Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

QUANTUM CHEMICAL CALCULATIONS OF THE STRUCTURE OF *N*-SILYLANILINE DERIVATIVES

J. NAGY and P. HENCSEI

Department of Inorganic Chemistry of the Technical University of Budapest, Budapest (Hungary)

(Received November 23rd, 1971)

SUMMARY

Quantum chemical calculations have been performed by the Del Re and Pariser–Parr–Pople methods for $Me_3SiNHPh$, $(Me_3Si)_2NPh$, and $(Me_2HSi)_2NPh$. The reliability of the results has been assessed by comparison with calculated ultraviolet spectra and dipole moments with the experimental values. It has been shown that a d_π–p_π linkage is formed between the silicon and the nitrogen atoms and that the molecules have a delocalised structure.

INTRODUCTION

The study of the silicon–nitrogen bond has been extended from the *N*-silylpyrroles to the *N*-silylanilines. The preparation of these compounds, their ultraviolet and infrared spectra and dipole moments are discussed elsewhere[1], and this paper deals with relevant quantum chemical calculations.

QUANTUM CHEMICAL CALCULATIONS

Our work involved the following compounds: *N*-(trimethylsilyl)aniline (I), hexamethyl-*N*-phenyldisilazane (II), *sym*-tetramethyl-*N*-phenyldisilazane (III). For comparison, previously published[2] results of our calculations for *N*-methylaniline (IV) and for *N,N*-dimethylaniline (V) are also listed here.

The calculation of the σ-bond system of the compounds was done by the Del Re method as modified by us and extended to organosilicon compounds[3]. For the calculation of the π-bond system the Pariser–Parr–Pople (PPP) methods has been used. In the application of the PPP method we employed the approximating relationships used in our earlier work[4] for the calculation of phenoxysilanes. It was assumed that the compounds have a planar structure, and calculations were made with a nitrogen atom in the sp^2 hybrid state. In the calculation of the electron interaction integral of *N*-(trimethylsilyl)aniline that steric structure was selected for which the plane determined by the $SiNC_{ar}$ atoms is perpendicular to the plane of the benzene ring, which leads to equal partial charges for centers of identical symmetry. Bond distances and bond angles used for the calculation, taken from the literature[5–7], were as follows: $r(CC) = 1.397$ Å, $r(CN) = 1.426$ Å, $r(NSi) = 1.72$ Å, $r(SiC) = 1.89$ Å, $r(C_{ar}H) = 1.084$ Å, $r(C_{alk}H) = 1.093$ Å, $r(NH) = 1.014$ Å, $\angle SiNSi = 140°$, $\angle SiNC(I) = 130°$, $\angle SiNC(II) = 110°$, $\angle SiNH = 115°$.

In the calculation of the overlap integral of the silicon–nitrogen bond account was taken of the fact that the overlap of the *p* orbital of nitrogen with the *d* orbital of silicon is not at a maximum along the bond axis; a similar consideration applied in the case of the Si–O bond in phenoxysilanes.

Basic data for computation are contained in Table 1. Calculations were made on the computer Razdan-3 of the Technical University of Budapest. The Z_i, U_i, α_i values were changed with the aid of the values obtained in the zeroth approximation, while the values of β_{ij} were taken as constant. The approximations were continued

TABLE 1

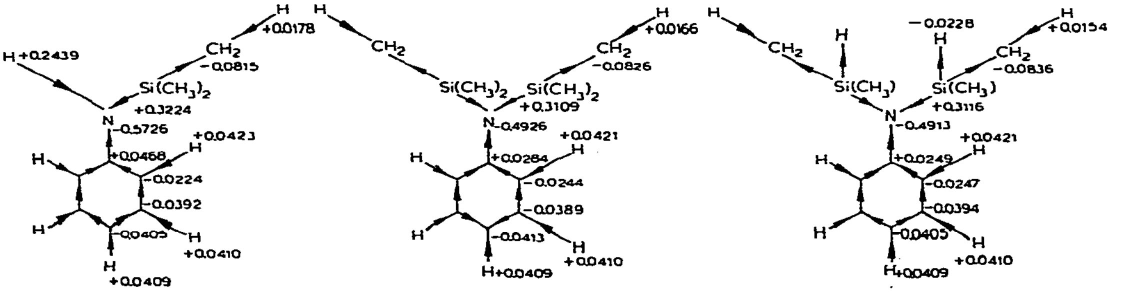
BASIC DATA FOR THE CALCULATION OF *N*-SILYLANILINES

$U_C = -0.61329 \exp(1.03616\, Z)$ $\gamma_{CC} = 11.13$ eV (ref. 8)
$U_{Si} = -0.20662 \exp(0.95552\, Z)$ $\gamma_{SiSi} = 3.762$ eV (ref. 9)
$U_{N^+} = -3.6528 \exp(0.54675\, Z)$ $\gamma_{NN} = 17.44$ eV (ref. 8)
$k = 0.6426$

TABLE 2

BASE DATA FOR THE CALCULATION OF THE π-SYSTEM OF *N*-SILYLANILINES BY THE PPP METHOD

	Z_{Si}	Z_N	Z_C	Z_C	Z_C	Z_C
(I)	1.863	3.600	2.816	2.792	2.786	2.786
(II)	1.859	3.628	2.810	2.791	2.786	2.786
(III)	1.859	3.628	2.809	2.791	2.786	2.786
	U_{Si}	U_N	U_C	U_C	U_C	U_C (eV)
(I)	−1.2251	−26.143	−11.351	−11.132	−11.003	−10.997
(II)	−1.2205	−26.546	−11.275	−11.062	−11.004	−10.994
(III)	−1.2208	−26.552	−11.261	−11.061	−11.002	−10.997
	β_{SiN}	β_{NC}	β_{CC}	β_{CC}	β_{CC}	(eV)
(I)	−1.4440	−2.1893	−2.4205	−2.4072	−2.3926	
(II)	−1.4436	−2.1828	−2.4048	−2.3997	−2.3923	
(III)	−1.4436	−2.1816	−2.4032	−2.3994	−2.3925	

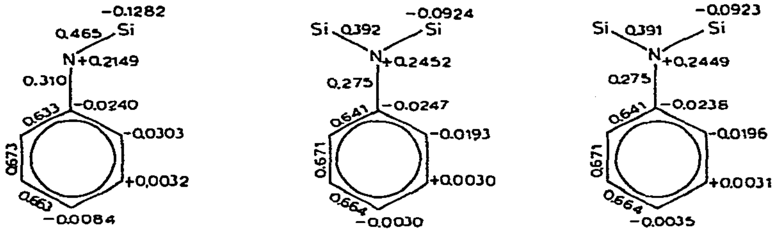


(I) (II) (III)

Fig. 1. σ-partial charges in *N*-silylanilines.

until selfconsistency. The eigenvalues, linear coefficients, electron densities, partial charges and bond orders have been determined for the single compounds. Configurational interactions have also been taken into account. With their aid the energy values of the singlet and triplet transitions and the oscillator strengths have been calculated. Input data are shown in Table 2.

Fig. 1 shows the σ-charge distribution and Fig. 2 the π-charge distribution, while Table 3 lists the results.



(I) (II) (III)

Fig. 2. π-partial charges and π-bond orders of *N*-silylanilines.

TABLE 3

EIGENVALUES, ENERGY VALUES OF SINGLET AND TRIPLET TRANSITIONS, AND OSCILLATOR STRENGTHS OF THE *N*-SILYLANILINES

	E (eV)	$^1E_{CI}$ (eV)	f	$^3E_{CI}$ (eV)
(I)	−14.0540	4.6858	0.016	3.0158
	−12.1269	4.9320	0.441	3.7978
	−10.2817	6.0748	0.006	3.9088
	−9.4951	6.5132	0.622	4.7593
	−1.3023	6.8267	0.793	4.8107
	−0.7145	6.9901	0.199	6.5113
	−0.3619	7.7280	0.167	6.6910
	2.3371	7.9208	0.333	6.9875
(II)	−14.3985	4.7522	0.007	3.0478
	−12.5501	5.0953	0.079	3.8795
	−10.3397	5.3565	0.361	3.9388
	−9.8133	6.1258	0.001	4.7890
	−1.6954	6.3423	0.103	5.0193
	−1.2614	6.6118	0.682	5.4891
	−0.7896	6.9911	0.767	6.1550
	−0.2946	7.1422	0.348	6.7620
	2.2542			
(III)	−14.3954	4.7516	0.007	3.0470
	−12.5504	5.0941	0.079	3.8786
	−10.3371	5.3563	0.360	3.9381
	−9.8108	6.1230	0.001	4.7885
	−1.6957	6.3407	0.102	5.0184
	−1.2604	6.6106	0.679	5.4894
	−0.7876			
	−0.2940			
	2.2558			

CONCLUSIONS

It can be seen from our calculations that the Si–N bond in *N*-phenylsilazanes has partial double bond character: a d_π–p_π linkage is formed between the empty 3*d* orbital of the silicon atom and the 2*p* electron pair of the nitrogen atom. According to the calculations, the value of the π-bond order is 0.391–0.465. A partial double bond is also formed between the nitrogen and carbon atoms, while the π-bond order of the CN bond is lower in the silicon derivatives (0.310–0.275–0.275) than in *N*-methylaniline and *N,N*-dimethylaniline (0.346–0.319).

Delocalised molecular orbitals with 8 and 9 centres, resp., are formed in the compounds from the *p* orbitals of the carbon and nitrogen atoms and the *d* orbitals of the silicon atoms. The computed values have been compared with experimental dipole moments and with the data of ultraviolet spectra. From the σ and π partial charges of the compounds the dipole moments μ_σ and μ_π have been calculated, and the $\mu_{\sigma\pi}$ values obtained by vectorial summation are compared with the experimental data in Table 4.

The ultraviolet absorption maxima of the compounds have been compared with the values of singlet energy transitions calculated taking account of configurational interaction. In Table 5, calculated oscillator strengths are compared with values determined from the UV spectra.

It can be shown from the data in Table 4 that the difference in calculated and observed dipole moments is greater for the silicon compounds than for the organic

TABLE 4

CALCULATED AND MEASURED DIPOLE MOMENTS OF ANILINE DERIVATIVES (in D)

	μ_σ	μ_π	$\mu_{\sigma\pi}$	μ_{exp}	*Difference* Δ
(I)	0.728	0.795	0.946	1.328 [1]	+0.382
(II)	0.231	0.000	0.231	0.556 [1]	+0.325
(IV)	0.163	1.460	1.615 [2]	1.67 [10]	+0.055
(V)	0.125	1.249	1.374 [2]	1.57 [10]	+0.196

TABLE 5

COMPARISON OF THE EXPERIMENTAL AND CALCULATED SINGLET TRANSITIONS AND OSCILLATOR STRENGTH OF THE *N*-SILYLANILINES

	$^1E_{CI}$ (*eV*)	*f*	^1E (*eV*)	*f*	*Difference* (*eV*)
	calc.		*exp.*		
(I)	4.69	0.016	4.32	0.026	0.37
	4.93	0.441	5.14	0.175	0.21
(II)	4.75	0.007	4.66	0.003	0.09
	5.10	0.079	5.28	0.068	0.18
(III)	4.75	0.007	4.59	0.012	0.16
	5.09	0.079	5.25	0.077	0.16

derivatives. Owing to presence of the electron pair on nitrogen, better agreement cannot be expected. Table 5 shows that there is good agreement between the experimental ultraviolet spectrum and the calculated singlet energy transitions; better agreement could be attained only after solution of the ultraviolet spectrum.

REFERENCES

1 J. Nagy, P. Hencsei and E. Hegedüs-Zimonyi, *Period. Polytech. Chem. Eng. (Budapest)*, in print.
2 J. Nagy and P. Hencsei, *Period. Polytech. Chem. Eng. (Budapest)*, in print.
3 J. Nagy, P. Hencsei and J. Réffy, *Acta Chim. (Budapest), 65 (1970) 51.*
4 J. Nagy and P. Hencsei, *J. Organometal. Chem.*, 32 (1971) 39.
5 *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Chemical Society, London, 1958.
6 W. R. Roper and C. J. Wilkins, *Trans. Faraday Soc.*, 58 (1962) 1686.
7 H. Bürger, *Monatsh. Chem.*, 97 (1966) 869.
8 K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, 4 (1966) 155.
9 K. A. Levison and P. G. Perkins, *Theor. Chim. Acta*, 14 (1969) 206.
10 A. L. McCellan, *Tables of experimental dipole moments*, Freeman, London, 1963.