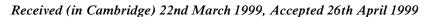# Spin isomerisation of *para*-substituted phenyl cations

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The singlet and triplet potential energy surfaces of a series of *p*-X-substituted aryl cations (X = H, CN, CH$_3$, F, OH, NH$_2$) are investigated computationally at the B3LYP/6-31G(d) level of theory. The first four species are found to be ground state singlets, the last has a triplet ground state, and the spin states of the OH derivative are almost isoenergetic. The minimum energy crossing points (MECPs) between the two surfaces are found to lie very little above the higher of the two minima in all cases, and the spin-orbit coupling is significant at those points. Therefore, it is expected that aryl cations will rapidly convert to their most stable spin state, and that in cases of near degeneracy such as for *p*-HO-C$_6$H$_4^+$, the states may interconvert rapidly enough to both be accessible in thermal reactions.

Introduction

Aryl cations[1] Ar$^+$ are intermediates in a number of organic reactions, of which by far the most important is dediazonation of arene diazonium salts ArN$_2^+$, that is, the loss of molecular nitrogen from these species.[2] They can also be formed in a variety of gas-phase reactions.[3] One particularily interesting feature of these aryl cations is that they have two close-lying spin states (Fig. 1): a closed-shell singlet state in which the aromatic ring has its usual 6 π electrons, the charge being formally associated with an empty in-plane σ-like orbital on the dicoordinate carbon atom; and a triplet state in which there are only 5 π electrons, the σ-like orbital containing a further unpaired electron.[4,5] It has been known for some time that the parent phenyl cation is a singlet in the ground state, and the energy gap between this state and the triplet has recently been established to be *ca.* 100 kJ mol^{-1} by two independent computational studies.[6] Matrix photolysis studies of a number of aryl diazonium salts bearing amino or alkoxy substituents on the ring were able to show that the corresponding aryl cations exist at least in part as triplets.[7] The fact that irradiation of most other aryl diazonium ions did *not* lead to the observance of triplet signals led to the conclusion that triplets were either not formed in those cases, or that they rapidly converted to the singlet states. This is consistent with an early computational study dealing with the stabilisation effect of substituents on phenyl cations,[8] which showed that π-donating substituents stabilise the triplet state much more than the singlet, and, within the accuracy available at that time, that the amino-substituted cations would have triplet ground states.

There has been considerable recent interest in the inter-conversion of spin states, and a number of cases have been described in which a molecule has been observed to react both as a singlet and as a triplet.[9] This implies that the two spin states are able to interconvert with little or no hindrance induced by the spin-forbidden nature of the process. This type of *spin isomerisation* should also be possible in condensed-phase reactions of substituted phenyl cations[10] having roughly isoenergetic triplet and singlet states, provided that they could readily interconvert. In this paper, we extend our recent computational study[11] of the spin interconversion of the singlet and triplet states of the parent phenyl cation to a range of *para*-substituted derivatives, in which the substituents have been chosen so as to yield a broad range of singlet–triplet energy gaps.

Fig. 1 Lewis structures of singlet and triplet states of the phenyl cation.

To characterise the relative stabilities of the states, we have performed standard *ab initio* density functional calculations on the substituted benzene derivatives and the corresponding singlet and triplet aryl cations. Evaluating the probability of spin isomerisation—a spin-forbidden process which, in the absence of spin-orbit coupling would simply not take place—cannot however be treated using standard methods, because it is a non-adiabatic process[12] which intrinsically involves several potential energy surfaces. Thus, it is not possible to locate a transition state between the singlet and triplet states, as one would do for 'ordinary' isomerisation processes. To evaluate the possibility of spin isomerisation, we have instead followed the procedure with which we have recently characterised a range of spin-forbidden processes.[11,13] This involves locating the lowest point on the seam of intersection of the singlet and triplet surfaces (minimum energy crossing point, MECP) and thus determining its energy relative to the two minima, which provides the equivalent of an activation energy for spin isomerisation; and then calculating the spin-orbit induced coupling between the surfaces at the MECP, to provide an estimate of the surface-hopping probability.

Computational details

The B3LYP density functional method[14] was chosen for the calculations relating to the potential energy surfaces because whilst computationally affordable, it has been shown[6a,11] to yield a good description of the singlet–triplet splitting and of the MECP for the parent phenyl cation. The standard 6-31G(d) basis set was used throughout, because preliminary calculations using larger basis sets did not show any significant change in the singlet–triplet energy splittings. The minima were fully optimised without symmetry constraints, and analytical second derivatives were computed at the optimised geometries to identify them as minima. The MECP geometries were located using the steepest descent method of ref. 11, which briefly involves following a generalised gradient which is a sum of one term orthogonal to the crossing seam of the two surfaces, and one which is directed towards the minimum within the seam.[15] The generalised Hessian matrix of second derivatives of the potential energy within the crossing seam was then constructed from the Hessians and gradients on the two surfaces as described in ref. 11. After projection[16] of this matrix to remove rotational and translational motions, and the direction of the gradient, it was diagonalised to yield 'frequencies' for the motions within the crossing seam at the MECP. This enables one to verify that the latter is indeed a minimum within the crossing space, and, together with the frequencies at the minima, to introduce a rather approximate correction for the zero-point vibrational energy (ZPVE) to the MECP relative energies. All DFT calculations were performed using the Gaussian program suite,[17] the

Table 1 B3LYP/6-31G(d) optimized minima: Representative structural data (R in Å, angles in degrees), total electronic energies, and harmonic zero point (ZPVE) energies (in Hartrees)

Species	Point group	State	$R(C_p–C_m)$	Angle ($C_m–C_p–C_m$)	Total energy	ZPVE
H-C$_6$H$_5$	D_{6h}	$^1A_{1g}$	1.397	120.0	−232.24866	0.10073
H-C$_6$H$_4$$^+$	C_{2v}	$^1A_1$	1.327	147.3	−231.26301	0.08513
H-C$_6$H$_4$$^+$	C_{2v}	$^3B_1$	1.412	127.7	−231.23412	0.08612
NC-C$_6$H$_5$	C_{2v}	$^1A_1$	1.397	120.2	−324.49222	0.09944
NC-C$_6$H$_4$$^+$	C_{2v}	$^1A_1$	1.328	147.5	−323.48082	0.08328
NC-C$_6$H$_4$$^+$	C_{2v}	$^3B_1$	1.405	127.9	−323.46257	0.08488
H$_3$C-C$_6$H$_5$	C_s	$^1A'$	1.396	119.4	−271.56665	0.12829
H$_3$C-C$_6$H$_4$$^+$	C_s	$^1A'$	1.327	146.7	−270.58543	0.11259
H$_3$C-C$_6$H$_4$$^+$	C_1	^3A	1.406	127.1	−270.56875	0.11368
F-C$_6$H$_5$	C_{2v}	$^1A_1$	1.397	119.8	−331.48230	0.09260
F-C$_6$H$_4$$^+$	C_{2v}	$^1A_1$	1.330	147.2	−330.48215	0.07675
F-C$_6$H$_4$$^+$	C_{2v}	$^3B_1$	1.410	127.6	−330.47103	0.07900
HO-C$_6$H$_5$	C_1	^1A	1.397	119.3	−307.46487	0.10480
HO-C$_6$H$_4$$^+$	C_1	^1A	1.338	142.9	−306.47653	0.08925
HO-C$_6$H$_4$$^+$	C_1	^3A	1.403	127.2	−306.48064	0.09200
H$_2$N-C$_6$H$_5$	C_s	$^1A'$	1.397	118.9	−287.60176	0.11739
H$_2$N-C$_6$H$_4$$^+$	C_s	$^1A'$	1.360	133.8	−286.62967	0.10296
H$_2$N-C$_6$H$_4$$^+$	C_s	$^3A'$	1.397	126.8	−286.64706	0.10503

construction of the generalised Hessian was performed with our own program,[11] and the projection and diagonalisation of the effective Hessian were performed using the Gamess-USA program.[18]

Root-mean-square spin-orbit coupling matrix elements between the singlet and triplet states at the respective MECPs were also computed with the Gamess program using an approximate one-electron operator.[19] This was done as in ref. 11, except that the standard 6-31G basis set was used instead of the 6-31G(d) one. The wavefunctions were expanded within the CASSCF method, the active space being comprised of 8 electrons in 7 orbitals (6 electrons in 7 orbitals for C$_6$H$_5$$^+$). The values reported are the root-mean-square values of the coupling between the singlet wavefunction and the three triplet sub-state wavefunctions. In ref. 11, we reported instead the value of the two non-zero coupling elements (the rms value is 0.82 times that value).

Results and discussion

Let us first address the question of the substituent effect on the individual stationary points of the aryl cations (Tables 1 and 2). As for the bare phenyl cation, two distinct minima are found corresponding to the singlet and the triplet. The main structural difference between these minima is at the dicoordinate carbon atom, *para* to the substituent, which adopts an sp^2 configuration in the triplet, similar to the neutral benzene species, but a rather sp-like structure in the singlet ions. In these last, the *para* carbon atom therefore forms significantly shortened bonds to the neighbouring (*meta*) carbon atoms, and the angle between these bonds is significantly larger than the sp^2 120 degrees. These structural data are shown in Table 1.

The stability of the spin isomers relative to each other and relative to the singlet phenyl cation (defined as the energy change of the reaction p-X-C$_6$H$_4$$^+$ + C$_6$H$_6$→X-C$_6$H$_5$ + ^{1}C$_6$H$_5$$^+$) are shown in Table 2. The conclusions to be drawn from these results are broadly similar to those obtained by Pople *et al.*,[8] with the main observation being that π-donating substituents such as F, OH and especially NH$_2$ stabilise the triplet relative to the singlet. Thus, our results confirm that amino-substituted aryl cations should have triplet ground states, as is indeed found experimentally.[7] Unlike the earlier study,[8] however, we predict that the hydroxy-substituted cations should have near-degenerate singlet and triplet states. Given the small difference in the energies, the level of theory used, and the expected and observed[7] sensitivity of the relative energetics to the medium, it is of course not possible to predict which state will be most stable under experimental conditions.

If one now considers the geometries of the MECPs (Table 3), it can be observed that they are intermediate between those of

Table 2 Relative energies ΔE(S–T) and stabilisation energies (SE, with respect to the singlet phenyl cation) of singlet and triplet *para*-substituted aryl cations X-C$_6$H$_4$$^+$, and relative energies of the MECP with respect to the singlet and triplet minima, at the B3LYP/6-31G(d) level of theory. All data are in kcal mol^{-1} and include an approximate correction for zero-point vibrational energy

X	ΔE(S–T)	Singlet SE	Triplet SE	ΔE(S-MECP)	ΔE(T-MECP)
H	18.8	0.0	−18.8	16.8	−1.9
NC	12.5	−15.8	−28.3	12.3	−0.1
H$_3$C	11.2	2.8	−8.3	10.5	−0.6
F	8.4	−8.9	−17.3	8.3	−0.1
HO	−2.6	−1.7	−0.9	3.0	3.9
H$_2$N	−10.9	7.8	17.4	−0.5	9.1

the respective singlet and triplet minima, being closest to the higher-lying isomer in each case. This can be considered to be a manifestation of an extended Hammond postulate applied to MECPs as analogues of transition states: the transition state (MECP) is 'early' for an exothermic reaction (or spin interconversion). The relative *energies* of the MECPs (Table 2) are in each case very low with respect to the higher lying isomer. In fact, although the *electronic* total energies of the MECPs are always slightly higher than those of the corresponding higher-lying minima, the inclusion of approximate zero-point vibrational energy (ZPVE), as in Table 2, actually leads to the MECPs lying *lower* than the close-lying minima in many cases. This effect, already noted in ref. 11, is probably due to the rather approximate nature of the harmonic ZPVE correction, especially at the MECP, but does underline how low the MECPs lie in most cases. Irrespective of whether one includes or not the ZPVE corrections, the results suggest that in the absence of constraints due to the spin-forbidden character of the transition, aryl cations formed in the less stable spin state will revert very rapidly to their ground state. The barrier with respect to the higher-lying state is highest for the hydroxy-substituted cation, which is again expected from the Hammond-like postulate since this is the case where the two states are nearly degenerate in energy. However, even in this case, the barrier is very low and lies in an energy range which should be accessible at all but the very lowest temperatures.

To pursue the analogy with transition state theory, the rate of interconversion between the isomers can be thought of as depending on the barrier height (relative energy of the MECP) and a transmission probability (spin-inversion probability at the MECP). This second term will obviously depend most on the spin-orbit coupling between the two surfaces. As can be seen in Table 3, the spin-orbit coupling constants calculated at the MECP are very similar for all the aryl cations, and are of

Table 3 B3LYP/6-31G(d) optimized MECPs: Representative structural data (R in Å, angles in degrees), total electronic energies, harmonic zero point (ZPVE) energies (in Hartrees), and rms spin-orbit coupling (SOC) matrix element (in cm^{-1})

Species	Point group	$R(C_p–C_m)$	Angle ($C_m–C_p–C_m$)	MECP energy	ZPVE	SOC
H-$C_6H_4^+$	C_{2v}	1.402	129.2	-231.23370	0.08264	5.8
NC-$C_6H_4^+$	C_{2v}	1.386	132.2	-323.45900	0.08111	5.4
H_3C-$C_6H_4^+$	C_1	1.383	132.0	-270.56600	0.10992	5.5
F-$C_6H_4^+$	C_{2v}	1.382	133.9	-330.46700	0.07481	6.9
HO-$C_6H_4^+$	C_1	1.368	135.1	-306.47050	0.08801	3.3
H_2N-$C_6H_4^+$	C_s	1.367	132.7	-286.62890	0.10142	4.7

non-negligible magnitude. The prediction emerging from our calculations is thus very similar to that reached for the parent species, phenyl cation: conversion of the less stable spin isomer to the more stable one is expected to be rapid, except perhaps for very low internal energies for the hydroxy-substituted aryl cation. More importantly, perhaps, it appears that for aryl cations in which the singlet and triplet states lie close in energy—like the hydroxy-substituted cation studied here—interconversion from one state to the other, or spin isomerisation, is likely to be fairly rapid. Thus, in the right experimental conditions, it should be possible to detect both spin states. It should be stressed that the spin-orbit coupling constants calculated here are in a range such that the probability of spin-hopping in the region of the seam of intersection will be very small in absolute terms, so that spin-forbidden events will be comparatively rare. However, because the MECPs lie so low in energy with respect to the minima, the ions will approach the seam of crossing very frequently, leading to a high *overall* spin isomerisation rate.

Conclusions

In the present study, *ab initio* computations have been used to determine the parameters that govern the rate of spin-forbidden interconversion of the triplet and singlet states of a series of p-X-$C_6H_4^+$ aryl cations. Thus, we have computed the energies of the relevant minima and of the MECP of the two potential energy surfaces using density functional methods. At the MECP, we have also computed the spin-orbit coupling matrix element. From these calculations, an interesting qualitative picture emerges, with a Hammond-like correlation between the singlet–triplet energy gap, and the position and energy of the MECP. Further, the latter is found to lie very low in energy above the less stable of the two minima. Since the spin-orbit coupling at the MECP is found to be non-negligible, we predict that regardless of how they are formed, aryl cations should convert to their most stable spin state (the singlet for X = H, CN, CH$_3$ and F, and the triplet for X = NH$_2$) very rapidly. For the hydroxy-substituted aryl cation, where the two spin states are near-degenerate in energy, the predicted rapid interconversion raises the interesting possibility of observing the *spin isomerisation* of this system, that is, its conversion from one spin state to the other, depending on the experimental conditions.

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