

## TRANSMISSION OF SUBSTITUENT EFFECTS IN N-(*p*-SUBSTITUTED PHENYL)-PHTHALIMIDES

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*Dedicated to Professor Otto Exner on the occasion of his 65th birthday.*

Chemical shifts of benzene part of the title compounds have been correlated with substituent-chemical shift (SCS) increments  $a$  for  $^1\text{H}$  and  $z$  for  $^{13}\text{C}$  NMR spectra. These correlations gave pieces of information not only about the through-conjugation of substituents but also about the change of the twist about the central N-C bond with the change of substituent in the *para*-position. In such a way the electronic effects of substituents have been studied together with the effects due to conformational changes which manifest themselves with the change in the van der Waals repulsion and/or diamagnetic anisotropy of double bond. Chemical shifts in phthalimide part of molecule have been related to the electronic effect of distant substituent after separation of the main source of variation from random error by principal component analysis.

Cumulative effect of two substituents on any measurable quantity is generally non-additive. Thus in benzene ring a substituent with a strong inductive effect might alter the electronic contribution of a second substituent; most often the deviations from additivity are found where the two substituents can conjugate with each other through the aromatic ring. If both substituents are  $\pi$ -donors or acceptors, then due to their competitive interaction their effective resonance parameters can become smaller in magnitude. On the contrary, if one substituent is a  $\pi$ -donor and the other is a  $\pi$ -acceptor then due to their cooperative interaction their effects can be enhanced.

The resonance part of dual-substituent-parameter equation<sup>1</sup> can be written according to Exner's proposal<sup>2</sup> as

$$Q_{XY} = Q_{HH} + \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \quad (1a)$$

$$Q_{XY} = Q_{HY} + \rho_X\sigma_X + \rho_{XY}\sigma_X\sigma_Y \quad (1b)$$

For one constant substituent (Y) the Eq. (1a) can be rewritten to Eq. (1b) where  $Q_{HY} = Q_{HH} + \rho_Y\sigma_Y$ . It can be shown that some other equations which take the electron demand of substituent in account and are more practical for calculations

( $\sigma_R$  for *ipso* position are not defined) might be considered as the other forms of Eq. (1b). E.g., for small values  $e_Y\sigma_X$  (which is mostly the case) Taft's effective resonance parameter<sup>3</sup>,  $\bar{\sigma}_X$ , Eq. (2a), can be substituted by the approximative value from Eq. (2b).

$$\bar{\sigma}_X = \sigma_X / (1 - e_Y\sigma_X) \quad (2a)$$

$$\bar{\sigma}_X = \sigma_X(1 + e_Y\sigma_X), \quad (2b)$$

where  $\sigma_X$  is the resonance parameter of substituent X not affected by substituent Y and  $e_Y$  is the electron demand characteristic of Y group. Then the resonance part of Taft's dual-substituent-parameter equation,  $Q_{XY} - Q_{HY} = \rho_X\bar{\sigma}_X$ , can be written as Eq. (3).

$$Q_{XY} = Q_{HY} + \rho_X\sigma_X + \rho_X e_Y\sigma_X^2 \quad (3)$$

$$e_Y = \rho_{XY}\sigma_X\sigma_Y / (\rho_X\sigma_X^2) \quad \text{for } \sigma_X \neq 0 \quad (4)$$

From the comparison of the Eq. (1b) and Eq. (3) it is clear that the electron demand of Y substituent,  $e_Y$ , depends on the nature of substituent X; when calculated from experimental data then probably the mean value of  $\sigma$ 's for given set of X substituents is involved.

The resonance part of Charton's three parameter equation<sup>4</sup>,

$$Q_{XY} = Q_{HY} + \rho_X\sigma_X + \rho_X\eta_Y\sigma_e \quad (5)$$

( $\rho_X = D$  and  $\rho_X\eta_Y = R$  in original assignment) can give electron demand of substituent Y,  $\eta_Y$ , in the similar form.

$$\eta_Y = \rho_{XY}\sigma_X\sigma_Y / (\rho_X\sigma_e) \quad \text{for } \sigma_e \neq 0 \quad (6)$$

It follows from the Eq. (4) and Eq. (6) that in the accuracy limits given by approximative substitution of Eq. (2a) by Eq. (2b) and if electron demand of Y substituent were the same in Taft's and in Charton's concept, i.e.,  $\eta_Y = e_Y$ , then Charton's  $\sigma_e$  constant would be equal to  $\sigma_X^2$ .

Data used for investigation of substituent effects by above-mentioned methods must meet certain strict requirements, namely that steric effects must be absent, constant, or negligible and conformation must be constant through the whole series. If this is not the case and the intention is to study conformation changes introduced by substituent, some other indicators of electron density changes must be used.

The NMR chemical shifts of the hydrogens attached to a benzene ring or of the <sup>13</sup>C carbon atoms of ring themselves reflect properly not only the electron density

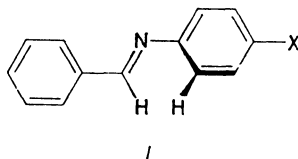
at the position in the question but also anisotropic and ring current effects which can vary with the conformational changes. It was shown<sup>5</sup> that chemical shifts of aromatic hydrogen atoms in *para*-disubstituted benzenes can be correlated with the substituent chemical shifts (SCS) values<sup>6</sup>,  $a_i$ , for one variable substituent X with the other substituent Y and its  $a_j$  SCS value being constant in the whole series.

$$\delta_{\text{H}} = 7.27 + a_j + a_i(1 + Ka_j) \quad (7)$$

The correlation equation, Eq. (7), for  $^1\text{H}$  chemical shifts takes into account the deviation of SCS increments  $a_i$  and  $a_j$  from additivity in the same way as does the Exner's equation, Eq. (1). It applies to the chemical shifts of hydrogens ortho to substituent X with  $a_j = a(\text{meta})$  and  $a_i = a(\text{ortho})$ , or those ones meta to X with  $a_j = a(\text{ortho})$  and  $a_i = a(\text{meta})$ .

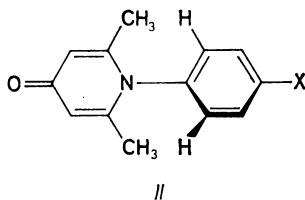
Correlation of  $\delta_{\text{H}}$  versus  $a_i$  can be used for (i) the assignment of signals to corresponding hydrogen atoms<sup>5</sup>; from graphical presentation it is easy to decide whether the assignment of particular pair of  $\delta_{\text{o}}-\delta_{\text{m}}$  is right or should be reversed; (ii) to estimate the degree of interaction of substituents<sup>5</sup>; the slope is about unity for negligible interaction and less than one if through-conjugation occurs; similar correlation with  $^{13}\text{C}$  SCS was introduced by Lynch<sup>7</sup> and Doucet<sup>8</sup> and later generalized for three substituents arbitrary situated on the benzene ring by Laatikainen<sup>9</sup>; (iii) to indicate conformational changes at the Y site which manifest themselves with the variation in the van der Waals repulsion, diamagnetic anisotropy, or ring current effects at the proximal H atoms<sup>10-13</sup>.

In benzylideneanilines<sup>10</sup> *para*-substituted in aniline ring (I) the CH=N and H-2 hydrogen atoms are close one another which results in a distortion of their electron clouds and a submission of them to the ring current or diamagnetic anisotropy effect of C=N group, respectively, causing low field shift of corresponding  $^1\text{H}$  NMR signals.

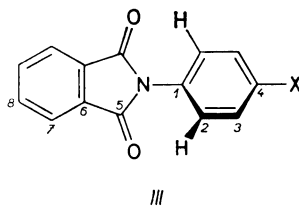


If going from  $\text{NMe}_2$  to  $\text{NO}_2$  substitution the twist angle between aniline ring and CH=N bond plane increases then the deshielding influence of neighbour hood decreases and the signals are shifted upwards. This results in drastical tilt of  $\delta$  versus  $a(\text{meta})$  correlation line; its slope approaches zero due to the practical compensation of electronical deshielding effect of substituent X by the decrease of the contribution due to the diamagnetic anisotropy of CH=N bond and/or the repulsive interaction of proximal atoms. Similar kind of compensation is the reason why the position of

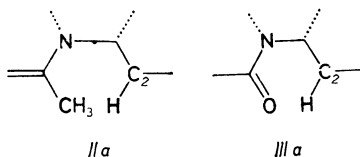
$^1\text{H}$  signal of  $\text{CH}=\text{N}$  group seemingly does not depend on the change of the substituent  $\text{X}$  and not the absence of any real effect of substituent, the explanation which is from time to time ever more presented in literature<sup>14-17</sup>.



The effect of conformational changes on the  $^1\text{H}$  NMR chemical shifts was observed<sup>13</sup> also in the series of 4'-substituted-N-phenyl-2,6-dimethyl-4-pyridones (II). The twist angle between both rings decreases when going from  $\text{NEt}_2$  to  $\text{NO}_2$  substituent; this fact can be deduced from the slope of the correlation  $\delta_{\text{H}}$  versus  $a(\text{meta})$ , which is larger than unity, since electronic effect of substituent and repulsive van der Waals interaction between methyl and H-ortho atoms act in the same direction.



Likewise, the N-(*p*-substituted phenyl)phthalimides (III) are non-planar due to the steric hindrance of the carbonyl oxygens and proximal hydrogen atoms on the phenyl ring; for sterically similar N-(*p*-substituted phenyl)maleimides<sup>18</sup> the twist angle between both rings was found in nematic solvent to be  $52.9^\circ$  for  $\text{X} = \text{H}$  and  $54.5^\circ$  for  $\text{X} = \text{Cl}$ . Relatively broader interval for twist angle was claimed after the investigation of  $^{15}\text{N}$  labelled N-(*p*-bromophenyl)maleimide in nematic phase<sup>19</sup>.



It was tempting to compare the effect of substituents in both the lately mentioned series II and III not only because of their similarity (two ring systems connected by  $\text{N}-\text{C}_{\text{arom}}$  bond) but also because of the subtle difference in the orientation of double bond ( $\text{C}=\text{C}$  or  $\text{C}=\text{O}$ ) with respect to *para*-substituted benzene ring.

## EXPERIMENTAL

N-(*p*-substituted phenyl)phthalimido derivatives<sup>20</sup> were prepared by melting together equimolar amounts of phthalic anhydride and respective *p*-substituted aniline. Products were recrystallized from ethanol-chloroform (2 : 3) or in the case of nitro and acetyl derivatives from acetic acid. All compounds gave satisfactory elemental analyses and were characterized by the melting point: OCH<sub>3</sub> (152–153°C), CH<sub>3</sub> (201–202°C), H (203–204°C), Cl (194–195°C), COOCH<sub>3</sub> (195 to 196°C), COCH<sub>3</sub> (242–243°C), NO<sub>2</sub> (263–264°C). The <sup>1</sup>H and <sup>13</sup>C NMR spectra verified their structure and showed no impurity signals. All spectra were recorded on Bruker WP80SY FT-NMR spectrometer; the <sup>13</sup>C NMR spectra were proton broad-band decoupled. Typical operating conditions are shown in the Table I.

Samples were run at concentrations 0.02 mol l<sup>-1</sup> (<sup>1</sup>H NMR) or 0.25 mol l<sup>-1</sup> (<sup>13</sup>C NMR) in deuteriochloroform; from sparingly soluble nitro and acetyl derivatives saturated solutions were prepared for <sup>13</sup>C NMR measurements. Tetramethylsilane (0.000 ppm) for <sup>1</sup>H NMR and central peak of deuteriochloroform (77.00 ppm) for <sup>13</sup>C NMR were used as internal standards. Accurate values of <sup>1</sup>H chemical shifts were obtained by iterative simulation of corresponding part of spectra with commercial program PANIC (Bruker Analytische Messtechnik, GmbH, B.R.D.); standard deviation between experimental and calculated spectra were about 0.02 Hz.

## RESULTS AND DISCUSSION

<sup>13</sup>C and <sup>1</sup>H NMR chemical shifts of N-(*p*-substituted phenyl)phthalimides are presented in Tables II, III, and V. For the convenience, chemically non-equivalent carbon atoms (and corresponding hydrogens) were numbered from 1 to 8 as given in formula III.

Tables II and III show <sup>13</sup>C and <sup>1</sup>H chemical shifts of NMR signals from *para*-substituted benzene ring and the results of linear regression of chemical shifts versus respective SCS (increments *a* for <sup>1</sup>H (ref.<sup>6</sup>) and *z* for <sup>13</sup>C (ref.<sup>21</sup>).

As expected, the correlations in Table II are all very good as evidenced not only by high correlation coefficients, *r*, but also by relative standard deviations of slope  $g = sb/b$ , and Ehrenson's goodness of fit parameter<sup>1</sup>  $f = se/sy$ . Decrease in the slope of the correlation of  $\delta(\text{C-1})$  versus  $z_p$  from unity confirms the presence of through-conjugation effect; i.e., the electron deficiency in the benzene ring caused by electron withdrawing substituent X is partially compensated by electron shift from phthalimide moiety and reversely the electron density surplus due to electron donating substituent X is partially transferred from the ring to the *para*-substituent group<sup>5</sup>.

In the Table III the present results of correlation of chemical shifts in position 2 are compared with those from pyridone II series<sup>13</sup>. In both series the slope of  $\delta(\text{H-2})$  versus  $a_m$  regression is higher than unity which could be explained by the same dependence of van der Waals repulsive interaction on the substituent X which shifts NMR signals the more downfields the shorter is the distance between proximal atoms. That means, the twist angle between both ring systems, i.e., benzene and

TABLE I  
Experimental conditions of NMR measurements

Parameter	$^1\text{H}$	$^{13}\text{C}$
Transmitter frequency, MHz	80.13	20.15
Spectral width, Hz	1 200	4 200
Data points	32 K	16 K
Digital resolution, ppm/point	0.001	0.025
Pulse width, $\mu\text{s}$	2.5	5
Pulse angle, deg	50	40
Relaxation delay, s	0	4

TABLE II  
Chemical shifts of signals in *ipso*, *ortho*, and *para* position in  $\text{III}$  (ppm) and results of regression with SCS<sup>a</sup> constants  $a$  and  $z$

X	C-1	C-3	H-3	C-4	X-4
$\text{OCH}_3$	124.34	114.45	7.019	159.26	3.847
$\text{CH}_3$	129.03	129.70	7.292	138.06	2.408
H	131.78	129.05	7.514	128.02	7.438
Cl	130.28	129.25	7.475	133.75	—
$\text{COOCH}_3$	135.65	130.34	8.183	129.28	3.950
$\text{COCH}_3$	136.14	129.15	8.103	136.14	2.644
$\text{NO}_2$	136.08	124.42	8.380	146.72	—

versus	$z_p$	$z_o$	$a_o$	$z_i$
$a$ (intercept)	131.63	129.06	7.485	127.71
$b$ (slope)	0.8887	1.0063	0.9654	1.0018
$r$	0.9928	0.9996	0.9989	0.9986
$s$	0.5799	0.1707	0.0262	0.6241
$sa$	0.2197	0.0710	0.0109	0.3487
$sb$	0.0479	0.0123	0.0202	0.0223
$g$	0.0539	0.0122	0.0209	0.0223
$sy$	4.4261	5.7081	0.5120	10.9642
$f$	0.1310	0.0299	0.0512	0.0569

<sup>a</sup> SCS constants taken from the literature:  $a$  (ref.<sup>6</sup>),  $z$  (ref.<sup>21</sup>).

pyridone in *II* and benzene and phthalimide in *III* depends on the substituent X in the same way; it increases with increasing electron donicity of substituent X.

The correlation of  $\delta(\text{C-2})$  with  $z_m$  is rather poor; the fact, that at least in some cases, can be explained by insufficient range of  $z_m$  values<sup>7</sup>. However, the scatter of points about the regression line shown in the Fig. 1 reveals surprising similarity in both cases; the scatter pattern for pyridone systems looks like a mirror image of that one of phthalimides.

We believe that this is the clear evidence for the variation of diamagnetic anisotropy contribution to the screening of C-2 carbon nucleus in the X-substituted series.

In pyridones *II* the change in the twist angle about N—(C-1) bond moves the C-2 nucleus in the deshielding zone of C=C double bond (*IIa*); for the more planar NO<sub>2</sub> derivative the deshielding is higher than for more twisted OCH<sub>3</sub> derivative. In phthalimides *III* the C-2 nucleus lies in the shielding zone of C=O double bond (*IIIa*); thus for the more planar NO<sub>2</sub> derivative the distance of C-2 to double bond is shorter and therefore also the shielding contribution to chemical shift is higher than for more distant C-2 in more twisted OCH<sub>3</sub> derivative.

TABLE III

Chemical shifts of signals in *meta* position in *II* and *III* and results of regression with SCS<sup>a</sup> constants *a* and *z*

X	$z_m$	C-2( <i>II</i> )	C-2( <i>III</i> )	$a_m$	H-2( <i>II</i> )	H-2( <i>III</i> )
OCH <sub>3</sub>	1.04	128.92	127.90	-0.09	7.118	7.337
CH <sub>3</sub>	-0.11	127.57	126.40	-0.12	7.085	7.325
H	0	127.95	126.54	0	7.235	7.417
Cl	1.4	129.44	127.62	-0.02	7.222	7.420
COOCH <sub>3</sub>	-0.1	128.32	125.86	0.11	7.361	7.603
COCH <sub>3</sub>	-0.1	128.58	126.10	0.14	7.401	7.633
NO <sub>2</sub>	0.9	129.81	126.33	0.26	7.581	7.777
<i>a</i> (intercept)		128.22	126.27		7.235	7.452
<i>b</i> (slope)		1.0001	0.9505		1.2751	1.2521
<i>r</i>		0.8214	0.8033		0.9980	0.9942
<i>s</i>		0.4980	0.5054		0.0122	0.0202
<i>sa</i>		0.2313	0.2347		0.0048	0.0080
<i>sb</i>		0.3105	0.3151		0.0365	0.0606
<i>g</i>		0.3105	0.3315		0.0286	0.0484
<i>sy</i>		0.7971	0.7747		0.1738	0.1710
<i>f</i>		0.6247	0.6524		0.0700	0.1181

<sup>a</sup> SCS constants taken from the literature: *a* (ref.<sup>6</sup>), *z* (ref.<sup>21</sup>).

Residuals from the regressions shown in Fig. 1 are collected in Table IV. In order to prove our hypothesis that these residuals  $R1$  and  $R2$  depend on the twist angle between rings and therefore on the nature of the X substituent we have subjected them to the principal component analysis<sup>22</sup> (PCA). This transformation corresponds to the rotation of coordinate system of  $R1$  and  $R2$  axes to the new one defined by  $F1$  and  $F2$  axes; then the main source of variability in residuals is described by coordinates of  $F1$  and the secondary source, which most probably reflects some measurement errors, by the  $F2$  coordinates.

In our case shown in the Fig. 2 the proper rotation angle is about  $45^\circ$ . The value of the first component  $F1$  results from the perpendicular projection of original points upon the  $F1$  axis. These values correlate very well with the  $\sigma_p$  values<sup>23</sup> of X substituent ( $\sigma_p$  axis coincides with  $F2$  axis in Fig. 2). This correlation is not expected to be linear since also the trajectory of the C-2 atom in the shielding and deshielding zones of double bond is not linear.

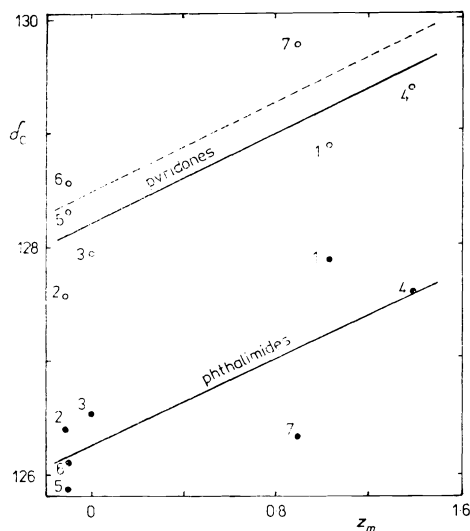


FIG. 1

Regression of C-2 chemical shifts in pyridones *II* and phthalimides *III* versus SCS increments  $z_m$ . Substituents: 1  $\text{OCH}_3$ , 2  $\text{CH}_3$ , 3 H, 4 Cl, 5  $\text{COOCH}_3$ , 6  $\text{COCH}_3$ , 7  $\text{NO}_2$ . Data for pyridones *II* and phthalimides *III* from Table III,  $z_m$  values from ref.<sup>21</sup>

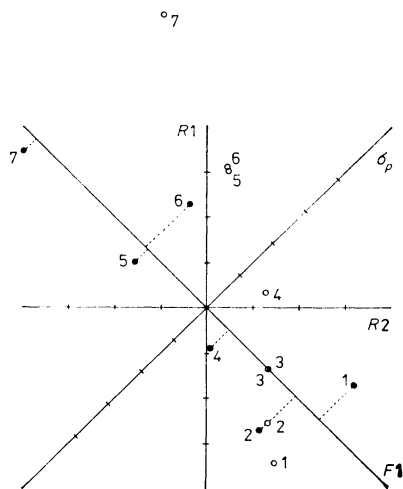


FIG. 2

Graphical extraction of the first principal component vector from residuals  $R1$  (pyridones) and  $R2$  (phthalimides) and its correlation with  $\sigma_p$  of substituents. Scaling step on all axis is 0.2 unit; the  $\sigma_p$  axis coincides with the  $F2$  one. ● Correlation of  $R1$  and  $R2$  residuals; ○ correlation of  $\sigma_p$  vs  $F1$  values



The broken line in Fig. 1 is the function line for monosubstituted benzenes, i.e.,  $\delta_C = 128.5 + z_m$ . Vertical distances at  $z_m = 0$  of pyridones and phthalimides regression lines to this broken line correspond to SCS of pyridone and phthalimide group to the *ortho*-position ( $z_o$ ), respectively, which is practically not affected by diamagnetic anisotropy of particular double bond.

Chemical shifts of  $^{13}\text{C}$  and  $^1\text{H}$  NMR signals of phthalimide group are given in Table V together with IR valence vibration of CO groups. Our assignment of chemical shifts agree with that one for N-substituted phthalimides in spectra cata-

TABLE IV  
Transformation of residuals from  $\delta(\text{C-2})$  vs  $z_m$  regression by PCA

X	R1(II)	R2(III)	F1	F2	$\sigma_p^a$
OCH <sub>3</sub>	-0.343	0.644	-0.459	0.473	-0.268
CH <sub>3</sub>	-0.543	0.237	-0.360	-0.506	-0.170
H	-0.273	0.273	-0.253	-0.077	0
Cl	-0.183	0.022	-0.094	-0.263	0.227
COOCH <sub>3</sub>	0.197	-0.312	0.236	-0.179	0.489
COCH <sub>3</sub>	0.457	-0.072	0.244	0.630	0.502
NO <sub>2</sub>	0.687	-0.793	0.687	-0.151	0.778

<sup>a</sup>  $\sigma_p$  values are taken from ref.<sup>23</sup>.

TABLE V  
Chemical shifts (ppm) from phthalimide ring and  $\nu_{\text{CO}}(\text{cm}^{-1})$

X	$\nu_{\text{CO}}$	C-5	C-6	C-7	H-7	C-8	H-8
OCH <sub>3</sub>	1 713	167.49	131.85	123.60	7.776	134.24	7.937
CH <sub>3</sub>	1 715	167.32	131.84	123.59	7.777	134.22	7.943
H	1 715	167.19	131.78	123.68	7.795	134.32	7.964
Cl	1 718	166.90	131.64	123.80	7.805	134.50	7.960
COOCH <sub>3</sub>	1 726	166.69	131.58	123.84	7.818	134.58	7.977
COCH <sub>3</sub>	1 726	166.77	131.65	123.96	7.824	134.69	7.983
NO <sub>2</sub>	1 731	166.39	131.42	124.18	7.847	134.98	8.003
preprocessing multiplication by	0.001	0.01	0.01	0.01	0.2	0.01	0.2

$\log^{24}$ . For limited number of substituents ( $\text{CH}_3$ ,  $\text{Cl}$ ,  $\text{NO}_2$ ) the correlation of  $\gamma_{\text{CO}}$  with  $\sigma_p$  constants was reported by Harfoush<sup>20</sup>. We have expected that also the chemical shifts values in Table V could correlate with  $\sigma_p$  Hammett constants<sup>23</sup>. However, since their variances are relatively small no statistics have been calculated for individual correlations.

Better we have used again principal component analysis to extract the main source of variation from the whole set of data. Before a singular value decomposition of data matrix the recommended procedure<sup>25,26</sup> is to ensure that different variables have similar errors. In our case,  $\gamma_{\text{CO}}$  values were multiplied by 0.001,  $^{13}\text{C}$  chemical shift data by 0.01 and  $^1\text{H}$  chemical shifts by 0.2 yielding a common experimental uncertainty of 0.001. PCA of such preprocessed  $7 \times 7$  data matrix  $\mathbf{D}$  showed that just one principal component ( $\mathbf{V1}$ ) accounted for 99.9995% of the whole variability which is given by the trace of the starting  $\mathbf{D}^T\mathbf{D}$  matrix. In such case of a single principal component it is not necessary to make any rotation to a real physical property vector. We have found (Table VI) that this vector  $\mathbf{V1}$  correlates fair to well

TABLE VI  
Results of principal component analysis of phthalimide group data; eigenvalue(1) = 99.9995% of the trace

X	V1	nV1	$\sigma_p$	$\sigma_{\text{IR}}^a$	$\sigma_{\text{Id}}^b$
OCH <sub>3</sub>	0.377319	-0.2012	-0.268	-0.18	-0.25
CH <sub>3</sub>	0.377374	-0.1685	-0.170	-0.15	-0.15
H	0.377657	0	0	0	0
Cl	0.377758	0.0601	0.227	0.23	0.19
COOCH <sub>3</sub>	0.378249	0.3524	0.489	0.44	0.48
COCH <sub>3</sub>	0.378464	0.4804	0.502	0.44	0.55
NO <sub>2</sub>	0.378928	0.7566	0.778	0.80	0.85
regression V1 vs $\sigma$					
a (intercept)			0.377627	0.377595	0.377613
b (slope)			$1.515 \cdot 10^{-3}$	$1.636 \cdot 10^{-3}$	$1.474 \cdot 10^{-3}$
r			0.9788	0.9819	0.9915
s			$1.348 \cdot 10^{-4}$	$1.244 \cdot 10^{-4}$	$8.561 \cdot 10^{-5}$
sa			$5.993 \cdot 10^{-5}$	$5.680 \cdot 10^{-5}$	$3.838 \cdot 10^{-5}$
sb			$1.419 \cdot 10^{-4}$	$1.411 \cdot 10^{-4}$	$8.656 \cdot 10^{-5}$
g			0.0936	0.0862	0.0587
sy	$6.002 \cdot 10^{-4}$				
f			0.2245	0.2074	0.1426

<sup>a</sup>  $\sigma_{\text{IR}} = \sigma_{\text{I}} + \sigma_{\text{R}}$  (Taft); <sup>b</sup>  $\sigma_{\text{Id}} = \sigma_{\text{I}} + \sigma_{\text{d}}$  (Charton).

with Hammett  $\sigma_p$  values; practically the same results have been obtained for 1 : 1 combination of Taft's  $\sigma_I$  and  $\sigma_R$  constants ( $\sigma_{IR}$ ) and Charton's  $\sigma_1$  and  $\sigma_d$  values ( $\sigma_{1d}$ ). For better visual comparison of  $\mathbf{V1}$  vector with  $\sigma$  values it is convenient to shift this vector to zero for unsubstituted compound and then to scale its length to unity giving  $n\mathbf{V1}$ .

From the trends in chemical shift changes in Table V we can follow the way how the substituents in phenyl ring change the polarization of the electron cloud in phthalimide group; electron-withdrawing substituents pull electrons of sixmembered ring toward the C-6 atom and electrons of carbonyl group to the C-5 atom; the electron-donating substituents push electrons in the opposite direction.

### CONCLUSIONS

$^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of *p*-disubstituted benzene part of the title compounds correlate well with substituent chemical shift increments  $a$  and  $z$ , respectively. Those regressions with the slope near to one can be used only for the verification of chemical shifts assignment. However, if the slope smaller than one is found at the site of substitution (C-1) then the clear evidence for the through-conjugation of both substituents is provided. In the position sensitive to conjugation changes (H-2) the electronic effect of substituent is amended by the contribution from the van der Waals interaction and/or diamagnetic anisotropy of near double bond. In suitable case the diamagnetic contribution can be extracted from residuals of regression  $\delta(\text{C-2})$  versus corresponding SCS increments  $z_m$  and then correlated to  $\sigma_p$  constants of the substituents.

In spite of the twist of the molecule about the central N—(C-1) bond the small changes of chemical shifts in phthalimide group can be related to the effect of X substituent after this source of variation has been separated from random error by principal component analysis.

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