

## Photoelectron Spectroscopic Investigation of Phenyl Isocyanato Silanes

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**Summary.** The HeI photoelectron spectra of compounds  $C_6H_5(CH_3)_nSi(NCO)_{3-n}$  were recorded and analysed using semiempirical AM1 quantum chemical calculations. The interaction between phenyl and pseudohalide groups is minimal. The splitting of bands originated from pseudohalide groups is not sensitive to the Si-N-C bond angle.

**Keywords.** AM1 calculations; PE-spectra; Silicon isocyanates.

### Photoelektronenspektroskopische Untersuchungen von Phenyl-isocyanato-silanen

**Zusammenfassung.** Es wurden die Photoelektronenspektren von Verbindungen  $C_6H_5(CH_3)_nSi(NCO)_{3-n}$  aufgenommen und die Spektren mit der Hilfe von semiempirischen quantenchemischen AM1 Rechnungen ausgewertet. Die Wechselwirkung zwischen den Phenyl- und Pseudohalogenidgruppen erwiesen sich als minimal. Die Aufspaltung der infolge der Pseudohalogenidgruppe entstandenen Bänder ist gegen den Bindungswinkel von Si-N-C unempfindlich.

### Introduction

As silicon isocyanates find an increasing application in polymer chemistry as important starting materials [1–8], there is an increasing interest in characterizing their structure by experimental and theoretical means. A better understanding of the electronic structure and its influence on the chemical behaviour of these species may help to find further applications.

The molecular structure of silicon isocyanates has been studied by several different experimental methods in recent years. These investigations were mostly aimed towards establishing the molecular geometry of these compounds. The most controversial question to be resolved was the linearity of the SiNCO chain. This question is especially intriguing because different experimental methods predict different geometries.

The equilibrium structure of silyl isocyanate ( $H_3SiNCO$ ) is now relatively well understood. It is now known that silyl isocyanate has a pseudolinear frame in the gas phase [9–11] which has been demonstrated by microwave spectroscopy.

The equilibrium structure of the trimethylsilyl (or other silyl substituted) an-

alogues is still very controversial due to the size of these molecules and the difficulties involved in their experimental study.  $(\text{CH}_3)_3\text{SiNCO}$  was predicted to have a bent structure by electron diffraction ( $r_a$  structure) [12]. The deviation from the expected linear geometry can be explained by the large amplitude motions of the Si-N-C-O frame [12]. Of these compounds, only the microwave spectrum of  $(\text{CH}_3)_3\text{SiNCO}$  has been studied [13]. This spectrum is rather complicated and an unambiguous structure cannot be deduced only on the basis of the spectrum. It has nevertheless been established that the equilibrium geometry must be linear or very close to it. The infrared spectrum of  $(\text{CH}_3)_3\text{SiNCO}$  also indicates a linear structure [14]. It is interesting to note that according to low temperature crystal structure studies,  $(\text{CH}_3)_3\text{SiNCO}$  is bent at the nitrogen with about  $20^\circ$  deviation from linearity [15].

The electronic structure of various isocyanates was studied by UV photoelectron spectroscopy [16–20]. In our earlier work [21] we investigated the electronic structure of compounds  $(\text{CH}_3)_n\text{Si}(\text{NCO})_{4-n}$  (where  $n = 0-3$ ). In the present work we study the electronic structure of some phenyl derivatives of silicon isocyanates. The spectra of compounds  $(\text{C}_6\text{H}_5)(\text{CH}_3)_n\text{Si}(\text{NCO})_{3-n}$  (where  $n = 0-2$ ) were recorded and analysed. Molecular orbital calculations have also been carried out in order to assign the experimental spectra. The aim of this work was to get a better understanding of the electronic structure of these molecules. It was also planned to study the dependence of the band positions in the photoelectron spectrum on the Si-N-C angle, in order to derive unambiguous information on the geometry of these molecules from the photoelectron spectra.

### Experimental and Calculations

The HeI photoelectron spectra were recorded using the apparatus described earlier [22, 23]. The resolution (FWHM) during measurements was ca. 40 meV for the Ar  $^2\text{P}_{3/2}$  line. All spectra were calibrated using the HeI photoelectron spectrum of  $\text{CH}_3\text{I}$ . The studied compounds were all synthesized

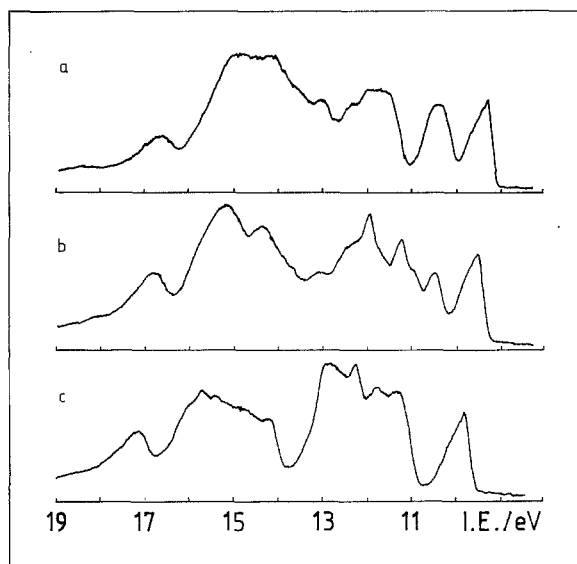


Fig. 1. Photoelectron spectra of silicon isocyanates, a.  $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiNCO}$ , b.  $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{Si}(\text{NCO})_2$ , c.  $(\text{C}_6\text{H}_5)\text{Si}(\text{NCO})(\text{NCO})_3$

by standard methods [24] and were purified by distillation. The purity of the samples was checked by GC-MS.

Semiempirical AM1 molecular orbital calculations [25] were performed on all of the investigated molecules in order to assist the assignment of the experimental photoelectron spectra. The vertical ionization energies were calculated for the minimum energy geometry of the molecules.

## Results and Discussion

The HeI photoelectron spectra of the investigated silicon isocyanates are shown in Fig. 1, the observed ionization energies are given in Table 1. The ionization energies calculated on the basis of Koopmans' theorem [26] and the assignments of the photoelectron peaks are also given in Table 1.

**Table 1.** Observed and calculated vertical ionization energies for the molecules  $(C_6H_5)(CH_3)_nSi(NCO)_{3-n}$  (where  $n=0-2$ )

$(C_6H_5)(CH_3)_2SiNCO$			$(C_6H_5)(CH_3)Si(NCO)_2$			$(C_6H_5)Si(NCO)_3$		
obs.	calc.	ass.	obs.	calc.	ass.	obs.	calc.	ass.
9.22	9.80	$\pi(C_6H_5), (e_{1g})$	9.46	10.00(a'')	$\pi(C_6H_5), (e_{1g})$	9.73	10.19	$\pi(C_6H_5), (e_{1g})$
	9.89			10.14(a'')			10.36	
10.32	10.57	$\pi_{nb}(NCO)$	10.36	10.78(a')	$\pi_{nb}(NCO)$	11.2	11.32	$\pi_{nb}(NCO)$
	10.60			11.17(a'')				
11.4	11.53	$\sigma(C_6H_5), (e_{2g})$	10.8	11.19(a'')	$\sigma(C_6H_5), (e_{2g})$	11.7	11.45	$\pi_{nb}(NCO)$
11.9	11.78	Si-C	11.12	11.23(a')				
12.3	12.10	$\sigma(C_6H_5), (e_{2g})$	11.85	12.02(a')	$\sigma(C_6H_5), (e_{2g})$	12.15	11.61	$\pi_{nb}(NCO)$
			12.3	12.25(a')				
12.9	12.75	Si-C			$\sigma(C_6H_5), (e_{2g})$	12.7	12.36	$\sigma(C_6H_5), (e_{2g})$
13	13.42		13.0	12.93(a')				
	13.55	CH	13	13.73(a')	CH	14.1	12.45	$\pi(C_6H_5), (a_{2u})$
	13.57			13.79(a'')	$\pi(C_6H_5), (a_{2u})$		14.00	
	13.66	$\pi(C_6H_5), (a_{2u})$		13.97(a'')	CH	14.1	14.41	$\sigma(C_6H_5), (e_{1u})$
	14.05	CH		14.41(a')			14.67	
	14.32	$\sigma(C_6H_5), (e_{1u})$		14.58(a')	$\sigma(C_6H_5), (e_{1u})$	16.01	16.01	$\sigma(C_6H_5), (b_{2u})$
	14.53			15.86(a')	$\sigma(C_6H_5), (b_{2u})$		16.33	
	15.64	$\sigma(C_6H_5), (b_{2u})$		16.14(a')	$\sigma(C_6H_5), (b_{1u})$	16.62	16.62	$\sigma(C_6H_5), (b_{1u})$
	16.00	$\sigma(C_6H_5), (b_{1u})$		16.37(a'')			16.63	
	16.21	$\pi_b(NCO)$		16.45(a'')	$\pi_b(NCO)$	16.68	16.68	$\pi_b(NCO)$
	16.24			16.56(a')				
16	16.24		16	16.61(a')	$\pi_b(NCO)$	16.75	16.75	$\pi_b(NCO)$
16.5	17.26	$n_0(NCO)$		16.61(a')				
	18.12	$\sigma(C_6H_5), (a_{1g})$		17.23(a'')	$n_0(NCO)$	16	16.89	$n_0(NCO)$
			16.7	17.70(a')			17.58	
				18.46(a')	$\sigma(C_6H_5), (a_{1g})$	17.1	17.59	$n_0(NCO)$
							18.01	
						17.1	18.79	$\sigma(C_6H_5), (a_{1g})$
							18.79	

<sup>a</sup> Bridging substituent

AM1 calculations show that the Si-N-C-O chains are linear for the equilibrium geometry, the phenyl ring and the NCO groups being not in the same plane. The rotation of the phenyl group around the Si-C axis is practically completely free, the potential barrier is less than 0.02 eV which indicates a slight interaction between the  $\pi$  system of phenyl and the NCO groups. On the basis of the calculations,  $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{Si}(\text{NCO})_2$  belongs to the point group  $\text{C}_s$ , the other two studied compounds can be related to the point group  $\text{C}_1$ .

The photoelectron spectra of the investigated phenyl derivatives are rather complicated, including quite a lot of partially or completely merged bands. On the basis of comparison of the spectra with those of benzene [27] and the methyl derivatives studied earlier [21], the shift of the bands related to the phenyl and NCO groups can fairly be followed making the assignment easier.

In the spectra of the phenyl derivatives the band corresponding to the lowest ionization energy can be derived from the two uppermost  $\pi$  orbitals of the phenyl group. These two orbitals for benzene ( $e_{1g}$ ) are degenerate and are split in the case of the silicon derivatives. In the experimental spectra this splitting cannot be observed albeit it is indicated by the existence of a broad asymmetric band. (To make the relationship with benzene clear, the orbitals of the phenyl group will be designated by the same symmetry symbols as in benzene). According to the calculations the mesomeric interaction between the  $\pi$  system of the phenyl group and that of the rest of the molecule is weak, which is supported by the absence of a splitting for the bands in the experimental spectra. The same conclusion was drawn on the basis of our earlier UV spectroscopic investigation [28]. As a consequence, the degree of splitting is expected to be proportional with the inductive effect of the substituent attached to the phenyl group. In the photoelectron spectra of the analogous fluorine and chlorine derivatives the splitting of these bands can be unambiguously observed (e. g. the splitting is 0.38 eV for  $\text{C}_6\text{H}_5\text{SiF}_3$ , 0.30 eV for  $\text{C}_6\text{H}_5\text{SiCl}_3$  [29]), the ionization energies corresponding to these bands and the splitting of the bands decrease gradually for the F, Cl, NCO derivatives indicating a smaller  $-I$  effect of the NCO group as those of fluorine and chlorine. The shift of the bands derived from the phenyl group into the direction of higher ionization energies going from the monofunctional derivative to the trifunctional derivative can be explained by the replacing of the  $+I$  effect of  $\text{CH}_3$  by a  $-I$  effect of the NCO group.

In the spectrum of  $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiNCO}$  the band at 10.32 eV can be related to the nonbonding  $\pi_{\text{nb}}$  orbitals of the NCO group. The splitting of the  $\pi_{\text{nb}}$  bands cannot be observed (similarly to the finding for  $(\text{CH}_3)_3\text{SiNCO}$  [21]) in spite of the fact that in these compounds the two  $\pi_{\text{nb}}$  orbitals are not degenerate even in the case of a linear Si-N-C-O chain. The  $\pi_{\text{nb}}$  bands in the spectra of the other phenyl isocyanato silanes are fairly merged with bands derived from the phenyl group but in the spectrum of  $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{Si}(\text{NCO})_2$  the band at 10.36 eV can be unambiguously assigned to a  $\pi_{\text{nb}}$  orbital on the basis of the calculations.

The bands in the region of the spectra between 11 and 16 eV are partially or completely merged, thus their unambiguous assignment is not possible. It can be observed that in the case of a replacement of a methyl group by an NCO group the orbitals related to the phenyl group and the NCO group are shifted in the direction of higher ionization energies, thus on the basis of the band shifts and the

spectral characteristics of benzene and the analogous methyl derivatives [21] the relative positions of the bands can be determined.

The band system in the spectrum of  $(C_6H_5)_3Si(NCO)_3$  between 11 and 13 eV can be related to the  $\pi_{nb}$  orbitals of the NCO groups and the  $\sigma(e_{2g})$  and  $\pi(a_{2u})$  orbitals of the phenyl group. It can be expected that the corresponding bands of benzene, when influenced by the  $-Si(NCO)_3$  group, are shifted in the direction of higher ionization energies [as it is shown by the shift of the  $\pi(e_{1g})$  bands], in contrary to the  $\pi_{nb}$  bands of the NCO group which are shifted to lower ionization energies in comparison to positions for  $Si(NCO)_4$  if they are affected by a phenyl group. On the basis of the mentioned trends the  $\pi_{nb}$  bands are likely to be found in the lower ionization energy region of the band system between 11 and 13 eV and the bands derived from the phenyl group contribute to the band system in the higher ionization energy side. Similarly, in the spectra of  $(C_6H_5)(CH_3)_2SiNCO$  and  $(C_6H_5)(CH_3)Si(NCO)_2$  the bands related to the  $\sigma(e_{2g})$  and  $\pi(a_{2u})$  orbitals of the phenyl group are expected between 11.5 and 12.5 eV, the further  $\pi_{nb}$  bands of the NCO groups have probable positions in the spectrum of  $(C_6H_5)(CH_3)Si(NCO)_2$  between 11 and 12 eV.

Informations given by the spectra of compounds  $(CH_3)_nSi(NCO)_{4-n}$  indicate that the bonding  $\pi_b$  bands derived from the NCO group are to be found at about 15–16 eV. In building up the strongly merged band system between 13 and 16 eV the participation of the  $\pi_b$  bands, the  $\sigma(e_{1u})$ ,  $\sigma(b_{2u})$ ,  $\sigma(b_{1u})$  bands of phenyl group

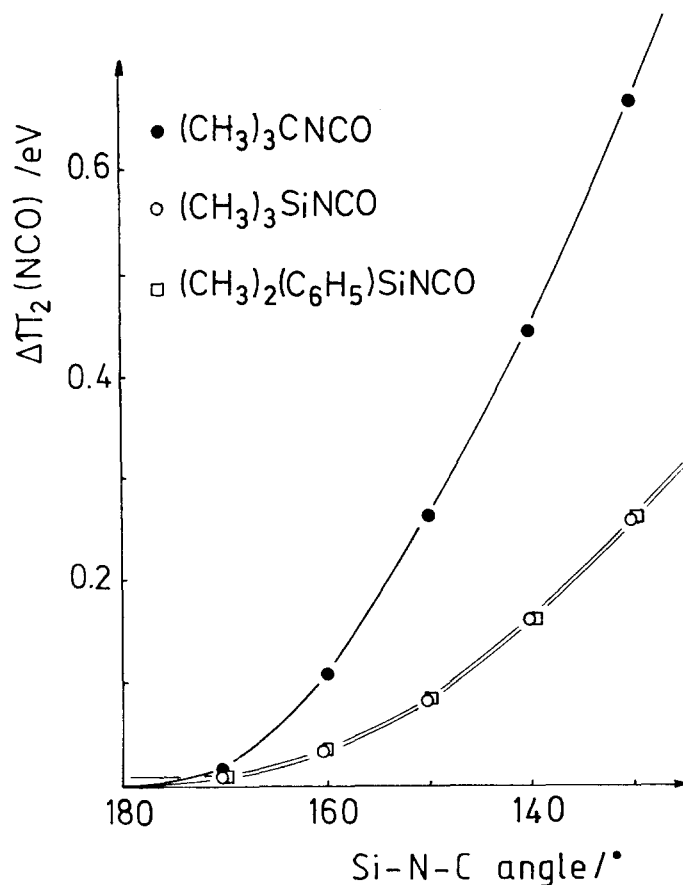


Fig. 2. Calculated  $\pi_2$  orbital splitting as a function of the Si-N-C angle

and the bands derived from the methyl group can be considered. According to the calculations the weak bands at 12.9 eV in the spectrum of  $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiNCO}$  and at 13.0 eV in the spectrum of  $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{Si}(\text{NCO})_2$  can be assigned to an ionization of the Si-C bond.

In the spectra of the phenyl derivatives the band observed at 16.5–17.1 eV can be related to the  $\sigma(\text{a}_{1g})$  orbital of the phenyl group and the  $\text{n}_0$  orbitals of the NCO groups.

After assignment of the photoelectron spectra an important question arises: what kind of conclusions can be drawn on the basis of these spectra on the linear or bent structure of the Si-N-C-O chains? In connection with compound  $(\text{CH}_3)_3\text{SiNCO}$  this problem was studied earlier by the help of ab initio Hartree-Fock method [21] and in this work the investigation of  $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiNCO}$  is supplemented by AM1 calculations. For the  $(\text{CH}_3)_3\text{SiNCO}$  molecule the two  $\pi_{\text{nb}}$  molecular orbitals are degenerate if the Si-N-C-O chain is linear and they are split in the case of a bent chain. For the phenyl derivative these two orbitals are not degenerate, but their splitting is expected to be small in the case of a linear Si-N-C-O chain and increases with diminishing SiNC angle. The splitting of bands derived from the mentioned orbitals cannot be observed in the spectrum of either  $(\text{CH}_3)_3\text{SiNCO}$  or  $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiNCO}$ . In the case of  $(\text{CH}_3)_3\text{CNCO}$  the situation is unambiguous: the molecule is bent and the corresponding bands are split [30]. To get information on the linear or bent structure of Si-N-C-O chains on the basis of photoelectron spectra first we have to estimate what splitting would be observable at all in the spectrum.

To give an answer for this question we optimized the geometries of  $(\text{CH}_3)_3\text{CNCO}$ ,  $(\text{CH}_3)_3\text{SiNCO}$ , and  $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiNCO}$  and studied the splitting of the  $\pi_{\text{nb}}$  orbitals in the function of the Y-N-C angle (where Y=C or Si). The results are summarised in Fig. 2. It can be seen that the splitting of the  $\pi_{\text{nb}}$  orbitals is much smaller for the silicon derivatives as for the *tert.*-butyl derivative. The calculations illustrate that, if the experimental resolution of the photoelectron spectrometer is about 40 meV, a relatively small deviation ( $>15^\circ$ ) from linearity can be observed by the splitting of the  $\pi_{\text{nb}}$  orbitals in the photoelectron spectrum of  $(\text{CH}_3)_3\text{CNCO}$ . In the case of silicon derivatives the observed deviation should be much larger ( $>25^\circ$ ). This means that for the silicon derivatives no unambiguous conclusion can be drawn on the linear or pseudolinear structure of these compounds based only on the photoelectron spectra.

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