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The singlet and triplet states of phenyl cation. A hybrid approach for locating minimum energy crossing points between non-interacting potential energy surfaces

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Abstract. The phenyl cation is known to have two low-energy minima, corresponding to $^1A_1$ and $^3B_1$ states, the first of which is more stable by ca. 25 kcal/mol. The minimum energy crossing point between these two surfaces, located at various levels including a hybrid method first described here, lies just above the minimum of the triplet, 0.12 kcal/mol at the CCSD(T)/cc-pVDZ//B3LYP/SV level, and there is significant spin-orbit coupling between the surfaces at this point. On the basis of these results, the lifetime of the triplet is expected to be very short.

Key words: Phenyl cation – Minimum energy crossing points

1 Introduction

Many molecular systems display a fascinating diversity of isomeric structures, which are, however, all local minima on the same potential energy surface (PES). In some cases, there may be different isomers which lie on *different* PESs. The interconversion of these species is then a non-adiabatic process [1], and obeys completely different rules to those describing molecular motion on a single PES. A good example of a species occupying multiple PESs is the phenyl cation. The ground state of this ion was not known unambiguously until quite recently. Various experimental and computational studies had led to contradictory conclusions, in that some favoured a ground state singlet, while others predicted a triplet ground state [2, 3]. In the $^1A_1$ singlet state, the π electrons of the benzene ring are left intact, and there is an empty, σ-type orbital in place of one of the C—H bonds of benzene. The triplet $^3B_1$ state, on the other hand, has one unpaired electron in the σ orbital, and another in a π orbital of B_1 orbital. Two recent high-level computational studies [2, 3] have readdressed this question and have definitively proved that the $^1A_1$ state is the ground state, situated approximately 25 kcal/mol below the $^3B_1$ state. These computational investigations were also able to explain why the experimental, photoelectron spectroscopy, studies led to contradictory and incorrect results. In fact, the $^3B_1$ state is rather close in geometry to the neutral phenyl radical, since it differs in electronic occupation only by the removal of a π electron, whereas the empty σ orbital present in the $^1A_1$ state leads to extensive rehybridization of the corresponding carbon atom and to a very different geometry from that of the phenyl radical. The Franck-Condon factor is thus expected to largely favour photoionization of the radical to form the $^3B_1$ state. Indeed, explicit calculation of the vibrational wavefunction overlap was performed in one of the studies [2], leading to the prediction that the bands for ionization to the $^1A_1$ state should be very weak, and indeed that the fundamental should not be observed.

In other words, the large difference in geometry between the two spin states of the phenyl cation means that the less stable triplet cation may be preferentially formed in some experimental conditions. The question then arises as to what then happens to this cation. Is it a stable species, what is its lifetime, and can it be made to undergo chemical reactions, or does it decay rapidly to the ground state? This decay is a spin-forbidden, non-adiabatic process [1], which can, in a first approximation, be considered to occur by weak spin-orbit coupling of the two PESs in the vicinity of areas where they cross. To estimate the speed of this process, it is necessary to determine the minimum energy crossing point (MECP) on the hyperline where the two surfaces cross, and the coupling constant between them at that point. In this communication, we have done this for the intersection between the $^1A_1$ and $^3B_1$ states of the phenyl cation. The methods used to locate and characterise the MECP are partly new, and are therefore presented in some detail in Sect. 3.

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2 Computational details

Hartree-Fock (HF) and density functional calculations using the B3LYP hybrid density functional were carried out using Gaussian 94 for Windows [4], on Pentium personal computers, with a split-valence (SV) basis set of double-zeta quality [5]. For the triplet, the unrestricted formalism was used. The two minima were characterized by analytical computation of the force constants at both levels of theory. The MECP was optimized using a simple, steepest-descent type approach [6] using the gradients described in Sect. 3, and was characterized as a minimum on the crossing line by diagonalization of the projected effective Hessian H_{eff} described in Eq. (4) of Sect. 3. The projection [7] and diagonalization were carried out using the Gamess for PC program package (version of 18 March 1997) [8]. The required Hessian was generated in three steps: (1) analytical computation of the Hessian on both surfaces in Gaussian; (2) translation of the Hessian as encoded in the corresponding Gaussian archive entry into a Hessian in Gamess format, using the GRABFF routine [9]; and (3) a Fortran routine [10] written to read in the two Hessians and gradients, to calculate the effective Hessian following Eq. (4), and to write this H_{eff} in Gamess format. Closed-shell and restricted open-shell [11] coupled-cluster calculations were carried out in Molpro [12] using the correlation consistent polarized valence double-zeta (cc-pVDZ) basis set [13].

Calculation of the spin-orbit coupling constant at the geometry of the B3LYP MECP was also performed using Gamess for PC, with the 6-31G(d) basis set [14]. The calculations use an approximate one-electron operator, with an effective nuclear charge $\mathrm{Z_{eff}}$ as an adjustable parameter to incorporate the missing two-electron terms [15, 16]. Values of 3.6 and 1.0 for $\mathrm{Z_{eff}}$(C) and $\mathrm{Z_{eff}}$(H), as recommended in the literature [15], were used in the present study. The spin-orbit coupling matrix element between the singlet wavefunction and each substate of the triplet wavefunction was calculated using complete active space self-consistent field (CASSCF) wavefunctions. The $^1A_1$ wavefunction was a fully optimized CASSCF wavefunction, with the active space including the three bonding π orbitals, the empty σ orbital, and the three empty anti-bonding π orbitals. The $^3B_1$ wavefunction was developed in the same active space, and the orbitals were also optimized, but under the constraint that the 17 core orbitals were identical to those of the singlet state. To test the effect of this approximation, the reverse operation was also carried out, that is the triplet orbitals were fully optimized, and the singlet orbitals optimized under the constraint of maintaining the triplet core orbitals frozen. This led to a nearly identical value of the coupling constant, 7.701 $\mathrm{cm^{-1}}$ vs 8.039 $\mathrm{cm^{-1}}$. This difference is well below the intrinsic error involved in using the approximate one-electron method. Note that we report the absolute value of the coupling constant between coupled substates.

3 Method for locating and characterizing MECPs

Methods for locating the MECP between two non-interacting PESs, e.g. corresponding to states of different spin, of different spatial symmetry, or of different number of electrons, have been described before in the literature [17–19]. These methods require analytical energy gradients, which, together with computational resources, place restrictions on the level of electronic structure theory which can be applied. On the other hand, the previous computational studies on the phenyl cation have shown that obtaining accurate state splittings requires large basis sets and a good level of correlation treatment [2, 3]. Of course, the same computational restrictions and requirements apply when considering the energy of stationary points on a single PES. The difference is that the geometry of stationary points is often relatively level-independent, so that their geometry can be obtained at a low level, and only single-point energy calculations are needed at the expensive correlated level. The geometry of MECPs, on the other hand, is usually strongly dependent on the level, because changing the level of theory can "shift" the PESs relative to one another by sometimes tens of kcal/mol. The MECP will be moved as well, since by definition it depends strongly on the relative energy of the two PESs. To circumvent the necessity of performing full optimization of the MECP in the phenyl cation system at the high levels of theory needed to reliably describe the singlet/triplet splitting, we have developed a hybrid approach for determining MECPs at one level with gradients at another level. This method is new, and may prove useful in many similar situations, so we here describe it in some detail.

It is most readily understood by comparison with the simpler procedure used for locating MECPs using gradients and energies at the same level. This is essentially a combination of the methods of Refs. [18] and [19]. As in Ref. [18], the energies E_{i} on the two PESs and corresponding energy gradients $(\partial E_i/\partial q)$ with respect to the nuclear coordinates q are combined to yield two effective gradients, ***f*** and ***g***. These vectors ***f*** and ***g*** are orthogonal, and go to zero at the MECP, where the energy gradients on the two surfaces are parallel. Around the MECP, ***f*** is orthogonal to the crossing hyperline, whereas ***g*** is parallel to the hyperline and points towards the minimum. These gradients are defined by:

$$f = (E_1 - E_2)\left[\left(\frac{\partial E_1}{\partial q}\right) - \left(\frac{\partial E_2}{\partial q}\right)\right] = (E_1 - E_2)x_1 \tag{1}$$

$$g = \left(\frac{\partial E_1}{\partial q}\right) - \frac{x_1}{|x_1|}\left[\left(\frac{\partial E_1}{\partial q}\right)\cdot\frac{x_1}{|x_1|}\right] \tag{2}$$

In the method of Ref. [18], as well as in other procedures for the location of MECPs [1, 17], the necessary energy gradients are derived from state-averaged complete active space self-consistent field (SA-CASSCF) calculations. Although CAS wavefunctions have undeniable advantages for the description of excited states and distorted geometries, which are often involved when MECPs are concerned, they lead to the recovery of only limited amounts of dynamic correlation energy, which means they are not always well adapted for locating the intersection of surfaces having different amounts of correlation energy. In the present case, for example, the $^3B_1$ phenyl cation is slightly *more* stable than the singlet using HF wavefunctions, and CASSCF only recovers about half of this differential correlation effect, leading to a ca. 50% underestimated state splitting [2]. It is therefore not always the best or only method for obtaining the gradients of Eqs. (1) and (2), and as shown in Ref. [19], it is more appropriate to derive the gradients from *any* electronic structure method, provided the method chosen is appropriate for the problem at hand. The geometry is then optimized using a minimization algorithm following the sum of the two gradients $\boldsymbol{f}$ and $\boldsymbol{g}$. With a simple to implement steepest descent method [6], the geometry can be rapidly (10–15 steps) converged, at least within *chemical* accuracy $\Delta E < 0.05$ mHartree, rms(g) < 0.001 Hartree/a.u.). To obtain a higher level of convergence, a more sophisticated optimization procedure can also be implemented [1, 18, 19].

In the hybrid method, the gradient $\boldsymbol{f}$ is approximated by the closely similar term $\boldsymbol{f}'$:

$$\boldsymbol{f}' = \left(E_1^{\mathrm{high}} - E_2^{\mathrm{high}}\right)\left[\left(\frac{\partial E_1^{\mathrm{low}}}{\partial q}\right) - \left(\frac{\partial E_2^{\mathrm{low}}}{\partial q}\right)\right] \tag{3}$$

In this equation, the subscripts ($^{\mathrm{high}}$) and ($^{\mathrm{low}}$) refer to the level at which the corresponding number or vector is calculated. The idea behind using the low-level gradients is that the overall shape of the two surfaces will be correctly reproduced by the lower level, even if their relative energies are not. Thus, the difference gradient x_1 should have the correct orientation, as should the gradient $\boldsymbol{g}$. Following the approximate gradients $\boldsymbol{f}'$ and $\boldsymbol{g}$ [20] will lead to a point where they are equal to zero, and should in most cases be a good approximation for the high-level MECP. The principle behind this hybrid method can also be expressed using the language of Lagrangian constraints. The standard method for locating MECPs is equivalent to a full geometry optimization on one of the PESs, with the constraint that the difference in energy of the surfaces is zero. The present hybrid method is a *low-level* geometry optimization on one of the surfaces, under the constraint that the difference of the *high-level* energies is zero. The approximate MECP which is located is then the low-level minimum along the high-level crossing hyperline. This approach is in many ways equivalent to that used when calculating high-level single point energies at stationary points optimized at a lower level. In fact, since an MECP located using Eq. (3) is optimized at the lower level, when computing a complete PES, the high-level energies computed at this point should be compared to high-level energies computed at lower-level stationary points [21]. Of course, like the single-point approximation to which it is related, the present approximate method for locating MECPs will fail in some cases, and as for the single-point approximation, this will be when the shape of one of the surfaces at the lower level is seriously wrong.

In symmetrical systems, the stationary point located in the 3N-7 dimensions of the crossing hyperline using either of the two methods described can be a minimum or a higher-order stationary point. Because the MECP is not a stationary point in the full 3N-6 dimensions of either of the PESs, it is not possible to perform a standard frequency analysis. However, an analogous procedure is possible, as suggested by the second-order Taylor expansion for the energy of both surfaces in the vicinity of the MECP, for a displacement Δq along the crossing hyperline (orthogonal to x_1):

$$\begin{aligned} E &= E_{\mathrm{MECP}} + \frac{1}{2}\Delta q^T \left(\frac{\left|\frac{\partial E_2}{\partial q}\right| H_2}{|x_1|} - \frac{\left|\frac{\partial E_2}{\partial q}\right| H_1}{|x_1|} \right) \Delta q \\ &= E_{\mathrm{MECP}} + \frac{1}{2}\Delta q^T H_{\mathrm{eff}}\ \Delta q, \end{aligned} \tag{4}$$

where H_1 and H_2 are the Hessian matrices of second derivatives of the energy with respect to the nuclear coordinates on the two surfaces, which can be calculated in the normal way. Diagonalization of the effective Hessian H_{eff}, should thus yield a set of normal modes and force constants for movement along the crossing hyperline. Because Eq. (4) is only valid for displacements orthogonal to x_1, it is actually necessary to first project out of H_{eff} the 6 rotations and translations and the direction of the difference gradient x_1 before diagonalization. The required projection is well known [7], so it is relatively easy to generate, project, then diagonalize H_{eff}, thus yielding a set of 3N-7 force constants along the crossing hyperline. As stated above, these can be useful for verifying that the MECP is indeed a minimum, and not a higher-order stationary point in the space of the crossing hyperline. They can also be used, for example, for approximate dynamical treatment of the non-adiabatic reaction on the two surfaces.

4 MECP between the $^1A_1$ and $^3B_1$ states of the phenyl cation

The main aim of the present work is to obtain energetics for the MECP between the singlet and triplet PESs of the phenyl cation at the CCSD(T) level of theory, which was shown [2, 3] to provide a very reliable description of the energetics in this $C_6H_5^+$ system. This was one of the motivations in developing the hybrid approach described above, because the geometry optimization of the MECP using CCSD(T) energies and gradients would be too expensive. First, some calibration calculations were, however, performed to test the reliability of the hybrid method. The MECP was optimized (within the C_{2V} point group to which both minima belong) first at the HF level, then at the B3LYP level, but using HF gradients, and finally at the B3LYP level alone. These methods were chosen because they give very different pictures of the energy relations between the triplet and singlet states (see Table 1). Thus, with the basis set we use, the $^1A_1$ state lies 13.2 kcal/mol *above* the $^3B_1$ state at their respective minima at the HF level, whereas with the DFT method, the state splitting is of the right sign and even its magnitude is roughly correct (16.1 kcal/mol). Unlike the relative energies, the geometries (Table 2, Scheme 1) are rather similar.

Table 1. Engergies of points on the $C_6H_5{}^+$ potential energy surfaces (PESs) in kcal/mol relative to ${}^1A_1$ $C_6H_5{}^+$, based on total energies with no zero-point energy correction. The total energies of the ${}^1A_1$ minimum are included for reference. For details of basis sets, see Sect. 2.

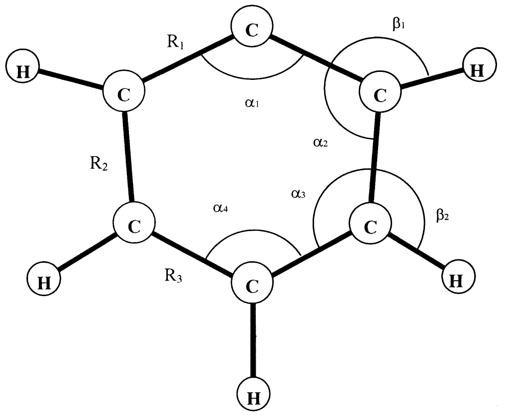
Method	$E_{tot}({}^1A_1$ min.)	E(MECP)	$E({}^3B_1$ min.)	$E({}^1A_1$ at ${}^3B_1$ min.)	$E({}^3B_1$ at ${}^1A_1$ min.)
HF	−229.474817	1.38	−13.23	23.01	12.05
B3LYP//HF	−231.021517	16.09	15.80	22.81	35.53
B3LYP	−231.023226	16.38	16.07	20.74	38.77
CCSD(T)//B3LYP	−230.600367	18.67	18.85	22.39	40.83

Table 2. Geometries of points on the $C_6H_5{}^+$ PESs. Bond lengths are in Å, angles in degrees. MECP, Minimum energy crossing point

	Method	R_1	R_2	R_3	α_1	α_2	α_3	α_4	β_1	β_2
${}^1A_1$ minimum	HF	1.340	1.422	1.401	143.7	106.1	121.1	121.9	129.0	117.7
	B3LYP	1.339	1.447	1.405	144.5	105.8	121.2	121.5	131.0	116.1
MECP	HF[a]	1.359	1.409	1.412	139.3	108.8	120.7	121.9	127.0	118.6
	B3LYP//HF[b]	1.408	1.378	1.433	129.1	114.8	119.5	122.4	121.8	121.5
	B3LYP[a]	1.415	1.392	1.437	128.9	114.9	119.4	122.5	122.3	120.6
	CCSD(T)//B3LYP[b]	1.418	1.390	1.441	128.7	115.1	119.2	122.7	122.2	120.7
${}^3B_1$ minimum	HF	1.422	1.371	1.439	125.5	117.0	119.2	122.1	120.9	121.4
	B3LYP	1.424	1.389	1.444	126.8	116.2	119.4	122.1	121.4	121.0

[a] MECP optimized with the normal procedure

[b] MECP optimized with the hybrid approach, using "high"-level energies and "low"-level gradients



Scheme 1

As could have been expected from the energetics, the HF method performs very poorly as compared to B3LYP for locating the MECP (see Tables 1, 2). At the B3LYP level, the MECP lies just above the triplet in energy, and has a rather similar geometry to that of the triplet minimum. The HF MECP, in contrast, lies just above the *singlet* in energy and has an energy similar to the singlet minimum. Despite this poor behaviour of the HF method, the MECP located using B3LYP energies but HF gradients (Eq. 3, above) is seen to lie very close to that obtained only with B3LYP. Thus, the failure of the HF method to locate the MECP is not due to the shape of the PESs, but only to their relative energies. The same trend is found upon inspecting the gradients at the respective MECPs. At the HF MECP, the gradient on the triplet PES is about three times larger than that on the singlet surface. At the B3LYP and B3LYP//HF MECPs, the situation is reversed with the singlet gradient being larger (6 and 4 times respectively) than the triplet one. To verify that there is no symmetry-broken crossing point which lies lower in energy than the present C_{2V} MECPs, the B3LYP analytical Hessians on both surfaces were computed, at the B3LYP MECP. The resulting effective Hessian H_{eff} of Eq. (4) was then projected and diagonalized, to give effective force constants along the crossing hyperline. These were all positive, indicating that the MECP is indeed a minimum and not a higher-order stationary point. The resulting (unscaled) vibrational frequencies can also be used to include a zero-point energy correction to the B3LYP data of Table 1; this actually leads to the MECP being *lower* than the ${}^3B_1$ minimum, the relative energies of the ${}^1A_1$ minimum, MECP and ${}^3B_1$ minimum being equal to 0.0, 14.9, and 16.7 kcal/mol. This zero-point energy correction may not be very meaningful at the MECP, so one should not take these energies literally, but they underline that the MECP is very close in energy to the triplet.

The data obtained at the B3LYP level should already be quite reliable, since as shown in the previous computational studies on the phenyl cation [2, 3], this method provides excellent geometries for both states, and quite good energetics. However, as stated, we also wanted to obtain coupled-cluster energetics for the crossing point, and therefore reoptimized the MECP at the CCSD(T) //B3LYP level of theory. As can be seen in Table 2, the geometry and relative energy obtained at this level are indeed similar to those obtained with B3LYP. However, the MECP is a little closer to the ${}^3B_1$ minimum, and lies even closer in energy to it, the difference being extremely small, at 0.1 kcal/mol [22]. This means that even in its ground vibrational state, the vibrational wavefunction of the phenyl cation will have a large amplitude in the whole region of the MECP, or, in classical terms, the system will repeatedly traverse the crossing seam. Even if the surface-hopping probability is small at each passage, the triplet state will rapidly decay into the ground, singlet, state.

In a first attempt to quantify this, we considered the spin-orbit coupling constant between the ${}^3B_1$ and ${}^1A_1$

states at the geometry of the B3LYP MECP. From the point of view of the group theory, the matrix element between a B_1 and A_1 state can be non-zero. Also, upon referring to the above description of the two wavefunctions, it can be seen that they differ essentially only in the position of a single electron, which is in an a_1 (σ-type) orbital in the triplet, and in a b_1 (π-type) orbital in the singlet. Therefore, the overlap factor between the two wavefunctions should also be quite large, and one can expect a relatively large spin-orbit coupling constant, considering the low nuclear charge of the nuclei involved. In agreement with these predictions, we obtained a calculated value of 8 cm^{-1}. using an approximate one-electron spin-orbit Hamiltonian operator [15, 16]. Although this coupling constant is rather small in absolute terms, it is certainly large enough to efficiently mediate transition of the triplet cation to the singlet.

5 Conclusions

In this study, we have shown that the intersection between the lowest triplet and singlet hypersurfaces of the phenyl cation lies very close in geometry and in energy to the triplet minimum. Also, the spin-orbit coupling between the two states in the vicinity of the crossing point is small but by no means negligible. It is therefore extremely likely that the triplet phenyl cation is only a very short-lived intermediate which rapidly undergoes spin-forbidden decay to the ground, singlet state. Given an experimental set-up in which the triplet could be unambiguously generated, and its decay to the singlet spectroscopically monitored, it would be possible to test the present prediction.

The location of the MECP at a reliably accurate level of theory required the development of a hybrid method for optimizing the geometry of such MECPs which is analogous to the "single-point" approximation for stationary points, in that it requires the calculation of energy gradients at some lower level of theory, but only of energies at the higher level of theory. This method should be of general use for many problems in non-adiabatic chemistry, where the computational resources required to perform full geometry optimization at a reliable level of theory are simply unavailable. One such area, for example, is the chemistry of transition metals, where spin changes are not at all infrequent and often play a key role [23, 24].

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20. The gradient $\boldsymbol{g}$ used is in fact $\boldsymbol{g}'$, an approximation to $\boldsymbol{g}$ derived from the low-level gradients. The expression used to derive it is identical to Eq. (2), and is therefore not repeated here
21. This is not entirely accurate, because whereas all 3N-6 internal coordinates are optimized at the lower-level for stationary points, for the MECP, only 3N-7 coordinates are, the extra coordinate set being set by the constraint that the high-level energies must be identical. This is, however, expected to make only a very small difference in energy
22. As already pointed out [4], the basis set we use for our CCSD(T) calculations, the cc-pVDZ basis set, is still rather modest. In Ref. [4], the authors performed CCSD(T) calculations using the slightly larger 6-311G(d, p) basis set, and using an extrapolation scheme, effective CCSD(T) calculations with the very large 6-311+G($3df$, $2p$) basis set. At this level, the splitting between the singlet and the triplet phenyl cation is still larger than the value obtained with CCSD(T)/cc-pVDZ. Although it would in principle be possible, we did not seek to locate the MECP using larger basis sets. One may expect the MECP to move still closer to the $^3B_1$ minimum
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