with dilute HCl, and extract into CH_2Cl_2) and recrystallization from ether/petroleum ether gave analytically pure **24**, mp 70–73 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (6 H, s), 3.71 (3 H, s), 5.83 (1 H, d, $J = 16$ Hz), 7.21 (1 H, d, $J = 16$ Hz), 10.48 (1 H, br s).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 6.97. Found: C, 55.43; H, 6.91.

Se-Methyl 4-Carbomethoxy-2,2-dimethylbut-3-eneselenoate (26). A 50-mL three-necked flask was equipped with a dry ice condenser, and ca. 20 mL of NH_3 was condensed. To the flask a total of 0.30 g (0.013 g atom) of sodium and 1.20 mL (14.7 mmol) of dimethyl diselenide were added alternately in several portions.[19b] After the addition was over, excess NH_3 was removed at room temperature. Dilute sulfuric acid was slowly added to the solid residue, and the evolved gas was carried in a current of nitrogen through two $CaCl_2$ drying tubes and condensed in a trap cooled in dry ice–acetone. The trap containing methyl selenol[19b] was allowed to attain room temperature slowly, and the gas was passed, via a current of nitrogen, through a mixture of 3.90 g (20.4 mmol) of acid chloride **6** and 1.97 mL (24.2 mmol) of pyridine in 5 mL of CH_2Cl_2 at −78 °C. The mixture was allowed to warm to room temperature and filtered. The filtrate was washed with water, dried (Na_2SO_4), and concentrated. The residue was purified by Kugelrohr distillation (130 °C/1.5 torr) to give 4.2 g (16.8 mmol, 82%) of **26**: ^{1}H NMR ($CDCl_3$) δ 1.36 (6 H, s), 2.16 (3 H, s), 3.71 (3 H, s), 5.91 (1 H, d, $J = 16$ Hz), 7.07 (1 H, d, $J = 16$ Hz).

Anal. Calcd for $C_9H_{14}O_3Se$: C, 43.38; H, 5.60. Found: C, 43.16; H, 5.77.

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Registry No. **1**, 20004-62-0; **3**, 518-82-1; **5**, 96328-29-9; **6**, 96328-30-2; **7**, 96328-31-3; **8**, 96328-32-4; **9**, 31469-25-7; **10**, 22852-03-5; **11**, 96328-33-5; **12**, 96328-34-6; **14**, 96328-35-7; **19**, 96328-36-8; **21**, 96328-37-9; **23**, 31469-15-5; **24**, 96328-38-0; **25**, 96328-39-1; **26**, 96328-40-4; **27**, 6414-42-2; **28**, 96328-41-5; **29**, 96328-42-6; **30**, 96328-43-7; methyl propiolate, 922-67-8; methylselenol, 6486-05-1.

Synthesis and Valence Orbital Structures of Azacycl[3.3.3]azines in a Systematic Series

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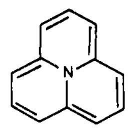
Abstract: The syntheses and spectroscopic properties of unsubstituted 1,3,4,6,7-pentaazacycl[3.3.3]azine (1,3,4,6,7,9b-hexaazaphenalene), 1,3,4,6-tetraazacycl[3.3.3]azine (1,3,4,6,9b-pentaazaphenalene), and 1,3,4,6,8-pentaazacycl[3.3.3]azine (1,3,4,6,8,9b-hexaazaphenalene) are reported. The syntheses were abbreviated in that they consisted of a two-step procedure whereby the appropriate diaminoazine was treated with methyl *N*-cyanomethanimidate and NaOMe in MeOH to give the corresponding bis(*N'*-cyano-*N*-formamidino)azines and these were subjected to short vacuum pyrolysis to afford the azacycl[3.3.3]azines. The valence orbital electronic structure of this series of molecules was examined using UV photoelectron spectroscopy. Interpretation of the spectra was aided by results from HAM/3 and GAUSSIAN 80 (STO-3G) ab initio SCF–MO quantum mechanical calculations. Spectroscopic and theoretical studies were also carried out on 1,3,4-triazacycl[3.3.3]azine and 1,3,6-triazacycl[3.3.3]azine. The results from studies of electronic structure were compared with those previously reported for 1,3,4,6,7,9-hexaazacycl[3.3.3]azine (tri-*s*-triazine) and for cycl[3.3.3]azine. In all of the azacycl[3.3.3]azines studied the highest occupied molecular orbital is a π orbital while the second and third highest occupied orbitals are lone-pair orbitals associated with N atoms. There is a significant variation (>1.3 eV) in the first π ionization potentials of these molecules, and the ionization potential decreases as the number of nitrogen atoms decreases. The ionization potentials of the highest occupied lone-pair orbitals, by contrast, do not change greatly when the number of N atoms changes or when the positions of the N atoms are varied. The quantum mechanical calculations indicate that the entire manifold of upper occupied π orbitals exhibits great sensitivity to heteroatom substitution. Both the HAM/3 and the ab initio GAUSSIAN 80 calculations predict that the ionization potentials of all six of the highest occupied orbitals decrease monotonically as the number of N atoms decreases. The empirically parameterized HAM/3 calculations predict that the total stabilization of the six highest occupied π orbitals is 1.9 eV for each peripheral N atom added. It is likely that these large differences in the stability of the manifold of upper occupied π orbitals play a large role in determining the different reactivities of members of this series of cycl[3.3.3]azines.

The cyclazines as a class of compounds consist of a fused conjugated ring system held planar by three covalent bonds to an internal nitrogen atom.[1,2] The first member of one series, cycl[3.3.3]azine (**1**),[3,4] isoelectronic with the phenalene anion,[5,6] is nonaromatic, contrary to early predictions.[1,7]



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Cycl[3.3.3]azine (**1**) was found to be a highly reactive compound, exhibiting a strong paramagnetic shift in the ^{1}H NMR signals[3,4,8] and a high susceptibility toward oxidation[3,4,9,10] and

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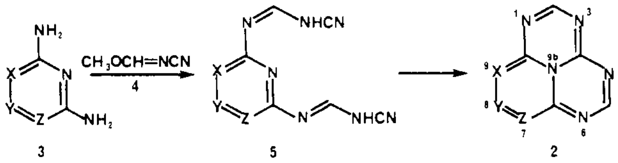
reduction.[9] Gradations in the properties of other members of the cycl[3.3.3]azine series containing 0 to 6 N atoms in the periphery are of interest with respect to the influence that the sequential introduction of nitrogens has on the π and lone-pair electronic structure.[11-14] The azacycl[3.3.3]azines have been the subject of numerous theoretical[6-14] and synthetic investigations.[3,4,15-18] Recently, we have synthesized tri-*s*-triazine (**2a**),[19] the ultimate member of the alternating C, N azacycl[3.3.3]azine series, via an abbreviated two-step procedure and have used photoelectron spectroscopy to assess its valence orbital structure.[20,21] In this paper we describe the extension of our abbreviated synthetic procedure to other azacycl[3.3.3]azines (1,3,4,6,7-pentaazacycl[3.3.3]azine (**2b**), 1,3,4,6-tetraazacycl[3.3.3]azine (**2c**), and 1,3,4,6,8-pentaazacycl[3.3.3]azine (**2d**)).



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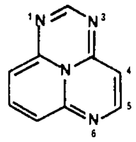
a, X=Z=N, Y=CH b, X=Y=CH, Z=N

c, X=Y=Z=CH d, X=Z=CH, Y=N

In the present investigation we have measured the photoelectron spectra of molecules **2b**, **2c**, and **2d** and of the additional cycl[3.3.3]azines, 1,3,6-triazacycl[3.3.3]azine (**6**) and 1,3,4-triazacycl[3.3.3]azine (**7**). Interpretation of the photoelectron spectra has been aided by results from semiempirical HAM/3, and from ab initio (SCF-MO) GAUSSIAN 80, quantum mechanical calculations using a STO-3G basis set. In conjunction with the photoelectron measurements, the quantum mechanical calculations provide detailed information about how the stepwise addition of heteroatoms influences π and lone-pair electronic structure in an extended series of cycl[3.3.3]azines.



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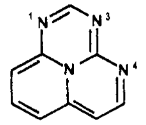

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Results and Discussion

Synthesis and Structure. In approaching the synthesis of tri-*s*-triazine (**2a**), it was found that the synthetic methodology which had been developed earlier for cycl[3.3.3]azine (**1**) and other aza-substituted members of this series[3,4,16-18] was not applicable. This was a consequence of the propensity of cyclizations on substituted pyrimidines and triazines to occur at distal nitrogens to afford intractable mixtures of undesired products.[17b,21] We found a remedy for this situation in an abbreviated synthesis consisting of a two-step procedure.[20,21] 2,4-Diamino-1,3,5-triazine (**3a**) was treated with methyl *N*-cyanomethanimidate (**4**)[22] and NaOMe in Me_2SO/MeOH to give 2,4-bis(*N'*-cyano-*N*-formamidino)-1,3,5-triazine (**5a**), which was then subjected to flash vacuum pyrolysis to afford tri-*s*-triazine (**2a**).[20,21]

The abbreviated synthesis of the azacycl[3.3.3]azines **2b**, **2c**,[17a,b] and **2d**[17f] is closely parallel to the method presented above. The key intermediates were the bis(*N'*-cyano-*N*-formamidino)azines **5b**, **5c**, and **5d**, obtainable in yields of 66–84% by treatment of the corresponding diamino compounds with methyl *N*-cyanomethanimidate (**4**) and NaOMe in MeOH at room temperature followed by neutralization with dilute HCl.

The ^{1}H NMR spectrum of **5b** in $(CD_3)_2SO$ shows four signals: two doublets at δ 6.8 and 8.5 assignable respectively to protons 5-H and 6-H, a multiplet at δ 9.6 assignable to the side-chain protons, and a broad signal at δ 10.8 corresponding to the N protons which were exchangeable with D_2O. The infrared spectrum revealed a strong C≡N stretching absorption at 2220 cm^{-1}. As in the case of **5a**,[20] the electron impact mass spectrum of **5b** at 70 eV exhibited a base peak at *m/e* 172 ($M^+ - 42$) corresponding to the loss of cyanamide. Similar ^{1}H NMR, IR, and mass spectroscopic data were obtained for the intermediates **5c** and **5d**, as described in the Experimental Section.

The ring closure of the intermediates **5b**, **5c**, and **5d** was effected by flash vacuum pyrolysis[20] to afford the desired azacycl[3.3.3]azines **2b**, **2c**,[17a,b] and **2d**[17f] in yields of 42–64%. The NMR assignments of **2b** merit a few remarks. The ^{1}H NMR spectrum of **2b** in $(CD_3)_2SO$ reveals four signals: two doublets at δ 6.20 and 7.95, with an integrated ratio of 1:1 and assignable respectively to protons 9-H and 8-H; two singlets at δ 7.77 and 7.82, each integrating for one proton and assignable to either 2-H or 5-H. Seven signals appeared in the ^{13}C NMR spectrum: one at δ 108.3 for C9, $^1J_{\mathrm{CH}} = 176.3$ Hz with the attached proton; three signals at δ 156.1, 159.2, and 160.5 corresponding to the three junctional carbons, respectively, C9a and either C3a or C6a; one signal at δ 162.5 for C8, $^1J_{\mathrm{CH}} = 184.0$ Hz with the attached proton; and two signals at δ 168.7 and 169.1 for either C2 or C5, $^1J_{\mathrm{CH}} = 205.3$ and $^1H_{\mathrm{CH}} = 204.6$ Hz with the attached protons. The mass spectrum of **2b** exhibited base peak at *m/e* 172, corresponding to the molecular ion, and fragment ions at 145 and 118, corre-

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sponding to the loss of 1 HCN and 2 HCN.

In this series of azacycl[3.3.3]azines, the arrangement of the nitrogen atoms is constant in two rings while the number and position of the nitrogen atoms vary in the third ring. This results in two trends which are noteworthy. First, the colors of the azacycl[3.3.3]azines range from yellow to orange, lavender, and blue for **2a**, **2b**, **2c**, and **2d**, respectively. The colors are in close agreement with those predicted by Leupin and Wirz.[12] Second, there is a substantial upfield shift in the ^{1}H NMR spectra for protons 2-H and 5-H in this series, ranging from δ 8.3 to 7.8 to 7.2 for **2a**, **2b**, and **2c**, respectively, and 7.39 for **2d**, all in $(CD_3)_2SO$. There is a slight upfield shift in the ^{13}C NMR signals for C2 and C5 in the series, ranging from δ 171 to 169 to 167, for **2a**, **2b**, and **2c**, respectively, and 169 for **2d**. For two additional members of the azacycl[3.3.3]azine series, namely the blue 1,3,6-triazacycl[3.3.3]azine (**6**)[16a,b] and the blue 1,3,4-triazacycl[3.3.3]azine (**7**),[16l] made by methods reported earlier, the ^{1}H NMR signals for 2-H were at δ 6.85 (**7**) and 6.50 (**6**) in $CDCl_3$, continuing the trend toward shielding described above for **2a**, **2b**, and **2c**.

There is interest in qualitative comparison of the electronic absorption spectra of our additions to the azacycl[3.3.3]azine series. In the long-wavelength region (390–640 nm), the absorptions responsible for the colors of the azacycl[3.3.3]azines **2a–d** consist of three bands of low intensity (ϵ 100–900) in acetonitrile. The wavelength (or frequency) values are close to those obtained by extrapolation by Leupin and Wirz,[12] and the observed hypsochromic shifts for the series **2c**, **2b**, and **2a** due to the substitution of the inductive acceptor nitrogen atoms at positions 7 and 9 are also as predicted.[12] A bathochromic shift and a hyperchromic effect are observed for **2d** (cf. **2b** with the same number of nitrogens), in which a nitrogen is in position 8, creating a pyrazine unit rather than a pyrimidine unit in one ring. The same trends observed in the visible spectra are also found in the UV region (see Experimental Section). Tri-*s*-triazine (**2a**) exhibits the simplest spectrum because of its high degree of symmetry, point group D_{3h}. Azacycl[3.3.3]azine **2b** does not contain any symmetry elements, while azacycl[3.3.3]azines **2c** and **2d**, each possessing C_{2v} symmetry, have very similar spectra, bathochromically shifted in the case of **2d**.

UV Photoelectron Measurements and Quantum Mechanical Calculations

Panel a of Figure 1 shows He I photoelectron spectra of tri-*s*-triazine (**2a**), 1,3,4,6,7-pentaazazacycl[3.3.3]azine (**2b**), and 1,3,4,6,8-pentaazazacycl[3.3.3]azine (**2d**). Panel b shows spectra of 1,3,4,6-tetraazazacycl[3.3.3]azine (**2c**), 1,3,6-triazacycl[3.3.3]azine (**6**), and 1,3,4-triazacycl[3.3.3]azine (**7**). Figure 1 also contains vertical ionization potentials for the highest occupied π orbitals in molecules **2a–d**, **6**, and **7**. The assignment of the spectrum of tri-*s*-triazine is the same as that previously reported.[21] The photoelectron spectrum of each of the six molecules exhibits one well-resolved band which arises from the highest occupied molecular orbital (HOMO).

In each spectrum in Figure 1 the photoelectron emission in the energy region above 9.5 eV arises from overlapping bands. Of all the molecules studied, the spectrum of tri-*s*-triazine (**2a**) in this energy region possesses the least detailed structure. Tri-*s*-triazine is also the most symmetric molecule. Ionization potentials above 9.5 eV which are denoted in Figure 1 correspond to maxima in the photoelectron spectra that occur in energy regions containing several closely spaced unresolved bands. Above 13.0 eV the spectra of molecules **2b–d**, **6** and **7** are very poorly resolved and are not shown in Figure 1. For these molecules the HOMO, like that in tri-*s*-triazine (**2a**)[21] and cycl[3.3.3]azine (**1**),[12,21] is a π orbital (π_1).

The results of Figure 1 indicate that the π_1 ionization potentials vary significantly from 9.16 eV for tri-*s*-triazine to 7.36 eV for 1,3,6-triazacycl[3.3.3]azine. The spectra indicate that the π_1 ionization potential decreases as the number of nitrogen atoms decreases. This is consistent with the electronic absorption spectra which are increasingly shifted to the red as the number of N atoms decreases. The results in Figure 1 also indicate that for the molecules studied the ionization potential of the π_1 orbital is more sensitive to changes in the number of N atoms than to changes in the positions of the N atoms. For example, the π_1 ionization potential of tri-*s*-triazine (**2a**) is more than 0.6 eV greater than that of either 1,3,4,6,7-pentaazazacycl[3.3.3]azine (**2b**) or 1,3,4,6,8-pentaazazacycl[3.3.3]azine (**2d**), but the ionization potentials of molecules **2b** and **2d** differ by only about 0.1 eV.

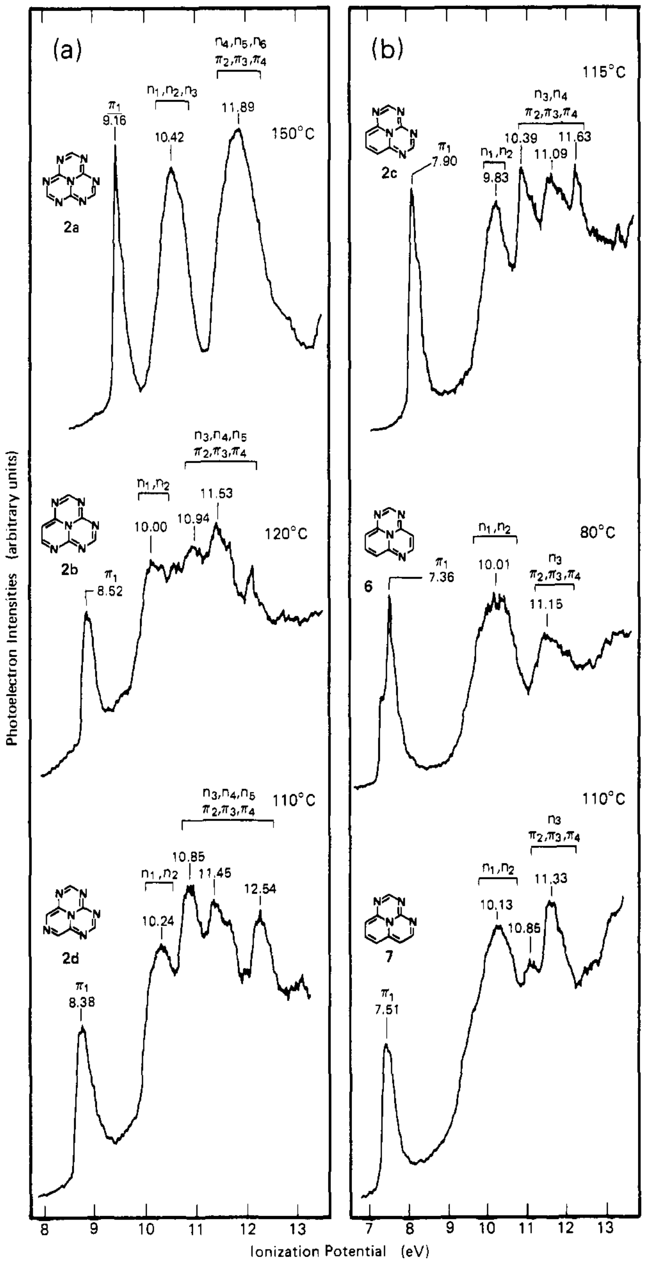

Figure 1. Photoelectron spectra of azacycl[3.3.3]azines along with assignments and π_1 vertical ionization potentials.

In each spectrum there is a significant energy gap (>1.2 eV) between the π_1 band and a broad region of high photoelectron intensity with a maximum that lies in the range 9.8 to 10.4 eV. In tri-*s*-triazine this energy region contains bands arising from the highest occupied lone-pair orbitals. The spectra of the other molecules in Figure 1 have been similarly assigned.

The observation that the ionization potentials of the highest occupied lone-pair orbitals do not change significantly as the number of N atoms is altered in this series is similar to results from previous photoelectron studies[21] of *s*-triazine and tri-*s*-triazine. For these two molecules (the former with three N atoms, the latter with seven N atoms) the n_1 ionization potentials differ by less than 0.1 eV. On the other hand, the difference in the π_1 ionization potentials is more than 2.5 eV. The strong dependence of π_1 ionization potentials on the number of N atoms is expected

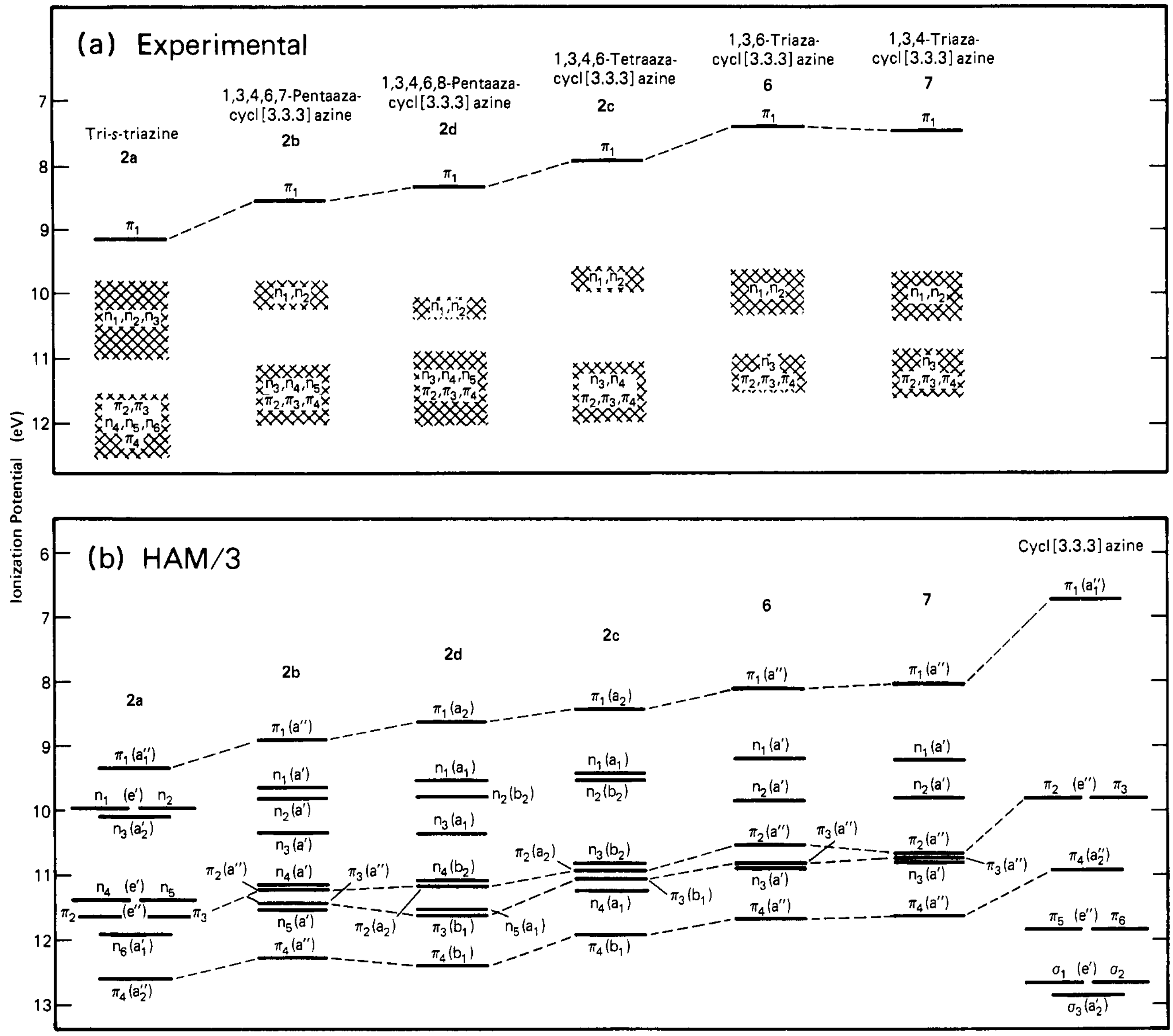

Figure 2. Energy level diagram comparing azacycl[3.3.3]azine experimental ionization potentials (panel a) with theoretical ionization potentials (panel b) obtained from HAM/3 calculations. Panel b also contains theoretical results for cycl[3.3.3]azine.

since, for all the molecules studied, this orbital is a nonbonding molecular orbital with nodes at alternate peripheral positions. The variation in π_1 ionization potentials arises from differences in the number of N atoms at the nonnodal positions.

Assignments of other bands appearing in the spectra of molecules **2b–d**, **6**, and **7** have been made with the aid of results from HAM/3[23] semiempirical and GAUSSIAN 80[24] (STO-3G) ab initio SCF-MO calculations. The HAM/3 calculations provide accurate descriptions of the energetic ordering of orbitals in s-triazine.[21,25] For HAM/3 the predicted energetic ordering of orbitals for s-triazine and tri-s-triazine was also found to agree well with results of STO-3G ab initio SCF-MO calculations.[21] The HAM/3 calculations are parameterized to provide directly the theoretically predicted ionization potentials. Koopmans' theorem was employed to obtain theoretical ionization potentials from the results of the ab initio calculations. The results are summarized in Figures 2 and 3.

For the molecules in Figures 2 and 3 crystal structures have been reported only for tri-s-triazine (**2a**)[20] and 1,3,4,6-tetraazacycl[3.3.3]azine (**2c**).[16c] In the calculations the geometries used for all of the molecules were based on averaged bond lengths and bond angles obtained from tri-s-triazine crystallographic data. For all molecules a planar geometry was employed with C–N and C–C bond lengths equal to 1.34 Å and C–H bond lengths equal to 1.10 Å. All bond angles were taken to be 120°.

In order to test the effects of geometry change on the computational results both HAM/3 and ab initio calculations were also carried out on **2a** and **2c** using the reported crystal structures. In both molecules and in both types of computation, it was found that for each of the 10 upper occupied orbitals the predicted ionization potentials differed by less than 0.56 eV for the two geometries used. For neither molecule did the different geometries used lead to different predictions concerning the energetic ordering of the 10 upper occupied orbitals.

Both HAM/3 and ab initio calculations were also carried out on tri-s-triazine to examine the effects that small deviations from planarity have on the theoretical results. For tri-s-triazine the averaged geometry was modified so that the central N was translated 0.1 Å out of the plane containing the remaining atoms. For the nonplanar geometry both calculations predict that the ionization potential of each of the 31 highest occupied orbitals changes less than 0.25 eV from that calculated for the planar geometry.

Figure 2 compares experimental and theoretical results obtained for the cycl[3.3.3]azines studied here. For the π_1 orbitals, panel a shows vertical ionization potentials obtained from the photoelectron spectra of Figure 1. In panel a the hatched regions

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(24) The GAUSSIAN 80 program was obtained from the Quantum Chemistry Program Exchange at the University of Indiana.

(25) Gleiter, R.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1972**, *55*, 255.

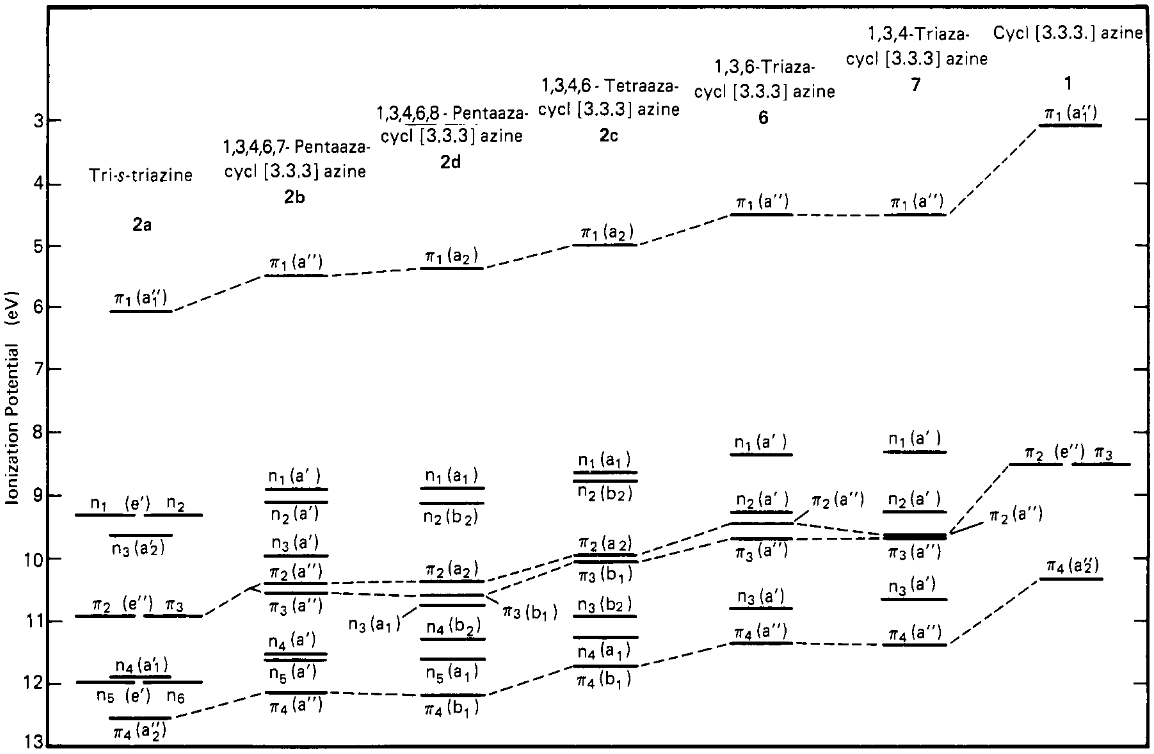

Figure 3. Theoretical energy level diagram for the azacycl[3.3.3]azines and cycl[3.3.3]azine obtained from results of GAUSSIAN 80 ab initio SCF–MO calculations.

correspond to the energy ranges which are bracketed in Figure 1. Panel b gives orbital symmetries and ionization potentials predicted by HAM/3. In addition to the molecules for which spectra have been measured, panel b also contains HAM/3 results for cycl[3.3.3]azine.

In cases where comparison with experiment is possible, an examination of Figure 2 indicates that HAM/3 predicts absolute ionization potentials for the first and second highest occupied orbitals in azacycl[3.3.3]azines to within 0.8 eV. The calculations also accurately predict the perturbation pattern of the π_1 orbitals which is observed experimentally as the number of N atoms is varied and the positions are changed. Finally, the calculations correctly indicate that the ionization potentials of the second highest occupied orbitals, the n_1 orbitals, are much less sensitive to variation in N atom substitution than the ionization potentials of the HOMO's. According to the calculations the n_1 ionization potentials differ by less than 0.8 eV among the azacycl[3.3.3]azines studied.

The HAM/3 calculations predict that the difference in the ionization potentials of the n_1 and n_2 orbitals increases in going from 1,3,4,6-tetraazacycl[3.3.3]azine (**2c**) to the triazacycl[3.3.3]azines (**6** and **7**). While the n_1 and n_2 bands are not resolved in the photoelectron spectra, this prediction is consistent with the data in panel b of Figure 1. Here, it is found that the energy region associated with photoelectron emission from the n_1 and n_2 orbitals broadens in going from molecules **2c** to **6** and **7**.

Consistent with assignments given in Figure 1, the HAM/3 calculations predict that the energy gap between the n_3 orbital and the degenerate or nearly degenerate n_1 and n_2 orbitals increases in going from tri-*s*-triazine (**2a**) to the pentaazacycl[3.3.3]azines (**2b** and **2d**) to 1,3,4,6-tetraazacycl[3.3.3]azine (**2c**).

Because of the poor resolution of the spectra in the energy region above 10.5 eV it is not possible to provide a detailed assignment of the high-energy bands at this time. According to the present assignments, the bands arising from the π_2, π_3, and π_4 orbitals occur between 11.1 and 12.8 eV in the spectrum of tri-*s*-triazine and between 10.5 and 11.8 eV in the spectrum of the triazacycl[3.3.3]azines **6** and **7**. For the pentaazacycl[3.3.3]azines **2b** and **2d** and for 1,3,4,6-tetraazacycl[3.3.3]azine (**2c**), the π_2, π_3, and π_4 bands lie in the range 10.5–12.5 eV.

The HAM/3 calculations indicate that in the energy regions containing the π_2, π_3, and π_4 bands the spectra of the azacycl[3.3.3]azines are made more complex by the presence of varying numbers of bands arising from lone-pair orbitals. In the spectra of tri-*s*-triazine the HAM/3 calculations predict that the n_4, n_5, and n_6 bands and in the pentaazacycl[3.3.3]azines the n_3, n_4 and n_5 bands lie in the energy region containing the π_2, π_3, and π_4 bands. In the spectrum of 1,3,4,6-tetraazacycl[3.3.3]azine the n_3 and n_4 bands are interspersed with the π_2, π_3, and π_4 bands. In the spectra of the triazacycl[3.3.3]azines calculations indicate that only the n_3 band lies in the region containing the π_2, π_3, and π_4 bands.

The prediction that the number of lone-pair bands interspersed with the π_2, π_3, and π_4 bands decreases as the number of N atoms in the molecules decreases is consistent with the observation that the spectra of the triazacycl[3.3.3]azines are less complex in the energy region assigned to the π_2, π_3, and π_4 bands than the spectra of the tetra-, penta- and hexaazacycl[3.3.3]azines.

Figure 3 shows an energy level diagram constructed from the results of the ab initio SCF–MO calculations. For all of the molecules studied the absolute values of ionization potentials obtained from the ab initio calculations show less correspondence than those obtained from HAM/3. However, the pattern of energy levels predicted by the ab initio calculation is very similar to that obtained with HAM/3 and agrees with the spectral assignments given in Figure 1.

For molecules **2b**, **2c**, and **2d** the ab initio and HAM/3 calculations predict a slightly different energetic ordering of the π_2 and π_3 orbitals relative to the manifold of occupied lone-pair orbitals. However, because of the complexity of the photoelectron spectra of molecules **2b**, **2c**, and **2d** in the energy regions containing the π_2 and π_3 bands, the discrepancies between the ab initio and the HAM/3 results cannot be resolved at present.

Lone-Pair Electron Distribution

An examination of electron distribution provides detailed information about differences in the lone-pair orbital structure in the molecules studied here. Panel a of Figure 4 shows electron density maps for the n_1, n_2, n_3, and n_4 orbitals of 1,3,4,6-tetraazacycl[3.3.3]azine. Panel b shows electron density maps for the n_3 orbitals of 1,3,4,6,7- and 1,3,4,6,8-pentaazacycl[3.3.3]azines (**2b**, **2d**) and the n_2 orbitals of 1,3,6- and 1,3,4-triazacycl-

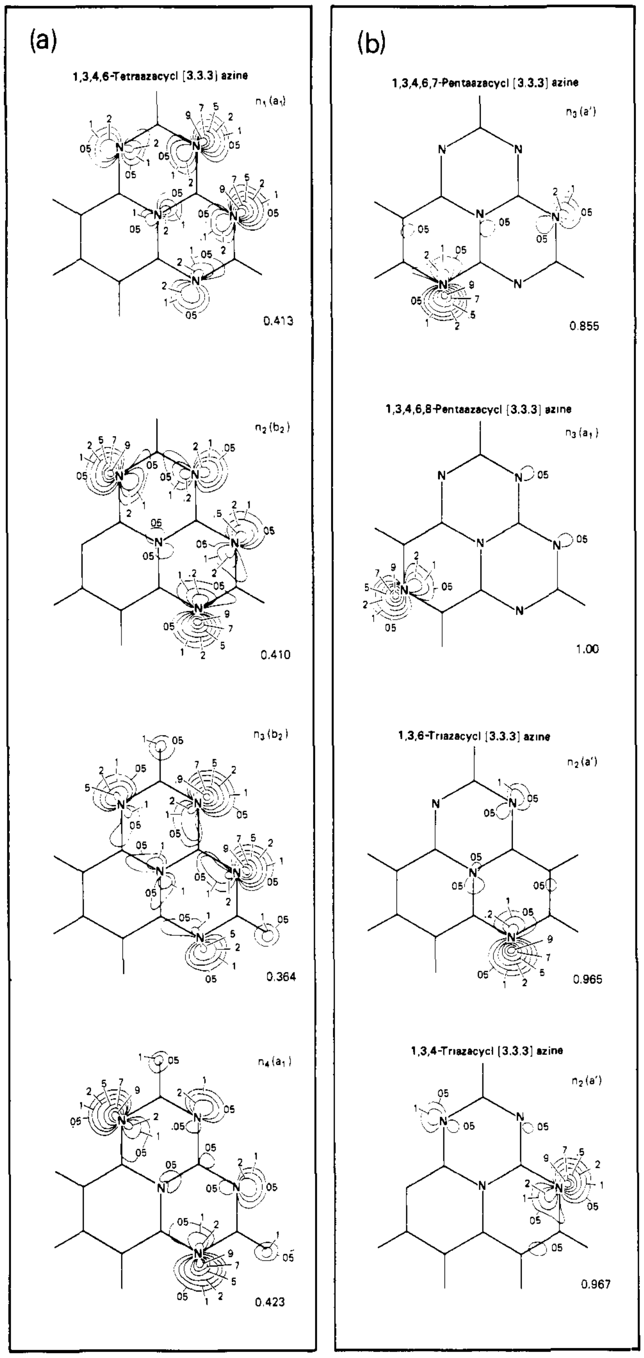

Figure 4. Lone-pair electron density maps. Panel a shows the electron distributions and symmetries for four lone-pair orbitals in 1,3,4,6-tetraazacycl[3.3.3]azine (**2c**). Panel b shows results for the n_3 orbitals of 1,3,4,6,7- and 1,3,4,6,8-pentaazacycl[3.3.3]azine (**2b** and **2d**, respectively) and for the n_2 orbitals of 1,3,6- and 1,3,4-triazacycl[3.3.3]azine (**6** and **7**, respectively). Values of electron density denoted on the contours are normalized to the maximum density in each of the orbitals. The relative magnitude for the maximum density occurring in each of the eight orbitals is given to the lower right of each map.

[3.3.3]azines (**6**, **7**). The electron density maps were generated from the results of the ab initio SCF–MO calculations using previously described methods.[26]

In our previous studies of tri-*s*-triazine[21] it was found that all six of the highest occupied lone-pair orbitals are highly delocalized with large contributions provided by several N atoms. This description is typical of many of the lone-pair orbitals occurring in the penta-, tetra-, and triazacycl[3.3.3]azines studied here, as demonstrated by the lone-pair maps in panel a for 1,3,4,6-tetraazacycl[3.3.3]azine (**2c**). The uniform delocalization of the lone-pair orbitals occurs in the cycl[3.3.3]azines when the member of this series has high symmetry [D_{3h} for tri-*s*-triazine (**2a**), C_{2v} for 1,3,4,6-tetraazacycl[3.3.3]azine (**2c**)] and when the peripheral N atoms are not separated by more than two bonds. In molecules **2a** and **2c** the peripheral N atoms all occupy alternating positions.

Most of the n orbitals in the penta- (**2b** and **2d**) and triazacycl[3.3.3]azines (**6** and **7**) are also delocalized. However, in contrast to molecules **2a** and **2c** the tri- and pentaazacycl[3.3.3]azines also contain highly localized lone-pair orbitals. Electron density maps of these orbitals are shown in panel b of Figure 4.

In the case of 1,3,4,6,7-pentaazacycl[3.3.3]azine (**2b**) the localized n_3 orbital on the N7 atom arises owing to the low C_s symmetry of the molecule. This is the same symmetry as that of 1,3,4-triazacycl[3.3.3]azine (**7**) in which the n_2 orbital is localized on the N4 atom. In 1,3,4,6,8-pentaazacycl[3.3.3]azine (**2d**) the localized n_3 orbital on the N8 atom arises because N8 occupies a nonalternate position. Finally, for 1,3,6-triazacycl[3.3.3]azine (**6**) in which the n_2 is localized on the N6 atom, both the symmetry is low (C_s) and the N6 atom occupies a nonalternating position.

π-Electron Distribution and Reactivity Indexes

In previous studies π-electron densities obtained from Hückel calculations[2d,16a] were used to predict the relative susceptibilities of different sites on 1,3,6-triazacycl[3.3.3]azine (**6**) to electrophilic substitution. It was found that among the carbon atoms C4 has the highest π charge. In agreement with the calculations,[2d,16i] it is found that electrophilic bromination of **6** carried out under mild conditions occurs preferentially at the 4 position.

In the present study it is found that the relative magnitudes of the π-electron densities obtained from the ab initio calculations on **6** are in agreement with the Hückel results. For the other molecules studied ab initio calculations predict that the preferred site (or sites) of electrophilic substitution is C6 followed by C7 in **7**, C9 in **2b**, C7 and C9 in **2c** and **2d**, and C1, C3, C4, C6, C7, and C9 in cycl[3.3.3]azine (**1**). In tri-*s*-triazine (**2a**) there are no C atoms with high π-electron density. The ab initio results point out, furthermore, that for cycl[3.3.3]azine and for molecules **2b–d**, **6**, and **7** the C atom sites of highest π-electron density are also sites of highest total electron density.

In addition to predicting sites of electrophilic substitution, Hückel calculations have also been used to develop a rule of topological charge stabilization for the cycl[3.3.3]azines.[15] This rule provides guidelines for predictions how the addition of peripheral N atoms stabilizes cycl[3.3.3]azines. This rule is based upon a consideration of the π-electron distribution in the phenalenide anion which is isoelectronic with the cycl[3.3.3]azines. According to the rule, the positions of highest π-electron density in the phenalenide anion will give rise to the greatest stabilization when a methine group is replaced by an N atom. The rule predicts that stabilization of cycl[3.3.3]azine (**1**) occurs most favorably when N atoms lie at the 1, 3, 4, 6, 7, and 9 positions. Occupation of all of these positions occurs in tri-*s*-triazine (**2a**) which, in agreement with the rule, is much more inert than cycl[3.3.3]azine. For the molecules studied here the rule predicts that stability increases in the order cycl[3.3.3]azine (**1**) < **6** ≈ **7** < **2c** < **2d** < **2b** < **2a**.

Finally, it is interesting to note the relationship between the predictions concerning the methine groups at which electrophilic substitution in cycl[3.3.3]azine and molecules **2b–d**, **6**, and **7** is preferred and the predictions concerning the methine positions in these molecules at which N-atom substitution most effectively leads to stabilization. For all six molecules, these two sets of positions correspond to the positions of the most negative methine groups and are identical.

Experimental Section

General. Proton nuclear magnetic resonance spectra were recorded on a Varian EM-390 or HR-220 spectrometer, operating at 90 or 220 MHz, respectively. ^{13}C NMR spectra were obtained on a Nicolet NTC-360 spectrometer operating at 90.5 MHz and are reported in parts per million from tetramethylsilane. Data are reported as follows:

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(26) Padva, A.; O'Donnell, T. J.; LeBreton, P. R. *Chem. Phys. Lett.* **1976**, *41*, 278.

chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration, and assignment. Mass spectra were obtained by J. Carter Cook and his staff on a Varian MAT CH-5 low-resolution spectrometer coupled with a 620i computer and a STATOS Recorder. Ultraviolet absorption spectra were obtained on a Beckman Acta MVI spectrometer. Infrared spectra were obtained on a Perkin-Elmer 337 spectrophotometer. Microanalyses were performed by Josef Nemeth and his staff. 1,3,6-Triazacycl[3.3.3]azine (**6**)[16a,b] and 1,3,4-triazacycl[3.3.3]azine (**7**)[161] were prepared by the published procedures.

General Procedure for Bis(*N′*-cyano-*N*-formamidino)azines (5b–d). To a solution made from 1.6 g (0.07 g-atom) of sodium in 20 mL of anhydrous methanol was added 1.0 g (9.0 mmol) of the diamino azine. The resulting solution was stirred at 25 °C for 30 min under N_2. Then 8.2 mL (9.5 mmol) of methyl *N*-cyanomethanimidate (**4**) was added. After the solution was stirred for 1 h, 10% aqueous HCl was added to bring the pH to 4.0–4.5. The precipitate was filtered through a medium porous sintered-glass funnel, washed with methanol followed by ethyl acetate, and air-dried to afford 1.30–1.60 g (66–84%) of compound. The product was dried overnight at 25 °C over P_2O_5 under high vacuum.

2,4-Bis(*N′*-cyano-*N*-formamidino)pyrimidine (5b): yield 1.3–1.4 g (66–71%); mp 204–207 °C; mass spectrum (70 eV), *m/e* 172 ($M^+ - NH_2CN$, 100%); ^1H NMR ($(CD_3)_2SO$) δ 6.8 (d, 1, 5-H), 8.5 (d, 1, 6-H), 9.6 (M, 2, side-chain CH), 10.8 (b, 2, NH, exchangeable with D_2O); IR (KBr) 2220 cm^{-1} ($C{\equiv}N$).

2,6-Bis(*N′*-cyano-*N*-formamidino)pyridine (5c): yield 1.57–1.60 g (80–84%); mp 165–167 °C; mass spectrum (70 eV), *m/e* 171 ($M^+ - NH_2CN$, 100%); ^1H NMR ($(CD_3)_2SO$) δ 6.7 (d, 2, 3-H and 5-H), 7.7 (t, 1, 4-H), 9.5 (s, 2, side-chain CH); IR (KBr) 2220 cm^{-1} ($C{\equiv}N$).

2,6-Bis(*N′*-cyano-*N*-formamidino)pyrazine (5d): yield 1.36 g (71%); mp 183–185 °C; mass spectrum (70 eV), *m/e* 172 ($M^+ - NH_2CN$, 100%); ^1H NMR ($(CD_3)_2SO$) δ 8.15 (s, 2, 3-H and 5-H), 9.65 (s, 2, side-chain CH); IR (KBr) 2210 cm^{-1} ($C{\equiv}N$).

General Procedure for Azacycl[3.3.3]azines (2b–d). Bis(*N′*-cyano-*N*-formamidino)pyrimidine, -pyridine, or -pyrazine (1.0 g, 4.6 mmol) was spread over the bottom of a sublimation apparatus and a vacuum was applied at 10^{-2} to 10^{-3} mmHg. The sublimation apparatus was immersed in a preheated (400 °C) lead bath for approximately 2 min and was then removed and allowed to cool to room temperature. The sublimation apparatus was opened, and extraction of the sublimate and residual material with anhydrous methyl Cellosolve, filtration, and evaporation afforded 332–506 mg (42–64%) of compound.

1,3,4,6,7-Pentaazacycl[3.3.3]azine (1,3,4,6,7,9b-Hexaazaphenalene) (2b). The general procedure was modified as follows. To the methyl Cellosolve filtrate was added approximately 5 g of flash silica gel, and the mixture was evaporated to dryness on a rotary evaporator under high vacuum. The orange solid was finely ground with a mortar and pestle and loaded upon a column of Woelm silica gel (100 g packed with $CHCl_3$) and eluted with $CHCl_3/MeOH$ (4:1). The orange band was collected, and the solvent was removed on a rotary evaporator to afford 332 mg (42%) of **2b**: mp 268–271 °C; mass spectrum (70 eV), *m/e* 172 (M^+, 100%), 145 ($M^+ - HCN$, 3), 118 ($M^+ - 2HCN$, 9); ^1H NMR ($(CD_3)_2SO$) δ 6.20 (d, 1, J = 6 Hz, 9-H), 7.77 (s, 1, 2-H or 5-H), 7.82 (s, 1, 5-H or 2-H), 7.95 (d, 1, J = 6 Hz, 8-H); ^{13}C NMR ($(CD_3)_2SO$) δ 108.3 ($^1J_{CH}$ = 176.3 Hz, C 9), 156.1 (C9a), 159.2 (C3a or C6a), 160.5 (C6a or C3a), 162.5 ($^1J_{CH}$ = 184.0 Hz, C8), 168.7 ($^1J_{CH}$ = 205.3 Hz, C2 or C5), 169.1 ($^1J_{CH}$ = 204.6 Hz, C5 or C2); color, orange: UV (CH_3CN) λ_{max} 531 (ϵ 144), 502 (289), 468 (173), 335 (8690), 320 sh (12550), 315 (15350), 309 (14860), 299 (14480), 231 (12740). Flash chromatography on silica gel with EtOAc/MeOH (4:1) as eluting solvent furnished analytically pure compound.

Anal. Calcd for $C_7H_4N_6$: C, 48.83; H, 2.34; N, 48.83. Found: C, 48.70; H, 2.43; N, 48.40.

1,3,4,6-Tetraazacycl[3.3.3]azine (1,3,4,6,9b-pentaazaphenalene) (2c):[17a,b] color, lavender; yield 497 mg (67%); mp 254–257 °C [lit.[17a,b] 258–260 C]; ^1H NMR ($(CD_3)_2SO$) δ 6.04 (d, 2, J = 8 Hz, 7-H and 9-H), 7.21 (s, 2, 2-H and 5-H), 7.36 (t, 1, J = 8 Hz, 8-H); ^{13}C NMR ($(CD_3)_2SO$) δ 111.76 (C7, C9), 146.35 (C8), 155.07 (C6a, C9a), 161.64 (C3a), 166.84 (C2, C5); UV (CH_3CN) λ_{max} 608 (ϵ 179), 565 (346), 526 (285), 495 sh (155), 363 (6590), 360 (5080), 351 (8370), 345 (7240), 336 (6830), 331 (16870), 302 sh (12600), 238 (16830).

1,3,4,6,8-Pentaazacycl[3.3.3]azine (1,3,4,6,8,9b-hexaazaphenalene) (2d):[17f] color, blue; yield 506 mg (64%); mp 246–249 °C [lit.[17f] 248–250 °C]; ^{13}C NMR ($(CD_3)_2SO$) δ 134.13 (C7, C9), 147.56 (C6a, C9a), 160.79 (C3a), 169.01 (C2, C5); UV (CH_3CN) λ_{max} 637 (ϵ 969), 592 (840), 550 (420), 386 (5180), 379 (4690), 368 (7120), 362 (6630), 352 (5500), 314 (17540), 302 sh (12130), 246 (11650).

Gas-phase UV photoelectron spectra were measured with a Perkin-Elmer PS-18 spectrometer. The $^2P_{3/2}$ and $^2P_{1/2}$ bands of Xe and Ar were used to calibrate the He I spectra of the molecules studied. The spectrometer probe temperatures at which the spectra were measured are given Figure 1. For each molecule several spectra from a single sample were measured over a period of 2 h and no signs of decomposition were observed.

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Registry No. 2b, 54499-06-8; **2c**, 38713-73-4; **2d**, 64323-57-5; **3b**, 156-81-0; **3c**, 141-86-6; **3d**, 41536-80-5; **4**, 51688-22-3; **5b**, 96445-61-3; **5c**, 96445-62-4; **5d**, 96445-63-5; **6**, 37159-99-2; **7**, 63325-76-8.