

PREPARATION AND SPECTROSCOPIC INVESTIGATION OF N-SILYL-PHENYLENEDIAMINES

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Introduction

In the course of the study on the Si-N bond, after the N-silyl-pyrroles and anilinosilanes, preparation UV and IR spectroscopic investigations phenylenediamines silylized on nitrogen followed, to be reviewed in the present paper. The following compounds are discussed: N,N'-bis-(trimethylsilyl)-ortho-phenylenediamine (I), N,N'-bis-(trimethylsilyl)-metaphenylenediamine (II), N,N'-bis-(trimethylsilyl)-paraphenylenediamine (III), and N,N,N',N'-tetrakis-(trimethylsilyl)-para-phenylenediamine (IV).

Literary Survey on Phenylenediamines

Few papers have been published on silyl-phenylenediamines so far. Some authors investigated these compounds but their works contain very few data. BIRKOFER et al. [1] reported on the preparation of the silicon derivatives of ortho-phenylenediamine. The reactions were carried out in toluene starting from ortho-phenylenediamine and trimethylchlorosilane in the presence of triethylamine at a yield of 95%. KLEBE [2] reported of the preparation of meta- and paraderivatives by the same method but in benzene solution. STEWART et al. [3] prepared the ortho-derivative from ortho-phenylenediamine with hexamethyldisilazane in the presence of trimethylchlorosilane in catalytic quantity, in absolute tetrahydrofuran, at a yield of 83%. This paper also contains some NMR and IR data of N,N'-bis-(trimethylsilyl)-ortho-phenylenediamine. Apart from the references these compounds are mentioned in some patents [4] but these give no further information of preparation and physical and chemical properties. N,N,N',N'-tetrakis-(trimethylsilyl)-para-phenylenediamine are mentioned in two papers by GERSON et al [5, 6] where the ESR spectrum of the compound is also reviewed. WITKE et al. [7] published the preparation and IR spectrum of the tetrasilyl-derivative. This compound was prepared from para-phenylenediamine with trimethyl-diethylamino-silane in the presence of $(\text{NH}_4)_2\text{SO}_4$ as catalyst, the product had a yield of 72%. The data of silyl-phenylenediamines found in the literature are compiled in Table I.

Table I
Data published on silyl-phenylenediamines

	I.	II.	III.	IV.
m.p. °C	23 32—34,5		103—05	96
b.p. °C/Hgmm	137/14 106—08/1,8—2	130/3,5		112—16/0,25
n_D^{20}		1,5266		
spectra data	NMR, IR			IR, Raman, ESR

The Preparation of the Compounds

Silyl-phenylenediamines were prepared from the respective phenylenediamines dissolved in organic solvents together with triethylamine as acid acceptor, and to this mixture trimethylchlorosilane was added. For the preparation of ortho-, meta- and para-derivatives toluene, benzene, and xylene was used as solvents. To 1 mole of phenylenediamine 2 moles of trimethylchlorosilane and 2 moles of triethylamine were taken. The crude ortho- and meta-derivatives were purified by fractionated vacuum distillation, the para-derivative was recrystallized from carbon tetrachloride. The yields were: I: 70%, II.: 80%, III.: 50% in this order. The tetrakis-silyl compound was prepared by the method reported in [7]. The purity of the products was checked in various ways: by C—H analysis, gas chromatography, ebullioscopic determination of the molecular weight in carbon tetrachloride and by measured and calculated molecular refraction. The physical and chemical data of each compound are shown in Table II.

Table II
Physical-chemical-data-of-silyl-phenylenediamines,

	I.	II.	III.	IV.
m.p. °C			104,5	95,5
b.p. °C/Hgmm	134/14	105—06/0,15		115—16/0,2
n_D^{25}	1,5051	1,5278		
d_4^{25} g/ml	0,9268	0,9616		
MR _D (exp)	80,82	80,83		
MR _D (calc)	79,66	79,66		

Spectroscopy

The UV absorption spectra of the compounds were recorded on a Spektromom 201 spectrophotometer. Cyclohexane (n-hexane in the case of compound IV) was used as solvent. The cell lengths were 0,2 and 1 cm, the concentrations

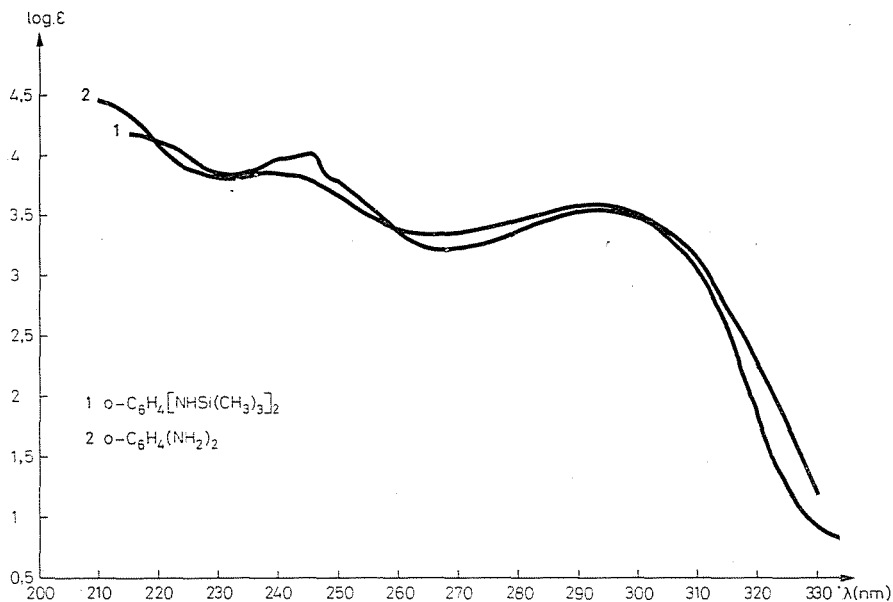


Fig. 1. UV absorption spectra of *N,N'*-bis-(trimethylsilyl)-ortho-phenylenediamine and ortho-phenylenediamine

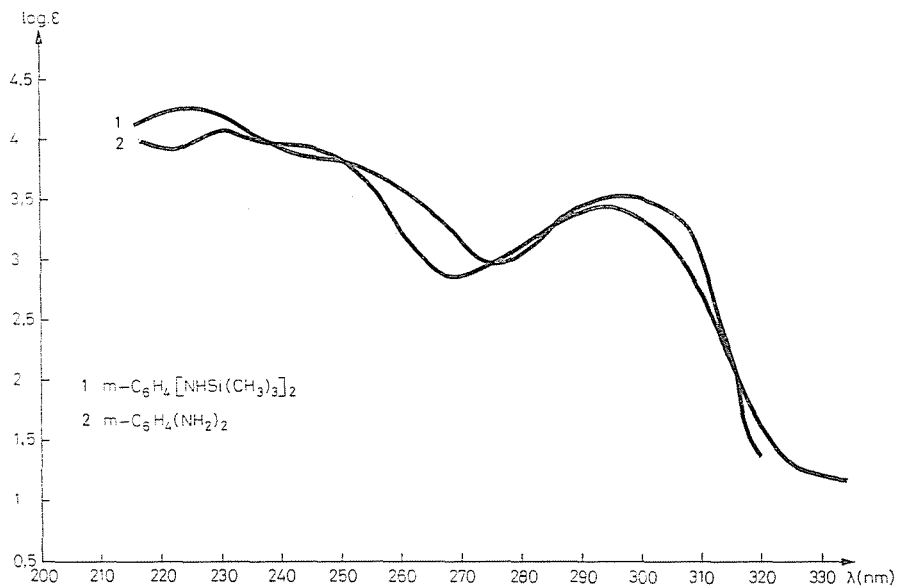


Fig. 2. UV absorption spectra of *N,N'*-bis-(trimethylsilyl)-meta-phenylenediamine and meta-phenylenediamine

ranged from 10^{-2} to 10^{-5} mole/l. The UV absorption spectrum of phenylenediamine was also recorded for the evaluation of the spectra. The spectra and the data for the absorption maxima are shown in Fig 1 to 3 and in Table III.

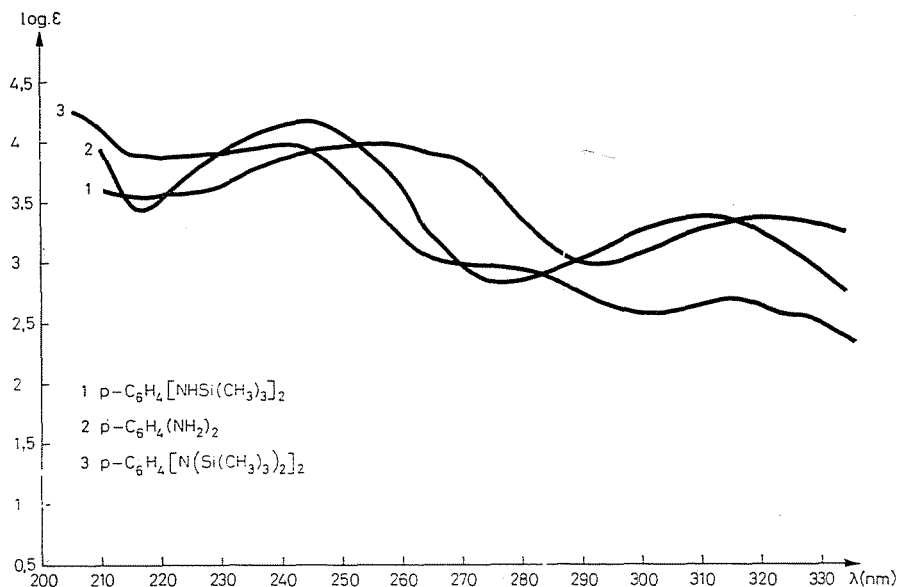


Fig. 3. UV absorption spectra of N,N' -bis-(trimethylsilyl)-para-phenylenediamine, N,N,N',N' -tetrakis-(trimethylsilyl)-para-phenylenediamine and para-phenylenediamine

Table III

UV absorption data of silyl-phenylenediamines

	λ nm	ν^* cm^{-1}	ϵ
I.	245	40 816	10 500
	294	34 014	3 690
II.	225	44 444	18 600
	250 inf.	40 000	6 260
	296	33 784	3 440
III.	257	38 911	9 440
	320	31 250	2 380
IV.	239	41 841	10 140
	279 inf.	35 842	910
	314	31 847	480

N,N' -bis-(tertiary-butyl)-phenylenediamine cannot be prepared because of steric hindrance and only few spectra of the N,N' -dimethyl-phenylenediamines are known so we compared the spectra to these of phenylenediamines.

The IR spectra were recorded on a UR-20 spectrophotometer. Recordings were performed on specimens in 0,02 mm tubes and between two plates in layers. The IR data and the assignments are shown in Table IV.

Table IV
IR spectroscopic data of silyl-phenylenediamines

I.	II.	III.
3372 s ν NH	3385 s ν NH	3382 m ν NH
3072 w ν (=CH)	3080 w ν (=CH)	3050 w ν (=CH)
3040 m ν (=CH)	3044 m ν (=CH)	3035 w ν (=CH)
2964 vs $\nu_{as}CH_3$	2962 vs $\nu_{as}CH_3$	2960 w $\nu_{as}CH_3$
2905 m ν_sCH_3	2905 s ν_sCH_3	2860 w ν_sCH_3
1620 s ν CC	1613 vs ν CC	1635 s ν CC
1604 vs ν CC	1595 s ν CC	1522 vs ν CC
1590 vs ν CC	1506 vs ν CC	1455 w ν CC
1508 vs ν CC	1455 m ν CC	1450 w $\delta_{as}CH_3(Si)$
1498 vs ν CC	1400 s $\delta_{as}CH_3(Si)$	1313 m ν CN
1463 m ν CC	1306 s ν CN	1266 s $\delta_sCH_3(Si)$
1406 s $\delta_{as}CH_3(Si)$	1255 vs $\delta_sCH_3(Si)$	1070 w $\beta(=CH)$
1305 vs ν CN	1093 w $\beta(=CH)$	1015 w $\beta(=CH)$
1255 vs $\delta_sCH_3(Si)$	1079 w $\beta(=CH)$	835 vs $\rho_{as}CH_3(Si)$, $\gamma(=CH)$
1102 m $\beta(=CH)$	855 vs $\rho_{as}CH_3(Si)$	800 m $\rho_sCH_3(Si)$
1047 s $\beta(=CH)$	843 vs $\rho_{as}CH_3(Si)$	730 s $\rho_sCH_3(Si)$
860 vs $\rho_{as}CH_3(Si)$	768 s $\rho_sCH_3(Si)$, $\gamma(=CH)$	518 s ν SiN (?)
835 vs $\rho_{as}CH_3(Si)$	692 m $\nu_{as}SiC_3$, γ CC	
780 s $\rho_sCH_3(Si)$	620 m ν SiN	
745 vs $\gamma(=CH)$		
690 s $\nu_{as}SiC_3$		
622 s ν SiN		

vs = very strong
s = strong
m = medium
w = weak

Discussion

From the study of the UV spectra of ortho- and meta-phenylenediamines and their silyl derivatives it was stated that the spectra showed small differences, only a small bathochromic shift was found in the case of the silyl derivatives compared to phenylenediamines. The bathochromic shift was more considerable in the spectra of para-phenylenediamine and bis-(trimethyl-silyl)-para-phenylenediamine and the run of the spectra was quite different in the case of the tetrakis-silyl derivative.

IR data have following conclusions. The valence vibration ν NH is assigned to the maximum about the wave number 3400. This single maximum found in this region affirms that the compounds contain only monosubstituted amino-groups and they have no unsubstituted NH_2 groups. The maxima corresponding to vibrations $\gamma(=CH)$ and $\gamma(CC)$ show up according to the differently substituted (ortho-, meta-, and para-) benzene ring: 745 (ortho-), 768 and 692 (meta-) and 835 (para-) wave numbers. The valence vibration of the Si—N bond was assigned to 622 and 620 cm^{-1} values. In connection with N-silyl-pyrroles, BÜRGER and BURCZYK [8] showed the ν Si—N vibration to

appear around 600 cm^{-1} . Assignment is uncertain in compound III where single maximum is found at 518 cm^{-1} in the IR spectrum.

From the UV and IR spectra of N-silyl-phenylenediamines an interaction can be stated to arise between nitrogen and silicon, inducing the formation of delocalized systems. This assumption is to be supported by quantum chemical calculations.

The authors wish to thank Dr. T. GÁBOR for recording the IR spectra.

Summary

The preparation of N-silyl-phenylenediamines is reported. The UV and IR absorption spectra were recorded and evaluated. Inferences were drawn on the structure of the molecules.

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