energy. Thus, for solution measurements employing donors having reasonably allowed emissions, contact singlet exchange energy transfer will probably be uncommon.

Acknowledgment. We gratefully acknowledge the Air Force Office of Scientific Research (Chemistry) (Grant AFOSR 78-3590) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. All lifetime measurements were performed on the University of Virginia laser facility which was purchased in part with NSF Grant CHE 77-09296.

Registry No. $[Ru(bpy)_3]^{2+}$, 15158-62-0; Rhodamine 101, 64339-18-0; cresyl violet, 18472-89-4; nile blue, 2381-85-3; oxazine 1, 24796-94-9.

Effects of Cyclic 8-π-Electron Conjugation in Reductively Silylated N-Heterocycles[1]

Wolfgang Kaim

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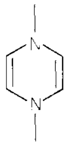
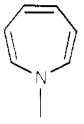
Abstract: A number of partly reduced N-heterocycles, **2–15**, have been prepared by reductive silylation of aromatic precursors. The *N*-silyl substituents stabilize unusual electronic structures such as the 1,4-dihydropyrazine system toward rearrangements. In addition, R_3Si substitution is likely to cause planarization at the amino nitrogen atoms. This may lead to cyclic 8-π-electron conjugation, as has been established, e.g., for 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**2**). The experimental results obtained for **2** by comparative ^{1}H NMR and photoelectron spectroscopic studies are a distinct paratropism, an exceptionally low ionization potential, and an enormous difference between the first and second ionization energy. These effects confirm the predictions made for planar 1,4-dihydropyrazine on the basis of HMO calculations. Corresponding to the very low ionization potentials of most of the reduced compounds, persistent radical cations such as $\mathbf{2}^{+\cdot}$ have been readily obtained and were fully characterized by ESR spectroscopy. Modification of the 1,4-dihydropyrazine **2** by methyl substitution or by extension of the π system results in an attenuation of the 8-π- electron conjugation through steric and/or electronic factors. The flexibility of this system toward steric requirements can be related to the redox behavior of flavoenzymes.

For a variety of reasons, the 1,4-dihydropyrazine structural unit

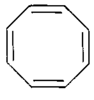


I

has attracted a great deal of attention: (1) It can be regarded as a potential "antiaromatic"[2] system due to the availability of 8 π electrons in a sterically constrained six-membered ring.[3-6] Such a system cannot deviate as much from planarity as the iso-π-electronic seven-[7,8] and eight-membered[9a] rings II and III.

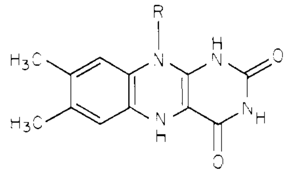


II

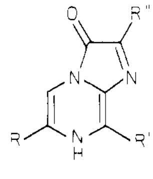


III

(2) The electronic structure of the cyclic six-center π-electron arrangement I may be conveniently described in terms of the familiar benzene HMO formalism.[9b,10] Calculations for planar 1,4-dihydropyrazine (**1**) have predicted the occupancy of an antibonding molecular orbital[9b] that would render such a compound extremely electron rich. (3) The 1,4-dihydropyrazine system is an essential constituent of biochemically important molecules, viz., of the 1,5-dihydroflavins IV[11-13] and of certain luciferins V.[14] (4)



IV



V

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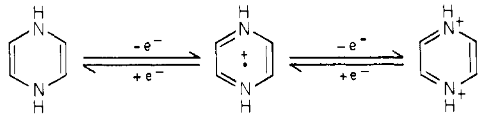
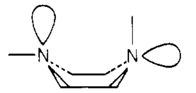
The reducing function of 1,4-dihydro-1,4-diazines[13] has also found application in the photographic process of silver color bleaching.[15]

Attempts to prepare unsubstituted 1,4-dihydropyrazine **1** have to date been unsuccessful. Protonation of electrochemically reduced pyrazines may lead to derivatives of **1** that undergo a rapid 1,3 shift[8] to yield the 1,2-dihydro isomers.[4d,16] However, the oxidized species $\mathbf{1}^{+\cdot}$ and $\mathbf{1}^{2+}$ are persistent, as has been shown by ESR[17] and UV spectroscopy.[18] Extension of the π system such as in 1,4-dihydroquinoxalines[19] or 5,10-dihydrophenazines[20] helps to stabilize the reduced form.



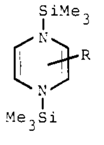
1 $1^{+\cdot}$ 1^{2+}

N,N'-Dialkyl or -diaryl derivatives of I have only been reported for 2,6-diaryl-substituted systems.[4,5] The structure of one such compound was determined by X-ray crystallography,[21] and may be described as a flat boat conformation with axial/equatorial N-substituents (VI) and hence interrupted π-electron conjugation.[22] Only the radical cations[24] or the fully oxidized dications[25] of unsubstituted *N,N'*-dialkyl-1,4-dihydropyrazines have been observed; however, extension of the π system such as in 5,10-dihydrophenazines[26] and -flavins[11-13] or incorporation of two more electronegative ring nitrogens such as in 1,4-dihydro-1,2,4,5-tetrazines[27] makes it possible to isolate the neutral compounds under ordinary laboratory conditions. More recently, unsubstituted *N,N'*-diacyl derivatives of I were obtained by a reductive procedure.[28] The stability of these molecules is attributable to the π-electron delocalization from the electron-rich ring π system into the carbonyl groups.[3,28]

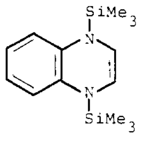


VI

Reductive processes have also been used to synthesize 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**2**), which was reported to be a highly oxidizable compound.[29,30] Since silyl substituents at the amino nitrogen flatten the pyramidal N configuration[31] without greatly changing the nitrogen lone pair ionization energy,[32] we have studied **2** and various other reductively silylated N-heterocycles **3**–**15** with respect to the possibility of cyclic π-electron conjugation.



2



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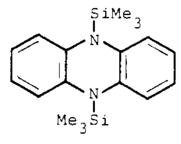


10

3, R = 2-Me

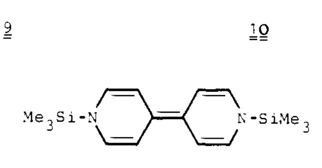
4, R = 2,5-Me$_2$

5, R = 2,3-Me$_2$

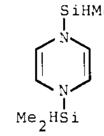
6, R = 2,6-Me$_2$

7, R = 2,3,5-Me$_3$

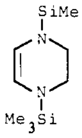
8, R = 2,3,5,6-Me$_4$



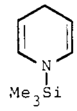
11



12



13



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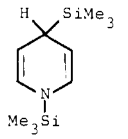

15

While the comparison of ^{1}H NMR data for **2**–**15** is expected to yield information on the paratropic[33] character ("antiaromaticity"[34]) of the compounds within the ring current concept,[35] the ionization energies as measured by photoelectron (PE) spectroscopy may be correlated with molecular orbitals obtained from π-electron model calculations.[10,36] As another set of parameters that correlates favorably with the results of HMO calculations, the ESR coupling constants[37] of the readily obtained[38] radical cations $\mathbf{2}^{+\cdot}$ and $\mathbf{12}^{+\cdot}$ may be compared with the data for other derivatives of reduced pyrazine.[17,39-41]

Experimental Section

All manipulations were carried out under an atmosphere of dry argon with rigorously dried solvents. The starting materials were obtained from Aldrich.

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Table I. Data of Characterization for the N-Silylated Heterocycles 2–15. ^{1}H NMR Parameters δ (ppm) from $CDCl_3/Me_4Si$ Solutions

		^{1}H NMR		
compd (color)	bp, °C (torr)	δ CH	δ CH_3	δ $SiCH_3$
2 (yellow)	sublimation 80 (0.1) mp 66	4.64 (s)		0.03 (s)
3 (yellow)	50 (0.01)	4.7–5.0 (m)	1.49 (d)^a	0.06 (s) 0.16 (s)
4 (pale yellow)	70 (0.01)	5.00 (m)	1.57 (d)^b	0.16 (s)
5 (pale yellow)	70 (0.01)	5.37 (s)	1.67 (s)	0.16 (s)
6 (pale yellow)	70 (0.01)	5.46 (m)	1.64 (d)^b	0.09 (s) 0.17 (s)
7 (very pale yellow)	70 (0.005)	5.49 (m)	1.68 (ps)	0.16 (ps)
8 (colorless)	sublimation 70 (0.01) mp 62		1.69 (s)	0.14 (s)
9 (yellow)	80 (0.005)	5.28 (s) 6.52 (m)		0.25 (s)
10 (colorless)	mp 92	6.84 (m)		0.25 (s)
11 (red)	mp 165	5.82 (m)		0.07 (s)
12 (yellow)	50 (0.05)	4.64 (s)	4.22^c	0.12 (d)
13 (very pale yellow)	65 (1) mp 25	5.38 (s)	3.14 (s)^d	0.08 (s)
14 (colorless)	30 (1)	5.93 (m) 4.60 (m)	3.16 (m)^d	0.00 (s)
15 (colorless)	50 (0.1)	5.70 (m) 4.35 (m)	2.25 (m)^e	−0.01 (s) 0.11 (s)

^{a} ^4J = 1.7 Hz. ^{b} ^4J = 1.0 Hz. ^{c} SiH protons, septet, ^3J = 3.2 Hz. ^{d} CH_2 protons. ^{e} CH proton.

The compounds 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**2**),[29] 5,10-bis(trimethylsilyl)-5,10-dihydrophenazine (**10**),[42] 1,1′-bis(trimethylsilyl)-1,1′-dihydro-4,4′-bipyridine (**11**),[43] 1-(trimethylsilyl)-1,4-dihydropyridine (**14**),[44] and 1,4-bis(trimethylsilyl)-1,4-dihydropyridine (**15**)[45] were prepared according to literature procedures.

The compounds 1,4-bis(trimethylsilyl)-2-methyl-1,4-dihydropyrazine (**3**), 1,4-bis(trimethylsilyl)-2,5-dimethyl-1,4-dihydropyrazine (**4**), 1,4-bis(trimethylsilyl)-2,3-dimethyl-1,4-dihydropyrazine (**5**), 1,4-bis(trimethylsilyl)-2,6-dimethyl-1,4-dihydropyrazine (**6**), 1,4-bis(trimethylsilyl)-2,3,5-trimethyl-1,4-dihydropyrazine (**7**), 1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyrazine (**8**), 1,4-bis(trimethylsilyl)-1,4-dihydroquinoxaline (**9**), and 1,4-bis(dimethylsilyl)-1,4-dihydropyrazine (**12**) have been synthesized by reacting the corresponding 1,4-diazine with potassium metal and the chlorosilane in THF. In a typical run, 10 mmol of the diazine was dissolved in 50 mL of THF, and 30 mmol of each R_3SiCl and clean-cut potassium were added, in that order. After stirring overnight at room temperature, the reaction mixture was filtered, the solvent removed, and the reductively silylated heterocycle purified by distillation (**3**–**7**, **9**, **12**) or sublimation (**8**) under reduced pressure. In all cases the yields were approximately 80%.

1,4-Bis(trimethylsilyl)-1,2,3,4-tetrahydropyrazine (**13**) was obtained in 84% yield by catalytic hydrogenation of **2** with Pd/C in THF under 760-torr H_2 pressure. The compound was purified by distillation and solidified while standing.

Elementary analyses of the reductively silylated compounds could not be carried out because of their extreme sensitivity toward hydrolysis and oxidation.[30] The characterization data are summarized in Table I.

^{1}H NMR spectra were recorded with a Varian T-60 spectrometer. The measurements were performed with air- and moisture-free $CDCl_3$ as solvent, Me_4Si served as internal standard.

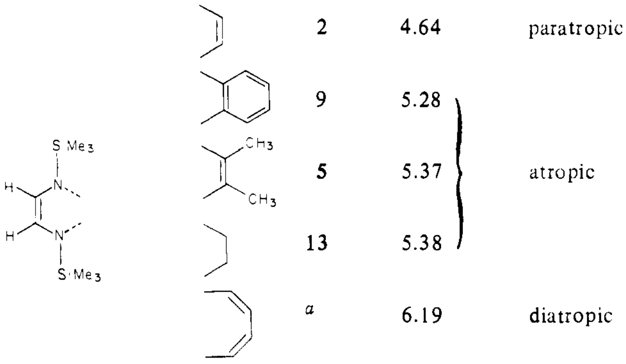
Photoelectron spectra were recorded on a Perkin-Elmer PS 16 spectrometer and were calibrated by using the $Xe(^2P_{3/2})$ = 12.13-eV and $Ar(^2P_{3/2})$ = 15.76-eV peaks.

Electron spin resonance spectra of $2^{+\cdot}$ and $12^{+\cdot}$ were recorded by using a Varian E 9 spectrometer in the X-band mode. Calibration was performed with the perylene radical anion in DME.[46] The program ESPLOT[47] was used for ESR spectra simulation. The radical cations were generated by treating the neutral compounds with a mixture of $AlCl_3$[47] and R_3SiCl in CH_2Cl_2. The chlorosilane was used to prevent hydrolysis.

Results and Discussion

^{1}H NMR Spectra. As reduced compounds, the heterocycles **2**–**15** generally exhibit ^{1}H NMR resonances at higher field than the corresponding aromatic starting materials.[48] The question as to whether cyclic 8-π-electron conjugation is effective in some of these molecules is advantageously discussed by comparing the NMR data of monocyclic derivatives. Cyclic conjugation of 4*n* π electrons should result in an induced paramagnetic ring current[35] in a magnetic field, which is expected to shift the outer protons upfield.[33,49] The concept of paramagnetic ring currents has been successfully applied before to a number of neutral molecules,[49,50] anions,[51] and dianions;[52] however, the problems associated with relating a "paramagnetic ring current" to "antiaromaticity" should be realized,[34] especially when dealing with polycyclic systems.

Chart I. Chemical Shifts δ_{en} for the Enamine Protons of the *N*,*N*′-Bis(trimethylsilyl)-1,2-diaminoethene Moiety in Various Cyclic Molecules



2	4.64	paratropic
9	5.28	atropic
5	5.37	
13	5.38	
^{a}	6.19	diatropic

^{a} Reference 54.

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(42) Birkofer, L.; Ramadan, N. *Chem. Ber.* **1975**, *108*, 3105.

(43) Hünig, S.; Schenk, W. *Liebigs Ann. Chem.* **1979**, 727.

(44) Cook, N. C.; Lyons, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 3396.

(45) Sulzbach, R. A. *J. Organomet. Chem.* **1970**, *24*, 307.

(46) Bolton, J. R. *J. Phys. Chem.* **1967**, *71*, 3702.

(47) Bock, H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 4429; *Acc. Chem. Res.* **1982**, *15*, 9.

(48) Cf. the spectra In "The Aldrich Library of NMR Spectra",. Pouchert, C. J.; Campbell, J. R., Eds.; Alrich Chemical Company, Inc.: Milwaukee, WI, 1974–1975.

(49) Haddon, R. C.; Haddon, V. R.; Jackman, L. M. *Fortschr. Chem. Forsch.* **1971**, *16*, 103.

(50) For representative examples, see: (a) Pyracyclene: Trost, B. M.; Bright, G. M.; Frihart, C.; Britelli, D. *J. Am. Chem. Soc.* **1971**, *93*, 737. (b) 1,3,5-Tri-*tert*-butylpentalene: Hafner, K.; Süss, H. U. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 575. (c) Tri-*tert*-butylcyclobutadiene: Masamune, S.; Nakamura, N.; Suda, M.; Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481. Maier, G.; Alzerreca, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1015. (d) Methanol[12]annulenes: Vogel, E.; Königshofen, H.; Müllen, K.; Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 281, 283. (e) Cycl[3.3.3]azine: Farquhar, D.; Gough, T. T.; Leaver, D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 341. (f) 1,2-Bis(trimethylsilyl)benzocyclobutadiene: Vollhardt, K. P. C.; Yee, L. S. *J. Am. Chem. Soc.* **1977**, *99*, 2010. (g) Naphtho[1,8-*c*,*d*:4,5-*c*′,*d*′]bis-[1,2,6]thia- and selenadiazine: Kaplan M. L.; Haddon, R. C.; Schilling, F. C.; Marshall, J. H.; Bramwell, F. B. *J. Am. Chem. Soc.* **1979**, *101*, 3306.

(51) Staley, S. W.; Orvedal, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 3382, 3384. Staley, S. W.; Heinrich, F.; Orvedal, A. W. *Ibid.* **1976**, *98*, 2681. Staley, S. G.; Linkowski, G. E. *Ibid.* **1976**, *98*, 5010. Anastassiou, A. G.; Kasmai, H. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 43. Anastassiou, A. G.; Kasmai, H. S.; Saadein, M. R. *Ibid.* **1981**, *20*, 115.

(52) Cox, R. H.; Terry, H. W., Jr.; Harrison, L. W. *Tetrahedron Lett.* **1971**, 4815. Huber, W.; Müllen, K.; Wennerström, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 624.

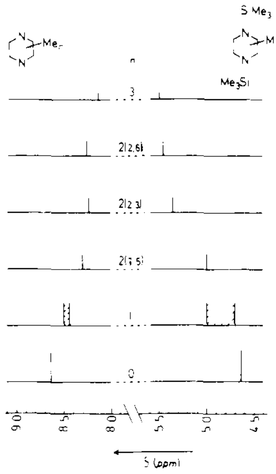
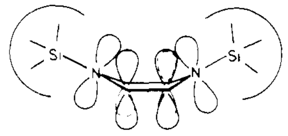


Figure 1. Ring proton chemical shifts of methylated pyrazines (left) and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazines (right), depending on the substitution pattern.

A first indication for paratropism[33] is obtained if the cyclic π-electron conjugation in **2** is interrupted by removal of one of the olefinic π bonds such as in **13** or one of the nitrogen lone pairs, as in **14** and **15**. These operations cause considerable changes of the enamine resonance, the absorption being shifted to lower field by at least 0.73 ppm[1] (Table I). This result is quite significant, allowing even for the different ring conformations of **2** and **13–15**.[53] Still more instructive is a comparison of the enamine chemical shifts δ_{en} for the *N,N'*-bis(trimethylsilyl)-1,2-diaminoethene moiety in various molecules as illustrated in Chart I. Closure of the enamine ring fragment by either an ethene (2 π) or a diene (4 π) unit leads to opposite shifts relative to compounds that allow little or no cyclic π interaction. The latter molecules, **4**, **9**, and **13**, seem to constitute an "atropic"[33] standard relative to which the 8 π system **2** exhibits a paratropic shift, while the 10-π-electron-containing 1,4-bis(trimethylsilyl)-1,4-dihydro-1,4-diazocine represents a diatropic, "aromatic", molecule.[54]

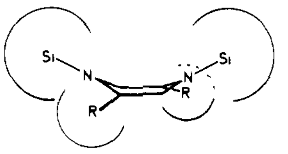
These results seen to verify the concept outlined above; i.e., *N*-silyl substitution causes a flattening of the pyramidal nitrogen configuration in **2** ($sp^3 \rightarrow \perp sp^2 + p$) and makes the N electron pairs available for cyclic 8-π-electron conjugation. The situation may be depicted qualitatively as shown for VII where the six-membered ring is assumed to adopt a flat boat conformation, similar to the one that has been found for an *N,N'*-diaryl derivative in the solid state.[21]



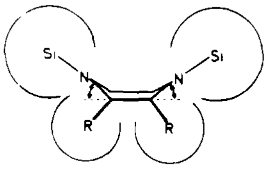
VII

^{1}H NMR of Methyl Derivatives. Further insight into the cyclic 8-π-electron conjugation mechanism is obtained if steric constraints are introduced by successive methyl substitution of **2** such as in compounds **3–8**. Figure 1 shows the effect of increasing methyl substitution on the ring proton chemical shifts of the heterocycles before and after reductive silylation. Whereas the series of the aromatic N-heterocycles shows the expected trend of a shift to higher field upon increasing methyl substitution, the reduced pyrazines display completely opposite behavior (Figure 1). Increasing methyl substitution causes a low-field shift of the ring proton resonances, in contrast to what would be expected if only an inductive substituent effect were operating.

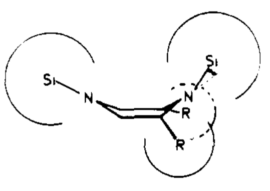
Especially intriguing are the rather different NMR resonances of the isomeric dimethyl derivatives **4**, **5**, and **6**, which provide some clues to the nature and sensitivity of the 8-π-electron conjugation. In the 2,5-dimethyl compound **4** the R_3Si and methyl groups are arranged in a 1,2,4,5-substitution pattern that minimizes steric repulsion and seems to allow at least some degree of cyclic π conjugation (VIII). In contrast, the 2,3-dimethyl isomer **5** has the larger substituents arranged in a 1,2,3,4-substitution pattern; obviously, this leads to considerable steric repulsion and hence to a more pronounced deviation from planarity (IX). In the 2,6 isomer **6** not only the ring conformation but also the nitrogen configuration are affected by steric repulsion. Two neighboring methyl groups are likely to enforce some bending of the 1-trimethylsilyl substituent toward an axial position at N(1), effectively interrupting the cyclic conjugation (VI, X).[5,13,21] Consequently, addition of another methyl substituent (**7**) does not change the chemical shift of the remaining ring proton, as the conjugation has already been effectively interrupted in **6**. The atropic character of **6** (δ_{en} 5.46) is also evident from the comparison with compounds **14** and **15** (δ_{en} 5.93 and 5.70), which do not have the electron-donating methyl substituents. Related organic derivatives, viz., 1,4-dimethyl-[4c] and 1,4-dibenzyl-2,6-diphenyl-1,4-dihydropyrazine,[4d] have δ_{en} 5.32 and 5.57, respectively. *N,-N'*-Diacyl compounds have still higher values, δ_{en} ≥5.80,[3,28] corresponding to a flow of π-electron density into the amide carbonyl groups.



VIII



IX



X

The characteristic dependence of the NMR resonances on the substitution pattern in methylated 1,4-bis(trimethylsilyl)-1,4-dihydropyrazines is displayed not only by the ring protons but also by the ring methyl and the silylmethyl hydrogens, albeit in less pronounced form (Table I). Similarly, the benzo AA'BB' multiplets in **9** and **10** are at rather high field[55] due to the delocalization of electron density from the fused electron-rich hetero system.

In summary, the ^{1}H NMR results for compounds **2–15** illustrate a rather delicate dependence of the "antiaromaticity" on geometry, a phenomenon that was also observed for some higher annulenes.[56]

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[53] The conformational situation is more complicated in the nine-membered ring system of 1,4,7-trimethyl-1*H*-4,7-dihydro-1,4,7-triazonine (Prinzbach, H.; Breuninger, M.; Gallenkamp, B.; Schwesinger, R.; Hunkler, D. *Angew. Chem.* **1975**, *87*, 350; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 348).

[54] Altenbach, H. J.; Stegelmeier, H.; Wilhelm, M.; Voss, B.; Lex, J.; Vogel, E. *Angew. Chem.* **1979**, *91*, 1028; Angew. *Chem. Int., Ed. Engl.* **1979**, *18*, 962. Cf. also: Breuninger, M.; Gallenkamp, B.; Müller, K. H.; Fritz, H.; Prinzbach, H.; Daly, J. J.; Schönholzer, P. *Angew. Chem.* **1979**, *91*, 1030; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 964.

[55] Cf. quinoxaline δ 7.99 (m, 4 H) or phenazine δ 8.04 (m, 4 H).[48]

[56] Staley, S. W.; Orvedal, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 3384. Brown, J. M.; Sondheimer, F. *Angew. Chem.* **1974**, *86*, 348. Angew. *Chem., Int. Ed. Engl.* **1974**, *13*, 339. Cf. also: Vogel, E.; Deger, H. M.; Hebel, P.; Lex, J. *Angew. Chem.* **1980**, *92*, 943; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 919.

Table II. Vertical Ionization Energies IE_n^{V} (eV) below 10 eV and Lone-Pair Splittings $\Delta^{\pi}{}_{n_+/n_-}$ (eV) of N-Silylated Heterocycles **2–15**[a]

compd	$IE^{\mathrm{V}}{}_1$	$IE^{\mathrm{V}}{}_2$	$IE^{\mathrm{V}}{}_3$	$\Delta^{\pi}{}_{n_+/n_-}$
2	6.16 $b_{3u}(\pi^*_S)$	9.5[b] $b_{2g}(\pi_A)$	9.5[b] $b_{1g}(\pi_S)$	3.34
3	6.37 $b_{3u}(\pi^*_S)$	9.20 $b_{2g}(\pi_A)$	9.50 $b_{1g}(\pi_S)$	3.13
4	6.45 $b_{3u}(\pi^*_S)$	8.75 $b_{2g}(\pi_A)$	9.25 $b_{1g}(\pi_S)$	2.80
5	6.47 $b_{3u}(\pi^*_S)$	8.65 $b_{2g}(\pi_A)$	9.05 $b_{1g}(\pi_S)$	2.58
6	6.48 $b_{3u}(\pi^*_S)$	8.70 $b_{2g}(\pi_A)$	9.10 $b_{1g}(\pi_S)$	2.62
7	6.50 $b_{3u}(\pi^*_S)$	8.45 $b_{2g}(\pi_A)$	8.95 $b_{1g}(\pi_S)$	2.45
8	6.48 $b_{3u}(\pi^*_S)$	8.10 $b_{2g}(\pi_A)$	8.70 $b_{1g}(\pi_S)$	2.22
9	6.50 b_1	8.25 a_2	9.00[c] b_1	1.75
10	6.5 b_{3u}	7.9 b_{1g}	8.9 b_{2g}, a_u	1.4
11	6.50 b_{3u}	8.35 b_{1g}	*d*	1.85
12	6.33 b_{3u}	9.7[b] b_{2g}	9.7[b] b_{1g}	3.37
13	6.60 b_1	8.80 a_2		2.20
14	7.30 b_1	9.55 a_2		
15	6.85 b_1	9.35 a_2		

[a] Idealized (planar) geometries were used for the π orbital assignment; the choice of coordinates was made according to ref 57. [b] Overlapping bands not resolved; see, however, ref 1. [c] Additional ionization at 9.65 eV. [d] Strongly overlapping bands.

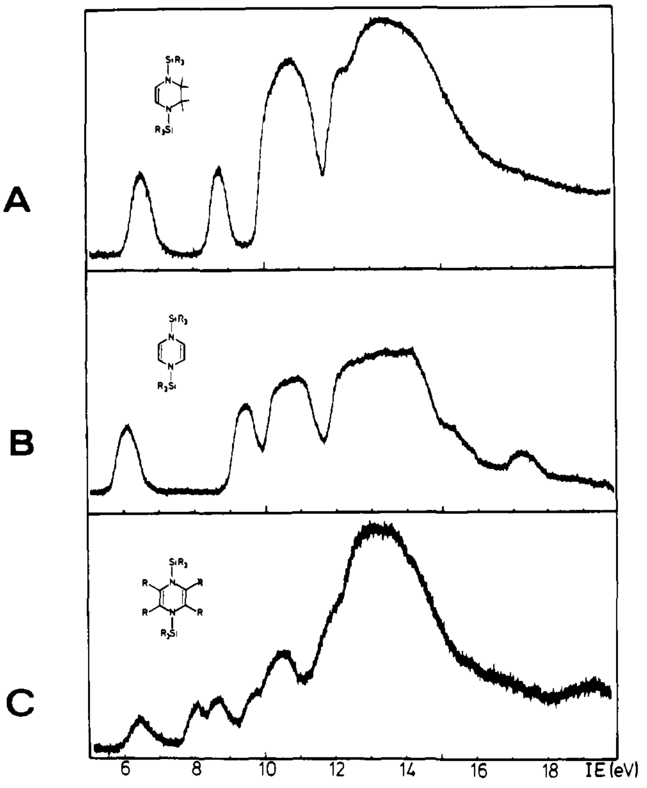
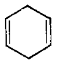
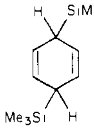
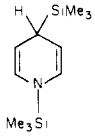
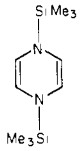


Figure 2. He (Iα) photoelectron spectra of compounds **13** (A), **2** (B), and **8** (C).

Photoelectron Spectra: The First Ionization Energy. The question of cyclic conjugation of π electrons in a six-membered ring such as in **1** or **2** constitutes an ideal problem for a Hückel molecular orbital treatment. Streitwieser's HMO calculation for the planar 8-π-electron system **1** with $h_N = 1$ and $k_{CN} = 1$ has suggested that the last two electrons must be placed in an antibonding orbital.[9b] Heilbronner and Bock have presented correlation diagrams of orbital energies as a function of the Coulomb integral parameter h_N.[10a] Calculated orbital energies may be correlated, via Koopmans' theorem,[36] with ionization energies as measured by UV photoelectron spectroscopy. This method has been applied to the compounds **2–15** in order to gain information on the extent of the π interaction. Some representative spectra are shown in Figure 2 and the data are summarized in Table II.

Table III. First and Second Vertical Ionization Energies $IE^{\mathrm{V}}{}_{1,2}$ (eV) of **1**,4-Cyclohexadienes and Related Molecules

compound		$IE^{\mathrm{V}}{}_1$	$IE^{\mathrm{V}}{}_2$
	ref 73	8.82	9.88
	ref 47	7.70	9.30
	**15**	6.85	9.35
	2	6.16	9.5

A first look at the ionization energies of compounds **2–15** reveals that these molecules are very electron rich. The vertical[58] ionization potentials (IPs) of the reduced 1,4-diazines are all smaller than 6.60 eV. These quantitative results complement the observations concerning the extreme reactivity of, e.g., **2**[29,30] and **11**[43,44], toward oxidants. The latter compound has also been studied electrochemically and exhibited an irreversible oxidation wave at −0.68 V vs. Ag/AgCl.[59] Extremely low ionization potentials as observed for **2** are not often encountered with nonmetal-centered species;[60] they may only be compared to the IPs of polyaminoethenes[61a] or phosphorus ylides.[61b]

Low first ionization energies alone cannot be taken as an indication for cyclic π-electron conjugation. However, it is remarkable that the methylated derivatives **3–8** or larger systems **9–11** have IPs *higher* than that of the unsubstituted compound **2** (Table II). Methyl substitution should *lower* the ionization potential of a molecule due to the donor effect of CH_3.[47,62] This has been observed for methylated pyrazines, too.[63] It should be noted that the increasing IP in the series **2–8** is accompanied by a gradual loss of color in going from the bright yellow **2** to the colorless tetramethyl derivative **8** (Table I). Both effects can be rationalized by assuming an energetic stabilization of the HOMO and a constant level of the LUMO.

Since it is unlikely that a charge delocalization *into* the methyl groups is occuring,[64] the explanation of the anomalous substituent effect may again be based on steric repulsion. Increasing methyl substitution impairs the cyclic 8-π- electron conjugation via conformational changes induced by steric interactions. Thus, in spite of the σ-donor effect of the methyl groups, the first ionization energy is raised instead of lowered. Both contributions, the additive[62] methyl σ-donor effect and the increasing steric repulsion, appear to nearly balance one another, so that several of the methyl

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(57) Gleiter, R.; Heilbronner, E.; Hornung, V. *Angew. Chem.* **1970**, *82*, 878; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 901; *Helv. Chim. Acta* **1972**, *55*, 255.

(58) The PE bands do not exhibit a fine structure due to the presence of highly flexible trimethylsilyl substituents; it is assumed that the band maximum represents the vertical ionization energy.

(59) Hünig, S.; Schenk, W. *Liebigs Ann. Chem.* **1979**, 1523. Hünig, S.; Berneth, H. *Top. Curr. Chem.* **1980**, *92*, 1.

(60) Cf.; Alder, R. W.; Arrowsmith, R. J.; Casson, A.; Sessions, R. B.; Heilbronner, E.; Kovac, B.; Huber, H.; Taagepera, M. *J. Am. Chem. Soc.* **1981**, *103*, 6137.

(61) (a) Cetinkaya, B.; King, G. H.; Krishnamurthy, S. S.; Lappert, M. F.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1971**, 1370. (b) Ostoja Starzewski, K. A.; Bock, H. *J. Am. Chem. Soc.* **1976**, *98*, 8486.

(62) Cf. e.g.: Bock, H.; Kaim, W. *Chem. Ber.* **1978**, *111*, 3552.

(63) Bischof, P.; Gleiter, R.; Hofmann, P. *J. Chem. Soc., Chem. Commun.* **1974**, 767.

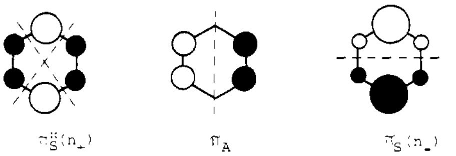
(64) CH_3 acts as electron donor in benzene radical anions: Bolton, J. R.; Carrington, A. *Mol. Phys.* **1961**, *4*, 497.

derivatives (**4**–**8**) have very similar IPs of approximately 6.45 eV (Table II).

Electronic effects due to π-electron delocalization and steric factors such as bending[12c,65] due to peri interactions (**9**, **10**) are likely to play a role in the increase of the ionization potentials of larger systems (**9**–**11**) relative to **2**. The results from HMO calculations for alternating π systems[10b] illustrate how increasing delocalization in extended π systems leads to a *reduction* in the energy of the lowest antibonding orbital: The observed IPs (Table II) confirm the antibonding character of the HOMO of **2**.

The first ionization energies of reductively silylated pyridine **15** lie almost exactly half way between the values for **2** and for reductively silylated benzene, i.e., *trans*-1,4-bis(trimethylsilyl)-1,4-cyclohexadiene.[47] The successive replacement of the hyperconjugatively interacting[47] σ_{C-Si} bonds by n_{N-Si} lone pairs that interact via direct conjugation brings about another decrease of the ionization potential (Table III).

Assignment of PE Bands. n_N/n_N Lone Pair Splitting. The antibonding character of the highest occupied MO in a molecule such as **2** is evident from the appearance of its photoelectron spectrum (Figure 2B). Basically, the spectrum is similar to that of an aromatic molecule[66] except for an additional peak at very low energy, corresponding to the occupation of an antibonding orbital.[9b] The assignment of the PE bands, i.e., of the individual radical cation states,[10] to molecular orbitals is, therefore, straightforward within the π-electron model. The LUMO of the aromatic precursor becomes the HOMO of the reduced molecule. In the series of the methylated derivatives, the second ionization energy is strongly affected by increasing methyl substitution; the corresponding MO is of the π_A type. Accordingly, this one ionization remains essentially constant upon variation of the nitrogen substituents from $SiHMe_2$ (**12**) via $SiMe_3$ (**2**) to $GeMe_3$.[1] Such a perturbation does, however, shift two other π ionizations to lower energies.[1] These two ionizations may be assigned to the π_S and π^*_S molecular orbitals, the uniform shift corresponding to a decrease of the Coulomb integral parameter h_N.[10a] Interestingly, the differemce between IE(π_S) and IE(π^*_S) stays approximately constant in the series **12** to **2** to the germanium analogue of **2**[1] and can be identified as the nitrogen "lone-pair splitting" Δ_{n_+/n_-}. This parameter has been discussed in great detail for a variety of nitrogen-containing molecules.[57,60,63,67-71]



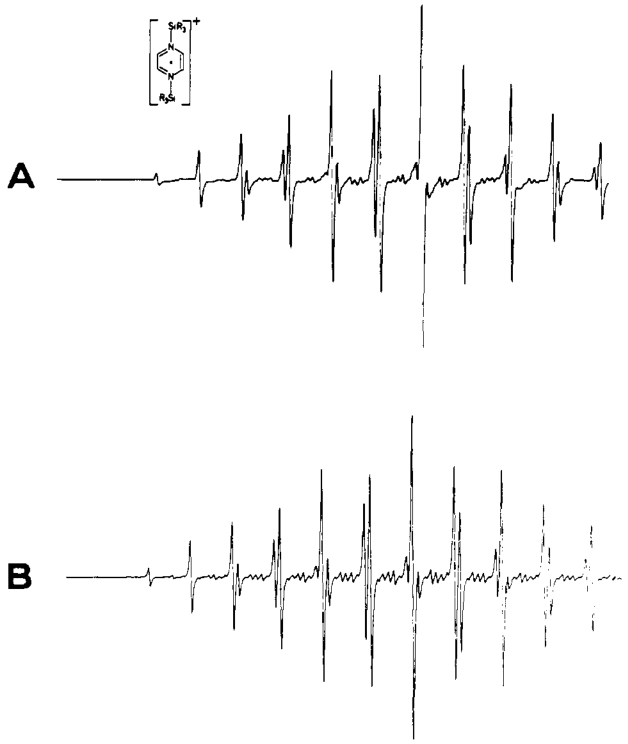


Figure 3. ESR spectrum (low field section) of the 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine radical cation $2^{+\cdot}$ (A) with a computer simulation (B) that accounts for ^1H, ^{14}N, ^{13}C, and ^{29}Si couplings.

Relative to the standard **13** that constitutes a noncyclic four-center 6-electron π system and has $\Delta_{n_+/n_-} = 2.20$ eV (Figure 2A and Table II), the unsubstituted 1,4-dihydropyrazines **2** and **12** exhibit an even larger lone-pair splitting of 3.35 eV. This value is quite extraordinary when compared to other relatively large n_+/n_- splittings for nitrogen-[67,69,70] or oxygen-containing molecules.[72]

The very large n_+/n_- splitting for **2** reveals a considerable "through-bond" π-electron conjugation. Methyl substitution causes a gradual decrease of the lone-pair splitting until a value similar to the one for the nonconjugated standard **13** is reached (Table II; Figure 2A,C). As in case of the NMR study, the isomeric dimethyl derivatives **4**–**6** exhibit a characteristic sequence of Δ_{n_+/n_-} (**4** > **5** > **6**) according to the individual steric situation (VIII–X). Extension of the system such as in **9**–**11** leads to a considerable reduction of the nitrogen lone-pair splitting because of the increased electron delocalization and/or steric repulsion. Thus, the reductively silylated phenazine **10** has ionization energies very similar to the values reported for *N,N'*-dialkyl derivatives.[65] It should be pointed out that the previous discussion uses arguments that refer to strictly planar molecules, in case of obvious deviation from planarity for steric reasons the σ contributions play an increasing role and lead to the observed breakdown of the π model.

ESR Spectra. After consideration of the very low ionization potentials measured for the compounds **2**–**12** (Table II) and the strong antibonding character of the HOMO of, e.g., **2**, it becomes immediately clear why radical cations have often been observed as one-electron oxidation products in the chemistry of 1,4-dihydro-1,4-diazines.[4,5,11,12d,17,74,75] On the other hand, *N,N'*-dialkylated pyrazines have proved to be rather sensitive toward even weak reductants such as alcohols;[24,25] obviously, the presumably planar[11,17] six-center 7-π electron system $I^{+\cdot}$ constitutes

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(65) Haink, H. J.; Huber, J. R. *Chem. Ber.* **1975**, *108*, 1118.

(66) The spectral regions above 10 eV are characterized by strongly overlapping bands from numerous σ-type ionizations; the hump at ~17 eV in Figure 2B may be tentatively assigned to 3s(Si) ionizations: Bock, H.; Ensslin, W.; Fehêr, F.; Freund, R. *J. Am. Chem. Soc.* **1976**, *98*, 668.

(67) Lone-pair splittings may be of the σ[57,60,63,68] or of the π type.[69,70,71b,c] The term refers to the difference between orbitals with predominant but not necessarily exclusive lone-pair character.

(68) Δ_{n_+/n_-}(1,4-diazabicyclo[2.2.2]octane) = 2.13 eV: Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Tetrahedron Lett.* **1969**, 4025. Heilbronner, E.; Muszkat, K. A. *J. Am. Chem. Soc.* **1970**, *92*, 3818. Δ_{n_+/n_-}(azomethane) = 3.3 eV: Haselbach, E.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 878.

(69) Δ_{n_+/n_-}(*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) = 1.6 eV: Kaim, W.; Bock, H. *J. Am. Chem. Soc.* **1978**, *100*, 6504; *Chem. Ber.* **1978**, *111*, 3843.

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(72) 1,4-Dioxin: IE_1^v = 8.13 eV; Δ_{n_+/n_-} = 2.57 eV: Bloch, M.; Brogli, F.; Heilbronner, E.; Jones, T. B.; Prinzbach, H.; Schweikert, O. *Helv. Chim. Acta* **1978**, *61*, 1388.

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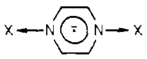
Table IV. ESR Coupling Constants a_x (*mT*) and *g* Values for Pyrazine-Centered Radical Ions



X		a_H^{CH}	a_C	a_N	a_X (X)	*g*
n_N	*a*	0.264	0.288	0.721		2.0035
$SiMe_3^+$	($2^{+\cdot}$)	0.313	0.11	0.664	0.279 (^{29}Si)	2.0033
$SiHMe_2^+$	($12^{+\cdot}$)	0.313	*b*	0.668	*b,c*	2.0033
H^+	($1^{+\cdot}$)	0.316	0.12	0.745	0.805 (^{1}H)	2.0034

[a] Reference 39. [b] Not observed. [c] $a_H^{SiH} = 0.103$ mT.

a favored oxidation state. It is not surprising, therefore, that the unpaired electron density in the flavin radical cations is also largely centered on the 1,4-dihydropyrazine moiety.[11,12d]

Radical cations can also be generated from several of the *N*-trimethylsilyl compounds using the one-electron oxidant $AlCl_3/CH_2Cl_2$[47] and an excess of the corresponding chlorosilane. An ESR study of the blue cation **11**$^{+\cdot}$ will be reported elsewhere; the spin distribution in this species is similar to the one found for the paraquat cation radical.[76] Attempts to oxidize **13** with $AlCl_3$ have resulted in the formation of **2**$^{+\cdot}$ as paramagnetic product; this reaction may be understood by considering the catalytic properties of $AlCl_3$[77] and the stability of the 7-π-electron system mentioned previously. The ESR spectrum of **2**$^{+\cdot}$, generated by $AlCl_3$ oxidation of **2**, is shown in Figure 3 together with a computer simulation that also reproduces ^{13}C and ^{29}Si satellites; an ESR spectrum of **12**$^{+\cdot}$ has been obtained in a similar manner.[78] The ESR data for **2**$^{+\cdot}$, **12**$^{+\cdot}$, **1**$^{+\cdot}$, and for the pyrazine radical anion are listed in Table III. It should be noted that the cation **2**$^{+\cdot}$ is isoelectronic to a number of other persistent radical ions[38] and related to organomagnesium and -aluminum complexes of reduced pyrazine.[40,41]

Table IV reveals that the spin distributions in **1**$^{+\cdot}$, **2**$^{+\cdot}$ and **12**$^{+\cdot}$ are virtually identical as shown by the comparable parameters a_H and $a_{^{13}C}$. It appears, therefore, that at least for the radical cation state the silylated derivative **2**$^{+\cdot}$ is a good model for the parent system **1**$^{+\cdot}$. The silylmethyl splitting in **2**$^{+\cdot}$ is not detected and must, therefore, be smaller than 0.005 mT. Accordingly, the a_H^{SiH} coupling constant in **12**$^{+\cdot}$ is also relatively small when compared to the value of 0.728 mT in the isoelectronic 1,4-bis(dimethylsilyl)benzene radical anion.[79]

Summary

The results presented in this study have demonstrated how reductive silylation of N-hetrocycles leads, in a simple way, to kinetically stable compounds with unusual electronic properties. *N*-Silyl substitution not only renders the molecules persistent toward rearrangements such as 1,3-shifts but allows as well for the possibility of cyclic 8-π-electron conjugation. In agreement with the Hückel rule, this interaction can then result in paratropism, extraordinarily large n_+/n_- splitting, and a strong tendency to lose an electron. However, the reduction of these effects by successive methyl substitution or other steric and electronic factors shows how flexibly such a system reacts to even minor perturbations. This propensity of the system to use any available route to avoid an unfavorable cyclic 8-π-electron configuration bears some significance as well in the explanation of flavocoenzyme reactivity.

It has been assumed[12a] that the variable electrochemical potentials of flavoenzyme redox systems are governed by the steric requirements imposed by the apoprotein.[11] The striking "reverse" substituent effects on ^{1}H NMR and PE spectra resulting upon methyl substitution of **2** constitute a confirmation of this assumption, using the model system at hand. Furthermore, the extremely low ionization potentials of reduced 1,4-diazines and their tendency to form very persistent radicals in single-electron-transfer reactions[75] may be related to the ability of compounds such as IV[75,80] and V[14] in the activation of paramagnetic $^3O_2$.

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Registry No. 2, 31639-80-2; **2**$^+$, 75533-79-8; **3**, 84073-74-5; **4**, 78167-43-8; **5**, 78167-44-9; **6**, 78167-45-0; **7**, 84073-75-6; **8**, 78279-92-2; **9**, 78279-93-3; **10**, 57027-17-5; **11**, 13032-12-7; **12**, 78279-91-1; **12**$^+$, 84073-76-7; **13**, 78167-46-1; **14**, 3337-18-6; **15**, 29173-25-9; $AlCl_3$, 7446-70-0.

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