grammer. Products were identified by spiking techniques. Calibration curves were prepared daily and employed for product quantitation. Analysis for methane gas was accomplished by gas chromatography with molecular sieve Type 5A columns.[41] Gas chromatographic analysis of other products was carried out on a Varian Aerograph Series 2100 gas chromatograph equipped with $^1/_8$-in., all-glass OV-17 columns and FID detectors.

Acknowledgment. Grateful acknowledgement is made to the U.S. Department of Energy for supporting this research through Grant No. DE-FG22-80PC30227. Financial support to M.D.K. was made possible by a North Dakota MMRRI Fellowship. The encouragement and initial support by Professor M. D. Hawley are gratefully acknowledged. We thank Dr. Virgil Stenberg for helpful discussions.

Registry No. 1, 6609-56-9; **1** radical anion, 89596-85-0; **2**, 1527-89-5; **2** radical anion, 68271-94-3; **3**, 874-90-8; **3** radical anion, 68271-93-2.

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(41) Gas analyses by gas chromatography were generously performed by the UND Engineering Experiment Station.

Tri-*s*-triazine: Synthesis, Chemical Behavior, and Spectroscopic and Theoretical Probes of Valence Orbital Structure

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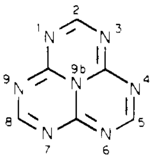
Abstract: The synthesis, physical properties, and chemical properties of unsubstituted tri-*s*-triazine (1,3,4,6,7,9,9b-heptaazaphenalene) are reported. The abbreviated synthesis consisted of a two-step procedure whereby 2,4-diamino-1,3,5-triazine was treated with methyl *N*-cyanomethanimidate and NaOMe in Me$_2$SO/MeOH to give 2,4-bis(*N*′-cyano-*N*-formamidino)-1,3,5-triazine, which was subjected to short vacuum pyrolysis to give tri-*s*-triazine. The compound gave no evidence of (a) formation of π complexes with either electron-donor or electron-acceptor organic partners, (b) protonation, (c) alkylation, or (d) N-oxidation, yet it formed complexes with silver salts and decomposed in water. Photoelectron spectroscopic studies of tri-*s*-triazine have provided ionization potentials associated with the six highest occupied π and six highest occupied lone-pair orbitals. Interpretation of the photoelectron spectrum has been aided by results from semiempirical HAM/3 and from ab initio, GAUSSIAN70, quantum mechanical calculations. The detailed picture of valence orbital structure provides insight concerning the low basicity and the overall high chemical stability of tri-*s*-triazine.

Tri-*s*-triazine (**1**)[1,2] is the ultimate member of the alternating C,N azacycl[3.3.3]azine series. The first member of the series is called cycl[3.3.3]azine (**2**)[3,4] and contains three fused conjugated six-membered rings held planar by three covalent bonds to an internal nitrogen atom.[5,6] Cycl[3.3.3]azine is formally isoelectronic with the phenalenide anion (**3**) containing an all-carbon skeleton[7,8] and, with the aza compounds in the series, has been the subject of numerous theoretical calculations and predictions.[9-16] The considerable theoretical interest in the cycl[3.3.3]azine series is derived from the 12-π-electron periphery and the question of the involvement of the n electrons of the central N. Moreover, although members of the series containing from 0 to 6 N atoms in the periphery are formally isoelectronic, they exhibit widely different electronic and chemical properties.[10] For example, cycl[3.3.3]azine (**2**) is chemically reactive and readily undergoes oxidation and addition reactions,[3,4] while 1,3,4,6,7,9-hexaazacycl[3.3.3]azine or tri-*s*-triazine (**1**)[2] is chemically unreactive except for its facile decomposition by water.



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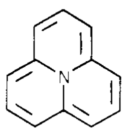

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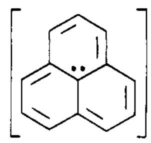

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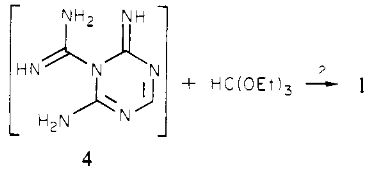
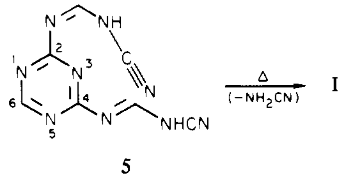
Scheme I



Scheme II



The properties of heat stability, low solubility, and little chemical reactivity are characteristic of a group of related nitrogen com-

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(1) Other names of **1** include cyamelurine, 1,3,4,6,7,9,9b-heptaazaphenalene, *s*-heptazine, and 1,3,4,6,7,9-hexaazacycl[3.3.3]azine.

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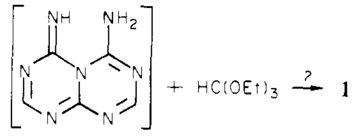
Scheme III



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pounds (hydromelonic acid, cyameluric chloride, cyameluric acid, melem, melon, etc.) that originated in the laboratories of Liebig[17] and Gmelin[18] from various pyrolysis and fusion reactions, e.g., of (a) potassium ferrocyanide and sulfur, (b) thiocyanogen, (c) thiocyanogen and chlorine, (d) potassium thiocyanate, and (e) potassium thiocyanate with antimony or bismuth trichloride. These compounds remained structural puzzles for more than a century until Pauling and Sturdivant[9] devised the correct formulation for their common nucleus, a coplanar arrangement of three fused *s*-triazine rings (**1**). Now, almost a century and a half after the first experiments of Liebig and Gmelin, we have synthesized the unsubstituted nucleus, tri-*s*-triazine (**1**), for the first time,[2] determined its structure by X-ray crystallography, and examined its physical, spectroscopic, and chemical properties.

Synthesis, Structure, and Chemistry. Although synthetic methodology had been developed earlier for cycl[3.3.3]azine (**2**) and for various aza-substituted members of the series,[3,4,19–21] the compound with six alternating nitrogens in the periphery, tri-*s*-triazine (**1**), had not yet been made. We sought to remedy this situation with the added intent of providing a simple and straightforward method of preparation. At first inspection, three possible routes to tri-*s*-triazine seemed viable: the addition of two separate carbon units to a 1-formamidino-substituted *s*-triazine (**4**) (Scheme I); the addition of a one-carbon unit to an appropriately substituted triazino[1,2-*a*]triazine (**5**) (Scheme II); and the intramolecular ring closure of a suitably derivatized 2,4-diamino-*s*-triazine (**6**) (Scheme III). In the first approach, *N*,*N'*-dicyanoformamidine, NCNH-CH=NCN (**7**), made from sodiocyanamide and methyl *N*-cyanomethanimidate, $CH_3OCH{=}NCN$ (**8**),[22,23] was treated with guanidine hydrochloride. The product was not the desired **4·HCl** but rather 2,4-diamino-*s*-triazine hydrochloride. In order to construct the substituted triazino[1,2-*a*]triazine (**5**) in Scheme II, regioselective formation of the second triazine ring was required in the condensation of 2,4-diamino-*s*-triazine with 1 mol equiv of methyl *N*-cyanomethanimidate (**8**). Under the conditions employed (Me_2SO at 100 °C), however, cyclization appeared to have taken place on N5 instead of N3 of the original 2,4-diamino-*s*-triazine, as in previously reported cases of ring closure to a distal nitrogen,[20b] and an additional molecule of cyanamide appeared to have been incorporated.[23] Scheme III was successful when we recognized that the mass spectrum of the intermediate **6** was giving us a cue as to the conditions necessary to convert **6** to tri-*s*-triazine (**1**).

2,4-Bis(*N'*-cyano-*N*-formamidino)-1,3,5-triazine (**6**) was obtained ($\geq$60% yield) from the reaction of methyl *N*-cyanomethanimidate (**8**; see text above) with 2,4-diamino-1,3,5-triazine and NaOMe in Me_2SO/MeOH at room temperature followed by neutralization with dilute HCl. The ^1H NMR in $(CD_3)_2SO$ had two sharp singlets at δ 8.8 and 9.7, with an integrated ratio of 1:2 and assignable, respectively, to the ring and side-chain protons. The broad signal at δ 12.4 corresponding to N–H integrated for two protons, which were exchangeable with D_2O. The infrared spectrum revealed a strong $C{\equiv}N$ stretching absorption at 2220 cm^{-1}. Formula **6** is not intended to portray a special tautomeric form or geometrical isomer but only to show the general placement of the atoms for construction of the second and third rings of tri-*s*-triazine (**1**).[2] Any tautomerism or isomerism of **6** prerequisite for the probably sequential ring closures to occur might be assumed to take place at elevated temperature. The electron impact mass spectrum of **6** at 10 eV exhibited a base peak at m/e 173 ($M^+ - 42$) corresponding to the loss of CH_2N_2 (cyanamide?), suggestive that the intended cyclization of **6** to **1** had occurred in the mass spectrometer. Supporting this conclusion was the fragmentation pattern that showed no ions resulting from the further loss of CH_2N_2 but showed instead two consecutive losses of HCN, a mass spectral behavior characteristic of nitrogen heterocycles.[24]

Intermediate **6** showed some interesting chemical properties. It dissolved readily in dilute aqueous NaOH, but after this solution was shaken for a few seconds at room temperature, colorless crystals separated. Isolation followed by characterization by TLC and ^1H NMR indicated it to be 2,4-diamino-*s*-triazine. Intermediate **6** is stable as a solid when stored under protection from atmospheric moisture but decomposes in common organic solvents in 1–2 days at room temperature. If compound **6** in DMF spotted on a TLC plate is evaporated with a stream of dry nitrogen and developed, it retains its chromatographic purity. By contrast, if after spotting it is evaporated with a heat gun, development shows a number of products to have been formed.

Inlet conditions in the mass spectrometer, i.e., short residence time, high temperature, and very low pressure, suggested a favorable vacuum pyrolysis method for the conversion of **6** to **1**, probably through the intermediacy of one ring closure and tau-

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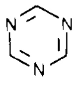
tomerization, followed by the other ring closure and elimination of cyanamide.[2] A sublimation apparatus containing 2,4-bis-(*N'*-cyano-*N*-formamidino)-1,3,5-triazine (**6**) maintained at <0.025 mmHg was immersed in a Wood's metal bath at ~400 °C for ~2 min. Extraction of the sublimate and residual material with acetonitrile, filtration, and evaporation in vacuo yielded (≥60%) tri-*s*-triazine, $C_6H_3N_7$ (**1**), which was obtained analytically pure by flash chromatography on Woelm silica gel with EtOAc/$CHCl_3$ (1:1) as the eluting solvent. The compound is yellow, with a lowest energy electronic transition (443 nm in CH_3CN) close to that predicted by Leupin and Wirz,[10] and it is also weakly fluorescent,[10] with an emission maximum at 517 nm when irradiated at 307 or 445 nm. The structural degeneracy of tri-*s*-triazine (**1**) is evident from its NMR spectra. In the ^1H spectrum in $(CD_3)_2SO$, a single C–H singlet appeared at δ 8.3, which is a greater chemical shift value than any previously observed for unsubstituted cycl[3.3.3]azines having a smaller number of nitrogens in the periphery,[6c,21g] greater also than that, δ 7.3, for the >N—CH=N—Ar model, *N*,*N*-dimethyl-*N'*phenylformamidine,[25] and smaller than the δ 9.2 value for the protons in "aromatic" *s*-triazine (**9**).[26] Two signals appeared in the ^{13}C NMR spectrum,



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one at δ 171.6 for the three peripheral carbons, $^1J_{CH} = 207.6$ Hz with their attached protons, and one at δ 159.7 for the three junctional carbons. The ^{15}N NMR chemical shift of the peripheral nitrogens in **1**, 133.8 ppm downfield from DMF or ~237 ppm downfield from ammonia,[27] with $^2J_{NCH} = 14.0$ Hz, is less than that for the monocyclic (^{15}N)-*s*-triazine, 282.9 ppm from ammonia.[28] The central ^{15}N signal was observed at 81.8 ppm downfield from DMF. Chemical shifts of the ^{15}N resonances, especially for the central ^{15}N in representative members of the azacycl[3.3.3]azine series, will be further investigated. The mass spectrum of tri-*s*-triazine (**1**) exhibited a base peak at *m/e* 173, corresponding to the molecular ion, and fragment ions at 146 and 119, corresponding to the loss of 1 HCN and 2 HCN, just as did the precursor **6** when released through the heated inlet system into the mass spectrometer.

Crystals of tri-*s*-triazine (**1**) for single-crystal X-ray examination[29] were grown by slow evaporation of a solution in anhydrous acetonitrile in an atmosphere of dry xylene. The molecular dimensions were reported in our communication and supplementary material.[2] The deviation of the central nitrogen from the weighted least-squares plane is −0.015 (2) Å, the peripheral bonds are uniform, averaging 1.33 Å, and the three central C–N bonds average 1.39 Å.[30] None of the 16 molecules per unit cell (Figure 1) lies on any of the symmetry elements of the cells.

While cycl[3.3.3]azine (**2**) is highly reactive and readily undergoes oxidation and addition reactions,[3,4] the introduction of electronegative N atoms at the alternating peripheral locations 1, 3, 4, 6, etc., in various azacycl[3.3.3]azines provides increasing stabilization with increasing N content.[19–21,31] Tri-*s*-triazine (**1**), the ultimate member in the alternating C, N series, shows remarkable chemical stability except toward water (see Experimental Section). It gave no evidence of formation of π complexes with either electron-donor or electron-acceptor organic partners. Despite the plethora of lone-pair electrons (14 on the N's), no protonation, alkylation, or N-oxidation was observed. Tri-*s*-triazine (**1**) formed 3:2 complexes with silver perchlorate and silver tetrafluoroborate. Additional complexes of tri-*s*-triazine (**1**) were formed with mercuric chloride, cupric chloride, zinc chloride, and cobaltous chloride but were of variable stoichiometry. No addition (cycloaddition) reactions were found to occur. Susceptibility to electrolytic reduction remains to be examined. The basicity of tri-*s*-triazine (**1**) appears to be lower than that of the monocyclic *s*-triazine (**9**), which is reported to have a pK_a value of 3.5 in CH_3NO_2 + 5% Ac_2O at 25 °C and an estimated pK_a value of −1.7 in H_2O at 25 °C.[32] The successive introductions of N atoms into the nucleus in the series pyridine, pyrimidine, and *s*-triazine reduces the pK_a value by 3–4 units at each step.[32] Chemical behavior of tri-*s*-triazine (**1**) similar to that of *s*-triazine (**9**) is observed in the rapid decomposition of both in water. In all spectroscopic determinations on tri-*s*-triazine, water must be rigorously excluded.

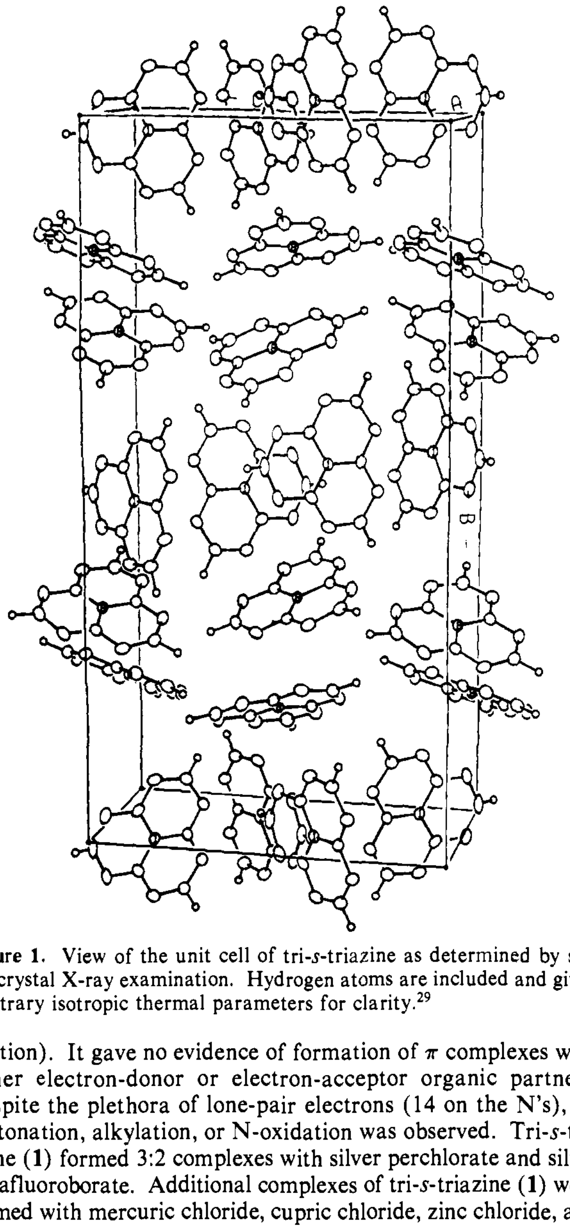

Figure 1. View of the unit cell of tri-*s*-triazine as determined by single-crystal X-ray examination. Hydrogen atoms are included and given arbitrary isotropic thermal parameters for clarity.[29]

UV Photoelectron Measurements and Quantum Mechanical Calculations. Photoelectron spectroscopy studies of tri-*s*-triazine (**1**) have provided ionization potentials associated with the six highest occupied π and six highest occupied lone-pair orbitals. Interpretation of the photoelectron spectrum has been aided by quantum mechanical calculations. Our goal has been to examine the manner in which valence orbital structure may influence the chemical properties of the molecule. The gas-phase UV photoelectron spectrum of tri-*s*-triazine (**1**) was measured at the vapor pressure corresponding to 155 °C, and, for comparison, the

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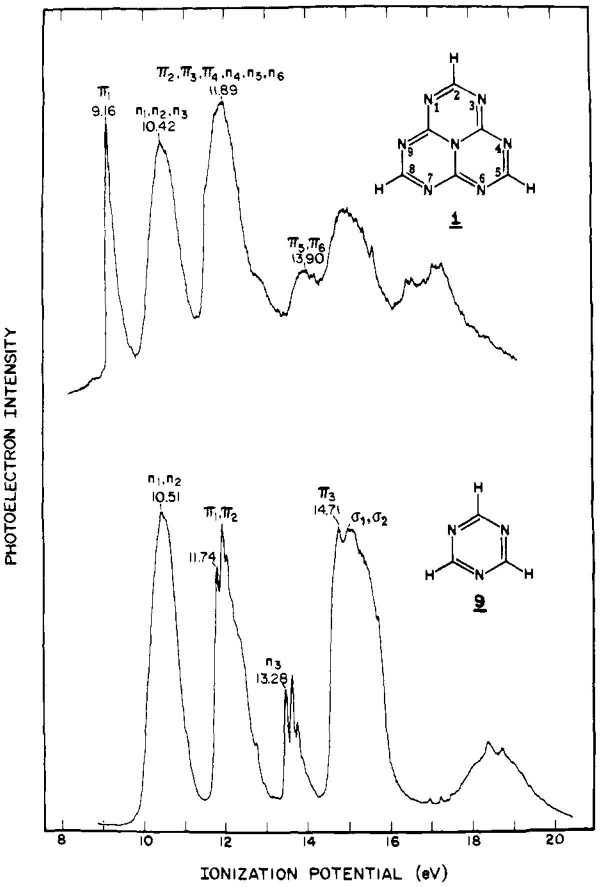

Figure 2. Photoelectron spectra of tri-*s*-triazine (**1**) and *s*-triazine (**9**), along with assignments and vertical ionization potentials.

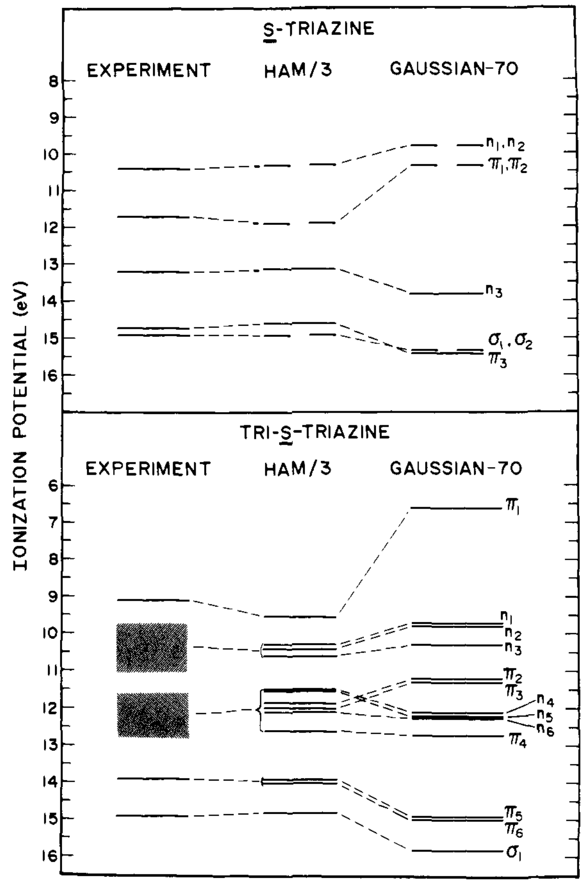

Figure 3. Energy level diagram comparing experimental and theoretical results for tri-*s*-triazine (**1**) and *s*-triazine (**9**). For the experimental energy level diagram, hatched areas represent broad regions of overlapping photoelectron bands.

spectrum of *s*-triazine (**9**) was measured at the vapor pressure corresponding to 0 °C.

Figure 2 shows He I photoelectron spectra of tri-*s*-triazine and *s*-triazine, along with vertical ionization potentials and assignments. For *s*-triazine the present assignments remain unchanged from those previously reported.[34a,b] They are also consistent with results from optical absorption measurements.[34c] The most striking difference between the photoelectron spectra of tri-*s*-triazine and *s*-triazine is that tri-*s*-triazine exhibits a very well resolved band at 9.10 eV associated with the highest occupied molecular orbital. Other regions of high photoelectron intensity in the spectrum of tri-*s*-triazine are less well resolved and are similar to those that appear in the spectrum of *s*-triazine. These broad regions arise from overlapping photoelectron bands.

In the spectrum of tri-*s*-triazine, the assignment of the first band to a π orbital is consistent with previous studies of complex heterocyclic aromatic molecules with diffuse π systems.[35,36] In this regard, tri-*s*-triazine differs from *s*-triazine[34] and 1,2,4-triazine.[37] In each of these monocyclic molecules the highest occupied molecular orbital is a lone-pair orbital.

The π_1 band of tri-*s*-triazine is followed by a structureless region of high photoelectron intensity peaking at 10.42 eV that arises from the three highest occupied lone-pair orbitals. A third region of high intensity has a maximum at 11.89 eV and a shoulder at 12.9 eV. This region contains the second, third, and fourth highest occupied π orbitals and the fourth, fifth, and sixth highest occupied lone-pair orbitals. The emission occurring in the region of 13.9 eV has been assigned to the nearly degenerate π_5 and π_6 orbitals. The assignments of the π_5 and π_6 orbitals are somewhat tentative. At ionization potentials above 12.0 eV the energetic ordering of closely spaced π and lone-pair or σ orbitals cannot be predicted accurately on the basis of SCF calculations.

The full assignment of the photoelectron spectrum of tri-*s*-triazine has been carried out by using HAM/3 semiempirical[38] and GAUSSIAN70 ab initio[39] molecular orbital calculations. The HAM/3 calculations are parameterized in such a manner as to provide direct predictions of experimental ionization potentials. Results from SCF GAUSSIAN70 calculations have been used in conjunction with Koopmans' theorem[40] to obtain ionization potentials. The molecular geometry used in the calculation for *s*-triazine was obtained directly from crystal data.[41] The geometry for tri-*s*-triazine was obtained by assuming D_{3h} symmetry and taking average bond angles and bond lengths from crystal data for structure A.[2]

Figure 3, which shows a comparison of experimental ionization potentials with theoretical ionization potentials obtained from the HAM/3 and GAUSSIAN70 calculations, indicates that the GAUSSIAN70 calculations predict ionization potentials for the π_1 orbitals of *s*-triazine and tri-*s*-triazine that are 1–3 eV lower than those observed experimentally. In this regard, HAM/3 is more

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[39] The GAUSSIAN70 program was obtained from the Quantum Chemistry Program Exchange at the University of Indiana. A STO-3G minimal basis set has been used.

[40] Koopmans, T. *Physica* (*The Hague*) **1933**, *1*, 104.

[41] Smith, J. H.; Rae, A. I. M. *J. Phys. C* **1978**, *11*, 1761.

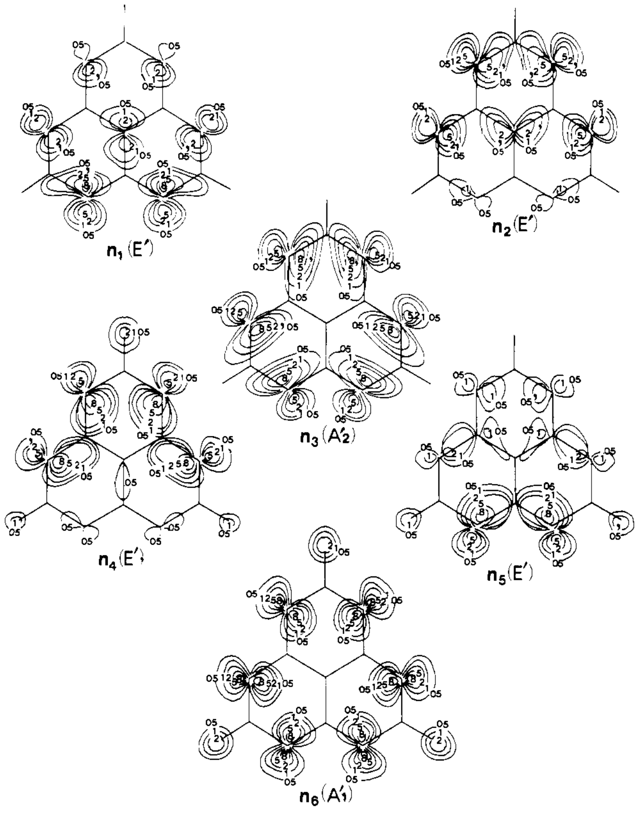

Figure 4. Electron density maps showing electron distribution and symmetries for the six highest occupied lone-pair orbitals in tri-*s*-triazine. Values of electron density, denoted on the contours, are normalized to the maximum density in each of the orbitals. The relative magnitudes for the maximum density occurring in each of the orbitals is 1.00, 0.88, 0.58, 0.67, 0.73, and 0.32, respectively, for the n_1 to n_6 orbitals.

reliable. The good agreement between the HAM/3 results and the experimental data is not surprising in view of the fact that photoelectron data from a large number of molecules, including *s*-triazine, have been used to parameterize this semiempirical calculation.

More important than the discrepancy between the absolute ionization potentials predicted by the two theoretical methods, however, is the good agreement reached with regard to the energetic ordering of valence orbitals. The patterns of energy levels predicted by both theoretical approaches and the pattern that is observed experimentally are remarkably similar. One difference between the HAM/3 and the GAUSSIAN70 results involves the relative energies of the π_3 orbital and the two degenerate highest occupied σ orbitals in *s*-triazine. Earlier photoelectron studies of *s*-triazine (**9**) indicated that the ionization potential of the π_3 orbital is 0.5 eV lower than those of the σ orbitals.[34] Another difference involves the energetic ordering of the π_2, π_3 vs. n_4, n_5 orbitals in tri-*s*-triazine. Due to the structureless nature of the photoelectron spectrum in the energy region between 11.2 eV and 12.6 eV this discrepancy has not been resolved.

In order to gain further detailed information about valence orbitals in tri-*s*-triazine, electron density maps were constructed from results of the theoretical calculations as previously described.[42] The electron distributions in individual orbitals predicted by the two calculations are essentially the same.

Figure 4 shows electron density maps and D_{3h} symmetry assignments describing the lone-pair orbital structure for tri-*s*-triazine (**1**). As in many other cyclic (aromatic) molecules containing several N atoms, the indication is that all the lone-pair orbitals of tri-*s*-triazine exhibit significant delocalization.[12,35] This delocalization is greater than that observed in a simpler lone-pair system such as that found in pyridine.[34a] The high degree of

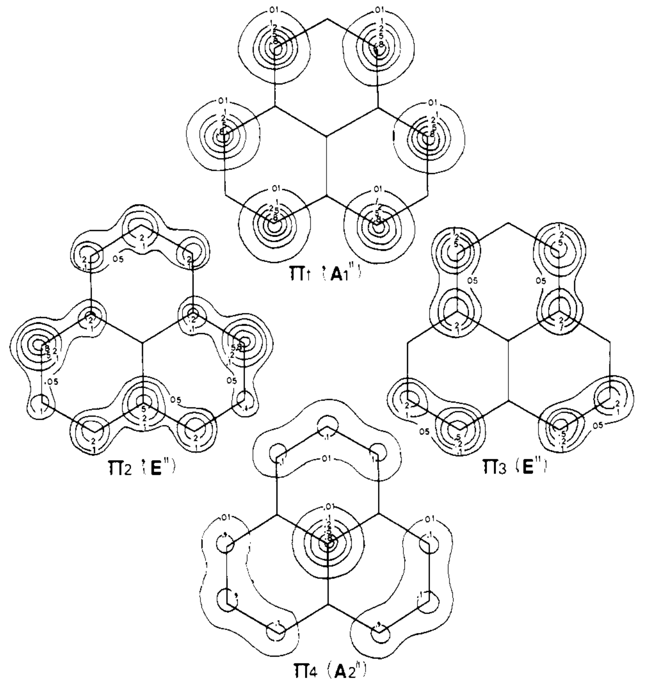

Figure 5. Electron density maps showing the electron distribution and symmetries for the four highest occupied π orbitals of tri-*s*-triazine. The maps show electron density 0.25 Å above a plane containing the molecule. Values associated with each of the contours were obtained in the same manner as those in Figure 4. The relative magnitude for the maximum in each orbital is 0.52, 0.52, 0.44, and 1.00, respectively, for the π_1 to π_4 orbitals.

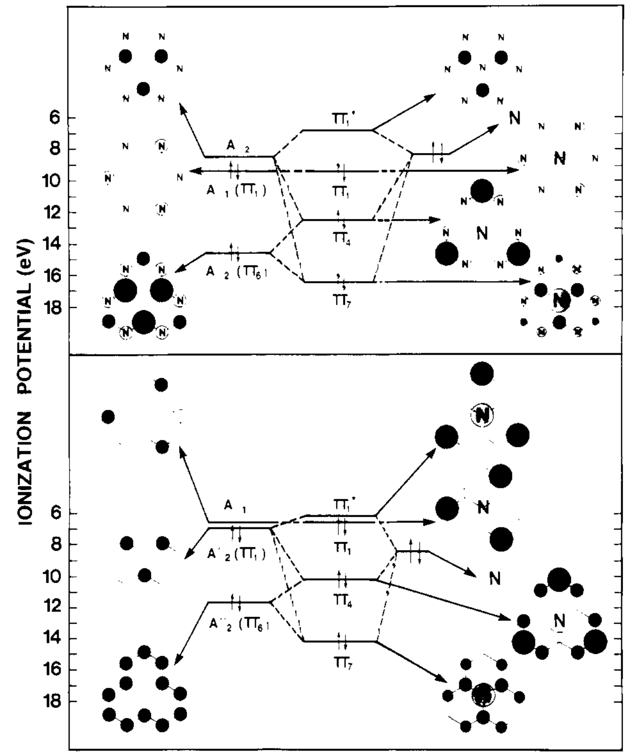

Figure 6. Construction of frontier A_1'' and A_2'' orbitals in tris-*s*-triazine (top) and cycl[3.3.3]azine (bottom) from cyclic π systems and a nitrogen p lone-pair orbital.

delocalization of the lone-pair orbitals[15] is consistent with the observation that tri-*s*-triazine (**1**), like *s*-triazine (**9**), is an extremely weak base.

Figure 5 shows electron density maps and symmetry assignments for the four highest occupied orbitals in tri-*s*-triazine. The highest occupied π_1 molecular orbital of tri-*s*-triazine is the most striking of those appearing in Figure 5. According to the molecular

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[42] Padva, A.; O'Donnell, T. J.; LeBreton, P. R. *Chem. Phys. Lett.* **1976**, *41*, 278.

Table I

compd	solvent	temp	time	result
A. Attempts To Form Charge-Transfer Complexes				
tetracyanoethylene	CH_3CN	RT	24 h	NR
		reflux	20 min	NR
7,7,8,8-tetracyanoquinodimethane	CH_3CN	RT	24 h	NR
		reflux	20 min	NR
2,4,7-trinitro-9-fluorenone	CH_3CN	RT	24 h	NR
		reflux	20 min	NR
picric acid	CH_3CN/Et_2O	RT	24 h	NR
N,N,N',N'-tetramethyl-*p*-phenylenediamine	CH_3CN	RT	24 h	NR
N,N,N',N'-tetramethyl-4,4-diaminobiphenyl	$CH_3CN/Et_2O/C_6H_6$	RT	24 h	NR
B. Attempts at Cycloadditions				
dimethyl acetylenedicarboxylate	dioxane	reflux	12 h	NR
	xylene	reflux	12 h	NR
DMAD + $AlCl_3$	xylene	reflux	20 min	dec
maleic anhydride	CH_3CN	reflux	12 h	NR
C. Miscellaneous				
methyl iodide	CH_3CN	RT	24 h	NR
m-chloroperbenzoic acid	dioxane	RT	24 h	NR
		reflux	24 h	NR
Cl_3CCO_2H	CH_3CN	RT	24 h	NR
perhydro-9b-boraphenalene	CH_3CN/C_6H_6	RT	24 h	NR
Br_2 vapor	CH_3CN	RT	3 h	complex mixture
H_2O	H_2O	RT	1 h	complex mixture
	H_2O vapor	RT	24 h	complex mixture

[a] NR = no reaction; RT = room temperature.

orbital calculations, this orbital exhibits antibonding nodes between all adjacent peripheral atoms.

Figure 6 shows a scheme for constructing the lowest unoccupied A_2'' and the highest occupied π_1 (A_1'') orbitals as well as the occupied π_4 and π_7 (A_2'') orbitals of tri-*s*-triazine from a hypothetical annulene-like molecule containing alternate N atoms (1,3,5,7,9,11-hexaaza[12][21]annulene) and a nitrogen p lone-pair orbital. The figure, based upon HAM/3 calculations, also shows an analogous construction of the A_1'' and A_2'' orbital structure of cycl[3.3.3]azine (**2**)[8,10,15,16] from [12][21]annulene and a nitrogen p lone-pair orbital. For the calculations in the second case, an idealized geometry of cycl[3.3.3]azine was used. All C–C bond distances were taken to be the same (1.39 Å) as those in benzene,[43] and the three C–N bond distances were taken to be the same as those to the central N atom in tri-*s*-triazine. The C–H bond lengths were taken as 1.10 Å.

For tri-*s*-triazine, where a comparison of HAM/3 and GAUSSIAN70 results has been carried out, both methods predict an identical mixing scheme.

The dashed lines in Figure 6 indicate basis orbitals which make major contributions to the A_1'' and A_2'' orbitals of tri-*s*-triazine (top) and cycl[3.3.3]azine (bottom). The ionization potential of the nitrogen p lone-pair orbital corresponds to that calculated for trimethylamine in a hypothetical D_{3h} geometry with N–C bond lengths taken to be the same as those to the central N atom in tri-*s*-triazine.

A frontier orbital mixing scheme for cycl[3.3.3]azine was previously reported from results of Hückel calculations.[10] Some differences occur between the earlier results and those in our Figure 6 (bottom). Most important in the earlier study, the highest occupied A_2'' (π_4) orbital was constructed from a simple linear combination of the upper A_2'' (π_1) orbital in [12][21]annulene and the nitrogen p lone-pair orbital. Figure 6 (bottom) indicates that both of the upper occupied A_2'' orbitals (π_4 and π_7) in cycl[3.3.3]azine contain significant contributions from two A_2'' (π_1 and π_6) orbitals in [12][21]annulene. The upper occupied A_2'' orbitals of tri-*s*-triazine (Figure 6, top) are similarly constructed.

Finally, the low susceptibility of tri-*s*-triazine (**1**) to electrophilic attack compared to cycl[3.3.3]azine (**2**) is demonstrated by its inertness in the presence of methyl iodide, *m*-chloroperbenzoic acid, trichloroacetic acid, perhydro-9b-boraphenalene, and oxidizing metal ions. This is understandable in view of the significant difference in ionization potentials (>2 eV) predicted by the HAM/3 calculations for tri-*s*-triazine vs. cycl[3.3.3]azine.

Experimental Section

General. Proton nuclear magnetic resonance spectra were recorded on a Varian EM-390 spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX-60 or a WCV-KLFT-100 Fourier transform instrument, operating at 15.03 and 25.2 MHz, respectively, and are reported in parts per million from tetramethylsilane. ^{15}N NMR spectra were obtained on a 250-MHz Fourier transform instrument operating at 25.37 MHz (see Acknowledgment). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration. 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 spectrophotometer. Fluorescence excitation and emission spectra were measured on a Spex Fluorolog spectrofluorometer. Fluorescence lifetimes were determined at 25 °C by using the cross-correlation spectrofluorometer described by Spencer and Weber.[44] The exciting light was modulated at 14.2 MHz and was filtered through a monochromator and a CS-7-54 Corning filter. The emission was observed through a CS-0-52 Corning filter. Microanalyses were performed by Mr. Josef Nemeth and his staff. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure and stored over 4-Å sieves. Dimethylformamide and acetonitrile were distilled from calcium hydride immediately before use. Xylene used in the crystallization of tri-*s*-triazine (**1**) was distilled from sodium benzophenone ketyl immediately before use.

***N,N'*-Dicyanoformamidine (7).** To a solution of 3.2 g (50 mmol) of sodiocyanamide in 300 mL of absolute methanol was added 4 mL (50 mmol) of methyl *N*-cyanomethanimidate (**8**), and the reaction mixture was stirred at 20 °C overnight. Formic acid (98%, 1.8 mL) was added to the reaction mixture, and the suspension was stirred for $^1/_2$ h. The solvent was removed on a rotary evaporator under high vacuum (1 mmHg) with a bath temperature <38 °C. The colorless solid was triturated with 50 mL of anhydrous diethyl ether, filtered, and air-dried to give 3.9 g (85%) of *N,N'*-dicyanoformamidine (**7**): mp 283–285 °C dec; mass spectrum, CH-5 *m/e* 94 (M^+); ^1H NMR ($(CD_3)_2SO$) δ 8.20 (br, 1, NH), 8.55 (s, 1, CH). An analytical sample of the sodium salt of this reagent was obtained prior to acidification by collecting a small portion from the reaction mixture by filtration and washing with methanol. Anal. Calcd. for C_3HN_4Na: C, 31.04; H, 0.87; N, 48.27. Found: C, 30.93; H, 0.67; N, 48.33.

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(44) Spencer, R. D.; Weber, G. *Ann. N.Y. Acad. Sci.* **1969**, *158*, 361.

2,4-Bis(*N′*-cyano-*N*-formamidino)-1,3,5-triazine (6). To a solution of 5.2 g (47 mmol) of 2,4-diamino-1,3,5-triazine in 208 mL of anhydrous dimethyl sulfoxide was added a solution made from 8.3 g (0.36 mol) of sodium in 104 mL of anhydrous methanol. The resulting solution was stirred at 25 °C for 30 min under N_2. Then 40 mL (0.50 mol) of methyl *N*-cyanomethanimidate (**8**)[22,23] was added. After the solution was stirred for 1 h, 5% aqueous HCl was added to bring the pH to 4.0–4.5. The colorless precipitate was filtered through a medium porous sintered glass funnel, washed with methanol, and air-dried to afford compound **6** in yields ranging from 4.6 to 6.1 g (46–62%). The $C_7H_5N_9$ product was dried overnight at 25 °C over P_2O_5 under high vacuum: mp >300 °C; mass spectrum (10 eV), *m/e* 173 ($M^+ - NH_2CN$) 100%; ^1H NMR ($(CD_3)_2SO$) δ 8.8 (s, 1, 6-H), 9.7 (s, 2, side-chain CH), 12.4 (br, 2, NH, exchangeable with D_2O); IR (KBr) 2220 cm^{-1}.

Tri-*s*-triazine (Cyamelurine, 1,3,4,6,7,9,9b-Heptaazaphenalene, 1,3,4,6,7,9-Hexaazacycl[3.3.3]azine (1)). 2,4-Bis(*N′*-cyano-*N*-formamidino)-1,3,5-triazine (6.0 g, 23 mmol) (**6**) was spread over the bottom of a sublimation apparatus, and a vacuum was applied at 10^{-3}–10^{-2} mmHg. The sublimation apparatus was immersed in a preheated (400 °C) Wood's metal or lead bath for ~2 min and was then allowed to cool to room temperature. The sublimation apparatus was opened, and extraction of the sublimate and residual material with anhydrous acetonitrile, filtration, and evaporation in vacuo yielded tri-*s*-triazine (2.9 g (61%)) (**1**): mp >300 °C dec; ^1H NMR ($(CD_3)_2SO$) δ 8.3 (s, CH); ^{13}C NMR δ 171.6 ($^1J_{CH}$ = 207.6 Hz, CH); 159.7 (junctional C); ^{15}N NMR ($(CD_3)_2SO$, DMF (2:1); downfield, DMF as internal standard) 133.8 ($^2J_{NCH}$ = 14.0 Hz), 81.8 ppm (central N); mass spectrum (10 eV), *m/e* 173 (M^+, 100%), 146 (M^+–HCN, 2), 119 (M^+–2HCN, 12), 94 ($C_3H_2N_4^+$, 13); color, yellow; UV (CH_3CN) λ_{max} 443 nm (ϵ 270), 416 (200), 391 sh (95), 305 (22 700), 298 sh (18 900), 293 (20 600), 279 sh (13 580), 219 (9660); fluorescence (CH_3CN) $\lambda^{em}{}_{max}$ 307 or 445, $\lambda^{em}{}_{max}$ 517 nm, ϕ 0.014 (relative to fluorescein, τ 9.5 ns (by phase), 15.4 ns (by modulation), corresponding to at least two emitting forms of the molecule in CH_3CN.[43] Flash chromatography on Woelm silica gel with EtOAc/$CHCl_3$ (1:1) as the eluting solvent furnished analytically pure compound.

Anal. Calcd for $C_6H_3N_7$: C, 41.62; H, 1.75; N, 56.63. Found: C, 41.74; H, 1.58; N, 56.66.

Crystals of tri-*s*-triazine (**1**) for single-crystal X-ray examination were grown by slow evaporation of a solution of **1** in anhydrous acetonitrile in an atmosphere of dry xylene. The crystallographic data, collected on an Enraf-Nonius CAD4 computer-controlled κ-axis diffractometer using ω–θ scan techniques and Cu Kα radiation (λ 1.54184 Å), are reported in ref 2 and the supplementary material.

Complex Formation with Tri-*s*-triazine (1). a. With Silver Perchlorate. To a solution of 100 mg (0.6 mmol) of tri-*s*-triazine in 25 mL of anhydrous acetonitrile was added a solution of anhydrous silver perchlorate (900 mg) in 25 mL of acetonitrile. A yellow solid formed immediately. The mixture was stirred for 15 min, filtered, washed with anhydrous diethyl ether, and dried to give 136 mg of complex. mp >300 °C.

Anal. Calcd for [$3C_6H_3N_7 \cdot 2AgClO_4$]: C, 23.14; H, 0.97; N, 31.49; Ag, 23.10. Found: C, 23.51; H, 0.78; N, 31.70; Ag, 22.75.

b. With Silver Tetrafluoroborate. To a solution of 50 mg (0.3 mmol) of tri-*s*-triazine in 25 mL of anhydrous acetonitrile was added a solution of anhydrous silver tetrafluoroborate (426 mg) in 15 mL of anhydrous acetonitrile. A yellow solid formed immediately. The mixture was stirred for 1 h, filtered, washed with anhydrous diethyl ether, and dried to give 28 mg of complex; mp >300 °C.

Anal. Calcd for [$3C_6H_3N_7 \cdot 2AgBF_4$]: C, 23.79; H, 1.00; N, 32.88; Ag, 23.71; F, 16.73. Found: C, 24.25; H, 0.84; N, 32.88; Ag, 23.80; F, 16.73.

Reactions Attempted with Tri-*s*-triazine (1). The lists in Table I summarize the accumulated evidence for the chemical stability of tri-*s*-triazine (**1**) (except with water). "NR" = no reaction as defined by the absence of a precipitate, visible color change, or new absorption bands in the ultraviolet spectrum.

Gas Phase UV Photoelectron Spectra were measured with a Perkin-Elmer PS-18 spectrometer equipped with a heated probe and a He I lamp. Ionization potentials were calibrated by using the $^2P_{3/2}$ and $^2P_{1/2}$ bands of Xe and Ar.

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Registry No. 1, 204-34-2; **6**, 82679-23-0; **7**, 89302-48-7; **8**, 51688-22-3; 2,4-diamino-1,3,5-triazine, 504-08-5.