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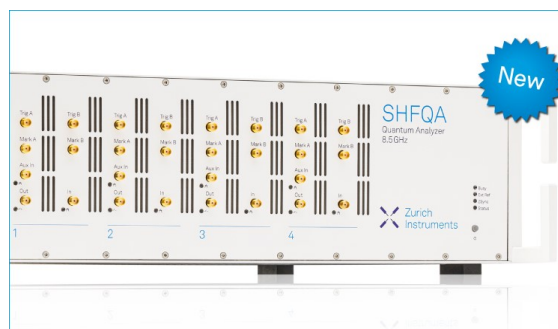
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# Automerization reaction of cyclobutadiene and its barrier height: An *ab initio* benchmark multireference average-quadratic coupled cluster study

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The problem of the double bond flipping interconversion of the two equivalent ground state structures of cyclobutadiene (CBD) is addressed at the multireference average-quadratic coupled cluster level of theory, which is capable of optimizing the structural parameters of the ground, transition, and excited states on an equal footing. The barrier height involving both the electronic and zero-point vibrational energy contributions is  $6.3 \text{ kcal mol}^{-1}$ , which is higher than the best earlier theoretical estimate of  $4.0 \text{ kcal mol}^{-1}$ . This result is confirmed by including into the reference space the orbitals of the CC  $\sigma$  bonds beyond the standard  $\pi$  orbital space. It places the present value into the middle of the range of the measured data ( $1.6\text{--}10 \text{ kcal mol}^{-1}$ ). An adiabatic singlet-triplet energy gap of  $7.4 \text{ kcal mol}^{-1}$  between the transition state  ${}^1B_{1g}$  and the first triplet  ${}^3A_{2g}$  state is obtained. A low barrier height for the CBD automerization and a small  $\Delta E({}^3A_{2g}, {}^1B_{1g})$  gap bear some relevance on the highly pronounced reactivity of CBD, which is briefly discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2222366]

## I. INTRODUCTION

Cyclobutadiene (CBD) has been a challenge for both theoretical and experimental chemists for many decades.<sup>1</sup> It is the smallest neutral organic compound that exhibits the effect of antiaromaticity<sup>2</sup>—one of the central notions in organic chemistry. In addition to that, its striking feature is a high angular strain,<sup>3</sup> which is another determining factor of chemical reactivity. It is widely accepted that a combined effect of these two electronic and structural features yields a very high energy content of CBD, thus leading to its strongly pronounced reactivity. Experimental efforts to synthesize cyclobutadiene and its remarkable chemistry have been the subject matter of several books and reviews.<sup>4–6</sup> Being an antipode to the aromatic benzene, CBD aroused a lot of interest of theoreticians too, which has resulted in numerous studies and research papers.<sup>7–25</sup>

In spite of its seemingly simple electronic structure, CBD exhibits some very interesting features. Remarkably, the first important pieces of information on its electronic structure, apart from a simple Hückel molecular orbital (HMO) theory, came from experiments. Early synthetic work of Pettit and co-workers<sup>26</sup> indicated that CBD was a singlet in its ground state and that its geometry was a planar rect-

angle. This hypothesis was experimentally confirmed later by many groups.<sup>27–29</sup> Furthermore, automerization reaction interconverting two equivalent  $D_{2h}$  structures via transition square structure  $D_{4h}$  (Fig. 1) was a topic of intensive investigations. Experimentally, the energy barrier for automerization of cyclobutadiene is predicted to be in the range of  $1.6\text{--}10 \text{ kcal mol}^{-1}$ .<sup>30</sup> Furthermore,  ${}^{13}\text{C}$  nuclear magnetic resonance (NMR) measurements of automerization of *tert*-butylcyclobutadiene have shown that the barrier should be less than  $2.5 \text{ kcal mol}^{-1}$ .<sup>31</sup> This large span of the experimental values calls for the use of the high-level *ab initio* calculations capable of discriminating the measured data. An intriguing hypothesis of the heavy atom tunneling as the main mechanism of the automerization, put forward by Carpenter,<sup>30</sup> triggered vivid discussions with no final conclusions.<sup>5,32–37</sup> It has been established beyond any reason-

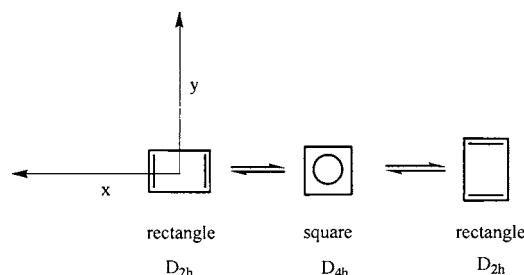


FIG. 1. Automerization reaction of cyclobutadiene in the ground state.

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able doubt, however, that two isomers of CBD and its deuterated derivatives underwent very rapid bond flipping interconversion<sup>38</sup> even at a very low temperature of 10 K.

Theoretically, the ground state (GS) of cyclobutadiene is found to be a closed shell singlet, implying that it is well described by the single reference methods.<sup>39</sup> Perusal of the occupation numbers of the natural orbitals (NOs) in the configuration interaction (CI) expansion reveals that this is really a fact. However, the transition structure has square geometry ( $D_{4h}$ ), being an open shell system, which requires the use of multireference methods. A comprehensive study of Balková and Bartlett<sup>40</sup> using multireference coupled cluster method including single and double excitations augmented by noniterative triplet excitations [MR-CCSD(T)] gave the energy barrier height of 6.6 kcal mol<sup>-1</sup>. Inclusion of zero-point vibrational energy (ZPVE) lowered this value to 4.0 kcal mol<sup>-1</sup> only. It should be mentioned that there is a large scatter of the theoretical estimates of the energy barrier height in the literature depending on the method employed, implying that the problem is not settled as yet, which should be rectified by using the state of the art methodology and computations.

The aim of this study is to provide the benchmark calculations of the barrier height for the bond flipping automerization of CBD by using the multireference average-quadratic coupled cluster (MR-AQCC) method<sup>41,42</sup> and to compare the present results with the earlier CI values. The main advantage of the adopted method is the combination of multireference and approximate size extensivity effects, which allow for a balanced description of the nondynamic and dynamic electron correlations. In addition, the availability of analytic energy gradients<sup>43-45</sup> enables the geometry optimization and location of the transition structures at a very high level of theory. Finally, it should be mentioned that the first excited triplet state and two lowest singlet states, apart from the ground state, will be considered and briefly discussed.

## II. COMPUTATIONAL DETAILS

Single state and state averaged multiconfiguration self-consistent field (denoted as SS-CASSCF and SA-CASSCF, respectively), multireference configuration interaction with single and double excitations (MR-CISD), and multireference average-quadratic coupled cluster (MR-AQCC) calculations were used for comparative purposes. Since the lowest triplet state is close to the transition structure, it is necessary to include it in the state averaging procedure too. Hence, two types of state averaging were considered: the first one is over the ground state and the lowest triplet state (SA-2) and the second, a larger one, is comprised of the ground state, lowest triplet state, and two lowest excited singlet states (SA-4). In the state averaged calculations equal weights were used for all states. The ground state energy surface has as a minimum the rectangular structure of  $D_{2h}$  symmetry ( $1^1A_g$  state). In contrast, the excited states  $1^3B_{1g}$  and  $1^1B_{1g}$  have as minima the square structures with the corresponding electronic symmetry labels  $1^3A_{2g}$  and  $1^1B_{2g}$ , respectively. It should be

pointed out that the square structure for the  $2^1A_{1g}$  excited state is not a true minimum, which in turn is slightly nonplanar (*vide infra*). Nevertheless, we shall consider the square structure of this state in some detail for the sake of comparison with other states. The transition structure related to the automerization reaction has a square geometry. In the first step, a complete active space<sup>46</sup> (CAS) was used in the multiconfigurational self-consistent-field (MCSCF) calculations. It was constructed within the  $\pi$ -electron orbital manifold, which includes four  $\pi$  electrons placed in two  $\pi$  and two  $\pi^*$  orbitals [CAS(4,4)]. The final expansion space in the MR-CISD and MR-AQCC calculations in terms of configuration state functions (CSFs) consisted of the CAS(4,4) reference configurations (utilized in the MCSCF calculations) and additional configurations derived by all single and double excitations involving transfer of electrons into all internal and external orbitals. In the geometry optimizations the symmetry of the reference configurations was restricted to the state symmetry. It should be mentioned that the interacting space restriction<sup>47</sup> was applied. The four core  $1s$  carbon orbitals were kept frozen in all post-MCSCF calculations. The computations were performed by using Dunning's correlation consistent cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, and aug'-cc-pVTZ basis sets<sup>48,49</sup> (the prime in the latter basis set implies that  $f$  functions on carbon and  $d$  functions on hydrogen were deleted in the augmented set). In addition, single-point calculations were performed using the basis set of cc'-pVQZ quality on carbons and cc'-pVTZ basis set on hydrogens (the prime denotes that  $g$  functions in cc-pVQZ and  $d$  functions in cc-pVTZ basis sets were deleted). The former basis set will be denoted by QZ'. A two-point extrapolation to the infinite basis set<sup>50</sup> has been performed using the cc-pVTZ and QZ' basis sets and will be denoted as (TQ). This procedure is very pragmatic in view of the limitations introduced into the QZ' basis. Nevertheless, it is expected to reflect certain trends in the basis set dependence of the total electronic energy. Geometry optimizations were performed in natural internal coordinates as defined by Fogarasi *et al.*<sup>51</sup> using the GDIIS procedure.<sup>52</sup> Size extensivity corrections for the MR-CISD calculations are taken into account by employing the Davidson correction,<sup>44,53,54</sup> which is denoted by + $Q$ . Orientation of the molecule is defined as presented in Fig. 1.

In order to separate orbitals describing CC and CH (localized) bonds, the restricted direct product (RDP) space<sup>55</sup> was used at the MCSCF level. Under  $D_{2h}$  symmetry restriction, the RDP space is formed by 16 orbitals grouped in four  $\sigma_{CC}\sigma_{CC}^*$  subspaces:  $(3a_g, 4b_{1u})$ ,  $(4a_g, 4b_{2u})$ ,  $(2b_{2u}, 3b_{3g})$ , and  $(3b_{1u}, 4b_{3g})$ , as well as four  $\sigma_{CH}\sigma_{CH}^*$  subspaces:  $(2a_g, 5a_g)$ ,  $(3b_{2u}, 5b_{2u})$ ,  $(2b_{1u}, 5b_{1u})$ , and  $(2b_{3g}, 5b_{3g})$ . Each subspace is restricted to singlet coupling of two electrons. Within the  $D_{2h}$  symmetry of the ground state, the appropriate symmetry adapted combinations of localized CC and CH bonds, respectively, were constructed. All configurations of the RDP space plus those of the CAS(4,4) space ( $\pi$ ,  $\pi^*$  orbitals) were used in the MCSCF calculations averaged over four states. In

general, the MCSCF calculations based on the RDP spaces result in orbitals localized in the chemical bonds similar to those obtained in the generalized valence bond (GVB) calculations.<sup>56</sup>

The orbitals obtained by using the CAS(4,4)+RDP space were subsequently employed in the MR-AQCC calculations. Two reference spaces were generated. The first one was composed of all configurations of the CAS(4,4) space ( $\pi$ ,  $\pi^*$  orbitals), supplemented by all configurations produced by single excitations from the two  $\pi$  and two  $\pi^*$  orbitals into the four  $\sigma_{CC}^*$  orbitals. In addition, all configurations obtained by single excitations from the four  $\sigma_{CC}$  orbitals into the two  $\pi$ , two  $\pi^*$ , and four  $\sigma_{CC}^*$  orbitals were taken into account. The  $\sigma_{CH}$  and  $\sigma_{CH}^*$  orbitals describing CH bonds were moved into the reference doubly occupied and virtual subspaces, respectively. The MR-AQCC calculations carried out with this reference space were performed by utilizing the aug-cc-pVDZ and cc-pVTZ basis sets, which will be abbreviated thereafter as A1 and A2, respectively. The second reference space included all configurations of the CAS(4,4) space ( $\pi$ ,  $\pi^*$  orbitals), complemented by all configurations generated by single excitations from the manifold formed by the four  $\pi$  and  $\pi^*$  orbitals into the eight  $\sigma^*$  orbitals (CC and CH), plus all configurations belonging to single excitations from the eight  $\sigma$  orbitals into the two  $\pi$ , two  $\pi^*$ , and eight  $\sigma^*$  orbitals. The calculations with this reference orbital space were performed only with the aug-cc-pVDZ basis set. They are denoted as A3.

ZPVE corrections were computed at the MR-AQCC/SS-CASSCF level of theory by using the cc-pVDZ and cc'-pVTZ basis sets (the prime in the latter basis set implies that  $f$  functions on carbon and  $d$  functions on hydrogen were deleted) for the  $1^1A_g$  state of CBD. Vibrational frequencies for the  $1^3A_{2g}$  state were computed at the MR-AQCC/SS-CASSCF/cc-pVDZ level of theory. On the other hand, vibrational frequencies for the  $2^1A_g$  state were computed by using the MR-AQCC/SA-4-CASSCF/cc-pVDZ method. The harmonic vibrational frequencies were obtained by the program SUSCAL developed by Pulay *et al.*,<sup>57</sup> whereas the force constants were computed by the finite differences of energy gradients. Normal modes of vibrations were calculated and the minimum energy of the ground state rectangular structure was verified by frequency analysis. It was found that the square structure in the  $1^1B_{1g}$  state possessed a single imaginary frequency, which corresponded to the C–C bond stretching mode along the reaction path of the automerization reaction. Finally, it should be noted that the square geometries are the equilibrium structures for the first triplet and the  $S_2$  singlet excited states.

The COLUMBUS suite of codes was employed in all calculations.<sup>58–61</sup> The atomic orbital (AO) integrals and AO gradient integrals have been computed with program modules taken from DALTON.<sup>62</sup> As the last technical remark we would like to mention that the tables in the supplementary material are denoted as S1–S4.<sup>63</sup>

TABLE I. Optimized structural parameters of the rectangular  $1^1A_g$  ground state and square transition state of cyclobutadiene as obtained by the MR-AQCC/SA-4-CASSCF method by using various basis sets.

		Bond distances <sup>a</sup>		Bond angles <sup>b</sup>
cc-pVDZ				
Rectangle	$R_{C=C}$	$R_{C-C}$	$R_{C-H}$	HCC <sup>c</sup>
	1.367	1.573	1.093	134.9
Square	$R_{C-C}$	$R_{C-C}$	$R_{C-H}$	HCC <sup>c</sup>
	1.461	1.461	1.092	135.0
aug-cc-pVDZ				
Rectangle	$R_{C=C}$	$R_{C-C}$	$R_{C-H}$	HCC <sup>c</sup>
	1.368	1.574	1.091	135.0
Square	$R_{C-C}$	$R_{C-C}$	$R_{C-H}$	HCC <sup>c</sup>
	1.463	1.463	1.090	135.0
cc-pVTZ				
Rectangle	$R_{C=C}$	$R_{C-C}$	$R_{C-H}$	HCC <sup>c</sup>
	1.349	1.562	1.077	134.9
Square	$R_{C-C}$	$R_{C-C}$	$R_{C-H}$	HCC <sup>c</sup>
	1.447	1.447	1.076	135.0

<sup>a</sup>Bond lengths are given in Å.

<sup>b</sup>Angles are given in degrees.

<sup>c</sup>Exterior angle between C–H and the longer C–C bond.

### III. RESULTS AND DISCUSSION

#### A. The double bond flipping automerization reaction of cyclobutadiene

##### 1. Structural parameters

The optimized structural parameters of the rectangular ground state and square transition structure of cyclobutadiene, obtained at the MR-AQCC/SA-4-CASSCF level of theory, are presented in Table I. It appears that the use of the triple zeta basis set leads to a decrease in the CC and CH bond distances by 0.01–0.02 Å relative to the cc-pVDZ results, leaving the bond angles virtually unchanged. On the other hand, inclusion of augmented functions is unimportant. With the aug'-cc-pVTZ basis set identical structural parameters are obtained as for the cc-pVTZ basis set. It should be mentioned that experimental data are not available for the parent CBD due to its elusive nature. There are numerous measured structures of the CBD derivatives, which are unfortunately biased by the substituent effects or by influence of the annelated rings. Hence, they will not be commented upon here. We just note in passing that CCSD(T)/cc-pVTZ calculations of Levchenko and Krylov<sup>25</sup> gave  $d(C-C) = 1.566$  Å,  $d(C=C) = 1.343$  Å, and  $d(C-H) = 1.074$  Å, in good agreement with our MR-AQCC/SA-4-CASSCF/aug'-cc-pVTZ values for  $d(C-C) = 1.562$  Å,  $d(C=C) = 1.350$  Å, and  $d(C-H) = 1.077$  Å. The latter values are probably very close to the true equilibrium bond distances. We believe that our estimate of the square structure characterized by the  $d(C-C) = 1.447$  Å,  $d(C-H) = 1.076$  Å, and bond angle HCC = 135.0° is reliable too. Two comments are in place here. First, the square structure has a  $d(CC)$  distance very close, but not equal to the average of the ground state  $d(C=C)$  and  $d(C-C)$  bond lengths, being 1.456 Å as obtained by the cc-pVTZ basis. It implies that the C=C and C–C bond distances are lengthened and shortened in the au-

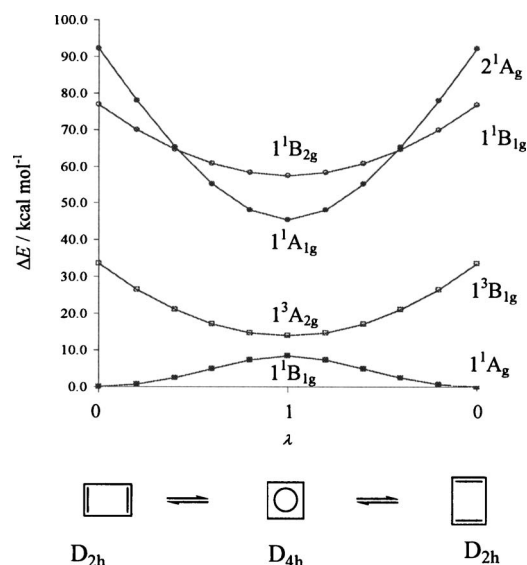


FIG. 2. Energy variation along the automerization path of cyclobutadiene for the ground state and the three lowest excited states.

tomerization process by 0.10 and 0.12 Å, respectively. Second, other structural parameters [the  $d(\text{CH})$  bond length and the HCC and CCC bond angles] are virtually unchanged, meaning that the double bond shift interconversion is a pure CC bond-stretch reaction.

## 2. Energetic properties

In order to obtain the potential energy curve for the automerization reaction of CBD in the ground state, an approximate reaction path connecting two rectangular structures via the intermediate square structure was used. This reaction path was obtained by linear interpolation of the selected internal coordinates  $l_i$  [Eq. (1)] (Ref. 64) related to the C–C optimized distances of the rectangular and square geometries used as the fixed boundary  $l_i(\text{rt})$  and  $l_i(\text{sq})$  structural parameters, respectively, calculated by the MR-AQCC/SA-4-CASSCF/cc-pVTZ method:

$$l_i(\lambda) = (1 - \lambda)l_i(\text{rt}) + \lambda l_i(\text{sq}). \quad (1)$$

Here, the index  $i$  assumes values of 1 and 2, implying that  $l_1(0)$  and  $l_2(0)$  correspond to the initial  $d(\text{C}=\text{C})$  and  $d(\text{C}-\text{C})$  double and single bond distances, respectively, in the ground state. The dimensionless parameter  $\lambda$  is varied in the 0–1 interval with consecutive steps of 0.2. Once the square structure is attained, the mirror image of the second half of the curve is obtained by symmetry. All other internal coordinates have been optimized at each point of the reaction path by the MR-AQCC/SA-4-CASSCF/cc-pVTZ approach (Fig. 2).

Let us first consider results of the calculations performed by using SS-CASSCF and SA-2-CASSCF orbitals. Barrier heights are given in Table II and total electronic energies, obtained by the MR-CISD, MR-CISD+Q, and MR-AQCC methods for the optimized rectangle and square structures of cyclobutadiene, are presented in Table S1.

Perusal of the presented data shows that the energy barrier spans a small range of 7.3–8.8 kcal mol<sup>-1</sup> depending on the basis set used. They compare rather well with the

TABLE II. Energy barriers obtained by the multireference methods based on the single state (SS-CASSCF) and the state averaged SA-2-CASSCF orbitals for automerization reaction of cyclobutadiene (barrier height are given in kcal mol<sup>-1</sup>). The SA-4-CASSCF results are given within the square parentheses.

	Barrier		
	MR-CISD	MR-CISD+Q	MR-AQCC
SS-CASSCF			
cc-pVDZ	7.3	7.6	7.7
aug-cc-pVDZ	7.4	7.6	7.7
cc-pVTZ	8.4	8.8	8.9
aug'-cc-pVTZ	8.4	8.7	8.8
SA-2-CASSCF			
cc-pVDZ	6.5	7.2	7.3[7.3]
aug-cc-pVDZ	6.3	7.1	7.4[7.4]
cc-pVTZ	7.3	7.9	8.4[8.4]
aug'-cc-pVTZ	7.1	8.1	8.3[8.3]
QZ'	...	...	[8.6]
(TQ) <sup>a</sup>	...	...	[8.8]

<sup>a</sup>Extrapolated value (see text).

results obtained by the MR-CCSD(T)/[3s2p1d/1s] (6.6 kcal mol<sup>-1</sup>) (Ref. 40) and multireference Brillouin-Wigner coupled cluster method with single and double excitations (MR-BWCCSD) employing the cc-pVDZ and cc-pVTZ basis sets (6.4 and 7.0 kcal mol<sup>-1</sup>, respectively).<sup>19</sup> It is interesting to note that the energy barrier increases with the flexibility of the basis set, which is compatible with the known fact that the dynamic correlation increases the barrier. The latter is also in harmony with a pronounced dependence of the dynamic electron correlation on the quality of the basis set in contrast to its nondynamic counterpart. More specifically, the increase in the barrier height by ca. 1 kcal mol<sup>-1</sup> on going from double zeta to triple zeta quality illustrates the point. The effect of more extended basis sets is described below. Inclusion of the augmented basis functions in the aug-cc-pVDZ and aug'-cc-pVTZ sets did not significantly change the energy barrier. It appears that the Davidson correction for size extensivity improves the MR-CISD values of the barrier height by making the MR-CISD+Q and MR-AQCC values almost identical. The barrier heights obtained by MR-CISD, MR-CISD+Q, and MR-AQCC methods based on the state averaged (SA-2-CASSCF) orbitals are lower in energy by ca. 0.5 kcal mol<sup>-1</sup> than those obtained from the single state orbitals.

Since the  $S_1$  and  $S_2$  excited states are of interest too, we decided to carry out computations by taking the ground state and the three lowest excited states into account by the multireference MR-AQCC/SA-4-CASSCF method in order to treat all of them on an equal footing. Table II displays the results obtained by the MR-AQCC/SA-4-CASSCF approach, which involves averaging over the indicated four states (Fig. 2). The results for the barrier height are identical to those obtained at the MR-AQCC/SA-2-CASSCF level. The energy barrier obtained by the MR-AQCC/SA-4-CASSCF/QZ'/MR-AQCC/SA-4-CASSCF/cc-pVTZ method is 8.6 kcal mol<sup>-1</sup>. The extrapolation technique explained

above<sup>50</sup> gives a value of 8.8 kcal mol<sup>-1</sup> for the barrier height. This result will be denoted by MR-AQCC/SA-4-CASSCF/(TQ) further in the text. Considering the fact that in the aug'-cc-pVTZ basis the MR-AQCC single state result (see Table II) for the barrier is 0.5 eV larger than the corresponding SA-4 result, it is plausible to assume that the barrier is slightly higher. From our results we also conclude that extension to higher excited states in the state averaging procedure would not significantly influence the barrier height for the CBD automerization. It is worth noting that inclusion of the four states offers a more balanced computation of the individual excited states under scrutiny, which is important *per se*.

It is of some interest to try to delineate the influence of dynamic and nondynamic correlations on the barrier height, at least in an approximate manner. As mentioned earlier, the nondynamic electron correlation effects are very important in the description of the transition structure square geometry due to its biradical character. The MCSCF results by Nakamura *et al.*<sup>34</sup> have shown that the energy barrier was only 2.5 kcal mol<sup>-1</sup> if the ZPVE effect was correctly taken into account as pointed out by Balková and Bartlett,<sup>40</sup> whereas the electronic contribution was 4.6 kcal mol<sup>-1</sup>. The present MR-AQCC/SA-2-CASSCF and MR-AQCC/SA-4-CASSCF barrier heights are ca. 3–4 kcal mol<sup>-1</sup> higher than the MCSCF results. It follows that the MCSCF method alone tends to overstabilize the transition structure due to the omission of the dynamic correlation effect as mentioned by Schmidt and Gordon<sup>65</sup> earlier and confirmed by the present study. It is, therefore, safe to conclude that only a balanced treatment taking into account both the nondynamical and dynamical correlation effects is capable of providing a correct barrier height.

In order to examine the effect of the size of the MCSCF space, we have systematically enlarged the original CAS(4,4) subspace. It is well known that the main contributions to the dynamic correlation come from the electron pairs of the (localized) chemical bonds. The RDP spaces offer a suitable way of including these contributions in the MCSCF formalism without blowing up the number of configurations occurring in the customary CAS subspaces. In the present calculations the RDP space included the electron correlation energy effects arising from the  $\sigma_{CC}$  and  $\sigma_{CH}$  orbitals. This contribution supplements the correlation energy derived from the  $\pi$  orbitals manifold, and provides the main component in the CAS(16,16) calculations. In the MR-CI and MR-AQCC calculations, we have increased the reference space by incorporating the most relevant configurations correlating the  $\pi$  and  $\sigma$  spaces. The corresponding A1, A2, and A3 computational methods were described earlier in Sec. II. Table III shows the energy barriers obtained by the RDP procedure. The results are quite similar to those obtained with CAS(4,4) space provided the same basis set is employed, which has led us to conclude that the CAS(4,4) approach involving four electrons in four  $\pi$  orbitals was good enough to produce reliable results for the energy barrier within the MR framework. More specifically, the energy barrier heights obtained by the A1 and A3 computational schemes employing the aug-cc-pVDZ basis set are 7.5 and 7.3 kcal mol<sup>-1</sup>, respectively,

TABLE III. The calculated barrier heights for CBD automerization estimated without and with ZPVE employing various basis sets. The electronic energy is obtained either by the MR-AQCC/SA-4-CASSCF approach or by the RDP formalism, whereas the zero-point vibrational energies are calculated by the MR-AQCC/SS-CASSCF method by using cc-pVDZ and cc'-pVTZ basis sets.

	Energy barrier height <sup>a</sup>		
	$\Delta E(\text{el})_{\text{tot}}$	$\Delta E(\text{el})_{\text{tot}}$ +ZPVE/BS1 <sup>b</sup>	$\Delta E(\text{el})_{\text{tot}}$ +ZPVE/BS2 <sup>c</sup>
MR-AQCC			
cc-pVDZ	7.3	4.8	4.8
aug-cc-pVDZ	7.4	4.9	4.9
cc-pVTZ	8.4	5.9	5.9
aug'-cc-pVTZ	8.3	5.8	5.8
QZ'	8.6	6.1	6.1
(TQ)	8.8	6.3	6.3
RDP			
A1 <sup>d</sup>	7.5	5.0	5.0
A2 <sup>e</sup>	8.6	6.1	6.1
A3 <sup>f</sup>	7.3	4.8	4.8

<sup>a</sup>In kcal mol<sup>-1</sup>.

<sup>b</sup>BS1=cc-pVDZ.

<sup>c</sup>BS2=cc'-pVTZ.

<sup>d</sup>A1=MR-AQCC( $\sigma_{CC}$ )/SA-4-[CAS(4,4)+RDP]/aug-cc-pVDZ.

<sup>e</sup>A2=MR-AQCC( $\sigma_{CC}$ )/SA-4-[CAS(4,4)+RDP]cc-pVTZ.

<sup>f</sup>A3=MR-AQCC( $\sigma_{CC}, \sigma_{CH}$ )/SA-4-[CAS(4,4)+RDP]/aug-cc-pVDZ.

thus comparing well with the MR-AQCC/SA-4-CASSCF value of 7.4 kcal mol<sup>-1</sup> obtained by the same basis set. The corresponding value obtained by the SA-2-CASSCF orbitals is 7.4 kcal mol<sup>-1</sup> (Table II). Furthermore, the A2 barrier height of 8.6 kcal mol<sup>-1</sup> is in good agreement with the multireference MR-AQCC/SA-4-CASSCF/(TQ) benchmark result of 8.8 kcal mol<sup>-1</sup> (Table II). The respective multireference results deduced from the MR-AQCC/SA-2-CASSCF approach are 8.4 and 8.3 kcal mol<sup>-1</sup> for the cc-pVTZ and aug'-cc-pVTZ basis sets, respectively, thus convincingly showing that the CAS(4,4)  $\pi$  subspace is sufficient.

Data describing the influence of the ZPVE corrections on the value of the energy barrier are collected in Table III. Survey of the results shows that the ZPVE correction lowers the barrier as expected. The  $\Delta$ ZPVE value calculated by the MR-AQCC/SS-CASSCF/cc-pVDZ method (2.5 kcal mol<sup>-1</sup>) is identical to the corresponding MR-AQCC/SS-CASSCF/cc'-pVTZ value, thus enabling the use of cc-pVDZ basis set in future calculations. Taking into account the ZPVE effect, it follows that the best estimate of the barrier height is 6.3 kcal mol<sup>-1</sup>, which is placed right in the middle of the range of the experimental values (1.6–10 kcal mol<sup>-1</sup>).<sup>30</sup> Hence, the present benchmark energy barrier height value is 2.3 kcal mol<sup>-1</sup> higher than that of Balková and Bartlett<sup>40</sup> provided the ZPVE effect is explicitly taken into account. The calculated vibrational frequencies are compared in Tables IV and V with earlier results<sup>13,40</sup> and measured data.<sup>38</sup> The imaginary frequency belonging to the CC bond stretch along the automerization pathway of 1579i cm<sup>-1</sup> is almost twice as large as that computed by Balková and Bartlett<sup>40</sup> (803i cm<sup>-1</sup>). This is compatible with the higher barrier obtained in our calculations.

TABLE IV. Frequencies, symmetry labels, and IR intensities calculated at the MR-AQCC/SS-CASSCF/cc'-pVTZ level of theory compared to experimental and reference frequencies.

Frequencies (cm <sup>-1</sup> )	Symmetry	Intensity (km mol <sup>-1</sup> )	Ref. 13	Ref. 40	Expt. (Ref. 38)
Rectangle					
501	<i>a<sub>u</sub></i>	0		509	
540	<i>b<sub>2g</sub></i>	0	500	540	531
564	<i>b<sub>1u</sub></i>	70.1	572	577	576
706	<i>b<sub>2u</sub></i>	4.1	721	760	721
767	<i>a<sub>u</sub></i>	0		754	
802	<i>b<sub>3g</sub></i>	0		776	
873	<i>b<sub>1g</sub></i>	0	861	867	723
921	<i>a<sub>g</sub></i>	0	992	925	989
1050	<i>b<sub>3u</sub></i>	0.1		1023	
1119	<i>a<sub>g</sub></i>	0	1150	1113	1059
1184	<i>b<sub>1g</sub></i>	0		1145	
1276	<i>b<sub>2u</sub></i>	17.1	1319	1253	1245
1489	<i>a<sub>g</sub></i>	0	1604	1469	1678
1545	<i>b<sub>3u</sub></i>	2.0	1620	1542	1526
3213	<i>b<sub>1g</sub></i>	0	3265	3157	3093
3230	<i>b<sub>2u</sub></i>	6.3	3275	3178	3107
3249	<i>b<sub>3u</sub></i>	10.1	3270	3195	3124
3263	<i>a<sub>g</sub></i>	0	3309	3206	3140
Square					
1579 <sub>i</sub>	<i>b<sub>1g</sub></i>	0		803 <sub>i</sub>	
451	<i>b<sub>1u</sub></i>	0		461	
509	<i>e<sub>g</sub></i>	0		512	
515	<i>a<sub>2u</sub></i>	63.5		539	
595	<i>b<sub>1u</sub></i>	0		620	
904	<i>e<sub>u</sub></i>	3.8		921	
947	<i>b<sub>1g</sub></i>	0		838	
1080	<i>b<sub>2g</sub></i>	0		949	
1199	<i>a<sub>2g</sub></i>	0		1224	
1244	<i>a<sub>1g</sub></i>	0		1273	
1331	<i>e<sub>u</sub></i>	2.1		1326	
3232	<i>b<sub>2g</sub></i>	0		3178	
3250	<i>e<sub>u</sub></i>	5.9		3198	
3275	<i>a<sub>1g</sub></i>	0		3217	

The low barrier height deserves a few words of comment. It was conjectured by Borden and shown by Kollmar and Staemmler<sup>8,11</sup> that the singlet transition state is lower than the first triplet state due to a specific dynamic spin polarization. Furthermore, Voter and Goddard<sup>15</sup> have shown, by using the generalized resonating valence bond (GRVB) method, that fully delocalized 4π electrons in the transition state (TS) contribute 21.8 kcal mol<sup>-1</sup> to the resonance energy of the square structure. These two effects lead to a low barrier height, which seems to be closely related to the high chemical reactivity of CBD (see below).

## B. The lowest excited states of cyclobutadiene

The excited states 1<sup>3</sup>A<sub>2g</sub> and 1<sup>1</sup>B<sub>2g</sub> have a planar equilibrium square structure of D<sub>4h</sub> symmetry just like the transition state 1<sup>1</sup>B<sub>1g</sub> for the double bond flipping interconversion reaction between two equivalent ground state singlet isomers (Fig. 2). It should be pointed out that the energy curves for the excited states against the automerization reac-

TABLE V. Frequencies and symmetry labels of the lowest triplet state (<sup>3</sup>A<sub>2g</sub>) of cyclobutadiene calculated at the MR-AQCC/SS-CASSCF/cc-pVDZ level of theory.

Symmetry	Frequency (cm <sup>-1</sup> )	
	This work	Ref. 40
<i>b<sub>1g</sub></i>	942	878
<i>b<sub>1u</sub></i>	456	476
<i>e<sub>g</sub></i>	548	535
<i>a<sub>2u</sub></i>	527	552
<i>b<sub>1u</sub></i>	609	615
<i>e<sub>u</sub></i>	897	885
<i>b<sub>1g</sub></i>	1369	1284
<i>b<sub>2g</sub></i>	999	953
<i>a<sub>2g</sub></i>	1190	1232
<i>a<sub>1g</sub></i>	1274	1292
<i>e<sub>u</sub></i>	1327	1294
<i>b<sub>2g</sub></i>	3260	3177
<i>e<sub>u</sub></i>	3260	3194
<i>a<sub>1g</sub></i>	3287	3217

tion coordinate shown in Fig. 2 are obtained for the ground state *l<sub>i</sub>(rt)*, *l<sub>i</sub>(sq)*, and *l<sub>i</sub>(λ)* CC bond distances. The first triplet state is of particular interest because of its alleged aromatic character<sup>7,12,66</sup> and close energetic vicinity to the transition state. Historically, the D<sub>4h</sub> structure of the <sup>3</sup>A<sub>2g</sub> state was first established by Borden<sup>67</sup> and Borden *et al.*<sup>10</sup> A steep stabilization of the <sup>3</sup>A<sub>2g</sub> state on going from rectangular to square geometry and a relatively deep minimum (Fig. 2) can be understood by a decrease in antiaromaticity and even by a certain amount of aromatic stabilization. The latter was introduced, defined, and advocated by Baird<sup>7</sup> as a stabilization of the <sup>3</sup>A<sub>2g</sub> state measured against the first ππ\* triplet state of the open-chain polyene containing the same number of carbon atoms. By using this concept, Gogonea *et al.*<sup>66</sup> estimated the aromatic stabilization of the <sup>3</sup>A<sub>2g</sub> state of CBD by employing a particular homodesmotic reaction and obtained a value of -7 kcal mol<sup>-1</sup>. This makes a large difference compared to the ground state characterized by the antiaromatic destabilization of 38 kcal mol<sup>-1</sup>.<sup>23</sup> We note in passing that the aromatic stabilization of benzene was estimated to be ~-38 kcal mol<sup>-1</sup> recently.<sup>68</sup> If the idea of the triplet state partial aromaticity of CBD is adopted, then it is intuitively clear that the energy splitting between the <sup>3</sup>A<sub>2g</sub> state and transition state, ΔE(<sup>3</sup>A<sub>2g</sub>, <sup>1</sup>B<sub>1g</sub>), should be small. In order to obtain an accurate value of the ΔE(<sup>3</sup>A<sub>2g</sub>, <sup>1</sup>B<sub>1g</sub>) energy gap, one should take into account the optimized geometry for <sup>3</sup>A<sub>2g</sub> state and the corresponding ZPVE correction. The latter is computed by the MR-AQCC/SS-CASSCF/cc-pVDZ method. It appears that the ZPVE contribution increases the ΔE(<sup>3</sup>A<sub>2g</sub>, <sup>1</sup>B<sub>1g</sub>) gap by 2.0 kcal mol<sup>-1</sup> *inter alia* due to an inactive CC bond stretch vibration in the transition state. The differences in the total electronic energies ΔE<sub>el</sub>(<sup>3</sup>A<sub>2g</sub>, <sup>1</sup>B<sub>1g</sub>) are presented in Table VI. The ΔE(<sup>3</sup>A<sub>2g</sub>, <sup>1</sup>B<sub>1g</sub>) splitting including ZPVE corrections is given within parentheses. It appears that the best estimate is 7.4 kcal mol<sup>-1</sup>. As to the total electronic ΔE<sub>el</sub>(<sup>3</sup>A<sub>2g</sub>, <sup>1</sup>B<sub>1g</sub>) gap, it is 5.4 kcal mol<sup>-1</sup> by the aug'-cc-pVTZ basis set, which is 1.5 kcal mol<sup>-1</sup> lower than

TABLE VI. Energy differences ( $\Delta E$ ) obtained by the MR-AQCC/SA-4-CASSCF calculations between the transition state  $1^1B_{1g}$  and the lowest optimized excited states in cyclobutadiene (adiabatic excitations).

	$\Delta E_{ei}^{a-c}$		
	$1^3A_{2g}$	$1^1A_{1g}$	$1^1B_{2g}$
cc-pVDZ	6.3(8.3)	32.6	46.9
aug-cc-pVDZ	5.8(7.8)	30.5	41.9
cc-pVTZ	5.5(7.5)	31.5	43.3
aug'-cc-pVTZ	5.4(7.4)	30.7	41.6

<sup>a</sup>In kcal mol<sup>-1</sup>.

<sup>b</sup>The structural parameters were optimized by the MR-AQCC/SA-4-CASSCF method. The energy differences involving the ZPVE corrections (calculated by the MR-AQCC/SS-CASSCF/cc-pVDZ method) are given in parentheses. The  $1^1A_{1g}$  is constrained to be a planar square structure (see text).

<sup>c</sup>The adiabatic electron excitation energies relative to the ground state are obtained by adding the energy of the transition state. If the aug'-cc-pVTZ basis set is employed, the  $\Delta E_{ei}$  excitation energies for  $1^3A_{2g}$ ,  $1^1A_{1g}$ , and  $1^1B_{2g}$  states are 13.7, 39.0, and 49.9 kcal mol<sup>-1</sup>, respectively. Strictly speaking, the electron excitation energy to the  $1^1A_{1g}$  excited state is not adiabatic, since square is not the equilibrium structure.

the best value of Balková and Bartlett (6.9 kcal mol<sup>-1</sup>).<sup>40</sup> A small  $\Delta E(^3A_{2g}, ^1B_{1g})$  energy gap and rapid interconversion of the two equivalent forms of CBD in the ground state<sup>38</sup> even at very low temperatures suggest that the lowest triplet state might play an important role in the reactivity of cyclobutadiene. Indeed, it was argued by Zilberg and Haas<sup>18</sup> and later by Shaik and Shurki<sup>69</sup> that CBD was very reactive due to its kinetic instability combined with the existence of a low-lying triplet state possessing spin-unpaired electrons, which in turn were capable of forming new coupled electron pairs created in new covalent bonds. Hence, the first triplet state might be a key feature in understanding the reactivity of CBD together with its inherent high angular strain and collective term describing the increased energy content, namely, antiaromaticity of  $4\pi$  electrons. This should be better investigated in some characteristic reactions by employing quantitative *ab initio* methods.

It is also of importance to estimate the singlet-triplet splitting  $\Delta E(^3A_{2g}, \text{ground state})$  between the first triplet and the energy minimum of the ground state. The experimental value for peralkylated CBD derived by the flash photolysis measurements<sup>70</sup> gave 12.0 kcal mol<sup>-1</sup>. A recent CCSD(T)/cc-pVDZ//B3LYP/6-311+G(*d,p*) calculation yields

11.5 kcal mol<sup>-1</sup>, but without the ZPVE contribution.<sup>66</sup> The corresponding MR-CCSD(T) value obtained by  $[3s2p1d/1s]$  basis set is 13.5 kcal mol<sup>-1</sup>.<sup>40</sup> The present MR-AQCC/SA-4-CASSCF/aug'-cc-pVTZ calculation yields for the electronic part of the adiabatic  $\Delta E_{ei}(^3A_{2g}, \text{ground state})$  singlet-triplet splitting a value of 13.7 kcal mol<sup>-1</sup>. The ZPVE vibrational energies for the ground state ( $^1A_g$ ) and triplet ( $^3A_{2g}$ ) states are 37.6 and 37.1 kcal mol<sup>-1</sup>, respectively, as calculated by the MR-AQCC/SS-CASSCF/cc-pVDZ method. Hence, we arrive at the final adiabatic  $\Delta E(^3A_{2g}, ^1A_g)$ , singlet-triplet gap of 13.2 kcal mol<sup>-1</sup>, which is in a remarkably good agreement with measurements carried out on the cyclobutadiene flanked by two seven-membered carbocyclic rings substituted by eight methyl groups at the  $\alpha$ -carbon atoms.<sup>70</sup>

Let us briefly consider the first two singlet excited states  $S_1(^1A_{1g})$  and  $S_2(^1B_{2g})$  in the square structure. It should be mentioned that the  $S_1$  state is constrained to be planar and squarelike. The electronic excitation energies from the ground state to the  $S_1$  and  $S_2$  states are 39.0 and 49.9 kcal mol<sup>-1</sup>, respectively (see footnote c in Table VI). Their structural parameters, obtained by the MR-AQCC/SA-4-CASSCF method, are compared against the triplet  $^3A_{2g}$  geometry given in Table VII. Once again it turned out that the cc-pVTZ and aug'-cc-pVTZ basis sets gave virtually the same structural parameters. The similarity between the CC and CH bond distances in the  $^1A_{1g}$  and  $^1B_{2g}$  states compared to that of the  $^3A_{2g}$  triplet state is striking. It appears that the *d*(CC) bond lengths in  $^3A_{2g}$  state are 0.005 Å shorter than those in the  $^1A_{1g}$  state as obtained by the aug'-cc-pVTZ basis set. At the same time they are 0.006 Å longer than their counterparts in the  $^1B_{2g}$  state. The C-H bond lengths are the same (1.076 Å). It is remarkable that the first singlet excited state  $^1A_{1g}$  with assumed square structure has the same geometry as the transition state (viz. Tables I and VII). To be quite specific, there are some differences in the higher decimal places, which are, however, negligible and consequently neglected. It should be strongly pointed out that the square planar structure of the  $S_1$  state is not a true minimum on the potential energy surface. Vibrational analysis carried out by the MR-AQCC/SA-4-CASSCF/cc-pVDZ method gave two imaginary frequencies of 568*i* and 573*i* cm<sup>-1</sup>. They correspond to the out-of-plane motions of two 1,3-hydrogen atoms in the opposite directions, whereas the 2,4-hydrogens remain in the molecular plane. In pursuit of finding the minimum of the  $S_1$  state, we have performed potential energy

TABLE VII. Optimized bond lengths in the square planar ( $D_{4h}$ ) structure of the lowest excited states in cyclobutadiene as obtained by MR-AQCC/SA-4-CASSCF calculations. [The square structure in the  $1^1A_{1g}$  excited state is not a true minimum (see text and Fig. 3).]

	Bond lengths <sup>a</sup>					
	$1^3A_{2g}$		$1^1A_{1g}$		$1^1B_{2g}$	
	$R_{C-C}$	$R_{C-H}$	$R_{C-C}$	$R_{C-H}$	$R_{C-C}$	$R_{C-H}$
cc-pVDZ	1.456	1.092	1.461	1.091	1.449	1.091
aug-cc-pVDZ	1.458	1.090	1.462	1.090	1.452	1.090
cc-pVTZ	1.442	1.076	1.447	1.076	1.436	1.076

<sup>a</sup>Bond lengths are given in Å.



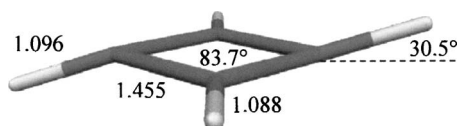


FIG. 3. The most stable structure of CBD in the first excited singlet state  $S_1$ . Bond distances are given in Å.

surface scans along these two modes of imaginary vibrations. The final structure, which served as a candidate for the minimum, was nonplanar with two opposite hydrogens lying out of the molecular plane (Fig. 3). Concomitantly, this excited state is only conditionally denoted by symmetry  ${}^1A_{1g}$  in its equilibrium structure. The MR-AQCC optimization calculations have been attempted for this structure. Unfortunately, the problem of “intruder states” did not render them possible. Therefore, the MR-CISD calculations, including Davidson correction, were carried out indicating that this nonplanar structure is more stable by  $3.7 \text{ kcal mol}^{-1}$ . This offset value can be safely used in considering the excitation energy of the  ${}^1A_{1g}$  state by using results presented in Table VI.

#### IV. CONCLUSIONS

A new benchmark value of the barrier height for the double bond shift automerization reaction of the CBD was computed by using the MR-AQCC/SA-4-CASSCF method. It is  $6.3 \text{ kcal mol}^{-1}$ , which is  $2.3 \text{ kcal mol}^{-1}$  higher than the best earlier theoretical result obtained by Balková and Bartlett.<sup>40</sup> This value includes both the electronic and zero-point vibrational energy contributions. The estimated barrier height lies in the middle of the experimental range of values ( $1.6\text{--}10 \text{ kcal mol}^{-1}$ ) obtained for various derivatives of CBD by using several experimental techniques. A low barrier is compatible with the rapid equilibration of the two isomers found by the ultraviolet and polarized IR spectroscopy measurements<sup>38</sup> at very low temperatures. Extended calculations employing the restricted direct product (RDP) method based on localized CC and CH bonding and antibonding orbitals yield the same barrier if the cc-pVTZ basis set is employed. It is noteworthy that the values for energy barrier height obtained by the MR-CISD+Q and MR-AQCC methods are almost identical. The energy minimum ground state, transition state, and excited state structures were computed by the MR-AQCC/SA-4-CASSCF approach. The minima of the  ${}^3A_{2g}$  and  ${}^1B_{2g}$  excited states on the corresponding potential energy hypersurfaces assume a square geometry of  $D_{4h}$  symmetry, whereas the planar form of the  $2{}^1A_{1g}$  state is not a true minimum. In this case, the out-of-plane motion of opposite 1,3-hydrogen atoms leads to a structure which is  $3.7 \text{ kcal/mol}$  more stable than the planar one.

The CC bond distances of all excited states differ very little from the transition state structure, whereas the CH bond lengths and the HCC bond angles are practically identical to those in the transition state, the first excited singlet state being an exception (*viz.* Fig. 3). One should point out that the difference in the ground state and transition state geometries lies only in the CC bond lengths, implying that the automerization reaction is a bond-stretch event.

The singlet-triplet splitting between the singlet transition state and the first excited triplet state  $\Delta E({}^3A_{2g}, {}^1B_{1g})$  is  $7.4 \text{ kcal mol}^{-1}$ , thus being rather small. Hence, it is concluded that the kinetic instability of CBD due to a small transition state barrier height (ca.  $6 \text{ kcal mol}^{-1}$ ), which in turn does not preclude interconversion of two equivalent isomeric forms, and a low  ${}^3A_{2g}$  state-transition state gap might strongly influence the reactivity of this elusive compound, together with its high energy content caused by the intrinsic structural strain and inherent antiaromatic destabilization in the ground state. Finally, the adiabatic singlet-triplet gap between the ground state and the triplet  ${}^3A_{2g}$  state is estimated to be  $13.2 \text{ kcal mol}^{-1}$ , in excellent agreement with the experimental result of  $12.0 \text{ kcal mol}^{-1}$  obtained for CBD fused to two seven-membered carbocycles substituted by eight methyl groups at four  $\alpha$ -carbon atoms.<sup>70</sup>

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