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UV SPECTROSCOPIC INVESTIGATION OF *N,N'*-PHENYLCYCLODISILAZANES

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Summary

The UV spectra of *N,N'*-phenylcyclodisilazanes, *N*-trimethylsilylaniline and *N,N*-bistrimethylsilylaniline have been investigated with the aid of UV and quantum mechanical calculations. The main difference between the spectra of *N,N'*-phenylcyclodisilazanes and that to aniline-like molecules is a strong bathochromic shift of 20—30 nm of the *p*-bands. This is explained in terms of significant through-space interaction between the N atoms and conjugation of in-plane phenyl groups.

Introduction

In our previous papers we have studied the molecular structure of some cyclodisilazanes with the help of X-ray diffraction [1—3] and IR and Raman spectroscopy [4]. We have now examined the UV spectra of some phenylcyclodisilazanes with the aim of studying the conjugation of the two opposite in-plane aniline-like parts of the molecules. The analysis was made with the help of CNDO/S quantum mechanical calculations.

Experimental

Cyclodisilazanes I—VII (Table 1), the *N*-trimethylsilylaniline (VIII) and *N,N'*-bistrimethylsilylaniline (IX) were specially made for these studies. Compounds I, III, VI and VII were prepared by pyrolysis from the corresponding bis-organoamino-diorganosilanes [5,6]. Cyclodisilazanes II, IV, V, VIII and IX were obtained from organo-lithium compounds [5,7—9].

The UV spectra were recorded with a SPEKORD UV-VIS spectrometer in i-octane using 1 cm quartz cells at the concentrations of 10^{-3}—10^{-5} mol/l. The spectra are shown in Fig. 1, and the maxima and the intensities of the absorption bands are listed in Table 2.

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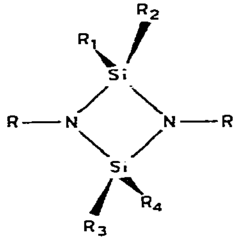
TABLE 1

EXAMINED CYCLODISILAZANES



Compound	R	R1	R2	R3	R4
(I)	C_6H_5	CH_3	CH_3	CH_3	CH_3
(II)	C_6H_5	C_6H_5	CH_3	CH_3	CH_3
(III)	C_6H_5	C_6H_5	CH_3	C_6H_5	CH_3
(IV)	C_6H_5	C_6H_5	C_6H_5	CH_3	CH_3
(V)	C_6H_5	C_6H_5	C_6H_5	C_6H_5	CH_3
(VI)	C_6H_5	C_6H_5	C_6H_5	C_6H_5	C_6H_5
(VII)	o-$CH_3C_6H_4$	CH_3	CH_3	CH_3	CH_3

TABLE 2

UV SPECTROPHOTOMETRIC DATA FOR CYCLODISILAZANES

Compound	CT_b; β(Si)		p(Si)		CT_a		α	
	ΔE (nm)	log ϵ	ΔE (nm)	log ϵ	ΔE (nm)	log ϵ	ΔE (nm)	log ϵ
I	205	4.57	221	3.75	260	4.57	282	3.55
							288	3.55
							301	3.36
II	201	4.53	220	4.00	259	4.35	273	3.60
							280	3.55
							291	3.38
III	198	4.92	221	4.52	256	4.64	291	3.78
							300	3.60
IV	198	5.00	222	4.40	256	4.62	290	3.70
							300	3.52
V	200	4.95	223	4.48	254	4.50	275	3.87
							291	3.63
							314	3.19
VI	197	5.05	225	4.53	254	4.38	266	3.89
							274	3.71
VII	210	4.80	—	—	245	4.18	269	3.28
							276	3.32
							285	3.22
							296	3.08
VIII					235	4.07	287	3.25
IX					234	4.02	272	3.57

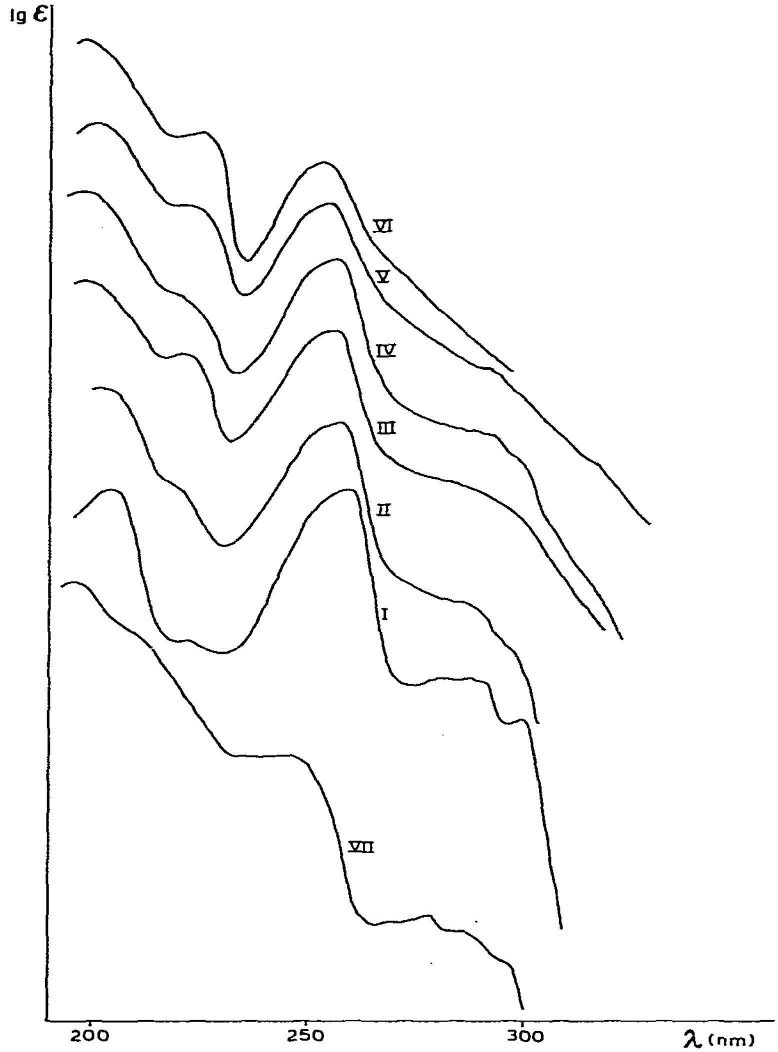


Fig. 1. UV spectra of phenylcyclodisilazanes.

Results

The UV spectra of cyclodisilazanes can be interpreted by analogy with the spectrum of aniline as analysed by Nagakura [10]. The α-band appears between 270—300 nm as a relatively wide shoulder. On the basis of X-ray diffraction data [1,2] the four membered ring and the phenyl groups are situated in the same plane so there is a possibility of a conjugation between the phenyl groups through the N atoms. Since two α-type transitions are expected in the long wave range of the spectrum, the breadth of the peak in this is understandable.

The most significant peak in the spectra is the charge-transfer band (CT_a) between 250—260 nm. This band shows a bathochromic shift of 20—30 nm compared with that of aniline. We thus assume that the ionization potential of

(continued on p. 168)

TABLE 3

CALCULATED AND EXPERIMENTAL UV TRANSITIONS (in eV)

Compound	CNDO/S [a]			CNDO/S [b]			Experimental	
	^1E	α	f [c]	^1E	α	f	^1E	f
$C_6H_5NH_2$ (X)				4,471 b_2	y	0,049	4,40	0,28 [10]
				5,444 a_1	z	0,304	5,39	0,14
				6,555 b_2	y	0,849	6,40	0,51
				6,570 a_1	z	0,882	6,88	0,57
				7,207 a_1	z	0,048	7,87	0,68
				8,076 b_2	y	0,020		
$C_6H_5NHCH_3$ (XI)				4,462	y	0,046	4,37	0,031 [10]
				5,378	z	0,321	5,20	0,190
				6,499	y	0,773	6,31	0.478
				6,550	z	0,837	6,88	0,556
				7,188	z	0,063	7,80	0,71
				8,017	y	0,019		
$C_6H_5N(CH_3)_2$ (XII)				4,405	y	0,050	4,30	0,044 [10]
				5,234	z	0,366	5,15	0,256
				6,392	y	0,632	6,25	0,350
				6,500	z	0,720	6,88	0,575
				7,098	z	0.103	7,68	0,81
				7,762	y	0,375		

$C_6H_5NHSi(CH_3)_3$ (VIII)	4.483	y	0,041	4,425	y	0,053	4,31	0,04
	5,410	z	0,317	5,337	z	0,334	5,28	0,28
	6,534	y	0,816	6,490	y	0,738		
	6,563	z	0,921	6,552	z	0,857		
$C_6H_5N[Si(CH_3)_3]_2$ (IX)	4.495 b_2	y	0,034	4,367 b_2	y	0,057	4,56	0,09
	5,372 a_1	z	0,335	5,211 a_1	z	0,366	5,30	0,25
	6,502 b_2	y	0,826	6,389 b_2	y	0,605		
	6,517 a_1	z	0,863	6,489 a_1	z	0,742		
$[(CH_3)_2SiNC_6H_5]_2$ (I)	4.439 b_{3g}		0,000	4,283 b_{3g}		0,000	4,12	0,06
	4.445 b_{2u}	y	0,098	4,295 b_{2u}	y	0,152	4,30	0,08
							4,40	0.08
	5,244 b_{1u}	z	0,894	5,127 b_{1u}	z	0,864	4,77	0,89
	5,412 a_g		0,000	5,287 a_g		0,000	5,611	0,13
	6,469 b_{3g}		0,000	6,170 b_{3g}		0,000		
	6,492 b_{2u}	y	0,486	6,171 b_{2u}	y	0,032	6,049	0,89
	6,506 b_{1u}	z	1,195	6,397 b_{1u}	z	0,072		
	6,574 a_g		0,000	6,400 a_g		0,000		
	6,577 b_{3g}		0,000	6,464 b_{3g}		0,000		
	6,620 b_{2u}	y	1,168	6,514 b_{2u}	y	1,247		
				6,557 b_{1u}	z	1,581		

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[a] Calculations with *d* orbitals. [b] Calculations without *d* orbitals. [c] *f* = oscillator strengths.

the nitrogen lone pair has decreased, indicating a strong through space interaction between the two nitrogen atoms. This is possible, because of the relatively short N···N′ distance (the N···N′ distance in I is 237 [1], and in VI is 236 pm [2]). Although the Si···Si′ distance is also rather small (the Si···Si′ distance in I is 256 [1] and in VI is 259 pm [2]), the phenomenon cannot be explained in terms of Si—Si bonding; not only would the transition be of the $\sigma \rightarrow \sigma^*$ type, and conjugation between the phenyl rings would be impossible, but the interpretation of the data for compound VII presents difficulties. The next CT-band lies between 195—205 nm. Its position is more or less invariant, but its intensity increases with the number of phenyl groups. The reason for this is that the β-bands of Si—Ph groups also appear in this range. The *p*-bands (*p*(Si)) of the phenyl groups joined to silicon are shifted slightly, in a hypsochromic direction, as the number of phenyl groups is decreased. The intensity of the peaks falls, as expected, with the decreasing number of the phenyl groups. Surprisingly I has a weak band in the range of the *p*(Si) band which is also probably of the CT-type, and in this compound only methyl groups are connected to the silicon.

It can be seen from Fig. 1 that the spectrum of compound VII differs from the others. The reason for this is that the phenyl groups are not in the same plane because of the steric effect of the *ortho*-methyl groups (as proved by X-ray diffraction studies [3]) and the conjugation is weakened. This is the cause of the hypsochromic shift of the CT-band and the lower intensity. The *p*-band is shifted to the red and the CT-band is observed.

TABLE 4

CALCULATED EIGENVALUES AND TRANSITIONAL WAVE FUNCTIONS

Compound	Orbital	E_i (eV)	Lin. coeff. of lone pair	Transition	Ψ
$C_6H_5NH_2$ (X)	π_5^*	—0.155	0.20	α	$0.85\psi_{3-4} - 0.51\psi_{2-5}$
	π_4^*	—0.388	—	*p*	$0.95\psi_{3-5} + 0.30\psi_{2-4}$
	π_3	—8.777	0.47	β	$0.52\psi_{3-4} + 0.85\psi_{2-5}$
	π_2	—9.834	—	β′	$0.28\psi_{3-5} - 0.93\psi_{2-4}$
	n	—12.568	0.65		
C_6H_5OH (XIII)	π_5^*	—0.457	0.14	α	$0.78\psi_{3-4} - 0.62\psi_{2-5}$
	π_4^*	—0.536	—	*p*	$0.88\psi_{3-5} + 0.47\psi_{2-4}$
	π_3	—9.469	0.32	β	$0.58\psi_{3-4} + 0.72\psi_{2-5}$
	π_2	—9.971	—	β′	$0.42\psi_{3-5} - 0.82\psi_{2-4}$
	n	—16.166	0.75		
C_6H_5Cl (XIV)	π_5^*	—0.687	0.09	α	$0.71\psi_{3-4} - 0.70\psi_{2-5}$
	π_4^*	—0.773	—	*p*	$0.81\psi_{3-5} + 0.59\psi_{2-4}$
	π_3	—9.995	0.26	β	$0.70\psi_{3-4} + 0.71\psi_{2-5}$
	π_2	—10.118	—	β′	$0.58\psi_{3-5} - 0.81\psi_{2-4}$
	n	—13.315	0.85		

In order to throw light on the UV spectra, quantum chemical calculations were carried out by a modified CNDO/S method [11]. The electronic transition energies of I, VIII, IX and, for comparison, the aniline (X), *N*-methylaniline (XI) and *N,N'*-dimethylaniline (XII) were calculated. Experimental geometries were used where possible, and in the case of compounds VIII and IX the experimental geometry for $HN[Si(CH_3)_3]_2$ [12] was used. The results are summarized in Table 3. For convenience Table 3 shows the polarization directions (α), and also in the case of C_{2v} and D_{2h} symmetry the group-theoretical designations. In the coordinate system, the $N—C_{Ar}$ direction coincides with the z axis and the phenyl groups are in the xy-plane.

The first three MOs of aniline have π character. Calculations and experimental analogies show that the third refers to the lone pair [13]. For the first two virtual orbitals the order and the symmetry are as follows: $n(b_1)$, $\pi_2(a_2)$, $\pi_3(b_1)$, $\pi_4^*(a_2)$, $\pi_5^*(b_1)$ of which only the b_1 type orbitals can have lone electron pair character with the next linear-coefficients: n: 0.65; π_3: 0.47; π_5: 0.20. In the configuration interaction (CI) the transitions are mixed and the first four transitions (after CI) always have n character by virtue of the π_3 and π_5 orbitals regardless of the symmetry of the transition. The situation is very similar to that in other benzene derivatives, as it can be seen from Table 4. Thus there is no reason to distinguish the spectra of aniline and its derivatives from other benzene derivatives. The considerable shift in its spectrum compared with e.g., that of phenol (XIII) or chlorobenzene (XIV) does not imply a different excitation mechanism. The main reason is the low ionization energy of the nitrogen lone pair. Thus the first four bands can be designated as α, p, β, β'. The same conclusion was reached by Kaito and Hatano [14] on the basis of CNDO/S calculations.

The progressive substitution of the hydrogen of the aniline by methyl groups causes a bathochromic shift of the p-band but a weak shift of the other bands is also observed. From the calculations this can be attributed to the destabilization of the π_3 orbital by about 0.2 eV. The introduction of a trimethylsilyl (TS) group causes a similar but a slightly stronger effect, reflecting the dominant +I effect of the TS group. For compound IX there is an unexpectedly strong hypsochromic effect which cannot be regarded as a d orbital effect. The steric effects of the two TS groups are evidently responsible for this phenomenon [15].

Compound I can be compared to IX. The main differences can be associated with the unusually short atomic distance between the N atoms. There is an interaction between the phenyl groups through the nitrogens, as confirmed by the coplanar dispositions. In consequence the bands are duplicated and furthermore β- and β'-type transitions are produced by the configuration interaction. Because of the D_{2h} symmetry some transitions are forbidden, e.g. that of the b_{3g}-type band. While the oscillator strength of the allowed band is also small, the transition b_{3g} may cause the broadening of the α-band. Similarly the weak maximum at 5.611 eV is probably the forbidden $p(a_g)$ band. The intensive band, appearing at 6 eV, probably arises from several transitions, and those of the β- and β'-type are the strongest.

The electron transitions for the other cyclodisilazanes were not calculated because of the large number of atoms, but the interpretation of the spectra is easy on the basis of the discussion above. The peaks of phenyl groups joined to silicon are independently superimposed on the spectrum of I.

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