

ture was stirred at room temperature for 10 min. The reaction mixture was poured into cold water (50 cm³). Precipitated 2-aminobenzimidazole was filtered off, dried and crystallized from the ethanol–water mixture. Yield 75 mg (93 %), m.p. = 233–235 °C. The properties of obtained product are identical with an authentic sample [7, 8].

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REFERENCES

1. Woodcock, D., in *Systemic Fungicides*. (Marshal, R. W., Editor.) P. 60. Longman, London, 1977.
2. Banks, B. J., Walshe, N. D., and Witty, M. J., in *Comprehensive Heterocyclic Chemistry*, Part I, p. 202. (Katritzky, A. R. and Rees, C. W., Editors.) Pergamon Press, Oxford, 1984.
3. *The Pesticide Manual*. (Worthing, C. R., Editor.) P. 32. The British Crop Protecting Council, London, 1979.
4. Omar, A. M. M. E., Habib, N. S., and Aboulwafa, O. M., *Synthesis* 1977, 864.
5. Ram, S., Wise, D. S., and Townsend, L. B., *Heterocycles* 22, 1789 (1984).

6. Hritzová, O. and Kristian, P., *Collect. Czech. Chem. Commun.* 43, 3258 (1978).
7. *The Aldrich Library of Infrared Spectra*, Edition III. (Pouchert, Ch. J., Editor.) P. 1272 A. Aldrich Chemical Company, Milwaukee, Wisconsin, 1981.
8. *The Aldrich Library of NMR Spectra*, Vol. 8. (Pouchert, Ch. J. and Campbell, J. R., Editors.) P. 89 A. Aldrich Chemical Company, Milwaukee, Wisconsin, 1974.
9. Dixon, A. E., *J. Chem. Soc.* 67, 565 (1895).
10. *Brit.* 880807 (1958); *Chem. Abstr.* 53, 5134 (1959).
11. Johnson, T. B. and Chernoff, L. H., *J. Am. Chem. Soc.* 34, 164 (1912).
12. Hoggarth, E., *J. Chem. Soc.* 1949, 1160.
13. Boeger, M. and Drabek, J., *Ger.* 3,504,016 (1985); *Chem. Abstr.* 103, P 215196r (1985).
14. Smith, H. E., Cook, S. L., and Warren, M. E., *J. Org. Chem.* 29, 2261 (1944).
15. Kristian, P., Dzurilla, M., and Kováč, Š., *Chem. Zvesti* 23, 173 (1969).
16. Kutschy, P., Dzurilla, M., Ficeri, V., and Koščik, D., *Collect. Czech. Chem. Commun.* 58, 575 (1993).
17. Dzurilla, M., Kristian, P., and Jurkechová, A., *Chem. Zvesti* 32, 402 (1978).
18. Lipp, M., Allacker, F., and Koenen, G., *Chem. Ber.* 91, 1660 (1958).
19. Kutschy, P., Imrich, J., and Bernát, J., *Synthesis* 1983, 929.

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Synthesis and the ¹³C NMR Spectra of *N,N'*-Disubstituted Benzoylthioureas and Their Seleno and Oxo Analogues

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The influence of substituents on the ¹³C NMR chemical shift values of the aromatic ring carbons and —CO—NH—C(=X)— groups (X = S, Se, O) of a series of 27 *N*-benzoyl-*N'*-(*Y*-aryl)- and -*N'*-alkylthioureas, selenoureas, ureas, thiourethanes and isothioureas was investigated. As found, the substituents in *N*-benzoyl-*N'*-(4-*Y*-phenyl)thio(seleno)ureas do not considerably influence the ¹³C NMR chemical shifts of C=X and C=O carbons; the marked substituent effect is observed for the aromatic ring carbons only. This conclusion was also confirmed by correlations with χ_s and σ_p^+ constants of substituents. Differences between the benzoyl $\delta(\text{CO})$ values of *N'*-monosubstituted and *N,N'*-disubstituted thioureas indicate the existence of an intramolecular hydrogen bond in the acylthiourea grouping, namely between the benzoyl CO and the N'H groups. The ¹³C NMR chemical shift values of C=Se carbons in *N*-benzoyl-*N'*-(4-*Y*-phenyl)selenoureas are higher than those of the analogous C=S carbons of the corresponding thioureas. The ¹³C spectral chemical shift increments $\Delta\delta$ of —NHCSNHCOPh and —NHCSenHCOPh groupings on the benzene ring were calculated.

Acylthioureas are known precursors of nitrogen or sulfur-containing heterocycles because of their reactive —CONHC(S)NH— grouping. Cyclization of acylthioureas can be well observed by ¹³C NMR spectroscopy. This paper presents the study con-

cerning the influence of substituents of the —CONHC(=X)NH— grouping (X = S, Se, O) on the chemical shift values of C=X and C=O groups and aromatic ring carbons in the *N*-benzoyl-*N'*-substituted thioureas *I*, *II*, selenoureas *III*, and isothioureas *V*.

The analogous *N*-benzoyl-*N'*-(4-*Y*-phenyl)ureas — excepting the 4-methoxy and 4-methyl derivatives *IVa*, *IVb* — are only little soluble in both deuteriochloroform and hexadeuterodimethyl sulfoxide and therefore, their ^{13}C NMR spectra could not be measured.

Pytela and coworkers [1] reported a relatively weak transmission of the substituent effect in their ^{13}C NMR study with a series of *N*-(4-*Y*-benzoyl)-*N'*-phenyl- and -*N'*-methylthioureas except for the benzoyl system. *Jirman* and *Lyčka* [2] compared the ^{15}N NMR signals of mono- and diacylated ureas and thioureas and found a better transmission of the electron-accepting effect of the N-1 acyl on N-2 through the C=S group of thioureas than through the C=O group of ureas. This fact was rationalized by a greater capability of the C=S group to lower the electron density at both nitrogen atoms in relation to the CO group of ureas.

EXPERIMENTAL

The ^{13}C NMR spectra of samples in deuteriochloroform containing tetramethylsilane were measured with a Tesla BS 567 spectrometer (25.156 MHz) at 27 °C. Compounds *IVa*, *IVb* were recorded in hexadeuterodimethyl sulfoxide at 70 °C and 110 °C; the δ scale was calibrated against the highest peak of the solvent ($\delta = 39.39$). Concentration of the samples was approximately 0.35 mol dm $^{-3}$. The broadband decoupled and the off-resonance spectra were run with each compound; moreover, proton-coupled spectra were taken with several compounds to identify and ascribe the respective signals. Digital resolution of the transformed spectrum was 0.93 Hz per point, *i.e.* $\delta = 0.0369$ per point. Measuring parameters: 3 μs (30°) pulse width, 3 s acquisition time, 1500 to 3000 accumulations, 7.6 kHz spectral width, 8K and 16K data memory size and 7 W decoupling power. Carbons in Tables 1 to 5 are numerated in accordance with formula 1.

The compounds synthesized were characterized by comparing their melting points with those reported; new substances were identified by elemental analyses (C, H, N) — the results agreed with those calculated within ± 0.3 mass %.

N-Benzoyl-*N'*-*R*-thioureas *Ia*–*Ih*, *Ila*–*Ilg*

The appropriate amine (0.15 mol) in dry acetone (15 cm 3) was added during 3 min to the stirred solution of benzoyl isothiocyanate (0.1 mol) [3] in dry acetone (15 cm 3). The required thioureas, separating on standing, were filtered off and crystallized from ethanol. This procedure was applied for obtaining compounds *Ia* (m.p. = 170–173 °C, 78 %), *Ib*–*Ie*

(melting points correspond to those given in [4–6]), *If* (m.p. = 145–147 °C, 65 %), *Ig* (m.p. = 159–160 °C, 82 %), *Ih* [7], *Ila* [8], *Ilb* [9], *Ilc* (m.p. = 121–122 °C, 43 %), *Ild*, *Ile* [10], *Ilf* [11], *Ilg* (m.p. = 134–136 °C, 76 %).

N-(4-Methylbenzoyl)-*N'*-phenylthiourea (*Ii*) was synthesized from 4-methylbenzoyl isothiocyanate and aniline according to [12]. *N*-Benzoyl-*O*-methylthiourethane (*Ijh*) [13] and *N*-benzoyl-*O*-methylthiourethane (*Iji*) [13] were obtained from benzoyl isothiocyanate (20 mmol) and an equimolar amount of the respective alcohol by a 6 h reflux in dioxane (10 cm 3). The precipitate, filtered after cooling, was dried and crystallized from hexane. Compound *Ilj* was synthesized according to [14].

N-Benzoyl-*N'*-(4-*Y*-phenyl)selenoureas *IIla*–*IIId* [15]

Benzoyl chloride (0.2 mol) in dry acetone (5 cm 3) was added dropwise to the stirred solution of KSeCN (0.2 mol) in dry acetone (30 cm 3) and the precipitated KCl was removed after 10 min. The respective amine (0.2 mol) in acetone (30 cm 3) was added to the filtrate with stirring and after 30 min the solution was poured into water (50 cm 3). The precipitate was filtered off, washed with water and crystallized three times from ethanol. *IIla*: m.p. = 159–161 °C, yield 71 %; *IIlb*: 139–141 °C, 73 %; *IIlc*: 150–152 °C, 76 %; *IIId*: 164–166 °C, 83 %.

N-Benzoyl-*N'*-(4-methoxyphenyl)urea (*IVa*) and -*N'*-(4-Methylphenyl)urea (*IVb*)

The title compounds were synthesized by reacting benzoyl isocyanate [16] and 4-anisidine or 4-toluidine employing the procedure described for preparation of substances *Ia*–*Ih*. Other derivatives of urea *IV* (Z = O, Y = OH, H, Br, NO $_2$) were not sufficiently soluble for the NMR measurements.

N-Benzoyl-*N'*-(4-dimethylaminophenyl)-*S*-ethylisothiourea (*Va*) and -*N'*-phenyl-*S*-ethylisothiourea (*Vb*)

Thiourea *Ia* or *Ie* (5 mmol) was added slowly to LiH (6 mmol) suspended in dimethylformamide (50 cm 3). The mixture was heated at 50 °C till the thiourea dissolved and then stirred till the liberation of hydrogen ceased (approx. 1 h); afterwards, ethyl iodide (5 mmol) was added, the mixture was stirred at room temperature for 1 h, filtered and poured slowly in an ice-cold water (100 cm 3). The precipitate was filtered off, washed with water and dried. Yield of *Va* (m.p. = 153–155 °C) was 47 % and that of *Vb* (m.p. = 67–68 °C) 36 %.

RESULTS AND DISCUSSION

Derivatives of general formulas I–IV obtained by addition of amines or alcohols to benzoyl iso(thio)cyanates, soluble in CDCl_3 (with the exception of *N*-benzoyl-*N'*-(4-*Y*-phenyl)ureas) are well crystallizing compounds. Thioureas I, II and ureas IVa, IVb were prepared from the relatively stable benzoyl iso(thio)cyanates, the selenoureas IIIa–IIIId, obtained from the crude benzoyl isoselenocyanate, have to be purified by a multiple crystallization. The attempts to *S*-alkylate thiourea I to the corresponding isothiurea failed, because cleavage of the starting *N*-benzoyl-*N'*-(4-nitrophenyl)thiourea (Ih) took place under the given reaction conditions.

The ^{13}C NMR spectral data of compounds prepared are listed in Tables 1 to 3. The chemical shift values were ascribed to the proper carbons according to signal multiplicities in the proton-coupled and off-resonance spectra, as well as by comparing them with the values calculated by the increment method on the basis of empiric constants of substituents [17] and spectral chemical shift (SCS) constants of the —CONHCSNH— grouping as obtained from the ^{13}C NMR spectrum of compound Ie. The chemical shifts of aliphatic carbons were assigned by analogy with the data reported in Ref. [18].

Compounds I–III with the not substituted *N*-benzoyl fragment reveal a typical tetrad of C-3 to C-6 signals in their ^{13}C NMR spectra; signal positions are — with the exception of C-6 — virtually independent of the replacement of C=S for C=Se and also of the change of the substituent at *N'*. The C-4 and

C-5 signals could be distinguished unambiguously from the doublet-triplet signal for C-4 carbons and the doublet-doublet signal for C-5 carbons in the proton-coupled spectra. Comparison of ^{13}C NMR shifts of carbons C=S, C-7 to C-10 of *N*-benzoyl-*N'*-(4-*Y*-phenyl)thioureas Ia–Ih shows that the substituent effect of *Y* in position 4 is virtually restricted to ^{13}C NMR shifts of aromatic carbons only and influences very little the C=S chemical shifts ($\delta = 177.83$ for Ia in respect of $\delta = 178.05$ to 178.80 for Ib–Ih). Similar observation also holds for the series of selenoureas IIIa–IIIId, where the substituent effect is seen with carbons C-7 to C-10, whilst the position of C=Se is almost constant ($\delta = 180.15$ to 180.37) except for IIIa ($\delta = 179.02$ — a little lower — analogous with Ia). The close range of ^{13}C NMR shifts of the C=S carbons of thiourea derivatives I (177.83 to 178.80) and C=Se carbons of selenourea derivatives III (179.02 to 180.37) indicates their chemical similarity. A little higher shift values $\delta(\text{C=Se})$ are associated probably with the higher polarity of the C=Se bond and the less perfect compensation of the partial positive charge at the C=Se carbon by the remaining moiety of the molecule [19, 20].

The ^{13}C NMR chemical shifts of aromatic C-7 carbons in the *para* position with respect to the substituent *Y* with compounds Ia–Ih displayed a Hammett correlation dependence on the σ_p^+ constants of substituents *Y* ($\rho = 6.84$, $r = 0.966$). This series also revealed an increasing trend of C-10 (*ipso*) shifts with rising electronegativity of the substituent χ_s [21, 22]. The correlation parameters of eight compounds Ia–Ih ($\rho = 18.94$, $r = 0.719$) improved when the chemi-

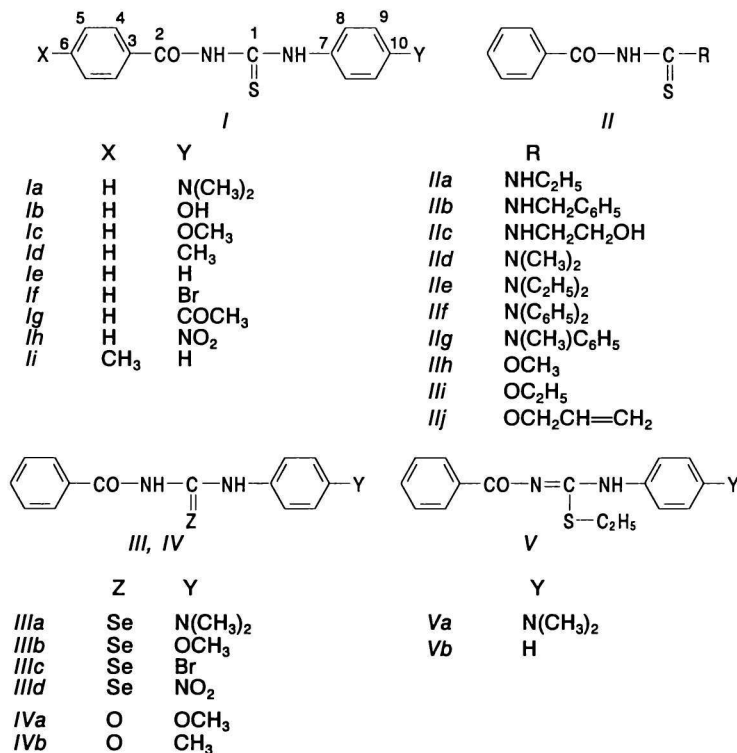


Table 1. ^{13}C NMR Chemical Shift δ Values for *N*-Benzoyl-*N'*-(4-*Y*-phenyl)thioureas *la–l* and *S*-Ethyl-*N*-benzoyl-*N'*-(4-*Y*-phenyl)isothioureas *Va, Vb*

Compound	Y	δ											
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-Y	
<i>la</i>	$\text{N}(\text{CH}_3)_2$	177.83	166.78	131.84	127.43	129.08	133.48	126.84	125.27	112.13	149.31	40.46	
<i>lb</i>	OH	178.80	167.00	131.76	127.51	129.30	133.78	130.79	126.16	115.71	154.46		
<i>lc</i>	OCH_3	178.48	166.91	131.67	127.49	129.14	133.61	130.63	125.78	114.06	158.17	55.46	
<i>ld</i>	CH_3	178.35	166.93	131.69	127.51	129.15	133.63	135.12 ^c	124.08	129.45	136.77 ^c	21.13	
<i>le</i>	H	178.27	166.93	131.62	127.51	129.15	133.63	137.66	124.00	128.85	126.84		
<i>lf</i>	Br	178.33	166.98	131.45	127.49	129.21	133.84	136.68	125.48	131.97	119.96		
<i>lg</i>	COCH_3	178.05	167.08	131.47	127.58	129.23	133.93	141.77	123.03	129.23	134.97	196.79, 26.58	
<i>lh</i>	NO_2	178.20	167.15	131.24	127.58	129.38	134.15	143.26	124.60	123.18	145.17		
<i>li</i>	H ^a	178.42	166.85	128.92	127.51	129.90	144.76	137.66	124.08	128.85	126.84	21.65	
<i>Va</i>	$\text{N}(\text{CH}_3)_2^b$	174.39	176.26	137.96	129.60 ^c	128.03 ^c	131.69	125.20	127.44	112.21	149.91	40.39	
<i>Vb</i>	H ^d	173.20	176.48	137.66	129.60 ^c	128.11 ^c	131.91	136.69	126.09	129.23 ^c	127.66		

a) X = CH₃; b) 25.98 and 14.63 (SCH₂CH₃); c) the values can be interchanged; d) 25.98 and 14.56 (SCH₂CH₃).

Table 2. ^{13}C NMR Chemical Shift δ Values for Substituted *N*-Benzoyl-*N'*-Alkylthioureas *IIa–IIg* and Substituted *N*-Benzoyl-*O*-alkylthiourethanes *IIh–IIj*

Compound	R	δ											CH ₂	CH ₃
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10			
<i>IIa</i>	NHC_2H_5	179.62	167.00	131.91	127.51	129.08	133.41						40.69	13.59
<i>IIb</i>	$\text{NHCH}_2\text{C}_6\text{H}_5$	180.07	166.85	131.77	127.51	129.08	133.48	136.24	127.88	128.85	127.88		49.79	
<i>IIc</i>	$\text{NHCH}_2\text{CH}_2\text{OH}$	180.89	166.93	132.06	127.58	129.15	133.48						48.00	
													60.69	
<i>IId</i>	$\text{N}(\text{CH}_3)_2$	180.22	163.57	132.36	127.96	128.70	132.89							43.00
														44.12
<i>IIe</i>	$\text{N}(\text{C}_2\text{H}_5)_2$	179.69	164.09	132.73	127.88	128.70	132.73						47.70	11.57
													47.70	13.14
<i>IIf</i>	$\text{N}(\text{C}_6\text{H}_5)_2$	182.75	162.60	132.81	127.81	128.78	132.81	145.80	126.99	129.30	127.51			
<i>IIg</i>	$\text{N}(\text{CH}_3)\text{C}_6\text{H}_5$	180.66	162.90	132.81	127.58	128.63	132.59	145.20	125.49	129.38	127.81			45.54
<i>IIh</i>	OCH_3	190.29	162.60	132.81	127.73	128.93	133.18							59.43
<i>III</i>	OC_2H_5	189.40	163.05	132.88	127.81	128.85	133.03						69.21	13.66
<i>IIj</i> ^a	<i>O</i> -allyl	188.88	163.19	132.81	127.88	128.63	132.96						72.79	

a) 130.42 and 119.30 (CH=CH₂).

Table 3. ^{13}C NMR Chemical Shift δ Values for *N*-Benzoyl-*N'*-(4-*Y*-phenyl)selenoureas *IIIa–IIIc* and *N*-Benzoyl-*N'*-(4-*Y*-phenyl)ureas *IVa, IVb*

Compound	Y	δ											
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-Y	
<i>IIIa</i>	$\text{N}(\text{CH}_3)_2$	179.02	166.85	131.46	127.51	129.23	133.71	127.51	125.57	111.98	149.68	40.46	
<i>IIIb</i>	OCH_3	180.15	166.93	131.47	127.59	129.16	133.79	131.32	126.17	114.15	158.65	55.47	
<i>IIIc</i>	Br	180.37	167.08	131.47	127.66	129.30	134.01	137.74	126.09	132.21	120.79		
<i>IIId</i>	NO_2	180.37	167.15	130.94	127.66	129.45	134.38	143.76	124.67 ^a	124.08 ^a	145.88		
<i>IVa</i> ^c	OCH_3	150.63	168.17	132.12	127.71 ^a	128.01 ^a	132.34	130.25	121.22	113.83	155.48	54.92	
<i>IVb</i> ^c	CH_3	150.33	168.10	132.12 ^b	127.64 ^a	127.93 ^a	132.41	134.65	119.50	128.76	132.26 ^b	19.76	

a, b) The values can be interchanged; c) in DMSO-*d*₆.

cal shift value for C-10 of the derivative *lf* (Y = Br) ($\rho = 16.38$, $r = 0.844$) was omitted. This improvement was rationalized [22] by the fact that bromine belongs to another period than the remaining seven substituents Y.

The chemical shift values of carbonyl carbons C-2 of derivatives *la–li*, *IIa–IIc*, and *IIIa–IIId* were almost identical (166.78 to 167.15); on the other hand, these values for thioureas and thiourethanes (*IIId–IIj*) were found to be by 2 to 4 lower (162.60 to

164.09), which evidences clearly the existence of an intramolecular hydrogen bond between the C-2 carbonyl and the N–H of the *N*-benzoyl-*N'*-mono-substituted thioureas *la–li*, *IIa–IIc* and selenoureas *IIIa–IIId*. The ^{13}C NMR chemical shift values $\delta(\text{C}=\text{S})$ of *N'*-alkyl-, dialkyl-, diaryl-, and alkylarylthioureas *IIa–IIg* showed a greater variability (179.62 to 182.75) than compounds *la–li*. As anticipated, the chemical shifts of C-1 carbons of thiourethanes *IIh–IIj* (188.88 to 190.29), ureas *IVa, IVb* (150.33 to

Table 4. ^{13}C SCS Increments $\Delta\delta$ of the $\text{C}_6\text{H}_5\text{—CO—NH—C(=Z)—NH}$ ($Z = \text{S, Se, O}$) Grouping on the Benzene Ring and the Standard Deviation s

X	$\Delta\delta$											
	$\text{C}_6\text{H}_5\text{—CO—NH—CS—NH—}$				$\text{C}_6\text{H}_5\text{—CO—NH—CSe—NH—}$				$\text{C}_6\text{H}_5\text{—CO—NH—CO—NH—}$			
	<i>i</i>	<i>o</i>	<i>m</i>	<i>p</i>	<i>i</i>	<i>o</i>	<i>m</i>	<i>p</i>	<i>i</i>	<i>o</i>	<i>m</i>	<i>p</i>
$\text{N}(\text{CH}_3)_2$	10.1	-4.0	-0.7	-1.6	10.8	-3.7	-0.8	-1.2				
OH	9.6	-3.7	-0.1	-0.9								
OCH_3	10.2	-3.6	0.3	-0.5	10.9	-3.2	0.4	-0.1	9.9	-8.2	0.0	-3.2
CH_3	9.7	-4.4	0.3	-1.0					9.3	-9.0	-0.3	-5.5
H	9.2	-4.5	0.4	-1.7								
Br	9.2	-5.2	0.2	-3.1	10.2	-4.6	0.4	-2.3				
COCH_3	9.1	-5.7	0.5	-2.8								
NO_2	8.8	-4.7	0.0	-2.9	9.3	-4.6	0.9	-2.2				
Mean values	9.5	-4.5	0.1	-1.8	10.3	-4.0	0.2	-1.4	9.6	-8.6	-0.2	-4.4
<i>s</i>	0.5	0.7	0.4	1.0	0.8	0.7	0.7	1.1	0.4	0.6	0.3	1.6

i — ipso, *o* — ortho, *m* — meta, *p* — para, *s* — standard deviation.

Table 5. ^{13}C SCS Increments $\Delta\delta$ of the —CO—NH—C(=Z)—NH—R ($Z = \text{S, Se, O}$) Grouping on the Benzene Ring and the Standard Deviation s

Z	R	<i>ipso</i>		<i>ortho</i>		<i>meta</i>		<i>para</i>	
		$\Delta\delta$	<i>s</i>	$\Delta\delta$	<i>s</i>	$\Delta\delta$	<i>s</i>	$\Delta\delta$	<i>s</i>
S	Aryl	3.1	0.2	-1.0	0.0	0.7	0.1	6.3	0.2
S	Alkyl	3.9	0.4	-0.8	0.2	0.4	0.2	4.6	0.4
Se	Aryl	2.8	0.3	-0.9	0.1	0.8	0.1	5.5	0.3
O	Aryl	3.6	0.0	-0.8	0.0	-0.5	0.1	3.9	0.0

150.63), and isothiureas *Va*, *Vb* (173.20 to 174.39) differ considerably, but only the chemical shift values for C-2 of thiureas (176.26 to 176.48) were quite different from those of compounds *I—IV* (162.26 to 167.15). The probable reason for this enhancement is the existence of a conjugated isothiurea system $\text{C}_6\text{H}_5\text{—C(=O)N=C}(\text{SC}_2\text{H}_5)\text{—NH—C}_6\text{H}_4\text{—Y}$ deshielding the carbonyl carbon [23].

The ^{13}C NMR chemical shifts of compounds under study served for calculation of ^{13}C SCS increments $\Delta\delta$ of the $\text{C}_6\text{H}_5\text{—CO—NH—C(=Z)—NH—}$ ($Z = \text{S, Se, O}$, Table 4) and —CO—NH—C(=Z)—NHR ($Z = \text{S, R} = \text{alkyl, aryl}$; $Z = \text{Se, R} = \text{aryl}$; $Z = \text{O, R} = \text{aryl}$, Table 5) groupings on the benzene ring. The results obtained showed similar SCS increments $\Delta\delta$ of the carbonylthiurea and carbonylselenourea groupings on the benzene ring as did $\text{C}_6\text{H}_5\text{—CO—NH—C(=Z)—NH—}$ ($Z = \text{S, Se}$) and —CO—NH—C(=Z)—NHR ($Z = \text{S, Se}$) substituents. Nonetheless, the carbonyl urea grouping $\text{C}_6\text{H}_5\text{—CO—NH—CO—NH—}$ is characterized by a relatively strong shielding effect on the *ortho* (-8.6) and *para* (-4.4) carbons in the benzene ring when compared with that of thio and seleno analogues (Table 4); this finding is in accordance with the higher electron density observed at both benzoylurea nitrogens in regard to benzoylthiureas [2, 24].

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REFERENCES

- Pytela, O., Jirman, J., and Lyčka, A., *Collect. Czech. Chem. Commun.* 54, 2399 (1989).
- Jirman, J. and Lyčka, A., *Collect. Czech. Chem. Commun.* 52, 2474 (1987).
- Johnson, T. B. and Chernoff, L. J., *J. Am. Chem. Soc.* 34, 164 (1912).
- Douglass, I. B. and Dains, F. B., *J. Am. Chem. Soc.* 56, 1408 (1934).
- Gach, I. G. and Nazarova, Z. U., *Zh. Obshch. Khim.* 30, 2183 (1960).
- Frank, Z. R. and Smith, P. A., *Org. Synth., Coll. Vol. III*, 735 (1955).
- Dyer, E. and Johnson, T. B., *J. Am. Chem. Soc.* 54, 777 (1932).
- Dixon, A. E., *J. Chem. Soc. (London)* 75, 383 (1899).
- Miquel, M. P., *Ann. Chim. Phys.* 11, 324 (1877).
- Vijayakumaran Nair, G., *J. Indian Chem. Soc.* 40, 953 (1963).
- Dixon, A. E. and Taylor, J., *J. Chem. Soc. (London)* 93, 693 (1908).
- Smith, P. A. and Kan, R. O., *J. Org. Chem.* 29, 2261 (1964).
- Dixon, A. E., *J. Chem. Soc. (London)* 75, 375 (1899).
- Kutschy, P., Dzurilla, M., Koščik, D., and Kristian, P., *Collect. Czech. Chem. Commun.* 52, 1764 (1987).
- Douglass, I. B., *J. Am. Chem. Soc.* 59, 740 (1937).
- Speziale, A. S. and Smith, K. R., *J. Org. Chem.* 28, 1805 (1963).
- Pretsch, E., Seibl, J., Simon, W., and Clerc, T., *Tables of Spectral Data for Structure Determination of Organic Compounds*, p. C212. Springer-Verlag, Berlin, 1983.
- Bremser, W., Ernst, L., Franke, B., Gerhards, R., and Hardt, R., *Carbon-13 NMR Spectral Data*. Verlag Chemie, Weinheim, 1981.
- Kristian, P. and Suchár, G., *Collect. Czech. Chem. Commun.* 37, 3066 (1972).
- Suchár, G. and Kristian, P., *Collect. Czech. Chem. Commun.* 40, 2998 (1975).
- Spiesecke, H. and Schneider, W. G., *J. Chem. Phys.* 38, 2803 (1963).
- Inamoto, N. et al., *Tetrahedron Lett.* 1976, 3707.
- Walter, W. and Ruback, W., *Liebigs Ann. Chem.* 1982, 231.
- Kaválek, J., El Bahaie, S., and Štěrbá, V., *Collect. Czech. Chem. Commun.* 49, 2103 (1984).

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