

Electronic Effects of CF₃ Group in Polyfluorinated Toluenes: Infrared, Raman, and Ultraviolet Spectra

O. Kh. Poleshchuk¹, I. K. Korobeinicheva², O. M. Fugaeva², and G. G. Furin²

¹Tomsk Pedagogical University, Tomsk, Russia

²Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—Relying on analysis of experimental infrared, Raman, and ultraviolet spectra and on calculation of frequencies and forms of normal vibrations of polyfluorinated toluenes these compounds were established to be prone to quinoid structure, and the interaction of the CF₃ group with the polyfluorinated benzene ring was found to occur predominantly through the π -system.

A considerable mesomeric effect of CF₃ group (σ_R 0.186) (for instance, σ_R of NO₂ group is 0.155 [1]) does not fit into the classical conjugation pattern. The various attempt of interpretation underlie two mechanisms [2]: (1) an interaction $\pi(F)-(Ph)$ which as inductive effect results in electron density transfer from the CF₃ group to the benzene ring; (2) an interaction $\pi(Ph)-\pi^*(CF_3)$ which causes the electron charge transmission from the benzene ring to the orbitals of π -symmetry belonging to the CF₃ group. However the dominant factor is the π -inductive effect caused by strong inductive attraction of electrons from the neighboring position of the ring; this effect is transmitted by the usual way involving the resonance in the *ortho*- and *para*-positions. A significant factor is the strong field effect of the CF₃ group. It was shown [3] for compounds PhCHlg₃ (Hlg = Cl, Br) that the interaction between Ph and CHlg₃ occurs via mechanism $\pi(Ph) - \pi^*(CHlg_3)$. With Hlg = F [3] as with substituted triphenylamines [4] the inductive effect prevails.

Investigations with the use of vibrational spectroscopy provide vast possibilities for the study of structural and electronic features of various compound classes. These methods give additional and sometimes essentially new information compared to the other analytical methods (including the popular NMR spectroscopy). The stretching vibrations of the CF₃ group in octafluorotoluene were the most thoroughly studied in [5–7]. The spectral bands corresponding to vibrations of the CF₃ group were identified, but significant discrepancies remained in their detailed assignment. For instance, in [6] were analyzed the IR spectra in vapor phase of C₆F₅CF₃

and C₆F₅¹³CF₃, and it was indicated that in the region 1250–1140 cm⁻¹ three bands suffer the strongest shifts on introduction of a ¹³C marker in the CF₃ group. The strongest two among them, at 1242 ($\Delta\nu$ 25) and 1176 ($\Delta\nu$ 35 cm⁻¹) were interpreted as asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of CF₃ group, and the weaker absorption band at 1200 ($\Delta\nu$ 28 cm⁻¹) was assigned to vibrations of the C_{ar}-CF₃ bond. At the same time in [5, 7] to $\nu_s(CF_3)$ was attributed a very strong band in the IR spectrum in the region 1348–1356 cm⁻¹, whereas $\nu_{as}(CF_3)$ according to the value of symmetry band b_1 and b_2 was considered to be in the range 1154–1177 cm⁻¹. In [7] the band at 717 cm⁻¹ was also assigned to vibration of CF₃ (a_1). No calculations of vibration frequencies of octafluorotoluene were published.

The goal of this study was to investigate IR and Raman spectra of a series of polyfluoroaromatic compounds of 4-XC₆F₄CF₃ type where X are substituents of various character, to perform a complete interpretation of vibration spectra of octafluorotoluene, and to reveal the effect of the *para*-substituent X on the frequencies and forms of vibrations corresponding to CF₃ and C₆F₅ groups. The vibration spectra of the polyfluoroaromatic compounds under study are compiled in Table 1, and for octafluorotoluene labeled with ¹³C the spectra are given in Table 2. The calculation of frequencies and forms of the normal vibrations for compounds C₆F₅CF₃ and C₆F₅¹³CF₃ was carried out in the valence-force field approximation by the program [8].

In calculations for the C₆F₅ fragment of octafluorotoluene was used the force field of a pentafluorobenz-

Table 1. Experimental frequencies of stretching vibrations of CF₃ group and C_{ar}-C bond in polyfluorinated toluenes 4-XC₆F₄CF₃ (cm⁻¹) (in solutions)

X	IR (CCl ₄)			Raman (C ₆ H ₁₂)	
	$\nu_{as}(\text{CF}_3)$	$\nu_{as}(\text{CF}_3)$	$\nu_s(\text{CF}_3)$	$\nu(\text{C}_{ap}-\text{C})$	$I_{\text{C}_{ap}-\text{C}}(-\log I)$
NH ₂	1135 m	1180 m	1239 w	1349 s	0.74 (0.132)
NMe ₂	1130 s	1170 m	1215 m	1349 s	0.74 (0.131)
NHMe	1132 s	1180 m	1245 m	1339 m	0.56 (0.252)
NHNH ₂	1145 s	1190 m	1235 m	1348 m	0.39 (0.409)
OMe	1145 s	1184 m	1237 v.s	1346 m	0.151 (0.820)
OEt	1143 s	1186 m	1230 v.s	1345 m	0.15 (0.827)
Me	1151 s	1186 m	1224 m	1344 m	0.11 (0.959)
SMe	1148 s	1170 m	1280 m	1338 m	0.10 (0.726)
SH	1160 s	1195 m	1296 m	1339 m	0.09 (1.018)
H	1156 m	1188 m	1275 m	1346 m	0.06 (1.222)
F	1159 s	1194 m	1236 s	1351 m	0.09 (1.046)
Br	1153 s	1180 m	1267 w	1336 m	0.09 (1.030)
CH=CH ₂	1150 m	1180 m	1235 m	1335 s	0.46 (0.140)
NO ₂	1170 m	1200 m	1267 m	1334 s	0.33 (0.481)

ene [9], and for the CF₃ group were taken the force constants of CF bonds and geometrical parameters from [10]. The variations of field were performed in the process of solving the inverse spectral problem. It should be noted that the force constants of the CF₃ group $q(\text{CF}_3)$ equal to 7.514 and are considerably smaller than those of the CF groups of the aromatic ring: $q(\text{CF})$ is 10.83, and $Q(\text{C}_{ar}-\text{C})$ 9.255 is larger than the value of the C-C R_{C-C} bond 7.0 [11] (force constants presented in 10⁶ cm²).

Nonempirical calculations were carried out with the use of GAUSSIAN'98W software [12]. The geometry optimization and subsequent calculation of vibration frequencies and wavelengths in the UV spectrum of the octafluorotoluene were performed by the density functional method B3LYP with Becke [13] exchange functional and correlation functional of Lee, Yang, and Parr [14]. The basis 6-31G* with accounting for diffuse functions on carbon and fluorine atoms was used in the calculations.

As seen from Table 2 the largest contribution (67 and 81%) the CF₃ group makes into the vibrations of b_2 and b_1 symmetry with the frequencies ν_{calc} of 1207 ($\Delta\nu$ 32) and 1177 ($\Delta\nu$ 36) cm⁻¹. The corresponding bands are very weak in the Raman spectrum and strong in the IR spectrum. The calculated forms of these vibrations essentially depend on the spatial position of the CF₃ group with respect to the plane of the polyfluorinated benzene ring. These are different for presumable conformations where one of the C-F

bonds of the trifluoromethyl group lies either in the plane of the aromatic fragment or is normal to it. We attempted to identify the conformations existing in solutions by recording the IR spectra of compounds C₆F₅CF₃ and C₆F₅¹³CF₃ at lower temperatures. The bands at 1159 and 1194 cm⁻¹ broadened and revealed a complex structure, and cooling to -50°C did not permit an unambiguous determination of the stable conformation. The vibration spectra of octafluorotoluene in different states of aggregation were described in [5]. In going from crystalline state to liquid to gas the significant shifts were observed for two bands: 1138-1154-1177 and 1158-1166-1172 cm⁻¹ respectively. These bands were attributed to antisymmetric (b_1 and b_2) stretching vibrations of the CF₃ group. The other bands suffer insignificant (up to 3 cm⁻¹) changes. These features of spectra were not discussed in [5]. The frequency ν_{calc} 1235 ($\Delta\nu$ 16) cm⁻¹ (a_1) corresponds to the mixed vibration of the benzene ring and the trifluoromethyl group with a large contribution from the bonds C_{ar}-C and C-F of the CF₃ group (Table 2), and it is assigned to the symmetric vibration of the CF₃ group. In the IR and Raman spectra the corresponding band is of moderate intensity. The form of this vibration is insensitive to conformations. The largest contribution (27%) of C_{ar}-C bond is made to the symmetric a_1 vibration, ν_{calc} 1348 ($\Delta\nu$ 12) cm⁻¹ (see Table 2). In the Raman spectrum it appears as a strong polarized (ρ 0.1) band, and in the IR spectrum it is observed as a medium

Table 2. Experimental and calculated frequencies of normal vibrations (ν , cm⁻¹) of octafluorotoluene enriched with ¹³C isotope in the CF₃ group

Raman	ν_{exp}		ν_{calc}	Symmetry	Distribution of potential energy (%)
	IR(CCl ₄)($\Delta\nu$ ¹³ C)	IR (gas) ($\Delta\nu$ ¹³ C)	($\Delta\nu$ ¹³ C)		
1665		1702	1684	a_1	73Q, 13 β
	1660	1698	1667	b_2	72Q, 12 β
	1530	1550	1556	a_1	46Q, 36Q, 12 β
	1515	1542	1542	b_2	47Q, 35q
1444	1433 (2)	1506 (6)	1457	a_1	35Q, 26Q (C _{ap} -C), 12 β
	1400	1388	1366	b_2	92Q
1351	1349 (8)	1348 (12)	1332	a_1	36q, 27Q (C _{ap} -C), 17Q
	1236 (22) ^b	1235 (16)	1249	a_1	47q, 13Q (C _{ap} -C), 8q (CF ₃)
1193	1194 (28) ^c	1207 (32)	1198	b_2	67q (CF ₃), 19 β
	1159 (35) ^d	1177 (36)		b_1	81q (CF ₃), 16 β
1158	1150	1134 (1)	1163	b_2	82q
1090	1090	1061 (3)	1103	a_2	52 q, 11 Q, 12 β
	1003	965 (1)	1018	b_2	54q, 19Q, 9q (CF ₃)
	879	877 (2)	886	a_1	43q, 21q (CF ₃), 13 β
	786	752 (1)	787	b_2	91 β
717	716 (4)	728 (2)	708	a_1	27 α , 24q (CF ₃), 20 γ
587		552 (1)	584	b_2	40Q, 31q
556		470 (1)	543	a_1	35 α , 20 β , 16q
467		469 (1)	446	b_1	80 γ , 20q (CF ₃)
444		433	434	b_2	55 α , 37 β
360		367 (1)	359	b_2	56 γ , 23q (CF ₃), 10Q
342		338	338	b_1	46 β , 52Q, 8 α
		326		a_1	93 γ
	304	313	300	b_2	80 γ , 8Q
284		292	280	b_2	62 β , 20Q, 16 γ
280		277	276	a_1	89 β
267		249	267	b_2	92 β
		231		a_1	40 γ , 18 β , 16Q (C _{ap} -C)
120			129	b_2	79 β , 14 γ

^a Calculation by software GAUSSIAN'98W [12]. IR (gas) ($\Delta\nu$ ¹³C). ^b 1241 (22). ^c 1201 (34). ^d 1177 (37).

band. According to the calculation this is a mixed vibration of the benzene ring and the trifluoromethyl group whose form is independent of the conformation of the compound. The strong band at 717 cm⁻¹ in the Raman spectrum shifted by 4 cm⁻¹ on labeling the CF₃ group with ¹³C, large contribution to the band was made by bonds and angles of the CF₃ group, and we assigned it to symmetric bending vibration of the trifluoromethyl group.

Our calculations of CF₃ group vibrations are well consistent with the data of [15] where the IR spectra have been studied and calculation of frequencies and forms of vibrations has been performed for *p*-, *m*-, and *o*-CNC₆H₄CF₃. For instance, the contributions into the potential energy of symmetric vibrations in

p-trifluoromethylbenzotrile involving the CF₃ group according to [15] are as follows: 1323 cm⁻¹, 20 (C_{ar}-C); 9 (CF₃); 1238 cm⁻¹, 14 (CF₃); for antisymmetric: 1176 cm⁻¹, 44 (CF₃); 1197 cm⁻¹, 81 (CF₃) (cf. with Table 2). The bands in the region 737–745 cm⁻¹ were assigned as in [15] to the symmetric stretching vibration of the CF₃ group. although its contribution to the potential energy was 8–21%, and the largest contribution to these vibrations made CCF angles.

As seen from Table 1, the frequencies of the stretching vibrations of CF₃ group and C_{ar}-C bond in the studied compounds 4-XC₆F₄CF₃ are independent of the character of the X substituent in the *para*-position to the CF₃ group: the frequencies of these

Table 3. UV absorption spectra of polyfluorinated toluenes 4-XC₆F₄CF₃

X	λ_{\max} , nm	ϵ , l mol ⁻¹ cm ⁻¹	σ_p [2]
NH ₂	249	15490	-0.66
	234 sh.	8910	
NMe ₂	282	16220	-0.6
	242	3310	
	220	8130	
NHMe	261	19060	-0.592
	240 sh.	8910	
NHNH ₂	258	15490	-0.55
OEt	268	1180	-0.25
	226	8510	
	213	8910	
Me	272	1950	-0.17
	210 sh.	6920	
SMe	278	10230	-0.0
	210 sh.	8510	
SH	300	16590	0.15
	250	5250	
	226	7240	
H	273	2360	0
	232 sh.	270	
F ^a	266	4860	0.062
	243	320	
I	272	2496	0.18
	242	9420	
	221	5470	
Br	278	2240	0.232
	228 sh.	8130	
	217	11750	
CF ₃	266	1410	0.551
	245	250	
CH=CH ₂	288	1820	
	245	16980	

^a Calculated for octafluorotoluene λ_1 239, λ_2 232 nm correspond to $\pi \rightarrow \pi^*$ -transition in the benzene ring.

vibrations do not undergo considerable changes. The intensity of the absorption bands assigned to C_{ar}-C bond vibrations in the Raman spectra of polyfluorinated toluenes (related to the band at 803 cm⁻¹ in the spectrum of cyclohexane) changes in parallel with σ_p substituent constants. Two linear relations are observed: for electron-donor substituents

$$\log I/I_0 = -(0.58 \pm 0.04)\sigma_p - (0.73 \pm 0.02), n 7, r 0.986;$$

and for electron-acceptor substituents

$$\log I/I_0 = -(0.58 \pm 0.04)\sigma_p + (1.35 \pm 0.14), n 5, r 0.969.$$

Similar correlations were first observed for *para*-nitro-substituted benzenes [13] and *para*-substituted anilines [14]. They were rationalized by assumption that the strongly pronounced electropositive and electronegative qualities of the substituents tended to induce a quinoid structure in nitrobenzenes and anilines, and in the region where the sign of σ_p changed this trend diminished.

Our calculations of frequencies and forms of octafluorotoluene (**I**) vibrations { $\sigma_p(\text{F})$ 0.062 [2]}, revealed the complex and mixed character of $\sigma_s(\text{CF}_3)$ and $\nu(\text{C}_{\text{ar}}-\text{C})$. Significant contributions thereto come both from vibrations of CF₃ group and from the polyfluorinated benzene ring (see Table 2). The increase in force constants (and, consequently, in orders) of C_{ar}-C bond and diminishing of the corresponding values for C-F bonds in the CF₃ group also evidences the efficient interaction between CF₃ and C₆F₅ and supports the notion of the trend of compound **I** to the quinoid structure. The high intensity of the $\nu(\text{C}_{\text{ar}}-\text{C})$ vibration in the Raman spectrum is well consistent with the distinguished direction of polarizability and its derivative with respect to the normal coordinate.

The hyperconjugation should result in a red shift of the longwave maximum in the UV absorption spectra, and the inductive effect is accompanied with a blue shift [4]. Actually in the spectra of a number of polyfluorinated toluenes (X = Br, CH₃, F etc.) a red shift is observed and increase in the intensity of the maximum of the longwave absorption band. In the presence of strong electron-donor substituents (X = NH₂, NMe₂) the UV spectra suffer significant changes at replacement of a fluorine atom by a trifluoromethyl group indicating a transformation of the π -electron system of these toluenes (Table 3).

EXPERIMENTAL

IR spectra were recorded on spectrometer Specord M-80 from pellets with KBr (2: 800 and 4: 800 mg) or from solutions in CCl₄ (*c* 5, 1, 0.5%; *d* 0.1, 0.4, 0.6 mm respectively). The spectra in gas phase were registered in a gas cell, *d* 10 mm. The recording at various temperatures was carried out in standard liquid cells from solutions in CCl₄ (*c* 1.7, 1.8, 1.9, 2.0%; *d* 0.1 mm). The cooling to desired temperature was performed by passing cooling mixture EtOH-liquid nitrogen from a thermostat. The temperature was measured in the thermostat, and it differed from that in the cell by 0.4°C.

Raman spectra were registered on spectrometer Coderg PH-1. As excitation source served a helium-neon laser Spectra-Physics 125 (λ_{excit} 6328 Å) and

argon laser ILA 120-1 (λ_{excit} 4880 Å). Internal intensities in the Raman spectra were estimated related to the line of internal reference cyclohexane at 803 cm⁻¹ (1 mol l⁻¹).

UV spectra of solutions in ethanol (c 1.10⁻⁴ mol l⁻¹) were recorded on spectrophotometers Specord UV-Vis and Beckman DU-8.

The isotope shifts of bands were measured with accuracy of 0.4 cm⁻¹. The content of isotope ¹³C in enriched samples was measured by mass spectra on Finnigan MAT MS-8200 (70 eV) (enrichment 60%).

The substances were recrystallized or distilled before registering IR, Raman, and UV spectra; the purity of samples was no less than 99.5% (GLC).

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