



Physical CHEMISTRY

An Indian Journal

Full Paper

PCAIJ, 8(4), 2013 [119-125]

A computational foray to structure and bonding of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_{4-n}\text{F}_n)$ (C_6H_4 =benzyne, $n=1-4$) complexes

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ABSTRACT

The electronic structure and properties of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_{4-n}\text{F}_n)$ (C_6H_4 =benzyne, $n=1-4$) complexes have been explored using hybrid density functional B3LYP theory. Both aromatic natures and nucleus independent chemical shift (NICS) of the benzyne rings have been investigated. Among mono-, di-, and tri-fluorinated complexes, *o*-F, F14, and *m*-H are the most stable isomers, respectively. NICS values calculated at the several points above the ring centers are consistent with those based on the relative energies of the complexes. The atoms in molecules (AIM) analysis indicates that $\Sigma\text{Ti-C}$ bond distance is well correlated with the electron density of a ring critical point ($\Sigma\rho_{\text{rcp}}$) in all species.

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KEYWORDS

Benzyne complexes;
Aromaticity;
Nucleus-independent
chemical shift (NICS);
Quantum theory Atoms in
molecules methodology
(QTAIM).

INTRODUCTION

Benzyne has been the subject of many theoretical and experimental investigations^[1-6] because it is found as an intermediate of many important organic or biochemical reactions^[3,7,8]. Since the first attempt for making metal complexes using benzyne by Wittig and Bickelhaupt in 1958^[9], many benzyne complexes have been successfully prepared^[10-13]. Benzyne complexes are strongly implicated as reactive intermediates in the thermal decomposition of perphenyl derivatives of the early transition elements, and of uranium and thorium; they can sometimes be isolated from such reactions. For example, $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_4)_2$ has been formed when TiCl_2Cp_2 is treated with *o*-bromofluorobenzene and magnesium^[14].

The structure and bonding of $\text{Ni}(\text{C}_6\text{H}_{4-n}\text{F}_n)(\text{CO})_2$ (C_6H_4 =benzyne, $n=1-4$) complexes have been studied theoretically^[15]. In the present study, the quantum chemical methods were used in order to increase a deeper insight into the structure and bonding of $\text{Ti}(\text{C}_6\text{H}_{4-n}\text{F}_n)(\text{CO})_2$ (C_6H_4 =benzyne, $n=1-4$) complexes and phenomena of the substituent effect in a benzyne ring.

Computational methods

All calculations were carried out with the Gaussian 03 suite of program^[16]. Light atoms (C, H, O and F) were described by the standard 6-31G (d,p) basis set^[17-21]. Ti was described by the effective core potential (ECP) of Wadt and Hay pseudo-potential^[22] with a double- ξ valance using the LANL2DZ basis set^[23,24,25].

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Geometry optimization was performed using Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP)^[26]. A vibrational analysis was performed at each stationary point which corresponds to an energy minimum.

The nucleus-independent chemical shift (NICS)^[27,28] has been defined as the absolute magnetic shielding computed at the center of a ring in a molecule. NICS (0.0), NICS (0.5), NICS (1.0), NICS (1.5) and NICS (2.0) were calculated at 0 (center), 0.5, 1.0, 1.5, and 2.0 Å above the ring, respectively.

The AIM2000 program^[29] was used for the topological analysis of electron density, and the characteristics of ring critical points (RCPs) were taken into account: density at RCP ($\rho(r_c)$), and its Laplacian ($\nabla^2\rho(r_c)$).

RESULT AND DISCUSSION

Energetic aspect

Figure 1 shows the optimized geometries the all molecule. The calculated energy values of the compounds in this work are listed along with the energy (E), relative energy (ΔE), and HOMO-LUMO gaps in TABLE 1. When the compounds are classified with geometric isomers, *o*-F, F14, and *m*-H are the most stable isomer in each group, and harder than the other isomers. As expected from the principles of minimum energy, and maximum HOMO-LUMO gaps (TABLE 3), that is, when an isomer changes from the most stable to other less stable species in most cases, the energy increases,

TABLE 1 : Energies (Hartree), relative energies (kcal/mol), and selected bond angle (deg) for of $Cp_2Ti(C_6H_{4-n}F_n)$ ($C_6H_4 =$ benzyne, $n = 1 - 4$) complexes.

	E (Hartree)	ΔE (kcal/mol)	$\angle C1-Ti-C2$ (deg)
H ₄	-676.2158	-	39.51
<i>m</i> -F	-775.4482	2.55	39.52
<i>o</i> -F	-775.4522	0.00	39.42
F12	-874.6781	5.09	39.47
F13	-874.6842	1.26	39.41
F14	-874.6862	0.00	39.34
F23	-874.6739	7.75	39.48
<i>m</i> -H	-973.9120	0.00	39.40
<i>o</i> -H	-973.9035	5.31	39.42
F ₄	-1073.1314	-	39.42

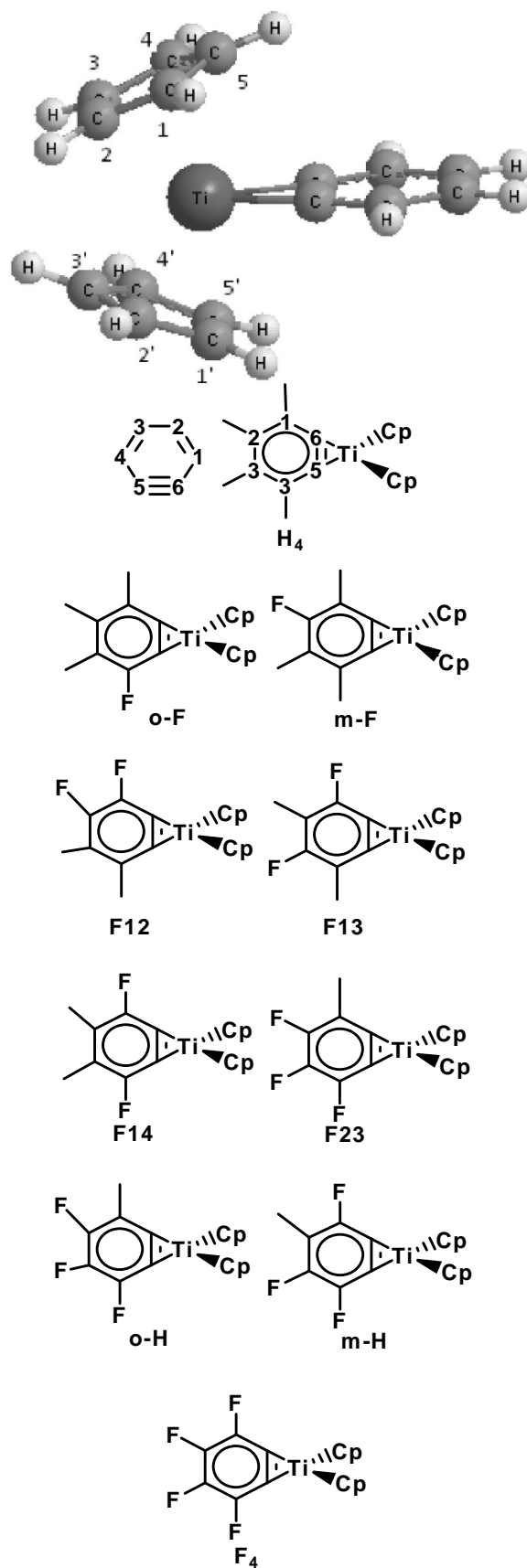


Figure 1 : Structures of $Cp_2Ti(C_6H_{4-n}F_n)$ ($n = 1-4$) complexes.

the HOMO-LUMO gaps decreases.

Geometry

The structures of the $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_{4-n}\text{F}_n)$ (C_6H_4 =benzyne, $n=1-4$) complexes were optimized by DFT calculations (Figure 1, TABLE 2). The C-C bond lengths in the benzyne-Ti complexes seem to be related with the changes in aromaticity. The C1-C6 bond distance of benzyne (1.384 Å) becomes elongated to 1.394 Å when benzyne forms a complex with TiCp_2 in H_4 . In contrast, this bond tends to decrease as the number of F atoms increase in the complex if the most stable isomers of the fluorinated complexes are considered: 1.379 Å (o-F), 1.380 Å (F14), 1.381 Å (m-H), and 1.376 Å (F_4).

TABLE 2 : The selected bond lengths (Å) for $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_{4-n}\text{F}_n)$ ($n = 1 - 4$) complexes.

	Ti-C6	Ti-C5	C1-C2	C2-C3	C3-C4	C4-C5	C5-C6	C6-C1
benzyne	-	-	1.412	1.406	1.412	1.384	1.251	1.384
H_4	2.038	2.038	1.402	1.403	1.402	1.394	1.377	1.394
m-F	2.038	2.036	1.395	1.398	1.401	1.395	1.378	1.393
o-F	2.044	2.036	1.403	1.402	1.396	1.380	1.376	1.394
F12	2.039	2.042	1.399	1.396	1.402	1.394	1.378	1.376
F13	2.036	2.046	1.395	1.397	1.396	1.392	1.377	1.380
F14	2.043	2.043	1.396	1.401	1.396	1.381	1.375	1.381
F23	2.038	2.038	1.392	1.403	1.392	1.395	1.377	1.395
m-H	2.041	2.045	1.397	1.395	1.400	1.376	1.377	1.380
o-H	2.045	2.038	1.394	1.402	1.397	1.377	1.377	1.393
F_4	2.044	2.044	1.398	1.400	1.398	1.376	1.378	1.376

The bond angles around Ti atom also show a systematic trend that the C1-Ti-C2 bond angles increase decrease in the fluorinated complexes (except in *m-F*).

Frontier orbitals

The HOMO and LUMO energies of the compounds in TABLE 3 show that all the Ti-complexes have lower HOMO—LUMO gap energies than those of $\text{C}_6\text{H}_{4-n}\text{F}_n$ ($n=0-4$). On the other hand, these values to decrease as the number of F atoms increases.

Nucleus-independent chemical shift (NICS)

As an effort to discuss the use of NICS as a measure of aromaticity, we have calculated NICS values from the center of the ring to 2.0 Å above the plane along the z-axis of the benzyne ring. The shape of NICS

TABLE 3 : HOMO, LUMO and HOMO-LUMO gap energies for $\text{C}_6\text{H}_{4-n}\text{F}_n$ and $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_{4-n}\text{F}_n)$ (C_6H_4 =benzyne, $n = 1 - 4$) complexes.

	Free benzyne				complex			
	HOMO	LUMO	ΔE	η	HOMO	LUMO	ΔE	η
H_4	-0.2587	-0.0701	5.1324	2.5662	-0.1986	-0.0695	3.5127	1.7564
m-F	-0.2545	-0.0826	4.6790	2.3395	-0.2001	-0.0748	3.4099	1.7049
o-F	-0.2565	-0.0840	4.6945	2.3473	-0.2054	-0.0765	3.5054	1.7527
F12	-0.2573	-0.0946	4.4295	2.2148	-0.2065	-0.0816	3.3995	1.6998
F13	-0.2625	-0.0976	4.4869	2.2435	-0.2064	-0.0816	3.3982	1.6991
F14	-0.2542	-0.1040	4.0880	2.0440	-0.2119	-0.0832	3.5027	1.7513
F23	-0.2560	-0.0914	4.4771	2.2386	-0.2016	-0.0794	3.3261	1.6630
m-H	-0.2595	-0.1152	3.9277	1.9639	-0.2119	-0.0881	3.3683	1.6841
o-H	-0.2659	-0.1054	4.3691	2.1845	-0.2083	-0.0861	3.3234	1.6617
F_4	-0.2699	-0.1240	3.9696	1.9848	-0.2147	-0.0927	3.3204	1.6602

profile with respect to the distance from the ring center falls into two categories. In addition, for all species, we have localized both the NICS maxima and minima, and determined the distances to the center of the ring at which they occur (TABLE 4). For each benzyne, di-, tri-, and tetra-fluorinated species, the highest absolute value of NICS closes to the center of the ring. Both non- and mono-fluorinated species have a maximum about 0.5 Å to the ring center. It is possible that induced magnetic fields generated by the σ -aromaticity are particularly large in the center of the ring. However, the molecular systems having π -aromaticity have a minimum NICS at the certain distances from the center of the ring. There is a linear correlation between NICS (0.0) and NICS (0.5) values in all complexes: $R^2 = 0.992$ (Figure 2).

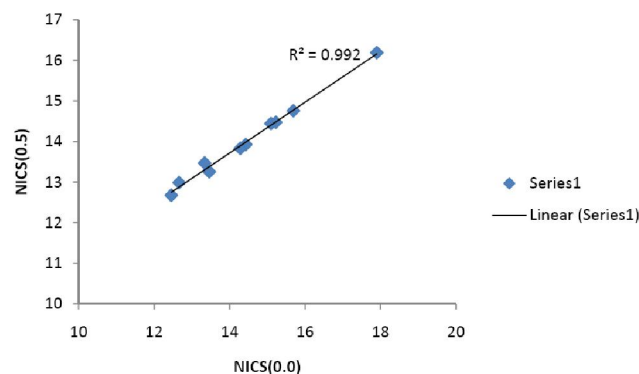


Figure 2 : Variations of NICS (0.0) and NICS (0.5) for $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_{4-n}\text{F}_n)$ ($n = 1 - 4$) complexes.

Natural bond orbital analysis

Natural bond orbital analysis stresses the role of

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TABLE 4 : NICS (0.0), NICS (0.5), NICS (1.0), NIS (1.5), and NICS (2.0) values for benzyne ring in (a) $C_6H_{4-n}F_n$ and (b) $Cp_2Ti(C_6H_{4-n}F_n)$ (C_6H_4 = benzyne, $n = 1 - 4$) complexes.

(a) $C_6H_{4-n}F_n$					
	NICS (0.0)	NICS (0.5)	NICS (1.0)	NICS (1.5)	NICS (2.0)
H ₄	-18.9713	-18.0774	-13.9476	-8.6423	-4.9038
m-F	-18.3075	-16.9203	-12.5940	-7.6053	-4.2027
o-F	-22.8492	-19.9027	-13.8523	-8.2350	-4.5877
F12	-20.7839	-18.3506	-12.8658	-7.5238	-4.0804
F13	-21.1874	-18.3460	-12.5979	-7.3148	-3.9508
F14	-21.9523	-19.6102	-13.8993	-8.1729	-4.4650
F23	-19.1460	-17.1578	-12.2774	-7.2356	-3.9219
m-H	-21.4969	-18.8450	-12.9060	-7.3527	-3.8968
o-H	-22.4316	-18.9332	-12.5357	-7.1163	-3.7773
F ₄	-24.0930	-20.0129	-12.8667	-7.1294	-3.7112
(b) $Cp_2Ti(C_6H_{4-n}F_n)$					
	NICS (0.0)	NICS (0.5)	NICS (1.0)	NICS (1.5)	NICS (2.0)
H ₄	-12.6585	-12.9854	-10.5225	-6.5273	-3.5261
m-F	-12.4522	-12.6735	-10.3253	-6.4250	-3.4752
o-F	-13.3366	-13.4690	-10.8517	-6.7215	-3.6177
F12	-13.4621	-13.2535	-10.5251	-6.4632	-3.4533
F13	-14.4252	-13.9228	-10.7279	-6.4493	-3.3855
F14	-15.0953	-14.4409	-11.0787	-6.6658	-3.5032
F23	-14.2831	-13.8287	-10.7276	-6.4927	-3.4235
m-H	-15.6887	-14.7562	-11.0526	-6.5405	-3.3797
o-H	-15.2248	-14.4712	-11.1932	-6.8121	-3.5952
F ₄	-17.9004	-16.1889	-11.4868	-6.5643	-3.3047

intermolecular orbital interaction in the complex, particularly charge transfer. This is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energetic importance by second-order perturbation theory. For each donor NBO (i) and acceptor NBO (j), the stabilization energy E^2 associated with electron delocalization between donor and acceptor is estimated as:

$$E^{(2)} = -q_i \frac{(F_{ij})^2}{\epsilon_j - \epsilon_i}$$

Where q_i is the orbital occupancy, ϵ_i , ϵ_j are diagonal elements and F_{ij} is the off-diagonal NBO Fock matrix element.

As illustrated in the NBO analysis, the Ti-C_{benzyne} bonds of the complexes show the σ bonds of Ni-C_{benzyne} bonds of the complexes are composed of $sp^m d^n$ hybrid orbital of nickel and sp^n hybrid orbital of the carbene carbon (TABLE 5). The occupation numbers of σ (Ti-

C_{benzyne}) are given in TABLE 5. This values decrease in fluorinated complexes. There is a good relationship between \langle occupancy \rangle and $\langle r(Ti-C_{benzyne}) \rangle$ (Figure 3).

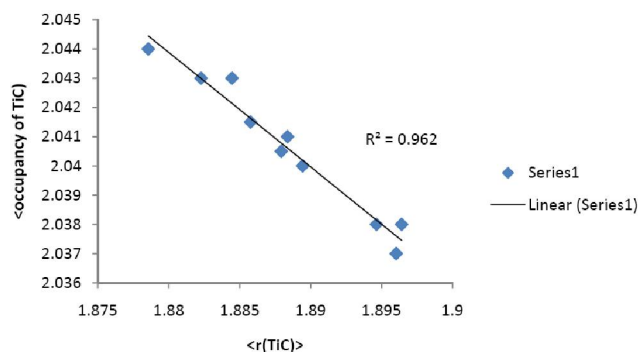


Figure 3 : Variations of \langle occupancy \rangle of $TiC_{benzyne}$ and $\langle r(TiC_{benzyne}) \rangle$ for $Cp_2Ti(C_6H_{4-n}F_n)$ ($n = 1 - 4$) complexes.

TABLE 6 gathers the most strongest donor-acceptor interaction energy (E^2) for $\sigma_n(C3) \rightarrow \pi^*(Ti)$ (in non-fluorinated complexes) and $\pi^*(C3' - C4') \rightarrow \pi^*(C1' - C5')$ (in fluorinated complexes). The minimum correspond to tetra-fluorinated complex.

QTAIM analysis

As it is difficult to separate the σ and π contributions to the electron density at the bond critical point, the $\rho(r)$ values can be used to evaluate bond strength for different types of bonds. The different values of $\rho(r)$ and $\nabla^2\rho(r)$ for the Ti-C_{benzyne} bonds evidently indicate the relative Ti-C_{benzyne} bond strengths (TABLE 7). On the other hand, the Ti-C_{benzyne} bonds in all structures have positive values of $\nabla^2\rho(r)$ which is indicative of the close shell interaction. The value of electron density and its Laplacian estimated at bond critical point of Ti-C_{benzyne} correlate very well with the strength of the bond, as well as with its length, since, as it is well known, both the strength and length of a bond are mutually dependent. A good relationship is present between the average electron density of Ti-C_{benzyne} values and average bond distance of Ti-C_{benzyne} ($R^2=0.976$, Figure 4). Similarly, $\Sigma\nabla^2\rho(Ti-C_{benzyne})$ values obeys a linear relationship ($R^2=0.851$, Figure 5), too.

The bond ellipticity is defined as $\epsilon = (\lambda_1/\lambda_2) - 1$, where $|\lambda_1| \geq |\lambda_2|$. It provides a quantitative measurement of the π character of the bond. The plane of the π distribution is uniquely specifies by the direction of the axis associated with the curvature of smallest magnitude, λ_2 . The $\epsilon(Ti-C_{benzyne})$ values show that the Ni-C

TABLE 5 : Occupancy of natural orbitals (NBOs) and hybrids of Ti-C_{benzyne} bonds of C₆H_{4-n}F_n and Cp₂Ti (C₆H_{4-n}F_n) (C₆H₄= benzyne, n = 1 - 4) complexes.

	Occupancy	Bond orbital	Hybrids
H ₄	1.89638	σ(Ti-C5)	0.6083*Ti sp 0.01d 8.91 + 0.7937* C 5 sp 2.57d 0.00
	1.89644	σ(Ti -C6)	0.6082*Ti sp 0.01d 8.89 + 0.7938* C 6 sp 2.56d 0.00
m-F	1.89553	σ(Ti-C5)	0.6046*Ti sp 0.01d 8.91 + 0.7966* C 5 sp 2.55d 0.00
	1.89652	σ(Ti -C6)	0.6066*Ti sp 0.01d 8.87 + 0.7950* C 6 sp 2.5d 0.00
o-F	1.88712	σ(Ti-C5)	0.5971*Ti sp 0.02d 8.51 + 0.8022* C 5 sp 2.42d 0.00
	1.89172	σ(Ti -C6)	0.6110*Ti sp 0.01d 8.97 + 0.7917* C 6 sp 2.71d 0.00
F12	1.88371	σ(Ti-C5)	0.5935*Ti sp 0.02d 8.50 + 0.8048* C 5 sp 2.45d 0.00
	1.89212	σ(Ti -C6)	0.6101*Ti sp 0.01d 9.00+0.7923* C 6 sp 2.67d 0.00
F13	1.88668	σ(Ti-C5)	0.5962*Ti sp 0.02d 8.51+0.8028* C 5 sp 2.38d 0.00
	1.89004	σ(Ti -C6)	0.6070*Ti sp 0.01d 8.97+0.7947* C 6 sp 2.70d 0.0
F14	1.88444	σ(Ti-C5)	0.5997*Ti sp 0.01d 8.61+0.8002* C 5 sp 2.55d 0.00
	1.88445	σ(Ti -C6)	0.5997*Ti sp 0.01d 8.61 + 0.8002* C 18 sp 2.55d 0.00
F23	1.89464	σ(Ti-C5)	0.6035*Ti sp 0.01d 8.87+0.7974* C 5 sp 2.50d 0.00
	1.89464	σ(Ti -C6)	0.6035*Ti sp 0.01d 8.87+0.7974* C 6 sp 2.50d 0.00
m-H	1.88442	σ(Ti-C5)	0.5986*Ti sp 0.01d 8.58+0.8010* C 5 sp 2.52d 0.00
	1.88012	σ(Ti -C6)	0.5962*Ti sp 0.01d 8.58 + 0.8028* C 6 sp 2.59d 0.00
o-H	1.88905	σ(Ti-C5)	0.6057*Ti sp 0.01d 8.92 + 0.7957* C 5 sp 2.67d 0.00
	1.88247	σ(Ti -C6)	0.5927*Ti sp 0.02d 8.48+0.8054* C 6 sp 2.42d 0.00
F ₄	1.87855	σ(Ti-C5)	0.5956*Ti sp 0.01d 8.56+0.8033* C5 sp 2.59d 0.00
	1.87856	σ(Ti -C6)	0.5955*Ti sp 0.01d 8.54 + 0.8034* C6 sp 2.59d 0.00

TABLE 6 : The results of second-order perturbation theory analysis of the Fock matrix within the NBO basis (E² energy values for the donor-acceptor interactions in kcal/mol) in C₆H_{4-n}F_n and Cp₂Ti (C₆H_{4-n}F_n) (C₆H₄ = benzyne, n = 1 - 4) complexes.

complex	donor→acptor	E (2), kcal/mol
H ₄	σ _n (C3) → π*(Ti)	96.09
m-F	π*(C3'-C4') → π*(C1' - C5')	181.12
o-F	π*(C3'-C4') → π*(C1' - C5')	172.27
F12	π*(C3'-C4') → π*(C1' - C5')	174.07
F13	π*(C3'-C4') → π*(C1' - C5')	175.06
F14	π*(C3'-C4') → π*(C1' - C5')	174.15
F23	π*(C3'-C4') → π*(C1' - C5')	183.85
m-H	π*(C3'-C4') → π*(C1' - C5')	182.23
o-H	π*(C3'-C4') → π*(C1' - C5')	180.46
F ₄	π*(C3'-C4') → π*(C1' - C5')	164.75

bond in fluorinated rings has a smaller π-character in comparison with H₄ (TABLE 7).

Further useful information on the chemical bond properties is obtainable from the total electron energy density (H(ρ)) and its components, a kinetic electron energy density (G(ρ), positive by definition) and a po-

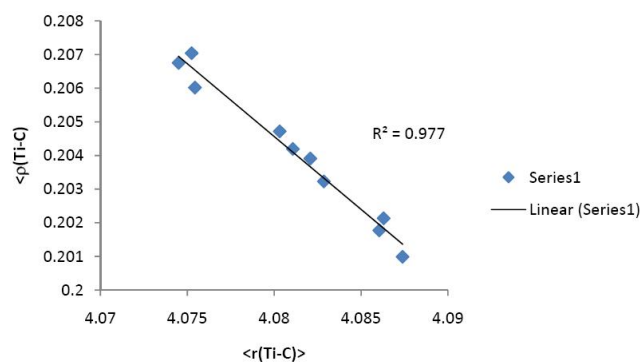


Figure 4 : Variations of $\langle \rho \rangle$ of TiC_{benzyne} and $\langle r \rangle$ TiC_{benzyne} for Cp₂Ti (C₆H_{4-n}F_n) (n = 1 - 4) complexes.

tential electron energy density (V(ρ), negative by definition). The following relation is known for H(ρ) and its components:

$$H(\rho) = G(\rho) + V(\rho)$$

For the strong covalent interactions (Ti-C_{benzyne}), V(ρ) dominates over the kinetic energy density (G(ρ)) and H(ρ) < 0. This usually accompany with ∇²ρ > 0 for H(ρ) > 0.

At the ring critical point of benzyne, both the electron density ρ(3,+1) and Laplacian of electron density

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TABLE 7 : Selected AIM based parameters for (a) Ti-C6(benzyne) and (b) Ti-C5(benzyne) bonds: Electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), kinetic electron energy density, $G(\rho)$, the total electron energy density, $H(\rho)$, potential electron energy density, $V(\rho)$, and ellipticity of the $Cp_2Ti(C_6H_{4-n}F_n)$ (C_6H_4 = benzyne, $n = 1-4$) complexes.

(a) Ti-C6									
Ti-C6	ρ	$\nabla^2\rho$	G	H	V	λ_1	λ_2	λ_3	ϵ
H ₄	0.10350	0.13896	0.07602	-0.04128	-0.11730	-0.14387	-0.13698	0.41982	0.05031
m-F	0.10309	0.14304	0.07646	-0.04070	-0.11715	-0.14301	-0.13610	0.42214	0.05077
o-F	0.10268	0.13528	0.07473	-0.04091	-0.11564	-0.14263	-0.13560	0.41352	0.05187
F12	0.10103	0.15620	0.07762	-0.03856	-0.11618	-0.13811	-0.13195	0.42626	0.04663
F13	0.10190	0.13927	0.07490	-0.04008	-0.11498	-0.14104	-0.13398	0.41429	0.05270
F14	0.10107	0.14859	0.07620	-0.03905	-0.11524	-0.13854	-0.13260	0.41973	0.04476
F23	0.10301	0.14403	0.07660	-0.04059	-0.11719	-0.14189	-0.13645	0.42237	0.03987
m-H	0.10145	0.15005	0.07674	-0.03922	-0.11596	-0.13846	-0.13379	0.42229	0.03488
o-H	0.10204	0.14031	0.07519	-0.04011	-0.11530	-0.14051	-0.13495	0.41577	0.04117
F ₄	0.10048	0.15329	0.07668	-0.03836	-0.11504	-0.13662	-0.13171	0.42161	0.03729
(b) Ti-C5									
Ti-C5	ρ	$\nabla^2\rho$	G	H	V	λ_1	λ_2	λ_3	ϵ
H ₄	0.10354	0.13876	0.07601	-0.04132	-0.11733	-0.14398	-0.13708	0.41982	0.05027
m-F	0.10366	0.14076	0.07645	-0.04126	-0.11771	-0.14332	-0.13756	0.42165	0.04187
o-F	0.10204	0.15236	0.07760	-0.03951	-0.11711	-0.13993	-0.13442	0.42671	0.04097
F12	0.10316	0.13597	0.07518	-0.04119	-0.11637	-0.14284	-0.13713	0.41593	0.04164
F13	0.10201	0.15318	0.07774	-0.03944	-0.11718	-0.13911	-0.13471	0.42700	0.03265
F14	0.10107	0.14858	0.07619	-0.03905	-0.11524	-0.13854	-0.13260	0.41972	0.04478
F23	0.10301	0.14402	0.07660	-0.04059	-0.11719	-0.14189	-0.13645	0.42237	0.03988
m-H	0.10032	0.15238	0.07638	-0.03829	-0.11467	-0.13714	-0.13076	0.42028	0.04875
o-H	0.10119	0.15654	0.07780	-0.03867	-0.11647	-0.13756	-0.13307	0.42717	0.03374
F ₄	0.10051	0.15319	0.07668	-0.03839	-0.11507	-0.13669	-0.13180	0.42168	0.03711

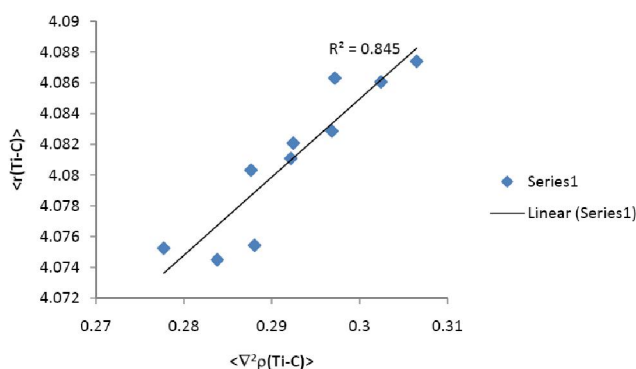


Figure 5 : Variations of $\langle \nabla^2\rho \rangle$ of $TiC_{benzyne}$ and $\langle \rho \rangle$ of $TiC_{benzyne}$ for $Cp_2Ti(C_6H_{4-n}F_n)$ ($n = 1-4$) complexes.

$\nabla^2\rho(3,+1)$ have been calculated for all complexes (TABLE 8). It is observed that these values become smaller in the complexes when they are compared with those of non-coordinated benzyne.

TABLE 8 : Electron density ($\rho(3,+1)$), Laplacian of electron density ($\nabla^2\rho(3,+1)$) at the ring critical point (RCP) of a benzyne ring in each $C_6H_{4-n}F_n$ and $Cp_2Ti(C_6H_{4-n}F_n)$ (C_6H_4 = benzyne, $n = 1-4$) complexes.

	ρ_{ring}		$\nabla^2\rho_{ring}$	
	$C_6H_{4-n}F_n$ ($n = 1-4$)	Complex	$C_6H_{4-n}F_n$ ($n = 1-4$)	Complex
H ₄	0.02595	0.02208	0.19984	0.17113
m-F	0.02593	0.02200	0.19553	0.16937
o-F	0.02639	0.02226	0.19808	0.17065
F12	0.02644	0.02202	0.19275	0.16729
F13	0.02615	0.02218	0.19396	0.16878
F14	0.02561	0.02236	0.19299	0.16929
F23	0.02592	0.02166	0.19071	0.16604
m-H	0.02552	0.02213	0.18785	0.16599
o-H	0.02613	0.02169	0.18804	0.16403
F ₄	0.02545	0.02166	0.18249	0.16132

CONCLUSION

We investigated the structure, properties and bonding of the $Cp_2Ti(C_6H_{4-n}F_n)$ (C_6H_4 =benzyne, $n=1-4$) complexes. The results suggest that o-F, F14, m-H isomers are most stable among the mono-, di-, tri-fluorinated complexes, respectively. The NICS calculations confirmed the aromaticity in the benzyne rings of the compounds. Using the analyses of both electron densities and energy densities, we could explain the characters of the Ti-C bonds in complexes.

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