Ab initio study of the energy difference between the cyclic and linear forms of the C_6 molecule

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The energy difference between the three lowest-lying isomers of C_6, the linear $^3\Sigma_g^-$ state, and the two ring forms, the benzene structure ($^1A_{1g}$) possessing D_{6h} symmetry and a distorted cyclic form ($^1A_1'$, D_{3h} symmetry) have been calculated using various *ab initio* methods. Variational methods such as multireference configuration interaction (MR-CI) and complete active space second order perturbation treatment (CASPT2) have been applied, as well as perturbational treatments and coupled cluster calculations (CCD). The correlation of all valence shell electrons is found to be important for a balanced description of the isomers of C_6. Methods which do not account for higher-order effects appropriately proved to be unsuitable for calculating the energy difference correctly. The results from multireference configuration interaction methods show that the isomers are close in energy with the cyclic forms somewhat lower than the linear form. The ring form possessing D_{3h} symmetry ($^1A_1'$) is found to be the lowest-lying structure.

I. INTRODUCTION

Carbon clusters have recently spurred the interest of the experimental and theoretical communities because of their possible astrophysical significance and their role in elementary chemical processes.[1,2] On the one hand, the nature of large clusters (C_n, $n>60$) has been studied by various methods. The properties of smaller clusters ($n<20$) are also very instructive and furthermore, they often serve as model systems for adjusting the parameters needed in empirical and semiempirical calculations.[3] Therefore, good knowledge of their nature is essential. However, for small carbon clusters (C_4–C_{10}) the discussion about the relative energetical position of the various isomers is still open. A prime example is the C_6 molecule. One of the first *ab initio* investigations on C_6 was performed by Raghavachari *et al.* in 1986[4] and 1987.[5] In their studies the geometries for all structures considered were completely optimized within the given symmetry constraints at the Hartree–Fock (HF) level of theory using a 6-31G* atomic orbital (AO) basis. For the calculation of the total and relative energies of the various isomers complete fourth-order Møller–Plesset perturbation theory (MP4) with the 6-31G* basis set was applied. As a result of their study they found the cumulene structure (structure I) with the valence electronic configuration

$$(\sigma_g)^2(\sigma_u)^2(\sigma_g)^2(\sigma_u)^2(\sigma_g)^2(\pi_u)^4(\sigma_g)^2(\sigma_u)^2(\pi_g)^4(\pi_u)^2$$

corresponding to a $^3\Sigma_g^-$ electronic state about 16 kcal/mol above the benzene form (structure II). The electronic ground state of the benzene form has $^1A_{1g}$ symmetry with the valence configuration

$$(a_{1g})^2(e_{1u})^4(e_{2g})^4(b_{1u})^2(a_{2u})^2(a_{1g})^2(e_{2g})^4(e_{1u})^4.$$

The absolute minimum of C_6 was found to be a planar D_{3h} structure (structure III) lying about 3 kcal/mol below the benzene form. The $^1A_1'$ electronic ground state of the D_{3h} form corresponds to the valence configuration

$$(a_1')^2(e')^4(e')^4(a_2')^2(a_2'')^2(a_1')^2(e')^4(e'')^4.$$

However, as noted in their publication the energy difference between the various structures depends greatly on the correlation treatment and based on coupled cluster calculations (CCD) they estimated the planar D_{3h} structure to lie about 10 kcal/mol below the cumulene structure. This conclusion seems to contradict the electron-spin resonance (ESR) results of VanZee *et al.*[6]

To resolve possible discrepancies between theory and experiment the C_6 molecule was reinvestigated by Parasuk and Almlöf.[7] In their study several geometries were optimized at the 10/10 complete active space self-consistent field (CASSCF) level using a $4s3p1d$ ANO contracted AO basis set.[8] The total energies at the optimized geometries were more accurately determined in the MR-CI calculations, in which ten electrons were correlated. Although the geometrical parameters for the cumulene and the benzene form are similar in both studies, e.g., all nuclear distances are equal within about 0.03 Å, their predictions concerning the relative energetical position of structure I and structures II and III is completely reversed with respect to the investigation of Raghavachari *et al.* According to the calculations of Parasuk and Almlöf the cumulene form (structure I) is the ground state, lying 37.2 kcal/mol below the benzene form. In summary, the predictions of both studies for the relative positions of the linear and the cyclic structures differ by more than 50 kcal/mol.

The idea that effects arising from the correlation of the inner valence electrons are responsible for the discrepancies of both studies was first formulated in Ref. 7. Correlating 24 electrons Parasuk and Almlöf found a reduction of the energy difference of both isomers between 7 and 29 kcal/mol depending on the correlation method used. However, as stated by the authors themselves these calculations were much less reliable than their ten electron calculations which indicated the cumulene form to be the ground state. A detailed investigation of the problem was not given. Furthermore, spin contamination effects for the cumulene form and basis set effects were addressed as possible errors in treat-

ments using the Møller–Plesset ansatz in combination with a 6-31G* basis set.

To the best of our knowledge to date no analysis of the various effects is performed with theoretical treatments appropriate for the description of such complicated systems. Various effects are examined which are responsible for this discrepancy between the energy difference of the linear and cyclic forms. These studies are performed in detail for structures I and II which can be computed economically due to high molecular symmetry. First of all, the influence of the correlation of the inner shell valence electrons is examined, an experience which is very important for reliable treatment of larger clusters. The next item concerns methods which can be applied to describe the relative energetical position of the isomers of C$_6$ properly. Variational correlation treatments such as SD-CI or MR-CI both with and without the Davidson correction and the CASPT2 approach as suggested by Roos and co-workers[9] are employed to elucidate to which extent higher-order effects have to be incorporated. Since in the work of Raghavachari et al.[4] all valence electrons are correlated at the unrestricted Møller–Plesset (UMP4) and coupled cluster (CCD) level, the correlation of the inner shell valence electrons is additionally examined using these perturbational treatments. Furthermore, the UMP4 calculations are extended by Feenberg scaling[10] to study the convergence of the perturbation series. In these computations the basis set used by Raghavachari et al. (6-31G*) is employed. In order to compare the results of these perturbational treatments with those of the variational methods, the effect of the basis set used in the work of Raghavachari et al. and that employed in the present work ([4s3p2d] ANO basis) is examined at the CASPT2 level.

Other findings also differ between the two investigations, i.e., Parasuk and Almlöf find the benzene form to be isoenergetic with the D_{3h} structure while Raghavachari et al. find the D_{3h} structure to be lower by 3.5 kcal/mol. Since the energy difference between structures II and III is expected to be small the energy of the D_{3h} form is calculated using the MRD-CI ansatz which was found to yield reliable results concerning the relative energetical position of the cyclic and linear isomers and to be stable with respect to the underlying CASSCF calculation. A low-lying linear triacetylenic form of $^3\Sigma_u^+$ symmetry is also imaginable. However, both studies agree that this form is much higher in energy than the cumulene form (33.3 kcal/mol according to Raghavachari et al. and 20.9 kcal/mol according to Parasuk and Almlöf). The triacetylenic form will not be considered in the following.

II. METHODS OF COMPUTATION

The AO basis set used in the present work originates from Widmark et al.[11] It consists of a 14s9p4d basis in a [4s3p2d] ANO contraction. Excluding the s components from the Cartesian d functions this yields a total of 138 basis functions for C$_6$.

In their calculations Parasuk and Almlöf used as starting point for the MR-CI calculations a 10/10 CASSCF calculation (all possible distributions of ten electrons in ten valence orbitals). In the present study in addition 12/12 and 14/14 CASSCF calculations were performed. For the calculations
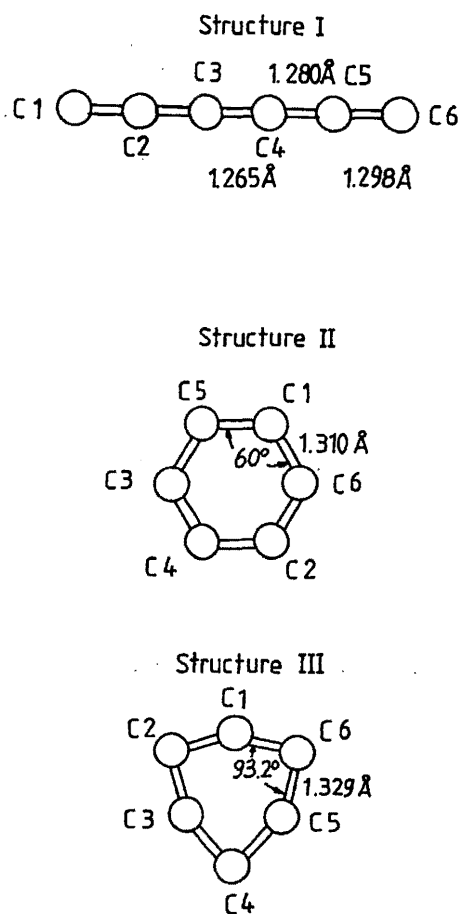

FIG. 1. Various structures of the C$_6$ molecule. Structure I: cumulene form; structure II: benzene form; structure III: distorted cyclic form; the corresponding point groups are $D_{\infty h}$ for structure I, D_{6h} for structure II, and D_{3h} for structure III, respectively. The bond lengths are given in Å.

of the total energies the influence of dynamic correlation effects were estimated using the CASPT2 scheme developed by Anderson et al.[9] Unless otherwise noted a diagonal zeroth-order Hamiltonian was used in the CASPT2 method. These calculations were performed with the MOLCAS program package.[12]

Furthermore, the energies of both isomers were calculated with the SD-CI and MR-CI method. Both were used with and without the Davidson correction.[13] For the MR-CI method the MRD-CI approach as advocated by Buenker and Peyerimhoff[14] was used. To diminish the influence of the perturbative correction the selection threshold T_{CI} was always kept lower than 0.5×10^{-6} hartree. Due to the small selection thresholds up to 600 000 configuration state functions (CSFs) were handled variationally. The influence of the neglected CSFs on the total energy were estimated via the Buenker–Peyerimhoff extrapolation scheme.[14] All calculations were performed with the DMRD-CI program.[15] The geometries given by Parasuk and Almlöf[7] are used throughout for structures I and II. The calculations for the D_{3h} form are performed at the geometry optimized by Hutter and Lüthi[18] on the CCSD(T) level using a TZ2P AO basis. The geometry is similar to those obtained by Raghavachari et al.[4]

TABLE I. Calculated energies for the two isomers, obtained by various methods, ten electrons correlated. Absolute energies in hartree, relative energies in kcal/mol.

$T_{CI} \times 10^6$	N_{sel}	$\Sigma\epsilon_i \times 10^3$	E_{diag}	ΔE_{diag}	E_{MRDCI}	ΔE_{MRDCI}	E_{Dav}	ΔE_{Dav}	Σc^2_{ref}
10ᵃ	3 575	82.5	−227.100 56	25.5	−227.165 14	38.0	−227.181 70	42.2	0.916
10ᵇ	2 609	57.3	−227.059 92		−227.104 56		−227.114 46		0.933
1ᵃ	22 006	24.4	−227.145 44	35.6	−227.165 17	34.9	−227.184 58	39.8	0.902
1ᵇ	14 111	22.8	−227.088 76		−227.109 51		−227.121 21		0.924
0.025ᵃ	164 658	3.6	−227.166 76	35.1	−227.172 28	35.9	−227.194 84	41.4	0.890
0.025ᵇ	239 395	1.7	−227.110 77		−227.115 02		−227.128 91		0.913
0.0ᵃ,ᶜ	1 780 649	0.0	−227.174 00	36.5	−227.174 00	36.5	−227.198 04	42.4	0.884
0.0ᵇ,ᶜ	1 156 165	0.0	−227.115 88		−227.115 88		−227.130 45		0.909

$T_{CI} \times 10^6$	N_{sel}	$\Sigma\epsilon_i \times 10^3$					E_{ACPF}	ΔE_{ACPF}	Σc^2_{rel}
0.0ᵃ,ᵈ	1 780 649	0.0					−227.198 69	43.0	0.965
0.0ᵇ,ᵈ	1 156 165	0.0					−227.130 16		0.974

ᵃCumulene form (structure I).
ᵇBenzene form (structure II).
ᶜMR-CI calculations performed with the MOLCAS program package.
ᵈACPF calculations performed with the MOLCAS program package.

The reliability of the MRD-CI extrapolation scheme is well established.[19] However, the extrapolation scheme can lead to larger uncertainties if the perturbational correction becomes very large.[14] Since for a comparison of both isomers of C₆ correlation effects are expected to be important, test calculations were performed for the cumulene and benzene forms to prove the reliability of the extrapolation for the present problem. The results are given in Tables I (correlating 10 electrons) and II (correlating 18 electrons). Due to the size of the MR-CI space (22×10⁶ CSFs) an unselected MR-CI calculation was not possible in the case of 18 correlated electrons but the results prove to be stable if the sum over the estimated energy contribution of the discarded CSFs ($\Sigma\epsilon_i$) is smaller than 40×10^{-3} hartree. Both tables show that the MRD-CI extrapolation scheme leads to values possessing an uncertainty of about 1–2 kcal/mol with respect to the unselected limit if $\Sigma\epsilon_i$ is smaller than 50×10^{-3} hartree. To

obtain this accuracy only about 1% of the total MR-CI space has to be treated variationally.

Size consistency is approximated in the present study by applying the Davidson correction to the energies obtained by the MRD-CI method (MRD-CI/DAV). In order to test the reliability of the Davidson correction a comparison to the averaged coupled pair functional (ACPF) method[20] is made. As Table I shows both the absolute energies and the energy difference obtained with the Davidson correction (ΔE_{Dav}=42.4 kcal/mol) is quite close to the value obtained from the ACPF approach (ΔE_{ACPF}=43.0 kcal/mol). This suggests that for the present case the ACPF results are well approximated by the Davidson correction. Including the effects arising from the extrapolation scheme as well as the Davidson correction for the present study an uncertainty of about 1–3 kcal/mol has to be considered.

III. RESULTS AND DISCUSSION

A. The energy difference between the cumulene and benzene structure

The complexity of the correlation effects can already be seen from the orbital diagram depicted in Fig. 2. Going from the electronic ground state of the cumulene form, $^3\Sigma_g^-$, to the benzene form with a $^1A_{1g}$ electronic ground state the characters of the orbitals change completely, a typical situation when π-type bonds are changed into σ bonds.

The nature of the various orbitals was already discussed by Raghavachari et al.[4] and Parasuk and Almlöf[7] so only a brief description necessary for an understanding of the CASSCF calculations will be given in the present work. Let us first focus on the cumulene form. The occupied π space (for an illustration of the orbitals see Ref. 7) consists of a fully occupied $1\pi_u(\epsilon_{1\pi_u}=-0.5682$ hartree) and $1\pi_g(\epsilon_{1\pi_g}=-0.4420$ hartree). The next π orbital, $2\pi_u(\epsilon_{2\pi_u}=-0.2254$ hartree) which possesses two nodal planes perpendicular to the molecular axis, is only half-filled, leading to an $^3\Sigma_g^-$ electronic state. The highest occupied σ orbitals $6\sigma_u,7\sigma_g$ are nearly degenerate ($\epsilon_{6\sigma_u}=-0.4877$

TABLE II. MRD-CI energies for both isomers, 18 electrons correlated. For notation see Table I. Absolute energies in hartree, relative energies in kcal/mol.

$T_{CI} \times 10^6$	N_{sel}	$\Sigma\epsilon_i \times 10^3$	E_{MRDCI}	ΔE_{MRDCL}
5ᵃ	18 639	200.0	−227.412 27	11.6
5ᵇ	14 518	144.8	−227.393 80	
1ᵃ	66 527	94.8	−227.405 27	7.9
1ᵇ	42 392	82.1	−227.392 72	
0.5ᵃ	101 816	69.8	−227.404 09	4.8
0.5ᵇ	65 356	65.8	−227.396 44	
0.25ᵃ	148 175	53.3	−227.404 63	3.0
0.25ᵇ	103 624	59.8	−227.399 78	
0.1ᵃ	244 176	38.4	−227.406 61	1.3
0.1ᵇ	202 192	37.2	−227.404 49	
0.05ᵃ	374 369	29.2	−227.408 70	1.2
0.05ᵇ	347 389	27.0	−227.406 71	
0.025ᵃ	593 433	21.6	−227.411 19	1.5
0.025ᵇ	587 717	18.6	−227.408 76	

ᵃCumulene form (structure I).
ᵇBenzene form (structure II).
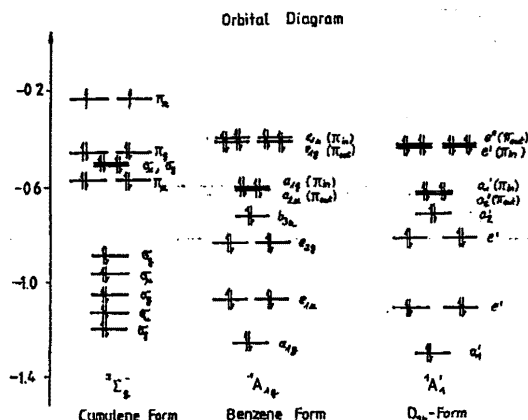
Orbital Diagram

FIG. 2. Orbital diagram of the cumulene, benzene, and D_{3h} forms, orbital energies in hartree.

hartree, $\epsilon_{7\sigma_g} = -0.4866$ hartree). All other occupied σ orbitals are much lower in energy. A CASSCF calculation including all π orbitals (ten electrons) is a good (and manageable) starting point for the cumulene structure.

For the benzene form the occupied π orbitals belong to $e_{1g} (\epsilon_{e_{1g}} = -0.3709$ hartree) and $a_{2u} (\epsilon_{a_{2u}} = -0.5614$ hartree) symmetry. They are very similar in energy to the e_{1u} ($\epsilon_{e_{1g}} = -0.3395$ hartree) and $a_{1g} (\epsilon_{a_{1g}} = -0.5412$ hartree) orbitals which, as pointed out by Raghavachari et al.,[4] can be considered as in-plane pseudo-π orbitals which become π orbitals in the case of a very large carbon ring. To distinguish between the two types of π orbitals they will be called π_{in} orbitals while π orbitals lying perpendicular to the molecular plane will be referred to as π_{out} orbitals. Since both types of π orbitals are very similar in energy, a 10/10 CASSCF calculation seems to be inappropriate as already stated by Parasuk and Almlöf.[7] A 12/12 CASSCF calculation which correlates both types of π electrons would be more adequate. However, in the cumulene form the $6\sigma_u$ and $7\sigma_g$ orbitals are nearly degenerate so that a 12/12 CASSCF calculation is unsuitable for the linear structure. To obtain a starting point of equal quality for both isomers the best treatment would be a 14/14 CASSCF calculation. In accord with the work of Parasuk and Almlöf one series of calculations was performed on the basis of a 10/10 CASSCF calculation for both isomers. As already pointed out all ten π electrons of structure I are correlated. As in the work of Parasuk and Almlöf for structure II the six π_{in} and the four degenerate π_{out} electrons are correlated. In the following they will be abbreviated as (10/10‖10/10). Effects arising from the inclusion of the a_{1g} into the CASSCF space of the benzene form were investigated by further calculations on the benzene form which started from a 12/12 CASSCF treatment. These calculations will be denoted by (10/10‖12/12). In the (14/14‖14/14) CASSCF treatment the highest 14 electrons of both isomers are included in the active space. Further CASSCF correlation schemes will be investigated along with the discussion of the CASPT2 treatment (see below).

As indicated in Fig. 2, in reasonable correlation schemes for the valence shell 14, 18, or 24 electrons are included in

TABLE III. Calculated energy difference between the cumulene and benzene structure ($\Delta E_{D_{6h}} = E_{\text{Benzene}} - E_{\text{Cumulene}}$) in dependence of the number of correlated electrons and the correlation treatment. A positive sign indicates that the cumulene form is lower in energy. All values in kcal/mol.

	$\Delta E_{D_{6h}}$			
	10ᵃ	14ᵃ	18ᵃ	24ᵃ
Based on ᵇ(10/10‖10/10) CASSCF				
SD-CI	53	41	30	30
MRD-CIᵉ	35ᶠ	17ᵍ	1ʰ	−2ⁱ
SD-CI/DAV	46	36	20	21
MRD-CI/DAVʲ	40	20	1	−1
CASPT2	33	9	−5	−10
Based on ᶜ(10/10‖12/12) CASSCF				
SD-CI	···	41	30	30
MRD-CIᵉ	···	17ᵍ	−1ʰ	−5ⁱ
SD-CI/DAV	···	36	21	21
MRD-CI/DAVʲ	···	20	1	−2
CASPT2	···	10	0	−5
Based on ᵈ(14/14‖14/14) CASSCF				
MRD-CIᵈ	···	···	···	−5ⁱ
MRD-CI/DAVʲ	···	···	···	−2

ᵃNumber of electrons correlated.
ᵇ(10/10‖10/10) indicates that in the CASSCF calculations of both structures ten electrons were distributed in ten valence orbitals (see the text).
ᶜ(10/10‖12/12) indicates that in the CASSCF calculations of the cumulene form 10 electrons were distributed in 10 valence orbitals while for the benzene form 12 electrons were distributed in 12 valence orbitals (see the text).
ᵈ(14/14‖14/14) indicates that in the CASSCF calculations of both structures 14 electrons were distributed in 14 valence orbitals (see the text).
ᵉThe reference space contains 35–50 configurations.
ᶠ2–4×10⁶ CSFs generated, 65 000–70 000 CSFs selected.
ᵍ8–17×10⁶ CSFs generated, 130 000–150 000 CSFs selected.
ʰ15–22×10⁶ CSFs generated, 300 000–380 000 CSFs selected.
ⁱ26–33×10⁶ CSFs generated, 440 000–590 000 CSFs selected.
ʲΣc²<0.9.

the treatment. The correlation of the $1s$ shells has only minor effects on the energy difference. At the CASPT2 level the correlation of all 36 electrons alters the energy difference between the benzene and the cumulene structure in favor of the cumulene form by 1 kcal/mol.

The results obtained for the various correlation schemes are summarized in Tables III and V, in which the energy difference between the two isomers, $\Delta E_{D_{6h}} = E_{\text{Benzene}} - E_{\text{Cumulene}}$, is given in dependence of the number of correlated electrons and of the correlation treatment. A positive sign indicates that the cumulene structure is lower in energy. While Table III contains the results of the variational treatments, the energy differences between both structures obtained with pure perturbational methods are given in Table V.

Before comparing the various treatments let us first focus on the energy changes when more and more valence electrons are correlated. For all methods used in the present work the correlation of all valence shells is essential. For the results of the variational calculations this is demonstrated by Table III. In accord to the work of Parasuk and Almlöf the cumulene structure is found to be much more stable than the benzene form if only ten electrons are correlated. As more and more electrons are correlated the benzene form is stabi-

lized with respect to the cumulene structure so that the energy gap between both isomers becomes smaller and for 24 correlated electrons a negative energy difference is found, i.e., the benzene form is more stable than the cumulene conformer. Even the correlation of the electrons in the binding linear combinations of the $2s$ orbitals (24 electrons vs 18 electrons correlated) is necessary.

A very important point for the treatment of even larger clusters is to elucidate to which extent higher-order effects (e.g., multireference effects) have to be considered for a reliable prediction of the energetical positions of various conformers. As was seen above the size of the energy gap, $\Delta E_{D_{6h}}$, between both isomers strongly depend on the correlation treatment. Let us first focus on treatments in which correlation effects are mainly taken into account variationally (SD-CI, MRD-CI, and CASPT2) given in Table III. First of all a large discrepancy between the single-reference CI (SD-CI) and multireference CI (MR-CI) calculations is observed. The Davidson correction reduces this difference to about 20 kcal/mol, a discrepancy which is still considerable. The discrepancy between the two methods is caused by the small weight of the leading reference configuration (0.79 for the cumulene form vs 0.71 for the benzene form).

As can be seen from Table III the influence of the Davidson correction on the energy difference between the various isomers is found to be small for the MRD-CI results.

As pointed out above a $(14/14\|14/14)$ CASSCF is more appropriate for a description of the problem. A comparison of the values in Table III shows that the MRD-CI/DAV calculations are nearly independent of the orbital optimization. For the CASPT2 method the deviations are 5 kcal/mol comparing the $(10/10\|10/10)$ calculation with the $(10/10\|12/12)$ treatment.

To study the dependence of the CASPT2 results on the underlying CASSCF calculation in more detail various different occupation patterns were tested in the CASSCF treatment. The CASSCF and CASPT2 results are given in Table IV. In the CASPT2 treatment 24 electrons were correlated. All $\Delta E_{D_{6h}}$ values are given with respect to a $(10/10\|10/10)$ treatment of the cumulene structure ($E_{CASSCF} = -227.032\ 38$ hartree, $E_{CASPT2D} = -227.672\ 23$ hartree, $E_{CASPT2N} = -227.670\ 21$ hartree). Besides calculations in which a diagonal form of the zeroth-order Hamiltonian is employed (CASPT2D) calculations with the nondiagonal form (CASPT2N)[9] were also performed. Since the effects arising from the different CASSCF treatments are qualitatively equivalent in both CASPT2 methods we will concentrate on the diagonal form.

As expected at the CASSCF level the energy of the benzene form strongly depends on the number of correlated electrons (Table IV). Table IV indicates that the CASPT2 energy of the benzene form is substantially influenced by the inclusion of both types of π orbitals into the CASSCF treatment. In order to obtain reliable values for $\Delta E_{D_{6h}}$ with the CASPT2 method a balanced correlation of π_{in} and π_{out} electrons within the underlying CASSCF treatment is essentially, e.g., by a 8/8 or 12/12 CASSCF calculation. Including pre-

TABLE IV. Calculated energy difference between the cumulene and benzene forms ($\Delta E_{D_{6h}} = E_{Benzene} - E_{Cumulene}$) using a CASPT2 treatment for the correlation of the 24 valence electrons. CASPT2D refers to a diagonal form of the zeroth-order Hamiltonian and CASPT2N to a nondiagonal form. Several different CASSCF wave functions were used as zeroth-order wave functions. A positive sign indicates that the cumulene form is lower in energy. All values in kcal/mol.

n_{el}^a/n_{orb}	$\Delta E_{D_{6h}}$(CASSCF)	$\Delta E_{D_{6h}}$(CASPT2D)	$\Delta E_{D_{6h}}$(CASPT2N)
6/6[b]	103.2	1.3	1.7
10/10[c]	46.5	−1.1	−0.5
6/6[d]	57.9	−8.7	−10.8
10/10[e]	13.9	−9.8	−10.4
8/8[f]	66.4	−5.6	−4.9
12/12[g]	−19.8	−4.8	−7.1

[a] n_{el} denotes the number of active electrons and n_{orb} the number of active orbitals within the CASSCF treatment. The following electrons are correlated in the underlying CASSCF treatment.
[b] Six π_{out} electrons.
[c] Four π_{in} electrons and six π_{out} electrons.
[d] Six π_{in} electrons.
[e] Six π_{in} electrons and four π_{out} electrons.
[f] Four π_{in} and four π_{out} electrons.
[g] Six π_{in} electrons and six π_{out} electrons.

dominantly either π_{in} or π_{out} orbitals in the CASSCF treatment large deviations (≈ 10 kcal/mol) are found in the CASPT2 results, which is shown by the 6/6 and 10/10 CASSCF treatments. If all π_{in} and π_{out} orbitals are optimized in the 12/12 CASSCF treatment a similar value as calculated with the MRD-CI approach is obtained. An analysis of the wave function shows that in the MRD-CI method the correlation of the π_{in} electrons is also more important than the correlation of the π_{out} electrons for the energy of the benzene form. In contrast to CASPT2 the MRD-CI method is found to be stable with respect to the one-particle basis set used.

In the present study it is found that the correlation of all valence shell electrons is essential for a reliable prediction of the relative energetical positions of the benzene and cumulene structures. Using the MRD-CI treatment all valence electrons an energy difference between structures I and II of −2 kcal/mol is computed. This reduces the large gap between the results of Raghavachari et al. (all valence electrons were correlated by means of UMP4) and Parasuk and Almlöf (only 10 valence electrons were correlated in an MR-CI treatment) from more than 50 to only 15 kcal/mol. To resolve the remaining differences the convergence of the perturbational series, the influence of geometry, and AO basis set effects were studied. The influence of the AO basis set on the computed energy difference between the cumulene and benzene forms was tested at the CASPT2 level. Within a 6-31G* AO basis the energy difference is computed to be −9.4 kcal/mol. Consequently, the 6-31G* basis set favors the benzene form by about 4 kcal/mol as compared to the more extensive ANO basis set used in the present work.

The results obtained with several perturbational treatments are summarized in Table V. In order to compare the results with the values reported by Raghavachari et al.[4] a 6-31G* AO basis set was again employed.

In accordance with the variational results the correlation of all valence shell electrons is found to be essential, as was

TABLE V. Results of the perturbation theory calculations using the 6-31G* AO basis set. A positive sign means that the cumulene structure is more stable. The units are kcal/mol. Note that the results for a UHF calculation is 82.1 kcal/mol, whereas the ROHF calculation results in 58.3 kcal/mol.

	14[a]	18[a]	24[a]
UMP2[b]	−6	−26	−35
UMP3[b]	22	10	8
UMP4[b]	8	−13	−22
E4$_{Feen}$	17	−2	−8
CCD[b]	19	6	0

[a]Number of electrons correlated.
[b]The calculations were performed with the GAUSSIAN92 program package (Ref. 21).

already pointed out by Raghavachari.[8] Therefore, only the 24 correlated electron calculations will be discussed. At the UMP4 level the benzene form is found to be −21.5 kcal/mol lower in energy than the cumulene structure. The deviation from the results of Raghavachari et al.[4] who found structure II to be 16.3 kcal/mol lower in energy is due to the different geometrical parameters.

An examination of the unrestricted MBPT calculations suggests that the perturbation series is not converged, in agreement with the values given by Raghavachari et al.[4] This is emphasized by the Feenberg scaling.[10] If it is used to estimate higher-order terms of the perturbation series, the computed energy difference between the two isomers moves markedly towards the variational results. The results obtained with the coupled cluster ansatz are also very close to the results of the variational treatments. Accounting for the 6-31G* basis set we roughly approximate $\Delta E_{D_{6h}}$ to be −4 kcal/mol using the Feenberg scaling and +4 kcal/mol using the CCD method if the larger [4s3p2d] ANO basis has been used.

B. Examination of the D_{3h} form

The results of Sec. III A suggest that the MRD-CI method is suited for a reliable description of the cyclic isomers of the C₆ molecule with respect to the cumulene form. The energy differences between the D_{3h} and the cumulene forms $\Delta E_{D_{3h}} = E_{D_{3h}} - E_{\text{Cumulene}}$ are shown in the upper half of Table VI. The energetical separation between the two cyclic forms $E_{D_{3h}} - E_{\text{Benzene}} = \Delta E_{D_{3h}} - \Delta E_{D_{6h}}$ is given in the bottom half of Table VI.

As for the cumulene and benzene forms the correlation of all valence shell electrons is essential for a balanced description of the D_{3h} form. Increasing the number of correlated electrons the D_{3h} form becomes more and more favored with respect to the cumulene form. However, the influence of the correlation of the σ-binding type orbitals on the energy difference $\Delta E_{D_{3h}}$ between structures I and III (upper half of Table VI) is less dramatic than on the energy difference between the cumulene and benzene forms $\Delta E_{D_{6h}}$ (Table III).

Correlating all 24 valence electrons the MRD-CI/DAV method predicts the D_{3h} form to be lower than the cumulene structure (−7 kcal/mol). Comparing the values of $\Delta E_{D_{3h}}$

TABLE VI. Calculated energy difference between the cumulene and D_{3h} structure ($\Delta E_{D_{3h}} = E_{D_{3h}} - E_{\text{Cumulene}}$) and between the D_{3h} form and the benzene form ($E_{D_{3h}} - E_{\text{Benzene}} = \Delta E_{D_{3h}} - E_{D_{6h}}$) in dependence of the number of correlated electrons and the correlation treatment. A negative sign indicates that the D_{3h} form is lower in energy than the cumulene form and the benzene form, respectively. All values in kcal/mol.

	$\Delta E_{D_{3h}}$		
	14[a]	18[a]	24[a]
	Based on [b](10/10‖12/12) CASSCF		
MRD-CI[c]	8[d]	−6[e]	−8[f]
MRD-CI/DAV[g]	12	−5	−7
		$\Delta E_{D_{3h}} - \Delta E_{D_{6h}}$	
	14[a]	18[a]	24[a]
	Based on [b](10/10‖12/12) CASSCF		
MRD-CI[c]	−9[d]	−5[e]	−3[f]
MRD-CI/DAV[g]	−8	−5	−5

[a]Number of electrons correlated.
[b](10/10‖12/12) indicates that in the CASSCF calculations of the cumulene form 10 electrons were distributed in 10 valence orbitals while for the cyclic forms 12 electrons were distributed in 12 valence orbitals (see the text).
[c]The reference space contains 35–50 configurations.
[d]8–17×10⁶ CSFs generated, 130 000–150 000 CSFs selected.
[e]15–22×10⁶ CSFs generated, 300 000–380–000 CSFs selected.
[f]26–33×10⁶ CSFs generated, 440 000–590 000 CSFs selected.
[g]$\Sigma c^2 < 0.9$.

with those of $\Delta E_{D_{6h}}$ (Table III) it is seen that the D_{3h} form is the energetically lowest structure of the three considered species of C₆. The lowering of the D_{3h} form with respect to the benzene form is suggested by the orbital scheme shown in Fig. 2. Going from structure II to structure III the π_{in} orbitals are especially lowered in energy. Nevertheless, the present calculations show that for a reliable calculation of the energy difference between both cyclic forms a balanced description of the correlation effects is required. On the HF level the D_{3h} form is favored by more than 40 kcal/mol with respect to the benzene form.[4] Including essentially static correlation by means of a 12/12 CASSCF calculation the relative ordering changes, i.e., the benzene form is favored by 3 kcal/mol over the D_{3h} form. The inclusion of the dynamic correlation by the MRD-CI method (including the Davidson correction) lowers structure III by 8 kcal/mol with respect to structure II.

IV. SUMMARY AND CONCLUSIONS

In the present study the energy differences ΔE between the cumulene form ($^3\Sigma_g^-$), the benzene structure ($^1A_{1g}$), and the D_{3h} form ($^1A_1'$) of the C₆ molecule were investigated using several ab initio methods. Variational methods (SD-CI, MR-CI, both with and without the Davidson correction and CASPT2) as well as perturbational treatments (UMP4, with and without Feenberg scaling and CCD) were applied. Such an investigation is of interest since previous studies show very large discrepancies in the predicted values of ΔE (up to 50 kcal/mol). This discrepancy indicates that the C₆ molecule is a complicated system so that high level ab initio treatments have to be employed in order to incorporate various effects which are necessary for a balanced description of the various structures.

Several reasons for the large discrepancy (number of correlated electrons, multireference effects, etc.) between the two studies were investigated and the various treatments in the present work were discussed in detail.

The correlation of all 24 valence electrons is found to be essential as was first formulated in a *Note added in proof* to the work of Parasuk and Almlöf.[7]

However, the computed energy gap depends greatly on the correlation treatment. SD-CI is found to be insufficient even if the Davidson correction is employed. Differences between the MRD-CI and CASPT2 approaches are found to be small, if the underlying CASSCF calculation is appropriate. However, the CASPT2 method was found to be sensitive to the underlying CASSCF calculation ($\sim$10 kcal/mol) while only minor influences on the MRD-CI treatment were seen ($<$2 kcal/mol).

The importance of higher-order effects can also be seen in the slow convergence of the perturbation series in Møller–Plesset calculations, as was already described by Raghavachari *et al.*[4] Use of the Feenberg scaling for an acceleration of the convergence causes the computed energy difference to move towards the variational results. If the coupled cluster (CCD) ansatz is used instead of the Møller–Plesset perturbation theory $\Delta E_{D_{6h}}$ is also calculated to be around 0 kcal/mol. The influence of the geometry optimization ($\sim$4 kcal/mol) and the AO basis set effect ($\sim$4 kcal/mol) are smaller than the effects discussed above.

The present work predicts the D_{3h} structure to be the lowest isomer. The benzene form is calculated to about 5 kcal/mol higher in energy while the energy of the cumulene form is found to be 7 kcal/mol higher than the D_{3h} form.

These results are in qualitative agreement with the calculations of Raghavachari *et al.* who found the same relative ordering of the considered isomers but disagree markedly concerning the absolute values of the energy differences between the various isomers. The quantitative agreement with recent investigations of Hutter and Lüthi[18] is very good. Using a similar ANO basis set in combination with the CCSD(T) method Hutter and Lüthi obtained a value of about 8 kcal/mol for the energy difference between the D_{3h} form and the benzene structure. For the energy difference between the D_{3h} form and the cumulene form they calculated a value of about 10 kcal/mol. The theoretical results seem to contradict experiments in which only the cumulene form is observed. However, our theoretical prediction is corroborated by the fact that elaborate methods such as MRD-CI or CCSD(T) which account for higher-order effects are in appropriately quantitative agreement.

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