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Singlet−Triplet Gap in α-*n*-Dehydrotoluene and Related Biradicals: An ab Initio Configuration Interaction Study

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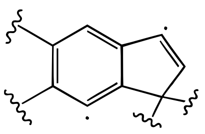
By means of ab initio difference-dedicated configuration interaction (DDCI2) calculations, singlet−triplet gaps of α-*n*-dehydrotoluene (*n* = 2, 3, or 4), **2-o**, **2-m**, **2-p**, and α-3-didehydro-5-methyl-6-hydroxybenzene, **4**, biradicals have been determined. Calculations have been performed with a 6-31G** basis set. A triplet ground state has been found for both the ortho and para isomers of **2**, with quite similar gaps: 6.5 and 6.8 kcal mol^{-1}, respectively. For the meta-substituted compounds, **2-m** and **4**, the ground state is found to be a singlet with a gap of −2.1 kcal mol^{-1} for both compounds. The intermediate in the synthesis of **4** and 2,6-dimethylcyclohexa-2,5-dien-1-on-4-ylidene, **3**, has also been considered. Its triplet ground state does not present a pure carbenic character, but the single electrons are strongly localized in different centers.

1. Introduction

The synthesis and characterization of magnetic molecular materials have been the object of many studies in the past 2 decades. Although an important part of this work has been devoted to materials with metallic magnetic centers, a lot of organic biradicals have also been described.[1] Among them, α-3-dehydrotoluene biradicals have aroused great interest as models for the substituted 3,7-dehydroindene biradical **1**, which is believed to be a key step in the DNA-cleaving action of neocarzinostatin.[2] Although **1** is supposed to be generated by a cycloaromatization reaction from an eneyne−allene precursor, no isolation or direct spectroscopic characterization has been reported, and many efforts have been devoted to generate analogues, such as α-3-dehydrotoluene, **2-m**, by the same synthetic procedure.[3] Wenthold et al.[4] were also able to generate **2-m** in the gas phase, and from collision-induced dissociation experiments, a singlet ground state was found for this biradical. From these experiments as well as from photoelectron spectroscopy,[5] the energy gap with the triplet state was estimated to be 3−5 kcal mol^{-1}. The ortho and para isomers, **2-o** and **2-p**, respectively, were also generated in the gas-phase experiment.



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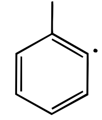
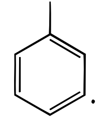
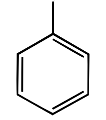


2-o

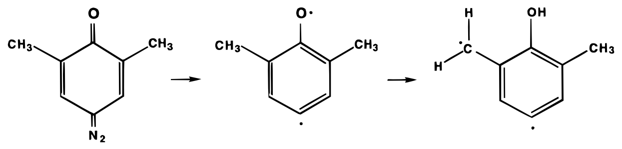


2-m



2-p

Recently,[6] another biradical of this family has been generated photochemically. From a diazocyclohexadienone as a precursor, an intermediate, **3**, is generated, that finally gives the hydroxy-substituted α-3-dehydrotoluene, **4**. **3** and **4** have been characterized by IR spectroscopy on matrix isolation.



3

4

On the basis of an early second-order perturbative treatment proposed by de Loth et al. for biradicals,[7] in previous papers[8−11] we presented a variational method especially conceived to determine energy transitions in these and more complex magnetic systems. This DDCI2 method is the version specifically suited for magnetic systems of the more general difference-dedicated configuration interaction method (DDCI).[12] The method starts by giving a simple zeroth-order description of the energy difference. Differential second-order contributions are then added variationally. DDCI2 has been applied successfully to other organic biradicals[10] and to transition metal binuclear complexes with different types of bridging ligands.[8,9,11] A brief summary of the DDCI2 method will be given in section 2.

Ab initio calculations at different accuracy levels have been performed on **2**[4] as well on **4**,[13] with large active spaces including all the bonding and antibonding π orbitals over the σ nonbonding orbital. Single reference configuration interaction of singles and doubles (SDCI) including Davidson's correction and correlation-consistent CI (CCCI)[14] have also been performed for **2**.[4] The aim of the present work is to show that for these systems with a small active orbital space with a σ orbital and one π orbital only, it is easy to include in a cheap and accurate way, through the DDCI2 method, the significant dynamic correlation, allowing calculations in large biradicalar systems.

2. DDCI2 Method To Evaluate the Singlet−Triplet Separation

The DDCI2 method, the reduced version of DDCI specifically designed for biradicals and for the more general case of magnetic

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systems, is a variational method in which the configuration interaction (CI) space is selected from second-order perturbation theory considerations. Grounded on the early perturbative calculations of singlet−triplet (S−T) gaps in biradicalar systems by De Loth et al.,[7] it was first derived to evaluate variationally this specific type of energy difference[8] and was then generalized for calculating the exchange coupling constant in problems with *n* unpaired electrons in *n* orbitals.[9]

The first step in the perturbative scheme is the definition of a minimal model space, *S*, from the *n* singly occupied "magnetic" orbitals. This model space is generated by the neutral determinants in the valence bond (VB) terminology, i.e., the subspace of the complete active space (CAS) generated from the *n* localized orbitals and the *n* electrons defined with determinants built from different spatial orbitals. In the special case of biradicals, if a and b are the magnetic orbitals, i.e. localized orbitals on each radicalar center, the two-dimensional model space is generated by the neutral determinants $|a\bar{b}\rangle$ and $|b\bar{a}\rangle$. The external correlation is evaluated in the framework of the quasi-degenerate perturbation theory. At this level of theory, it has been demonstrated[8a,9] that from the double excitations contributing to the second-order development of the effective Hamiltonian built on the previously defined model space, only those involving at most two inactive orbitals (doubly occupied or virtual) are significant for the energy differences. The remaining double excitations, although they give very important contributions to the correlation energy, only shift by the same value the diagonal elements of the effective Hamiltonian and thus do not contribute to the spectrum. By only taking into account this small part of the double excitations, the physical effects included at this second-order level are, as discussed by de Loth et al.,[7] the potential and the kinetic exchange, the dynamic spin polarization, and the charge transfer. However, higher order effects may be important, among which the contributions enabling relaxation of the energy of the ionic determinants, in the VB terminology, that appear only at the fourth order. As discussed in ref 7a, this last effect is important because the magnetic orbitals are well adapted to describe the neutral forms, where they are singly occupied, but not the ionic determinants whose energy is largely overestimated.

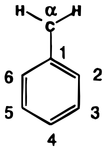
To include higher orders of perturbation, as well as to avoid intruder states, a well-known problem of perturbative effective Hamiltonians,[15] the above perturbative arguments are extrapolated to build a CI space that includes all the second-order excitations that are significant in the spectrum evaluation. It means that the same contributors to the perturbative calculation are included in a CI space, which will be treated variationally. In that way, interactions between double excitations are automatically allowed (enabling, for instance, the relaxation of the ionic forms that appear at the fourth order, as previously mentioned). In a strict sense, for a biradical, the CI subspace would thus include the neutral determinants $|a\bar{b}\rangle$ and $|b\bar{a}\rangle$ and single and double excitations on them involving at most two inactive orbitals (occupied or virtual). This subspace of the CAS single and double CI (CAS*SDCI) is then treated variationally. The method thus gives energy differences from purely variational calculations in magnetic systems and, in particular, in biradicalar systems.

Since we deal now with a CI space, some additional considerations are to be made. The first is the interest in working with symmetry-adapted active orbitals instead of localized ones. Some complementary determinants are added to ensure the invariance of the wave function under unitary transformations of the active orbitals and to obtain S^2 eigenfunctions. The DDCI2 space thus includes the CAS generated from the *n* electrons and the *n* active symmetry-adapted molecular orbitals (MO), which are essentially bonding and antibonding combinations of atomic orbitals centered on the magnetic centers, and all singles and doubles on the CAS involving at most two inactive orbitals. The main characteristics of the DDCI2 method may be summarized in four points: (i) it is a variational method; (ii) for this reason, it is an uncontracted method that allows the external correlation to modify the coefficients of the CAS; (iii) the DDCI2 matrix is invariant under rotations of the molecular orbitals in the active, doubly occupied or virtual subsets, and therefore, the method takes advantage of working with symmetry-adapted MOs; (iv) the number of determinants in the DDCI2 space is proportional to the square of the MO set dimension instead of to the fourth power, as it would be in a CAS single and double CI (CAS*SDCI) calculation. It is worth mentioning that DDCI2 is well designed to give vertical energy differences from a common set of molecular orbitals for all states, but since only a small part of the correlation is included, the absolute energies are not well estimated. On the other hand, because the most important contribution to the total correlation energy comes from the double excitations as pq → rs, where p and q are doubly occupied and r and s virtual spin orbitals, it is also the most significant in the size-inconsistency problems. So DDCI2 is not strictly a size-consistent method, but the size-consistency error is quite small. Several methods have been described to correct size inconsistency in truncated CI calculations such as the self-consistent size-consistent $(SC)^2$ method.[16] This method consists of adding corrections to the diagonal elements of the CI matrix to cancel the unlinked contributions that are responsible for the size-inconsistency (for more details, see ref 16). A quantitative estimation of DDCI2 size-consistency error by using the $(SC)^2$ procedure will be given in the next section.

Another aspect that has to be pointed out is that the arguments that lead to the DDCI or DDCI2 selected space are only strictly correct for vertical transitions. When adiabatic transitions are to be evaluated, the contributions of the neglected double excitations to the correlation energy of each state are to be included. These contributions vary with the geometry, and their effect must be evaluated and added to the results of the DDCI or DDCI2 calculations. In previous studies[12c−e] we proposed that this quantity should be estimated at the MP2 level; in substituted carbenes, where there are significant differences between the geometries of the singlet and the triplet state,[12d] this correction gives about 10% of the gap. When the perturbative estimation is not accurate enough, a previous good knowledge of the ground-state potential energy surface is needed (obtained either from an independent accurate calculation or from experimental information). Then, the transition between the ground state and the excited state(s), calculated at the DDCI level for each geometry is(are) added to the energy of the ground state. Very accurate potential energy curves for K_2 excited states[12g] have been calculated in this way. Since the optimized geometries of both states in the molecules presented are quite similar, the calculation of the vertical transitions is sufficient for the scope of the present work.

A last point should concern the choice of the molecular orbitals. Since the results depend on the MOs used in the CI step, an iterative improvement in the active orbitals has been proposed[12c] to avoid this difficulty. Average orbitals iteratively adapted to both the singlet and the triplet states may be obtained from a single-particle density matrix, $\bar{R}$, obtained by the average of the density matrices of both states, after diagonalizing the

TABLE 1: Optimized Bond Lengths (Å) at the CASSCF(2,2)/6-31G Level for the $^{1,3}A''$ States of α-*n*-Dehydrotoluene, *n* = 2 or 3, 2-o and 2-m, and for the $^{1,3}B_2$ States of α-4-Dehydrotoluene, 2-p**



isomer	state	$C_\alpha-C_1$	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_1-C_6
2-o	$^3A''$	1.444	1.382	1.370	1.389	1.389	1.382	1.404
	$^1A''$	1.454	1.388	1.364	1.395	1.382	1.389	1.395
2-m	$^3A''$	1.448	1.402	1.368	1.373	1.391	1.384	1.400
	$^1A''$	1.449	1.402	1.368	1.373	1.390	1.384	1.399
2-p	$^3B_2$	1.446	1.400	1.386	1.373			
	$^1B_2$	1.456	1.397	1.387	1.371			

DDCI2 matrix. The procedure is iterated to self-consistency. To avoid large computational costs, this iterative procedure is shortened by using only the determinants obtained by single excitations over the CAS, CAS*S, since it is the only subset directly coupled to the determinants of the CAS through the single-particle density operator. Once the self-consistency has been reached and a new set of orbitals adapted to the calculation of the gap has been obtained, only one diagonalization is performed with the whole DDCI2 space. The above procedure is not the only way to obtain mean natural orbitals; state-averaged CASSCF calculations can also provide active orbitals well suited for determining electronic transitions. However, the general advantage of the IDDCI procedure is that it allows, without any difficulty, mixing of states belonging to different irreducible representations.

3. Results

3.1. Computational Details. All the calculations were performed with the standard 6-31G** basis set. The geometries were optimized without symmetry constraints with the GAUSSIAN 94 package[17] at the CASSCF(2,2) level for both the triplet and the open-shell singlet.

The vertical S−T gap was calculated at the DDCI2 level. For all systems, at the optimized geometry of the ground state, an open-shell calculation of the triplet gives the starting MOs. These MOs are iteratively improved by the IDDCI procedure as described in section 2 (CAS*S). When self-consistency of the MOs is achieved, the DDCI2 space is generated and diagonalized. At this step, the calculations were performed with the MOLCAS 4.0 package[18] until the two-electron integral transformation was reached. The DDCI-SCIEL programs[19,20] were then used in the CI calculations.

3.2. α-*n*-Dehydrotoluene Biradicals, 2. The three isomers ortho, meta, and para (**2-o**, **2-m**, **2-p**) of α-dehydrotoluene have been calculated. At the CASSCF(2,2) level, the stability of the three isomers is quite similar, within a range of 5.8 kcal mol^{-1} and within the reported experimental heats of formation.[4] The optimized bond lengths, reported in Table 1, are in agreement with the results of Wenthold et al.[4] As shown in Table 1, the geometries of both states are quite similar, since the largest difference in the bond lengths is lower than 0.01 Å. The angles do not differ more than 0.2°. It justifies the calculation of the vertical transitions. The active orbitals are an a′ (σ) MO (a_1 for **2-p**, since it belongs to C_{2v} point group) basically localized at the ortho, meta, or para position of the benzene ring and an a″ (π) MO (b_2 for **2-p**). The biradicalar singlet and triplet states belong to the A″ irreducible representation (B_2 for **2-p**), and since both magnetic orbitals are well localized, they may be described at the zeroth-order by

$$^3A'' = \frac{1}{\sqrt{2}}[|\sigma\bar{\pi}\rangle - |\pi\bar{\sigma}\rangle]$$

$$^1A'' = \frac{1}{\sqrt{2}}[|\sigma\bar{\pi}\rangle + |\pi\bar{\sigma}\rangle]$$

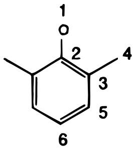
So, for the three isomers, only the A″ (or B_2) DDCI2 space is generated and the lowest roots correspond to the searched $^{1,3}A''$ states. The size of the space is quite small, since it ranges from 7000 determinants for the C_{2v} geometry to 13 000 for the C_s one.

TABLE 2: Singlet−Triplet Energy Separations ($E_S - E_T$), in kcal mol^{-1}, for α-*n*-Dehydrotoluene

	2-o	2-m	2-p
CASSCF(8,8)/6-31G*[a]	6.86	−2.52	6.76
SDCI+DV/pVDZ[a]	4.11	−0.31	3.10
CCCI/pVTZ′[a]	4.22	−0.95	4.99
DDCI2(2,2)/6-31G**	6.45	−2.05	6.79

[a] Reference 4.

TABLE 3: Optimized Bond Lengths (Å) at the CASSCF(2,2)/6-31G Level for the $^{1,3}B_2$ States of 2,6-Dimethylcyclohexa-2,5-dien-1-on-4-ylidene, 3**



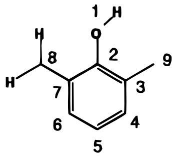
state	O_1-C_2	C_2-C_3	C_3-C_4	C_3-C_5	C_5-C_6
$^3B_2$	1.312	1.412	1.508	1.387	1.372
$^1B_2$	1.328	1.407	1.509	1.391	1.370

The active orbitals have been optimized by using the IDDCI procedure as described in section 2, starting with the CASSCF(2,2) orbitals of the triplet (in fact, OSRHF orbitals). As an example, for **2-o**, which has a triplet ground state, the vertical S−T gap ($E_S - E_T$) calculated from these active orbitals at the DDCI2 level is 6.63 kcal mol^{-1}. The weights of the wave function on the model space are 0.89 and 0.88 for the triplet and the singlet, respectively. When the self-consistency of the orbitals is achieved, the gap is 6.45 kcal mol^{-1}, and the weight of the wave function on the model space has increased to 0.93 for the triplet and 0.96 for the singlet, which shows that the iterative improvement of the active orbitals improves the zeroth-order description of the transition.

Table 2 shows the results of the vertical DDCI2 S−T gaps ($E_S - E_T$) for all isomers. As expected from the local Hund's rule, the ground state of the ortho and para isomers is a triplet, with quite similar gaps (6.5−6.8 kcal mol^{-1}). The singlet and the triplet lie closer in the meta isomer. These results are in a very good agreement with CASSCF(8,8) calculations with the 6-31G* basis set.[4] The SDCI including Davidson's correction and CCCI calculations[4] reported in the table give the same signs but smaller gaps.

Since the quality of our basis set is quite comparable with that of Wenthold et al.,[4] we have performed some additional calculations on **2-o** to evaluate the importance of taking into account the different geometries of both states. A complete SDCI calculation has been performed for both states at the optimized geometry of the triplet state, with the MOs obtained from CASSCF(8,8) calculations. The purely SDCI variational cal-

TABLE 4: Optimized Bond Lengths (Å) at the CASSCF(2,2)/6-31G Level for the $^{1,3}A''$ States of α-3-Didehydro-5-methyl-6-hydroxybenzene Biradical, 4**

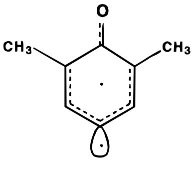


state	O_1-C_2	C_2-C_3	C_3-C_9	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7	C_7-C_8	C_2-C_7
3A″	1.357	1.391	1.512	1.394	1.370	1.367	1.400	1.446	1.403
1A″	1.357	1.392	1.511	1.393	1.370	1.366	1.399	1.447	1.402

culation gives a gap of 2.74 kcal mol^{-1} and, when Davidson's correction is added, of 4.02 kcal mol^{-1}. This last value is very similar to the adiabatic gap of 4.11 kcal mol^{-1} reported by these authors. This result allows us to conclude that the geometries are close enough to neglect this effect.

Regarding size-consistency errors, they are expected to have small effects in DDCI2 calculations, as discussed in section 2. To give a quantitative estimation of this error on the gap, a DDCI2+(SC)^2 calculation[16c] has been performed on both states, giving only an increase of 0.3 kcal mol^{-1} on the gap. So, the size-consistency error is significantly smaller than for the complete SDCI given by the less accurate Davidson's correction, 1.3 kcal mol^{-1}.

3.3. 2,6-Dimethylcyclohexa-2,5-dien-1-on-4-ylidene, 3. Compound **3**, an intermediate in the synthesis of the substituted α-3-dehydrotoluene biradical **4**, generated by visible light irradiation from quinone diazide in matrix isolation,[6] has also been calculated. The optimized bond lengths of both $^{1,3}B_2$ states at the CASSCF(2,2) level are reported in Table 3. As for the precedent compound, the geometries are quite similar for both states. The unsubstituted biradical cyclohexa-2,5-dien-1-on-4-ylidene was already described by Solé et al.,[21] with a comparable geometry. In agreement with the results of these authors, one of the active orbitals belongs to the a_1 irreducible representation and is essentially located in the para position. The second one belongs to the b_2 symmetry and, because of the strong electronegative character of the oxygen, is predominantly located on it, although delocalized on the π system of the ring. Thus, **3** is rather a biradical with strongly separated single electrons compared with a typical carbenic system, and as indicated in ref 21, the electronic structure may be represented as



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The $^1A_1$ singlet state as well as the $^{1,3}B_2$ biradicalar states have been calculated. The triplet $^3B_2$ is the ground state of this system, the corresponding $^1B_2$ singlet lying 8.8 kcal mol^{-1} higher, which compares quite well with the result of Solé et al.[21] The energy of the $^1A_1$ is much higher than both biradicalar states, with a difference of 45.7 kcal mol^{-1} from the triplet. Since the method used here, DDCI2, is especially designed for biradicalar species, this last result gives only the order of magnitude of the closed-shell state relative energy. A complete DDCI[12] calculation, taking into account the relaxation of the geometry, should be performed to obtain a more accurate transition. The wave function for this state shows that the closed-shell configuration has a weight of 0.68 and the double excitation of 0.12.

The intermediate **3** is found to be around 6 kcal mol^{-1} more stable than **4**, at the CASSCF(2,2) level, in agreement with the experimental observation of the stability of this intermediate,[6] which gives **4** after 2 h of UV irradiation.

3.4. α-3-Didehydro-5-methyl-6-hydroxybenzene Biradical, 4. Biradical **4** is an analogue of **2-m**, obtained[6] from UV irradiation of **3**, and a singlet state is expected as the ground state. The geometries of both the singlet and the triplet states are reported in Table 4. As for α-*n*-dehydrotoluene biradicals, **2**, the greatest difference found in the bond lengths is 0.01 Å. The active orbitals are quite similar to those of **2-m**, slightly less localized because of the OH substituent. So these active MOs belong to the a′ and a″ irreducible representations and the singlet and the triplet lowest states are the $^{1,3}A''$ states. The DDCI2 energy difference is found to be −2.14 kcal mol^{-1}, which, compared to **2-m**, −2.05 kcal mol^{-1}, shows a small influence of the substituents on the gap. This result is in agreement with previous MCSCF(9,8) calculations with the small 3-21G basis set,[13] giving −3.5 kcal mol^{-1}.

4. Conclusion

The results give a new confirmation of the good behavior of the DDCI2 method on biradicalar systems. The method includes in the CI space all the correlation contributions to the energy difference between the singlet and the triplet states, selected from second-order perturbative considerations. Thus, the CI space includes as well nondynamical as dynamical correlation but remains quite small, since its size is proportional to the square of the basis set dimension, which makes possible the study of systems that go further than the academic interest. The dynamical correlation is included at the variational level, which gives flexibility to the wave function, since the weight on the model space is allowed to be modified. On the other hand, the iterative improvement of the orbitals from an average density matrix gives active orbitals that progressively concentrate the weight of the wave function on the model space. At self-consistency, the results are independent of the starting MOs used in the calculation. Furthermore, the size-consistency error is quite small and further corrections are not necessary.

The minimal model space of two active orbitals and two electrons is sufficient for the description at the DDCI2 level, since all the remaining orbitals are included in the calculation of the differential correlation. Since the size of the space is also proportional to the CAS dimension, this last aspect gives a definitive advantage when considering the computational cost.

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