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Substituent Effects on the Electronic Ground State (Singlet *versus* Triplet) of Indenyl Cations: DFT and CASPT2 Studies

Ma-aya Takano,[a] Ivana Antol,*[b] and Manabu Abe*[c]

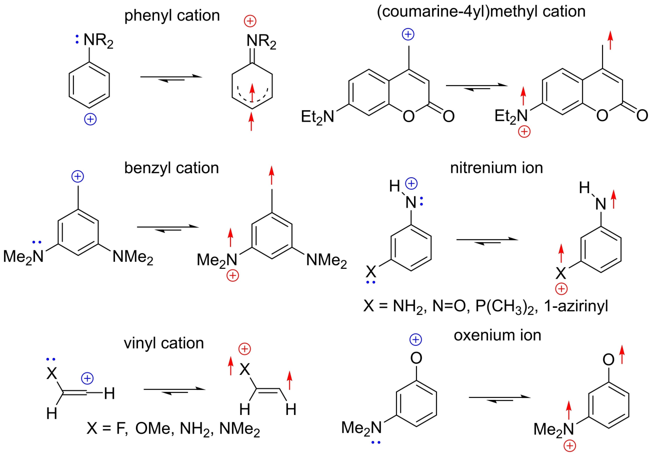
This paper is dedicated to Professors Dennis Curran and Shigeru Yamago on their 70th and 60th birthdays, respectively.

The electronic ground states of cations (singlet *versus* triplet) attract significant attention in the discovery of novel carbocation chemistry. Although the cyclopentadienyl cation exhibits a triplet ground state because of the antiaromaticity of the closed-shell singlet state, the ground state of the indenyl cation, which is a benzene-fused derivative of the cyclopentadienyl cation, is reportedly a closed-shell singlet state rather than a triplet state. In this study, in order to establish a strategy for controlling the ground state of indenyl cations, the substituent effects at the C2 and C5 positions of their structures were computed using density functional theory and complete active space multiconfiguration second order perturbation levels of theory.

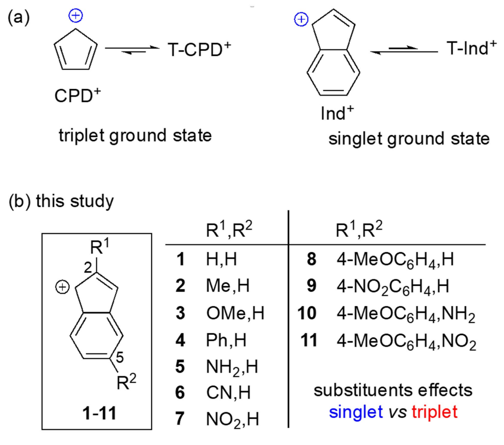
Introduction

Carbocations are essential intermediates in thermal and photochemical reactions. Their generation, observation, and reactivities have been thoroughly studied since the last century[1–3] to reveal that the electronic ground state of cation is supposed to be closed-shell singlet (S) state. Recently, however, the ground states of phenyl,[4–8] (coumarin-4-yl)methyl,[9,10] benzyl,[11,12] vinyl[13] cations were reportedly switched to their triplet (T) states via the introduction of substituents with lone-pair electrons, such as amino groups (NR_2) (Scheme 1). Furthermore, the T ground states of nitrenium[14,15] and oxenium ions[11,16] were also obtained by introducing NR_2 at the *meta*-positions of the phenyl rings. The recent studies are opening new areas of cation chemistry.

The cyclopentadienyl cation (CPD^+) exhibits a T ground state ($\Delta E_{ST} = 8.7$ kcal mol^{-1})[1–19] because of its Hückel antiaromaticity, which destabilizes the S state, and Baird aromaticity,[20,21] which stabilizes T-CPD^+ (Scheme 2). Remarkably, however, the electronic ground state of the indenyl cation (Ind^+), which is a benzene-fused derivative of CPD^+, is the S ground state ($\Delta E_{ST} \approx -10$ kcal mol^{-1}).[19] The resonance stabilization of the positive charge (22.0 kcal mol^{-1})[19] by the fused benzene ring is key in



Scheme 1. Triplet ground states of carbocations and the nitrenium and oxenium ions.



Scheme 2. (a) Ground states of the cyclopentadienyl (CPD^+) and indenyl (Ind^+) cations. (b) This study: effects of the substituents (R^1 and R^2) on the ground states (singlet *versus* triplet) of indenyl cation derivatives **1**–**11**.

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stabilizing the S state. In this study, the novel C2 (R^1) and C5 (R^2) substituents effects on the electronic

ground states of Ind^+ derivatives **1**–**11** are investigated for the first time using quantum chemical calculations, such as density functional theory (DFT) and complete active space multiconfiguration (CAS) second order perturbation theory (CASPT2/CASSCF) calculations to establish a strategy for controlling the ground state. The ground state is found to be significantly affected by the substituent at the C2 and C5 positions.

Results and Discussion

Electronic structure and configuration of 1–11

Firstly, geometries of the S and T state of **1** ($=Ind^+$; $R^1,R^2=H,H$) were respectively optimized at the restricted (R) and unrestricted (U) B3LYP/6-31G(d,p) level of theory (Figure 1). The energies were further refined at the CASPT2/cc-pVDZ level of theory (entry 1 in Table 1). It was shown that the singlet state is 13.1 kcal mol^{-1} (CASPT2) and 9.99 kcal mol^{-1} (RB3LYP) more stable than the triplet state in accordance with literature available estimates.[19] Analysis of the CASSCF reference wavefunction confirmed domination of only one leading configuration in the wavefunction for both singlet (weight 83%) and triplet (weight 84%) states. See the details in Tables S9-S11 in Supporting Information. Thus, the singlet state can be properly described by the closed shell singlet electronic configuration. To understand the electronic character of **1**, its NBO charges and NBO spin densities were computed in the S (S-**1**) and T states (T-**1**) at the (R/U)B3LYP/6-31G(d,p) level of theory (Figure 1). In S-**1**, the positive charges are delocalized at the benzylic positions C1/C3 (0.34) and the benzene ring C4/C7 (0.21) (Figure 1a). Whereas in T-**1**, the positive charge at C2 (0.20) is larger than that at C1/C3 (0.16). Interestingly, the considerable positive charge is found at C5/C6 (0.15). On the other hand, the spin density at C1 (0.39) is higher than that at C2 (0.31) (Figures 1b, c). These results suggest that the substituents at C2 and C5 might significantly affect the energetic stability of triplet state of indenyl cation derivatives. Thus, the electron-donating (EDG) and electron-withdrawing group (EWG) effects at C2 and C5 on the electronic ground states (singlet *versus* triplet) of **1**–**11** were investigated via DFT and CASPT2/CASSCF quantum chemical calculations.

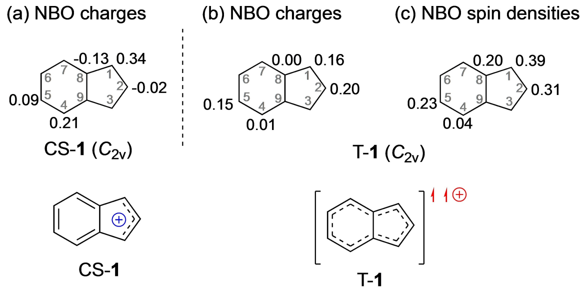
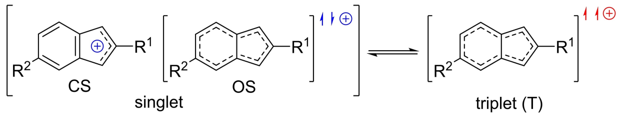


Figure 1. (a) NBO charges of the closed-shell singlet indenyl cation S-**1** in C_{2v} symmetry at the RB3LYP/6-31G(d,p) level of theory; (b) the NBO charges; (c) NBO spin densities of the triplet indenyl cation T-**1** at the UB3LYP/6-31G(d,p) level of theory;

Table 1. Singlet-triplet energy gaps in kcal mol^{-1} (ΔE_{RST} = singlet (RS) energy from RDFT− triplet (T) energy, ΔE_{UST} = singlet (US) energy from UDFT − T energy, as calculated using DFT[a] and ΔE_{ST} = singlet energy−-triplet energy as calculated using CASPT2/CASSCF[b] methods).



entry	cation R^1, R^2	ΔE_{RST} DFT	ΔE_{UST} DFT ($<S^2>$)[c]	ΔE_{ST} CASPT2	ground stateCASPT2
1	**1** (=**Ind$^+$**) H, H	−9.99	−9.99 (0.00)	−13.14	S
2	**2** Me, H	−5.31	−5.31 (0.00)	−9.49	S
3	**3** OMe, H	5.38	1.13 (0.96)	0.46	T
4	**4** Ph, H	5.48	1.74 (0.88)	−1.32	S
5	**5** NH_2, H	13.15	6.95 (1.05)	4.66	T
6	**6** CN, H	−6.52	−6.52 (0.00)	−11.25	S
7	**7** NO_2, H	−11.17	−11.17 (0.00)	−14.45	S
8	**8** 4-$MeOC_6H_4$, H	9.62	3.31 (1.03)	7.37	T
9	**9** 4-$NO_2C_6H_4$, H	2.06	0.38 (0.70)	−4.33	S
10	**10** 4-$MeOC_6H_4$, NH_2	−2.11	−2.77 (0.18)	−7.65	S
11	**11** 4-$MeOC_6H_4$, NO_2	9.09	3.67 (1.02)	6.77	T

[a] The closed-shell singlet (S) and triplet (T) states were computed at the R and UB3LYP/6-31G(d,p) levels of theory, respectively. Similar substituent effects were also found at the CAM-B3LPY, ωB97XD, and M06-2x/6-31G(d,p) levels of theory (Tables S6, S7). The singlet states (noted US) were also calculated using the broken-symmetry (BS) unrestricted singlet method by including "guess=mix,always" in the keywords at the UB3LYP/6-31G(d,p) level of theory. [b] CASPT2/CASCF/cc-pVDZ level of theory. [c] $<S^2>$: expectation values of the spin operators in the BS calculations of the singlet states using unrestricted approach.

The geometries of the singlet and triplet states of indenyl cations **2**–**11** were also optimized using DFT calculations at the (R or U)B3LYP/6-31G(d,p) level of theory (SI(S16–43), Table 1). The broken-symmetry[22–25] (BS) UB3LYP/6-31G(d,p) method was used to re-evaluate geometries and energies of the singlet states, resulting in more stable minima (noted as US) for derivatives **3**–**5** ($R^1,R^2=OMe,H$; Ph,H; NH_2,H) and **8**–**11** ($R^1,R^2=4$-

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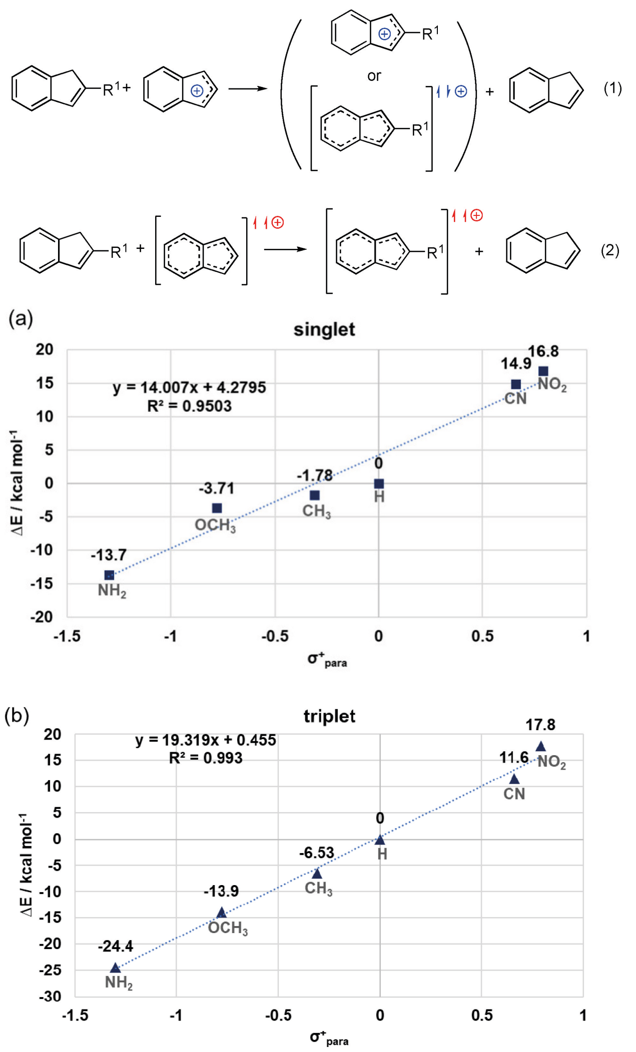


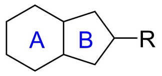
Figure 2. Hammett plots (HPs) of the (a) singlet (Equation (1)) and (b) triplet (Equation (2)) states.

$MeOC_6H_4$,H; 4-$NO_2C_6H_4$,H; 4-$MeOC_6H_4$,NH_2; 4-$MeOC_6H_4$,NO_2), whose vibration analyses of all molecules reveal no imaginary frequencies, indicating that the optimized structures are at their potential energy minima. Single point calculations of energies were conducted with multireference CASPT2 method using geometries from UB3LYP calculations (entries 3–5, 8–11). Wavefunction details and natural occupation numbers of active orbitals are listed in Tables S9–S11 in Supporting Information. In contrast to parent cation **1** with closed shell configuration (entry 1, spin-expectation value $<S^2>=0.00$), most of the substituted indenyl cation derivatives have multiconfigurational character of the wavefunction for singlet states ($<S^2>\neq 0.00$). It is particularly emphasized for cations **3** (R^1,R^2=OMe,H; entry 3), **5** (R^1,R^2=NH_2,H; entry 5) and **8** (R^1,R^2=4-$MeOC_6H_4$,H; entry 8) where the weight of leading configuration (classical HF closed-shell configuration) is substantially decreased with respect to parent unsubstituted indenyl cation **1** and second configuration (double excitation) contribute more than 10% (weights = 0.19, 0.12 and 0.20 for **3**, **5** and **8**, respectively). Natural occupation numbers of frontier orbitals (1.46 and 0.55 for **3**, 1.62 and 0.41 for **5**, and 1.39 and 0.65 for **8**) significantly deviate from 2 and 0. In view of these results it is apparent that the singlet states of these cations have significant diradical character. It is well known that such species with diradical character obtained from mixing of two closed shell configurations are not properly described by the restricted DFT methods and therefore the energies of singlets profit a lot using broken symmetry unrestricted approach.[11,13,26–30] Indeed singlets optimized by BS-UB3LYP for cations **3**, **5** and **8** are more stable by 4.3, 6.2 and 6.3 kcal mol^{-1}, respectively. On the other side, restricted and unrestricted calculations resulted in the same geometries and energies for singlet states of **2** (R^1,R^2=Me,H; entry 2), **6** (R^1,R^2=CN,H; entry 6), **7** (R^1,R^2=NO_2,H; entry 7) and **10** (R^1,R^2=4-$MeOC_6H_4$,NH_2; entry 10). As previously shown for singlet of parent indenyl cation **1**, the singlets of these cations have more than 80% of leading configuration vs. less than 6% of second configuration.

Singlet-Triplet energy splitting

The energy gaps determined using the total electronic energies (*E*), including zero-point energy corrections between the S and T states ($\Delta E_{RST}=E_{RS}-E_T$ and $\Delta E_{UST}=E_{US}-E_T$), are shown in Table 1. A positive value indicates that the T state is more energy-stable than the corresponding singlet state, i.e., the T state is the ground state. The methyl derivative **2** (R^1,R^2=Me,H, entry 2) as determined previously for parent cation **1**, exhibit singlet ground state ($\Delta E_{RST}=\Delta E_{UST}=-5.31$ kcal mol^{-1}). However,

Table 2. NICS(1)$_{zz}$ values of **1**, **4**, **5**, and **7**.



		1 (R^1,R^2=H,H)	4 (R^1,R^2=C_6H_5,H)[a]	5 (R^1,R^2=NH_2,H)[a]	7 (R^1,R^2=NO_2,H)
S	A	49.2	41.0	42.4	48.2
	B	104	89.7	81.0	99.0
T	A	−20.7	−20.3	−23.7	−19.2
	B	−32.5	−15.3	−18.2	−28.9

[a] UDFT calculations were used for singlet states of cations **4** and **5**.

Table 3. ACID plots of **1**, **4**, **5** and **7**.

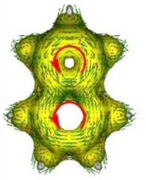
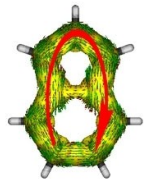
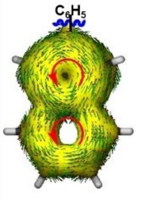
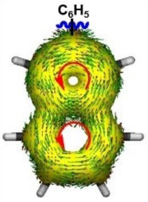
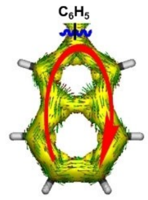
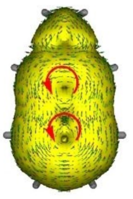
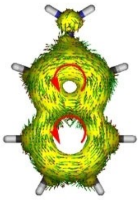
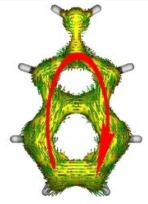
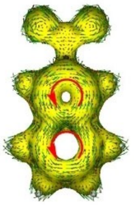
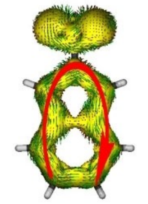
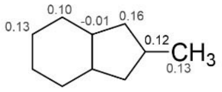
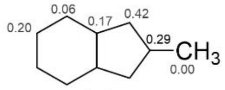
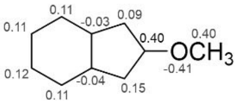
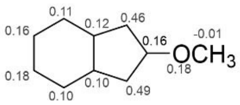
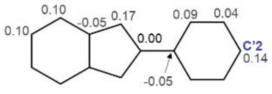
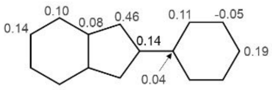
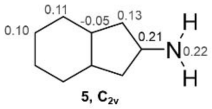
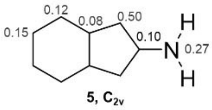
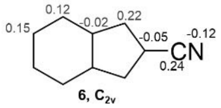
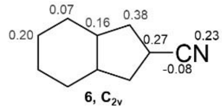
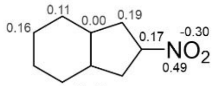
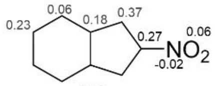
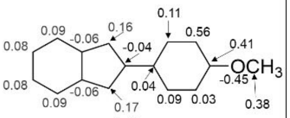
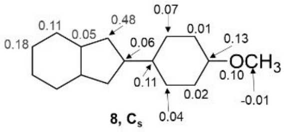
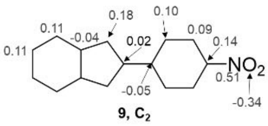
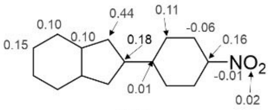
Cation	R^1, R^2	Singlet (RDFT)	Singlet (UDFT)	triplet
1	H,H		–[a]	
4	C$_6$H$_5$, H			
5	NH$_2$,H			
7	NO$_2$,H		–[a]	

Table 4. NBO charges and NBO spin densities of **2–9** determined at the (U)B3LYP/6-31G(d,p)) level of theory.

NBO charges of triplet	NBO spin densities of triplet
 **2**, C$_s$	 **2**, C$_s$
 **3**, C$_s$	 **3**, C$_s$
 **4**, C$_{2v}$	 **4**, C$_{2v}$
 **5**, C$_{2v}$	 **5**, C$_{2v}$
 **6**, C$_{2v}$	 **6**, C$_{2v}$
 **7**, C$_2$	 **7**, C$_2$
 **8**, C$_s$	 **8**, C$_s$
 **9**, C$_2$	 **9**, C$_2$

as compared with $\Delta E_{RST} = -9.99$ kcal mol^{-1} for **1** the weak EDG decreases the energy space. The later conclusion is corroborated by CASPT2 calculations where ΔE_{ST} for **2** is 3.65 kcal mol^{-1} smaller than for **1**. Both DFT and CASPT2 methods agree that cations **3–5**, **8** and **11** (R^1,R^2=OMe,H; Ph, H; NH$_2$,H; 4-MeOC$_6$H$_4$,H; 4-MeOC$_6$H$_4$,NO$_2$), with strong EDGs at C2, display T ground states. Also, cations **6** (R^1,R^2=CN,H entry 6), **7** (R^1,R^2=NO$_2$,H entry 7), and **10** (R^1,R^2=4-MeOC$_6$H$_4$,NH$_2$; entry 10), with EWGs at C2 and EDG at C5, display singlet ground states. In the case of cation **9** (R^1,R^2=4-NO$_2$C$_6$H$_4$,H, entry 9) with EWG at C2 triplet and singlet states are approximately the same energy (triplet state is only 0.38 kcal mol^{-1} lower than singlet) at the DFT level of theory while CASPT2 method predicts singlet ground state 4.33 kcal mol^{-1} below the triplet state. The quantum chemical calculations were rationalized using the electronic character of indenyl cation **1** (Figure 1). Thus, substituents, EDG/EWG, at C2/C5 may determine the electronic ground states of the indenyl cation derivatives.

Quantitative evaluation of the substituent effect

To understand more clearly the substituent effect at C2 on the electronic ground state in more detail, the singlet and triplet states of **1–3** (R^1,R^2=H,H; R^1,R^2=Me,H; R^1,R^2=OMe,H) and **5–7** (R^1,R^2=NH$_2$,H; R^1,R^2=CN,H; R^1,R^2=NO$_2$,H) in the isodesmic reactions shown in Equations (1) and (2) were respectively calculated at the (R/U)B3LYP/6-31G(d,p) level of theory. The obtained reaction energies (ΔE) are plotted against the Hammett parameters (σ^+_{para}, ΔE *versus* σ^+_{para}) to understand the substituent effects (Figure 2). The Hammet σ^+_{para} can directly evaluate the cationic character at C2. The positive and negative ΔE values indicate that the products of Equations (1) and (2) are respectively less and more energetically stable.

The correlation coefficient (R^2) and substituent constant (ρ= slope) of the Hammett plot (HP) of the singlet states (Equation (1)) are lower (R^2=0.95) and smaller (ρ=14) than those of the HP of the T states, respectively (Figure 2a). A considerably higher R^2 (0.99) and larger (ρ=19) are observed for the T states

^{3}[Ind$^+$] (Figure 2b). These results support a considerably larger substituent effect in the T state compared to that in the singlet state.

Nucleus-independent chemical shift (NICS) values (NICS(1)$_{zz}$) and Anisotropy of the induced current density (ACID) plots

NICS(1)$_{zz}$ values were calculated for the six- (A) and five-(B) membered rings in the singlet (RS from RDFT, US from UDFT calculations), and T states of **1**–**11** at the (R or U)B3LYP/6-31G(d,p) levels of theory.[31] The NICS(1)$_{zz}$ values of **1**, **4**, **5**, and **7** are shown in Table 2, and the NICS values of the other cations are shown in Table S1. Positive and negative values are obtained for the singlets (RS and US) and T states, respectively. Notably, the NICS(1)$_{zz}$ values of the T states are not highly dependent on the EDGs and EWGs, suggesting that the T ground state is formed via the energetic stabilization of the positive charge at the C2 position by an EDG. ACID plots were also calculated for singlet (RS, US) and T states of **1**–**11** at the (R or U)B3LYP/6-31G(d,p) level of theory. ACID plots of **1**,**4**,**5**, and **7** are shown in Table 3, and are qualitatively consistent with the NICS(1)$_{zz}$ analysis, in which the singlet and triplet states have an antiaromatic and aromatic character, respectively.

NBO charges and NBO spin densities

Finally, the NBO charges and NBO spin densities of the T, singlet (RS and US) states of **2**–**9** were examined at the (R or U) B3LYP/6-31G(d,p) level of theory, and the values are summarized in Table 4, Table S3, and Table S4, respectively. The positive charges are localized at C2 in the T state of **3** ($R^1,R^2=OCH_3,H$) and **5** ($R^1,R^2=NH_2,H$). In **2** ($R^1,R^2=CH_3,H$), **6** ($R^1,R^2=CN,H$), and **7** ($R^1,R^2=NO_2,H$), the positive charge are localized at C1 and also delocalized to the phenyl ring of indene structure, indicating that EDG at C2 effectively stabilizes the positive charge of T state. In the T state of **4** ($R^1,R^2=Ph,H$), **8** ($R^1,R^2=4\text{-}MeOC_6H_4,H$), **9** ($R^1,R^2=4\text{-}NO_2C_6H_4,H$), the positive charges are mainly located at C2′ which is para-position of the phenyl rings whereas in the singlet state, the positives charges are localized at C1 position. The relatively high spin density at C1 and C3 is confirmed in all T cations **2**–**9**.

Conclusions

In this study, the effects of substituents on the electronic ground states (singlet *versus* triplet) of indenyl cation derivatives were investigated for the first time. Computational studies using CASPT2 and DFT methods revealed that an electron-donating substituent at C2 resulted in a triplet ground state. In contrast, singlet ground states were observed for cations with electron-withdrawing substituents at the CASPT2/cc-pVDZ level of theory. The novel substituent effect on the ground state of indenyl cation may be rationalized by the selective stabilization of the triplet state energy by an EDG. These computational findings contribute significantly in developing novel cation chemistry.

Supporting Information

The authors have cited additional references within the Supporting Information.[32–34]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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