Photolysis Procedures. The light source most frequently used was a 400-W, medium-pressure, mercury, General Electric lamp H400 A-33-1. However, removal of the outer glass shell from this street lamp and slight bending of the electrical connections make it suitable as an inexpensive source of ultraviolet radiation. Light in the vicinity of 313 nm was isolated by placing the mercury lamp in a water-cooled quartz well filled with an aqueous solution, 0.0025 M in K_2CrO_4 and 1% in K_2CO_3.[27] The jacket surrounded the lamp with a 7-nm thickness of filter solution.

The solutions to be photolyzed were placed in 75-mm long, cylindrical, 20 mm o.d. Pyrex tubes. The tops of the tubes were fitted with 14/20 ST outer joints. The tubes could be sealed with a 14/20 ST inner joint to which was attached a Pyrex ST stopcock.

The contents of the tubes were first frozen with either liquid nitrogen or a dry ice–acetone slurry. The stopcock to the tube was then opened, and the tube was evacuated to 0.005 Torr. The stopcock was closed and the contents of the tube was allowed to thaw. The cycle was repeated four times.

To ensure that the samples received equal amounts of incident light during the quantum yield determinations, the tubes to be photolyzed were rotated about the light source at 5 revolutions/min with a Southern New England Ultraviolet Company Model MGR 500 "merry-go-round".

The samples to be irradiated for quantum yield determinations were maintained at 30 ± 0.4° throughout the photolysis by immersing the samples, "merry-go-round", and light source into a constant-temperature bath.

For product studies, samples were photolyzed in degassed Pyrex tubes, suspended in a Rayonet photochemical reactor, equipped with 300-nm bulbs. The light from the bulbs was filtered by suspending the solutions in the same dichromate carbonate solution used as a filter in quantum yield determinations and quencher studies.

References and Notes

(1) H. G. Kuivila and P. L. Maxfield, *Inorg. Nucl. Chem. Lett.*, 1, 29 (1965).
(2) H. G. Kuivila, *J. Organomet. Chem.*, 10, 41 (1967).
(3) A. G. Brook and J. M. Duff, *J. Am. Chem. Soc.*, 91, 2118 (1969).
(4) A. G. Brook, P. J. Dillon, and R. Pearce, *Can. J. Chem.*, 49, 133 (1971).
(5) J. M. Duff and A. Brook, *Can. J. Chem.*, 51, 2869 (1973), and references cited therein.
(6) Preliminary observations have been reported: H. G. Kuivila, K.-H. Tsai, and P. L. Maxfield, *J. Am. Chem. Soc.*, 92, 6696 (1970).
(7) H. G. Kuivila, J. E. Dixon, P. L. Maxfield, N. M. Scarpa, T. M. Topka, K.-H. Tsai, and K. R. Wursthorn, *J. Organomet. Chem.*, 86, 89 (1975).
(8) C. Deblandre, M. Gielen, and J. Nasielski, *Bull. Soc. Chim. Belg.*, 73, 214 (1964)
(9) C. Moureu, M. Murat, and L. Tampier, *Ann. Chim. (Rome)*, 15, 221 (1921).
(10) H. G. Kuivila and C. H.-C. Pian, *Tetrahedron Lett.*, 2561 (1973).
(11) L. Wilputte-Steinert and J. Nasielski, *J. Organomet. Chem.*, 24, 113 (1970).
(12) N. C. Yang and E. D. Feit, *J. Am. Chem. Soc.*, 90, 504 (1968).
(13) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 4009 (1965).
(14) M. A. El-Sayed, *J. Chem. Phys.*, 41, 2462 (1964).
(15) P. J. Wagner, *J. Chem. Phys.*, 45, 2335 (1966).
(16) Product determinations were not made in connection with the quenching studies so the results do not tell us whether only one or both primary chemical reactions are being quenched. The increase in quenching efficiency with chain length parallels the increase in the proportion of type II reaction cited in Table II and is of the order expected (P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 4009 (1965)). Thus, the tin–carbon cleavage may not be quenched by piperylene in these compounds.
(17) J. O. Pavlik, P. I. Picoard, A. C. Somersall, and J. E. Guillet, *Can. J. Chem.*, 51, 1435 (1973). References to other ketone-sensitized reactions of alkyl halides are contained in this paper.
(18) S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965). This statement ignores the often significant effect that a proximate radical center has on a given bond dissociation energy.
(19) R. A. Jackson in "Advances in Free Radical Chemistry", G. H. Williams, Ed., Academic Press, New York, N.Y., 1969, p 234.
(20) J. Meinwald and R. A. Chapman, *J. Am. Chem. Soc.*, 90, 3218 (1968).
(21) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Am. Chem. Soc.*, 92, 2564 (1970).
(22) See, for example, J. D. Kennedy and H. G. Kuivila, *J. Chem. Soc., Perkin Trans. 2*, 1812 (1972), and references cited therein.
(23) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Synth.*, 45, 77 (1965).
(24) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1970.
(25) D. Doddrell, I. Burfit, W. Kitching, M. Bullpit, C.-H. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila, and R. H. Sarma, *J. Am. Chem. Soc.*, 96, 1640 (1974).
(26) E. Lippmaa, T. Pehk, J. Paasivirta, N. Belikova, and A. Plate, *Org. Magn. Reson.*, 2, 581 (1970).
(27) F. D. Lewis and N. J. Turro, *J. Am. Chem. Soc.*, 92, 311 (1970).

Photoelectron Spectra and Molecular Properties. L.[1-3] On the Blue Color of Bis(trimethylsilyl)diimine

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Abstract: Photoelectron (PE) and uv spectra of group 4 azo compounds $R_3X—N{=}N—YR_3$ (X, Y = C, Si) and $H_5C_6—N{=}N—XR_3$ (X = C, Si, Ge) are reported. A comparative discussion, based on CNDO calculations, attributes the low ionization potentials of the trimethylsilyl derivatives to substantial electron donation from the R_3Si substituents. The unique electronic spectrum of the title compound can be rationalized considering in addition electron–electron interaction as well as Rydberg excitations.
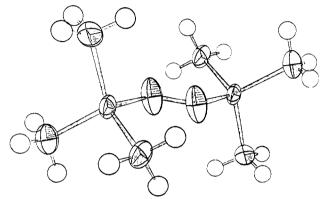
It is the blue color of bis(trimethylsilyl)diimine which has stimulated investigation of its molecular properties[3,4] as well as those of related compounds.[2,3,5] In spectroscopic terms, its long wavelength $n_N^+ \rightarrow \pi^*$ transition[6-9] is batho-

chromically shifted by more than 14000 cm^{-1} (!) relative to that of the isoelectronic *tert*-butyl derivative.[3,6,7] As pointed out for the corresponding ketones,[5] analogous substituent dependent shifts of the long wavelength absorption are also observed for other chromophoric systems. For bis(trimethylsilyl)diimine and its challenging spectroscopic prop-

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$\nu_m(n \longrightarrow \pi^*)$

$$\begin{array}{cc} & XR_3 \\ & | \\ N = N \\ | \\ R_3X \end{array} \qquad \begin{array}{c} R_3X \\ \diagdown \\ C = O \\ \diagup \\ R_3X \end{array}$$

(X = C) 27200 cm⁻¹   33600 cm⁻¹
(X = Si) 12750 cm⁻¹   18500 cm⁻¹
(R = CH₃)

erties tentative explanations range from inductive destabilization of the nitrogen electron pairs and/or silicon acceptor orbital participation[2-6] to a widening of the angle NNSi.[3] In the meantime the question of $d_\pi p_\pi$ bonding in organometalloids is widely accepted to be a rather semantic one[10-12] and a recent x ray structure determination proved an angle NNSi of 120°.[13] Although other silicon nitrogen com-
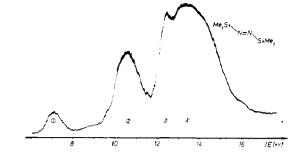

pounds exhibit a comparable angle[13] of ~120°, it is increased relative to angles CNN ~ 106-113° found for unstrained azo alkanes. The most striking difference, however, is the rather short NN bond length $d_{NN} = 1.17$ Å,[13] halfway between values for carbon azo compounds with $d_{NN} = 1.23-1.27$ Å and the nitrogen molecule with $d_{NN} = 1.11$ Å. This finding can be attributed to an unusual high electron density in the NN bond of bis(trimethylsilyl)diimine and already suggests a considerable electron donation from the adjacent silicon substituents.
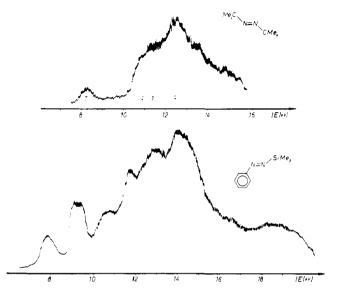
PE Spectra and Assignment

In order to support the remaining explanation for the blue color of bis(trimethylsilyl)diimine, i.e., a model emphasizing inductive effects, PE spectra of some group 4 azo compounds were recorded (Figure 1 and Table I).

The first PE band—well separated in the spectra of most azo compounds[7,14]—is readily assigned to ionization from the nitrogen electron pairs (Figure 2: n_N^+). This can be substantiated not only by the results of CNDO calculations but also by comparison with the carefully analyzed PE spectrum of azomethane[14] and by general uv spectroscopic arguments.[6-9] As expected,[15] the corresponding ionization energy, IE₁, is lowered on replacing tert-butyl by trimethylsilyl or trimethylgermyl substituents (Table I). Thereby a nearly constant shift ΔIE_1 occurs on stepwise substitution for the diimine derivatives R₃X—N=N—XR₃. This observation favors the application of an inductively dominated model, in agreement with, e.g., the CNDO charge densities at the nitrogen atoms q_N of the neutral molecules (values

$$\begin{array}{ccc} & \overset{0.14}{SiR_3} & \overset{-0.24}{CR_3} \\ \overset{}{N=N}\diagup & \overset{}{N=N}\diagup & \overset{}{N=N}\diagup \\ R_3Si\diagup_{-0.20} & R_3Si\diagup_{-0.09} & R_3C\diagup_{-0.12} \\ 0.53 & 0.53 & 0.14 \end{array}$$

for R = CH₃ are omitted). Thus the trimethylsilyl substituent, by its electron donating properties, considerably destabilizes the nitrogen lone pair electrons of the azo group. Ad-
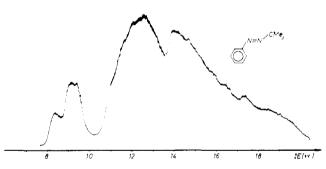
Figure 1. PE spectra of bis(trimethylsilyl)diimine, bis(tert-butyl)diimine, and of corresponding phenyl azo derivatives.
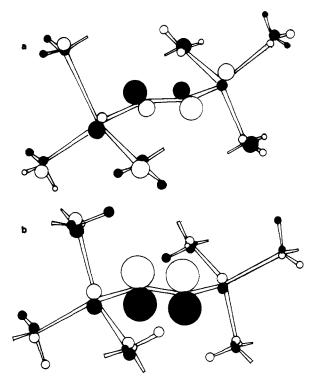
Table I. Vertical Ionization Potentials (IE_n, eV) of Bis(trimethylsilyl)diimine, 1-Trimethylsilyl-2-tert-butyldiimine, Bis(tert-butyl)diimine, and of Some Group 4 Phenylazo Compounds, C₆H₅—N=N—X(CH₃)₃

	X	Y	IE₁	IE₂	IE₃	IE₄	IE₅
	Si	Si	7.1	10.6	12.45	13.5	
	Si	C	7.6	10.4	11.0	12.6	
	C	C	8.2	10.9	11.5	12.5	
	C		8.35	9.1	9.35	11.1	12.5
	Si		7.85	9.1	9.4	10.7	11.8
	Ge		7.65	9.0	9.35	10.2	11.6

ditional CNDO calculations including 3d$_{Si}$ orbitals into the basis set did neither significantly improve the results nor provide new insight. In accordance with previous PE spectroscopic assignments based on CNDO calculations,[11] the conclusion therefore remains that there seems to be no way to definitely prove or disprove 3d$_{Si}$ orbital participation.[10-12]

Very little else can be assigned in the rather featureless diimine PE spectra (Figure 1); even the number of ionizations hidden under the humps cannot be extracted. This is due to the numerous σ-type ionizations in the 28-atom molecules $(H_3C)_3X$—N=N—$X(CH_3)_3$ containing 60 valence electrons. In general, three characteristic molecular orbitals are expected for the azo group: the nitrogen electron pair combinations n_N^+ and n_N^- and the π bonding orbital π_{NN}. The relative energies of these orbitals have been discussed[14] in terms of a through space splitting[16] into n_N^-/n_N^+ with a subsequent through bond destabilization[15] shifting the n_N^+ orbital above n_N^-. The lowest ionization potential therefore is assigned to the n_N^+ orbital combination (Figures 1 and 2).

However, semiempirical MO calculations even on simple azo compounds such as azomethane suggest that the classification given in Figure 2 represents an unrealistically oversimplified picture.[14] All the more, for the complicated molecules dealt with in this paper any such classification hardly seems possible. Judging from the CNDO calculation only the n_N^+ and π_{NN} orbitals can still be recognized, whereas n_N^- is heavily mixed with numerous σ-bonding orbitals of the substituents $X(CH_3)_3$. This is illustrated by, e.g., a sketch of the disilyldiimine molecular orbitals ψ_{24} (a) and ψ_{23} (b) with highest n_N^- and π_{NN} contributions, respectively:

For example, in $\psi_{23}(n_N^-)$ the nitrogen orbital components amount to only one-third of the total, and thus the interesting problem of substituent dependent magnitude of the n_N^+/n_N^--splitting finally must be abandoned because no (canonical) molecular orbital can be identified as n_N^- in more complex azo compounds.

To end the PE spectroscopic discussion of the diimine derivatives R_3X—N=N—XR_3, in Figure 3 the detectable lower ionization potentials (Table I) are compared with the CNDO eigenvalues assuming validity[17] of Koopmans theorem $IE_n = -\epsilon_J^{SCF}$.

In view of the complexity of the molecules dealt with, the overall PE spectroscopic pattern is satisfactorily reproduced, e.g., the 3-eV gap between the first two ionizations. According to the calculations, some σ orbitals are inserted
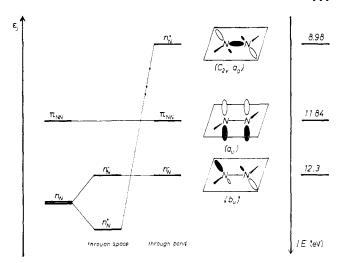

Figure 2. Qualitative splitting scheme for the characteristic molecular orbitals of an azo group and the first three ionization energies of azomethane.[12]
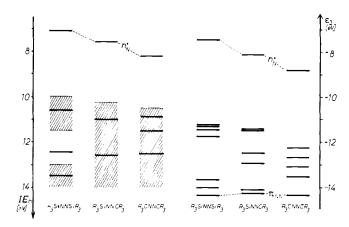

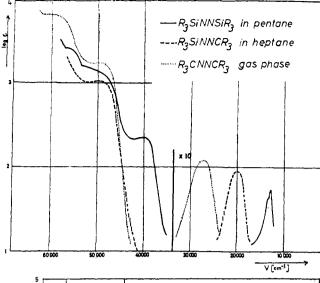Figure 3. Comparison of ionization energies IE_n (eV) and CNDO eigenvalues ϵ_J^{CNDO} (eV).

between n_N^+ and π_{NN}, which also seems reasonable with respect to the PE spectra of tetramethylsilane[18] and 2,2-dimethylpropane.[19] However, no evidence can be gathered from the PE spectra as to where to locate the π_{NN} ionizations. An approximate estimate based on the $IE_n/-\epsilon_J^{SCF}$ correlation (Figure 3) yields for bis(trimethylsilyl)diimine a difference $IE(\pi_{NN}) - IE(n_N^+)$ of more than 3 eV.

For the PE spectra of the phenyl azo derivatives C_6H_5—N=N—XR_3 (Figure 1 and Table I) a perturbation approach suggests that the degeneracy of e_{2g} benzene orbitals $(IE_1(C_6H_6) = 9.24$ eV[15]$)$ is removed by inductive and conjugative effects of the azo group. The shift of the first PE band again reflects increasing (inductive + hyperconjugative) electron donation from the substituents $CR_3 < SiR_3 < GeR_3$.

Summarizing, the PE spectra of the group 4 azo compounds are rather poorly structured and thus—besides some phenyl-type ionizations—only the strongly substituent dependent first bands can be unambiguously assigned. Nevertheless, based on the energies of the n_N^+ orbital combinations—established above within the limits and implications of Koopmans' theorem[17]—some comments on the optical absorption spectra and especially on the electronic transitions of bis(trimethylsilyl)diimine are rendered possible.

Absorption Spectra

The optical absorption spectra (Figure 4) have been recorded in hydrocarbon solvents except for the gaseous phase
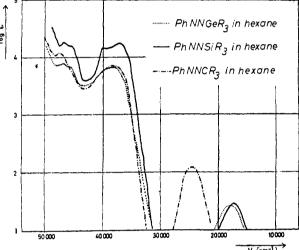
Figure 4. Optical absorption spectra of some group 4 azo compounds $R_3X—N=N—XR_3$ and $H_5C_6—N=N—XR_3$.[20]

spectrum of bis(*tert*-butyl)diimine. Transition energies and molar extinction coefficients are given in Table II.

In all electronic spectra[20] the $n^+ \rightarrow \pi^*$ bands are well-separated from the high intensity absorption regions, displaying a characteristic long wavelength shift on $R_3C \rightarrow R_3Si$ substituent exchange. The $n^+ \rightarrow \pi^*$ excitation energies of the R_3Si and R_3Ge derivatives differ only little. The uv region of the phenylazo compounds is dominated by transitions from the aromatic system[21]—also in accord with the assignment of the second and third ionization potentials (Table I) to predominantly phenyl-type molecular orbitals. In contrast, the $R_3X—N=N—XR_3$ derivatives show intense absorptions only near 50000 cm⁻¹, and again bis(tri-

methylsilyl)diimine exhibits a special feature. Besides the lowest $n_N^+ \rightarrow \pi^*$ excitation energy observed so far for an azo compound at the borderline between the visible and infrared spectral regions, there appears a second band of moderate intensity at about 40000 cm⁻¹ (Figure 4 and Table II).

The electronic spectra even of simple azo compounds are still puzzling; in general, only the $n_N^+ \rightarrow \pi^*$ transition can be unequivocally assigned, whereas, e.g., the location of the $\pi \rightarrow \pi^*$ band has been disputed again and again.[6-9,22] For a discussion of the bis(trimethylsilyl)diimine excitations we start with an approach applied to azomethane by Haselbach and Schmelzer.[8] On the same level of approximation as Koopmans' theorem,[17] the electronic excitation energies are given by[23]

$$\Delta E_{i \rightarrow k} = \epsilon_k - \epsilon_i - J_{ik} + 2K_{ik}$$

correcting the orbital energy difference $\epsilon_k - \epsilon_i$ for changes in interelectronic repulsions, i.e., by coulomb integral J_{ik} and by exchange integral K_{ik} terms. Within the CNDO approximation and parametrization,[23] values of

$$J_{ik} = \int\int \psi_i^+(1)\psi_k^+(2)r_{12}^{-1}\psi_i(1)\psi_k(2) \, d\tau_1 d\tau_2$$

$$K_{ik} = \int\int \psi_i^+(1)\psi_k^+(2)r_{12}^{-1}\psi_k(1)\psi_i(2) \, d\tau_1 d\tau_2$$

have been calculated for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of bis(trimethylsilyl)diimine.

Transition	J_{ik}	K_{ik}	$J_{ik} - 2K_{ik}$	$\Delta E_{i \rightarrow k}$	
$n_N^+ \rightarrow \pi^*$	8.65	0.00	8.6	0.9	(eV)
$\pi \rightarrow \pi^*$	8.65	1.36	5.9	10.5	(eV)

Although no emphasis is put on the actual numerical values, obviously the K_{ik} terms differ considerably for the different electronic transitions of the disilyl azo compound. According to ref 8, small K_{ik} values can be traced back to only minor contributions of same basis functions to the two molecular orbitals under consideration, whereas small J_{ik} values indicate considerable orbital extension outside the region of the azo group.[8] All in all, reasoning along these lines Hasselbach and Schmelzer[8] have accounted for the fact that the difference between n_N^+ and π ionization potentials in azomethane is smaller than the difference between $n_N^+ \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies. For bis-(trimethylsilyl)diimine a difference in $J_{ik} - 2K_{ik}$ of 2.7 eV is calculated, suggesting a much larger distance between n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands in the electronic spectrum than expected from the ionization potential difference IE ("π_{NN}") − IE(n_N^+) alone. Finally, the CNDO excitation energy $\Delta E_{\pi \rightarrow \pi^*}$, even though its numerical accuracy might be questioned, would place the $\pi \rightarrow \pi^*$ band in the vacuum uv region at about 80000 cm⁻¹.
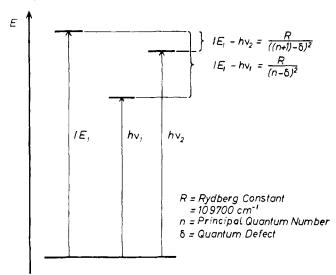
As pointed out before, the assignment of the $\pi \rightarrow \pi^*$ transition in the electronic spectra of azo compounds R—N=N—R is not yet settled.[8,9,22] In azoalkanes the $\pi \rightarrow \pi^*$ excitation energy possibly exceeds 70000 cm⁻¹.[9,22] For the observed transitions in between $n_N^+ \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ two

Table II. Transition Energies (ν_m, cm⁻¹) and Molar Extinction Coefficients(ϵ_m, l./(mol cm)) of Bis(trimethylsilyl)diimine,[b] 1-Trimethylsilyl-2-*tert*-butyldiimine,[b] Bis(*tert*-butyl)diimine, and of Phenylazo Compounds, $C_6H_5—N=N—X(CH_3)_3$[b] with X = C, Si, Ge[20]

	X	Y	$\tilde{\nu}_1/\epsilon_1$	$\tilde{\nu}_2/\epsilon_2$	$\tilde{\nu}_3/\epsilon_3{}^a$	$\tilde{\nu}_4/\epsilon_4{}^a$
R,X—N=N—YR,	Si	Si[b]	12750/5	40000/260	52100/1660	57000/2680
	Si	C[b]	20000/9		50000/1080	
	C	C[c]	27200/12		50000/1800	59500/6800
(Ph)—N=N—XR,	C	b	24400/144	38400/8400	47600/11900	
	Si	b	17250/29	37500/16350	40000/14750	45500/15400
						46600/18100
	Ge	b	17800/26	39200/6780		46800/7840

[a] Maxima of undeconvoluted bands. [b] Solvent: hydrocarbon (pentane, hexane, or heptane). [c] Gas phase.

assignments are discussed in the literature: $n_N^- \rightarrow \pi^*$[6,8,22] and $n_N^+ \rightarrow np$ Rydberg.[9] The latter proposal by Robin[9] is based on the following general procedure.[24] The Rydberg term value $R/(n - \delta)^2$ is obtained by subtracting the uv excitation energy $h\nu_1$ from the photoelectron spectroscopic ionization potential IE_1. The quantum defect δ calculated from the term value allows one to predict the excitation energies $h\nu_{1+m}$ of higher members $n + m$ ($m = 1, 2, 3 \ldots$)

$$IE_1 - h\nu_2 = \frac{R}{((n+1)-\delta)^2}$$

$$IE_1 - h\nu_1 = \frac{R}{(n-\delta)^2}$$

R = Rydberg Constant = 109700 cm^{-1}
n = Principal Quantum Number
δ = Quantum Defect

of the corresponding Rydberg series.[24] For azomethane, the $n_N^+ \rightarrow 3p$ Rydberg assignment of the band at 54000 cm⁻¹ is not only supported by the correct prediction $\nu(n_N^+ \rightarrow 4p$ Rydberg) ~63000–64000 cm⁻¹ of the next band but also by the vanishing vibrational fine structure in the spectrum recorded under 119 atm of nitrogen pressure.[9]

Comparison of the azomethane values with those for the symmetrically disubstituted azo compounds R—N=N—R shows term values $IE_1 - \nu_1$, quantum defects δ, and band distances $\nu_2-\nu_1$ of the same order of magnitude (Table III). In addition, the $n_N^+ \rightarrow 5p$ Rydberg excitation is predicted analogously at about 52000 cm⁻¹ (cf. Figure 4). The satisfying fit of both the presumably 4p and 5p Rydberg transitions to the recorded spectrum lends some credit to a tentative assignment $n_N^+ \rightarrow 3p$ Rydberg for the long wavelength band at 40000 cm⁻¹ of bis(trimethylsilyl)diimine. Its rather low intensity (ϵ_{mol} ~260 l./(mol cm)) is in accord with the uv spectra of azo alkanes which show for the corresponding band a considerable drop of the molar extinction with increasing size of the alkyl group, e.g., for H_3C- 7500, and for $(H_3C)_2HCCH_2$- 1200 l./(mol cm).[9] This observation can probably be explained by a distortion of the symmetry of lower Rydberg states accompanied by intensity redistribution.[9]

Concluding Remarks

Summarizing facts and speculations, the electronic spectrum of the blue title compound, bis(trimethylsilyl)diimine, is unique not only because of the tremendous $n_N^+ \rightarrow \pi^*$ shift relative to azo alkanes but also due to the strong electron donation by R_3Si substituents. In addition, there is some evidence for a low-lying 3p Rydberg state.

Rydberg states of polyatomic molecules, as defined in ref 24, can play a rôle in photochemistry.[25] For example, Sakurai and co-workers[26] reported that 1,2,3-trisilacycloheptanes expel almost quantitatively dialkylsilylenes when irradiated with a low pressure mercury arc lamp. Ramsey[27] has suggested a three-membered ring transition state for this reaction. The first ionization potential of octamethyltrisilane[28] amounts to $IE_1 = 8.19$ eV $\simeq 66000$ cm⁻¹, and the

Table III

R	CH_3	$C(CH_3)_3$	$Si(CH_3)_3$	
IE_1	72400	66100	57300	cm⁻¹
ν_1	54200	49000ᵃ	40000	cm⁻¹
$IE_1 - \nu_1$	18400	17100	17300	cm⁻¹
δ	0.56	0.47	0.48	
$(n_N^+ \rightarrow 4p)$calcd	63000	57500	48500	cm⁻¹
ν_2	63000–64000	58000ᵃ	49000ᵃ	cm⁻¹

ᵃ Corrected for tentative deconvolution (cf. Figure 4 and Table II).

mean first uv excitation energy of trisilacycloheptanes[26] to ν_m ~ 46000 cm⁻¹. Substituting these values into the Rydberg formula yields a term value $R/(n - \delta)^2$ ~ 20000 cm⁻¹, which could correspond to a $4p_{Si}$ Rydberg state.[24] If

so, then under local C_{2v} symmetry only the two transitions $\sigma_{SiSiSi} \rightarrow 4p_{Si}$ in the SiSiSi plane would be allowed (trisilacycloheptanes: $\epsilon_{max} = 6700$–8700 l./(mol cm)[26]), fitting nicely into the suggested three-membered ring transition state model. Proof or disproof of assumptions like the ones above is presently attempted by combined PE and uv spectroscopy.[29]

Experimental Section

Syntheses. All compounds have been prepared following literature routes: bis(trimethylsilyl)diimine,[30] 1-trimethylsilyl-2-tert-butyldiimine,[31] bis(tert-butyl)diimine,[32] phenylazo-tert-butyl,[31] phenylazotrimethylsilyl,[31] phenylazotrimethylgermyl.[31] Their purity has been controlled by standard techniques.

Spectra. The PE spectra were recorded using a Perkin-Elmer PS 16. Due to the thermal instability—especially of bis(trimethylsilyl)diimine—the compounds were evaporated directly into the ionization chamber from a bulb cooled by a dry ice bath. Regulating the height of the dry ice bath allowed the maintenance of an approximately constant vapor pressure of the substance. This technique, however, unfortunately did not yield high quality spectra, and therefore ionization energies are only reliable to 0.1–0.2 eV. Uv spectra were recorded in the gas phase on a McPherson 224 equipped with a Hinteregger hydrogen lamp and in solution on a Cary 14. All hydrocarbon solvents have been of spectral purity.

Calculations. The CNDO calculations have been performed at the Hochschul-Rechenzentrum at Frankfurt University, using a modified version[33] of the QCPE program 141. Bond lengths of bis(trimethylsilyl)diimine have been taken from the structure determination,[13] whereas the bond angles and dihedral angles have been idealized. For the di-tert-butyl and the unsymmetrically substituted compound, standard geometries have been used. The uv transition energies have been calculated by adding a subroutine, where K_{ik} and J_{ik} are computed from the CNDO LCAO expansion coefficients and the CNDO atomic electron–electron repulsion integrals γ_{AB}.[23]

References and Notes

(1) Part XLIX: H. Bock, "Photoelectron Spectra of Boron/Nitrogen Compounds" in Gmelin, Handbuch der Anorganischen Chemie, K. Niedenzu, Ed., Erg. Werk 8. Aufl., Bd. 23: Bor-Verbindungen Teil 5, Springer, Berlin, 1975.
(2) Also part XI of Color and Constitution of Azo Compounds; for X see H. Seidl, H. Bock, N. Wiberg, and M. Veith, Angew. Chem., 82, 42 (1970); Angew. Chem., Int. Ed. Engl., 9, 379 (1970).
(3) Also part XVIII of Diimine and Derivatives; for XVII see N. Wiberg, W. Joo, and E. Weinberg, J. Organomet. Chem., 73, 49 (1974); cf. also the review N. Wiberg, Angew. Chem., 83, 379 (1971); Angew Chem., Int. Ed. Engl., 10, 374 (1971).
(4) U. Krynitz, F. Gerson, N. Wiberg, and M. Veith, Angew. Chem., 81, 745 (1969); Angew. Chem., Int. Ed. Engl., 8, 755 (1969).
(5) B. G. Ramsey, A. D. Brook, and H. Bock, J. Organomet. Chem., 74,

C41 (1974); H. Bock, H. Alt, and H. Seidi, *J. Am. Chem. Soc.*, **91**, 355 (1969), and literature cited; especially A. G. Brook and C. J. D. Peddle, *J. Organomet. Chem.*, **5**, 106 (1966).

(6) H. Bock, *Angew. Chem.*, **77**, 469 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 457 (1965); H. Rau, *Angew. Chem.*, **85**, 248 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 224 (1973), and literature quotations given in both.

(7) Recently K. N. Houk, Y.-M. Chang, and P. S. Engel, *J. Am. Chem. Soc.*, **97**, 1824 (1975), reported ionization potentials and $n^+ \rightarrow \pi^*$ transitions of alkyl azo compounds, reviewing previous work.

(8) E. Haselbach and A. Schmelzer, *Helv. Chim. Acta*, **54**, 1575 (1971), and literature quotations given.

(9) M. B. Robin "Higher Electronic States of Polyatomic Molecules", Vol. 2, Academic Press, New York, N.Y., 1975, p 68ff, and references quoted there. Cf. also the addendum on p 327, pointing out that Rydberg transitions generally are not expected to survive in paraffin solution spectra.

(10) G. Bieri, F. Brogli, E. Heilbronner, and E. Kloster-Jensen, *J. Electron Spectrosc.*, **1**, 67 (1972/73).

(11) W. Ensslin, H. Bock, and G. Becker, *J. Am. Chem. Soc.*, **96**, 2757 (1974).

(12) R. L. DeKock and D. R. Lloyd, *Adv. Inorg. Chem. Radiochem.*, **16**, 98 (1974).

(13) M. Veith and H. Bärnighausen, *Acta Crystallogr., Sec. B*, **30**, 1806 (1974).

(14) E. Haselbach and H. Heilbronner, *Helv. Chim. Acta*, **53**, 684 (1970); E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem.*, **81**, 897 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 878 (1970).

(15) H. Bock and B. G. Ramsey, *Angew. Chem.*, **85**, 773 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 734 (1973), and literature quoted therein.

(16) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).

(17) Cf. E. Heilbronner "Some Aspects of UPS" in Proceedings of the I. International Congress of Quantum Chemistry at Mentone, 1973, R. Daudel and B. Pullmann, Ed., D. Reidel Publishing Co., Dordrecht, Holland, p 211. For the original publication see T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).

(18) S. Evans, J. C. Green, P. J. Joachim, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, 905 (1972); see also M. C. Green, M. F. Lappert, J. B. Pedley, W. Schmidt, and B. T. Wilkins, *J. Organomet. Chem.*, **31**, C55 (1971).

(19) W. Schmidt and B. T. Wilkins, *Angew. Chem.*, **84**, 168 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 221 (1972).

(20) Thesis, M. Veith, University of Munich, 1971.

(21) Cf., e.g., T. E. Peacock "Electronic Properties of Aromatic and Heterocyclic Molecules", Academic Press, London, 1965, or J. N. Murrell "The Theory of the Electronic Spectra of Organic Molecules", Methuen & Co, London, 1963.

(22) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Am. Chem. Soc.*, **89**, 1564 (1967), and literature quotations given.

(23) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

(24) M. B. Robin, "Higher Electronic States of Polyatomic Molecules", Vol. 1, Academic Press, New York, N.Y., 1974.

(25) Cf., e.g., C. Sandorfy, P. Ausloos, and M. B. Robin, Ed., "Chemical Spectroscopy and Photochemistry in the Vacuum-Ultraviolet," D. Reidel Publishing Co, Dordrecht, Holland, 1974.

(26) H. Sakurai, Y. Kobayashi, and Y. Nakadaira, *J. Am. Chem. Soc.*, **93**, 5273 (1971).

(27) B. G. Ramsey, *J. Organomet. Chem.*, **67**, C67 (1974).

(28) H. Bock and W. Ensslin, *Angew. Chem.*, **83**, 435 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 404 (1971).

(29) Cf., e.g., for boron nitrogen compounds W. Fuss and H. Bock, *J. Chem. Phys.*, **61**, 1613 (1974), or W. Fuss, *Z. Naturforsch. B*, **29**, 514 (1974).

(30) N. Wiberg, W. Joo, and W. Uhlenbrock, *Angew. Chem.*, **80**, 661 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 640 (1968).

(31) N. Wiberg and M. Veith, *Chem. Ber.*, **104**, 3191 (1971).

(32) E. Farenhorst and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **75**, 993 (1953).

(33) J. Kroner, D. Proch, W. Fuss, and H. Bock, *Tetrahedron*, **28**, 1585 (1972).

Reaction of Thiol Anions with Benzene Oxide and Malachite Green

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Abstract: The second-order rate constants for the reactions of a number of thiol anions with benzene oxide (BO) have been determined as have the rate constants and equilibria for the reaction of thiol anions with the acid–base equilibria species of malachite green (MG). β constants for reaction of thiol anion and amines with the nonprotonated species of malachite green are comparable ($\sim$0.3) to the β constants for the reactions of amines and thiol anions with ethylene oxide (EO) and thiol anions with BO. In addition the rate constants for the reaction of thiol anions with BO and EO are comparable. These results are discussed in terms of attack of RS^- directly upon BO and EO in an SN2 reaction vs. trapping of intimate ion pairs by RS^-. As compared with the ability of ethylene oxide to react with nucleophiles possessing basicities as low as that of water, benzene oxide is attacked by only the more polarizable nucleophile as N_3^-, RS^-, etc. This is shown to be due not to the greater selectivity of benzene oxide toward soft bases, but to the fact that the spontaneous aromatization rate (i.e., water rate) of benzene oxide exceeds the rate of reaction of ethylene oxide with water by ca. 10^3. It is predicted that benzene oxides substituted with highly electron-withdrawing groups will exhibit reactivity to a broad range of nucleophiles. This prediction is predicated on the previously determined fact that aromatization of benzene oxide is associated with a $\rho \simeq -7$. For the purposes of this study, it was desirable to determine the microscopic pK_a values for the thiol species under the conditions of the kinetic and thermodynamic studies (30°, solvent water, $\mu = 1.0$). These constants are reported herein and compared with literature values.

As part of the normal metabolic paths of catabolism and detoxification, both biotic and exobiotic aromatic structures are converted to arene oxides. However, these normal metabolic processes may result in the assassination of the subject. Thus, arene oxide moieties formed from exobiotic aromatic hydrocarbons have been implicated as causative agents in mutagenesis, carcinogenesis, and tissue necrosis.[2,3] The pathological effects of arene oxides have been attributed to their acting as alkylating agents.[4-7] The enzyme[8] and nonenzyme mediated 1,2-addition of the sulfhydryl group of glutathione to arene oxides appears as a major

means of protection from the cytotoxic effects of these agents. Thus, both the cytotoxic effects of arene oxides and the detoxification of these substances involve nucleophilic addition to the oxide moiety. The importance of understanding the mechanisms of nucleophilic addition to arene oxides is obvious. Important studies dealing with the formation of products and their stereochemistry have been published[9-16] but, with the possible exception of the hydration of 8,9-indane oxide,[16] no kinetic investigations of the nucleophilic addition to arene oxide have appeared.[17] The present investigation deals with the kinetics of addition of thiol anions to benzene oxides. The magnitude of the rate constants and their sensitivity to the proton basicity of the