KINETICS AND MECHANISM OF HYDROLYSIS OF BENZHYDRYL N-ARYLTHIOCARBAMATES AND STUDY OF THEIR IR SPECTRA

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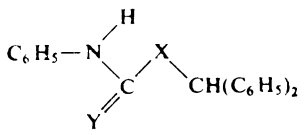
Received August 30th, 1983

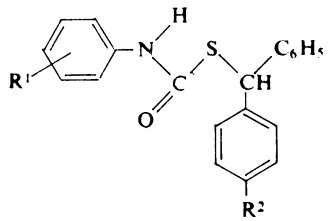
The hydrolysis of benzhydryl N-arylthiocarbamates proceeds by the ElcB mechanism. The reaction mechanism of S-benzhydryl N-arylthiocarbamates has been determined by trapping the reactive intermediate phenyl isocyanate (as N-phenyl-N'-morpholinourea) and by following the substituent effects in benzene ring of the benzhydryl group. The hydrolysis mechanism of O-benzhydryl N-arylthiocarbamates has been confirmed by spectral and kinetic determination of phenyl isothiocyanate. The hydrolysis of the primary formed phenyl isothiocyanate is almost 10 times slower than that of the starting thiocarbamate. With O-benzhydryl N-arylthiocarbamates at pH below 9 there takes place, at first, a rapid rearrangement to S-benzhydryl N-arylthiocarbamates, and benzhydrol is the reaction product. The rearrangement rate is pH independent. At pH above 11·5 the hydrolysis of O-benzhydryl N-arylthiocarbamates is much faster than the rearrangement, and thiobenzhydrol is the reaction product. Using the deuterated derivatives, the IR spectra of carbamates and thiocarbamates have been interpreted with respect to coupled vibrations of carbamic, thiocarbamic, and dithiocarbamic groups.

Recently a number of pesticides have been used based on S-alkyl thiocarbamates which have higher selectivity and efficiency than their oxygen analogues[1,2]. The present communication deals with kinetics and mechanism of hydrolysis of benzhydryl N-arylthiocarbamates which are more complex than those of the compounds studied so far.

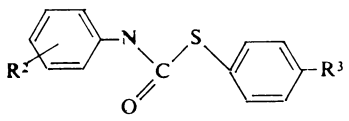
In contrast to secondary amides and thioamides[3], which were studied in detail, there exist only sporadic papers dealing with vibrational analysis of IR spectra of carbamates[4] and thiocarbamates[5]. The reason lies perhaps in the difficulties connected with the vibrational coupling of secondary amide and, especially, secondary thioamide groups, such interpretations being often different with different authors even in the cases of small molecules[6]. The present communication attempts to assign some bands of characteristic group vibrations of the studied O-benzhydryl N-phenyl carbamates (*I*), S-benzhydryl N-phenylthiocarbamates (*II*), and O-benzhydryl N-phenylthiocarbamates (*III*), as well as that of S-benzhydryl N-phenyldithiocarbamates (*IV*) and derivatives *IIa*–*IVa* (ref.[7]).



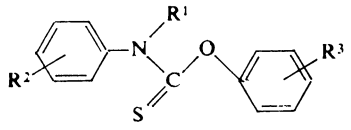
I, X = Y = O
III, X = O, Y = S
IV, X = Y = S



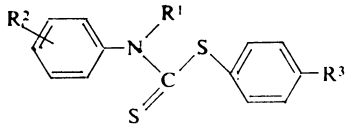
II, R^1 = H, 4-CH_3, 3-OCH_3, 3-Cl,
R^2 = H, CH_3, Cl



IIa, R^1 = H, CH_3
R^2 = H, 4-NO_2, 3-Cl
R^3 = H, CH_3



IIIa, R^1 = H, CH_3
R^2 = H, 4-NO_2
R^3 = H, 4-CH_3, C—Cl



IVa, R^1 = H, CH_3
R^2 = H, 3-Cl, 4-Br
R^3 = H, Cl, CH_3

EXPERIMENTAL

Reagents

Thiobenzhydrol and its 4-methyl- and 4-chlorosubstituted derivatives were prepared in the standard way[8] from S-benzhydrylthiouronium salts. The said compounds were purified by transformation to the corresponding lead(II) salts by reaction with methanolic lead(II) acetate and decantation with methanol. The salts were decomposed with aqueous 5% sulphuric acid (boiling) and extracted with ether after cooling. 4-Methylthiobenzhydrol b.p. 160—162°C/1·6 kPa, n_D^{20} 1·6285; 4-chlorothiobenzhydrol b.p. 168—170°C/1·3 kPa, n_D^{20} 1·6222. The benzhydryl chlorides were prepared according to Nishida[9]. 4-Nitrophenyl isocyanate was prepared from 4-nitroaniline[10].

S-*Benzhydryl* N-*arylthiocarbamates*: Solution of 0·01 mol of the respective thiobenzhydrol in 5 ml benzene was mixed with solution of the substituted phenyl isocyanate in 5 ml benzene. After addition of two drops of pyridine, the mixture was heated in a sealed glass ampoule on boiling water bath 2 h. After cooling the separated product was recrystallized from n-heptane, col-

lected by suction, washed with pentane, and dried. The yields varied within the limits 48—75%. Table I gives melting points and elemental analyses of the products.

O-Benzhydryl N-phenylthiocarbamate: Solution of 1·85 g (0·01 mol) benzhydrol in 10 ml dioxane was treated with 0·3 g (0·013 mol) sodium hydroxide added within 15 min with stirring. Thereafter 1·5 g (0·01 mol) phenyl isocyanate was added, and the mixture was heated on boiling water bath with stirring 30 min. After cooling the mixture was poured in 100 ml water and 3 ml acetic acid. The separated solid was collected, dried, and recrystallized from a 1 : 1 mixture of ethyl acetate and hexane. Yield 2 g (62%), m.p. 128—129°C in accordance with ref.[11].

S-Benzhydryl N-phenyldithiocarbamate was prepared from thiobenzhydrol and phenyl isothiocyanate in similar way as that given previously[12] for diaryldithiocarbamates. Yield 73%, m.p. 129—130°C (in accordance with ref.[13]). Benzhydryl N-phenylcarbamate was prepared from benzhydrol and phenyl isocyanate[14]. N-Phenyl-N'-morpholinourea was prepared by reaction[15] of morpholine and phenyl isocyanate in ether; m.p. 162—163°C.

Hydrolysis of S-Benzhydryl N-Phenylthiocarbamate and of Its Hydrolysis Intermediate

A) Solution of 0·25 g S-benzhydryl N-phenylthiocarbamate in 5 ml dioxane was mixed with solution of 1 ml morpholine in 10 ml dioxane and 15 ml borax buffer of pH 8·40 (pH of the mixture was 10·15 at 25°C). The mixture was refluxed on water bath 1 h, cooled, and extracted with 2 × 25 ml ether. The extract was washed with 3 × 25 ml water, 2 × 25 ml 1M-HCl, and again with 25 ml water. After drying with anhydrous sodium sulphate, the solvent was evaporated,

TABLE I

Elemental analyses and physical constants of the substituted S-benzhydryl N-phenylthiocarbamates $XC_6H_4NHCOSCH(C_6H_5)C_6H_4Y$

X Y	M.p., °C	Formula (mol.mass)	Calculated/Found		
			% C	% H	% N
H		$C_{21}H_{19}NOS$	75·64	5·74	4·20
4-CH_3	117—118	(333·4)	75·14	6·60	4·21
H		$C_{20}H_{16}ClNOS$	67·88	4·55	3·98
4-Cl	112—113	(353·8)	68·02	4·79	4·37
4-NO_2		$C_{20}H_{16}N_2O_3S$	65·92	4·42	7·68
H	174 (decomp.)	(364·4)	65·99	4·47	7·40
3-CH_3		$C_{21}H_{19}NOS$	75·18	5·47	4·01
H	125—127	(333·4)	75·07	5·89	3·90
4-CH_3		$C_{21}H_{19}NOS$	75·64	5·74	4·20
H	154—156	(333·4)	76·40	6·80	4·30
3-Cl		$C_{20}H_{16}ClNOS$	67·89	4·55	3·96
H	130—131	(358·8)	67·86	4·40	4·00

and the residue was decanted with 2 × 5 ml pentane. Yield of N-phenyl-N'-morpholinourea was 0·04 g (25%), m.p. 159–161°C.

B) Mixture of 0·2 ml phenyl isocyanate, 1 ml morpholine, 25 ml dioxane, and 5 ml aqueous buffer of pH 8·40 was heated at 80°C 10 min, cooled, and extracted with 30 ml ether. The extract was washed successively with water, 5% hydrochloric acid, and water, and the solvent was evaporated to give 0·137 g (38%) N-phenyl-N'-morpholinourea, m.p. 158–161°C.

C) Solution of 0·2 g N-phenyl-N'-morpholinourea in 25 ml dioxane and 5 ml borax buffer of pH 8·40 was heated on boiling water bath 1 h. The starting substance, separated on cooling, was isolated in the same way as sub *A*) (except for the decantation with pentane). Yield 0·08 g (40%), m.p. 161–163°C.

D) Solution of 0·2 g S-benzhydryl N-phenylcarbamate in 5 ml dioxane was mixed with 5 ml 5% aqueous sodium hydroxide and boiled 15 min. The mixture was cooled and acidified to pH 5 and extracted with ether. According to chromatography the extract contained thiobenzhydrol and aniline.

Hydrolysis of O-Benzhydryl N-Phenylthiocarbamate

A) Solution of 0·1 g O-benzhydryl N-phenylthiocarbamate in 10 ml dioxane was mixed with 100 ml 50% aqueous–dioxane buffer of pH 10·22, and the mixture was boiled 15 min. After cooling the mixture was extracted with ether, the extract was washed with water and concentrated to 2 ml. Chromatographic analysis of this sample gave the following results: 3 mg aniline, 35 mg phenyl isothiocyanate, 26 mg benzhydrol, 30 mg thiobenzhydrol. The last component of the mixture was separated by reaction with methanolic lead(II) acetate; the obtained lead(II) salt was decomposed with 5% aqueous sulphuric acid, and thiobenzhydrol was identified again by GLC.

B) O-Benzhydryl N-phenylthiocarbamate (0·1 g) was hydrolyzed similarly as sub *A*) in a buffer of pH 6·51 for 5 min. Thereafter pH of the solution was adjusted at 12·71 by addition of solid potassium hydroxide, and the mixture was boiled 30 min. The product contained 25 mg aniline, 4 mg benzhydrol, and 49 mg thiobenzhydrol.

C) Solution of 0·1 g O-benzhydryl N-phenylthiocarbamate in 10 ml dioxane was mixed with 100 ml 50% aqueous–dioxane buffer of pH 12·5, and the mixture was treated as sub *A*). The GLC analysis found only 25 mg aniline and 54 mg benzhydrol.

Kinetic Measurements

The hydrolysis kinetics of the studied thiocarbamates, dithiocarbamate, carbamate, and phenyl isothiocyanate were measured spectrophotometrically in 50% aqueous dioxane in phosphate, borax, and carbonate buffers with constant ionic strength $\mu = 0{\cdot}1$, or in solutions of potassium hydroxide. The measurements were carried out in the pH range from 7 to 13·2 at 50°C or different temperatutures (in the latter case the reaction rate was recalculated according to the Arrhenius relation). The reaction mixture was prepared by injecting 1 µl dioxane solution of the substrate to 5 ml buffer solution in a temperated cell. The substrate concentration in the solution was within 1 to 2 . 10^{-5} mol l^{-1}. A Unicam SP 800 B or a Specord UV-VIS apparatus was used for the measurements, and a Durrum–Gibson model D-110 was used for the hydrolyses with half-lives below 20 s. The reaction was followed by the substrate absorbance decrease at 260 nm. The hydrolysis of O-benzhydryl N-phenylcarbamate at pH above 11 was followed at λ 247 nm at which the absorbance of phenyl isothiocyanate is much greater than that of the starting thio-

carbamate. The rate constants of formation and subsequent hydrolysis of phenyl isothiocyanate were calculated numerically from kinetic equation for consecutive reactions using an EC 1033 computer.

To prove phenyl isocyanate as the reaction intermediate, the hydrolysis kinetics of S-benzhydryl N-phenylthiocarbamate was measured at pH 8·50 and 10·15 in the presence of morpholine of the concentrations $2 . 10^{-2}$ and 10^{-1} mol l^{-1}. The values of the individual samples were measured with a pH Meter 4c (Radiometer, Copenhagen) at 25°C.

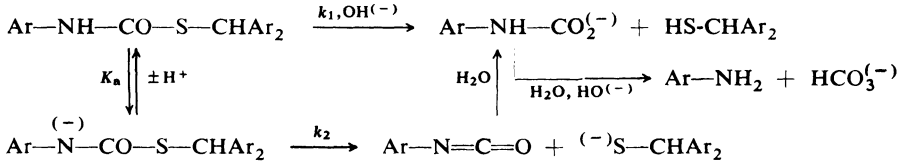
The rearrangement rates of O-benzhydryl N-phenylthiocarbamate were measured by the method of withdrawing samples from the solution of 0·6 g substrate and 0·25 g 4-chlorobenzonitrile in 3 ml dioxane and 750 ml 50% aqueous–dioxane buffer (pH 4·8, 6·4, and 7·4) temperated at 50°C. The 50 ml samples were diluted each with 100 ml ether (cooled at −5°C), and the ether extracts were washed with water, dried with sodium sulphate, and the solvent was evaporated. The IR spectra of these samples were measured in tetrachloromethane or Nujol using a Specord 75 IR, or a Perkin–Elmer 684, or a Spektromom 2000 apparatus. The wave number scale was calibrated with polystyrene. The deuterium exchange reaction was carried out by precipitation of solutions of 0·2 to 0·5 g of the compounds *I*—*III* in dioxane with heavy water. The rate constants were calculated from the relation $k_{obs} . t = -2{\cdot}3 \log ((A^{CO}/A^{CN})_t - (A^{CO}/A^{CN})_\infty) +$ + const. The A^{CO} values of the absorbance of the band of valence vibration of carbonyl group (at 1 662 cm^{-1}) of the S-benzhydryl N-phenylthiocarbamate being formed were determined from the height of the band. Similarly the values A^{CN} were determined from the band height at 2 233 cm^{-1} of the spectrum of the standard.

All the GLC analyses were carried out with a gas chromatograph Carlo Erba model GV with a column of 1 m length packed with Chromosorb A/SE 30 at 190°C.

RESULTS AND DISCUSSION

Hydrolysis of S-*Benzhydryl* N-*Phenylthiocarbamate*

In the solutions used for the kinetic measurements the hydrolysis of S-benzhydryl N-phenylthiocarbamate produced aniline and thiobenzhydrol. Two mechanisms (Scheme 1) can be considered for this hydrolysis.



SCHEME 1

The hydrolysis going *via* $B_{Ac}2$ mechanism involves direct attack of carbonyl group of the neutral substrate by hydroxyl ion with simultaneous splitting off of thiobenzhydrol. In ElcB mechanism the conjugated base of the substrate is decomposed to phenyl isocyanate and diphenylmethanethiolate anion in the rate-limiting step. Phenyl isocyanate then reacts rapidly with water (or with hydroxyl ion – at higher

pH values) to give the carbamate ion which is thus the intermediate of the both mechanisms. Its decarboxylation is acid catalyzed[16], hence the decarboxylation rate decreases with increasing pH value until – at sufficiently high pH values – carbamate ion accumulates in the reaction mixture. Therefore, the hydrolysis rate was followed by the absorbance decrease at 260 nm, where the absorbance of the substrate is high, whereas those of phenylcarbamate ($C_6H_5NHCO_2^{(-)}$) and aniline are small and approximately the same, so that the conversion of carbamate to aniline does not make itself felt spectrally. Under these conditions the hydrolysis was first-order reaction in all the cases. The pH dependence of log k_{obs} was linear in the whole range measured with the slope 1, *i.e.*, dissociation of the substrate is slight even at the highest pH values. The rate constants of the two reaction paths are defined by Eqs (*1*) and (*2*).

$$k_{obs} = k_1[OH^{(-)}] \tag{1}$$

$$k_{obs} = k_2 \,.\, K_a/[H^{(+)}] = k_2 \,.\, K_a[HO^{(-)}]/K_{H_2O} \tag{2}$$

Two methods were used for determination of the reaction mechanism, *viz.* trapping of the reactive intermediate – phenyl isocyanate – and determination of substituent effects on k_{obs}. In the former case we used morpholine to trap phenyl isocyanate in the form of N-phenyl-N′-morpholinourea, because aromatic amines used in great excess for this purpose interfere (due to their strong absorptions at 260 nm) with spectrophotometric measurement of the reaction rate. When the parent phenyl isocyanate was used for the reaction, the yield of N-phenyl-N′-morpholinourea was 38%, *i.e.*, the same as in the isolation of the separately prepared N-phenyl-N′-morpholinourea carried out under the same conditions. The yield of the substituted urea was 25% in the hydrolysis of X-benzhydryl N-phenylthiocarbamate in the presence of morpholine carried out under the same conditions as in the reaction of phenyl isocyanate. This decrease in the yield is mainly due to the fact that a part of the urea remained dissolved in the thiobenzhydrol formed simultaneously.

As the urea could also be formed by direct attack of S-benzhydryl N-phenylthiocarbamate by morpholine, the hydrolysis kinetics was studied in the presence of morpholine, too. The obtained k_{obs} values were practically the same as those obtained in pure buffers, *i.e.*, the reaction with morpholine takes place after the rate-limiting step, hence, morpholine reacts with phenyl isocyanate. The ElcB mechanism agrees therewith.

The substituent effects in N-phenyl ring and in phenyl ring of benzhydryl group on k_{obs} at pH 9·35 are presented in Fig. 1 giving the Hammett plot of log k_{obs} *vs* σ constants. The found value of the reaction constant $\varrho = 0{\cdot}8$ for the N-phenyl substitution is similar to that of N-arylcarbamates[17] and thiocarbamates[7,18] in which the hydrolysis goes exclusively by the ElcB mechanism. A similar value can be presumed

also in the $B_{Ac}2$ mechanism[17] which involves direct attack of carbonyl group by hydroxyl ion, so that the value of ϱ constant does not include the acid–base pre-equilibrium.

Much more significant is the relatively high value $\varrho = 1{\cdot}8$ found for the substituents in the phenyl ring of benzhydryl group, although it is determined from three points only. In the case of substituted phenyl N-phenylcarbamates[17,19] and thiocarbamates[7,18,20] the found values of ϱ constant of the hydrolysis going by the ElcB mechanism are within the limits of 2·9 to 3·6. For the N,N-disubstituted thiocarbamates, which are hydrolyzed exclusively by the $B_{Ac}2$ mechanism, it was found[18,20] $\varrho = 1{\cdot}05$. The CH group in thiobenzhydrols will lower the substituent effects and, hence, also the ϱ constant to one half, *i.e.*, to 0·5 and 1·6 for the $B_{Ac}2$ and ElcB mechanisms, respectively. The found value $\varrho = 1{\cdot}8$ indicates unambiguously the ElcB mechanism. As the kinetic experiments were carried out in 50% aqueous dioxane at 50°C, the effect of decreased polarity of medium (which increases the ϱ constant) and that of the enhanced temperature (which decreases the ϱ constant) compensate each other to considerable extent.

Hydrolysis of O-*Benzhydryl* N-*Phenylthiocarbamate*

Aniline and benzhydrol are the only hydrolysis products of O-benzhydryl N-phenylthiocarbamate in the buffer of pH 12·5. In the buffer of pH 10·22 we found – besides aniline – benzhydrol and thiobenzhydrol at a ratio of 1 : 1, and the reaction mixture from the buffer of pH 6·5 contained (after alkalization) benzhydrol and thiobenzhydrol at the ratio of 1 : 12. On the basis of composition of the reaction mixture the following hydrolysis mechanism (Scheme 2) can be suggested.

Rate of the rearrangement is independent of pH of the medium, and at pH < 10 it is faster than the hydrolysis of O-benzhydryl thiocarbamate, so the starting thiocarbamate predominantly rearranges, and thiobenzhydrol is the main reaction product. At pH 12 the hydrolysis of the substrate is much faster than its rearrange-

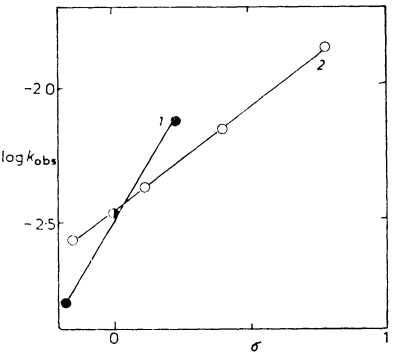
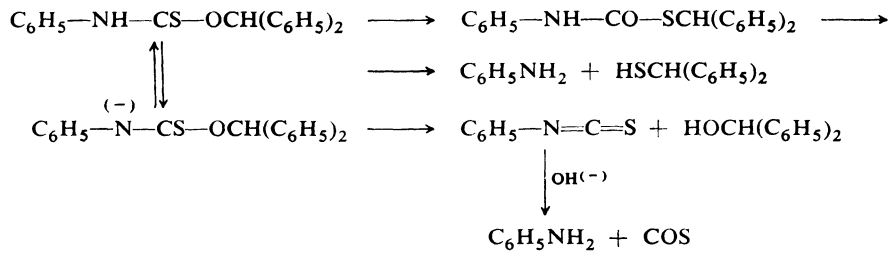


FIG. 1

Dependence of the hydrolysis rate constants of S-benzhydryl N-arylthiocarbamates on the substituent σ constants (pH 9·35, 50°C, 50% aqueous dioxane). *1* substituent in benzhydryl group, *2* substituent in N-phenyl group

ment, and benzhydrol is produced along with phenyl isothiocyanate which is hydrolyzed to aniline.



SCHEME 2

The hydrolysis kinetics were followed at pH below 9 and above 11·5. In the pH range in which the rearrangement and hydrolysis rates are comparable the reaction course is much too complex for spectrophotometric measurements. At pH > 11 the hydrolysis proceeds as the consecutive reaction: thiocarbamate → phenyl isothiocyanate → aniline. The reaction was followed spectrophotometrically in the region of the maximum absorption of phenyl isothiocyanate, and the rate constants of decomposition of thiocarbamate and phenyl isothiocyanate were determined which differ by about one order of magnitude (Fig. 2). Values of the hydrolysis rate constants of phenyl isothiocyanate were also determined from the hydrolysis rates of pure phenyl isothiocyanate in the same buffers.

Fig. 2 gives the pH dependence of all the log k_{obs} inclusive of the hydrolysis rate constants of dithiocarbamate and carbamate. The rate is controlled by both magnitude of the dissociation constants and rate constants of splitting of the con-

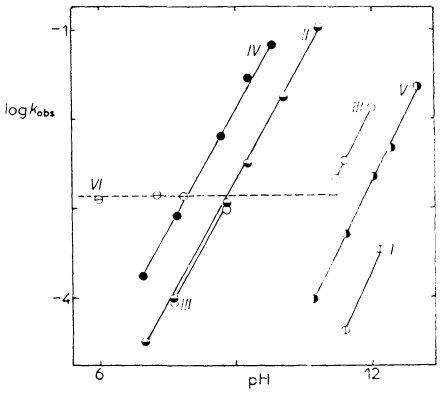


FIG. 2

pH Dependence of the hydrolysis rates (50°C, 50% aqueous dioxane) of benzhydryl N-phenylcarbamates (*I*), S-benzhydryl N-arylthiocarbamates (*II*), O-benzhydryl N-arylthiocarbamates (*III*), benzhydryl N-phenyldithiocarbamate (*IV*), phenyl isothiocyanate (*V*) and that of the rearrangement rate of O-benzhydryl N-arylthiocarbamate (*VI*)

jugated base: Substitution of oxygen (be it in carbonyl or in ether group) by sulphur increases the K value by 3–4 orders of magnitude[12] which affects decisively the hydrolysis rate order: dithiocarbamates > thiocarbamates > carbamates. As compared with C=O the C=S group retards splitting off of $ArX^{(-)}$, because the dipolar resonance structure $\overset{(+)}{C}—\overset{(-)}{S}$ is much more significant than the corresponding CO grouping[7,12]. Relative ease of splitting off of $ArS^{(-)}$ depends on structure of the remaining fragment[21]. If phenyl isocyanate is produced, then benzenethiolate ion is split off more easily, whereas, on the contrary, phenoxide is better leaving group, if phenyl isothiocyanate is formed[7].

IR *Spectra of the Carbamates* I *and Thio-analogues* II–IV

A decrease in the range 3 438–3 368 cm^{-1} was found for the wave numbers of ν(N—H) bands in the series of the derivatives *I–IV* (Tables II–VI) measured in dilute tetrachloromethane solutions, which indicates operation of the mass effect of sulphur when replacing one or two oxygen atoms in the carbamate molecule *I*. To evaluate the vibrational coupling, we also measured the spectra of the deuterated derivatives *I–III*, and we found the ratios ν(NH)/ν(ND) = 1·34 and 1·31 for the derivatives *I*, *II* (with secondary amide groups) and *III* (with thioamide group), respectively. The same difference also follows from the literature data for methyl N-methylcarbamate[4] and -thiocarbamate[5].

TABLE II

Wave numbers (in cm^{-1})[a] of absorption bands in IR spectra of O-benzhydryl N-phenylcarbamates (*I*)

Medium	ν(N—H)	ν(C=O)	δ(N—H)	ν(C—N—C—O)		ν(O—C)
Nujol	3 330 s	1 702 s	1 536 vs	1 450 vs	1 315 s	1 080 m
				1 296 m	1 231 vs	1 057 vs
[b]	2 357 s	1 696 vs	1 505 s	1 416 vs	1 368 s	1 085 s
				1 240 m	1 237 s	1 065 vs
CCl_4	3 438 s	1 749 vs	1 518 vs	1 439 vs	1 308 s	1 078 m
				1 295 sh	1 178 s	1 045 s
$CHCl_3$	3 435 s	1 727 vs	1 525 vs	1 440 vs	1 319 s	1 080 m
				1 298 sh	1 180 s	1 047 vs

[a] The band intensities: vs very strong, s strong, m medium, sh shoulder, [b] the deuterated derivative.

TABLE III

Wave numbers (in cm^{-1})[a] of absorption bands in IR spectra of S-benzhydryl N-phenylthiocarbamates *II*

R^1/R^2	Solvent	ν(N—H)	ν(C=O)	δ(N—H)	ν(C—N—C—S)			ν(C—S)
H/H	CCl_4	3 416 m	1 702 s	1 515 vs	1 305 s	1 235 m	1 135 vs	880 s
	$CHCl_3$	3 415 m	1 680 s	1 518 vs	1 308 s	1 236 s	1 139 vs	880 s
	Nujol	3 335 m	1 656 s	1 520 vs	1 310, 1 295 s	1 236 s	1 148 vs	880 s
[b]		2 488 m	1 647 s	1 458 s 1 373 vs	1 315 s, 1 187 s	1 170 s	988 s, 979 s	870 s
4-CH_3/H	Nujol	3 202 m	1 645 s	1 536 vs	1 308 m, 1 289 m	1 250 s	1 160 vs	888 s
3-OCH_3/H	Nujol	3 335 s	1 665 s	1 525 vs	1 301 s, 1 260 s	1 210 vs	1 144 s	890 s
3-Cl/H	Nujol	3 250 m	1 640 s	1 523 s	1 300 m	1 267 s 1 247 s	1 159 s	870 s
H/4′-CH_3	Nujol	3 345 m	1 660 s	1 516 vs	1 310 m	1 234 s	1 146 vs	870 s
H/4-Cl	Nujol	3 314 m	1 661 vs	1 523 vs	1 309 s	1 236 s	1 149 vs	878 s

[a,b] See footnotes in Tables II.

In contrast to compounds *I*, *II*, and *IV*, the O-benzhydryl derivative *III* in dilute tetrachloromethane solution exhibits two ν(N—H) bands. The wave number difference $\Delta\tilde{\nu}$ 34 cm^{-1} is close to the value published[5] for methyl N-methylthiocarbamate. The two bands were assigned to the respective *s-cis* and *s-trans* conformers according to the wave number decrease in the spectrum of derivative *III* when measured in chloroform instead of tetrachloromethane. The more intensive band at 3 416 cm^{-1} belongs to the *s-trans* conformer ($\Delta\tilde{\nu} = -11$ cm^{-1}), and that at 3 382 cm^{-1} is due to the *s-cis* conformer ($\Delta\tilde{\nu} = -2$ cm^{-1}).

The carbonyl frequency of thiocarbamate *II* is lower than that of carbamate *I* because of lower electronegativity of sulphur. The both carbonyls are sensitive to the solvent polarity and to change of state due to association by hydrogen bonds; in dilute tetrachloromethane solutions secondary carbamates absorb in the region of ν(C=O) absorption of carboxylic esters, thiocarbamates in condensed phases absorb in the region of absorption of secondary amides. The wave number values in the interval 1 640–1 670 cm^{-1} of our N,S-diphenylcarbamates do not correspond to polar effects of the substituents in the N-phenyl group. The wave number decrease of the ν(C=O) bands after deuterium exchange was greater in the thioderivative *II* than in carbamate *I*, it did not, however, reach the value of N-methylacetamide[1].

The changes of state and of solvent polarity have different effects on the frequency δ(N—H) (amide II): in this respect the carbamate *I* resembles secondary amides. The wave number decrease is accompanied by a small increase in the band intensity.

TABLE IV

Wave numbers (in cm^{-1})[a] of absorption bands in IR spectra of N,S-diphenylthiocarbamates (*IIa*) (in Nujol suspension)

R^2/R^3	ν(N—H)	ν(C=O)	δ(N—H)	ν(C—N—C—S)		ν(S—C)
H/H	3 240 m	1 655 vs 1 740 m	1 538 s	1 305 s	1 235 s 1 155 vs	880 s
4-NO_2/H	3 245 m	1 658 vs	1 550 vs	1 300 s	1 248 s 1 145 vs	890 s
4-NO_2/H[b]	—	1 672 vs 1 658 vs	—	1 305 s	1 248 s 1 105 vs	890 s
3-Cl/H	3 230 m	1 656 vs	1 535 s	1 301 m	1 240 vs 1 150 vs	890 s
4-NO_2/4-CH_3	3 280 m	1 670 vs	1 542 s	1 300 s	1 242 s 1 142 vs	885 s

[a] See footnote in Table II, [b] N-methyl derivative.

A lower sensitivity to the solvent polarity is seen in the δ(N—H) vibration of the thioderivative *II* as well as in thiocarbamate *III*. The dithiocarbamate *IV*, on the contrary, exhibits in solutions a greater value of wave number of δ(N—H) band

TABLE V

Wave numbers (in cm^{-1})[a] of absorption bands in IR spectra of O-benzhydryl- (*III*) and N,O-diphenylthiocarbamates (*IIIa*)

Sample	Medium	ν(N—H)	δ(N—H)	ν(C—N— C̈—O)		
IIIa	Nujol	3 240 m	1 545 vs	1 455 s	1 390 vs 1 380 vs	1 180 vs
4-NO_2	Nujol	3 230 m	1 555 vs	1 460 s	1 380 s	1 205 m
4-NO_2[b]	Nujol	—	—	1 460 s	1 380 s	1 200 s
III	Nujol	3 205 m	1 538 vs	1 450 m	1 375 m	1 190 vs 1 010 vs
[c]	Nujol	2 360 m	1 428 vs	1 420 vs	1 370 vs 1 260 s	1 198 s 1 000 vs
III	CCl_4	3 382 m 3 416 m	1 517 vs	1 441 s	1 369 vs	1 177 vs 1 010 s
III	$CHCl_3$	3 380 m 3 405 m	1 517 vs	1 444 s	1 373 vs	1 173 vs 1 010 s

[a] See footnote in Table II, [b] N-methyl derivative, [c] the deuteriated derivative.

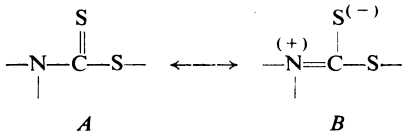
TABLE VI

Wave numbers (in cm^{-1}) of absorption bands in IR spectra of N,S-diphenyldithiocarbamates (*IVa*) (in tetrachloromethane)

Sample	ν(N—H)	Thioamide bands			
		I		II	III
IVa	3 350 m	1 520 sh[b] 1 480 s	1 440 s	1 350 vs	996 s
IVa[c]	—	1 500 vs 1 462 s	1 480 s 1 440 s	1 358 vs	1 108 s 1 087 s

[a] See footnote in Table II, [b] the δ(N—H) band, [c] N-methyl derivative.

1 510 – 1 520 cm^{-1}, relative intensities of these bands being approximately the same. This fact supports the idea[22] that the discussed band does not correspond to the δ(N—H) mode but rather to the valence vibration of C=N group. Contribution of the resonance structure *B* in the dithiocarbamate molecule strenghtens the C—N bond to the detriment of C=S bond. The authors do not explain the sensitivity of the band to the deuterium exchange, but it is understandable with respect to the vibrational coupling in thioamides.



A *B*

Intensive bands at 1 524 and 1 536 cm^{-1} in the spectrum of carbamate *I* in solid state are assigned to the δ(N—H) mode; the deuterated derivative exhibits new bands at 1 505 and 1 416 cm^{-1}. The isotopic exchange is connected also with a weakening of intensity of the band at 1 443 cm^{-1}. With respect to these frequency shifts, the δ(N—H) vibration resembles the same vibration of N-methylacetamide[3] more than that of methyl N-methylcarbamate[4] (the wave number value δ(N—D) $\sim$ $\sim$ 1 100 cm^{-1} was calculated for the latter compound). The intensity increase of the band at 1 085 cm^{-1} in the spectrum of the deuterated derivative *I* was not considered, because this is obviously no new band. The splitting of the δ(N—H) band is not seen in the spectra of compound *I* in solutions, and it is connected probably with properties of the crystal lattice. Besides the mentioned frequency shifts, the isotopic exchange also causes disappearance of intensive bands at 1 315 and 1 296 cm^{-1} and appearance of new bands at 1 368 and 1 240 cm^{-1}. The two bands are assigned to the amide *III* mode and valence vibration ν(phenyl-N). Small changes in intensity and wave number of the bands of valence vibrations of the ester group C—O—C indicate the effect of substituents at nitrogen atom and extent of vibrational coupling. Tables II and III also give the wave number value $\sim$880 cm^{-1}, which is found in the spectra of all the studied thiocarbamates *II* and is due probably to the ν(C—S). mode. The band ω(N—H) could not be identified due to intensive absorption of the benzene nuclei in the region below 800 cm^{-1}.

Besides the band δ(N—H) at 1 519 cm^{-1}, the spectrum of the deuterated thioderivative *II* lacks also the bands at 1 439, 1 295, 1 236, and 1 148 cm^{-1}. Out of the new bands it is possible to assign by analogy the band at 1 373 cm^{-1} to the δ(N—D) mode (the most intensive band in the spectrum). The bands at 1 295 and 1 236 cm^{-1} correspond most probably to the vibrations ν(phenyl-N) and to the amide III mode, the other value of Table III are not assigned. The bands at the given wave numbers are found in the spectra of the N,S-diphenylthiocarbamates *IIa*, too (Table IV). Especially sensitive to changes of state and solvent polarity is the band at 1 148 cm^{-1}.

A close value 1 149 – 1 162 cm^{-1} is given by Nyquist[23] for the band of characteristic group frequency of S-alkyl N-arylthiocarbamates; our S-benzhydryl derivatives exhibit the interval of 1 124 – 1 148 cm^{-1}. In contrast to the almost constant value of the wave number 1 236 cm^{-1}, the band at 1 148 cm^{-1} shows a decrease of the value by 9 and 13 cm^{-1} in chloroform and tetrachloromethane, respectively. The spectrum of N-methyl derivative *IIa* lacks this band, and a new intensive band at 1 105 cm^{-1} is due probably to the $\nu(N—CH_3)$ mode. The discussed band belongs obviously to the vibration with a greater proportion of N—H group vibration than is that in the band at 1 236 cm^{-1}.

The absorption band at 1 530 cm^{-1} of methyl N-methylthiocarbamate[5] was assigned to the vibration of almost pure $\delta(N—H)$ type. The following frequency shifts were found in the spectra of our thio derivative *III* and its deuterated analogue: 1 538 → 1 428, 1 450 → 1 420, and 1 375 → 1 260 cm^{-1}. The second of the given bands corresponds to the "pure vibration" $\nu(C—N)$, the third one is sensitive to the deuterium exchange and is not found in the spectrum of the N,O-dimethyl analogue[5]. The frequency shifts of the bands $\nu(C—O)$ 1 220 – 1 175 and (O—C) 1 010 – 1 000 cm^{-1} indicate vibrational coupling with $\delta(N—H)$. The intensive band at 1 190 cm^{-1} corresponds[24] to a vibration with participation of the $\nu(C=S)$ mode (Table V).

Due to extensive vibrational interactions it is impossible to assign bands in the spectrum of dithiocarbamate *IV* to localized bonds. Individual groups of bands of the functional group N—CS—N can be diagnostically characterized[3,25] as the thioamide bands I – III. The discussed vibration $\delta(N—H)$ can be assigned to the band at 1 520 cm^{-1} found in the spectrum of our N,S-diphenylthiocarbamate *IVa* and absent from the spectrum of the N-methyl derivative (Table VI).

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Translated by J. Panchartek.