-Fard, Sh. Moradi, B. Adib, and M. Matlobi, *Monatsh. Chem.*, **134** (2003) 23.
9. W. R. Moore and T. M. Ozretich, *Tetrahedron Lett.*, (1967) 3205.
10. D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4** (1965) 127.
11. A. D. Strickland and R. A. Caldwell, *J. Phys. Chem.*, **97** (1993) 13394.
12. M. J. S. Dewar, E. G. Zeobish, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107** (1985) 3907; M. J. S. Dewar and K. M. Dieter, *J. Am. Chem. Soc.*, **108** (1986) 8072.
13. J. J. P. Stewart, QCPE 581, Department of Chemistry, Indiana University, Bloomington, IN; J. J. P. Stewart, *J. Comput. Aided Mol. Des.*, **4** (1990) 1.
14. M. J. S. Dewar, E. F. Healy, and J. J. P. Stewart, *J. Chem. Soc., Faraday Trans.*, **80** (1984) 227.
15. Gaussian 98, Revision A. 6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Startmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rubuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Oritz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Comperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian. Inc., Pittsburgh PA 1998.
16. F. Jensen, "*Introduction to Computational Chemistry*", Wiley, New York, 1999; W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople., "*Ab Initio Molecular Orbital Theory*", Wiley, New York, 1986.
17. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28** (1973) 213.
18. R. S. Grev, C. L. Janssen, and H. F. Schaefer, *Chem. Phys.*, **95** (1991) 5128.