Tetrahedron. Vol. 29, pp. 3189 to 3194. Pergamon Press 1973. Printed in Great Britain

APPLICATION OF THE SETH-PAUL–VAN DUYSE EQUATION – I

A SIMPLE RELATION DEFINING NEW $X^+(R)$ SUBSTITUENT CONSTANTS ON THE BASIS OF ELECTROPHILIC σ^+ CONSTANTS

A. PERJÉSSY*
Department of Organic Chemistry, Komensky University, 801 00 Bratislava, Czechoslovakia

(*Received in UK* 23 *March* 1973; *Accepted for publication* 22 *May* 1973)

Abstract – The Seth-Paul-Van Duyse equation (SPVDE) correlating the C═O stretching frequencies of a great number of R_1COR_2 molecules with X (R) substituent constants has been reinvestigated. A simple empirical relation defining new $X^+(R)$ constants on the basis of electrophilic σ^+ constants has been derived:

$$X^+(R) = 0{\cdot}238\,\sigma^+ + 1{\cdot}077.$$

The three earlier reported relationships between the X(R) constants and Hammett σ values have been replaced by this single relationships and a set of new $X^+(R)$ constants has been calculated. The new $X^+(R)$ constants applied to 287 R_1COR_2 compounds containing *para*- or *meta*-substituted benzene rings fit very well the SPVDE. It has been possible to extend the SPVDE to various aromatic systems.

Seth-Paul and Van Duyse[1] investigated the C═O stretching frequencies of a great number of simple R_1COR_2 molecules measured in diluted carbon tetrachloride. Applying the concept of group electronegativity they developed a new X(R) substituent constants bridging the scale of Hammett σ and Taft δ constants. They have found that the C═O stretching frequencies of 457 R_1COR_2 molecules are proportional to the substituent constants X(R) ($r = 0{\cdot}995$ and $s = 2{\cdot}86$) according to the equation:

$$\nu_{CO} = 38{\cdot}2[X(R_1) + X(R_2)] + 1583{\cdot}2. \qquad (1)$$

Defining the X(R) values for a substituted methyl and phenyl group as

$$X(R) = X(Me) + \delta' \qquad (2)$$

and

$$X(R) = X(Ph) + \delta \qquad (3)$$

they have found, for substituents possesing negative Taft constants,

$$\delta' = 0{\cdot}482\,\sigma^*. \qquad (4)$$

For a substituted phenyl group with electron-attracting substituents in the *para*-position

$$\delta = 0{\cdot}2\,\sigma. \qquad (5)$$

For electron-donating substituents in *para* position

$$\delta = 0{\cdot}5\,\sigma \qquad (6)$$

and for substituents in *meta* position

$$\delta = 0{\cdot}3\,\sigma \qquad (7)$$

where σ refers to the Hammett constants defined in the region from $\sigma_p(NO_2) = 1{\cdot}28$ to $\sigma_p(NH_2) = -0{\cdot}66$ and $\sigma(H)$ being 0.

Among the 457 compounds used in the Eq 1 there are 305 compounds containing *para* or *meta* substituted benzene rings i.e. compounds fitting the Eqs 5–7. A great number of papers published recently e.g.[2–7], however, have drawn attention to the fact that the C═O stretching frequencies of *para* and *meta* substituted aromatic CO compounds correlate more significantly with the Brown-Okamoto's electrophilic σ^+ constants than with the Hammett σ constants. There are also some examples[2,8] of successful use of the σ^+ constants in the correlations with the C═O stretching frequencies of aromatic heterocyclic carbonyl compounds. Traylor and Ware,[2] Eaborn *et al.*[9] and recently Krygowski[10] have suggested the unification of Traylor's σ_α^+, Eaborn's σ_{Ar}^+, Brown-Okamoto's σ_p^+ and σ_m^+ and Streitwieser's σ_r^+ constants on the basis of an only scale of electrophilic σ^+ constants. This unification permits more general linear free-energy relationships for a wide range of aromatic compounds. The purpose of this work was therefore to define new $X^+(R)$ constants based on the electrophilic σ^+ constants fitting the SPVDE and allowing the extension of its validity. To derive such constants we reinvestigated the CO stretching frequencies of the 457 R_1COR_2 compounds used[1] in the construction of the original SPVDE.

The data have been arranged before treatment as follows:

(i) Among the 457 reported[1] R_1COR_2 compounds only 439 were taken into consideration for this investigation. The remaining 18 compounds were those containing *para*- or *meta*- substituents on a benzene ring for which the electrophilic σ^+ constants were uncertain during this investigation (i.e. compounds containing 3-OH, 3-N(Me)$_2$, 3-OEt, 3-COMe and 4-COMe groups).

(ii) The CO stretching frequencies selected[1] for derivation of the original SPVDE were used in this investigation.

(iii) The compounds and their corresponding CO frequencies were divided formally into three groups: The first group (I) consists of all aliphatic compounds and compounds containing unsubstituted or *ortho* substituted benzene rings. The second group (II) are the compounds containing *meta* and *para* substituted benzene rings and their corresponding unsubstituted parent compounds. The third group (III) contains all 439 compounds i.e. compounds included in groups I and II together with 104 compounds containing such *meta* and *para* substituents which are lacking in the original Brown-Okamoto's collection of σ^- constants[11] and *meta* and *para* substituted compounds with *ortho* substituents and such *meta* and *para* substituted compounds for which the corresponding unsubstituted parent compounds were not available.

In the process of investigating new $X^+(R)$ constants we constructed for the 206 compounds of group II linear relationships between the $\Delta\nu_{CO}$ values (CO frequency shifts) and Brown-Okamoto's[11] σ^+ constants, Seth-Paul-Van Duyse[1] δ values and McDaniel-Brown[12] σ constants respectively. It follows from the statistical treatment (Table 1) that the most significant is the correlation using electrophilic σ^+ constants:

$$\Delta\nu_{CO} = 9{\cdot}106 \sum \sigma^+ + 0{\cdot}284 \qquad (8)$$

where

$$\Delta\nu_{CO} = \nu_{CO}(R_1COR_2) - \nu_{CO}(PhCOR_2). \qquad (9)$$

Eq 8 was therefore chosen to derive new $X^+(R)$ constants.

Correlating the CO frequencies of the 152 compounds of group I with original Seth-Paul-Van Duyse X(R) constants[1] we obtained:

$$\nu_{CO} = 37{\cdot}759 \sum X(R) + 1584{\cdot}323 \qquad (10)$$

which can be written as follows:

$$\nu_{CO}(R_1COR_2) = 37{\cdot}759[X(R_1) + X(R_2)] + 1584{\cdot}323 \qquad (11)$$

and

$$\nu_{CO}(PhCOR_2) = 37{\cdot}759[X(Ph) + X(R_2)] + 1584{\cdot}323. \qquad (12)$$

Comparing Eqs 11 and 12 and introducing δ and $\Delta\nu_{CO}$ from the Eqs 3 and 9 we obtained:

$$\Delta\nu_{CO} = 37{\cdot}759\, \delta. \qquad (13)$$

Generally, for the compounds containing more than one substituent on the benzene ring (13) can be written:

$$\Delta\nu_{CO} = 37{\cdot}759 \sum \delta. \qquad (14)$$

The comparison of Eqs 8 and 14 led to a simple relation defining new primary δ values (denoted as $\delta^+_{pr.}$) on the bases of electrophilic σ^+ constants:

$$\delta = \delta^+_{pr.} = 0{\cdot}241\, \sigma^+ + 0{\cdot}008. \qquad (15)$$

Using new $\delta^+_{pr.}$ values for *meta* and *para* substituents (i.e. replacing the original Eqs 5–7 by the Eq 15) and original δ values for *ortho* substituents

Table 1. Statistical treatment of linear correlations

Eq No	Correlation	Group of compounds	n[a]	r[b]	ρ[c]	q[d]	s_ρ[e]	s[f]	s[g]
8	$\Delta\nu_{CO}$ *vs.* $\Sigma\, \sigma^+$	II	206	0·922	9·106	0·284	0·267	0·330	2·238
—	$\Delta\nu_{CO}$ *vs.* $\Sigma\, \delta$	II	206	0·911	36·111	−0·460	1·145	0·018	2·387
—	$\Delta\nu_{CO}$ *vs.* $\Sigma\, \sigma$	II	206	0·874	12·691	−1·554	0·493	0·588	2·813
10	ν_{CO} *vs.* Σ X(R)	I	152	0·992	37·759	1584·323	0·393	16·778	3·731
19	ν_{CO} *vs.* Σ X(R)	III	439	0·995	38·207	1583·169	0·183	12·620	2·974
16	ν_{CO} *vs.* $\Sigma\, X^+_{pr.}(R)$	III	439	0·995	38·215	1583·419	0·184	12·667	2·991
18	ν_{CO} *vs.* $\Sigma\, X^+(R)$	III	439	0·995	38·219	1583·426	0·185	12·694	2·998

[a] Number of compounds used in correlation. [b] Correlation coefficient. [c] Slope. [d] Intercept. [e] Standard deviation of ρ. [f] Standard deviation of q. [g] Standard deviation.

we calculated new X(R) values (denoted as $X^{+}_{pr.}(R)$) for 287 compounds containing *meta* or *para* substituted benzene rings. The SPVDE constructed by using the original X(R) values for the 152 compounds of group I and the new $X^{+}(R)$ values for the remaining 287 compounds is the following:

$$\nu_{CO} = 38{\cdot}215 \sum X^{+}_{pr.}(R) + 1583{\cdot}419. \quad (16)$$

Table 2. New $X^{+}(R)$ constants, δ^{+} values and corresponding electrophilic σ^{+} constants[a] for *meta* and *para* substituted benzene ring

	meta			*para*		
Substituent	$X^{+}(R)$	δ^{+}	σ^{+}	$X^{+}(R)$	δ^{+}	σ^{+}
H	1·070	0·000	0·00	1·070	0·000	0·00
$N(Me)_2$				0·672	−0·398	−1·70
NHPh				0·744	−0·326	−1·40
NH_2	1·039	−0·031	−0·16	0·768	−0·302	−1·30
OH				0·858	−0·212	−0·92
NHCOMe				0·934	−0·136	−0·60
NHCOPh				0·934	−0·136	−0·60
OMe	1·089	0·019	0·05	0·891	−0·179	−0·78
OPh	1·101	0·031	0·10[b]	0·958	−0·112	−0·50
SMe	1·115	0·045	0·16	0·934	−0·136	−0·60
Me	1·060	−0·010	−0·07	1·003	−0·067	−0·31
Et	1·063	−0·007	−0·06	1·006	−0·064	−0·30
iPr	1·063	−0·007	−0·06	1·010	−0·060	−0·28
tBu	1·063	−0·007	−0·06	1·015	−0·055	−0·26
Ph	1·103	0·033	0·11	1·034	−0·036	−0·18
CH_2COOEt	1·075	0·005	−0·01	1·039	−0·031	−0·16
CH_2Cl	1·110	0·040	0·14	1·075	0·005	−0·01
$Si(Me)_3$	1·079	0·009	0·01	1·082	0·012	0·02
F	1·160	0·090	0·35	1·060	−0·010	−0·07
Cl	1·172	0·102	0·40	1·103	0·033	0·11
Br	1·172	0·102	0·40	1·113	0·043	0·15
I	1·163	0·093	0·36	1·108	0·038	0·13
COOH	1·153	0·083	0·32	1·177	0·107	0·42
COOMe	1·165	0·095	0·37	1·194	0·124	0·49
COOEt	1·165	0·095	0·37	1·191	0·121	0·48
CF_3	1·201	0·131	0·52	1·222	0·152	0·61
CN	1·210	0·140	0·56	1·234	0·164	0·66
NO_2	1·236	0·166	0·67	1·265	0·195	0·79
$COO^{-}K^{+}$	1·070	0·000	−0·03	1·072	0·002	−0·02
$N(Me)_3^{+}Cl^{-}$	1·163	0·093	0·36	1·175	0·105	0·41
CHO				1·186	0·116	0·46[c]
OEt				0·906	−0·164	−0·72[d]
$N(Et)_2$				0·739	−0·331	−1·42[e]
$Sn(Me)_3$				1·048	−0·022	−0·12[f]
SO_2Me				1·251	0·181	0·73[g]
COMe				1·201	0·131	0·52[g]
COPh				1·179	0·109	0·43[h]
C≡CH	1·156	0·086	0·33[i]	1·120	0·050	0·18[i]
2-Thi	1·113	0·043	0·15[j]	0·987	−0·083	−0·38[j]
3-Thi	1·096	0·026	0·08[k]	0·987	−0·083	−0·38[k]
2-Fu	1·101	0·031	0·10[j]	0·970	−0·100	−0·45[j]
CH_2Ph	1·060	−0·010	−0·07[b]	1·022	−0·048	−0·23[b]
SPh				0·970	−0·100	−0·45[b]
Fer	1·070	0·000	0·00[l]	0·908	−0·162	−0·71[l]

Thi = thienyl
Fu = furyl
Fer = ferrocenyl

[a] Brown-Okamoto's σ^{+} constants from ref 11, [b] From ref 9, [c] From ref 13, [d] From ref 14, [e] From ref 15, [f] From 16, [g] From ref 17, [h] From ref 18, [i] From ref 19, [j] From ref 20, [k] From ref 21, [l] From ref 2.

Table 3. $X^+(R)$ values of various aromatic systems applicable in the SPVDE and corresponding electrophilic σ^+ constants

Aromatic system	Position	$X^+(R)$	σ^+	Ref
Naphtalene	1	0·994	−0·35	9
	2	1·018	−0·25	9
Biphenylene	1	1·022	−0·23	9
	2	0·965	−0·47	9
Fluorene	1	1·041	−0·15	9
	2	0·963	−0·48	9
	3	1·020	−0·24	9
	4	1·029	−0·20	9
Indene	5	0·979	−0·41	9
Anthracene	1	0·979	−0·41	10
	2	0·991	−0·36	10
	9	0·906	−0·72	10
9,10-Dihydroanthracene	1	1·006	−0·30	9
	2	1·001	−0·32	9
5,6,7,8-Tetrahydro-naphtalene	2	0·979	−0·41	9
Phenanthrene	1	0·996	−0·34	9
	2	1·018	−0·25	9
	3	1·008	−0·29	9
	4	0·998	−0·33	9
	9	0·991	−0·36	9
9,10-Dihydrophenanthrene	2	0·984	−0·39	9
Triphenylene	1	1·001	−0·32	10
	2	1·015	−0·26	10
Pyrene	1	0·918	−0·67	9
	2	1·025	−0·22	9
	4	0·991	−0·36	9
Naphtacene	5	0·887	−0·80	10
Benz[a]anthracene	7	0·925	−0·64	10
Perylene	3	0·901	−0·74	10
Chrysene	6	0·970	−0·45	9
Benzo[a]pyrene	6	0·872	−0·86	10
Dibenz[a, h]anthracene	7	0·922	−0·65	10
Anthanthrene	6	0·884	−0·81	10
Coronene	1	0·972	−0·44	10
Fluoranthene	1	1·010	−0·28	9
	2	1·027	−0·21	9
	3	0·970	−0·45	9
	7	1·013	−0·27	9
	8	0·979	−0·41	9
Triptycene	1	1·032	−0·19	9
	2	1·008	−0·29	9
Furan	2	0·853	−0·94	22
	3	0·970	−0·45	23
Thiophene	2	0·682	−1·66	2[a]
	3	0·960	−0·49	9
Benzo[b]furan	2	0·965	−0·47	22
	3	0·968	−0·46	22
Dibenzo[b, d]furan	1	1·020	−0·24	9
	2	0·982	−0·40	9
	3	1·010	−0·28	9
	4	1·018	−0·25	9
Pyridine	2	1·267	0·80	24
	3	1·148	0·30	24
	4	1·284	0·87	24
4-Pyridone	3	1·517	1·85	25
Pyridine 1-oxide	3	1·267	0·80	25
	4	1·132	0·23	26
1-Hydroxy-4-pyridonium	3	1·577	2·10	25
4-Pyrone	3	1·791	3·00	25
4-Thiapyrone	3	1·839	3·20	25
Indol	3	0·492	−2·46	2[a]
Quinoline	2	1·094	0·07	27
	3	1·096	0·08	27
	4	1·256	0·75	27
	5	1·051	−0·11	27
	6	1·091	0·06	27
	7	1·113	0·15	27
	8	1·091	0·06	27
Ferrocene	1	0·708	−1·55	22

[a] Calculated according to the equation $\sigma^+ = 0{\cdot}0877\,(\nu_{CO} - 1691{\cdot}1)$ reported by Traylor and Ware,[2] where ν_{CO} refers to the carbonyl frequency of corresponding arylmethylketone.

Following an analogous procedure using Eqs 8 and 16 we obtained an improved relation between new δ values (denoted as δ^+) and the electrophilic σ^+ constants:

$$\delta = \delta^+ = 0{\cdot}238\,\sigma^+ + 0{\cdot}007. \tag{17}$$

The use of these δ^+ values to calculate new X(R) constants (denoted as $X^+(R)$) led to the improved SPVDE:

$$\nu_{CO} = 38{\cdot}219 \sum X^+(R) + 1583{\cdot}426. \tag{18}$$

Repeating the above procedures with Eqs 8 and 18 we obtained practically the same Eqs as 17 and 18. Therefore, the Eqs 17 and 18 can be considered as definitive.

Using the original $\Sigma\,X(R)$ values[1] for all the 439 investigated compounds we obtained the equation:

$$\nu_{CO} = 38{\cdot}207 \sum X(R) + 1583{\cdot}169. \tag{19}$$

Comparing the regression parameters of Eqs 18 and 19 (see Table 1) it can be concluded that the new $X^+(R)$ values fit the slightly modified SPVDE (Eq 18) so good as the original X(R) values fit the original SPVDE (Eq 19).

Defining X(Ph) = 1·070 the new $X^+(R)$ constants of a *meta* or *para* substituted phenyl group can be calculated (for $\sigma^+ \neq 0$) as follows:

$$X^+(R) = 0{\cdot}238\,\sigma^+ + 1{\cdot}077 \tag{20}$$

and those of phenyl group containing more than one *meta* or *para* substituent equal:

$$X^+(R) = 0{\cdot}238 \sum_{i=1}^{n} \sigma_i^+ + 0{\cdot}007n + 1{\cdot}070. \tag{21}$$

The new $X^+(R)$ values for *meta* and *para* substituted phenyl groups together with the

Table 4. Carbonyl stretching frequencies (CCl_4) and Σ $X^+(R)$ values of aromatic R_1COR_2 compounds

Compound No	R_1^a	R_2^a	ν_{CO}(observed)^b (cm^{-1})	Ref	$\Sigma X^-(R)$	ν_{CO}(calculated)^c (cm^{-1})
1	2-Fu	H	(1682) 1699	28	2·983	1697·4
2	2-Fu	OMe	1726 (1740)	29	3·623	1721·9
3	2-Fu	OEt	1718 (1733)	29	3·423	1714·2
4	2-Fu	Me	1687	2	2·660	1685·1
5	2-Fu	CH=CHPh	1642 (1669)	*d*	1·426	1637·9
6	2-Thi	H	(1679) 1689	30	2·812	1690·9
7	2-Thi	Me	1673	31	2·489	1678·6
8	2-Thi	Et	1674	31	2·440	1676·7
9	2-Thi	nPr	1672	32	2·433	1676·4
10	2-Thi	tBu	1664	32	2·340	1672·9
11	2-Thi	OMe	1721	29	3·452	1715·4
12	2-Thi	CH=CHPh	1636 (1661)	*d*	1·245	1631·0
13	2-Thi	CH_2Cl	1685^e	31	2·700	1686·6
14	2-Py	Me	1705	*d*	3·074	1700·9
15	2-Py	H	1722	*d*	3·397	1713·3
16	3-Py	H	1714	*d*	3·278	1708·7
17	3-Py	Me	1697	*d*	2·955	1696·4
18	3-Py	OH	1756	*d*	4·248	1745·8
19	4-Py	Me	1706	*d*	3·091	1701·6
20	4-Py	H	1722	*d*	3·414	1713·9
21	3-Ind	Me	1663	2	2·299	1671·3
22	3-Ind $(CH_2)_3$	OH	1762	*d*	4·848	1768·7
23	1-Fer	OMe	1722	33	3·478	1716·4
24	1-Fer	Me	1676	2	2·515	1679·5
25	1-Fer	$(CH_2)_2Cl$	1676	*d*	2·497	1678·9
26	1-Fer	$(CH_2)_3Cl$	1676	*d*	2·463	1677·6
27	1-Fer	Ph	1649	*d*	1·778	1651·4
28	1-Fer	$(CH_2)_2Br$	1679	*d*	2·485	1678·4
29	1-Fer	OH	1736	*d*	3·808	1729·0
30	1-Fer	2-Fu	(1634) 1639	*d*	1·561	1643·1
31	1-Fer $(CH_2)_2$	Me	1725	*d*	3·544	1718·9
32	1-Fer	H	(1670) 1692	*d*	2·838	1691·9
33	1-Fer	$CHBrCH_2Br$	1683	*d*	2·614	1683·3
34	1-Fer	CH_2Ph	1671 (1682)	*d*	2·383	1674·5
35	1-Fer	1-Fer	1640	*d*	1·416	1637·5
36	1-Fer	2-Thi	1639	*d*	1·390	1636·6
37	1-Fer	CH_2Cl	1689^e	*d*	2·726	1687·6
38	1-Fer	Et	(1663) 1684	*d*	2·466	1677·7
39	1-Fer	$CH=CH_2$	1644 (1668)	*d*	1·648	1646·4
40	1-Naph	H	1698	34	3·124	1702·8
41	1-Naph	Me	1681	2	2·801	1690·5
42	1-NaphCH$_2$	OH	1764	*d*	4·769	1765·7
43	1-Naph	H	1698	34	3·148	1703·7
44	2-NaphCH$_2$	OH	1764	*d*	4·771	1765·8
45	3-Phen	Me	1691	*d*	2·815	1691·0
46	9-Phen	H	1698	34	3·121	1702·7
47	9-Phen	Me	1681	2	2·798	1690·4
48	1-Pyr	H	1696 (1687)	34	3·048	1699·9
49	1-Pyr	Me	1686 (1682)	35	2·725	1687·6
50	1-Pyr	nBu	1686 (1681)	35	2·669	1685·4

[a] Abbrevations: Fu – furyl, Thi – thienyl, Py – pyridyl, Ind – indolyl, Fer – ferrocenyl, Naph – naphtyl, Phen – phenanthryl, Pyr – pyrenyl, Ph – phenyl

[b] In the case of some compounds two bands are observed due to the rotational isomerism or Fermi resonance. Therefore, the frequencies of bands which not obeyed the SPVDE are between brackets.

[c] Calculated by means of Eq 18

[d] Frequencies measured in this laboratory in diluted carbon tetrachloride using a Zeiss UR 20 spectrophotometer.

[e] When, because of field effects, two bands are observed, the average value is given (similarly as in the original SPVDE[1]).

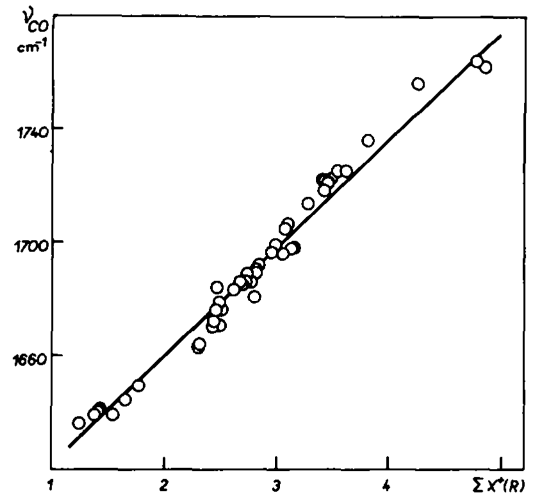

Fig 1. Carbonyl stretching frequencies (in CCl_4) of 50 aromatic R_1COR_2 compounds *vs.* corresponding $\Sigma X^+(R)$ values. The straight line is constructed according to the improved SPVDE (Eq 18).

corresponding electrophilic σ^+ constants are listed in the Table 2.

Considering the above mentioned unification of the scale of electrophilic σ^+ constants[2,9,10] and defining:

$$\sigma^+_\alpha(\mathrm{Ph}) \equiv \sigma^+_{\mathrm{Ar}}(\mathrm{Ph}) \equiv \sigma^+_r(\mathrm{Ph}) \equiv \sigma^+_{\mathrm{p,m}}(\mathrm{H}) \equiv 0$$

we can extend the use of the Eq 20 for calculating $X^+(R)$ constants for various aromatic groups. In the Table 3 is given a set of new $X^+(R)$ constants together with the corresponding σ^+ values for a large variety of common aromatic systems applicable in the SPVDE.

To establish the possibility of the above mentioned extension of the SPVDE we have compiled from the literature or measured in this laboratory the carbonyl frequencies (in diluted CCl_4) of the fifteen aromatic heterocyclic, organometallic and polycyclic hydrocarbon derivatives. The data together with the corresponding $\Sigma X^+(R)$ values are given in the Table 4. The data given in this table indicate that the CO stretching frequencies calculated by means of Eq 18 are in good agreement with those observed for all aromatic compounds. The applicability of the improved SPVDE for these compounds (from the Table 4) is illustrated by the graph in the Fig 1.

Acknowledgements—We express our thanks to Assoc. Prof. Š. Toma for samples of some ferrocene derivatives.

REFERENCES

[1] W. A. Seth-Paul and A. Van Duyse, *Spectrochim. Acta* **28A**, 211 (1972)

[2] T. G. Traylor and J. C. Ware: *J. Am. Chem. Soc.* **89**, 2304 (1967)

[3] I. N. Juchnovski, *Dokl. Bolg. Akad. Nauk* **20**, 33 (1967)

[4] I. N. Juchnovski and N. Christov, *Ibid.* **22**, 1401 (1969)

[5] N. L. Silver and D. W. Boykin, Jr., *J. Org. Chem.* **35**, 759 (1970)

[6] W. F. Weincoff, III and D. W. Boykin, Jr., *Ibid.* **37**, 673 (1972)

[7] A. Perjéssy, D. W. Boykin, Jr., L. Fišera, A. Krutošíková and J. Kováč, *Ibid.* **38**, 1807 (1973)

[8] A. Perjéssy, P. Hrnčiar and R. Frimm, *Acta Fac. Rerum Nat. Univ. Comen. Chimia* **18**, 89 (1973)

[9] R. Barer, C. Eaborn and R. Taylor, *J. Chem. Soc.* Perkin Trans. II 97 (1972)

[10] T. M. Krygowski, *Tetrahedron* **28**, 4981 (1972)

[11] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.* **80**, 4979 (1958)

[12] D. M. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958)

[13] H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.* **80**, 3277 (1958)

[14] B. B. Tice, J. Lee and F. H. Hendall, *Ibid.* **85**, 329 (1963)

[15] O. F. Ginsburg, E. N. Kviat and G. C. Idlis, *Zh. Obschei Khim.* **32**, 2633 (1962)

[16] O. Buchman, M. Grosjean and J. Nasielski, *Helv. Chim. Acta* **47**, 2037 (1964)

[17] N. C. Deno and W. L. Ewans, *J. Am. Chem. Soc.* **79**, 5804 (1957)

[18] W. N. White, D. Gwynn, R. Schlitt, Ch. Girard and W. Fife, *Ibid.* **80**, 3271 (1958)

[19] J. A. Landgrebe and R. H. Rymbrandt, *J. Org. Chem.* **31**, 2585 (1966)

[20] F. Fringuelli, G. Marino and A. Taticchi, *J. Chem. Soc.* Perkin Trans. II 158 (1972)

[21] F. Fringuelli, G. Marino and A. Taticchi, *Ibid.* B 2302 (1971)

[22] A. Hill, M. L. Gross, M. Stasievicz and M. Manion, *J. Am. Chem. Soc.* **91**, 7381 (1969)

[23] R. Taylor, *J. Chem. Soc.* B 1364 (1970)

[24] R. Taylor, *Ibid.* 4881 (1962)

[25] P. Bellingham, C. D. Johnston and A. R. Katritzky, *Ibid.* B 866 (1968)

[26] H. Shindo, *Chem. Pharm. Bull. Tokyo* **6**, 117 (1958)

[27] R. Taylor, *J. Chem. Soc.* B 2382 (1971)

[28] I. N. Juchnovski and J. Kaneti, *Tetrahedron* **27**, 4269 (1971)

[29] D. J. Chadwick, J. Chambers, G. D. Meakins and R. L. Snowden, *Chem. Commun.* 626 (1971)

[30] C. Andrieu, R. Pinel and Y. Mollier, *Bull. Soc. Chim. Fr.* 1314 (1971)

[31] J. J. Peron, P. Saumagne and J. M. Lebas, *Spectrochim. Acta* 26A, 1651 (1970)

[32] J. M. Angelelli, A. R. Katritzky, R. F. Pinzelli and R. D. Thompson, *Tetrahedron* **28**, 2037 (1972)

[33] G. G. Dvoryantseva, M. I. Struchkova, Y. N. Sheinker, K. I. Grandberg and S. P. Gubin, *Izvest. Akad. Nauk SSSR, Ser. Khim.* **37**, 945 (1967)

[34] H. P. Figeys and J. Nasielski, *Spectrochim. Acta* **23A**, 465 (1967)

[35] H. P. Figeys, *Ibid.* **23A**, 1281 (1967)