

dimethyl sulfoxide (DMSO) and not in water. Separation of nucleosides on a preparative scale ought to be possible, therefore, on organic polymer gels which swell in these solvents and which contain covalent nucleoside residues.

We have prepared such gels and tested their separation efficiency regarding the nucleosides thymidine (T), adenosine (A), cytidine (C), and guanosine (G). 1-[2,3,4-*O*-tris(trimethylsilyl)-6-methacryloyl- β -D-glucopyranosyl]thymine (1) and *N*⁴-benzoyl-*O*^x,*O*^y'-bis(trimethylsilyl)-*O*^x'-methacryloylcytidine (2)^[5] were copolymerized radically with tetramethylene dimethacrylate to give insoluble thymine- and cytidine-containing polymer gels that swell in organic solvents. Cleavage of the trimethylsilyl groups with HCl/acetone and of the trimethylsilyl- and benzoyl groups with NH₃/methanol afforded T gels and G gels, which swell in DMSO or DMSO/CHCl₃ and exhibit very good flow rates.

With T gels it was not possible to separate the 1 : 1 complex of the two corresponding nucleosides formed from equimolar amounts of T and A in DMSO. On the other hand it was possible to separate the excess amounts of A from the 1 : 1 complex formed from a mixture of T and an excess of A. In experiments with an analogous sample gel that did not contain T species, no interactions took place and consequently there was no separation effect.

In separation experiments carried out with CG mixtures on C gels similar results were obtained as with TA mixtures on T gels. With C gels, however, it was found that not only good separation of the 1 : 1 TA complex could be accomplished but also that the separation could be improved by lengthening the column. The two non-classical 1 : 1 complexes between A and G and between T and G can be completely separated on C gels. These results confirm indirectly the interaction energies^[6] calculated for vacuum for the classical and non-classical base pairs. Accordingly, the value for the base pair CG (-19.2 kcal/mole) is almost three times higher than that for the other combinations (AT = -7.0, AC = -7.8, AG = -7.5, TG = -7.4, and TC = -6.5 kcal/mole).

Chromatographic procedure:

Glass columns, 48 cm in length and 1 cm in diameter, were filled with 18 g of swollen T- or C-gel — a mixture of DMSO/CHCl₃ (2 : 3) being used as swelling agent. For separation, up to 100 mg of mixed nucleosides was dissolved in DMSO (ca. 20 mg/ml), transferred to the column, and then developed at room temperature with a mixture of DMSO/CHCl₃ (2 : 3), the flow rate being about 38 ml/h. The separation process was monitored in a measuring cell using a Uvicord-Ultraviolet absorptiometer and recorded in the form of a UV absorption diagram by an LKB pen recorder. Samples of the eluate were collected at regular intervals and the separation of the nucleosides examined by UV absorption measurements using a Zeiss spectrophotometer PMQ 11 at E₂₈₀/E₂₆₀ nm.

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[1] H. Tuppy and E. Küchler, Biochem. biophysica Acta 80, 669 (1964); Mh. Chem. 95, 1677, 1691 (1964).

[2] J. D. Watson and F. H. C. Crick, Cold Spring Harbor Sympos. quantitat. Biol. 18, 123 (1953); Nature (London) 171, 737 (1953).

[3] R. A. Newmark and C. R. Cantor, J. Amer. chem. Soc. 90, 5010 (1968).

[4] B. W. Bangert and S. C. Chan, Biopolymers 6, 983 (1968).

[5] Synthesis of (1) and (2): G. Greber, M. L. Hallensleben, L. Bucsis, and H. Schott, and G. Greber and H. Schott, Makromolekulare Chem., in press.

[6] B. Pullman, P. Claverie, and J. Caillet, J. molecular Biol. 22, 373 (1966).

The Color of Trimethylsilyl Derivatives of Diimine^[1]

By H. Seidl, H. Bock^[*], N. Wiberg, and M. Veith^[**]

The $n \rightarrow \pi^*$ excitation energies of hetero atom chromophores are lowered drastically by trimethylsilyl substituents (Table 1); for instance bis(triphenylsilyl) ketone^[2,3] is violet in contrast to the colorless dialkyl ketones, and bis(trimethylsilyl)diimine^[5] is blue in contrast to the colorless dialkyldiimines^[6].

Table 1. $n \rightarrow \pi^*$ excitation energies (cm⁻¹) of silyl- and alkyl-substituted hetero atom chromophores [R = C₆H₅ in (R₃Si)₂CO, otherwise CH₃].

X	$\begin{array}{c} \text{X} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{X} \end{array}$ [3]	$\begin{array}{c} \text{R}_3\text{C} \\ \diagdown \\ \text{C}=\text{N}-\text{X} \\ \diagup \\ \text{H} \end{array}$ [4]	X-N=N-X [5, 6]
CR ₃	35 800	40 200	27 200
CR ₃ /SiR ₃	26 800		20 000
SiR ₃	18 500	33 400	12 750

On the basis of experimental data^[7] the color of the silyl ketones has to be ascribed to the strong inductive rise of the highest occupied n -orbital of the oxygen atom due to the R₃Si group in the β -position and to the lowering of the π^* -orbital by Si \leftarrow C π interaction with unoccupied atomic orbitals of silicon in α -position to the C=O π -system. The long-wavelength shift of the $n \rightarrow \pi^*$ absorption band of bis(trimethylsilyl)diimine whose R₃Si groups are in α -position to both the N=N π -system and to the nitrogen lone pairs n_N is, however, still unexplained.

For a study of the substituent effects on the azo chromophore^[8] we selected the more stable phenyl derivatives (1)^[9] and (2)^[10], for which additional experimental data can be obtained. Their ionization energies (determined by mass spectroscopy^[11]), electron-spectroscopic excitation energies, and half-wave reduction potentials^[12] are collected in Table 2.

Table 2. Experimental data for *tert*-butyl- (1) and trimethylsilyl-phenyldiimine (2).

C ₆ H ₅ -N=N-C(CH ₃) ₃ (1)	C ₆ H ₅ -N=N-Si(CH ₃) ₃ (2)	
IE(n_N) (eV)	7.75	7.05
$\bar{\nu}_m^{n \rightarrow \pi^*}$ (cm ⁻¹) [13]	24 400	17 250
$\bar{\nu}_m^{\pi \rightarrow \pi^*}$ (cm ⁻¹) [13]	38 400	37 500
E _{1/2} ^{Red} (V)	-1.35	-1.13

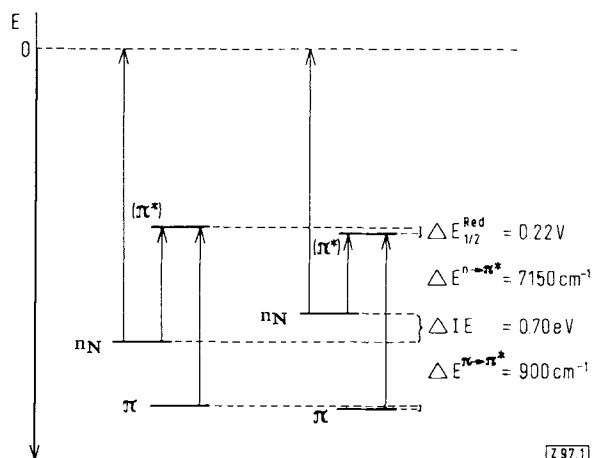


Fig. 1. Experimental energy level schemes for *tert*-butyl- (1) and trimethylsilyl-phenyldiimine (2).

Comparison of the energy level schemes for the inner molecular orbitals of (1) and (2) drawn up from the data in Table 2 shows that the R₃Si substituent in phenyldiimine derivatives also increases the energy of the nitrogen lone pair n_N whilst lowering the π-molecular orbitals. The decreased n → π* excitation energy of (2), and thence also of bis(trimethylsilyl) diimine, is then to be explained as in the case of the silyl ketones^[7]. However, as the rise in the n_O level of the oxygen due to silicon in the β-position amounts to 0.9 eV relative to the standard *tert*-butyl phenyl ketone^[7], a difference in the ionization potential Δ*I*E > 1 eV would be expected between the alkyl- and the silyl-substituted phenyldiimine derivatives, because the inductive effect of substituents in the α-position should be enhanced by a factor I_α/I_β ≈ 1.6^[14].

The observed difference of only 0.7 eV can be accounted for by an additional Si ← n_N interaction (in the direction opposite to the inductive increase) of the n_N lone pair with unoccupied atomic orbitals of the silicon in α-position to the nitrogen^[15]. The interaction should lead to an increase in the NNSi angle since a wider angle favors the overlap^[16].

Neither the NNSi angles^[13] in the trimethylsilyldiimine derivatives nor the interaction between the two n_N electron pairs discussed for azo compounds^[6,8] is known. Since, however, the whole visible and ultraviolet region of the electronic spectrum of bis(trimethylsilyl)diimine shows only the n → π* absorption at 12750 cm⁻¹, the n_a/n_s splitting must exceed 4.7 eV^[17].

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[1] Part 22 of d-Orbital Effects in Silicon-substituted π-Electron Systems. — Part 21: F. Gerson, U. Krynitz, and H. Bock, *Helv. chim. Acta* 52, 2512 (1969). Also Part 4 of Derivatives of Diimine. — Part 3: U. Krynitz, F. Gerson, N. Wiberg, and M. Veith, *Angew. Chem.* 81, 745 (1969); *Angew. Chem. internat. Edit.* 8, 755 (1969).

[2] A. G. Brook and G. J. D. Peddle, *J. organometallic Chem.* 5, 107 (1966).

[3] A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davies, *J. Amer. chem. Soc.* 89, 431 (1967).

[4] H. Bock and U. Krynitz, unpublished results.

[5] N. Wiberg, W.-Ch. Joo, and W. Uhlenbrock, *Angew. Chem.* 80, 661 (1968); *Angew. Chem. internat. Edit.* 7, 640 (1968).

[6] M. B. Robin and W. T. Simpson, *J. chem. Physics* 36, 580 (1962); cf. also M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Amer. chem. Soc.* 89, 1564 (1967).

[7] H. Bock, H. Alt, and H. Seidl, *Angew. Chem.* 80, 906 (1968); *Angew. Chem. internat. Edit.* 7, 885 (1968); *J. Amer. chem. Soc.* 91, 355 (1969).

[8] H. Bock, *Angew. Chem.* 77, 469 (1965); *Angew. Chem. internat. Edit.* 4, 457 (1965).

[9] P. O'Connor, *J. org. Chemistry* 26, 4375 (1961).

[10] U. Wannagat and C. Krüger, *Z. anorg. allg. Chem.* 326, 288, 296, 304 (1964).

[11] Measured on an Atlas CH-4 mass spectrometer with an FOX ion source. The data have a scatter of ±0.02 eV. — Cf. H. Bock, H. Seidl, and M. Fochler, *Chem. Ber.* 101, 2815 (1968).

[12] Measured in a 0.1 M *N,N*-dimethylformamide solution of tetrabutylammonium iodide against the mercury pool at 25 °C.

[13] The corresponding extinction values ε_m^{n→π*} and ε_m^{π→π*} (l · mole⁻¹ · cm⁻¹) are for (1) 100 and 7100, respectively, and for (2) 29 and 16350, respectively. As for the (trimethylsilyl)styrenes, the differences in the π → π* transitions are explained by expansion of the π-system in (2); for the n → π* transitions they possibly can be interpreted on the basis of increased p hybridization of the lone pair due to widening of the angle and the thus more strongly overlap-forbidden transition in the case of the silicon compound.

[14] O. Exner and J. Jonas, *Collect. czechoslov. chem. Commun.* 27, 2296 (1962).

[15] Experimental results for silyl- and alkyl-substituted aldimine derivatives RHC=N₂X, whose n → π* excitation energies (Table 1) also differ by more than 0.8 eV, prove also that Si → n_N interaction occurs between the n_N electron pair and unoccupied orbitals of the silicon atom in the α-position [4].

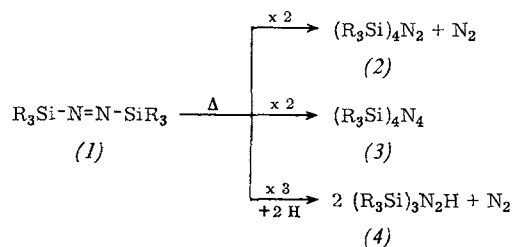
[16] Cf. the ESR data for the radical anion of *N,N'*-bis(trimethylsilyl)benzoquinone diimine [F. Gerson, U. Krynitz, and H. Bock, *Helv. chim. Acta*, in press].

[17] Note added in proof: The n_a/n_s splitting in azomethane has been found by photoelectron spectroscopy to amount to 3.3 ± 0.2 eV [E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem.* 81, 897 (1969); *Angew. Chem. internat. Edit.* 8, 878 (1969)].

1,1,4,4-Tetrakis(trimethylsilyl)tetrazene [1]

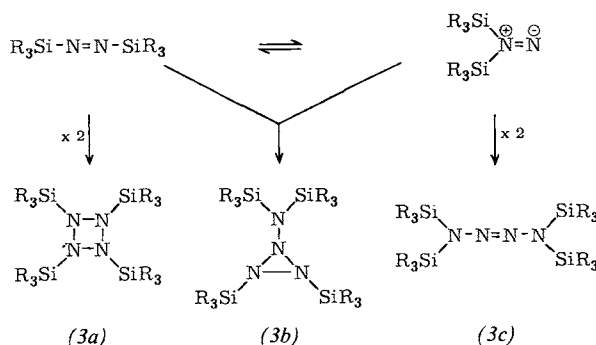
By N. Wiberg and W. Uhlenbrock [*]

Thermal decomposition of bis(trimethylsilyl)diimine (1) below 0 °C affords almost exclusively tetrakis(trimethylsilyl)hydrazine (2) and nitrogen^[2]. We have now found that an increase in thermolysis temperature reduces the yield of these two products; instead, other thermolysis products are formed, and in particular a compound having the composition (R₃Si)₄N₄ (3) (R = CH₃; elemental analysis, mass spectrum) as well as tris(trimethylsilyl)hydrazine (4).



The hydrogen required for formation of (4) comes from methyl groups; those molecules affected by hydrogen abstraction react further to give various products that have not yet been examined in detail.

The ¹H-NMR spectrum of compound (3) contains only one signal in the (CH₃)₃Si region [δ = -16.7 Hz, measured against TMS as internal standard in benzene^[3]]. Thus, of the isomers (3a), (3b), and (3c) that are formally possible according to



(3b) can be ruled out (the same applies to the compound (R₃Si)₂N—N(SiR₃)—N=N(SiR₃)). The IR and Raman spectra indicate the presence of (3c) rather than (3a); unequivocal evidence for an atomic skeleton containing an N=N bond comes, in particular, from the position, intensity, and polarization of a band at 1444 cm⁻¹ that is absent from the Raman spectrum of (2)^[4]. The electronic spectrum of the compound also lends support to the 2-tetrazene structure: as in the case of organic tetrazenes^[5] an n → π* transition of medium intensity is observed at about 280 nm, λ_{max} = 293 nm, (ε = 5820).