

**^{13}C NMR SPECTRA AND SUBSTITUENT EFFECTS
OF *meta* AND *para* SUBSTITUTED BENZOYL ISOTHIOCYANATES**

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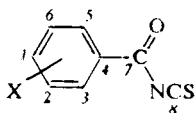
^{13}C NMR spectra have been studied of 20 *meta* and *para* substituted benzoyl isothiocyanates and corresponding benzoyl chlorides. The ^{13}C SCS values of the carbon atom in NCS group have been found to correlate linearly with the Hammett $\sigma_{m,p}$ constants of the substituents as well as with the corresponding π electron charges. The ^{13}C SCS (substituent chemical shift) values of the carbonyl carbon atom of the compounds investigated are little sensitive to substituent effects and are analyzed on the basis of the dual-substituent-parameter approach. Also discussed are the intercorrelation relations of the ^{13}C SCS values of benzoyl isothiocyanates and phenyl isothiocyanates and substituent effects on chemical shifts of carbon atoms of the benzene nucleus. For the benzoyl isothiocyanates the ^{13}C NMR increments of chemical shifts and $\sigma_{m,p}$ substituent constants of CONCS group have been determined.

Our previous papers¹⁻³ dealt with substituent effects on the ^{13}C NMR chemical shifts and quantum-chemical characteristics of *meta* and *para* substituted phenyl isothiocyanates. High reactivity of benzoyl isothiocyanates⁴ and their applications to organic syntheses^{5,6} also directed our attention to study of their ^{13}C NMR spectra which have not been described in literature yet. The acyl isothiocyanate group of benzoyl isothiocyanates belongs to groups possessing two reaction centres (C=O and NCS), and it is interesting from the point of view of ^{13}C NMR spectroscopy, too. Low sensitivity of the ^{13}C chemical shifts of carbonyl carbon atom in side chain of aromatic systems to *meta* and *para* substituents was dealt with in several studies⁷⁻¹⁰. In the case of carbon atom of the NCS group, however, it was found^{1-3,11} that – in analogous studies – the carbon atom of NCS group is much more sensitive to substituent effects, and the ^{13}C substituent chemical shift (SCS) values give good linear correlations with the Hammett substituent constants $\sigma_{m,p}$. With regard to chemical cognateness the corresponding benzoyl chlorides were chosen as model compounds, these compounds being intermediates in the preparations of the isothiocyanates studied. In this communication we have focused our attention to investigation of the substituent effects on ^{13}C NMR chemical shifts of carbon atoms of *meta* and *para* substituted benzoyl isothiocyanates and corresponding benzoyl chlorides. Changes in the ^{13}C chemical shifts of the benzoyl

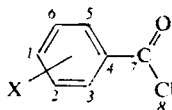
isothiocyanates caused by substituents (the SCS values) are interpreted by means of the corresponding electronic changes obtained by the MO-LCAO approach in π electronic approximation.

EXPERIMENTAL

The compounds investigated. 4-Dimethylaminobenzoyl isothiocyanate¹² (I); 4-methoxybenzoyl isothiocyanate¹³ (II); 4-methylbenzoyl isothiocyanate¹⁴ (III); benzoyl isothiocyanate¹⁵ (IV); 4-fluorobenzoyl isothiocyanate¹⁶ (V); 4-chlorobenzoyl isothiocyanate¹⁷ (VI) 4-bromobenzoyl isothiocyanate¹⁸ (VII); 4-cyanobenzoyl isothiocyanate¹⁹ (VIII); 4-nitrobenzoyl isothiocyanate¹² (IX); 1,4-bis(isothiocyanatocarbonyl)benzene²⁰ (X); 3-dimethylaminobenzoyl isothiocyanate (XI) was prepared by heating 3-dimethylaminobenzoyl chloride with $\text{Pb}(\text{SCN})_2$ for 1 h, m.p. 45°C (chloroform–light petroleum), for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{OS}$ (206.3) calculated: 58.23% C, 4.89% H, 13.58% N; found: 58.02% C, 5.01% H, 13.42% N; 3-methoxybenzoyl isothiocyanate¹⁴ (XII); 3-methylbenzoyl isothiocyanate¹⁴ (XIII); 3-fluorobenzoyl isothiocyanate (XIV) was prepared in the same way as XI, b.p. 76°C/250 Pa, for $\text{C}_8\text{H}_4\text{FNOS}$ (181.2) calculated: 53.03% C, 2.23% H, 7.73% N; found: 52.90% C, 2.31% H, 7.62% N; 3-trifluoromethylbenzoyl isothiocyanate (XV) was prepared in the same way as XI, m.p. 35°C, yellow crystals from light petroleum, for $\text{C}_9\text{H}_4\text{F}_3\text{NOS}$ (231.2) calculated: 46.76% C, 1.74% H, 6.06% N; found: 46.88% C, 1.70% H, 5.98% N; 3-chlorobenzoyl isothiocyanate¹⁶ (XVI); 3-bromobenzoyl isothiocyanate¹⁶ (XVII); 3-cyanobenzoyl isothiocyanate (XVIII) was prepared by heating 3-cyanobenzoyl chloride with NH_4SCN in acetone 20 min, yellow crystals (light petroleum–chloroform), m.p. 53°C, for $\text{C}_9\text{H}_4\text{N}_2\text{OS}$ (188.2) calculated: 57.44% C, 2.14% H, 14.88% N; found: 57.65% C, 2.19% H, 14.99% N; 3-nitrobenzoyl isothiocyanate²¹ (XIX); 1,3-bis(isothiocyanatocarbonyl)benzene²² (XX). 4-Dimethylaminobenzoyl chloride (XXI), 4-methoxybenzoyl chloride (XXII), 4-methylbenzoyl chloride (XXIII), benzoyl chloride (XXIV), 4-fluorobenzoyl chloride (XXV), 4-chlorobenzoyl chloride (XXVI), 4-bromobenzoyl chloride (XXVII), 4-cyanobenzoyl chloride (XXVIII), 4-nitrobenzoyl chloride (XXIX), 1,4-bis-(chlorocarbonyl)benzene (XXX), 3-dimethylaminobenzoyl chloride (XXXI), 3-methoxybenzoyl chloride (XXXII), 3-methylbenzoyl chloride (XXXIII), 3-fluorobenzoyl chloride (XXXIV), 3-trifluoromethylbenzoyl chloride (XXXV), 3-chlorobenzoyl chloride (XXXVI) 3-bromobenzoyl chloride (XXXVII), 3-cyanobenzoyl chloride (XXXVIII), 3-nitrobenzoyl chloride (XXXIX), and 1,3-bis(chlorocarbonyl)benzene (XL) were prepared from the corresponding acids by reaction with SOCl_2 or PCl_5 according to ref.²³.



I–XX



XXI–XL

Measurements. The ¹³C NMR spectra were measured with a Tesla BS 567 A (25.15 MHz) apparatus in deuteriochloroform at concentrations about 1 mol dm⁻³ at 28°C. The chemical shifts are given with respect to tetramethylsilane with the accuracy of ±0.07 ppm. The spectra were measured by a 3 μs pulse (30°) at the band width of 7 600 Hz. The method of key decoupling with retention of NOE contributions was used for interpretation of the ¹³C NMR signals of the aromatic carbon atoms of the nonsubstituted benzoyl isothiocyanate. In the case

of substituted benzoyl chlorides and benzoyl isothiocyanates the signals were assigned by comparison of the data from the noise-decoupled and off-resonance spectra with the values calculated by the increment method for disubstituted benzenes. The value of increments of CONCS group calculated from experimental chemical shifts of benzoyl isothiocyanate was used in the calculation. The ^{13}C — ^{19}F interactions in the compounds containing fluorine were interpreted on the basis of known literature data^{24,25}.

Calculations. The PPP calculations of benzoyl isothiocyanates were carried out according to the standard SCF-LCI theory^{26,27} (20 monoexcited configurations) with approximation of bicentric repulsion integrals $\gamma_{\mu,\nu}$ according to Mataga and Nishimoto²⁸. The geometry and parametrization of the substituents and of CONCS group were used according to refs^{1,29}. The possible planar conformers were considered, and the ^{13}C SCS values were correlated with the π electronic charges δQ_{π} for the conformer with the lowest value of total π electron energy involving repulsion of the nuclei.

RESULTS AND DISCUSSION

From the ^{13}C NMR spectra of the isothiocyanates investigated it follows that the resonance signals of the carbon atom of NCS group are located (due to electron-acceptor effect of carbonyl) at considerably higher ppm values than the resonance signals of the corresponding phenyl isothiocyanates^{2,11}. This fact is in accordance with higher reactivity of benzoyl isothiocyanates towards nucleophilic reagents^{4,30} as well as with higher positive values of π electronic charges as compared with those of phenyl isothiocyanates³. So *e.g.* ^{13}C signals of phenyl isothiocyanate: (NCS) = 135.2 ppm, $Q_{\pi} = 0.133$ e; for benzoyl isothiocyanate: (NCS) = 147.6 ppm, $Q_{\pi} = 0.179$ e. For evaluation of substituent effects on the ^{13}C NMR chemical shifts we used the ^{13}C SCS values calculated according to the relation $^{13}\text{C SCS} = \delta 13\text{-C}(\text{X}\neq\text{H}) - \delta 13\text{-C}(\text{X}=\text{H})$. The values thus obtained for benzoyl isothiocyanates are given in Table I and for the respective benzoyl chlorides in Table II. Comparison of the ^{13}C SCS values of the carbon atom of NCS group of the benzoyl isothiocyanates with the corresponding values of phenyl isothiocyanates^{2,3,11}, moreover, shows that the chemical shifts of benzoyl isothiocyanates are less sensitive to a change of the substituent X. Whereas with benzoyl isothiocyanates the extent of these changes is 5.4 ppm, with phenyl isothiocyanates it is 8.3 ppm. The sensitivity of the ^{13}C SCS values to substituents makes itself felt also in the linear correlation with the Hammett substituent constants $\sigma_{m,p}$ (Fig. 1). There exists a statistically significant linear correlation between the $^{13}\text{C}_8$ SCS values and the corresponding relative π electronic charges δQ_{π} (Fig. 2). The above-mentioned extent of changes in the ^{13}C SCS values of the carbon atom of NCS group in benzoyl isothiocyanates and phenyl isothiocyanates also corresponds to the extent of changes in the π electronic charges (0.0082 e and 0.0202 e for benzoyl isothiocyanates and phenyl isothiocyanates³, respectively) which are even more distinct in this case. In the calculations of π electronic energies and charges of the X-substituted benzoyl isothiocyanates we took into account the planar conformers, *viz.* Z and E in the *para* substituted series and Z.

. *syn* (X, CO), *Z anti* (X, CO), *E syn* (X, CO), *E anti* (X, CO) in the *meta* substituted series. In the series mentioned the total π electronic energies involving repulsion of the nuclei attain considerably different values for these conformers (e.g. X = NO₂: the energy differences for the *para* and the *meta* conformers are 0.0496 and 1.3833 eV, respectively), and the respective δQ_π are significantly different, too, both in value and sign from the point of view of the correlations given (e.g. X = *p*-NO₂: $\delta Q_\pi = -0.0030$ and 0.0039 e for the *E* and *Z* conformers, respectively). It was shown that significant linear correlations with the ¹³C₈ SCS values are obtained from the δQ_π values of those conformers whose total π electronic energies attain lower or the lowest values. They are *Z* conformers in the *para* substituted benzoyl isothiocyanate series, and *Z syn* (X, CO) and *Z anti* (X, CO) in the *meta* substituted series with electron-donor and -acceptor substituents, respectively (Scheme 1). Table III gives the δQ_π values of these benzoyl isothiocyanate conformers.

TABLE I
¹³C Substituent chemical shifts (ppm) in *meta* and *para* substituted benzoyl isothiocyanates (solutions in C²HCl₃)

X	C ₍₁₎ ^a	C ₍₂₎	C ₍₃₎	C ₍₄₎	C ₍₅₎	C ₍₆₎	C ₍₇₎	C ₍₈₎
<i>p</i> -NMe ₂	19.6	-18.0	2.4	-13.9	2.4	-18.0	-1.8	-2.2
<i>p</i> -OMe	30.1	-14.6	2.4	-7.7	2.4	-14.6	-1.1	-0.4
<i>p</i> -Me	11.3	0.8	0.2	-2.6	0.2	0.8	-0.3	-0.2
<i>p</i> -F	31.9	-12.6	2.8	-3.6	2.8	-12.6	-1.0	1.1
<i>p</i> -Cl	6.7	0.4	1.3	-2.6	1.3	0.4	-0.6	1.3
<i>p</i> -Br	-6.8	2.9	2.0	-1.1	2.0	2.9	-0.3	1.8
<i>p</i> -CN	-17.0	3.5	0.3	3.4	0.3	3.5	-0.6	2.3
<i>p</i> -NO ₂	16.4	-4.9	1.1	5.0	1.1	-4.9	-0.7	2.9
<i>p</i> -CONCS	0.8	1.8	0.3	5.0	0.3	1.8	-0.3	2.2
<i>m</i> -NMe ₂	-16.2	21.5	-17.2	0.6	-11.8	0.6	0.5	-0.7
<i>m</i> -OMe	-13.3	31.0	-16.1	1.2	-7.4	1.0	-0.1	0.3
<i>m</i> -Me	0.6	10.0	0.5	-0.1	-3.1	0.0	0.0	-0.1
<i>m</i> -F	-13.0	38.7	-13.4	2.1	-4.2	1.7	-0.7	1.4
<i>m</i> -CF ₃	-3.3	1.7	-3.0	0.4	3.2	0.8	-0.3	2.6
<i>m</i> -Cl	0.2	6.3	0.8	1.6	-1.9	1.3	-0.8	1.6
<i>m</i> -Br	2.7	-5.9	2.9	2.2	-1.5	1.5	-0.8	1.7
<i>m</i> -CN	2.6	-15.2	3.5	1.3	3.8	1.2	-0.9	2.8
<i>m</i> -NO ₂	-4.8	19.7	-5.2	1.8	5.4	0.3	-0.9	3.2
<i>m</i> -CONCS	1.0	3.0	1.7	1.0	5.7	0.9	-0.5	2.5

^a Values of the chemical shifts (ppm) for the non-substituted benzoyl isothiocyanate (with respect to tetramethylsilane): 135.1 C₍₁₎; 128.9 C₍₂₎; 130.4 C₍₃₎; 130.9 C₍₄₎; 161.6 C₍₇₎; 147.6 C₍₈₎. For *meta*-substituted derivatives X is attached to C₍₂₎ carbon.

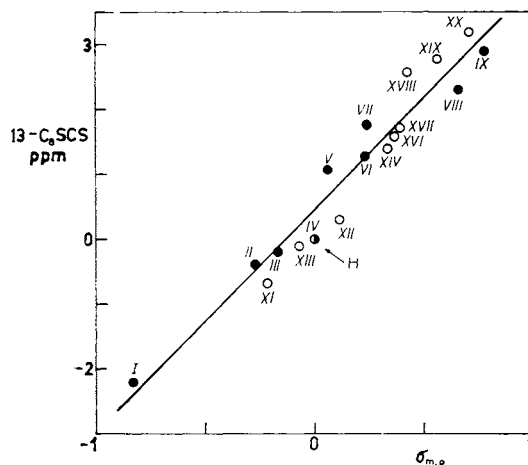


FIG. 1

Correlation of the $^{13}\text{C}_8$ SCS values with the Hammett substituent constants for *meta* (○) and *para* (●) substituted benzoyl isothiocyanates: slope = 3.5 ppm, $r = 0.969$, $n = 17$. Similar correlation of *meta* and *para* substituted phenyl isothiocyanates³ gave the slope = 5.9 ppm, $r = 0.982$, $n = 17$

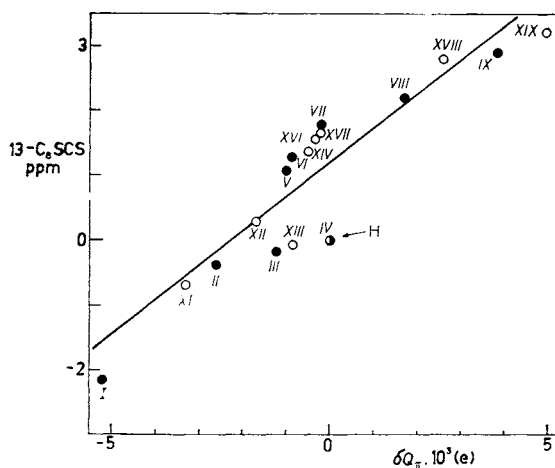
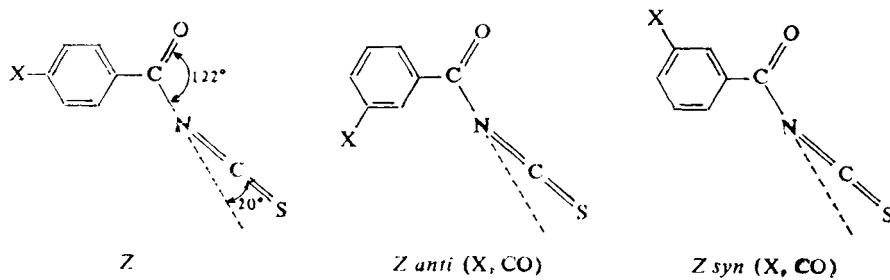


FIG. 2

Correlation between the $^{13}\text{C}_8$ SCS values and the corresponding relative π electronic charges δQ_π for *meta* (○) and *para* (●) substituted benzoyl isothiocyanates: slope = 645.9 ppm/e, $r = 0.970$, $n = 11$. Similar correlation of *meta* and *para* substituted phenyl isothiocyanates³ gave the slope = 278.3 ppm/e, $r = 0.902$, $n = 17$



SCHEME 1

On the basis of the correlations discussed a close interdependence could be expected between the ^{13}C SCS values of the carbon atom of NCS group in benzoyl

TABLE II
 ^{13}C Substituent chemical shifts (ppm) in meta and para substituted benzoyl chlorides (solutions in C^2HCl_3)

X	$\text{C}_{(1)}^a$	$\text{C}_{(2)}$	$\text{C}_{(3)}$	$\text{C}_{(4)}$	$\text{C}_{(5)}$	$\text{C}_{(6)}$	$\text{C}_{(7)}$
<i>p</i> - $\text{N}(\text{CH}_3)_2$	29.5	-9.2	2.1	-14.0	2.1	-9.1	-1.5
<i>p</i> - OCH_3	30.2	-14.6	2.6	-7.7	2.6	-14.6	-1.2
<i>p</i> - CH_3	11.5	0.8	0.1	-2.6	0.1	0.8	-0.3
<i>p</i> -F	31.9	-12.5	2.9	-3.5	2.9	-12.5	-1.4
<i>p</i> -Cl	7.0	0.5	1.2	-1.5	1.2	0.5	-1.0
<i>p</i> -Br	-4.1	3.5	1.2	-1.3	1.2	3.5	-0.7
<i>p</i> -CN	-16.7	3.8	0.1	3.4	0.1	3.8	-1.0
<i>p</i> - NO_2	16.4	-4.8	0.9	4.2	0.9	-4.8	-1.2
<i>p</i> -COCl	3.0	2.6	0.1	5.1	0.1	2.6	-0.8
<i>m</i> - $\text{N}(\text{CH}_3)_2$	-15.6	21.4	-17.3	0.7	-12.4	0.6	0.0
<i>m</i> - OCH_3	-13.5	31.0	-15.9	1.3	-7.3	1.0	-0.1
<i>m</i> - CH_3	0.8	10.1	0.3	0.0	-2.7	-0.2	0.0
<i>m</i> -F	-12.8	33.7	-13.3	2.1	-4.3	1.7	-1.0
<i>m</i> - CF_3	-3.5	1.0	-3.4	-0.5	3.0	-0.7	-0.8
<i>m</i> -Cl	0.0	6.4	0.3	1.7	-2.0	1.4	-1.1
<i>m</i> -Br	2.8	-5.9	2.5	1.8	-1.6	1.5	-1.2
<i>m</i> -CN	2.7	-15.1	3.2	1.3	3.4	1.3	-1.5
<i>m</i> - NO_2	-4.9	19.6	-5.4	1.6	4.9	0.6	-1.6
<i>m</i> -COCl	1.7	4.8	3.1	0.5	5.6	1.1	-1.1

^a Values of the chemical shifts (ppm) for the non-substituted benzoyl chloride (with respect to tetramethylsilane): 135.3 $\text{C}_{(1)}$; 128.9 $\text{C}_{(2)}$; 131.4 $\text{C}_{(3)}$; 133.2 $\text{C}_{(4)}$; 168.3 $\text{C}_{(7)}$.

isothiocyanates and phenyl isothiocyanates. This presumption was confirmed by finding linear correlation between the given values (^{13}C SCS (benzoyl isothiocyanates) = $0.61 \cdot ^{13}\text{C}$ SCS (phenyl isothiocyanates) + 0.26 ; correlation coefficient $r = 0.972$; number of points $n = 13$). Interestingly, no such correlation was found between the $^{13}\text{C}_8$ SCS values of benzoyl isothiocyanates and ^{19}F SCS values of benzoyl fluorides³¹. The correlation of these values is composed of two linear correlations, one for *meta* and the other for the *para* substituted series, the slope of the former straight line being about $3 \times$ greater than that of the latter. This result is probably connected with large contribution of inductive effect to transmission of substituent effects in the *meta* substituted series as compared with the *para* substituted series of benzoyl fluorides³¹, whereas no such drastic changes take place with benzoyl isothiocyanates (Table IV).

An interesting problem is presented by the transmission of the substituent effects to the carbonyl carbon atom in side chain of aromatic compounds whose $^{13}\text{C}_7$ SCS values do not give monoparameter correlations with the σ constants of substituents⁷⁻¹⁰. The carbonyl carbon atom of the benzoyl isothiocyanates studied by us shows a similar behaviour. It was proved^{9,31,32} that, also in conjugated sys-

TABLE III
Relative π electronic charges δQ_π ($\cdot 10^4$ e) of *meta* and *para* substituted benzoyl isothiocyanates

X	$C_{(1)}^a$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	O	N	$C_{(8)}$	S
<i>p</i> -N(CH ₃) ₂	42	-870	94	-511	94	-870	-27	-139	57	-55	-96
<i>p</i> -OCH ₃	323	-543	68	-284	68	-543	-7	-68	27	-26	-47
<i>p</i> -CH ₃	93	-47	-6	-44	-6	-47	2	-15	8	-12	-13
<i>p</i> -F	321	-315	41	-156	41	-315	-2	-36	13	-10	-24
<i>p</i> -Cl	207	-196	23	-101	23	-196	-1	-24	9	-9	-17
<i>p</i> -Br	128	-317	35	-177	35	-317	-5	-44	19	-2	-33
<i>p</i> -CN	-217	214	-1	167	-1	214	-13	40	-23	17	41
<i>p</i> -NO ₂	-693	281	42	283	42	281	-23	78	-55	39	91
<i>m</i> -N(CH ₃) ₂	-892	74	-737	48	-649	35	32	-44	43	-20	-49
<i>m</i> -OCH ₃	-549	342	-426	41	-405	20	15	-19	22	-17	-23
<i>m</i> -CH ₃	-45	118	70	-11	-154	-39	5	-10	7	-8	-10
<i>m</i> -F	-317	340	-203	26	-272	1	8	-9	11	-5	-12
<i>m</i> -Cl	-196	228	-83	13	-215	-20	6	-7	8	-3	-9
<i>m</i> -Br	-319	152	-198	18	-294	-143	10	-14	16	-2	-17
<i>m</i> -CN	209	-218	111	20	279	48	-8	12	-30	26	43
<i>m</i> -NO ₂	413	-685	322	57	450	84	-18	22	-62	50	95

^a Values of the π electronic charges δQ_π ($\cdot 10^4$ e) for the non-substituted benzoyl isothiocyanate: 110 $C_{(1)}$; -66 $C_{(2)}$; 311 $C_{(3)}$; -56 $C_{(4)}$; 2891 $C_{(7)}$; 1790 $C_{(8)}$; -4503 O; -3256 N; -2533 S.

tems, local polarization – and especially π polarization of functional groups – can play a more important role in the transmission of substituent effects than the total π polarization of the molecule does. Moreover, it was shown³³ that the ratio of inductive effect to resonance effect depends on electronic requirements of the reaction centre and is not constant. Therefore, we decided to investigate the substituent effects on the $^{13}\text{C}_7$ SCS and $^{13}\text{C}_8$ SCS values of the benzoyl isothiocyanates studied by means of the dual-substituent-parameter approach³⁵ which enables the analysis of the ^{13}C SCS values on the basis of the following relation:

$$^{13}\text{C SCS} = A \cdot F + B \cdot R,$$

where F and R are inductive and resonance parameters³⁶. The results of this approach are summarized in Table IV, wherefrom it follows that the resonance effect

TABLE IV

The A/B ratio of the inductive (A) and resonance contribution (B) to the transmission of substituent effects evaluated on the basis of the dual-substituent-parameter approach³⁵

Position of substituent X	BzITC ^a for C ₍₇₎	BzITC ^a for C ₍₈₎	BzCl ^a for C ₍₇₎	PhITC ^{3a} for C in NCS	BzF ^{31a} for 19-F
<i>para</i>	0.3	1.1	1.1	0.9	0.6
<i>meta</i>	0.7	1.4	8.9	0.7	8.3

^a The abbreviations: BzITC = benzoyl isothiocyanates, BzCl = benzoyl chlorides, PhITC = phenyl isothiocyanates, BzF = benzoyl fluorides.

TABLE V

Additive increments of CONCS group on aromatic nucleus

Position	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>
Z _i ^{CONCS}	2.4	1.9	0.2	5.8
S ^a	0.8	0.8	0.6	1.5
A ^b	16	23	23	16
B ^c	1	5	1	6

^a Standard deviation, ^b number of the experimental points used in the calculation, ^c and, out of them, number of those with the increment differing more than by ± 1 ppm from the average value of Z_i^{CONCS}.

is more important in the *para* substituted benzoyl isothiocyanates than in the *meta* substituted series, the resonance effect being more significant in the transmission to the carbonyl carbon atom, and the inductive effect being more significant in that to C atom of NCS. In the both series of benzoyl chlorides inductive effect predominates in the transmission of the substituent effects to the carbonyl carbon atom, its contribution in the *meta* substituted series being greater than in the *para* substituted series.

The ^{13}C SCS values of the carbon atoms of benzene nucleus are very close in the benzoyl isothiocyanates *I-XX* and benzoyl chlorides *XXI-XL*, which indicates similar transmission of the substituent effects to the side chain in the both cases. Very close linear correlations were also found for the corresponding ^{13}C SCS values at the carbon atoms of benzene ring in the case of benzoyl isothiocyanates and phenyl isothiocyanates³. An informative investigation of the ^{13}C SCS values in limited series (*i.e.* from the point of view of the minimum basis set³⁵) of benzoyl isothiocyanates, phenyl isothiocyanates, and benzoyl chlorides indicates that the ^{13}C SCS values for the carbon atoms of benzene rings of these systems are not precisely additive (this problem is dealt with in detail in ref.³⁴). Nevertheless, the additive increments are practically important in orientation analyses of NMR spectra. Therefore, we determined the values of additive increments of CONCS group at aromatic nucleus (Table V) from the relation

$$Z_i^{\text{CONCS}} = C_i^{\text{X}} - Z_j^{\text{X}} - 128.5$$

as average values for the non-substituted benzoyl isothiocyanate and the series of *meta* and *para* substituted benzoyl isothiocyanates. In the above relation, Z_i^{CONCS} means the additive increment of CONCS group for the *i*-th aromatic carbon atom, C_i^{X} is the chemical shift measured for the *i*-th carbon atom of the ring in the derivative carrying the X substituent, and Z_j^{X} is the additive increment of the X substituent³⁷. The indexes *i* and *j* denote the positions of CONCS group and the X substituent with respect to the aromatic carbon atom followed. Experimental values of the chemical shifts for X = *p*-CONCS, *m*-CONCS, *m*-F, *m*-CF₃ were not involved in the calculation because of the missing or ambiguous Z_j^{X} increments.

From the correlation between the ^{13}C SCS values and substituent constants (Fig. 1) we found the following values for CONCS group: $\sigma_p = 0.50$, $\sigma_m = 0.59$.

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