



Polarizability effect in transition metal carbonyl complexes

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ABSTRACT

The literature data on substituent influence on the carbonyl stretching frequencies (ν), CO stretching force constants (k), as well as ^{13}C NMR carbonyl chemical shifts (δ) have been analyzed for 19 series of the transition metal carbonyl complexes. It was established for the first time that the ν , k and δ values depend not only on the inductive and resonance effects but also on the polarizability of substituents. The polarizability contribution ranges up to 37%.

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1. Introduction

The carbonyl group constitutes one of the most common ligands in inorganic and organometallic chemistry. Because of this, the transition metal carbonyl complexes (TMCC) serve as examples of the well-studied donor–acceptor complexes [1–3].

Systematic investigations of TMCC using IR and NMR spectroscopy have begun since 1960s [4–6]. The studies of the carbonyl fragments of TMCC have a significant place in this work [4–41]. A great body of information was obtained from the measurement of the carbonyl stretching frequencies ν , ^{13}C NMR carbonyl chemical shifts δ as well as from the calculation of the CO stretching force constants k . The spectroscopic investigations of the CO–transition metal bond are based on the following grounds, see, e.g. [1,2,25].

The HOMO and LUMO of free carbon monoxide are 5σ (unshared electron pair located on C atom) and the degenerate set $2\pi^*$, respectively. Both of these orbitals are antibonding in character.

There is an abundant evidence that the complexation between CO and a transition metal M is carried out by two mechanisms.

1. A donor–acceptor σ -interaction $5\sigma(\text{CO}) \rightarrow d(\text{M})$, i.e. electron donation from the 5σ orbital to the unfilled M orbitals, leads to strengthening the C–O bond and an increase in the ν and k values.

2. A dative π -interaction $d\pi(\text{M}) \rightarrow 2\pi^*(\text{CO})$, i.e. electron donation from the relevant filled metal d orbitals to the unfilled $2\pi^*$ orbitals, results in weakening the C–O bond and a decrease in the ν and k values.

Hence, the two oppositely directed interactions influence the carbonyl stretching frequency ν and force constant k ; the latter being a more accurate measure of C–O bond strength.

There is evidence that in M–CO fragments carbonyl resonance is deshielded with increasing electron density on M atom and the chemical shifts δ reflect the electronic effects of groupings bonded to M [30,36]. Besides, the combined influence of the two interactions gives rise to the positive charge q^+ on the carbonyl carbon [22,30,42].

All the series of TMCC may be written as $X_n\text{BM}(\overset{q+}{\text{C}}\text{O})_m$, where CO (or C atom) is a reaction (indicator) centre, X_n are substituents, and B is a bridge between X_n and atom M. In the following, we will consider so-called narrow series of TMCC, e.g., $(\eta^6\text{-XC}_6\text{H}_5)\text{Cr}(\text{CO})_3$, $\text{X}_3\text{SnMn}(\text{CO})_5$ with B, M, n, and m variables being fixed. Therefore, the narrow series carry information on the influence of X substituents on the properties P (ν , k , δ).

In our opinion this influence is still not clearly understood. The distinctive feature of the intermolecular $[\text{X}_n\overset{q+}{\text{D}}\cdot\overset{q-}{\text{A}}\text{Hal}_m]$ ($\text{D} = \text{N, O, S}$; $\text{A} = \text{B, Al, Ga, Sn, Sb}$) and intramolecular [atranes

$\text{XM}^{\overset{q-}{\uparrow}}(\text{OCH}_2\text{CH}_2)_3\text{N}^{\overset{q+}{\downarrow}}$ ($\text{M} = \text{Si, Ge, Sn, Pb}$)] donor–acceptor complexes is the occurrence of the polarizability effect [43–45]. The

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
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appearance of an excess charge q on the reaction centre (atom D or M) is the cause of this effect. The charge q polarizes a substituent X, thus inducing a dipole. The energy of the electrostatic ion–dipole attraction is given by

$$E_{es} = -q^2\alpha/(2\epsilon r^4), \quad (1)$$

where α is the polarizability of X substituent, ϵ is a dielectric constant, and r is the distance between the charge q and the induced dipole.

The energy E_{es} varies in proportion to r^{-4} , thus being strongly dependent on the distance r . Therefore, the polarizability effect

does not seem to occur in the so-called classic X––R_C^q systems that are traditionally used in studies of interaction between the X substituents and the charged reaction centre R_C (⁺Alk₂, NO₂[−], etc.).

According to Hammett and Taft [46], the electronic interactions in the charged classic systems include an inductive effect and conjugation. The chemical and physical properties P of these systems are given by the equations

$$P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-), \quad (2)$$

where P_H is P value when $X = H$, and σ_I is a universal inductive constant of the X substituents. The conjugation is quantitatively characterized by the resonance constants σ_R , σ_R^+ , or σ_R^- , depending on the magnitude and sign of the charge on R_C.

The non-classic systems, e.g. XCH=CHR_C^q, XC≡CR_C^q, XR_C^q, differ from the classic analogs by the shorter distances r between X and R_C. The properties P of these systems are described by three-parameter equations

$$P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) + c\sigma_\alpha. \quad (3)$$

The universal σ_α constant of the X substituents serve as a measure of the polarizability effect [43–47]. It is more convenient to use σ_α constants (they are tabulated for most of the substituents [46]) rather than carry out laborious calculations using formula (1).

As indicated above, TMCC are representative examples of the donor–acceptor complexes. It is probable that the series of TMCC X_nBM(CO)_m are either classic or non-classic depending on the type of B bridge. In spite of this, the polarizability effect in TMCC, as far as we know, has not yet been taken into account.

The aim of this work was to elucidate quantitative relationships between the properties P (ν , k , δ) of the narrow series of the transition metal carbonyl complexes and the inductive, resonance, and polarizability effects of substituents.

2. Results and discussion

Using 19 narrow series of TMCC (Tables 1–7, series I–XIX), it is possible to consider the effects of substituents X on the carbonyl stretching frequencies ν , on the CO stretching force constants k as well as on the ¹³C NMR carbonyl chemical shifts δ .

The designations of the frequencies, force constants, and chemical shifts discussed below are given in Table 8.

One can see from Tables 1–7 that in the narrow series I–XIX values of ν , k , and δ are substituent dependent. It is generally believed that this is due to the electronic effects of substituents X [1,29,30,32,33,36,48–52]. There are several arguments in favour of the opinion.

- (1) It is well known that both ν and k values are linear with the chemical shifts δ , e.g. [30,53]. For example, the following equations are valid for series VII and XVII:

Table 1

Carbonyl stretching frequencies ν (cm^{−1}) and force constants k (mdyn Å^{−1}) for I–III series.

X ₆	Series I (X ₃ P) ₂ Co(CO)(NO)		Series II (X ₃ P)Cr(CO) ₂ (η ⁶ -Me ₆ C ₆)			Series III (X ₃ P)Mn(CO) ₂ (η ⁵ -MeC ₅ H ₄)		
	ν (I) ^a	X ₃	ν_1 (II) ^b	ν_2 (II) ^b	k (II) ^b	ν_1 (III) ^c	ν_2 (III) ^c	k (III) ^c
Bu ₆	1957	Et ₃	–	–	–	1937	1874	14.88
Ph ₆	1957	Me ₂ Ph	1850	1787	13.36	–	–	–
(MeO) ₆	1983	MePh ₂	1853	1793	13.43	1940	1878	14.72
(PhO) ₆	2004	Ph ₃	1857	1796	13.48	1944	1884	14.80
(CF ₃) ₄ F ₂	2072	Ph ₂ (MeO)	–	–	–	1944	1884	14.80
(CF ₃) ₂ F ₄	2065	(MeO) ₃	1870	1808	13.66	1947	1892	14.88
F ₆	2059	(PhO) ₃	1886	1825	13.90	1970	1910	15.20

^a Refs. [8,10,17,34], measured in the vapour phase.

^b Ref. [31], solutions in CH₂Cl₂.

^c Ref. [38], solutions in heptane.

Table 2

Carbonyl stretching frequencies ν (cm^{−1}) and ¹³C NMR chemical shifts δ (ppm) for IV–VI series.

X ₃	Series IV (X ₃ Ge)Fe(CO) ₂ (η ⁵ -C ₅ H ₅)		Series V (X ₃ P)Co(CO) ₂ (NO)		Series VI (X ₃ P)W(CO) ₂ (SnMe ₃ (η ⁵ -C ₅ H ₅))
	ν_1 (IV) ^a	ν_2 (IV) ^a	ν_1 (V) ^b	ν_2 (V) ^b	δ (VI) ^c
H ₃	–	–	2057	2006	–
Me ₃	1988	1933	–	–	−223.0
Et ₃	–	–	2032	1969	–
Me ₂ Ph	–	–	–	–	−223.2
MePh ₂	–	–	–	–	−223.3
Ph ₃	1998	1947	2035	1981	–
(N≡C) ₃	–	–	2102	2064	–
(MeO) ₃	–	–	2050	1996	−220.6
(PhO) ₃	–	–	2061	2004	−220.5
F ₃	2046	2001	2087	2044	–
MeCl ₂	2028	1979	–	–	–
Cl ₃	2043	2000	2073	2030	–
Br ₃	2043	2001	–	–	–

^a Ref. [19], solutions in THF.

^b Refs. [9,11,13,14,20,26], solutions in toluene.

^c Ref. [29], solutions in C₆H₆, δ values are reported in ppm downfield from Me₄Si.

Table 3

Carbonyl stretching frequencies ν (cm^{−1}), force constants k (mdyn Å^{−1}) and ¹³C NMR chemical shifts δ (ppm) for VIII–IX series.

X	Series VII (η ⁶ -XC ₆ H ₅)Cr(CO) ₃		Series VIII (η ⁵ -XC ₅ H ₄)Mn(CO) ₃		Series IX (η ⁵ -XC ₅ H ₄)Re(CO) ₃		
	ν_1 (VII) ^a	ν_2 (VII) ^a	δ (VII) ^{b,c}	k (VIII) ^{c,d}	δ (VIII) ^{c,e}	ν_1 (IX) ^d	k (IX) ^d
H	1987	1917	−233.34	26.77	−224.9	2030	26.67
Me	1983	1914	−233.64	26.65	−224.4	2028	26.61
Et	–	–	–	26.65	−224.7	–	–
<i>i</i> -Pr	–	–	–	–	−225.1	–	–
<i>t</i> -Bu	–	–	–	–	−225.3	–	–
ClCH ₂	–	–	–	26.82	–	–	–
HOC	–	–	–	27.13	–	–	–
MeOC	–	–	–	27.01	−223.2	2036	26.89
PhOC	–	–	–	27.02	–	2035	26.87
MeOOC	1997	1927	−231.23	–	−222.7	2035	26.89
N≡C	–	–	–	27.24	–	2041	27.08
H ₂ N	1977	1906	−234.62	26.49	–	2023	26.44
Me ₂ N	1969	1895	−235.05	–	–	–	–
MeO	1982	1910	−233.53	–	–	–	–
F	1990	1929	−232.05	–	–	–	–
Cl	1992	1930	−231.99	–	–	2034	26.82
Br	–	–	–	–	–	2034	26.84

^a Refs. [4,7,35], solutions in cyclohexane.

^b Ref. [30], solutions in CHCl₃.

^c Chemical shifts are reported in ppm downfield from Me₄Si.

^d Refs. [15,21], solutions in cyclohexane.

^e Ref. [27], solutions in CHCl₃.

Table 4Carbonyl stretching frequencies ν (cm^{-1}) for X and XI series.

X_3	Series X (X_3P)Ni(CO) ₃			Series XI (X_3P) ₃ Mo(CO) ₃				
	$\nu_1(X)^a$	$\nu_2(X)^a$	X_3	$\nu_1(X)$	$\nu_2(X)$	X_9	$\nu_1(XI)^b$	$\nu_2(XI)^b$
Me ₃	2064.1	1982	Ph ₂ (EtO)	2071.6	1994	Et ₉	1937	1841
Et ₃	2061.7	1978	Ph(EtO) ₂	2074.2	1997	(PhO) ₉	1994	1922
<i>i</i> -Pr ₃	2059.2	1977	(MeO) ₃	2079.5	2000	(EtO) ₃ Cl ₆	2027	1969
Bu ₃	2060.3	1976	(EtO) ₃	2076.3	1996	F ₉	2090	2055
<i>t</i> -Bu ₃	2056.1	1971	Ph ₂ (PhO)	2074.6	1998	Cl ₉	2040	1991
H ₂ Ph	2077.0	1998	(PhO) ₃	2085.3	2012	–	–	–
HPh ₂	2073.3	1995	F ₃	2110.8	–	–	–	–
MePh ₂	2067.0	1987	PhCl ₂	2092.1	2016	–	–	–
Ph ₃	2068.9	1990	Cl ₃	2097.0	–	–	–	–
Me ₂ CF ₃	2080.9	2004	–	–	–	–	–	–

^a Ref. [23], solutions in CH₂Cl₂.^b Ref. [37], solutions in CH₂Cl₂.**Table 5**Carbonyl force constants k ($\text{mdyn } \text{Å}^{-1}$) for XII–XIV series.

X	Series XII ($X_2PCH_2CH_2PX_2$)Cr(CO) ₄		Series XIII ($X_2PCH_2CH_2PX_2$)Mo(CO) ₄		Series XIV <i>cis</i> -(X_3P) ₂ Mo(CO) ₄		
	$k_1(XII)^a$	$k_2(XII)^a$	$k_1(XIII)^a$	$k_2(XIII)^a$	X_6	$k_1(XIV)^b$	$k_2(XIV)^b$
Me	15.30	14.83	15.46	14.98	Me ₆	15.02	15.21
C ₆ H ₁₁	15.17	14.71	15.32	14.78	Et ₆	14.83	15.29
Ph	15.32	14.75	15.48	14.87	Ph ₆	15.01	15.43
MeO	15.71	15.11	15.82	15.18	(MeO) ₆	15.32	15.65
F	16.39	15.94	16.57	16.04	(EtO) ₂ Cl ₄	15.97	16.33
Cl	16.30	15.87	16.43	15.98	Cl ₆	16.22	16.55

^a Ref. [39], solutions in CS₂.^b Ref. [24], solutions in saturated hydrocarbons.**Table 6**Carbonyl stretching frequencies ν (cm^{-1}), force constants k ($\text{mdyn } \text{Å}^{-1}$) and ¹³C NMR chemical shifts δ (ppm) for XV–XVII series.

X_3	Series XV $X_3AsCr(CO)_5$		Series XVI $X_3SnMn(CO)_5$			Series XVII $X_3PmO(CO)_5$			
	$\delta_1(XV)^a$	$\delta_2(XV)^a$	$\nu_1(XVI)^b$	$\nu_2(XVI)^b$	$\nu_3(XVI)^b$	$k_1(XVII)^c$	$k_2(XVII)^c$	$\delta_1(XVII)^c$	$\delta_2(XVII)^c$
Me ₃	10.89	5.44	2089	1991	1998	–	–	–	–
Bu ₃	10.89	6.06	–	–	–	15.58	15.84	–209.65	–206.32
Ph ₃	10.76	5.37	2094	2004	2004	15.49	15.96	–210.21	–205.66
Me ₂ (F ₃ C)	–	–	2105	2010	2018	–	–	–	–
(MeO) ₃	–	–	–	–	–	15.90	16.06	–208.16	–204.37
(PhO) ₃	–	–	–	–	–	15.93	16.19	–206.92	–203.09
Me ₂ Cl	–	–	2101	2006	2015	–	–	–	–
Ph ₂ Cl	9.34	3.23	2103	2018	2018	–	–	–	–
MeCl ₂	–	–	2114	2030	2019	–	–	–	–
PhCl ₂	7.96	1.26	2113	2031	2023	–	–	–	–
Cl ₃	–	–	2126	2046	2039	16.43	16.46	–206.02	–200.78
Me ₂ Br	–	–	2099	2005	2014	–	–	–	–
Br ₃	–	–	2122	2043	2037	–	–	–	–

^a Ref. [36], solutions in CDCl₃, δ values are reported in ppm downfield from Cr(CO)₆.^b Refs. [12,16,18], solutions in cyclohexane.^c Ref. [32], solutions in CHCl₃, δ values are reported in ppm downfield from Me₄Si.**Table 7**Carbonyl force constants k ($\text{mdyn } \text{Å}^{-1}$) and ¹³C NMR chemical shifts δ (ppm) for XVIII and XIX series.

Series XVIII $X_2CW(CO)_5$			Series XIX $XRe(CO)_5$				
X_2	$\delta_1(XVIII)^{a,b}$	$\delta_2(XVIII)^{a,b}$	X	$k_1(XIX)^c$	$k_2(XIX)^c$	$\delta_1(XIX)^{b,d}$	$\delta_2(XIX)^{b,d}$
Me(H ₂ N)	–203.83	–198.45	Me	16.03	16.94	–181.3	–185.2
Ph(H ₂ N)	–203.83	–198.21	Ph	16.11	17.05	–181.7	–183.6
Me(MeO)	–203.40	–197.17	MeOC	16.32	17.01	–181.2	–183.0
Me(EtO)	–203.43	–197.17	PhOC	16.31	17.07	–181.0	–182.9
Ph(MeO)	–203.60	–197.22	Br	16.03	17.44	–176.3	–177.8
Ph(EtO)	–203.52	–197.29	–	–	–	–	–

^a Ref. [28], solutions in CHCl₃.^b Chemical shifts are reported in ppm downfield from Me₄Si.^c Ref. [33], solutions in cyclohexane.^d Ref. [33], solutions in CDCl₃.

Table 8
Designations of carbonyl stretching frequencies, force constants, and chemical shifts.^a

Fragment	Point group	Symmetry of CO stretching modes	Designations of infrared-active stretching frequencies	Designations of stretching force constants ^b	Designations of ¹³ C NMR carbonyl chemical shifts ^b
MCO	C _{∞v}	a ₁	ν	k	δ
M(CO) ₂	C _s	a'	ν ₁	k	δ
		a''	ν ₂		
M(CO) ₃	C _{3v}	a ₁	ν ₁	k	δ
		e	ν ₂		
M(CO) ₄ ^c	C _{2v}	a ₁ ⁽¹⁾	ν ₁	k ₁	δ ₁
		b ₁	ν ₂		
		b ₂	ν ₃	k ₂	δ ₂
		a ₁ ⁽²⁾	ν ₄		
M(CO) ₅	C _{4v}	a ₁ ⁽²⁾	ν ₁	k ₁	δ ₁
		b ₂	ν ₂	k ₂	δ ₂
		a ₁ ⁽¹⁾	ν ₃		

^a Refs. [5,30,41].

^b k₁ and δ₁ refer to CO which is trans to X substituent.

^c For cis-M(CO)₄(L)₂ complexes.

$$\nu_1(\text{VII}) = (3495 \pm 155) - (6.48 \pm 0.66)\delta(\text{VII})$$

$$S_Y = 2 \quad R = 0.970 \quad n = 8, \quad (4)$$

$$k_2(\text{XVII}) = (38.04 \pm 1.07) + (0.11 \pm 0.01)\delta_2(\text{XVII})$$

$$S_Y = 0.02 \quad R = 0.996 \quad n = 5 \quad (5)$$

Hence the distinct properties (ν and δ or k and δ) are related by linear dependences. From this results the conclusion that the regularities of the X substituent influence are common to all properties under consideration. Because of this there is ample evidence that the substituent effect the ν, k, and δ values through electronic effects.

(2) Using hexacarbonyls of the transition metals it was established that in the vibration ν(CO) there was an essential contribution of the stretching vibration of the M–C bond [42]. Nevertheless, in the narrow series I–XIX (when M = const) the stretching vibrations of CO bonds, apparently, are rather characteristic. However, the ν values do not remain constant when the substituents bonded to M are changed. This is due to the substituent electronic effects which cause changes in the force constants k.

Table 9
Coefficients and their standard deviations (P_H ± S_p, a ± S_a, b ± S_b, c ± S_c) of equations P = P_H + aΣσ_I + bΣσ_R + cΣσ_α (or P = P_H + aΣσ_I + bΣσ_R⁺ + cΣσ_α), standard errors of approximation (S_Y), correlation coefficients (R), and sample size (n).^a

Property P	Equation	P _H ± S _p	a ± S _a	b ± S _b	σ	c ± S _c	S _Y ^b	R ^b	n
ν(I)	(6)	2023 ± 6	26 ± 2	20 ± 1	σ _R	14 ± 1	3(20)	0.998(0.923)	7
ν ₁ (II)	(7)	1871 ± 2	47 ± 1	22 ± 1	σ _R	9 ± 1	1(4)	0.999(0.971)	5
ν ₂ (II)	(8)	1806 ± 6	48 ± 3	21 ± 4	σ _R	8 ± 2	1(3)	0.997(0.980)	5
k(II)	(9)	13.64 ± 0.04	0.69 ± 0.02	0.31 ± 0.03	σ _R	0.12 ± 0.02	0.01(0.04)	0.999(0.978)	5
ν ₁ (III)	(10)	1983 ± 8	53 ± 5	44 ± 6	σ _R	17 ± 3	2(6)	0.988(0.851)	6
ν ₂ (III)	(11)	1909 ± 10	48 ± 6	31 ± 8	σ _R	13 ± 4	2(5)	0.982(0.921)	6
k(III)	(12)	15.27 ± 0.13	0.79 ± 0.08	0.57 ± 0.10	σ _R	0.23 ± 0.05	0.03(0.08)	0.986(0.899)	6
ν ₁ (IV)	(13)	2015 ± 6	46 ± 3	30 ± 8	σ _R	10 ± 2	2(6)	0.996(0.974)	6
ν ₂ (IV)	(14)	1968 ± 4	51 ± 1	24 ± 3	σ _R ⁺	7 ± 1	1(5)	0.999(0.985)	6
ν ₁ (V)	(15)	2058 ± 1	33 ± 1	18 ± 1	σ _R	11 ± 1	1(11)	0.998(0.883)	8
ν ₂ (V)	(16)	2004 ± 2	44 ± 2	14 ± 1	σ _R ⁺	11 ± 1	3(12)	0.996(0.928)	8
δ(VI)	(17)	-221.2 ± 0.2	2.5 ± 0.1	0.6 ± 0.1	σ _R	1.2 ± 0.1	0.04(0.4)	0.999(0.954)	5
ν ₁ (VII)	(18)	1987 ± 1	22 ± 3	20 ± 2	σ _R	0	2	0.983	8
ν ₂ (VII)	(19)	1918 ± 2	33 ± 7	13 ± 2	σ _R ⁺	0	3	0.954	8
δ(VII)	(20)	-233.19 ± 0.12	4.44 ± 0.35	2.58 ± 0.18	σ _R	0	0.18	0.991	8
k(VIII)	(21)	26.77 ± 0.03	0.85 ± 0.06	0.24 ± 0.02	σ _R ⁺	0.08 ± 0.06	0.029(0.032)	0.993(0.992)	9
δ(VIII)	(22)	-224.8 ± 0.3	9.1 ± 1.8	-4.0 ± 1.7	σ _R ⁺	1.0 ± 0.6	0.27(0.34)	0.962(0.941)	7
ν ₁ (IX)	(23)	2030 ± 1	17 ± 2	11 ± 1	σ _R	3 ± 2	1(1)	0.984(0.982)	9
k(IX)	(24)	26.67 ± 0.02	0.58 ± 0.06	0.37 ± 0.04	σ _R	0	0.03	0.985	9
ν ₁ (X)	(25)	2081.0 ± 1.0	27.2 ± 0.8	6.7 ± 0.4	σ _R ⁺	6.8 ± 0.5	1.3(4.4)	0.996(0.949)	19
ν ₂ (X)	(26)	2001 ± 1	38 ± 1	19 ± 1	σ _R	7 ± 1	1(4)	0.996(0.950)	17
ν ₁ (XI)	(27)	2015 ± 14	24 ± 3	8 ± 2	σ _R ⁺	11 ± 2	8(31)	0.989(0.842)	5
ν ₂ (XI)	(28)	1949 ± 18	36 ± 4	12 ± 3	σ _R ⁺	15 ± 3	11(40)	0.990(0.865)	5
k ₁ (XII)	(29)	15.68 ± 0.15	0.53 ± 0.06	0.12 ± 0.04	σ _R ⁺	0.12 ± 0.04	0.10(0.17)	0.983(0.948)	6
k ₂ (XII)	(30)	15.32 ± 0.22	0.55 ± 0.10	0.18 ± 0.06	σ _R ⁺	0.14 ± 0.07	0.15(0.22)	0.964(0.917)	6
k ₁ (XIII)	(31)	15.88 ± 0.11	0.53 ± 0.05	0.14 ± 0.03	σ _R ⁺	0.13 ± 0.03	0.08(0.18)	0.990(0.943)	6
k ₂ (XIII)	(32)	15.48 ± 0.21	0.54 ± 0.09	0.20 ± 0.06	σ _R ⁺	0.16 ± 0.06	0.14(0.23)	0.970(0.911)	6
k ₁ (XIV)	(33)	15.79 ± 0.10	0.53 ± 0.02	0.36 ± 0.04	σ _R	0.18 ± 0.03	0.05(0.22)	0.996(0.920)	6
k ₂ (XIV)	(34)	15.93 ± 0.18	0.53 ± 0.04	0.32 ± 0.06	σ _R	0.12 ± 0.04	0.09(0.17)	0.987(0.956)	6
δ ₁ (XV)	(35)	0.83 ± 0.26	-6.36 ± 0.11	-20.00 ± 0.61	σ _R	-1.82 ± 0.03	0.02(0.68)	0.999(0.824)	5
δ ₂ (XV)	(36)	-2.62 ± 1.09	-6.79 ± 0.46	-13.30 ± 2.60	σ _R	-2.15 ± 0.13	0.07(0.80)	0.999(0.915)	5
ν ₁ (XVI)	(37)	2105 ± 2	29 ± 1	12 ± 4	σ _R	7 ± 1	1(4)	0.996(0.944)	10
ν ₂ (XVI)	(38)	2005 ± 3	42 ± 2	11 ± 8	σ _R	5 ± 2	2(3)	0.991(0.982)	10
ν ₃ (XVI)	(39)	2019 ± 5	28 ± 3	12 ± 7	σ _R ⁺	5 ± 3	3(4)	0.965(0.950)	10
k ₁ (XVII)	(40)	16.60	0.51	0.29	σ _R ⁺	0.43	<0.01(0.24)	1.000(0.757)	5
k ₂ (XVII)	(41)	16.18 ± 0.02	0.43 ± 0.01	0.14 ± 0.01	σ _R ⁺	0.10 ± 0.01	0.01(0.06)	0.999(0.970)	5
δ ₁ (XVII)	(42)	-205.35 ± 2.02	2.64 ± 0.64	2.29 ± 1.00	σ _R	1.96 ± 0.84	0.61(1.08)	0.940(0.791)	5
δ ₂ (XVII)	(43)	-202.09 ± 0.26	3.99 ± 0.08	2.96 ± 0.13	σ _R	1.60 ± 0.11	0.08(0.81)	0.999(0.930)	5
δ ₁ (XVIII)	(44)	-202.30 ± 0.22	0	1.60 ± 0.27	σ _R	0.18 ± 0.12	0.07(0.08)	0.934(0.902)	6
δ ₂ (XVIII)	(45)	-195.84 ± 0.81	3.46 ± 1.34	2.33 ± 1.15	σ _R	1.18 ± 0.55	0.14(0.20)	0.973(0.939)	6
k ₁ (XIX)	(46)	16.07 ± 0.002	0.08 ± 0.003	0.78 ± 0.003	σ _R	-0.16 ± 0.003	0.001(0.04)	0.999(0.965)	5
k ₂ (XIX)	(47)	16.87 ± 0.02	0.86 ± 0.08	-0.78 ± 0.09	σ _R	0	0.03	0.988	5
δ ₁ (XIX)	(48)	-180.5 ± 1.1	10.4 ± 1.7	-8.8 ± 1.9	σ _R	4.1 ± 1.8	0.6(1.1)	0.961(0.880)	5
δ ₂ (XIX)	(49)	-185.1 ± 0.3	13.8 ± 0.5	-8.9 ± 0.6	σ _R	1.6 ± 0.6	0.2(0.4)	0.998(0.990)	5

^a Standard sets of the σ_I, σ_R, σ_R⁺, and σ_α constants are the same as those used previously [43–46].

^b The S_Y and R values calculated with using equations P = P_H + aΣσ_I + bΣσ_R(σ_R⁺) are given in parenthesis.

- (3) The ^{13}C NMR chemical shifts are used to calculate the σ constants of substituents for years, e.g. [54,55]. The foundation of this technique is the proposition that the magnitude of the chemical shift depends solely on the electronic effects of substituent.

We used all of the preceding as the basis for the following discussion.

The statistical characteristics of the correlation equations of the (2) and (3) types for series I–XIX are listed in Table 9. Going from the two-parameter to three-parameter equations of type (3) is accompanied by an increase in the correlation coefficients R and by a decrease in the standard errors of approximation S_Y for series I–VI, VIII, and X–XVIII. Improvement of the statistical characteristics of equations points to statistical significance of the term $c\Sigma\sigma_x$. For each narrow series I–VI, VIII, and X–XVIII the coefficient c is much larger than the corresponding standard deviation S_c .

Therefore, the partial charge q^+ appearing on the carbonyl carbon as a result of the formation of $X_n\text{BM}(\text{C}^{\text{O}})_{\text{m}}$ complexes I–VI, VIII, and X–XVIII brings about the specific interaction between the substituents X and the reaction centre (CO bond or C atom). We call this interaction a “polarizability effect”, using the conventional term, e.g. [43–47]. Hence, it follows that the properties P (ν , k , δ) of the non-classic narrow series I–VI, VIII, and X–XVIII depend not only on the inductive and resonance effects but also on the polarizability effect of the X substituents.

Correlation equations (3), (6)–(17), (21)–(23), (25)–(46), (48), (49) can be written in the general form

$$P = P_{\text{H}} + \text{Ind} + \text{Res} + \text{Pol}, \quad (50)$$

where $\text{Ind} = a\Sigma\sigma_{\text{I}}$, $\text{Res} = b\Sigma\sigma_{\text{R}}$ or $b\Sigma\sigma_{\text{R}}^+$, and $\text{Pol} = c\Sigma\sigma_x$ are respectively the contributions of the inductive, resonance, and polarizability effects to the overall change in P properties caused by the influence of substituents X .

Using (6)–(17), (21)–(23), (25)–(46), (48), and (49), we calculated the Ind, Res, and Pol contributions (see Table 10). The inductive Ind, resonance Res, and polarizability Pol contributions are determined by the type of the corresponding series. The data given in Table 10 indicate that a change in the ν , k , and δ values when X varies from 6% to 37% is due to the polarizability effect of these substituents.

In the narrow series I, IV, X–XIII, and XV–XVIII (see (6), (13), (14)–(25), (27)–(32), (36)–(40), (42), (45)) the Pol contribution is comparable to the Res value. Because of this, the influence of substituents on the properties ν , k , and δ cannot be estimated ignoring the polarizability effect.

The foregoing does not contradict the fact that the polarizability effect was not found for series VII, IX, and XIX (see Table 10, (18)–(20), (24), (47)).

It is particularly remarkable that the Pol contribution is zero for classic series VII. From Eq. (1) it follows that the energy E_{es} depends strongly on the distance r .

The molecules of series VII are characterized by the longest r values. Therefore, the E_{es} value seems to be zero so that the polarizability contribution Pol is also zero.

In the molecules of series VIII the distance r is smaller than in series VII. This causes the appearance of a small Pol contribution. Because the R_{C} atom is large in size, on going from series VIII to series IX the distance r increases and thus the Pol contribution decreases. The atomic size of R_{C} , probably, is one of the reasons for small Pol contribution in the series XIX.

Series V, VIII, XVII, and XIX each allows one to compare the Pol contributions to the frequency ν (or force constant k) and chemical shift δ (Table 10). As may be seen from the comparison of (16) and (17), (21) and (22), (41) and (43), (47) and (49), the influence of the polarizability effect on the chemical shifts is stronger than that on

Table 10

Contributions Ind, Res, and Pol (%) to the overall change in P properties of I–XIX series due to the influence of substituents X .

Property P	Equation	Ind	Res	Pol
$\nu(\text{I})$	(6)	35 ± 3	29 ± 1	36 ± 2
$\nu_1(\text{II})$	(7)	53 ± 1	30 ± 1	17 ± 2
$\nu_2(\text{II})$	(8)	54 ± 3	30 ± 6	16 ± 4
$k(\text{II})$	(9)	54 ± 2	29 ± 3	17 ± 3
$\nu_1(\text{III})$	(10)	42 ± 4	38 ± 5	20 ± 4
$\nu_2(\text{III})$	(11)	47 ± 6	33 ± 9	20 ± 6
$k(\text{III})$	(12)	45 ± 4	35 ± 6	20 ± 4
$\nu_1(\text{IV})$	(13)	57 ± 4	20 ± 5	23 ± 5
$\nu_2(\text{IV})$	(14)	66 ± 1	17 ± 2	17 ± 2
$\nu_1(\text{V})$	(15)	44 ± 1	31 ± 2	25 ± 2
$\nu_2(\text{V})$	(16)	47 ± 2	33 ± 2	20 ± 2
$\delta(\text{VI})$	(17)	55 ± 2	14 ± 2	31 ± 3
$\nu_1(\text{VII})$	(18)	34 ± 5	66 ± 7	0
$\nu_2(\text{VII})$	(19)	39 ± 8	61 ± 9	0
$\delta(\text{VII})$	(20)	44 ± 4	56 ± 4	0
$k(\text{VIII})$	(21)	50 ± 4	44 ± 4	6 ± 5
$\delta(\text{VIII})$	(22)	59 ± 12	29 ± 12	12 ± 7
$\nu_1(\text{IX})$	(23)	44 ± 5	46 ± 4	10 ± 7
$k(\text{IX})$	(24)	48 ± 5	52 ± 6	0
$\nu_1(\text{X})$	(25)	52 ± 2	24 ± 1	24 ± 2
$\nu_2(\text{X})$	(26)	54 ± 1	32 ± 2	14 ± 2
$\nu_1(\text{XI})$	(27)	50 ± 6	21 ± 5	29 ± 5
$\nu_2(\text{XI})$	(28)	52 ± 6	21 ± 5	27 ± 5
$k_1(\text{XII})$	(29)	56 ± 6	20 ± 7	24 ± 8
$k_2(\text{XII})$	(30)	50 ± 9	26 ± 9	24 ± 12
$k_1(\text{XIII})$	(31)	53 ± 5	23 ± 5	24 ± 6
$k_2(\text{XIII})$	(32)	46 ± 8	28 ± 8	26 ± 10
$k_1(\text{XIV})$	(33)	47 ± 2	31 ± 4	22 ± 4
$k_2(\text{XIV})$	(34)	53 ± 4	31 ± 6	16 ± 5
$\delta_1(\text{XV})$	(35)	51 ± 1	31 ± 1	18 ± 1
$\delta_2(\text{XV})$	(36)	57 ± 4	21 ± 4	22 ± 1
$\nu_1(\text{XVI})$	(37)	71 ± 2	12 ± 4	17 ± 2
$\nu_2(\text{XVI})$	(38)	82 ± 4	8 ± 6	10 ± 4
$\nu_3(\text{XVI})$	(39)	74 ± 8	13 ± 8	13 ± 8
$k_1(\text{XVII})$	(40)	32	31	37
$k_2(\text{XVII})$	(41)	53 ± 1	30 ± 2	17 ± 2
$\delta_1(\text{XVII})$	(42)	35 ± 8	30 ± 13	35 ± 15
$\delta_2(\text{XVII})$	(43)	44 ± 1	32 ± 1	24 ± 2
$\delta_1(\text{XVIII})$	(44)	0	80 ± 14	20 ± 13
$\delta_2(\text{XVIII})$	(45)	52 ± 20	23 ± 11	25 ± 12
$k_1(\text{XIX})$	(46)	10 ± 1	73 ± 1	17 ± 1
$k_2(\text{XIX})$	(47)	59 ± 6	41 ± 5	0
$\delta_1(\text{XIX})$	(48)	49 ± 8	33 ± 7	18 ± 8
$\delta_2(\text{XIX})$	(49)	62 ± 2	31 ± 2	7 ± 2

the frequencies and force constants. In NMR and IR experiments the reaction centres are carbonyl carbon atom and CO bond, respectively. The distance r between the substituent X and the carbonyl carbon atom is shorter than that between X and CO bond. According to Eq. (1), a decrease in r implies an increase in the polarizability effect.

In general, the inductive, resonance, and polarizability effects of substituents X are interdependent. The narrow series $X_n\text{BM}(\text{CO})_5$ and $\text{XRe}(\text{CO})_5$ (XV–XIX, Table 10) are examples. Let us consider contributions Ind, Res, and Pol in these series. The series XV–XIX each contain the CO groups located both *trans*- and *cis*- to the $X_n\text{B}$ fragment or X substituent.

It is apparent that the r distance (see Eq. (1)) between the reaction centre (the carbonyl carbon atom or CO bond) and X substituent is longer for *trans* CO groups. However, contrary to the expectations the Pol contribution to the overall change in k_2 and δ_2 properties is larger than that in k_1 and δ_1 . This is caused by the interrelation of the Ind, Res, and Pol contributions.

From Table 10 it follows that the influence of inductive effect on k_2 and δ_2 properties is stronger (i.e. Ind contribution is greater) than that on k_1 and δ_1 properties. The finding is in line with the evidence for the predominant role of the inductive influence on the stretching frequencies ν of the CO groups located *cis*- to the X sub-

stituents [50,56,57]. Therefore, in the molecules of series XV–XIX, as a rule, the influence of the resonance and polarizability effects on k_2 and δ_2 properties is weaker than that on k_1 and δ_1 properties.

Thus, the ν , k , and δ properties of TMCC depend on the inductive, resonance, and polarizability effects of X substituents. At the same time, the interplay of Ind, Res, and Pol contributions to the change in these properties is still not clearly understood. In particular, according to Eq. (1), the contribution Pol must increase with increase in the positive charge on the reaction centre (the carbonyl carbon atom, CO bond). An investigation of this problem is in progress.

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