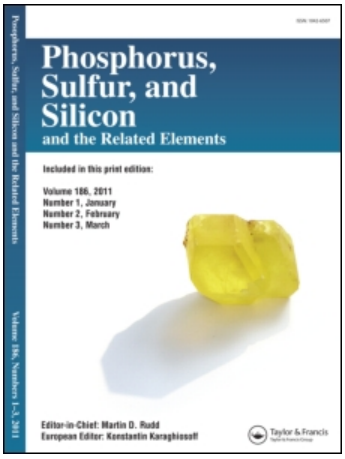

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SOLVENT EFFECTS ON THE INFRARED AND ^{1}H-NMR SPECTRA OF N,N'-THIODIANILINES

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SOLVENT EFFECTS ON THE INFRARED AND ^{1}H-NMR SPECTRA OF N,N′-THIODIANILINES

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The influence of various common basic solvents on the IR and ^{1}H-NMR spectra of a series of N,N′-thiodianilines, $S(HN-C_6H_4-X)_2$, X = H, OMe, Br, Cl, and m-NO_2 has been studied.

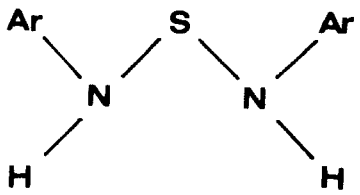
The solvent shifts of both, frequencies ϑ(NH) and chemical shifts δ(NH), show a near linear dependence on solvent basicity, DN (DN: Donor Number).

The sensitivity of the thiodianilines to the solvent, expressed as the slopes in the curves δ(NH) and ϑ(NH) vs. DN, are determined by the inductive effect of the substituents on the amino group. The anomalous behavior of the m-NO_2 derivative is attributed to strong intermolecular interactions.

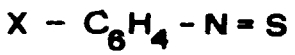
Key words: N,N′-Thiodianilines; solvent effect; IR and ^{1}H-NMR spectra; thionitrosobenzene precursors; sulfur (II) compounds.

INTRODUCTION

N,N′-thiodianilines (1) are known as a source of thionitrosobenzene derivatives (2)[1,2]



(1)



(2)

The relatively easy conversion of (1) into (2) together with the formation of X—$C_6H_4NH_2$ by thermal (decomposition), is to be contracted with the relatively high stability observed for its substituted analogues the N,N,N′,N′-tetraorganylthiodiamines R_2N—S—NR_2,[3] appear to be related to the lability of the N—H bonds. Although reactivity of the thiodianilines and their potential as precursors or intermediates in the synthesis of other sulfur-nitrogen compounds should be connected to the acidity of these N—H protons, little is known about their acidic properties.

In order to obtain information about the acidic properties of the N—H protons in derivatives with S—N—H backbone, we have investigated the influence of the Lewis acid-base properties of the medium on the IR and ^{1}H-NMR spectra of a series of thiodianilines.

RESULTS AND DISCUSSION

The infrared spectra of the thiodianilines $S(NHC_6H_4X)_2$ with X = H (**1a**), p-Cl (**1b**), p-Br (**1c**), p-OMe (**1d**) and m-NO_2 (**1e**) in the solid state as well as when dissolved in the solvents 1,2-dichloroethane (DEC), dioxane (Dx), tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and hexamethylphosphoric triamide (HMPA),

TABLE I

Selected values from IR spectra of thiodianilines[a]

Compound	ν(HN) (Δν/2)		ν(SN)
	Solid[b]	Solution[c]	Solid[b]
$S(NHC_6H_4\ H)_2$	3310,3260(20,50)	3220(100)	860
$S(NHC_6H_4\ Cl)_2$	3390(60)	3220(150)	870
$S(NHC_6H_4\ Br)_2$	3380(20)	3220(130)	860
$S(NHC_6H_4\ MeO)_2$	3325(60)	3210(80)	872
$S(NHC_6H_4\ NO2)_2$	3350(50)	3190(180)	940

a) frequency and mean band width values in cm^{-1}. b) KBr. c) Solution, DMSO.

TABLE II

Solvent effects on the IR and ^{1}H-NMR spectra of thiodianilines

Solvent	DN[a]	Compound							
		1a		1b		1c		1d	
		ν(NH) (Δν/2)[b]	δ(NH)[c]	ν(NH) (Δν/2)	δ(NH)	ν(NH) (Δν/2)	δ(NH)	ν(NH) (Δν/2)	δ(NH)
DCE	0	3380(80)	6,2	3380(60)	6,2	3380(50)	6,2	3380(40)	6,2
Dx	14	3310(70)		3300(110)		3300(110)		3320(50)	
AN	14.1		6.9		7.0		7.0		6.9
ES	15.3		6.9		7.0		7.0		
AC	17		7.6		7.9		7.9		7.2
THF	20	3290(110)	7.5	3280(160)	7.7	3280(140)	7.7	3300(60)	7.1
TMP	23		8.0		8.3		8.3		7.7
DMSO	29.8	3220(100)	8.2	3220(150)	8.5	3220(130)	8.5	3210(80)	7.9
DEAC	32.2		8.4		8.7		8.7		8.1
HMPA	38.8	3200(180)	9.0	3190(120)	9.4	3190(130)	9.4	3220(110)	8.6

a) Solvent Donor Numbers from ref. 5.

b) frequency values and mean band width values in cm^{-1}

c) δ in ppm from TMS.

were studied at room temperature. The nitro derivative, **1e**, is only very slightly soluble in every solvent except in DMSO. The assignment of the bands S—N was intended by comparing the IR spectra of the solids with those of substituted analogues $R_2N—S—NR_2$.[4] They are shown in Table I, in which also relevant features of the solid IR spectra of compounds **1a–1e** are compared with those from the spectra in solution.

Although significant effects on the absorptions associated to the N—H bonds can be observed in the IR spectra, strong absorptions of the solvents in the range 1000–800 cm^{-1} prevent the detection of possible effects on the vibrations associated to the S—N bonds. The frequency of the stretching vibrations ϑ(N—H) decreases with increasing basicity of the solvent. Data are shown in Table II. As illustrated in Fig. 1 for compound **1a**, there is a nearly linear dependence of ϑ(N—H) on the solvent donor number DN.[5] At the concentration ranges used for the experiments, the concentration effects on ϑ(NH) were negligible. Compounds **1b–1d** show a similar behavior. Data from regression analysis are reproduced in Table III.

The ^{1}H-NMR spectra of compounds **1a–1d** in the solvents dichloroethane (DCE), acetonitrile (An), ethylene sulfite (ES), acetone (Ac), tetrahydrofuran (THF), trimethylphosphate (TMP), dimethylsulfoxide (DMSO), diethylacetamide (DEAC), and hexamethylphosphoric triamide (HMPA) were examined at room temperature. Chemical shifts were determined using TMS as the internal reference standard. The shapes of the spectra depend certainly on the nature of the substituents but also on the solvent. In solid sharp bands are observed, $\Delta\vartheta/2$ 20–60 cm^{-1} (see Table I) while that in solution broadening in going from DCE to more donor solvent is observed. As reported in Table II, significant solvent shifts are observed for N—H protons. Concentration effects on the spectra were negligible. Similarly to ϑ(N—H),

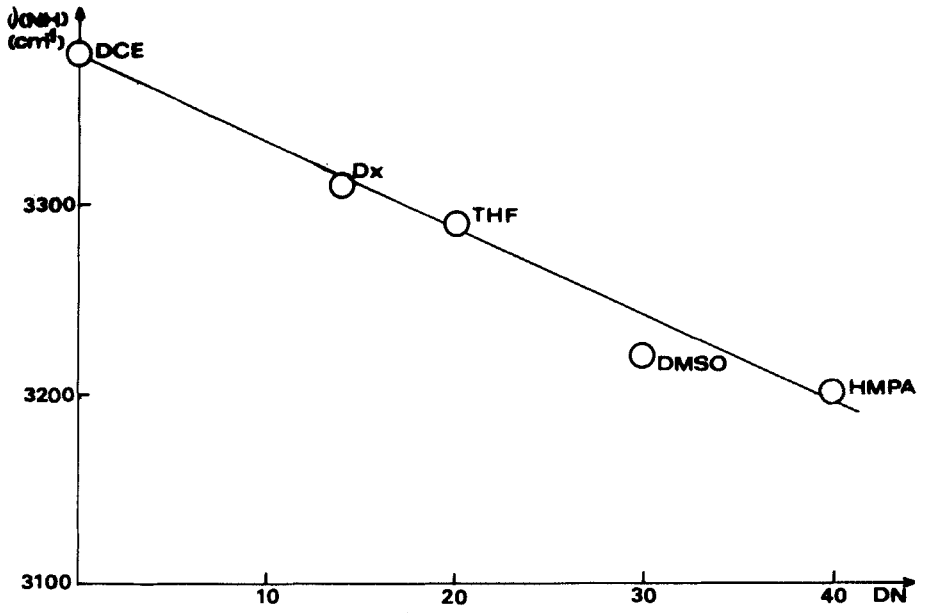


FIGURE 1 Influence of solvent donor strength of the N—H frequency shifts for N,N'-thiodianilines.

TABLE III

Regression parameters for ϑ(HN) vs. DN and δ(HN) vs. DN $Y = a_1 DN + a_0$

Compound			Y = ϑ(N-H)			Y = δ(N-H)		
Nr.	Substituent	σ^a	a_1	a_0	r^b	a_1	a_0	r
1a	p-H	0	-4.83	3379	0.99	0.073	6.07	0.97
1b	p-OMe	-0.268	-4.60	3380	0.96	0.064	6.01	0.97
1c	p-Br	0.232	-4.96	3375	1.0	0.083	6.08	0.97
1d	p-Cl	0.227	-4.96	3375	1.0	0.083	6.08	0.97
1e	m-NO_2	0.718	-	-	-	-	-	-

a) Values for Hammett Inductive Parameter from ref. 6.

b) Correlation Coefficient.

the chemical shift of the N—H protons show a nearly linear relationship with DN (Fig. 2). Regression data are reported in Table III.

The behavior of the N—H bond of thiodianilines in donor solvents, namely the weakening of the N—H linkage as well as the decrease of the electron density in the neighbor of the N—H proton with increasing donor strength of the medium, is the typical one of a system interacting *via* hydrogen bonding. From data reproduced in Table III and exemplified in Figs. 1 and 2 it is possible to evaluate the relative acidities of thiodianilines from the slopes of the curves $\Delta[\vartheta(H—N)]/\Delta DN$ and $\Delta[\delta(N—H)]/\Delta DN$. As shown in Fig. 3 for the chemical shifts, these parameters

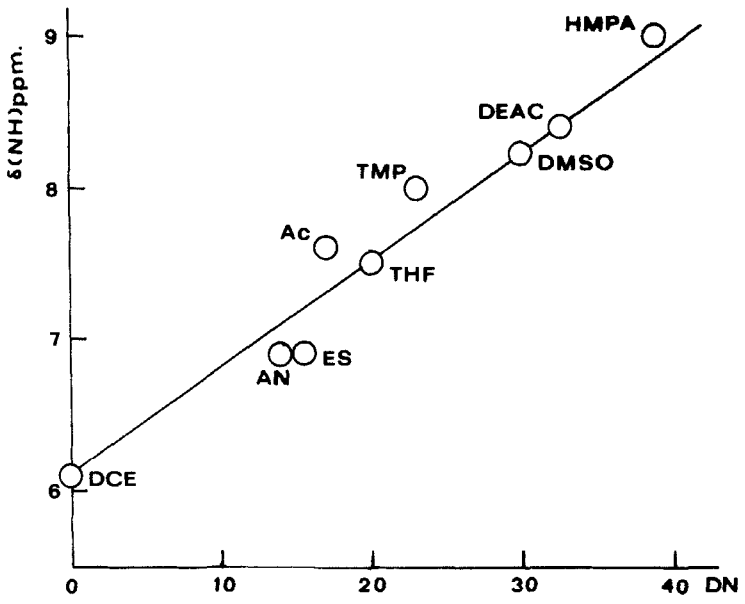
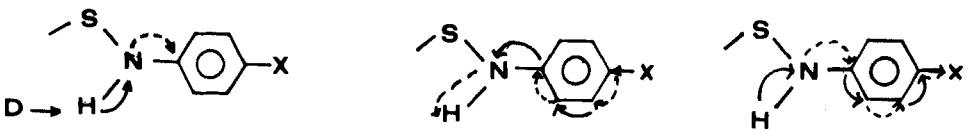


FIGURE 2 Influence of solvent donor strength on the chemical shifts of the amide proton δ(NH) for N,N'-thiodianilines.



depend on the inductive effects of the substituents. With increasing electron withdrawn capacity (+I effect) of X increases the acidity of the N—H proton. As shown in the following schemes, the formation of hydrogen bond with a donor and the +I effect of the substituents are cooperative. From data in Table III, specifically from the intercepts in the curves ϑ(N—H) and δ(N—H) vs. DN, a_0, the effect of the substituents on the N—H bond in absence of solvent can be also evaluated. As expected, a_0 correlates with the inductive effect of the substituents and therefore with the sensitivity of the N—H bonds towards the donor strength of the solvent analyzed above.

The anomalous behaviour of the nitro derivative **1e** which, as mentioned above, shows in DMSO a shielding of the N—H proton larger and solvent shifts smaller than those expected for an interaction with that solvent, could be due to strong intermolecular interactions. A similar effect but *via* intramolecular interaction has been detected for o-nitromethylaniline.[7]

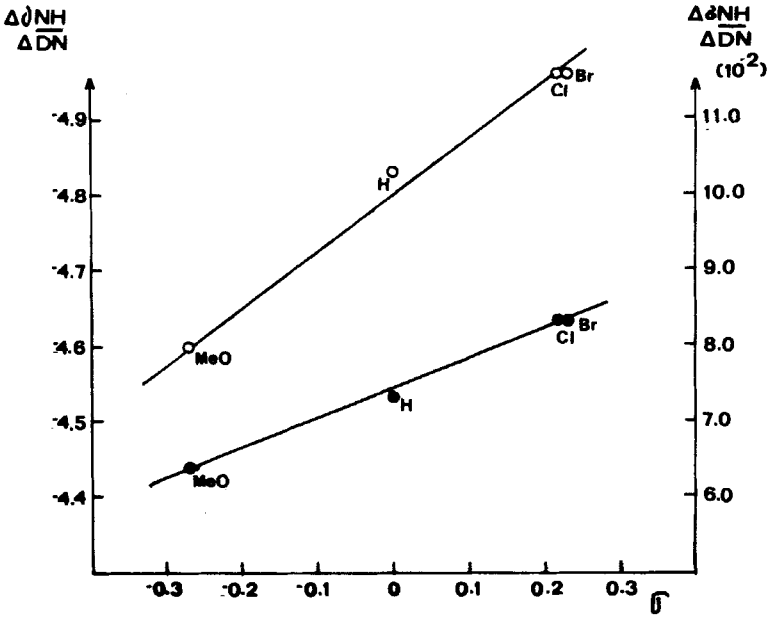


FIGURE 3 Influence of the Hammett Inductive Effect σ of the substituents on the sensitivity to the basicity of the solvent, $\Delta\vartheta$NH/ΔDN and $\Delta\delta$NH/ΔDN, of N,N'-thiodianilines.

The acidity of the thiodianilines **1a–1d** determined by solvent effects as described above correlates with the thermal stability of the same compounds

$$OMe < H < Br, Cl$$

that point out to a mechanism for the thermal decomposition of thiobisamines involving hydrogen abstraction, similar to that found for sulfenamides.[8]

EXPERIMENTAL

Solvents were purified by standard techniques[9] and stored in dark bottles over molecular sieves. Solvent purity was checked by IR spectroscopy. N,N'-thiodianilines were prepared by literature methods.[2] The N—H stretching frequencies were measured with a Perkin Elmer 621 spectrophotometer using liquid cells with sodium chloride windows (thickness 0.5 mm). An equivalent cell with the pure solvent was used in the reference beam. The concentrations of the N,N'-thiodianilines solutions usually were in the range 0.01–0.02 g/ml. In general, the frequencies reported are accurate to ± 1 cm^{-1}.

^{1}H-NMR spectra were run on a Varian T-60 spectometer using 5 mm o.d. tubes. The chemical shifts were determined using tetramethylsilane (TMS) as internal standard. For each solvent the concentration dependence was studied in the 0.003–0.006 g/ml range by adding pure solvent to the initial probe. IR spectra of the synthesized compounds are:

1a. m.p. 73–75°C IR (KBR, Pellet); 3310 (s) [ϑ(N—H], 3260 (s) [ϑ(N—H)], 1592 (s), 1492 (s), 1470 (m), 1405 (w), 1280 (w), 1210 (vs), 1175 (m), 1075 (w), 1024 (w), 898 (m), 860 (m) [ϑ(S—N)], 760 (vs), 750 (vs), 690 (vs), 612 (m), 505 (m), 280 (vw).

1b. m.p. 100°C IR (KBr, Pellet); 3390 (s) [ϑ(N—H)], 1590 (m), 1498 (vs), 1440 (m), 1370 (w), 1270 (m), 1220 (s), 1668 (w), 1112 (w), 1088 (m), 1008 (w), 870 (m) [ϑ(S—N)], 820 (s), 780 (w), 652 (w), 507 (m), 450 (s), 380 (vw), 345 (vw).

1c. m.p. 105°C IR (KBr, Pellet); 3380 (s) [ϑ(N—H)], 1585 (m), 1480 (vs), 1440 (m), 1370 (w), 1270 (m), 1220 (s), 1170 (w), 1110 (vw), 1070 (w), 1000 (w), 868 (m) [ϑ(S—N)], 815 (m), 775 (w), 630 (vw), 505 (m), 430 (w), 345 (vw).

1d. m.p. 102°C IR (KBr, Pellet); 3325 (vs) [ϑ(N—H)], 3040 (m), 3000 (s), 2980 (m), 2920 (m), 2850 (m), 2025 (vw), 1860 (w), 1642 (w), 1595 (w), 1500 (vs), 1455 (s), 1445 (s), 1390 (w), 1300 (m), 1275 (s), 1220 (vs), 1180 (s), 1110 (m), 1030 (s), 925 (w), 900 (m), 872 (s) [ϑ(S—N)], 820 (s), 805 (w), 730 (w), 605 (m), 570 (w), 525 (w), 445 (vw), 375 (vw).

1e. m.p. 185–187°C. 3350 (vs) [ϑ(N—H)], 3100 (w), 1615 (m), 1585 (w), 1520 (vs), 1470 (m), 1345 (vs), 1260 (vw), 1230 (m), 1070 (w), 995 (w), 940 (m) [ϑ(S—N)], 870 (m), 850 (m), 800 (m), 735 (s) 668 (m), 572 (vw), 420 (vw).

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