# Ab Initio Calculations on 1,2,4,5-Tetramethylenebenzene at Geometries Optimized by π-CI Calculations. Prediction of a Singlet Ground State for a Disjoint Diradical

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Abstract: The geometries of the lowest singlet and triplet states of 1,2,4,5-tetramethylenebenzene have been optimized, using the STO-3G basis set, by π-CI calculations that included all excitations through quadruples. In contrast to results reported previously, the optimized bond lengths in both states are found to be very similar and close to those of the optimized UHF geometry for the triplet. Additional π-CI calculations have been performed with a split-valence basis set at the UHF geometry. All these CI calculations predict a singlet ground state for this diradical, with the lowest triplet computed to be 5–7 kcal/mol higher in energy. In order to aid in the detection of the diradical by optical spectroscopy, the energies of some of the low-lying singlet and triplet excited states have been calculated.

Ab initio calculations have recently been reported on 1,2,4,5-tetramethylenebenzene (1).[2] Since 1 is a diradical in which the nonbonding MOs are essentially those for two pentadienyl radicals, the disjoint nature of these MOs should result in the lowest singlet and triplet state of 1 being nearly degenerate at the SCF level of theory.[3] Inclusion of electron correlation should favor the singlet state, as it does in tetramethyleneethane (2).[3a] In fact, the singlet was computed to be the ground state of 1.[2]
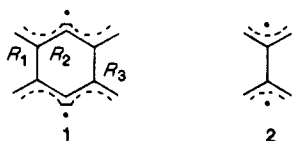
However, there were some puzzling features of the results of these calculations.[2] Because 1 is disjoint, the lowest singlet (^1A_g) and triplet ($^3B_{1u}$) states should have very similar spatial wave functions.[3] Nevertheless, it was found that with the STO-3G basis set[4] and configuration interaction (CI) in the π space that included all single and double (SD) excitations, the singlet and triplet apparently preferred rather different geometries. The energy of the triplet was lower by 33.7 kcal/mol at a geometry that had been optimized at the restricted Hartree–Fock (RHF) level of theory than at one that had been optimized with an unrestricted (UHF) wave function. In contrast, for the lowest singlet state the UHF optimized geometry was found to give an SD–CI energy 2.9 kcal/mol lower than the RHF geometry.

The strong preference of the triplet for the RHF geometry is in itself quite surprising. A UHF wave function provides some correlation between electrons of opposite spin; hence, it should furnish a better geometry for a CI calculation than an RHF wave function.[5] Indeed, as noted above, the singlet was found to prefer the UHF geometry.

Finally, at the SD–CI level of theory the triplet at the RHF geometry was found to lie *below* the singlet at the UHF geometry by 27.4 kcal/mol. The prediction of a triplet ground state for 1 at this level of theory contrasts with the results of additional calculations that included CI through quadruple excitations

(SDTQ–CI). These larger calculations reversed the energy ordering of the ^1A_g and $^3B_{1u}$ states, leading to the conclusion that the singlet was the ground state of 1.

However, the larger CI calculations for $^3B_{1u}$ with both STO-3G and Dunning's double-ζ basis set were performed at the RHF geometry. If the UHF geometry were actually preferred not only for the singlet but also for the triplet, the SDTQ–CI calculations would have been biased in favor of ^1A_g. Thus, we began by investigating whether the triplet actually prefers the RHF or UHF geometry.

SD–CI calculations were performed in the π space of 1 at both geometries,[2] using the STO-3G basis set. The results, which are shown in the first two lines of Table I, indicate that $^3B_{1u}$ prefers the UHF geometry by 7.1 mhartree.[6] Analogous SD–CI calculations, performed for ^1A_g with a two-configuration reference wave function, revealed that the singlet too prefers the UHF geometry. As shown in Table I, at both geometries the singlet was computed to lie below the triplet in energy.

In order to optimize the geometry of both states, additional π CI calculations were performed at points around the UHF geometry. The bond angles and C–H bond lengths were fixed at the UHF values, and calculations were carried out at five additional combinations of R_1 and R_2, with R_3 held at its UHF value. The energies at the six geometries were fitted with a quadratic potential and the optimal values of R_1 and R_2 determined. The remaining C–C bond length, R_3, was then optimized by quadratic fitting.

The CI calculations were performed in D_{2h} symmetry, starting with $^3B_{1u}$ RHF MOs. Because the MOs for $^3B_{1u}$ were expected to be essentially the same as those for ^1A_g, it was anticipated that the MOs from a two-configuration (TC) SCF calculation on the latter state would yield the same CI energies as those from an RHF calculation on the former. This was confirmed at one of the geometries, and it was found that the TCSCF energy of ^1A_g was the same to 0.1 mhartree as the RHF energy of $^3B_{1u}$.

At each geometry both SD and SDTQ–CI calculations were performed for each state. As shown in Table I, the optimized geometries differ slightly, with the smaller CI calculations giving a more highly bond-alternated geometry for each state. The larger CI calculations, by including more electron correlation, favor more delocalized wave functions and, hence, less bond-alternated geometries.[5] The singlet and triplet geometries that were optimized with SDTQ–CI are both very close to the optimized UHF ge-

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(6) The calculations were carried out with MELD, a package of ab initio programs developed at the University of Washington by E. R. Davidson and his collaborators. Although the previously reported calculations[2] were also performed with MELD, it now appears that incorrect lists of configurations were generated for the SD–CI calculations.

Table I. Results of Calculations with the STO-3G Basis Set

geometry[a]	R_1	R_2	R_3	calculation	state	energy[b]
$^3B_{1u}$ UHF	1.385	1.432	1.538	SD–CI[c]	$^3B_{1u}$	–379.8123
$^3B_{1u}$ RHF	1.326	1.472	1.510	SD–CI	$^3B_{1u}$	–379.8052
$^3B_{1u}$ UHF	1.385	1.432	1.538	SD–CI	^1A_g	–379.8169
$^3B_{1u}$ RHF	1.326	1.472	1.510	SD–CI	^1A_g	–379.8086
$^3B_{1u}$ SD–CI	1.365	1.450	1.543	SD–CI	$3^B{}_{1u}$	–379.8143
^1A_g SD–CI	1.368	1.447	1.535	SD–CI	^1A_g	–379.8184
$^3B_{1u}$ SDTQ–CI	1.383	1.437	1.540	SDTQ–CI[d]	$^3B_{1u}$	–379.8475
^1A_g SDTQ–CI	1.384	1.436	1.532	SDTQ–CI	^1A_g	–379.8564

[a] Level of theory at which geometry was optimized; bond lengths in Å. [b] Energy in hartrees. [c] π CI through double excitations from one reference configuration for $^3B_{1u}$ (241 spin-adapted configurations in the CI wave function) and from two reference configurations for ^1A_g (174 spin adapted configurations in the CI wave function). [d] π CI through quadruple excitations from one reference configuration for $^3B_{1u}$ (3613 spin-adapted configurations in the CI wave function) and from two reference configurations for ^1A_g (2350 spin adapted configurations in the CI wave function).

Table II. Results of Calculations with the SV Basis Set[a]

calculation	state	energy[b]
RHF	$^3B_{1u}$	–384.2389
TCSCF	^1A_g	–384.2417
SDTQ–CI[c]	$^3B_{1u}$	–384.3740
SDTQ–CI	^1A_g	–384.3820
MRSD–CI[d]	$^3B_{1u}$	–384.3991
MRSD–CI	^1A_g	–384.4096

[a] Calculations performed at the UHF optimized geometry for $^3B_{1u}$. [b] Energies in hartrees. [c] π CI through quadruple excitations in the 10 orbital space of a conceptual minimal basis set, using K orbitals generated from $^3B_{1u}$ RHF MOs, one reference configuration for $^3B_{1u}$, and two for ^1A_g. Similar CI calculations using K orbitals generated from ^1A_g TCSCF MOs gave the same energy for $^3B_{1u}$ and 0.0002 hartree lower energy for ^1A_g. [d] π CI through double excitations from a 9-configuration reference for $^3B_{1u}$ (38 129 spin adapted configurations in the CI wave function) and from a 10-configuration reference for ^1A_g (21 200 spin adapted configurations in the CI wave function).

ometry. This finding supports the general contention that triplet UHF geometries provide reasonable approximations to triplet CI geometries and hence are useful in diradicals where geometry optimization at the CI level is not feasible.[5]

Because the ^1A_g state of **1** has a very similar spatial wave function to that of $^3B_{1u}$, the two states have nearly the same optimized geometries. The largest difference between the optimized geometries is in the optimal value of R_3, the length of the bonds connecting the pentadienyl fragments at the nodal carbons of the nonbonding MOs. A CI wave function for pentadienyl radical gives negative spin densities at these carbons. In the ^1A_g CI wave function for **1** the spin polarization is opposite in the two pentadienyl fragments, whereas, in the $^3B_{1u}$ wave function it is the same. Thus, in the singlet there is additional π bonding between the two fragments that is not present in the triplet.[3] The additional π bonding is responsible for the smaller optimized value of R_3 in the singlet, and this additional bonding is what causes the energy of the singlet to fall below that of the triplet on inclusion of CI.

In order to verify that a singlet ground state would still be predicted for **1** if a better basis set was employed, additional calculations were performed with Dunning's [9s,5p] → [3s,2p] split-valence (SV) basis set.[7] The calculations were carried out at the UHF geometry that was optimized with the STO-3G basis set.[8] As shown in Table II, at this geometry, even at the SCF level of theory (RHF for $^3B_{1u}$ and TCSCF for ^1A_g), the singlet is computed to be the ground state with the SV basis set.

This change from the results with the STO-3G basis set, where the two states have the same energy at the SCF level of theory,

is due to the greater flexibility of the larger basis set. With the SV basis set the atomic orbitals in the in-phase combination of the nonbonding pentadienyl π orbitals ($2b_{2u}$) can be more diffuse than with the STO-3G basis set, thus allowing for greater direct bonding interaction between the AOs of the two pentadienyl fragments. This is reflected in the larger energy difference between $2b_{2u}$ and its out-of-phase counterpart ($2b_{3g}$) with the SV basis set (18.6 mhartrees) than with STO-3G (1.2 mhartrees).

Consequently, in the TCSCF wave function for ^1A_g the occupation number of b_{2u} is larger with the SV basis set (1.28) than with STO-3G (1.02). Of course, in the RHF wave function for $^3B_{1u}$ the $2b_{2u}$ and $2b_{3g}$ nonbonding orbitals both have occupation numbers of one. Since the singlet can take advantage of the larger energy difference between $2b_{2u}$ and $2b_{3g}$ with the SV basis set, the singlet lies below the triplet at the SCF level when this basis set is employed.

As expected, inclusion of CI further stabilizes the singlet with respect to the triplet. Since we were unable to perform SDTQ–CI in the full π space, which consists of 20 orbitals with the SV basis set, we carried out two different types of CI with this basis set. First, we performed SDTQ–CI in the conceptual minimal basis set consisting of 10 π orbitals. In order to ensure that the virtual orbitals used would provide effective correlation for the filled MOs, K orbitals[9] were employed. The results of these 10 orbital SDTQ–CI calculations are shown in Table II.

Also shown are the results of SD–CI calculations for both states in which all twenty orbitals were used. In order to allow some inclusion of higher excitations from the configuration(s) that appear in the RHF and TCSCF wave functions, the reference space was expanded to include all those singlet and triplet configurations with coefficients greater than 0.1 in the SD–CI wave functions for the two states. The singlet and triplet configurations were compared to ensure that corresponding excited configurations were included in both sets of reference spaces. These multireference (MR) SD–CI calculations give lower energies than the SDTQ–CI calculations in the space of the conceptual minimal basis set. A slightly larger singlet–triplet splitting (6.6 vs. 5.0 kcal/mol) is also obtained with the MRSD–CI calculations.

It has previously been shown that in neutral alternant hydrocarbons like **1**, CI in just the π space can be expected to give energy differences of about the same size as CI calculations in which σ orbitals are included.[10,11] Therefore, there is good reason to believe that the singlet–triplet splitting in **1**, computed with inclusion of more electron correlation, would be on the order of 5–7 kcal/mol, with ^1A_g the ground state.[12] We hope that this prediction will receive experimental test in the near future.

If our prediction of a singlet ground state for **1** is correct, the ground state of this diradical will not reveal itself directly by EPR.[13] Therefore, we have calculated the energies of some of

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(8) In response to the concern of a referee about the possible dependence of the optimized geometry on basis set, we reoptimized the STO-3G UHF geometry with the SV, 3-21G basis set. The 3-21G values of R_1, R_2, and R_3 found were respectively 1.371, 1.408, and 1.564 Å. As expected, each is within 0.03 Å of the corresponding STO-3G value in Table I. Because ^1A_g and $^3B_{1u}$ have very similar optimal geometries, as shown by the first four lines of Table I, the energy difference between them is rather insensitive to the geometry at which it is computed.

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(11) Feller, D.; Davidson, E. R.; Borden, W. T. *Isr. J. Chem.* **1983**, *23*, 105.

(12) Semiempirical INDO/S–CI calculations give a value of 9 kcal/mol for the singlet–triplet splitting, with the singlet again computed to be the ground state: Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273.

Table III. π CI Energies (eV) of Some Low-Lying States[a]

state	SDTQ[b]	MRSD[c]	state	SDTQ[b]	MRSD[c]
^1A_g	0	0	$^3B_{1u}$	0.22	0.29
$^1B_{3u}$	3.45	2.98	$^3B_{3u}$	2.77	2.46
$^1B_{2g}$	3.78	3.40	$^3B_{2g}$	3.28	3.08
2^1A_g	3.94	d	^3A_g	4.44	3.92
$^1B_{1u}$	5.08	4.94	2^3B_{1u}	4.76	d

[a] Calculations carried out at the optimized UHF geometry for $^3B_{1u}$, using K orbitals generated from $^3B_{1u}$ RHF MOs with the SV basis set. [b] π CI wave function with excitations through quadruples in the 10 orbital space of a conceptual minimal basis set and one reference configuration for all states except ^1A_g, for which two reference configurations were employed. Energies are relative to that (−384.3820 hartrees) of ^1A_g. [c] π CI wave function with excitations through doubles in the full 20 orbital space of the basis set from all configurations with coefficients >0.2 in the SDTQ–CI wave function, except for the lowest singlet and triplet states, for which the reference configuration cutoff was a coefficient >0.1. Energies are relative to that (−384.4096) of ^1A_g. [d] MRSD–CI energy not computed.

the low-lying singlet and triplet states of **1**, so that the singlet can be identified by UV spectroscopy. The calculations were performed with the SV basis set at the UHF geometry.

Two types of CI calculations were carried out. The first included SDTQ–CI in the 10 π orbitals of the conceptual minimal basis set. The second consisted of MRSD–CI calculations with the full set of 20 π orbitals, in which all configurations with coefficients larger than 0.2 in the SDTQ–CI were included in the

reference space for the excited states of each multiplicity. The results are shown in Table III.

Not surprisingly, the CI calculations that utilize the full set of 20 π orbitals give lower excitation energies, since they allow greater flexibility in the description of the excited states. However, even these MRSD–CI calculations give excitation energies that are probably too high, since the reference space for the lowest singlet and triplet included all configurations with coefficients larger than 0.1, instead of the 0.2 cutoff used for the excited states. Inclusion of σ–π correlation would probably also tend to lower at least some of the excitation energies by selectively stabilizing those excited states that are more ionic than the lowest singlet and triplet. Therefore, the vertical excitation energies given in Table III should be regarded as upper limits.

The data shown in Table III suggest that ^1A_g should have an absorption spectrum that is distinguishable from that of $^3B_{1u}$. Both states are predicted to have an allowed absorption around or slightly below 3.0 eV, polarized along the long molecular axis.[14] However, the triplet is expected also to have an absorption at lower energy, corresponding to the dipole-forbidden excitation to $^3B_{3u}$.

(13) A singlet ground state could be revealed indirectly by EPR if the singlet–triplet separation were small enough to permit detection of the signal from the triplet and if the Curie plot (signal intensity vs. $1/T$) were found to be convex.

(14) The oscillator strength calculated for the excitation in the singlet manifold is 7.6×10^{-2}, while that for the triplet is 5.9×10^{-2}. The lowest energy transitions that are polarized along the short molecular axis [$^1A_g \rightarrow {}^1B_{1u}$ and $^3B_{1u} \rightarrow {}^3A_g$] are calculated, respectively, to have $f = 3.0 \times 10^{-2}$ and 3.5×10^{-5}.

The Quenching of Aromatic Ketone Triplets by Oxygen: Competing Singlet Oxygen and Biradical Formation?
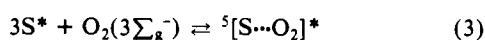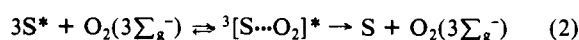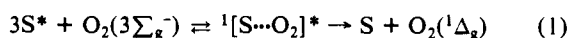
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Abstract: Singlet oxygen, $^1\Delta_g$, has been produced by pulsed laser excitation of benzophenone, acetophenone, 3′-methoxy-acetophenone, and 2-acetonaphthone in benzene and acetonitrile. In some cases second-order decay of the $O_2(^1\Delta_g)$ luminescence, monitored at 1270 nm, has been observed and a similar effect was apparent when $O_2(^1\Delta_g)$ was produced in the initial presence of ketyl radicals. It is proposed that the general inefficiency of $O_2(^1\Delta_g)$ production on sensitization by aromatic ketone triplets is a consequence of competitive biradical formation. Subsequent reaction of these biradicals gives rise to one or more long-lived species which react with $O_2(^1\Delta_g)$.

I. Introduction

The mechanism of the oxygen quenching of triplet states is a subject of some discussion and controversy. The collision complex can have singlet, triplet, or quintet multiplicity (eq 1–3), and it was originally concluded on both theoretical[1] and experimental[2] grounds that quenching proceeds exclusively via the singlet com-

plex and that each quenching act leads to a molecule of $O_2(^1\Delta_g)$. However, work by Garner and Wilkinson[3] and ourselves[4] presented evidence that the oxygen quenchings of several triplet states in benzene do not lead to $O_2(^1\Delta_g)$ with unit efficiency. Although the results were based on indirect techniques and have been

$$3S^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^1[S\cdots O_2]^* \rightarrow S + O_2(^1\Delta_g) \quad (1)$$

$$3S^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^3[S\cdots O_2]^* \rightarrow S + O_2(^3\Sigma_g^-) \quad (2)$$

$$3S^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^5[S\cdots O_2]^* \quad (3)$$

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