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Influence Parameters. A Quantitative Characteristic of the Capacity of Ligands to Exert Mutual Influence

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The dependence of characteristics of $A–X_i$ *bonds in octahedral and square complexes,* $AX_1\cdots X_i\cdots X_{n-1}L$, *on the properties of variable ligand L are examined. Within the perturbation theory using localized* $A–X_i$ *orbitals it is shown that, under certain conditions, the physico-chemical characteristics of* $A–X_i$ *bonds may be represented by a linear function of a quantity that is mainly determined by ligand L. These quantities are referred to as influence parameters (IP). Analysis of 149 series of* cis *and* trans *influence established a high correlation of experimental and calculated characteristics.*

On the basis of more than 600 experimental points obtained by IR, NMR and NQR spectroscopy IP's are determined for 22 neutral and 17 acido ligands by the least squares method. In accordance with the theory, IP values reflect the degree of covalence of the A–L bond and correlate with the ionization potential of the lone electron pair of donor ligands and with electron affinity and Taft's inductive constants for acido ligands. The reversibility of cis *and* trans *series is analysed using the IP values. The possibility of calculating characteristics of* $A–X_i$ *bonds with the help of IP within the additive scheme is noted. Inductive parameters for 16 donor ligands in octahedral compounds of Sn and Sb were determined accordingly. The obtained values correlate well with IP and donor numbers.*

Introduction

The mutual influence of ligands in chemical compounds is revealed in a variation of the reactivity of $A–X_i$ bonds and in variation of different characteristics of these bonds in the ground state of AX_nL compounds on varying the ligand L and the angle between $A–X_i$ and A–L bonds. The dependence of the ligand effect on the angle between $A–X_i$ and A–L bonds has been discussed earlier [1–6].

In the present work we attempted to find a quantitative characteristic of the capacity of neutral and acido ligands to affect other bonds. The fact that such a characteristic, that is mainly determined by the ligand and only slightly depends on the compound and type of physico-chemical property of the $A–X_i$ bond studied, may exist follows from numerous correlations [7, 8] between various properties of $A–X_i$ bonds on varying the nature of the ligand L.

The material is presented as follows. In the first part it is shown that, provided certain conditions are met, the dependence of characteristic T of the $A–X_i$ bond on ligand L in AX_nL compounds is given by

$$T(L) = T(0) + CP \qquad (1)$$

where T(0) and C are constant for a given characteristic in the studied series of compounds (AX_nL) and the dimensionless quantity, P, which we shall refer to as the influence parameter, depends mainly on the ligand L. In the second part numerous physical characteristics of $A–X_i$ bonds in series of transition element compounds are considered. Analysis is carried out separately for *cis* and *trans* arrangement of $A–X_i$ bonds in relation to the A–L bond and separately for acido and neutral ligands. Using the least squares method such values of P are determined that provide the best representation of experimental data for all the series studied in the form of (1), independently of T and the type of AX_nL compound. Correlation of influence parameters P with other ligand characteristics is discussed. The third part deals with the problem of the reversibility of *trans* and *cis* series and the fourth with the additivity of $A–X_i$ bond characteristics in different compounds. The influence parameters for compounds of nontransition elements are considered in the last-section.

Theoretical Study of Correlations between Various Characteristics

Numerous series of *cis* and *trans* influence of neutral and acido ligands are known at present. Thus, on the basis of the decrease of nuclear spin–spin coupling constants, $^1J(Pt–C)$, in *trans*-$[PtL(CO)X_2]Br_4$ compounds, where X = PR_3, the following series [9] of *trans* influence of acido ligands can be proposed

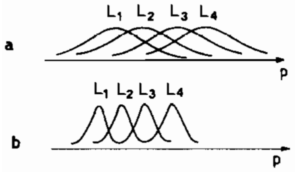

Figure 1. Various dependence of *trans* and *cis* influence series of ligands L on influence parameters, P.

$$\mathrm{PhCH_2 > ClC_6H_4 > H > I > Br > Cl > NCS > NO_3} \qquad (2)$$

The decrease of ν(Pt–P) stretching frequencies in *cis*-$\mathrm{PtL_2(PEt_3)_2}$ compounds [7] renders the following order of *trans* influence

$$\mathrm{Ph > C_6F_5 > NCS > Br \geqslant Cl} \qquad (3)$$

Even from these two examples it is obvious that such series are not of universal character, a fact that naturally follows from the diversity of factors affecting these series. Therefore the task of finding a quantitative characteristic of the ligand L capacity to alter A–X_i bonds in AX_nL compounds can only be solved statistically. In principle two extreme cases are possible.

In the first place the effect of the type of compound or of the characteristic of the A–X_i bond is decisive, so that series of *trans* and *cis* influence of the type (2) and (3) are not determined by ligand properties. In this case determination of a certain averaged series of ligands is of no interest since most of the experimental series will not correlate with this series. If the distribution of ligand locations in various series is represented, for instance, by a dispersion curve, the width of such curves would be considerable in relation to the difference of maxima positions corresponding to the averaged series (Fig. 1a).

In the second case the location of a ligand in series of *trans* and *cis* influence mainly depends on the ligand itself and therefore only adjacent ligands can change places in different series. Determination of an averaged series is meaningful in this case since most series will correlate satisfactorily with the averaged series. Furthermore, it makes sense to establish a quantative characteristic of ligand capacity to exert mutual influence. Here, the width of the dispersion curves is small relative to the difference between positions of distribution maxima (Fig. 1b).

The fact that the second case may be realized follows from numerous correlations [7, 8] between various properties of A–X bonds on varying ligand L. It should be determined whether these correlations are accidental or may be substantiated theoretically.

Such an a substantiation may be given within the perturbation theory.

Let T be a physical characteristic of A–X_i bond in compound $AX_1 \cdots X_i \cdots X_k$ and $\bar{T}$ an operator such that

$$T = \langle \chi_i | \bar{T} | \chi_i \rangle \qquad (4)$$

where χ_i is a localized orbital of A–X_i σ-bond. Replacement of one of the ligands, for instance $X_1 \rightarrow L$ will change orbital $\chi_i \rightarrow \chi_i'$. As was shown [1, 2] within the framework of the perturbation theory χ_i' may be represented by

$$\chi_i' = \chi_i + \delta m_i \chi_i^* \qquad (5)$$

where χ_i^* corresponds to the antibonding excited orbital of the A–X_i bond and δm_i is given [1–4] by

$$\delta m_i = da \sum_{k,l} \frac{n_{kl}}{a_k - a_l^*} \qquad (6)$$

where dA is a perturbation parameter that characterises the change of orbital energy of the L ligand relative to X_1. Values of a_k and a_l^* are the orbital energies of occupied and vacant σ-MO.

In accordance with (4) and (5) T will change to

$$T' = T + 2\delta m_i \langle \chi_i | \bar{T} | \chi_i^* \rangle \qquad (7)$$

On the basis of expression (7) it can be expected that (1) will be approximately correct provided that the following conditions are met.

1. The first order perturbation theory should be sufficient for investigation of the mutual influence of ligands.

One of the required conditions of application of the first order perturbation theory is fulfilled, since usually CP < T(0) (see below).

2. The A–X_i bond and characteristic T should be sufficiently localized to provide adequate accuracy of expressions (4) and (5).

3. The quantity δm_i should be mainly determined by the nature of L.

This condition is not necessary for obtaining linear dependences, such as (1), from (7). Nevertheless it means that constant C in (1) will mainly be dependent upon T and not upon the type of compound.

This condition is fulfilled when the range of A variation is wider than the range of $\sum_{kl}(6)$, therefore for comparatively similar compounds a certain average value may be expected

$$\sum_{k,l} \frac{n_{kl}}{a_k - a_l^*} = C_\sigma', \; C_\sigma = 2C_\sigma' \langle \chi_i | \bar{T} | \chi_i^* \rangle \qquad (8)$$

Such an approximation is to a certain extent similar to the average excitation energy approximation which is frequently used in the analysis of various characteristics (*e.g.*, NMR parameters). Although it is not generally sufficient to obtain quantitative results it is useful for understanding qualitative relationships.

4. Characteristics T should to approximately the same relative extent depend both on the σ- and π-components of the A–X_i bond. Quantities C and

TABLE I. Correlation Coefficients r and $\bar{r}$ for Series of *Trans* Influence of Neutral Ligands[a].

N	Series	Characteristics	Number of points	References	r × 1000	$\bar{r}$ × 1000	T(0)	C
1.	*trans*-$PtLCl(PEt_3)_2^+$	ν(Pt–Cl)	8	7	−817	−261	352.6	−4.45
2.	$PtCl_3L^-$	ν(Pt–Cl)	5	7	−922	−285	326.5	−4.60
3.	*cis*-$PtCl_2L_2$	ν(Pt–Cl)	8	7	−943	−892	334.7	−3.18
4.	*trans*-$[PtLCl(NH_3)_2]BPh_4$	ν(Pt–Cl)	7	10, 11	−744	−245	347.2	−3.11
5.	*trans*-$[PtLCl(NH_3)_2]ClO_4$	ν(Pt–Cl)	5	10, 11	852	659	329.7	4.47
6.	*trans*-$PtLCl(NH_3)_2]NO_3$	ν(Pt–Cl)	5	10, 11	−973	−970	333.2	−3.90
7.	*trans*-$PtLH(PR_3)_2^+$	ν(Pt–H)	9	7	−959	−955	2189.7	−10.26
8.	*trans*-$PtLMe(PMe_2Ph)_2^+$	ν(Pt–C)	7	7	−996	−933	554.9	−2.79
9.	$PtL_2Me_2(PMe_2Ph)_2^{2+}$	ν(Pt–C)	6	12	−960	−967	549.7	−2.61
10.	$PtLMe_3(PMe_2Ph)_2^+$	ν(Pt–C)	4	13	−967	−952	567.5	−3.35
11.	*trans*-$PtL(C_2H_4)Cl_2$	ν(Pt–C)	4	14	−827	−877	390.9	−1.39
12.	*trans*-$PtL(C_2H_4)Cl_2$	ν(C=C)	4	14	992	735	1255.3	1.68
13.	*trans*-$PtL(PMeR_2)_2Me^+$	^2J(Pt–C–H)	12[b]	7	−957	−918	74.2	−1.62
14.	$PtL_2Me_2(PMe_2Ph)_2^{2+}$	^2J(Pt–C–H)	9[c]	7	−925	−791	63.2	−0.90
15.	$PtLMe_3Bipy^+$	^2J(Pt–C–H)	4	7	−959	−984	69.3	−0.88
16.	$PtLMe_3(PMe_2Ph)_2^+$	^2J(Pt–C–H)	7	7	−949	−908	67.1	−0.96
17.	*trans*-$PtLMe(AsMe_3)_2^+$	^2J(Pt–C–H)	5	15	−894	−980	71.9	−1.23
18.	*trans*-$PtL(CF_3)(PMe_2Ph)_2^+$	^2J(Pt–C–F)	10	22	−885	−773	722.7	−13.23
19.	$PtLMe(COD)^+$	^1J(Pt–C)	5	16	−990	−951	172.7	−8.61
20.	*trans*-$PtLMe(AsMe_3)_2^+$	^1J(Pt–C)	6	15	−914	−844	553.2	−11.01
21.	*trans*-$PtLMe(PMe_2Ph)_2^+$	^1J(Pt–C)	9	15	−928	−873	598.1	−11.85
22.	*trans*-$PtLPh(AsMe_3)_2^+$	^1J(Pt–C)	5	17	−845	−970	741.5	−11.24
23.	*trans*-$PtL(C_2H_4)Cl_2$	^1J(Pt–C)	4	14	−966	−466	172.6	−4.67
24.	*trans*-$PtL(PBu_3)Cl_2$	^1J(Pt–P)	5	18	−985	−955	3369.3	−85.39
25.	*trans*-$PtLH(PMe_2Ph)_2^+$	^1J(Pt–H)	4	7	−965	−945	1088.6	−38.07
26.	*trans*-$PtLH(PEt_3)_2^+$	^1J(Pt–H)	5	7	−893	199	1031.1	−18.75
27.	$W(CO)_5L$	^1J(W–C)	3	19	988	−600	118.9	1.96
28.	*trans*-$PtLF(PEt)_2^+$	^1J(Pt–F)	3	20	987	−587	52.2	16.77
29.	TaF_5L	$\delta(^{19}F)$	3	21	631	838	44.2	0.66
30.	*trans*-$PtLF(PEt_3)_2^+$	$\delta(^{19}F)$	3	20	−998	666	303.7	−4.42
31.	$PtLMe(COD)^+$	$\delta(^{13}C_{COD})$	5	16	−957	−945	−97.7	−1.67
32.	*trans*-$PtLMe(AsMe_3)_2^+$	$\delta(^{13}C)$	6	15	−560	−851	21.1	−0.83
33.	*trans*-$PtLMe(PMe_2Ph)_2^+$	$\delta(^{13}C)$	9	15	−587	−667	11.5	−0.93
34.	*trans*-$PtLPh(AsMe_3)_2^+$	$\delta(^{13}C)$	6	17	−945	−958	−132.1	−1.36
35.	*trans*-$PtL(C_2H_4)Cl_2$	$\delta(^{13}C)$	4	14	978	727	74.6	1.05
36.	$Cr(CO)_5L$	$\delta(^{13}C)$	8	19	−884	560	−209.1	−1.18
37.	$Mo(CO)_5L$	$\delta(^{13}C)$	5	19	−970	709	−194.5	−1.60
38.	$W(CO)_5L$	$\delta(^{13}C)$	4	19	−995	668	−186.2	−1.26
39.	*trans*-$PtL(PBu_3)Cl_2$	$\delta(^{31}P)$	4	18	−966	−942	7.42	−1.24
40.	*trans*-$PtL(CF_3)(PMe_2Ph)_2^+$	$\delta(^{19}F)$	10	22	505	667	15.54	0.25
41.	$PtLMe(COD)^+$	$\delta(^{13}C_{COD})$	5	16	949	926	28.12	0.14
42.	$PtLMe_3bipy^+$	$\tau(^1H)$	4	7	807	697	9.42	0.013
43.	*trans*-$PtLMe(AsMe_3)_2$	$\tau(^1H)$	5	15	422	412	0.51	0.014
44.	$MoL_2Cl_2O_2$	$\nu_1(MoO_2)$	3	23	−368	−000	933.9	−1.49
45.	$MoL_2Cl_2O_2$	$\nu_2(MoO_2)$	3	23	−398	−036	899.7	−1.24

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[a] r and $\bar{r}$ are correlation coefficients between experimental data and P_{trans} and $\bar{P}$, respectively. Series 40–45 were not used for P_{trans} determination. Values of T(0) and C determine the linear dependence between the characteristic and P_{trans} (see (1)). [b] Data of the $PtMe_3L_3^+$ series are also taken into account. [c] Data of the $PtLMe_2J(PMe_2Ph)_2^+$ series are also taken into account.

TABLE II. Correlation Coefficients r and $\bar{r}$ for Series of *Cis* Influence of Neutral Ligands[a].

N	Series	Characteristic	Number of points	References	r × 1000	$\bar{r}$ × 1000	T(0)	C
46.	*trans*-$\mathrm{PtL(C_2H_4)Cl_2}$	ν_s(Pt–Cl)	4	14	993	475	340.2	0.325
47.	*trans*-$\mathrm{PtL(C_2H_4)Cl_2}$	ν_{as} (Pt–Cl)	4	14	983	644	342.2	0.589
48.	$\mathrm{W(CO)_5L}$	^1J(W–C)	7	19	−825	−822	129.8	−0.248
49.	*trans*-$\mathrm{PtLF(PEt_3)_2^+}$	^1J(Pt–P)	3	20	−985	−913	2598.3	−24.04
50.	*trans*-$\mathrm{PtLCl(PEt_3)_2^+}$	^1J(Pt–P)	3	20	−954	−852	2433.0	−20.74
51.	$\mathrm{PtLMe(diars)^+}$	^1J(Pt–C)	6	24	−960	−760	568.5	−4.83
52.	$\mathrm{PtLMe(COD)^+}$	$^1J(\mathrm{Pt{-}C})_{\mathrm{Me}}$	5	16	−895	−662	630.3	−5.73
53.	$\mathrm{PtLMe(COD)^+}$	$^1J(\mathrm{Pt{-}C_{COD}})$	5	16	−363	−620	−36.4	−0.324
54.	*trans*-$\mathrm{PtLMe(AsMe_3)_2^+}$	^2J(Pt–AsC)	6	15	−789	−523	50.7	−0.400
55.	$\mathrm{PtLMe(diars)^+}$	^2J(Pt–CH)	6	24	579	782	61.7	0.195
56.	*trans*-$\mathrm{PtLMe(AsMe_3)_2^+}$	^3J(Pt–AsCH)	5	15	524	299	22.4	0.078
57.	$\mathrm{PtLMe(diars)^+}$	$\delta(^{13}\mathrm{C})$	6	24	−873	−763	−5.06	0.461
58.	$\mathrm{PtLMe(COD)^+}$	$\delta(^{13}\mathrm{C_{Me}})$	5	16	648	353	−5.71	0.368
59.	$\mathrm{PtLMe(COD)^+}$	$\delta(^{13}\mathrm{C_{COD}})$	6	16	773	941	−113.6	0.337
60.	$\mathrm{Cr(CO)_5L}$	$\delta(^{13}\mathrm{C})$	7	25	931	844	−220.7	0.377
61.	$\mathrm{Mo(CO)_5L}$	$\delta(^{13}\mathrm{C})$	4	25	983	858	−209.8	0.379
62.	$\mathrm{W(CO)_5L}$	$\delta(^{13}\mathrm{C})$	4	25	996	862	−201.6	0.432
63.	*trans*-$\mathrm{PtLF(PEt_3)_2^+}$	$\delta(^{31}\mathrm{P})$	3	20	−906	−982	124.9	−0.746
64.	*trans*-$\mathrm{PtLCl(PEt_3)_2^+}$	$\delta(^{31}\mathrm{P})$	3	20	−840	−947	133.1	−0.828
65.	*trans*-$\mathrm{PtL_2J_2}$	$e^2qQ(^{129}\mathrm{J})$	4	26	967	999	32.4	0.355
66.	*trans*-$\mathrm{PdL_2Cl_2}$	$\nu(^{35}\mathrm{Cl})$	3	27, 28	882	536	0.329	0.0062
67.	$\mathrm{PtLMe(diars)^+}$	$\tau(^1\mathrm{H})$	6	24	855	552	0.653	0.021
68.	*trans*-$\mathrm{PtLMe(AsMe_3)_2^+}$	$\tau(^1\mathrm{H_{AsMe}})$	5	15	610	342	1.250	0.017
69.	$\mathrm{PtLMe_3(bipy)^+}$	$\tau(^1\mathrm{H})$	3	29	−344	−990	8.68	−0.0068
70.	$\mathrm{PtLMe(COD)^+}$	$\delta(^{13}\mathrm{C_{COD}})$	5	16	468	659	−30.51	0.029
71.	*trans*-$\mathrm{PtL_2Cl_2}$	$\nu(^{35}\mathrm{Cl})$	4	27, 28, 30	886	822	19.42	0.21
72.	$\mathrm{PtLMe_3(bipy)^+}$	^2J(Pt–C–H)	3	29	−594	−425	68.21	−0.047

[a] r and $\bar{r}$ are correlation coefficients between experimental data and P_{cis} and $\bar{P}$ values, respectively; series 67–72 were not used for P_{cis} determination. Values of T(0) and C determine the linear dependence between the characteristic and $\bar{P}_{cis}$ (see (1)).

TABLE III. Correlation Coefficients r and $\bar{r}$ of Series of *Trans* Influence of Acido Ligands X[a].

N	Series	Characteristic	Number of points	References	r × 1000	$\bar{r}$ × 1000	T(0)	C
73.	*trans*-$\mathrm{PtHX(PEt_3)_2}$	ν(Pt–H)	12	31	−920	−985	2222.3	−25.87
74.	*trans*-$\mathrm{PtClX(PEt_3)_2}$	ν(Pt–Cl)	5	7	−986	−962	338.5	−6.69
75.	*trans*-$\mathrm{PdHX(PCy_3)_2}$	ν(Pd–H)	4	7	−871	−882	2011.5	−60.62
76.	*trans*-$\mathrm{NiHX(PCy_3)_2}$	ν(Ni–H)	5	7	−670	−437	1934.9	−10.76
77.	$\mathrm{PtMe_3Xbipy}$	ν(Pt–C)	10	29	−950	−974	574.5	−9.01
78.	*trans*-$\mathrm{PtMeX(PEt_3)_2}$	ν(Pt–C)	7	7	−884	−856	555.2	−6.73
79.	*trans*-$\mathrm{CoHX(diars)_2^+}$	ν(Co–H)	6	32	−692	−540	1916.7	−29.90
80.	1,6[$\mathrm{Co(DH)_2thioX}$]	ν(Co–S)	6	33	661	228	262.8	2.00
81.	*trans*-$\mathrm{RhX_2(cyclam)^+}$	ν_1(Rh–N)	6	7	−466	−678	500.8	−11.00
82.	*trans*-$\mathrm{RhX_2(cyclam)^+}$	ν_2(Rh–N)	6	7	−776	−775	462.4	−19.77
83.	*trans*-$\mathrm{PtX(CO)(PR_3)_2^+}$	ν(CO)	6	9	−474	−553	2123.6	−3.33

(continued on facing page)

TABLE III. *(continued)*

N	Series	Characteristic	Number of points	References	r × 1000	$\bar{r}$ × 1000	T(0)	C
84.	*trans*-$RuHX(C_2H_4PMe_2)_2$	νRu–H)	6	34	–965	–845	1903.6	–25.37
85.	*trans*-$RuHX(C_2H_4PEt_2)_2$	νRu–H)	6	34	–996	–976	1953.4	–29.78
86.	*trans*-$RuHX(PHPh_2)_4$	ν(Ru–H)	4	35	–310	–234	1979.4	–10.03
87.	*trans*-$PtHX(PEt_3)_2$	^1J(Pt–H)	12	7, 37, 45	–873	–658	1250.1	–81.98
88.	*trans*-$Pt[(PhO)_2PO]X(PBu_3)_2$	^1J(Pt–P)	10	38	–963	–758	5593.3	–277.94
89.	$PtX(PEt_3)_3^+$	^1J(Pt–P)	7	39	–945	–725	3418.8	–184.70
90.	$PtX(PMe_3)_3^+$	^1J(Pt–P)	3	40	–900	–871	3413.5	–79.14
91.	*trans*-$PtMeX(PEt_3)_2$	^2J(Pt–C–H)	9	22	–972	–816	83.2	–4.26
92.	*trans*-$PtMeX(PMe_2PH)_2$	^2J(Pt–C–H)	5	22	–977	–979	81.8	–3.86
93.	$PtMe_3Xbipy$	^2J(Pt–C–H)	11	29	–983	–951	74.8	–3.17
94.	*trans*-$Pt(CF_3)X(PMe_2Ph)_2$	^2J(PtC–F)	9	22	–961	–802	757.6	–36.90
95.	*trans*-$Pt(SCF_3)X(PEt_3)_2$	^3J(Pt–SCF)	13	36	–974	–925	124.1	–7.66
96.	*trans*-$PtMeX(PMe_2Ph)_2$	^1J(Pt–C)	5	15	–961	–766	661.5	–31.14
97.	*trans*-$Pt(CO)X(PR_3)_2^+$	^1J(Pt–C)	6	9	–987	–967	1760.3	–76.60
98.	$PtX(PMe_2Ph)_3^+$	^3J(Pt–PCH)	5	15	–958	–878	39.1	–2.03
99.	*trans*-$Pt(GeMe_3)X(PEt_3)_2$	^3J(Pt–GeCH)	5	41	–943	–838	19.7	–1.42
100.	$Rh(PPh_3)_3X$	^1J(Rh–P)	3	42	–944	–963	–189.6	–6.17
101.	$Co(NH_3)_5X^{2+}$	$\delta(^{15}N)$	3	43	–1000	–995	18.0	–32.06
102.	*trans*-$Pt(CO)X(PR_3)_2^+$	$\delta(^{13}C_{CO})$	6	9	–993	–972	–158.1	–2.16
103.	$Re(CO)_5X$	$\delta(^{13}C)$	3	44	–986	–988	–176.2	–0.55
104.	$Rh(PPh_3)_3X$	$\delta(^{31}P)$	3	42	998	993	–48.1	6.48
105.	$PtX(PMe_3)_3^+$	$\delta(^{31}P)$	3	40	–539	–590	26.9	–1.38
106.	*trans*-$PtHX(PEt_3)_2$	τ(H)	4	45, 50	610	–534	24.8	1.50
107.	*trans*-$CoHX(diars)_2^+$	τ(H)	6	32	–958	–988	40.8	–9.23
108.	*trans*-$RuHX(PHPh_2)_4$	τ(H)	4	35	–669	–718	27.2	–2.25
109.	*trans*-$RtMeX(PMe_2Ph)_2$	$\delta(^{13}C_{Me})$	5	15	–229	–634	18.6	–0.78
110.	*cis*-$PtX_2(PEt_3)_2$	ν(Pt–P)	5	7	–979	–971	433.5	–1.97
111.	$PtMe_3Xbipy$	τ(H)	11	29	845	724	9.42	0.081
112.	$PtX(PEt_3)_3^+$	$\delta(^{31}P)$	7	39	356	–065	107.1	1.13
113.	*cis*-$PtX_2(NH_2CH_3)_2$	ν_1(Pt–N)	5	46	075	–859	501.3	0.99
114.	*cis*-$PtX_2(NH_2CH_3)_2$	ν_2(Pt–N)	5	46	162	–891	486.5	2.75

[a] r and $\bar{r}$ are correlation coefficients between experimental data and values of P_{trans} and $\bar{P}$, respectively. Series 109–114 were not used for P_{trans} determination. T(0) and C, see Table I.

TABLE IV. Correlation Coefficients r and $\bar{r}$ of Series of *Cis* Influence of Acido Ligands X[a]).

N	Series	Characteristic	Number points	References	r × 1000	$\bar{r}$ × 1000	T(0)	C
115.	1,6-$[Co(DH)_2(thio)X]$	$\nu_1(Co–N_{DH})$	6	33	–608	097	352.9	–2.99
116.	1,6-$[Co(DH)_2(thio)X]$	$\nu_2(Co–N_{DH})$	6	33	–507	043	401.7	–1.27
117.	*trans*-$Pt[OP(OPh)_2]X(PBu_3)_2$	^1J(Pt–P)	10	38	–875	–866	2465.9	–36.35
118.	*trans*-$PtX_2(PBu_3)_2$	^1J(Pt–P)	9	47	–720	–515	2362.3	–54.5
119.	*trans*-$PtMeX(PEt_3)_2$	^1J(Pt–P)	9	48	–827	–911	2802.5	–37.34
120.	*trans*-$PtHX(PPh_3)_2$	^1J(Pt–P)	7	47	–981	–902	3012.7	–23.36
121.	*trans*-$PtJX(PEt_3)_2$	^1J(Pt–P)	4	49	864	884	2172.0	37.77

(continued overleaf)

TABLE IV. *(continued)*

N	Series	Characteristic	Number of points	References	r × 1000	$\bar{r}$ × 1000	T(0)	C
122.	*trans*-$PtHX(PEt_3)_2$	$^1J(Pt–P)$	10	31	–974	–681	2722.6	–26.36
123.	*trans*-$PtX_2(PBu_3)_2$	$^1J(Pt–P)$	8	39	–767	–583	2367.7	–54.50
124.	$PtX(PEt_3)_3^+$	$^1J(Pt–P)$	7	39	–776	–751	2283.5	–34.41
125.	*trans*-$PtHX(PEt_3)_2$	$^1J(Pt–P)$	4	49, 50	–646	–985	2737.5	–39.43
126.	$PtX(PMe_3)_3^+$	$^1J(Pt–P)$	3	40	–964	–959	2264.3	–5.26
127.	$PtX(PMe_2Ph)_3^+$	$^3J(Pt–PCH)$	5	22, 48	967	900	22.8	0.97
128.	$PtXMe_3bipy$	$^2J(Pt–C–H)$	11	29	881	888	69.6	0.31
129.	$RhX(PPh_3)_3$	$^1J(Rh–P)$	3	42	999	1000	–142.0	0.92
130.	*trans*-$PtX_2(PBu_3)_2$	$\delta(^{31}P)$	7	47	909	727	–7.35	4.28
131.	*trans*-$PtMeX(PEt_3)_2$	$\delta(^{31}P)$	9	48	889	735	–15.9	1.26
132.	*trans*-$PtJX(PEt_3)_2$	$\delta(^{31}P)$	4	49	–834	–907	–1.61	–1.04
133.	$RhX(PPh_3)_3$	$\delta(^{31}P)$	3	42	–1000	–1000	31.5	–1.33
134.	*trans*-$PtHX(PEt_3)_2$	$\delta(^{31}P)$	10	31	896	881	–22.7	0.77
135.	*trans*-$PtX_2(PBu_3)_2$	$\delta(^{31}P)$	8	39	662	317	106.8	1.84
136.	$PtX(PEt_3)_3^+$	$\delta(^{31}P)$	7	39	776	729	97.1	1.54
137.	*trans*-$PtHX(PEt_3)_2$	$\delta(^{31}P)$	4	49, 50	973	813	–23.0	1.17
138.	*trans*-$PtX_2(PMe_3)_2$	$\delta(^{31}P)$	4	51	832	193	14.8	4.07
139.	$PtX(PMe_3)_3^+$	$\delta(^{31}P)$	3	40	939	986	13.0	2.35
140.	*trans*-$PdX_2(PMe_3)_2$	$\delta(^{31}P)$	4	51	709	006	11.0	3.57
141.	*trans*-$PtX_4(PMe_3)_2$	$\delta(^{31}P)$	3	51	1000	1000	11.7	16.0
142.	$Re(CO)_5X$	$\delta(^{13}C)$	3	44	–991	–993	–76.8	–0.7
143.	*trans*-$PtX_2(PEt_3)(carbene)$	$\delta(^{13}C)$	3	52	–987	–995	–195.5	–2.24
144.	$Co(NH_3)_5X^{2+}$	$\delta(^{14}N)$	3	43	807	817	4.05	0.43
145.	*cis*-$Pt(SCF_3)X(PEt_3)_2$	$^3J(Pt–F)$	6	36	158	758	63.3	0.44
146.	*trans*-$PtHX(PPh_3)_2$	$\delta(^{31}P)$	7	47	–273	–341	–28.1	–0.20
147.	*trans*-$Pt(CN)X(PPh_3)_2$	$^1J(Pt–P)$	3	47	–995	–412	2462.1	99.3
148.	*trans*-$Pt(CN)X(PPh_3)_2$	$\delta(^{31}P)$	4	47	352	310	–17.4	0.30
149.	$PtMe_3Xbipy$	$\tau(H)$	11	29	334	441	8.47	0.014

[a] r and $\bar{r}$ are correlation coefficients between experimental data and P_{cis} and $\bar{P}$ values, respectively. Series 145–149 were not used for P_{cis} determination. T(0) and C, see Table II.

P may then be represented by a certain average magnitude

$$C = \alpha^2 C_\sigma + \beta^2 C_\pi;\ \Delta P = \alpha^2(\Delta A_\sigma) + \beta^2(\Delta A_\pi);$$
$$\alpha^2 + \beta^2 = 1 \qquad (9)$$

Evidently all these conditions are not fulfilled equally for different characteristics and for different compounds. This explains the non-universal character of experimental series of *cis* and *trans* influence. Just for these reasons formula (1) describes with sufficient accuracy only the majority of series known to date, at best. The degree of accuracy of (1) may only be determined by analysis of experimental data.

Calculation and Analysis of Influence Parameters

Vast experimental material was examined on *cis* and *trans* series of influence in order to determine whether it is possible to find quantities P* that characterise only the ligand L and are independent of the characteristic of the A–X bond and of the compound (Tables I–IV). Among other characteristics the $\nu(A–X)$ stretching frequencies, nuclear spin–spin coupling constants $^nJ(A–X)$, NMR chemical shifts $\delta(X^N)$ or $\tau(H)$ of X atoms and $\nu(X^N)$ frequencies in NQR spectra of X atoms were considered. By the least squares method such P were determined (Tables V–VI) that provide the maximal average correlation coefficient between T(L) (1) and experimental values (see *Appendix 1* for more detail). It is natural to refer to these quan-

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*From formulae (8) and (9) it follows that P has the dimension of energy and C'_σ the dimension $(energy)^{-1}$. For convenience we consider P and C'_σ to be formally dimensionless; dimensions of T, T(0) and C then coincide. In Tables I–IV T(0) and C are given in the dimensions cited in the original works.

TABLE V. Influence Parameters P_{trans}, P_{cis}, $\bar{P}$ and Ionization Potentials (ev) [53–55] of Neutral Ligands.

Ligand	n_{trans}[a]	n_{cis}[a]	P_{trans}	P_{cis}	$\bar{P}$	I
Carbenes	11	4	13.72	8.36	11.19	
PEt_3	11	8	11.65	9.90	9.04	8.0
PPh_3	19	15	10.00	10.00	10.00	7.85
SbR_3	8	0	9.46	–	11.92	8.48
$AsPh_3$	16	12	8.84	13.03	10.82	8.03
$P(OR)_3$	14	8	8.48	18.83	13.38	
RNC	19	10	6.56	14.72	10.42	
PhNC	8	0	6.45	–	8.40	
CO	19	9	3.88	23.13	12.99	
SR_2	3	1	3.63	–0.31	1.76	8.67
C_2H_4	9	0	1.58	–	2.71	
NH_3	12	4	0.56	–6.90	–2.97	10.92
Py	30	13	0.00	0.00	0.00	9.67
$RC{\equiv}CR$	3	0	–0.04	–	0.81	
OMe_2	4	0	–0.56	–	0.21	9.01
bipy	3	0	–3.25	–	–2.93	
Phen	3	0	–3.53	–	–3.26	
RCN	5	12	–3.72	5.23	0.51	
PhCN	13	0	–5.46	–	–5.52	
$OCMe_2$	4	0	–9.08	–	–9.75	9.72
Me_2NCHO	8	2	–10.05	–1.40	–5.96	9.77
H_2O	3	0	–16.09	–	–17.94	12.62

[a] n is the number of *trans* and *cis* series in which the corresponding ligand is included.

TABLE VI. Influence Parameters P_{trans}, P_{cis}, $\bar{P}$, electron Affinity E(ev) [56] and α_{av} Values [8] of Acido Ligands.

Ligand	n_{trans}[a]	n_{cis}[a]	P_{trans}	P_{cis}	$\bar{P}$	E	α_{av}
H	7	3	11.13	15.86	13.16	0.77	–
CH_3	6	6	10.00	10.00	10.00	1.1	1.61
CF_3	2	1	9.41	5.31	7.66	2.1	–
Ph	7	2	8.91	9.33	9.09	2.2	1.56
CN	16	19	5.48	2.51	4.21	3.82	1.82
C_6F_5	1	–	4.26	–	4.12	2.1	–
NO_2	17	14	2.65	–1.29	0.97	3.1	1.94
NCO	9	11	1.00	–0.00	0.57	1.56	1.99
SCN	10	6	0.96	3.81	2.18	2.17	1.96
N_3	9	10	0.91	–1.01	0.09	–	1.97
I	31	26	0.75	3.30	1.84	3.08	2.00
Br	32	27	0.23	1.25	0.66	3.37	2.02
NCS	17	11	0.09	0.40	0.22	3.5	2.00
Cl	34	27	0.00	0.00	0.00	3.61	2.02
RCOO	7	2	–0.18	–3.07	–1.42	3.7	2.03
NO_3	17	12	–0.39	–3.43	–1.69	2.8	2.08
ClO_4	2	–	–3.06	–	–3.95	5.82	–

[a] n is the number of *trans* and *cis* series in which the corresponding ligand is included.

tities as influence parameters. As can be seen from Tables I–IV (see also data for $r_{av}(i)$, Table VII), a considerable number of series of *cis* and *trans* influence may be represented by influence parameters (P) with sufficient accuracy. Therefore they may be considered as numeric characteristics of the ligand capacity to influence other bonds in compounds. The dependence of several characteristics on P are shown in Fig. 2.

It is evident from the theoretical consideration and method of determination that magnitudes P are of a statistical nature in that they describe only the overall tendency: series exist for which P does not represent

TABLE VII. Correlation Coefficients: $r_{av}(i)^a$ and $\bar{r}_{av}(i)$ – Average for *trans* and *cis* Series with P_i and $\bar{P}$; r(i, k) for Values i and k.

	r_{av}(*trans*)	r_{av}(*cis*)	$\bar{r}_{av}$ (*trans*)	$\bar{r}_{av}$ (*cis*)	r ($\bar{P}$, P_{trans})	r ($\bar{P}$, P_{cis})	r (P_{cis}, P_{trans})
Acido Ligands	0.88	0.83	0.81	0.70	0.97	0.96	0.87
Neutral Ligands	0.90	0.81	0.77	0.72	0.94	0.89	0.53

[a] The value r_{av} is defined in the Appendix.

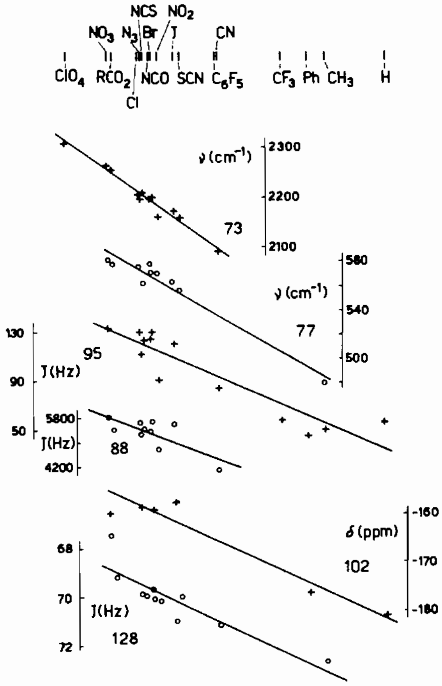

Figure 2. Correlation of various physical characteristics with influence parameters $\bar{P}$ for acido ligands. Digits indicate the numbers of series in Tables III–IV.

the change of T(L) with variation of the ligand (Table I–IV)*.

Analysis of the stability of the obtained values of P depending on the number of series and analysis of the signs of the correlation coefficients for separate series and their stability (see below) shows that the available experimental material is sufficiently extensive for producing reliable values of P_{trans} for the majority of neutral and acido ligands. The stability of P_{cis} values for acido ligands is somewhat lower. Nevertheless, although further accumulation of experimental data may lead to certain revision of P_{trans} and P_{cis} values for acido ligands and of P_{trans} values for neutral ligands, it may be considered that on the whole the set of these values is correctly determined from the available data. The situation with P_{cis} for neutral ligands is somewhat different. Experimental material is noticeably more scarce in this case (compare the number of series and their length in Table II, with those in Tables I, III, IV) and to a great extent is related to carbonyl and π-complexes. On account of this, values of P_{cis} obtained for neutral ligands reflect the capacity of neutral ligands to exert mutual influence through π-bonds considerably more than other P values. Consequently, obtained values of P_{cis} for neutral ligands can only be considered preliminary. The above-mentioned observations apparently explain the relatively poor correlation of P_{cis} and P_{trans} for neutral ligands (see below and Table VII).

Let us now examine qualitatively the numerical results obtained for T(0), P and C (equation 1, Tables I–IV) for different characteristics.

First of all it should be emphasised that equation (1) gives influence parameters P only up to the accuracy of the linear transformation. For calibration, the following values were taken: in the case of neutral ligands, $P_{cis} = P_{trans} = 10.00$ for PPh_3 and $P_{cis} = P_{trans} = 0.00$ for Py; in the case of acido ligands, $P_{trans} = P_{cis} = 10.00$ for CH_3 and $P_{trans} = P_{cis} = 0.00$ for Cl. In other words with the growth of the capacity of L to mutual influence P increases. The value of T(0) in Tables I–IV, therefore, corresponds to the value of the characteristic of $A–X_i$ bond in the series of compounds studied when Py (for neutral ligands) or Cl (for acido ligands) are *cis* or *trans* to the bond. Note that in all cases (Tables I–IV)* inequality $T(0) > C \cdot \Delta P$ is satisfied ($\Delta P \sim 10$).

Let us now study the signs of C (or of correlation coefficients r) for various T in series of *trans* influence of neutral and acido ligands**. According to the

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*Most of such series were not used for determination of P_{cis} and P_{trans}, so as not to distort these values significantly. Several other series listed in Tables I–IV were not used in calculations because they came to our knowledge only after calculations were completed.

*An obvious exception is NMR chemical shifts δ(X), since the T(0) value depends on the reference point chosen.

***Cis*-influence series are discussed in Section III in connection with the problem of reversibility of *cis* and *trans* influence series.

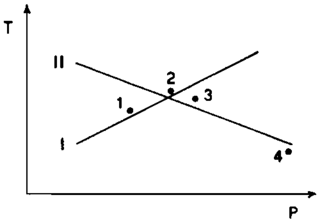

Figure 3. The necessity of large values of ΔP for obtaining correct T *vs.* P dependences.

traditional, somewhat simplified approach [7], the increase of the capacity of L to *trans* influence, *i.e.* increase of P_{trans}, should decrease the A–X stretching frequencies and NMR J(A–X) spin–spin coupling constants (by absolute values). Therefore all values of C (or r) in Tables I, III for ν(A–X) and J(A–X) should be negative. Indeed, in 53 out of 59 cases C (or r) is negative. Furthermore, analysis of series where C is positive shows that the ligands in these series have a too small range of ΔP variation, rendering correlation of T and P meaningless. Below, several examples are given to illustrate this.

Series 5 (Table I) is similar to series 4 and 6, however it has a positive value of C due to the fact that, unlike series 4 and 6, the value of ν(Pt–Cl) for L = PPh_3 is absent. On account of this the maximum value of ΔP in series 4 and 6 is 10.6 while in 5 it is only 4.4. If the value of ΔP is small various secondary reasons as well. Ligand L = $SOMe_2$ is present only in the sign of C and the value of T(0). Fig. 3 shows an equation of the type 1 for case I (points 1–3 with small ΔP) and for case II (points 1–4 with large ΔP). The positive sign in series 5 is explained by other reasons as well. Ligand L = $SoMe_2$ is present only in three other series (Table V). In series 29 (Table I) the value $\delta(^{19}F)$ for L = $SOMe_2$ falls between the values for L = H_2O and Me_2NCHO and the corresponding value of P is thus considerably underestimated, since these ligands have largely negative values of P. The latter fact also distorts the correlation between ν(Pt–Cl) values in series 5 and influence parameters P_{trans}.

The small value of ΔP and the small number of points also explains the distorted pattern of correlation for series 27, 28 (Table I), 113 and 114 (Table III). It is significant that a slight change in the values of P connected with transition from P_{trans} to $\bar{P}$ (the mean value for P_{trans} and P_{cis}) changes the sign of C in these series (from positive to negative). As for deviation of series 80 (Table III) from the general trend concerning the sign of C, in our opinion it is associated more with the complex nature of the dependence of ν(CO ← S) on the σ- and π-components of the variable ligand L.

Let us now examine the agreement between the obtained values of P and the theoretical considerations discussed in section 1. In the ideal simplified case P_{trans} and P_{cis} should be equal (separately for neutral and acido ligands) and a linear dependence should exist between P_i and the magnitude characterising the change of orbital energy of the ligand (ΔA) that is responsible for the formation of a bond with the central atom. Obviously, due to the statistical nature of P_{cis} and P_{trans}, one can hardly expect exact equality between them.

The obtained values of P_{cis} and P_{trans} for neutral and acido ligands are given in Tables V and VI. The values of $\bar{P}$ calculated by averaging P_{trans} and P_{cis} with regard to the number of experimental points used for their determination are also listed in these Tables. The P_{trans} and P_{cis} series for acido ligands are very similar, the correlation coefficient being equal to 0.87 (Table VII)*. The correlation coefficients between $\bar{P}$ and P_{trans}, $\bar{P}$ and P_{cis} and between T(L) and $\bar{P}$ (Tables I–IV) are sufficiently high both for neutral and acido ligands.

Thus, in accordance with the analysis described above, magnitudes P_{trans}, P_{cis} and $\bar{P}$ indeed describe the properties of ligands and should be proportional to ΔA_σ and ΔA_π (formula 9). Since for most characteristics in Tables I–IV the most important factor is σ-interaction of the studied ligand with the central atom, the inequality $\alpha^2 > \beta^2$ should presumably be valid in expressions (9)**.

Consequently, influence parameters $\bar{P}$ should correlate with characteristics that determine σ-bonds of the ligands with the central atom. We shall first consider ligands that form a mainly σ-bond with the central atom. Typical π-ligands NO and CO are examined below.

Electron affinity for acido ligands and the ionization potential of the level the wave function of which most adequately describes the lone electron pair that acts as a donor for neutral ligands may be employed as such characteristics. Indeed, the correlation coefficient between influence parameters $\bar{P}$ of acido ligands and electron affinity is –0.76 and between $\bar{P}$ for neutral ligands and ionization potentials is –0.90. Hence, in complete agreement with theoretical considerations [1–3], acido ligands forming covalent bonds with the central atom and strong donors are characterised by high influence parameters. It should also be noted that parameters [8] α_{av} which should also characterise the capacity of acido ligands to mutual influence well correlate with $\bar{P}$ (r = –0.97). However the method of determination and meaning of quantities in the cited study greatly differ from those of influence parameters described in the present work. Good correlation (r = -0.79) is also observed

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*As shown above, the set of influence parameters P is accurate to the linear transformation, therefore the difference between P_{trans} and P_{cis} is actually less than it appears at first glance.

**This inequality is valid apparently to a lesser extent for P_{cis} of neutral ligands than for the other P.

TABLE VIII. Interatomic Distances (Å).

Compound	R(A–X$_{trans}$)	R(A–X$_{cis}$)	<ANO°	References
[Co(NH$_3$)$_5$NO]Cl$_2$	2.22(NH$_3$)^a	1.98(NH$_3$)	119	64
[Coen$_2$(NO)Cl]ClO$_4$	2.58(Cl)	2.27^b	121	
[Ru(NH$_3$)$_5$(NO)]Cl	2.017(NH$_3$)	2.09(NH$_3$)	173	65
[Ru(NH$_3$)$_5$NO$_2$]$^{4+}$	2.199(NH$_3$)	2.127(NH$_3$)	–	
[Ru(OH)(NH$_3$)$_4$NO]$^{2+}$	–	2.102(NH$_3$)	174	
(NH$_4$)$_2$[RuCl$_5$NO]	2.357(Cl)	2.376(Cl)	177	66
K$_2$[RuCl$_5$NO]^c	2.359(Cl)	2.372(Cl)	177	67
Cs$_2$[RuCl$_5$H$_2$O]	2.31(Cl)	2.35(Cl)	–	68
K[IrCl$_5$NO]	2.286(Cl)	2.338(Cl)	174	69
K[IrBr$_5$NO]	2.419(Br)	2.480(Br)	170	
Na$_2$[Fe(CN)$_5$NO]·2H$_2$O	1.90(C)	1.92(C)	178	70
K$_3$[Mn(CN)$_5$NO]·2H$_2$O	2.01(C)	1.98(C)	174	71
[Coen$_3$][Cr(NO)(CN)$_5$]·2H$_2$O	2.075(C)	2.033(C)	176	72
K$_4$[Mo(CN)$_5$NO]	2.20(C)	2.12(C)	175	73

[a] Ligand X is given in brackets. [b] The Co–Cl distance in [Co(NH$_3$)$_5$Cl]Cl$_2$. [c] These data should be appreciated with certain caution since the structure is partially disordered.

between values of $\bar{P}$ for acido ligands and Taft inductive coefficients [57].

Consider the correlation of P values with the position of ligands in the X-ray-photoelectron series. According to X-ray photoelectron data [58], the capacity of acido ligands to attract electron density from the central atom follows the order

$$F > NO_3 \cong NO_2 \gtrsim CN \cong 1/2C_2O_4 \cong NCS > Cl > Br \cong SCN > I > CH_3 \qquad (A)$$

A similar sequence for neutral ligands takes the form of

$$N_2 \geqslant CO \cong C_2H_4 > C_2Ph_2 > PhCN > NH_3 > Py > R_2S \cong Thio > PPh_3 \qquad (B)$$

Molecules to the left of PhCN are generally acceptors and those to the right donors.

Series (A) is consistent with the appropriate influence parameters (Table VI) with the exception of data for CN and NO$_2$. Series (B) for donor molecules also well correlates with values of P$_{trans}$ (Table V).

Thus, the influence parameters characterise the capacity of acido and neutral ligands to transfer electron density to the central atom and through the latter to another ligand. This is in complete accord with the arguments developed in the preceding section and in studies [1–3]. Increase of electron density transfer to another ligand (X), as shown [1–3], weakens the A–X bond. Indeed, with the increase of P$_{trans}$ of ligand L as shown above, the ν(A–X) stretching frequencies decrease. P$_{trans}$ also correlate with interatomic distances R(A–X): increase of P$_{trans}$ of ligand L is accompanied by lengthening of the A–X bond, X being *trans* to L. The Pt–Cl length in compounds *trans*-PtClL(PR$_3$)$_3$, where L is an acido ligand changes for various L as follows [7, 59, 60] (Pt–Cl distances are given in brackets, Å):

$$SiR_3(2.45) > H(2.422) \geqslant CH_2SiMe_3(2.415) > C{\equiv}CPh(2.407) > Cl(2.294)$$

This is consistent with the general trend of the corresponding P$_{trans}$ values (Table VI).

The length of the Pt–Cl bond *trans* to L changes in the order:

$$\mathit{Cis}\text{-}PtCl_2(PR_3)L\ [7, 60]: PR_3(2.37) \geqslant \text{carbene-}(2.365) > CNR\ (2.314) > CO(2.277)$$

$$PtCl_3L^-\ [7, 61–63]: PET_3(2.382) > C_2H_4(2.340) > NH_3\ (2.395)$$

This is also in accordance with variation of P$_{trans}$ (Table V). It can be shown as well that the length of Pt–P bond also increases with increasing P$_{trans}$ of the ligand *trans* to this bond.

Finally, what determines the value of the influence parameter at neutral molecules–acceptors? We shall restrict ourselves to consideration of the simplest molecules CO and NO (for linear fragments, A–NO). Along with the comparatively weak σ-donor capacity, the π-acceptor interaction with the central atom should be taken into account in these molecules, since it usually plays the major role in formation of A–CO and A–NO bonds and may predominate in the influence on other A–X bonds. The latter obviously takes place when the A–X bond has a considerable π-component or, more precisely, when CO (NO) and X compete for the acception of the electron density of atom A. Two limiting cases should be considered in this respect.

1. If the A–X bond is mainly of σ-type, then for instance transition $AX_6 \rightarrow AX_5NO$ (where X is an acido ligand or a stronger σ-donor than NO) corresponds to introduction of a weaker σ-donor that usually leads [2] to strengthening of all bonds, the $A–X_{trans}$ being more strengthened than the $A–X_{cis}$ bond. Certain experimental data in Table VIII (for Cl, Br and NH_3) illustrate this case. Data for several similar compounds are also listed: for instance, strengthening of $Ru–Cl_{trans}$ bond as compared with $Ru–Cl_{cis}$ in $Cs_2[RuCl_5(H_2O)]$ is essentially caused by the same reasons as in $(NH_4)_2[RuCl_5NO]$. A further illustration is the relatively weak influence of CO on the decrease [7] of Pt–Cl and Pt–H stretching frequencies. Note also the decrease [60] of Pt–Cl distances *trans* to CO down to 2.277 Å in *cis*-$PtCl_2(CO)PPh_3$ in relation to 2.37 Å in *cis*-$PtCl_2(PMe_3)_2$. In all cases small values of P_{trans} should be expected for the CO molecule.

2. When the A–X bond has a considerable π-component, A–NO and A–CO π-interactions weaken [74, 75] the bond especially when it is in *trans*-position. Data for X = CN (Table VIII) illustrate this. Due to the considerable π-interaction in A–CN, in certain nitrosyls $R(A–CN)_{trans} > R(A–CN)_{cis}$*. It is also known [77–79] that CO weakens the $Pt–PR_3$ bond due to the appreciable π-interaction of $Pt–PR_3$. In these cases large values of P_{trans} should be expected for the CO molecule.

In the series that we used for determination of P_{trans} most of the A–X bonds are of a σ-nature, consequently P_{trans} for CO is comparatively small. However, due to the weak σ-influence of molecules of the CO and NO type, a large contribution to the overall value of P_{trans} is made by π-interaction. The high value of P_{cis} for CO (Table V) is possibly caused by the fact that in the *cis* influence series (Table II) many A–X bonds have a noticeable π-character. However, as mentioned above, the values of P_{cis} cannot be considered entirely reliable for neutral molecules.

It follows from the method of their determination that influence parameters reflect the capacity of ligands to exert mutual influence on characteristics of other ligands or of bonds in the ground state of the compound. Nevertheless, it is interesting to compare influence parameters with the *trans* influence series derived from chemical data on reactions of substitution, exchange, *etc.* Ligands are ordered [80] as follows:

$$CN, C_2H_2, NO > Thio, R_2S, R_3P, NO_2, I, SCN > Br > Cl > OH, RNH_2 > NH_3 > H_2O \qquad (C)$$

Comparison of this sequence with P_{trans} parameters for acido and neutral-donor ligands shows that ligands with high values of P_{trans} indeed exert a strong *trans* effect in chemical reactions. Note that in contrast to series A (donor–acceptor capacity of acido ligands) anions CN and NO_2 conform with the general trend. This indicates that not only the overall capacity of acido ligands to withdraw electron density from the central atom A which is determined by the position of the ligand in series A, but also more intricate details of σ- and π-interaction of the central atom with the ligand considerably affect the capacity of acido ligands to influence other ligands.

The existence of a correlation between the position of acido and neutral-donor ligands in series C and values of P shows that weakening of A–X bonds in the ground state, due to influence of ligand L, is, if not the main, at least one of the causes of the kinetic *trans* effect. The considerable *trans* effect of π-acceptors such as NO, C_2H_2 and CO which have small P_{trans} values demonstrates the importance of the state of the transition complex in the reaction process in this case.

Reversibility of *Trans* and *Cis* Influence Series

The tendency of *trans* and *cis* influence series to reversibility has been reported in several works (see, for instance [26, 28, 81]. Particularly convincing results were obtained [36, 81] where the following series of *trans*[*trans*-$PtX(SCF_3)(PR_3)_2$] and *cis*[*cis*-$Pt(SCF_3)X(PR_3)_2$] influence are proposed:

$$Trans\text{: } CN(82.0) > NO_2(88.6) > N_3(110.5) > I(118.8) > NCS(122.6) > NCO(123.0) > Br(128.0) > Cl(129.0) > NO_3(131.4);$$

$$Cis\text{: } NO_3(58.5) > Cl(61.2) > NCO(61.8) \cong NCS(61.8) > N_3(64.0) > NO_2(70.0).$$

The $^3J(Pt–F)$ constants, Hz, are given in brackets.

The reversible nature of *cis* and *trans* series for acido ligands is clearly seen from the variation of the sign of correlation coefficients in Tables III and IV. As already mentioned, for characteristics ν, J and δ the signs of r are mainly negative for *trans* series, whereas more than half of the signs are positive in the case of *cis* series (Table IV). The reversible character of *cis* and *trans* sereis is especially distinct in series

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*[*] *Trans* A–X bonds are especially weakened by bent A–NO groups (Table VIII). As explained [76], the NO group in this case should be considered as an σ-acido ligand, derivative of HNO molecule, rather than as a π-acido ligand.

TABLE IX. Correlation Coefficients $\bar{r}$ and Coefficients $\bar{C}$ for *cis* and *trans* Series of Acido Ligands.

Series Number in Tables III, IV	Compound	Characteristic	1000 × $\bar{r}_{trans}$	1000 × $\bar{r}_{cis}$	$\bar{C}_{trans}$	$\bar{C}_{cis}$
89, 124	$PtX(PEt_3)_3^+$	$^1J(Pt–P)$	–725	– 751	–159.33	–42.61
90, 126	$PtX(PMe_3)_3^+$	$^1J(Pt–P)$	–871	– 959	– 31.66	– 9.34
100, 129	$RhX(PPh_3)_3$	$^1J(Rh–P)$-	–963	1000	– 2.60	1.64
93, 128	$PtXMe_3$bipy	$^2J(Pt–C–H)$	–951	888	– 3.00	0.36
98, 127	$PtX(PMe_2Ph)_3^+$	$^3J(Pt–P–C–H)$	–873	900	– 1.69	1.09
104, 133	$RhX(PPh_3)_3$	$\delta(^{31}P)$	993	–1000	2.66	– 2.38
105, 139	$PtX(PMe_3)_3^+$	$\delta(^{31}P)$	–590	986	– 0.62	4.18
112, 136	$PtX(PEt_3)_3^+$	$\delta(^{31}P)$	–065	729	– 0.23	1.86
103, 142	$ReX(CO)_5$	$\delta(^{13}C)$	–988	– 993	– 0.58	– 0.75
101, 144	$CoX(NH_3)_5^{2+}$	$\delta(^{14}N)$	–995	817	– 8.20	0.87
111, 149	$PtXMe_3$bipy	$\tau(H_{Me})$	724	441	0.068	0.022

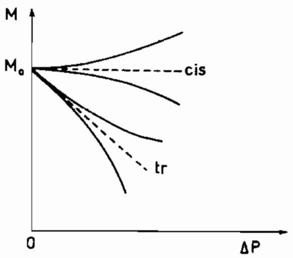

Figure 4. Dependence of $A–X_i$ bond strength, M, on the difference of influence parameters of L and X ligands. Dashed lines show results obtained from the first-order perturbation theory.

composed by identical compounds, for example $^1J(Rh–P_{trans})$ and $^1J(Rh–P_{cis})$ for $Rh(PPh_3)_3X$ compounds. All such pairs of series for acido ligands are listed in Table IX. These data show that whilst in the majority of instances the signs of $\bar{r}$ and $\bar{C}$ are reversed this reversibility is not a general rule. The absence of reversibility may to a certain extent be due to differences in ligand–ligand interactions for the *cis* and *trans* positions. Unfortunately, the scarcity of appropriate experimental data does not allow a more detailed study of this problem. It is of interest to compare the values of $\bar{C}$ for *cis* and *trans* series given in Table IX. For spin–spin coupling constants values $\bar{C}_{trans}$ are negative and $|\bar{C}_{trans}|$ greatly exceed $|\bar{C}_{cis}|$. This is in accord with the predominantly *trans*-direction of mutual influence of ligands in transition element compounds. As for NMR chemical shifts, in the first place $\bar{C}_{trans}$ may be both negative and positive and secondly, in certain cases, $|\bar{C}_{trans}| < |\bar{C}_{cis}|$. These results emphasize the fact that the relationship between various characteristics of the mutual influence of ligands may be very complex.

The possibility of reversal of *cis* and *trans* series for such characteristics as $\nu(A–X)$ and $J(A–X)$(which, in the first approximation, reflect the strength of A–X bonds) may be understood from results obtained in [1–3]. The increase of influence parameter $\bar{P}$ of ligand L in relation to X in transition element compounds, AX_5L or AX_3L, always leads to weakening of $A–X_{trans}$ bonds relative to A–X bonds in AX_6 and AX_4. The $A–X_{cis}$ bond, however, may either weaken or strengthen. In other words, the sign of δm in (5) may be different for $A–X_{trans}$ and $A–X_{cis}$, *i.e.* $\sum_{k,1}$ (6) has different signs. Therefore, increase of P for L relative to X may lead to reversibility of *cis* and *trans* series.

Strengthening of $A–X_{cis}$ bonds in AX_5L and AX_3-L occurs when the orbital energies of σ-levels of initial complexes, AX_6 and AX_4, are ordered as follows:

$$e_g < a_{1g} < a_{1g}^* < e_g^* < 0 \text{ or}$$

$$a_{1g} < e_g < e_g^* < a_{1g}^* < 0 \ [1–3].$$

The $A–X_{cis}$ bond weakens when $a_{1g} < e_g < a_{1g}^* < e_g^* < 0$ or $e_g < a_{1g} < e_g^* < a_{1g}^*$. It is significant that both strengthening and weakening of the bond should be rather small, since the a_{1g} and e_g levels and a_{1g}^* and e_g^* levels should have close orbital energies. It was theoretically established in [2, 3] that weakening of the $A–X_{cis}$ bond is invariably smaller than weakening of $A–X_{trans}$. Analysis of experimental data shows that change of the strength of the *cis* bond (independently of the sign) is usually appreciably less than that of the *trans* bond. Therefore, the effect of secondary factors should be higher in the case of *cis* series. Indeed, the values of r_{av}(*trans*) and $\bar{r}_{av}$(*trans*) are higher than r_{av}(*cis*) and $\bar{r}_{av}$(*cis*) (Table VII).

It should be remembered that conclusions about the signs of δm_i and C'_σ (see (8)) were obtained [1–3] in the first order perturbation theory, *i.e.* concern the sign of the derivative $dM/d(\Delta P)$, where M is a characteristic of A–X bond strength (Fig. 4). Due to the strong dependence of M(A–X_{trans}) on P in a certain initial point ($\Delta P = 0$) (Fig. 4), the secondary factors according to analysis of numerous experimental data, practically never alter the results obtained from the first order perturbation theory, *i.e.* $M(A–X_{trans})_{\Delta P>O} < M(A–X_{trans})_{\Delta P=O} = M$, where ΔP is the difference between influence parameters of L and X.

On the other hand, the weak dependence of M(A–X_{cis}) on ΔP in the initial point $\Delta P = 0$, independently of the sign of δm_i or C'_σ (and, thus, of the sign of $dM/d(\Delta P)$) may lead to distortion of the value of M (or T, in the general case) with the increase of ΔP by secondary factors (Fig. 4). The direction of this distortion depends on the nature of M or T. Therefore the reversibility of *cis* and *trans* series depends not only on the type of compound (C'_σ or C'_π) but also on the type of characteristic.

The conclusion about the possibility of *cis*-strengthening and, thus, indirectly about possible reversal of *cis* and *trans* influence series was first reached by Syrkin [82].

Additivity of Characteristics of A–X Bonds

By analogy with [1–3] it may be shown that the quantity δm_i in expression (5) is additive. For instance, for transition $AX_4 \rightarrow$ cis-AX_2L_2 the value of δm_i for an A–X bond is equal to $\delta m_{trans} + \delta m_{cis}$. Therefore equation (1) may be generalised*

$$T(X_i) = T(0) + \sum_k C_k P_k \qquad (10)$$

where subscript k relates to ligands $X_k \neq X_i$.

Equation (10) reflects the additivity of the characteristic $T(A–X_i)$ of $AX_1 \cdots X_i \cdots X_n$ compounds and there are only five parameters T(0), C_{cis} and C_{trans} for neutral and acido ligands for every T, provided that values of P are known.

Since it has already been established that the accuracy of (1) is sufficient for most series of compounds (Tables I–IV) it is very likely that equation (10) is also sufficiently accurate. Equation (10) has not been verified so far**. Nevertheless, the near equality of T(0) and C values for the same T in different compounds (Tables I–IV) suggests that the average correlation coefficient between $T(X_i)$ values, calculated according to (10) and established experimentally, will be sufficiently high. Obviously the correlation coefficient may be improved by discarding the general approach described by formulae (1) and (10) in favour of a more specific procedure of P determination, *e.g.* by considering only certain types of compounds or characteristics. This would lead to several sets of influence parameters. We have determined P_{trans} (neutral ligands) separately for ν, J and δ and obtained a fairly good correlation for the three sets. However, we consider such an approach somewhat premature, since the accumulated experimental material is not yet sufficiently representative for calculation of the statistical influence parameters.

Inductive Ligand Parameters in Octahedral Compounds of Nontransition Elements

At present, the accumulated experimental data is not extensive enough to determine P_{cis} and P_{trans} for neutral and acido ligands in octahedral compounds of nontransition elements. Nevertheless, by combining series of characteristics reflecting the mutual ligand influence with characteristics that reflect the ligand capacity to an inductive effect (transfer of electron density upon coordination) it is possible to obtain a sufficient number of series for P_{ind} determination (Table X) for neutral donor ligands. These parameters characterise the tendency of ligands to an inductive effect, since both theory [1–4] and experimental results (see above) indicate that influence parameters are associated with the inductive capacity of ligands.

The obtained values of P_{ind} are listed in Table XI. The mean correlation coefficient for series 150–171 and P_{ind} is 0.86. P_{ind} (as P_{trans} and P_{cis} for transition element compounds) well correlates with ionization potentials of lone pairs (–0.835). The correlation coefficient with donor numbers [95] (which are frequently used for describing the donor capacity) is also extremely high (0.93). The correlation coefficient of P_{ind} and P_{trans} for transition element compounds is 0.72 and increases to 0.89 if the data for NMe_2CHO is discarded (the discrepancy between P_{ind} and P_{trans} is especially great for this ligand).

Let us examine the signs of coefficients r in Table X. The values of r are negative for all stretching and NQR frequencies (Table X), as follows from general considerations. The only exception is series 159, which however is composed of ligands with very close P_{ind} values and, therefore, correlation of experimental data with P_{ind} is meaningless (see above). In all the series studied $^2J(Sn–C–H)$ constants have a positive correlation coefficient, whilst $^2J(Sn–C–F)$ have a negative value: presumably these constants have opposite signs. The value of quadrupole splitting is not directly related to donor properties of the ligand and depends on the geometry of the complex. Consequently coefficient r takes up different signs for different compounds in this case.

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*Evidently this equation may be also used for calculating influence parameters.

**One of the reasons being the insufficient reliability of P_{cis} values for neutral ligands.

TABLE X. Correlation Coefficients r for Series of Characteristics that reflect the Inductive Effect of Neutral Ligands in Sn and Sb Compounds[a].

N	Series	Characteristic	References	Number of points	r × 1000	T(0)	C
150.	*trans*-$SnCl_4L_2$	ν(Sn–Cl)	83	4	−992	326.1	− 2.04
151.	*trans*-$SnBr_4L_2$	ν(Sn–Br)	83	3	−970	234.4	− 2.31
152.	$Me_2SnBr_2L_2$	^2J(Sn–C–H)	84, 85	6	936	110.7	3.90
153.	$Me_2SnCl_2L_2$	^2J(Sn–C–H)	84, 85	6	895	110.4	3.83
154.	$MeSnCl_3L_2$	^2J(Sn–C–H)	85	8	916	69.4	0.79
155.	$MeSnBr_3L_2$	^2J(Sn–C–H)	85	8	928	68.9	0.78
156.	$SbCl_3L$	ν(^{35} Cl)	86	5	−586	24.8	− 0.081
157.	$Me_2SnBr_2L_2$	ν(^{81} Br)	87	8	−976	67.5	− 4.64
158.	$Me_2SnCl_2L_2$	ν(^{35}Cl)	87	3	−957	4.08	− 1.75
159.	*trans*-$SnCl_4L_2$	ν(^{35}Cl)	88–90	4	918	22.3	0.46
160.	$SbCl_5L$	IS(Sb)[b]	91	6	834	2.37	0.021
161.	$MeSnCl_3L_2$	IS(Sn)	92	10	−982	0.94	− 0.035
162.	$MeSnBr_3L_2$	IS(Sn)	92	10	−946	1.07	− 0.045
163.	$SbCl_5L$	QS(Sb)[c]	91	6	985	−5.44	0.14
164.	$Me_2SnBr_2L_2$	QS(Sn)	92	10	616	4.14	0.057
165.	$Me_2SnCl_2L_2$	QS(Sn)	92	10	806	4.18	0.052
166.	$MeSnCl_3L_2$	QS(Sn)	92	10	−695	2.01	− 0.052
167.	$MeSnBr_3L_2$	QS(Sn)	92	10	−680	1.96	− 0.054
168.	*cis*-$SnCl_4L_2$	QS(Sn)	93	4	−933	0.91	− 0.089
169.	$Me_2SnL_4^{2+}$	QS(Sn)	93	4	−1000	6.77	− 1.76
170.	$SbCl_5L$	DN[d]	94	10	932	29.2	1.25
171.	*cis*-$SnCl_4 \cdot 2L$	ν(^{35}Cl)	88–90	4	−990	18.7	− 0.19
172.	*trans*-Me_3SnClL	^2J(Sn–C–H)	85, 95	11	671	68.6	0.56
173.	*trans*-Me_3SnBrL	^2J(Sn–C–H)	85	9	765	68.5	0.54
174.	*trans*-Me_3SnBrL	ν(^{81}Br)	87	10	−823	63.8	− 2.70
175.	*trans*-$Me_3Sn(CF_3)L$	^2J(Sn–C–H)	95	10	678	64.4	0.56
176.	*trans*-$Me_3Sn(CF_3)L$	^2J(Sn–C–F)	95	10	−750	182.2	−11.69
177.	*trans*-$SnBr_4L_2$	ν(^{81}Br)	87	5	−984	124.3	− 2.03

[a] r is the correlation coefficient between experimental data and P_{ind} values. Series 172–176 were not used for P_{ind} determination, since they correspond to pentacoordinate compounds. [b] Isomeric shift of NGR. [c] Quadrupole splitting of NGR spectra. [d] Donor numbers.

TABLE XI. P_{ind} Values in Sn and Sb Compounds and Ionization Potentials I (ev) [53–55].

L	PPh_3	$AsPh_3$	NMe_2CHO	Me_2SO	$OP(NMe_2)_3$	OPR_3	Py	TMEDA
P_{ind}	10.00	8.40	1.43	1.28	1.24	1.15	0.00	−1.20
n[a]	2	1	15	16	13	4	13	8
I	7.85	8.03	9.77	9.01	10.44	–	9.67	–

L	Et_2O	Dimethoxyethane	Dioxan	Me_2CO	THF	RCN	$OPCl_3$	RNO_2
P_{ind}	−5.24	−5.52	−6.45	−6.46	−6.90	−11.81	−13.05	−23.47
n[a]	9	13	14	14	11	6	6	4
I	9.61	9.67	–	9.72	9.57	12.12	11.91	11.3

[a] The number of series in which the corresponding ligand is included.

Appendix

We posed the following problem: to find for substituents $L_1, L_2 \cdots L_i \cdots L_m$ such a set of numbers $P_1, P_2 \cdots P_i \cdots P_m$ so that the values of $T(L_i)$ calculated as

$$T(L_i) = T(0) + CP_i$$

best fitted the experimental values of T(L) for all T_k series. The notion "best fitted" is somewhat ambiguous. We applied one of the possible versions of this notion and required the maximum of the function

$$r_{av} = F(P) = \sum_{k=1}^{n} w_k |r_k| / \sum_{k=1}^{n} w_k \qquad (1)$$

where r_k is the correlation coefficient* between the k-th experimental series and parameters P, w_k is the weight assigned to this series (we took $w_k = n_k - 2$, where n_k is the number of points in the k-th series).

For maximization of functional F we employed a combination of Newton–Raphson method and the steepest ascent method. Defining vectors $\vec{P} = (P_1, P_2 \cdots P_m)$, $\vec{G} = (\partial F/\partial P_1, \partial F/\partial P_2, \cdots \partial F/\partial P_m)$ and matrix $N = \| \partial^2 F/\partial P_i \partial P_j \|$ the increment of vector $\vec{P}$ at the (t + 1)th step of iteration will be: ($\vec{\Delta}^{(t)} = \vec{P}^{(t+1)} - \vec{P}^{(t)}$).

For the Newton–Raphson method

$$\vec{\Delta}_N^{(t)} = -\vec{G}N^{-1} \qquad (2)$$

For the steepest ascent method

$$\vec{\Delta}_G^{(t)} = \lambda \vec{G} \qquad (3),$$

all the derivatives being calculated at $\vec{P} = \vec{P}^{(t)}$

Multiplier λ in (3) may be estimated theoretically:

$$\lambda = \vec{G}^2 / \vec{G}N\vec{G}^{+}.$$

At each iteration step we found the values of $\vec{\Delta}_G^{(t)}$ and $\vec{\Delta}_N^{(t)}$ from formulae (2) and (3), and then determined K_G and K_N from the requirement of the maximum of $F(\vec{P}^{(t)} + K\vec{\Delta}^{(t)})$. The increment of vector $\vec{P}$ was assumed equal to $K_G\vec{\Delta}_G^{(t)}$ or $K_N\vec{\Delta}_N^{(t)}$ depending on which selection gave the highest value of functional (1). Iteration was terminated when the Euclidean norm of the increment had become less than a pre-set value (usually 10^{-6}). For determining F, $\vec{G}$ and N the following formulae may be used:

$$r_k = C_k/(D_k D_k')^{1/2}: \qquad (4)$$

$$\frac{\partial |r_k|}{\partial P_i} = \frac{\gamma_{ki} |r_k|}{D_k C_k} (E_k + T_{ki} D_k - P_i C_k) \qquad (5)$$

$$\frac{\partial^2 |r_k|}{\partial P_i \partial P_j} = -\delta_{ij} \gamma_{ki} |r_k| / D_k + \frac{\gamma_{ki} \gamma_{kj} |r_k|}{D_k^2 C_k} \times$$

$$\{P_i P_j \cdot 3C_k - (P_i T_{kj} + P_j T_{ki}) D_k -$$

$$(P_i + P_j)(E_k + 2S_k^p C_k/n_k) + (T_{ki} + T_{kj}) S_k^p D_k/n_k +$$

$$S_k^{pt} D_k/n_k + 3S_k^p E_k/n_k\} \qquad (6)$$

where

$$D_k = S_k^{pp} - (S_k^p)^2/n_k;$$

$$D_k' = S_k^{tt} - (S_k^t)^2/n_k;$$

$$C_k = S_k^{pt} - S_k^p S_k^t/n_k;$$

$$E_k = (S_k^p S_k^{pt} - S_k^t S_k^{pp})/n_k;$$

$$n_k = \sum_i \gamma_{ki};$$

$$S_k^p = \sum_i \gamma_{ki} P_i;$$

$$S_k^{pp} = \sum_i \gamma_{ki} P_i^2;$$

$$S_k^t = \sum_i \gamma_{ki} T_{ki};$$

$$S_k^{tt} = \sum_i \gamma_{ki} T_{ki}^2;$$

$$S_k^{pt} = \sum_i \gamma_{ki} P_i T_{ki};$$

In these expressions T_{ki} corresponds to the k-th T characteristic for compound with the i-th substituent, γ_{ki} is equal to 1 or 0 depending on the availability of the experimental value, T_{ki}.

It should be noted that influence parameters in this algorithm are determined with accuracy up to the linear transformation $P_i' = \alpha P_i + \beta$ (i = 1,2,... m), since such transformation does not alter the correlation coefficients, r. Therefore the algorithm should provide for selection from several equivalent sets of P. This was achieved either by pre-setting two parameters (*i.e.* $P_i^{(t)} = P_i^{(0)}$ for $i = i_1, i_2$) or by setting one parameter and defining the total range of P_i (*i.e.* $P_{i_1}^{(t)} = P_{i_1}^{(0)}$ and $P_{max}^{(t)} - P_{min}^{(t)} = d$).

The algorithm was implemented by an ALGOL program. Translations and computations were carried out on a BESM-4 computer. Depending on the number of series, their composition and selection of the initial vector $\vec{P}$, the problem required from tens to hundreds of iterations.

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*The necessary information about the correlation coefficient and minimization methods may be found in Ref. [96].

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