

Ni(C₆H_{4-n}F_n)(CO)₂ (C₆H₄=benzyne, n=1-4) 착물의 구조 및 화학결합

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(접수 2010. 8. 20; 수정 2010. 10. 18; 게재확정 2010. 12. 6)

Structure and Bonding of Ni(C₆H_{4-n}F_n)(CO)₂ (C₆H₄=benzyne, n=1-4) Complexes

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(Received August 20, 2010; Revised October 18, 2010; Accepted December 6, 2010)

요약. Ni(C₆H_{4-n}F_n)(CO)₂ (C₆H₄=benzyne, n=1-4) 착물의 전자구조 및 성질을 혼성 밀도 함수 B3LYP 이론을 이용하여 조사하였다. Benzyne 고리에 대한 방향족 성질과 벤젠핵과 무관한 화학적 이동(NICS)을 분석하였다. 일-, 이- 및 삼-플루오르화 착물 중에서 3-F, 3, 6-F, 및 4-H는 각기 가장 안정한 이성질체였다. 고리 중심 상단의 여러 점에서 계산한 NICS 수치는 이들 착물의 상대 에너지에 의해 구한 값들과 일치하였다. 분자-내-원자(AIM) 분석에서 얻어진 Ni-C 결합거리는 모든 화학종에 대한 고리 임계점의 전자밀도(ρ_{rcp})와 좋은 상관성을 보였다.

주제어: Benzyne 착물, 방향족성, 벤젠핵-무관-화학적 이동 (NICS), 분자-내-원자 방법에 의한 양자이론 (QTAIM)

ABSTRACT. The electronic structure and properties of Ni(C₆H_{4-n}F_n)(CO)₂ (C₆H₄=benzyne, n=1-4) complexes have been investigated using hybrid density functional B3LYP theory. Both aromatic natures and nucleus independent chemical shift (NICS) of the benzyne rings have been analyzed. Among mono-, di-, and tri-fluorinated complexes, 3-F, 3,6-F, and 4-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 Ni-C bond distance is well correlated with the electron density of a ring critical point (ρ_{rcp}) in all species.

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 investigations¹⁻⁶ 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 for example, M. A. Bennett *et al.*¹⁴ synthesized organometallic compounds, NiL₂(C₆H₄)(L = PCy₃, PⁱPr₃; Cy = cyclohexyl, ⁱPr = isopropyl). K. R. Deaton and M. S. Gin studied the reactions of nickel(0)-benzyne complexes with symmetrically substituted 1,3-diyne in the presence of triethylphosphine, which lead to the regioselective formation of 2,3-dialkynyl naphthalenes¹⁵. In the present study, the quantum chemical methods were used in order

to gain a deeper insight into the structure and bonding of Ni(C₆H_{4-n}F_n)(CO)₂ (C₆H₄= 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 6-31+G(d) basis set.¹⁷ Ni was described by the effective core potential (ECP) of Wadt and Hay pseudo-potential²¹ with a double- ξ valance using the LANL2DZ basis set.¹⁸⁻²⁰ Geometry optimization was performed using Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP).²² A vibrational analysis was performed at each stationary point which corresponds to an energy minimum.

The nucleus-independent chemical shift (NICS)^{23,24} 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 program²⁵ 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

Energy and geometry

The calculated energy values of the compounds in this work are listed along with the selective bond angles in Table 1. When the compounds are classified with geometric isomers, 3-F, 3,6-F, and 4-H are the most stable isomer in each group.

Table 1. Energies (Hartree), relative energies (kcal/mol), and selected bond angles (deg) for of benzyne and Ni(C₆H_{4-n}F_n)(CO)₂ (C₆H₄ = benzyne, n = 1-4) complexes. See Fig. 1 for their structures

Compounds	E (Hartree)	DE (kcal/mol)	∠C1-Ni-C2 (deg)	∠C7-Ni-C8 (deg)
benzyne	-230.9221	-	-	-
H₄	-626.9823	-	40.79	111.89
3-F	-726.2170	0.00	41.04	111.15
4-F	-726.2142	1.77	40.95	111.42
5,6-F	-825.4426	26.03	41.20	110.71
4,6-F	-825.4487	22.25	41.17	110.66
3,6-F	-825.4841	0.00	41.30	109.79
3-H	-924.6683	31.09	41.29	110.32
4-H	-924.7179	0.00	41.44	109.34
F₄	-1023.8941	-	41.54	109.71

The structures of the Ni(C₆H_{4-n}F_n)(CO)₂ complexes were optimized by DFT calculations (Fig. 1). The C-C bond lengths in the benzyne-Ni complexes seem to be related with the changes in aromaticity. The C1-C6 bond

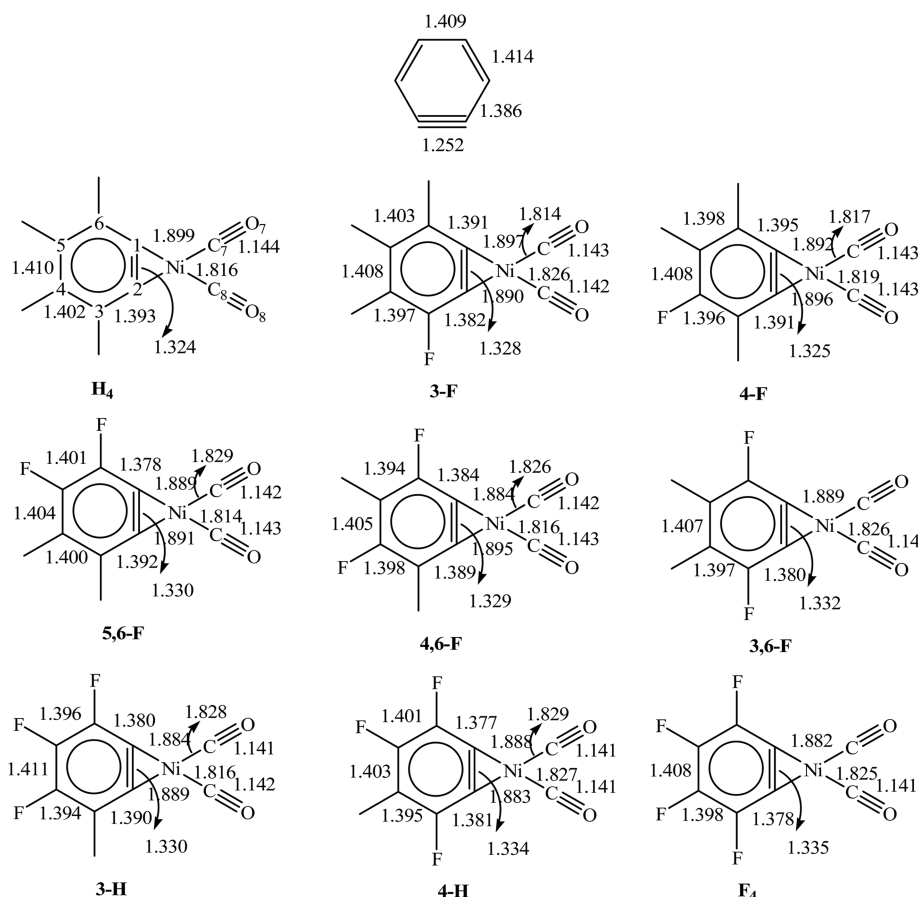


Fig. 1. Optimized structures of the compounds are displayed with bonds distances. Notice that the compounds can be classified into six groups according to their chemical natures, complexation or the number of F atoms: (**benzyne**), (**H₄**), (**3-F**, **4-F**), (**5,6-F**, **4,6-F**, **3,6-F**, **4,5-F**), (**3-H**, **4-H**), and (**F₄**). In the multi-fluorinated compounds, **3-F**, **3,6-F**, and **4-H** are the most stable ones which are used for the discussion of their representative properties in this work.

Table 2. Charges of Ni, C and O atoms calculated by NBO analysis for benzyne and Ni(C₆H_{4-n}F_n)(CO)₂ complexes.

	Ni	C1	C2	C3	C4	C5	C6	C7	C8	O7	O8
benzyne	-	0.019	0.019	-0.284	-0.244	-0.244	-0.284	-	-	-	-
H₄	0.420	-0.263	-0.215	-0.215	-0.263	-0.240	-0.240	0.470	0.470	-0.453	-0.453
3-F	0.421	-0.287	-0.180	-0.294	0.385	-0.302	-0.224	0.479	0.470	-0.442	-0.447
4-F	0.414	-0.243	-0.277	-0.205	-0.323	0.413	-0.293	0.474	0.474	-0.445	-0.445
5,6-F	0.429	-0.271	-0.192	-0.290	0.326	0.354	-0.284	0.481	0.479	-0.439	-0.443
4,6-F	0.430	0.399	-0.307	-0.171	-0.347	0.420	-0.361	0.478	0.487	-0.443	-0.439
3,6-F	0.432	0.364	-0.258	-0.258	0.364	-0.284	-0.284	0.484	0.484	-0.435	-0.435
3-H	0.431	0.310	-0.272	-0.251	0.377	-0.338	0.367	0.483	0.484	-0.434	-0.433
4-H	0.432	0.339	-0.301	-0.181	0.334	0.372	0.299	0.481	0.483	-0.430	-0.435
F₄	0.438	0.321	-0.265	-0.265	0.321	0.311	0.311	0.488	0.488	-0.429	-0.429

distance of benzyne (1.386 Å) becomes elongated to 1.393 Å when benzyne forms a complex with Ni(CO)₂ in **H₄**. 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: 1.382 Å (**3-F**), 1.380 Å (**3,6-F**), 1.377 Å (**4-H**), and 1.378 Å (**F₄**).

The bond distances of Ni-C(benzyne) decrease, and the Ni-C(O) bonds increase, revealing that the fluorination of benzyne reduces the back-donation of electron densities of Ni to the carbonyls. This observation is supported by the increase of Ni charges in the fluorinated complexes (Table 2): 0.420 (**H₄**) to 0.421 (**3-F**), 0.432 (**3,6-F**), 0.432 (**4-H**), and 0.438 (**F₄**). The bond angles around Ni atom also show a systematic trend that the C1-Ni-C2 bond angles increase while the C7-Ni-C8 ones decrease in the fluorinated complexes.

Frontier orbitals

The HOMO and LUMO energies of the compounds in Table 3 show that all the Ni-complexes have higher HOMO and lower LUMO energies than those of benzyne, respectively. The HOMO—LUMO gap energies tend to

decrease as the number of F atoms increases.

Vibration Analysis

The symmetric and asymmetric stretching modes of CO are displayed in Fig. 2 and the calculated frequencies of CO ligands, $\nu(\text{CO})$, have been presented in Table 3. These values increase in fluorinated complexes when the most stable isomers are considered.

The IR spectroscopy experimental results show that in NiL₂(C₆H₄) (L=PCy₃, Cy = cyclohexyl), the C1-C2 bond length of 1.332 Å is greater than the value of 1.29 Å typical of most ML₂(alkyne) complexes, but the lengthening on coordination relative to the free ligand ($\Delta r = 0.08\text{--}0.09$ Å) is about the same.¹¹ Correspondingly, the $\nu(\text{C}\equiv\text{C})$ value of ca. 1580 cm⁻¹ in ML₂(C₆H₄) (M = Ni, Pt) complexes is less than the value of ca. 1700 cm⁻¹ found in ML₂ (alkyne) complexes, but the decrease relative to the free ligand is of the same order ($\nu(\text{C}\equiv\text{C}) = 400\text{--}500$ cm⁻¹) in both series. In the Ni(C₆H_{4-n}F_n)(CO)₂ systems, the $r(\text{C1-C2})$ in complexes is greater than free benzyne ($\Delta r_{\text{max}} = 0.083$ Å in F₄ molecule). On the other hand, the $\nu(\text{C}\equiv\text{C})$ values increase in complexes rather than free benzyne (Table 3).

Table 3. HOMO, LUMO and HOMO-LUMO gap energies for benzyne and Ni(C₆H_{4-n}F_n)(CO)₂ (C₆H₄=benzyne, n=1-4) complexes. The vibration frequencies involving C≡C and carbonyls are also listed

	$\nu(\text{C}\equiv\text{C})$ (cm ⁻¹)	$\Delta\nu(\text{C}\equiv\text{C})$ (cm ⁻¹)	$\nu(\text{CO})_{\text{asy}}$ (cm ⁻¹)	$\nu(\text{CO})_{\text{sym}}$ (cm ⁻¹)	HOMO (Hartree)	LUMO (Hartree)	ΔE (eV)
benzyne	2017.11	-	-	-	-0.2717	-0.0872	5.02
H₄	1729.45	287.66	2145.54	2182.48	-0.2468	-0.0887	4.30
3-F	1717.22	299.89	2153.65	2189.95	-0.2555	-0.0949	4.37
4-F	1727.99	289.12	2149.78	2185.38	-0.2478	-0.0944	4.17
5,6-F	1715.59	301.52	2157.77	2193.13	-0.2548	-0.1004	4.20
4,6-F	1719.64	297.47	2158.23	2193.41	-0.2559	-0.1004	4.23
3,6-F	1704.16	312.95	2154.91	2191.24	-0.2534	-0.1017	4.13
3-H	1726.67	290.44	2161.27	2195.96	-0.2599	-0.1054	4.20
4-H	1717.22	299.89	2160.09	2195.14	-0.2587	-0.1071	4.12
F₄	1727.99	289.12	2170.25	2203.24	-0.2683	-0.1113	4.27

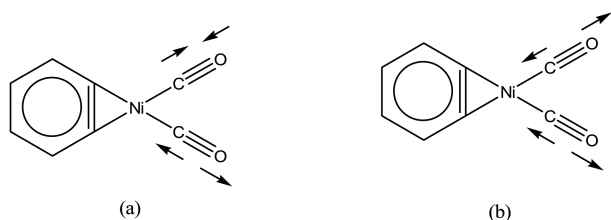


Fig. 2. Stretching modes of carbonyl groups in the Ni-complexes: (a) asymmetric, (b) symmetric.

Table 4. Calculated proton chemical shifts (ppm) values for of benzyne and $\text{Ni}(\text{C}_6\text{H}_{4-n}\text{F}_n)(\text{CO})_2$ (C_6H_4 =benzyne, $n=1-4$) complexes

Compounds	Chemical Shift (ppm)			
	H3	H4	H5	H6
benzyne	6.34	7.05	7.05	6.34
H₄	7.54	7.30	7.30	7.54
3-F	-	6.76	7.29	7.18
4-F	7.04	-	6.91	7.46
5,6-F	6.99	7.06	-	-
4,6-F	6.91	-	7.44	-
3,6-F	-	6.83	6.83	-
3-H	7.01	-	-	-
4-H	-	6.58	-	-
F₄	-	-	-	-

¹H, ¹³C-NMR

Along with the vibration analysis, we could compute ¹H-NMR chemical shifts for the set of compounds by GIAO method. The calculated chemical shifts of protons are listed in Table 4. The H3 - H6 signals of **H₄** are expected to appear at down-field compared with those in benzyne, indicating that the complexation makes the benzyne ring more electron-deficient. When the F atom is introduced to H4, some of protons shift to up-field although a systematic trend is not clearly detected. This is probably due to the induction effect of the electronegative F atom which attracts electrons again from Ni to the benzyne moiety.

The benzyne ¹³C chemical shifts provide some support for aromaticity. The experimental δ values for C1 and C2 in $\text{NiL}_2(\text{C}_6\text{H}_4)$ ($\text{L}=\text{PCy}_3$, $\text{Cy}=\text{cyclohexyl}$) are 145.2 ppm.¹¹ Also, the computed ¹³C NMR chemical shifts of the Ni ($\text{C}_6\text{H}_{4-n}\text{F}_n$)(CO)₂ are compatible with aromaticity (Table 1).

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 profile with respect to the distance from the ring center falls into two

Table 5. NICS(0.0), NICS(0.5), NICS(1.0), NICS(1.5), and NICS(2.0) values for benzyne ring in benzyne and $\text{Ni}(\text{C}_6\text{H}_{4-n}\text{F}_n)(\text{CO})_2$ (C_6H_4 =benzyne, $n=1-4$) complexes. The values in the parentheses show the distances in Å

	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
benzyne	-17.5675	-16.7084	-12.9513	-8.2404	-4.8850
H₄	-9.4885	-11.3675	-11.1670	-8.0751	-5.2098
3-F	-10.8810	-12.0664	-11.1773	-7.9206	-5.0660
4-F	-9.5709	-10.9448	-10.4704	-7.5293	-4.8449
5,6-F	-11.1714	-11.9407	-10.7238	-7.5047	-4.7662
4,6-F	-11.8219	-12.2890	-10.7318	-7.4256	-4.6958
3,6-F	-12.7603	-13.0210	-11.0626	-7.5479	-4.7474
3-H	-13.1612	-13.0230	-10.7906	-7.2991	-4.5734
4-H	-13.4067	-13.1599	-10.8065	-7.2749	-4.5387
F₄	-15.6948	-14.6049	-11.2443	-7.3494	-4.5355

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 5). For each benzyne, tri-, and tetra-fluorinated species and **H₄**, the highest absolute value of NICS closes to the center of the ring. Both mono- and di-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: $R^2=0.968$, not shown.

AIM 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 (Table 6). The different values of $\rho(r)$ and $\nabla^2\rho(r)$ for the Ni-C bonds evidently indicate the relative Ni-C bond strengths. This result is in agreement with the geometrical analysis, showing that the Ni-C bond of $\text{Ni}(\text{C}_6\text{H}_4)(\text{CO})_2$ is longer than other species. On the other hand, the Ni-C 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 NiC(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 $\Sigma\rho(\text{NiC}_{\text{benzyne}})$ values and $\Sigma r(\text{NiC}_{\text{benzyne}})$ ($R^2=0.994$). Similarity, $\Sigma\nabla^2\rho(\text{NiC}_{\text{benzyne}})$ values obeys a linear relationship ($R^2=0.941$), too.

Table 6. Selected AIM based parameters for (a) Ni-C(benzyne) and (b) NiC(O) 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 Ni(C₆H_{4-n}F_n)(CO)₂ (C₆H₄=benzyne, n=1-4) complexes

(a) Ni-C(benzyne)

	Bond	ρ	$\nabla^2\rho$	$G(\rho)$	$H(\rho)$	$V(\rho)$	λ_1	λ_2	λ_3	$\varepsilon(\text{NiC})$
H4	Ni-C	0.1097	0.3717	0.1235	-0.0306	-0.1541	-0.1496	-0.0879	0.6092	0.7010
3-F	Ni-C1	0.1108	0.3670	0.1233	-0.0315	-0.1548	-0.1523	-0.0902	0.6095	0.6883
	Ni-C2	0.1110	0.3836	0.1278	-0.0319	-0.1597	-0.1519	-0.0912	0.6267	0.6659
4-F	Ni-C1	0.1104	0.3775	0.1255	-0.0311	-0.1566	-0.1509	-0.0884	0.6167	0.7076
	Ni-C2	0.1114	0.3684	0.1243	-0.0322	-0.1565	-0.1524	-0.0927	0.6136	0.6439
5,6-F	Ni-C2	0.1111	0.3898	0.1293	-0.0319	-0.1612	-0.1521	-0.0898	0.6317	0.6942
	Ni-C1	0.1125	0.3631	0.1239	-0.0331	-0.1570	-0.1552	-0.0957	0.6140	0.6210
4,6-F	Ni-C2	0.1113	0.3731	0.1251	-0.0319	-0.1570	-0.1533	-0.0903	0.6166	0.6974
	Ni-C1	0.1125	0.3806	0.1285	-0.0334	-0.1619	-0.1544	-0.0956	0.6306	0.6149
3,6-F	Ni-C	0.1119	0.3784	0.1272	-0.0326	-0.1599	-0.1542	-0.0934	0.6260	0.6499
3-H	Ni-C2	0.1126	0.3714	0.1259	-0.0331	-0.1590	-0.1549	-0.0940	0.6204	0.6478
	NiC1	0.1129	0.3896	0.1309	-0.0335	-0.1644	-0.1558	-0.0954	0.6407	0.6333
4-H	Ni-C1	0.1121	0.3849	0.1289	-0.0327	-0.1616	-0.1545	-0.0923	0.6317	0.6743
	NiC2	0.1135	0.3753	0.1279	-0.0341	-0.1620	-0.1567	-0.0982	0.6302	0.5954
F4	Ni-C	0.1136	0.3825	0.1297	-0.0341	-0.1638	-0.1570	-0.0967	0.6363	0.6234

(b) NiC(O)

	Bond	ρ	$\nabla^2\rho$	$G(\rho)$	$H(\rho)$	$V(\rho)$	λ_1	λ_2	λ_3	$\varepsilon(\text{NiC})$
H4	Ni-C	0.1300	0.5556	0.1902	-0.0513	-0.2416	-0.1759	-0.1713	0.9029	0.0268
4-F	Ni-C1	0.1310	0.5555	0.1913	-0.0524	-0.2437	-0.1772	-0.1729	0.9056	0.0244
	Ni-C2	0.1270	0.5478	0.1856	-0.0486	-0.2342	-0.1698	-0.1652	0.8828	0.0281
4-F	Ni-C1	0.1297	0.5536	0.1895	-0.0511	-0.2406	-0.1753	-0.1709	0.8999	0.0255
	Ni-C2	0.1291	0.5531	0.1889	-0.0506	-0.2395	-0.1737	-0.1694	0.8963	0.0255
5,6-F	Ni-C2	0.1309	0.5534	0.1907	-0.0523	-0.2430	-0.1770	-0.1728	0.9032	0.0245
	Ni-C1	0.1262	0.5450	0.1843	-0.0481	-0.2324	-0.1682	-0.1637	0.8769	0.0275
4,6-F	Ni-C2	0.1303	0.5530	0.1901	-0.0518	-0.2419	-0.1751	-0.1711	0.8992	0.0272
	Ni-C1	0.1269	0.5460	0.1851	-0.0487	-0.2338	-0.1698	-0.1653	0.8810	0.0272
3,6-F	Ni-C	0.1272	0.5452	0.1853	-0.0490	-0.2343	-0.1699	-0.1653	0.8804	0.0276
3-H	Ni-C2	0.1304	0.5496	0.1894	-0.0521	-0.2415	-0.1759	-0.1718	0.8972	0.0242
	NiC1	0.1264	0.5437	0.1842	-0.0483	-0.2324	-0.1681	-0.1638	0.8756	0.0273
4-H	Ni-C1	0.1262	0.5419	0.1837	-0.0482	-0.2319	-0.1677	-0.1632	0.8729	0.0273
	NiC2	0.1270	0.5427	0.1845	-0.0488	-0.2333	-0.1696	-0.1650	0.8773	0.0275
F4	Ni-C	0.1275	0.5427	0.1851	-0.0494	-0.2345	-0.1703	-0.1660	0.8789	0.0257

The comparison of electron density in the bond critical points of Ni-C(benzyne) and Ni-C(O) shows that $\rho(\text{Ni-C}_{\text{benzyne}})$ is smaller than $\rho(\text{Ni-C(O)})$. This trend is well-matched with the results of the geometrical analysis.

The bond ellipticity is defined as $\varepsilon=(\lambda_1/\lambda_2)-1$, 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 specified by the direction of the axis associated with the curvature of smallest magnitude, λ_2 . The $\varepsilon(\text{Ni-C})$ values show that the Ni-C bond in fluorinated rings has a smaller π -character in comparison with Ni(C₆H₄)(CO)₂ (Table 6).

Further useful information on the chemical bond properties is obtainable from the total electron energy density ($H(\rho)$) and its components, a kinetic electron energy density ($G(\rho)$, positive by definition) and a potential electron energy density ($V(\rho)$, negative by definition). The following relation is known for $H(\rho)$ and its components:

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

In the region of the bond critical point for the weak closed-shell inter-atomic interactions (Ni-C), the kinetic energy density dominates with the $G(\rho)$ magnitude being slightly greater than the potential energy density $|V(\rho)|$,

Table 7. 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 $\text{Ni}(\text{C}_6\text{H}_{4-n}\text{F}_n)(\text{CO})_2$ (C_6H_4 =benzyne, $n=1-4$) compound

	$\rho(3,+1)$	$\nabla^2(3,+1)$
benzyne	0.0259	0.1967
H₄	0.0236	0.1813
2-F	0.0236	0.1789
3-F	0.0235	0.1781
5,6-F	0.0234	0.1744
4,6-F	0.0236	0.1758
3,6-F	0.0234	0.1750
2-H	0.0239	0.1727
3-H	0.0233	0.1709
F₄	0.0229	0.1660

which implies that the total energy density $H(\rho)$ is positive and closes to zero. For the strong covalent interactions (Ni-C), $V(\rho)$ dominates over the kinetic energy density and $H(\lambda) < 0$. This usually accompany with $\nabla^2\rho > 0$ for $H(\lambda) > 0$, and $\nabla^2\rho < 0$ for $H(\rho) < 0$.

At the ring critical point of benzyne, both the electron density $\rho(3,+1)$ and Laplacian of electron density $\nabla^2\rho(3,+1)$ have been calculated for all complexes (Table 7). It is observed that these values become smaller in the fluorinated complexes when they are compared with those of benzyne and **H₄**.

CONCLUSION

We investigated the structures and frontier orbitals of the $\text{Ni}(\text{C}_6\text{H}_{4-n}\text{F}_n)(\text{CO})_2$ (C_6H_4 =benzyne, $n=1-4$) complexes. The results suggest that **3-F**, **3,6-F**, **4-H** isomers are most stable among the mono-, di-, tri-fluorinated complexes, respectively. Using the stable ones, both vibration and ¹H-NMR shifts were calculated and analyzed. 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 Ni-C bonds in complexes.

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