Interconversion of diborane (4) isomers

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Highly correlated electronic structure calculations using many-body perturbation theory (MBPT) and coupled-cluster (CC) gradient techniques are applied to a study of a reaction pathway which links the two forms [C_{2v} and D_{2d}] of diborane(4) [B_2H_4]. A reaction coordinate which preserves C_2 symmetry is studied, as this mechanism is allowed by orbital symmetry rules. However, calculations show that the minimum energy path does not conform to this idealized mechanism. Rather, the reaction coordinate bifurcates, and the transition state contains no nontrivial elements of symmetry. At the level of partial fourth-order many-body perturbation theory [SDQ-MBPT(4)] with a large triple-zeta plus double polarization basis set, differences in distances between the hydrogen atoms corresponding to the bridge atoms in the C_{2v} form and the two boron atoms [$\delta r(\text{B–H}) = |r(\text{B}_1\text{–H}) - r(\text{B}_2\text{–H})|$] are 0.14 and 0.81 Å, reflecting the pronounced asymmetry of the transition state structure. We find that the C_{2v} isomer should be the thermodynamically favored form of B_2H_4. At the coupled-cluster singles and doubles level with a noniterative treatment of triple excitation effects, the barrier to isomerization is found to be 6.3 kcal/mole using a large generally contracted basis set. This result, along with statistical arguments concerning the rate of reaction, suggest that equilibrium may be established relatively rapidly, and that rigid molecule treatments of B_2H_4 spectra may not be appropriate.

I. INTRODUCTION

In the past two decades, the diborane(4) [B_2H_4] molecule has been the subject of considerable theoretical study.[1–11] Recent investigations[7–11] have demonstrated that there are at least two minima on the global B_2H_4 potential energy surface. One of these forms has two three-center two-electron hydrogen bridge bonds and a butterfly-shaped structure with C_{2v} symmetry, while the other has no bridge bonds and a staggered D_{2d} structure like that found in the V state of ethylene (see Fig. 1). This system is particularly appealing for theory because it is one of the simplest boron hydrides which exhibits structural isomerism. In addition, the recent preparation of B_2H_4 by successive proton abstraction from B_2H_6 and its subsequent characterization by photoionization mass spectrometry[12] offers hope for experimental confirmation of theoretical predictions concerning this system.

Calculations by Lipscomb and co-workers[8,9] and by Curtiss and Pople[10,11] have unanimously predicted that the C_{2v} and D_{2d} isomers of B_2H_4 (hereafter referred to as I and II, respectively) have nearly identical energies, with the most recent calculations[10] predicting an energy difference of only 0.1 kcal/mole which favors I. Calculated vertical and adiabatic ionization potentials[10,11] of both forms were used to interpret the photoionization experiments carried out by Ruscic, Schwarz, and Berkowitz (RSB),[12] who observed

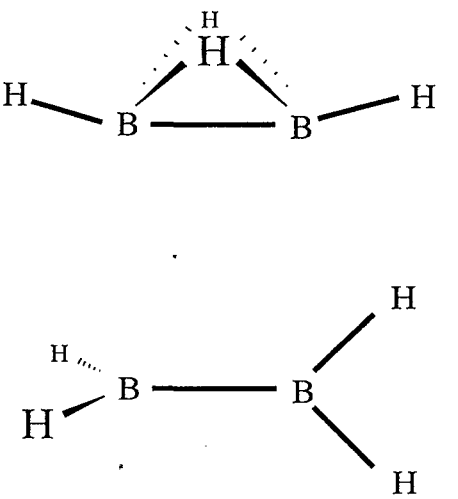

FIG. 1. Structures of the two stable B_2H_4 isomers, I (C_{2v} symmetry) and II (D_{2d} symmetry).

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ionization of B_2H_4 at photon energies which indicate that the $B_2H_4^+$ precursor is the C_{2v} isomer. The photoionization onset of the D_{2d} form has not been directly observed, but is predicted to lie at approximately 10.5 eV by theory.[10] At first glance, one might conclude that these results suggest that the C_{2v} form is the kinetically favored product of proton abstraction from B_2H_5 and that the barrier to isomerization is quite high. However, RSB argue that ionization of II may be occurring, but is difficult to resolve from the already strong ionization signal of I, which begins to appear at $\sim$9.7 eV. In addition, they suggest that II may be the precursor of $B_2H_2^+$, which is formed by fragmentation of a B_2H_4 cation and has been observed experimentally. If the latter suggestion is correct, then RSB argue that the relative abundance of the two isomers is roughly 1:1, based on the relative intensities of $B_2H_4^+$ and $B_2H_2^+$ photoion signals. This possibility alternatively suggests a rapid establishment of isomeric equilibrium.

From the above discussion, it is clear that an understanding of the isomerization pathway in B_2H_4 will be useful in the interpretation of new experiments and further analysis of those carried out by RSB. In addition, a detailed exploration of the isomerization mechanism may be useful in establishing models for similar processes in the higher boranes, including the rapid hydrogen scrambling which is observed in essentially all of the boron hydrides.[36] RSB[12] have suggested that the two isomers interconvert by a stepwise mechanism, involving planar D_{2h} structures as intermediates. By using a combination of experimental data and theoretical calculations, they estimate that the barrier height associated with such a process would be approximately 30 kcal/mole, sufficiently high to "freeze" out the isomeric components. However, they also suggest that a lower energy mechanism might be possible. Indeed, it is a straightforward matter to show that a single-step mechanism involving a reaction pathway which preserves C_2 symmetry[13] is allowed by orbital symmetry rules. This possibility has not previously been addressed in the literature, and its study forms the principal focus of this paper.

II. THEORETICAL METHODS

All calculations reported here were carried out with the newly developed ACES II program system.[14] This program package has been designed to take full advantage of Abelian point group symmetry, and has been optimized for modern vector supercomputers such as the Cray YMP, which was used for all calculations reported here. Most of ACES II has been written at the University of Florida in the past two years, but it also includes the MOLECULE[15] and ABACUS[16] programs for evaluation of integrals and derivatives of the integrals, the latter of which is required to compute the gradient of the electronic energy. Both programs are ideally suited to ACES II, as they exploit symmetry through the use of symmetry adapted basis functions and perform impressively on vector supercomputers. In addition, they have been written to handle generally contracted basis sets[17] in an efficient way.

Structures of isomers I and II were first located using second-order many-body perturbation theory[18] [MBPT(2)] and partial fourth-order MBPT [SDQ-MBPT(4)] with the double-zeta basis sets of Dunning,[19] augmented with our usual set of polarization exponents.[20] Starting with the DZP-SDQ-MBPT(4) structures, additional geometry optimizations were carried out with a larger triple-zeta plus double polarization basis set [TZ2P[21]] at the SDQ-MBPT(4) level. Geometry optimizations for the two stable structures were also performed at the coupled-cluster singles and doubles (CCSD) level. However, the results were not significantly different from those obtained with SDQ-MBPT(4) to warrant the cost of optimizing the transition state structure (C_1 symmetry) at this level of theory. As a result, the TZ2P-SDQ-MBPT(4) structures were used in all of the high-level single point calculations discussed in the following section. All geometry optimizations were performed with recently developed analytic gradient techniques;[22] minimizations used the Morse-adjusted Newton–Raphson algorithm,[23] while transition state searches were performed with eigenvector following methods.[24] In the latter optimizations, the exact Hessian was used to begin the calculation, and Hessian update procedures were used subsequently.

To obtain accurate estimates of the energy difference between I and II as well as the height of the barrier which separates them, single point energy calculations were carried out at various levels of MBPT as well with the CCSD,[25] CCSD + T(CCSD),[26] and CCSD(T)[27,28] coupled-cluster[29] approaches. To gain some understanding of basis set effects, these calculations were carried out with both the DZP and TZ2P basis sets, and with the PVTZ correlation consistent generally contracted basis set of Dunning.[30] The latter basis has been optimized specifically for correlated calculations, and contains 30 functions for each boron atom ($4s3p2d\,1f$) and 14 functions on the hydrogen atoms ($3s2p1d$). In the single point calculations, the d and f polarization functions were composed of the set of pure spherical harmonics corresponding to each angular momentum, while a full set of six Cartesian d functions were used in the optimizations. Zero-point vibrational contributions to the isomerization energy and barrier height were estimated from the DZP-MBPT(2) harmonic force fields, which were evaluated by numerical differentiation of analytical gradients.[31]

III. RESULTS

Geometrical parameters optimized at the DZP-MBPT(2) and TZ2P-SDQ-MBPT(4) levels for both I and II as well as the transition state are presented in Table I; Table II contains a complete set of Cartesian coordinates corresponding to the TZ2P-SDQ-MBPT(4) structures. At the DZP-MBPT(2) level, harmonic frequencies and infrared intensities were evaluated for all three structures; these results are presented in Table III.

A. Interconversion pathway

Initial transition state searches using the eigenvector following algorithm were performed at the DZP-MBPT(2) level. Searches were started at the DZP-SCF minimum energy geometry of isomer II, using eigenvectors obtained from

TABLE I. Energies and geometrical parameters for the two structures of B_2H_4 and the transition state for their interconversion. Energies are given in hartree, bond distances in Å, angles in degrees.

(a) C_{2v} form (I)	DZP-MBPT(2)	TZ2P-SDQ-MBPT(4)
Energy	− 51.833 20	− 51.907 24
r(BB)	1.484	1.458
$r(BH_t)$	1.176	1.169
$r(BH_b)$	1.354	1.333
$\alpha(BBH_t)$	173.5	174.0
$\alpha(H_bBH_b)$	83.2	84.3
(b) D_{2d} form (II)		
Energy	− 51.836 19	− 51.909 71
r(BB)	1.671	1.648
r(BH)	1.200	1.191
α(HBB)	121.6	121.9
(c) Transition state		
Energy	− 51.821 86	− 51.896 29
r(BB)	1.541	1.517
$r(B_1H_{t1})$	1.181	1.171
$r(B_2H_{t2})$	1.184	1.177
$r(B_2H_{b1})$	1.323	1.303
$r(B_2H_{b2})$	2.063	2.026
$r(B_2H_{b1})$	1.465	1.444
$r(B_2H_{b2})$	1.220	1.213
$\alpha(B_2B_1H_{t1})$	168.0	168.4
$\alpha(B_1B_2H_{t2})$	139.8	141.5
$\theta(H_{t1}B_1B_2H_{t2})$	160.4	160.2
$\alpha(H_{b1}B_1H_{b2})$	67.7	68.4
$\alpha(H_{b1}B_2H_{b2})$	94.8	94.9
$\alpha(H_{t1}B_1H_{b1})$	116.7	116.9
$\alpha(H_{t1}B_1H_{b2})$	132.1	131.9
$\alpha(H_{t2}B_2H_{b1})$	111.4	111.8
$\alpha(H_{t2}B_2H_{b2})$	123.5	122.6

the internal coordinate harmonic force constant matrix (Hessian). From this point, the eigenvector corresponding to the second smallest eigenvalue of the Hessian[32] was followed out of the potential well and a stationary point was located after 12 geometry steps. Subsequent calculation of the harmonic force constants at this geometry, however, revealed that the Hessian contained two negative eigenvalues. One of these belonged to a mode of a symmetry and corresponds to the presumed reaction coordinate, while the other is associated with a nonsymmetric b mode and indicates that this structure is unstable with respect to a lowering of symmetry to C_1. Following this, an additional search was launched from this second-order saddle point; the a mode having a negative eigenvalue was searched uphill, while the energy was minimized along all other modes (including the b mode mentioned above). Convergence to a true transition state was extremely rapid, and its character was confirmed by evaluation and diagonalization of the harmonic force constant matrix. A final estimate of the transition state geometry was obtained by location of the stationary point at the SDQ-MBPT(4) level with a TZ2P basis set, which contains polarization functions that have been optimized for correlated calculations.[21] The process of locating this transition state clearly illustrates the power of the eigenvector following method,[24] as the two separate searches started from regions with zero and two negative eigenvalues in the Hessian matrix, respectively, and standard Newton–Raphson approaches will fail in either case.

Our calculations indicate that the isomerization pathway linking I and II through the C_2 region of configuration space is not preferred by nature, even though such a route is consistent with orbital symmetry rules. In the language of Dewar,[33] this reaction is concerted, but not synchronous. As the C_2 pathway is followed from the D_{2d} structure, the surface contains a branch point which represents the confluence of two different but equivalent pathways which pass through transition states on their way to structure I. It is significant to note that the energy difference between the second-order saddle point having C_2 symmetry and the true transition state geometries on either side of it is small (< 1 kcal/mole). This is due to the soft nature of a transverse mode which acts to interchange the positions of the two hydrogen atoms. Consequently, the potential energy surface exhibits a soft double-minimum perpendicular to the direction of net reactive flux (see Fig. 2), and the conformational freedom afforded in the isomerization is extremely high. Although it would be meaningless to calculate partition functions based on the *harmonic* vibrational frequency for this transverse mode, the entropy of activation is probably large, suggesting a rapid isomerization process. Furthermore, the rate of reaction is additionally enhanced by the large number of equivalent reaction channels on the potential energy surface relative to starting materials, which is given by the one half the rotational symmetry number of the stable isomers [2 for I→TS and 4 for II→TS].[34]

TABLE II. Cartesian coordinates for isomers I and II and the transition state linking them, optimized at the SDQ-MBPT(4) level of theory with the TZ2P basis set. All coordinates are in bohr, and the molecules have been placed in the principal axis orientation.

	Isomer I			Isomer II			Transition state		
	X	Y	Z	X	Y	Z	X	Y	Z
B	1.3778	0.000	− 0.1155	0.000	− 1.8897	0.000	1.4682	− 0.0766	0.1161
B	− 1.3778	0.0000	− 0.1155	0.0000	1.8897	0.0000	− 1.3966	0.0188	− 0.0930
H	0.0000	1.6911	1.1461	1.3508	− 1.3508	2.7483	0.2750	− 0.5788	1.9793
H	0.0000	− 1.6911	1.1461	− 1.3508	1.3508	2.7483	3.6493	0.2628	0.0303
H	3.5756	0.0000	0.1150	− 1.3508	− 1.3508	− 2.7483	− 1.5242	2.2547	0.3981
H	− 3.5756	0.0000	0.1150	1.3508	1.3508	− 2.7483	− 3.1821	− 1.3056	− 0.1241

TABLE III. Harmonic frequencies (ω) and infrared intensities (I) for structures I and II and the transition state linking them. All values computed at the DZP-MBPT(2) level by finite difference of analytic energy gradients and dipole moments. Frequencies are in cm^{-1} intensities in km/mole.

	Isomer I C_{2v}			Isomer II D_{2d}			Transition state C_1		
	Mode symmetry	ω	I	Mode symmetry	ω	I	Mode symmetry	ω	I
ω_1	a_1	2874.3	0.7	a_1	2637.5	···	a	2835.7	20.5
ω_2	a_1	2148.5	14.8	a_1	1241.2	···	a	2788.0	49.9
ω_3	a_1	1346.1	1.8	a_1	859.6	···	a	2523.0	19.1
ω_4	a_1	1130.8	0.0	b_1	515.3	···	a	2066.2	90.6
ω_5	a_1	736.2	3.6	b_2	2615.4	87.1	a	1293.4	64.5
ω_6	a_2	1346.1	···	b_2	1177.8	9.7	a	1167.6	76.8
ω_7	a_2	651.5	···	e	2705.4	165.1	a	1137.0	0.3
ω_8	b_1	2831.9	32.3	e	1029.5	45.1	a	1014.4	0.9
ω_9	b_1	1391.5	232.9	e	444.3	3.2	a	844.6	20.2
ω_{10}	b_1	494.2	35.1	···	···	···	a	831.5	5.2
ω_{11}	b_2	2153.5	44.2	···	···	···	a	468.7	84.2
ω_{12}	b_2	808.5	0.8	···	···	···	a	343.9i	22.7

From Fig. 3, which shows a ball and stick representation of the transition state geometry, we see that the two hydrogens corresponding to bridging hydrogen atoms in isomer I are not in symmetrically equivalent environments. Some idea of the asymmetry can be gained by comparing the difference in B–H bond lengths for both hydrogens. While one of the protons is in a relatively symmetrical environment [$\Delta r(\text{B–H}) = |r(\text{B}_1\text{–H}) - r(\text{B}_2\text{–H})| = 0.14$ Å], indicating a partially formed bridge bond, the other still resembles a terminal hydrogen [$\Delta r(\text{B–H}) = 0.81$ Å]. The difference between these two values (0.67 Å) provides a quantitative measure of the asymmetrical nature of the transition state geometry.

B. Correlation and basis set effects

In order to investigate the effects of basis set extension and electron correlation effects, single point calculations were performed at the TZ2P-SDQ-MBPT(4) stationary points using the following levels of theory: MBPT(2), MBPT(3) SDQ-MBPT(4), MBPT(4), CCSD, CCSD + T(CCSD) and CCSD(T), using the DZP and TZ2P basis sets as well as the PVTZ correlation consistent basis set of Dunning.[30] Results of these calculations are reported in Table IV. Consistent with all of our previous studies of the boranes,[35] the infinite order effects included in the coupled-cluster models have only slight effects on the predicted energy differences; the CCSD and CCSD(T) [or CCSD + T(CCSD)] models agree quite well with their fourth-order MBPT approximations, SDQ-MBPT[4] and MBPT[4], respectively. Also in line with previous work, contributions of triple excitations favor the isomer with more hydrogen bridge bonds. The near equivalence of results obtained with the CCSD(T) and CCSD + T(CCSD) models reflects the fact that triple excitation effects are well approximated by a low-order treatment in the present case. The CCSD + T(CCSD) method is exact through fourth order in perturbation theory, while the CCSD(T) model includes one of three terms which occur in fifth order. For difficult cases, this additional term tends to offset the tendency for CCSD + T(CCSD) to overestimate these effects but differences are negligible for well-behaved molecules such as the boron hydrides. This property of the boranes is due to the

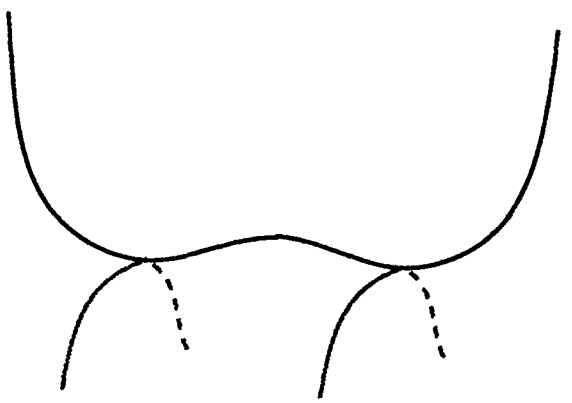

FIG. 2. Schematic cross-sectional view of the isomerization channel. The inverted parabolas normal to the plane of the page pass through equivalent transition states. The apparent maximum of the curve is the second-order saddle point along the pathway which conserves C_2 symmetry.

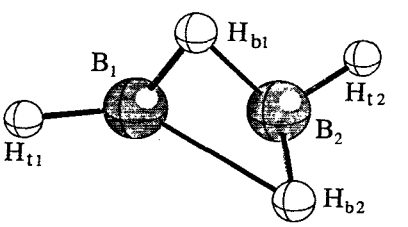

FIG. 3. Ball and stick representation of the transition state geometry. The atomic labels are consistent with Table I.

TABLE IV. Isomerization energy and barrier height for the conversion of the C_{2v} isomer of B_2H_4 to the D_{2d} form. All values (kcal/mole) represent *electronic* energy differences and were calculated at the corresponding TZ2P-SDQ-MBPT(4) geometries. Zero-point corrections listed at the bottom of the table were calculated from the harmonic vibrational frequencies presented in Table III.

	ΔE (I→II)	$\Delta E^{\neq}$
DZP basis		
MBPT(2)	−1.8	7.1
MBPT(3)	−4.3	5.9
SDQ-MBPT(4)	−5.6	5.1
MBPT(4)	−3.6	5.9
CCSD	−6.0	4.9
CCSD + T(CCSD)	−3.9	5.4
CCSD(T)	−4.0	5.4
TZ2P basis		
MBPT(2)	2.3	9.1
MBPT(3)	−0.7	7.6
SDQ-MBPT(4)	−1.5	6.8
MBPT(4)	−0.8	7.8
CCSD	−2.3	6.5
CCSD + T(CCSD)	0.2	7.2
CCSD(T)	0.2	7.3
PVTZ basis		
MBPT(2)	3.3	9.5
MBPT(3)	0.3	8.0
SDQ-MBPT(4)	−1.0	7.2
MBPT(4)	1.9	8.3
CCSD	−1.4	6.9
CCSD + T(CCSD)	1.1	7.7
CCSD(T)	1.2	7.7
DZP-MBPT(2) zero-point correction		
	−0.6	−1.4

isolated nature of electronic states in these molecules and the resulting lack of near-degeneracy effects such as those present in multiply bonded molecules.[29] Nevertheless, dynamical electron correlation is extremely important in these systems, since the SCF approximation tends to grossly exaggerate the stability of two-center bonds relative to the three-center bonds which are ubiquitous in boron hydrides.[36] However, these effects are easily handled by perturbation theory, and the MBPT expansion of the correlation energy therefore converges rapidly for these molecules.

Basis set effects are modest in the present case. Improvement from DZP to PVTZ tends to favor isomer I. This too is consistent with previous experience, as the nonclassical hydrogen bridge bonds found in the boranes make more demands on the basis set than the simpler terminal B–H units. At the highest level of theory [CCSD(T) with the PVTZ basis set], we find that isomer I is approximately 1.2 kcal/mole more stable than II, and that the transition state lies only 7.7 kcal/mole above I. The error due to neglect of residual correlation effects is likely to be small (<1 kcal/mole) and might favor either isomer. However, further improvement of the basis would probably favor the nonclassical form (I) and further lower the barrier. The magnitude of these effects is difficult to estimate, but is probably not more than ~ 2 kcal/mole. Addition of zero-point energy corrections estimated from the DZP-MBPT(2) harmonic frequencies (see Table IV) reduce the PVTZ-CCSD(T) isomerization energy to 0.6 kcal/mole and the barrier heights to 6.3 and 5.1 kcal/mole for the transitions from I and II, respectively.

IV. DISCUSSION AND CONCLUSIONS

The results of this study indicate that a low energy pathway exists for interconversion of the two low-lying isomers of diborane(4). Unlike the stepwise process previously suggested in the literature, the mechanism proposed here consists of a single concerted, but unsynchronous, rotation of the BH_2 groups. The pathway initially follows an idealized reaction coordinate which preserves C_2 symmetry, but then bifurcates at a branch point leading to two equivalent transition states which lack nontrivial elements of symmetry.

The magnitude of the barrier height found in the present study [~ 6 kcal/mole] suggests that establishment of equilibrium should occur rapidly under ambient conditions. Consequently, experimentalists studying this molecule should expect to find both isomers in comparable proportions, although the results of the present calculations and those presented previously[10,11] indicate a slight preference for isomer I. Statistical considerations favor this isomer as well, as the number of distinct permutational structures is twice that for II [24 vs 12] and the equilibrium constant for I→II would be approximately equal to two even if the corresponding points on the energy surface were degenerate. In addition, the low barrier height and flat nature of the transition state region found in the present study suggests that a standard rigid-molecule interpretation of the spectra of B_2H_4 may not be entirely appropriate. This possibility needs to be considered in future experimental analyses.

It should be pointed out that the transition state obtained in the present study does not necessarily correspond to the lowest energy mechanism linking isomers I and II, since B_2H_4 has 12 conformational degrees of freedom and an exhaustive search of such a surface is an intractable problem. Nevertheless, the pathway studied here is intuitively appealing, as it roughly follows an idealized symmetry-conserving reaction coordinate which is allowed by orbital symmetry rules; in our opinion, it is probable that it does indeed represent the minimum energy path for this process. In any event, the activation energy corresponding to the pathway studied here necessarily represents an upper limit to the true value. The value of 6.3 kcal/mole calculated at the PVTZ-CCSD(T) level is probably within 3 kcal/mole of the exact nonrelativistic result for these geometries, so that reasonable estimates for the barrier height (I→TS) and isomerization energy (I→II) are 6 ± 3 and 1 ± 3 kcal/mole, respectively.

While the barrier height found here seems to be small for such an extensive rearrangement of the nuclear skeleton, one must remember that intermolecular hydrogen scrambling and other rearrangements in the boron hydrides and related compounds typically occur faster than the NMR time scale. In this regard, the isomerization of B_2H_4 studied here might help to serve as a model for certain classes of these reactions.

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[13]The C_2 axis which is preserved corresponds to one of the two perpendicular C_2 axes in the D_{2d} structure, not the principal S_4 axis.

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[15]MOLECULE is a vectorized Gaussian integral program, written by J. Almlof and P. R. Taylor.

[16]ABACUS is a program which calculates derivatives of Gaussian integrals, written by T. Helgaker, P. Jørgensen, H. J. A. Aa. Jense, and P. R. Taylor; the version of ABACUS used in ACES II is a 1988 version of the code which has been appropriately modified to perform large-scale CC/MBPT gradient calculations.

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