Conclusions

We have shown that, at least at the levels of approximation employed herein, there are three pentacoordinated compounds of nitrogen, i.e., NF_3H_2, NF_4H, and NF_5, that are structurally stable. Examination of several sets of computed properties, particularly their molecular structures, vibrational frequencies, and multicenter energies, shows that in addition they are truly pentacoordinated species with appreciable and distinct bonding to the central atom. This study has not rigorously ruled out the existence of other NF_nH_{5-n} compounds, but their structural stabilities now appear unlikely. Also it should be emphasized that the role played by electron correlation in determining the shapes of the energy surfaces in such compounds is presently not well understood. Although the methods we employed in this study are quite adequate based on our experience to date, energies and structures of fluorine compounds are notoriously difficult to compute accurately, and the numerical values reported here may exhibit lower accuracy than would be expected from similar computations on other nitrogen-containing molecules. This is reflected to some extent by the computed structures in Table II.

Our computed properties of NF_3H_2, NF_4H, and NF_5 are to our knowledge the first evidence of stable pentacoordinated nitrogen compounds. There is little evidence for neutral highly coordinated compounds (with distinct and separate linkages to the central atom) of any of the other first-row elements except for a small number of experimental studies involving bi- and tridentate ligands.[40]

Further it now appears that the ability to form pentacoordinated compounds such as NF_5 is unique to nitrogen among the first-row elements. For example, calculation of the structural stablity of the isoelectronic species OF_5^+ employing the same techniques as described above showed it to be stable at the RHF/basis I level, but unstable with MP2/basis I. (A similar situation was found for OF_4, which is stable with RHF/basis I but unstable with MP2/basis I.) Conversely we found the isoelectronic carbon compound, CF_5^-, to be *unstable* with RHF/basis I but *stable* with MP2/basis I. Hence, although the stabilities of these two species is still uncertain, it now appears unlikely that they will be found to be stable at higher levels of approximation. The isoelectronic boron and fluorine compounds, BF_5^{2-} and F_6^{2+}, were found to be structurally unstable at both of the levels of approximation discussed above.

Finally, our computed results suggest several other types of compounds that may be structurally stable. The considerable affinity of PF_5 for fluoride ions to form PF_6^- suggests that there should be a similar tendency of NF_5 to form NF_6^-, and we have found that, in fact, NF_6^- is structurally quite stable. Thus this line of investigation leads to the conclusion that the existence of pentacoordinated and hexacoordinated compounds of first-row elements is possible, and these should be amenable to synthesis providing that the thermodynamic instabilities which usually characterize them can be overcome.

Acknowledgment. The authors are indebted to Professor J. C. Martin for several helpful discussions. This work was supported by the Air Force Office of Scientific Research, AFSC, under Grant AFOSR-86-0146. The computations were performed on an SCS-40 computer acquired with the assistance of SCS Corp., Vanderbilt University, and NSF Grant CHE-8808018.

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[40] (a) Forbus, T. R.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5057. (b) Lee, D. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 5745.

Azines. A Theoretical Study of π-Electron Delocalization

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Abstract: π-Electron delocalization in benzene and the azines has been studied theoretically in several ways: via an analysis of the first $\pi \rightarrow \pi^*$ transitions, via calculation of hydrogenation energies, and via an analysis of the wave functions. The electronic transitions suggest that the delocalization energies are essentially the same for all the compounds. The calculated energies for the addition of 1 equiv of hydrogen suggest that the "resonance energies" of benzene, pyridine, pyrazine, and pyrimidine are essentially the same. The values for the other azines appear to be smaller, but this may in part arise from changes in the σ-systems. The distribution of π-electron density around the rings does not appear to be strongly perturbed by the replacement of CH by N.

1. Introduction

The azines form the basic structures of some of the most important compounds in nature. As such, they deserve especially careful examination. One of the most important characteristics of these compounds is π-electron delocalization,[1] which leads to reduced reactivity,[2] marked changes in keto/enol equilibria,[3] and substitution rather than addition.[4] A study of the monocyclic azines should provide useful information on the origin of this interaction. This would appear particularly appropriate at this time in view of the recent interest in the subject. Although benzene and the azines are generally considered to have significant resonance stabilization,[5] we may note the calculations of Berry in 1965,[6] which suggested that it is the σ-bonds that cause benzene to be a regular hexagon and that the π-electrons would prefer a "Kekule"-like structure. The suggestion has recently been further amplified by Shaik and Hiberty, et al.,[7] and Epiotis has called into question the entire notion of π-electron delocalization.[8]

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[1] For an excellent general summary of the aromaticity problem, see: Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.

[2] Barnes, R. A. In *Pyridine and its Derivatives*; Klingsberg, E., Ed.; Interscience: New York, 1960; pp 12ff.

[3] Meislich, H. In *Pyridine and its Derivatives*; Klingsberg, E., Ed.; Interscience: New York, 1962; pp 614ff.

[4] Illuminati, G. *Adv. Heterocycl. Chem.* **1964**, *3*, 285. Abramovitch, R. A.; Saha, J. G. *Ibid.* **1966**, *6*, 229.

[5] Byström, K. *J. Chem. Thermodyn.* **1982**, *14*, 865. Byström has calculated resonance energies for the azines using a new set of bond energies and concluded that they had comparable values. The bond energies are, however, not well established.

[6] Berry, R. S. *J. Chem. Phys.* **1961**, *35*, 29, 2253.

[7] Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J. M. *Nouv. J. Chim.* **1985**, *9*, 385. Hiberty, P. C.; Shaik, S. S.; Lefour, J. M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4659. Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Phys. Chem.* **1988**, *92*, 5086.

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We have begun a combined theoretical and experimental study of a variety of properties of the azines. We have reported a study of the vibrational spectra of pyridine[9] and of *s*-tetrazine,[10] and the spectra of the other monocyclic azines are being investigated. We now report a theoretical study of electron delocalization and of thermochemical stabilization of these compounds (**1**–**8**). Subsequently, we present experimental thermochemical data dealing with the same problem.


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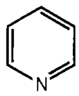
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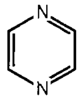
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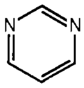

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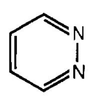

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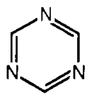

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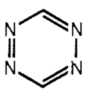

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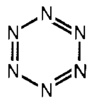

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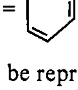
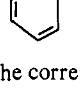
2. Delocalization Energies

The subject in question has three aspects: spectroscopic, thermodynamic, and kinetic. A quantity of particular interest is the vertical delocalization energy, which in the case of benzene is the difference in energy between a "Kekule" structure and benzene with both having the same geometry. This cannot readily be obtained from thermochemical measurement because of the uncertainty in estimating the "compression energy" involved in distorting the bond lengths in a normal Kekule structure to those found in the actual molecule and because of the uncertainty in the values of the bond energy terms that should be used.

The delocalization energy may be obtained for those compounds having two equivalent resonance structures by a method developed by Simpson.[9,10] Consider the Kekule forms of benzene: Each

$\psi_I^2 =$  $\psi_{II}^2 =$ 

structure may be represented by the square of the corresponding wave function, and the wave functions for the two forms may properly be considered as linearly independent and therefore orthogonal. The formation of benzene from these structures involves changing the bond length and may be considered to be a perturbation. The operator will then be $H = H° + V$ where $H°$ is the operator appropriate to ψ_I and ψ_{II} and V is the perturbation. Using the definitions

$$H_{11} = \int \psi_I H° \psi_I \, d\tau = H_{22} = \int \psi_{II} H° \psi_{II} \, d\tau$$

$$V_{11} = \int \psi_I V \psi_I \, d\tau = V_{22} = \int \psi_{II} V \psi_{II} \, d\tau$$

$$V_{12} = \int \psi_I V \psi_{II} \, d\tau$$

where H_{11} is the energy of one of the Kekule structures, the secular determinant becomes

$$\begin{vmatrix} H_{11} + V_{11} & V_{12} \\ V_{12} & H_{22} + V_{22} \end{vmatrix} = 0$$

The solution is

$$E = H_{11} + V_{11} \pm V_{12}$$

and is shown diagrammatically in Figure 1.

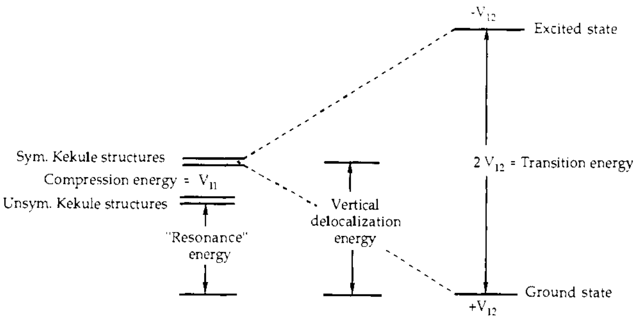


Figure 1. Relationship between the transition energy and the delocalization energy for benzene and some azines.

Table I. Azine $\pi \rightarrow \pi^*$ Transitions and Estimated Delocalization Energies

compd	transition, nm	DE	compd	transition, nm	DE
benzene	262.6[a]	55	pyridazine	254.7[d]	
pyridine	260[b,c]	55	s-triazine	~228[e]	63
pyrazine	263.9[c]	54	s-tetrazine	~262[f]	55
pyrimidine	247.0[c]	58			

[a] Benzene.[14] [b] The n–π^* transition for pyridine is found on the high-wavelength side of the π–π^* transition. Therefore, it is difficult to locate the 0–0 transition, and the value is approximate. [c] Lewis, T. P. Ph.D. Thesis, Yale University, 1968. [d] Two identical Kekule structures cannot be written for this compound, and therefore the delocalization energy was not calculated. [e] The location of the band is somewhat doubtful. The 228-nm band is commonly considered to be the first π–π^* transition. However, it may easily be part of the broad absorption from 250 to 295 nm. [f] The absorption band for s-tetrazine shows no structure. The location of the 0–0 transition was estimated as the point at which the intensity reached 25% of the maximum value.

The lower energy state formed via the interaction has the wave function $\Psi = 2^{-1/2}(\psi_I + \psi_{II})$ and corresponds to the ground state of the molecule with bond lengths shorter than the average of normal C—C and C═C lengths.[13] The upper state has the wave function $\Psi = 2^{-1/2}(\psi_I - \psi_{II})$ and corresponds to the first excited state of benzene having bond lengths longer than average. Since the transition energy for benzene is 109 kcal/mol,[14] $V_{12} = 55$ kcal/mol. The difference in energy between a normal Kekule structure and one having equal bond lengths (but no interaction between the double bonds) is the compression energy, which has been estimated to be about 20 kcal/mol.[15,16] The Kekule structure is then about 35 kcal/mol above the ground state, and this should correspond to the conventional thermochemically determined resonance energy. The latter is 36 kcal/mol, in good agreement with this estimate. Correspondingly, the delocalization energy is equated with V_{12} and is 55 kcal/mol. Thus, this simple model

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(8) Epiotis, N. *Nouv. J. Chim.* **1984**, *8*, 11.

(9) Wiberg, K. B., Walters, V. A.; Wong, K.; Colson, S. D. *J. Phys. Chem.* **1984**, *88*, 6067.

(10) Spencer, G. H., Jr.; Cross, P. C.; Wiberg, K. B. *J. Chem. Phys.* **1961**, *35*, 1939. A more recent study has been presented by: Franks, L. A.; Merer, A. J.; Innes, K. K. *J. Mol. Spectrosc.* **1968**, *26*, 458.

(11) Simpson, W. T. *J. Am. Chem. Soc.* **1953**, *75*, 597. It is important to note that this model is appropriate only for molecules whose ground state is reasonably well described by a single-determinant wave function (i.e., having a large π-HOMO–LUMO gap) and is not appropriate for molecules for which this is not the case (i.e., cyclobutadiene).

(12) The importance of two equivalent canonical structures cannot be overemphasized. Consider the polyenes. Here, the second canonical structure (diradical or zwitterionic) would have a much higher energy, resulting in little mixing. As a result, they have alternating single and double bonds, and at least a part of the apparent conjugative stabilization results from the stronger sp^2–sp^2 C–C bonding as compared to sp^3–sp^3 in alkanes: Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166; *Ibid.* **1960**, *11*, 96). This may be contrasted with the polymethinium ions (Me_2N^+═CH(CH═CH)$_n$NMe_2), which have two equivalent canonical structures and have equal bond lengths and whose electronic transitions may be modeled using a free electron approximation. Cf.: Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964; p 9.

(13) The C-C bond length in benzene is 1.397 Å, which is shorter than the average of C═C (1.33 Å) and sp^2–sp^2 C–C (1.49 Å) lengths: Stoicheff, B. P. *Can. J. Phys.* **1954**, *32*, 339. The first excited state has a C–C length of 1.431 Å, which is longer than the average: Parmenter, C. S.; Tang, K.; Ware, W. R. *Chem. Phys.* **1976**, *17*, 359.

(14) The first benzene $\pi \rightarrow \pi^*$ transition in benzene is at 262.6 nm, which corresponds to 109 kcal/mol: Sponer, H.; Nordheim, C.; Sklar, A. L.; Teller, E. *J. Chem. Phys.* **1939**, *7*, 207.

(15) Cf.: Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1965; p 57.

(16) It should be recognized that the force constant for stretching a C═C is greater than that for C—C, and so a large part of the compression energy is associated with the stretching of the C═C bonds of the Kekule structure. This appears to be a central part of the arguments of Shaik and Hiberty, et al.[7]

Table II. Calculated Energies of Azines, 6-31G* (Hartrees)

	6-31G*			6-31G**[a]		
compd	RHF	MP2	MP3	RHF	MP2	MP3
benzene	−230.703 14	−231.456 48	−231.485 20	−230.713 86	−231.504 58	−231.536 30
pyridine	−246.695 82	−247.480 36	−247.502 44	−246.704 61	−247.520 03	−247.544 65
pyrazine	−262.683 00	−263.500 21	−263.515 70	−262.689 96	−263.531 63	−263.549 19
pyrimidine	−262.693 49	−263.506 48	−263.522 48	−262.700 34	−263.537 80	−263.555 87
pyridazine	−262.650 03	−263.469 88	−263.485 46	−262.657 07	−263.501 36	−263.518 95
s-triazine	−278.695 84	−279.535 02	−279.545 49	−278.700 75	−279.558 06	−279.570 13
s-tetrazine	−294.592 93	−295.477 48	−295.480 82	−294.596 37	−295.492 81	−295.497 15
hexazine	−326.448 96	−327.406 32	−327.396 25	−326.448 96	−327.406 32	−327.396 25
HC≡CH	−76.817 83	−77.064 63	−77.075 05	−76.821 84	−77.079 47	−77.090 68
HC≡N	−92.875 20	−93.154 51	−93.156 94	−92.877 14	−93.161 70	−93.164 48
N_2	−108.943 9	−109.248 2	−109.245 3	−108.943 9	−109.248 2	−109.245 34
H_2	−1.126 83	−1.144 10	−1.149 25	−1.131 33	−1.157 66	−1.163 16

[a] Obtained at the 6-31G* geometry.

allows one to easily relate these three quantities.

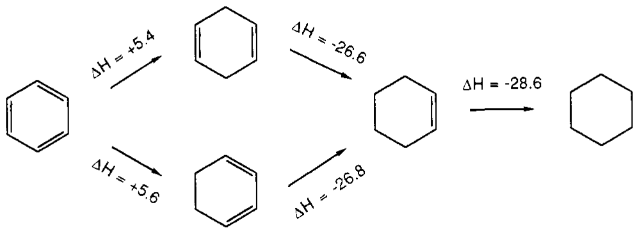
This treatment may be applied to each of the azines having two equivalent resonance structures, and the delocalization energy (DE) will be given by half the transition energy for the first $\pi \rightarrow \pi^*$ transition.[17] The data are shown in Table I. It can be seen that, by this simple criterion, each of the azines has about the same delocalization energy as benzene.

The transition energies are properly examined by considering the configurations that might be formed by electronic excitation and then allowing these states to mix, thereby giving the electronically excited states. However, in a qualitative sense, they may be thought of as being related to the energy difference between the highest occupied π MO and the lowest unoccupied π MO. The observation of essentially constant transition energies then implies relatively constant π HOMO–LUMO energy differences. As will be shown in the following section, this is the case.

3. "Resonance" Energies

We now examine the results of applying other criteria for delocalization to these compounds. Here it is useful to first turn to the conventional "resonance energy", which is the difference between the *observed* energy of a molecule and that of a suitable nondelocalized model. The question of which model should be chosen has been the subject of much controversy,[1,2,18] but to begin with, we shall choose the simplest model. In the case of benzene, this is the difference between the enthalpy of hydrogenation of benzene and 3 times the enthalpy of hydrogenation of cyclohexene,[19] leading to the commonly quoted 36 kcal/mol.

Further information may be gained by examining each of the steps in the reduction of benzene to cyclohexane, and the enthalpy changes are[19]



The first step is endothermic, indicating a loss of π-electron stabilization. A comparison of the enthalpies of reduction for the first and last steps leads to 34 kcal/mol as the minimum stabilization energy for benzene, for it neglects any possible stabilization in the dienes.

These considerations provide the best evidence for special stabilization of benzene. This stabilization could involve either or both of the π- or σ-systems. It is unlikely to involve the latter since 1,4-cyclohexadiene is planar but gives a normal enthalpy of hydrogenation. Thus, despite the questions which have been raised, π-electron delocalization remains the best explanation for the "resonance" stabilization of benzene.

Similar data are not available for the azines, and the reactivities of some of the intermediates are such that it is unlikely that these data could be obtained experimentally.[20] This is a case in which theoretical calculations may prove valuable. It will first be necessary to demonstrate that the structures and relative energies of the azines may be correctly calculated. Then, it will be necessary to demonstrate that the known enthalpies of hydrogenation may be correctly reproduced.

Ab initio calculations for benzene and the azines have been reported.[21,22] However, with few exceptions,[22] they have not included polarization functions at both carbon and nitrogen. It is known that these functions are needed in calculations of structures of compounds containing heteroatoms.[23] Therefore, all of the geometry optimizations were carried out using the 6-31G* basis set,[24] which includes a set of d-type functions at the carbons and nitrogens. We have shown that, with most hydrocarbons, we can convert the 6-31G* total energies to enthalpies of formation with an average error of only 1 kcal/mol using a set of group equivalents that we have derived.[25] In the case of benzene, however, the estimated ΔH_f was considerably in error, showing that the electron correlation energy per CH group was significantly different from that for ordinary alkenes. For this reason, we have corrected the energies for the effect of electron correlation using the Møller–Plesset perturbation method[26] through the third order (MP3). The energies for most of the known monocyclic azines are given in Table II, and their structures are compared with the experimental data[27] in Table III. In

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(17) This treatment is exact for monocyclic planar systems with a 3-fold or greater rotational axis and a large HOMO–LUMO gap. However, it should also be a reasonable approximation for the monocyclic azines.

(18) Dewar, M. J. S.; deLlano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. Hess, B. A., Jr.; Schaad, L. J. *Ibid.* **1971**, *93*, 305. George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 1357.

(19) Kistiakowsky, G. B.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1935**, *57*, 876. *Ibid.* **1936**, *58*, 146, 237.

(20) As an example, 2,3,4,5-tetrahydropyridine can only be isolated as its trimer: Nomura, Y.; Bando, T.; Takeuchi, Y.; Tomoda, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1271.

(21) Pang, F.; Pulay, P.; Boggs, J. E. *J. Mol. Struct.* **1982**, *88*, 79. Price, S. L.; Stone, A. J. *Chem. Phys. Lett.* **1983**, *98*, 419. Fos, E.; Vilarrasa, J.; Fernandez, J. *J. Org. Chem.* **1985**, *50*, 4894. Mo, O.; De Paz, J. L. G.; Yanez, M. *THEOCHEM* **1987**, *35*, 135.

(22) de Brouckere, G.; Berthier, G. *Mol. Phys.* **1982**, *47*, 209. Radom, L.; Nobes, R. H.; Underwood, D. J. *Pure Appl. Chem.* **1986**, *58*, 75.

(23) Boggs, J. E.; Niu, Z. *J. Comput. Chem.* **1985**, *6*, 46.

(24) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

(25) Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285.

(26) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(27) Structural data. (a) Benzene: Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243. (b) Pyridine: Mata, F.; Quintana, M. J.; Sorensen, G. O. *J. Mol. Struct.* **1977**, *42*, 121. Pyckhout, W.; Horemans, N.; van Alsenoy, C.; Geise, H. J.; Rankin, D. W. H. *J. Mol. Struct.* **1987**, *156*, 315. (c) Pyrazine: Bormans, B. M. J.; DeWith, G.; Mijlloff, F. C. *J. Mol. Struct.* **1977**, *42*, 121. (d) Pyrimidine: Farberg, S.; Grogaard, J.; Smedsrud, B. *Acta Chem. Scand.* **1979**, *B33*, 715. Fernholt, L.; Romming, C. *Ibid.* **1978**, *A32*, 271. (e) Pyridazine: Almenningen, A.; Bjoernsen, G.; Gutmund, A. T.; Seip, R. *Acta Chem. Scand.* **1977**, *A31*, 63. (f) *s*-Triazine: Pyckhout, W.; Callaerts, I.; Van Anselnoy, C.; Rae, A. I. M.; Pawley, G. S. *J. Mol. Struct.* **1986**, *147*, 321. (g) *s*-Tetrazine: Jobs, V. A.; Innes, K. K. *J. Mol. Spectrosc.* **1978**, *71*, 299. Bertinotti, F.; Giacomello, G.; Liquori, A. *Acta Crystallogr.* **1956**, *9*, 510.

Table III. Calculated Structures of Azines, 6-31G*[a]

compd	param	calc	obs[27]
benzene	r(CC)	1.386	1.396 (1)
pyridine	r(CN)	1.321	1.338 (2), 1.341 (1)
	r(C2C3)	1.385	1.394 (2), 1.396 (6)
	r(C3C4)	1.384	1.392 (2), 1.395 (6)
	∠CNC	117.7	116.9 (1), 116.2 (1)
	∠NCC	123.6	123.8 (1), 124.6 (3)
	$\angle C_2C_3C_4$	118.2	118.5 (1)
	$\angle C_3C_4C_5$	118.6	118.4 (1)
pyrazine	r(CN)	1.319	1.335 (2)
	r(CC)	1.386	1.387 (2)
	∠CNC	116.6	116.3 (1)
	∠NCC	121.7	121.9 (1)
pyrimidine	r(C2N1)	1.319	1.340 (2)
	r(N3C4)	1.321	1.340 (2)
	r(CC)	1.382	1.392 (2)
	∠CNC	116.2	115.5 (2)
	∠NCN	126.9	127.6 (3)
	∠NCC	122.3	122.3
	∠CCC	116.0	116.8
pyridazine	r(CN)	1.310	1.341 (2)
	r(NN)	1.310	1.330 (1)
	r(C2C3)	1.394	1.393 (2)
	r(C3C4)	1.367	1.375 (1)
	∠NCC	123.3	123.7 (1)
	∠CNN	120.0	119.3 (1)
	∠CCC	116.7	117.1 (1)
s-triazine	r(CN)	1.318	1.338 (1)
	∠CNC	114.4	113.9 (1)
	∠NCC	125.6	126.1
s-tetrazine	r(CN)	1.318	1.341 (6)
	r(NN)	1.291	1.326 (16)
	∠NCN	125.1	126.4 (7)
	∠CNN	117.4	

[a] Bond lengths are given in angstroms, and bond angles, in degrees.

addition, the energy of the hypothetical hexazine also was obtained.[28]

In studying the hydrogenation enthalpies (see below), it was found that a more flexible basis set for the hydrogen might be needed. Therefore, we also have obtained the 6-31G** energies using the 6-31G* geometries. These data are given in Table II.

In order to see if the relative energies are correctly reproduced, we have derived group equivalents for CH and N groups, which give a best fit to the equation

$$\Delta H_f = 627.5(E_T - nE_{CH} - mE_N)$$

for the compounds with known heats of formation.[29] Here, 627.5 is the conversion factor from atomic units to kcal/mol, E_T is the calculated total energy in hartrees, n is the number of CH groups, and m is the number of nitrogens. A calculation using all the experimental ΔH_f fit the data satisfactorily except for pyrimidine. The analysis was repeated deleting pyrimidine, giving the results shown in Table IV. It can be seen that with the above exception the available enthalpies of formation are reproduced to within ±1 kcal/mol. The ΔH_f of s-tetrazine is not known and was predicted using the group equivalents. The ΔH_f of hexazine also was estimated.

The deviation found for pyrimidine led to the following analysis. The calculated (MP2 or MP3/6-31G* or 6-31G**) energy difference between pyrazine and pyridazine was 19.0 kcal/mol, which is in very good agreement with the experimental difference in ΔH_f corrected to 0 K and for zero-point energy differences (19.3 kcal/mol). The calculated energy difference between pyrazine and pyrimidine (3.9–4.2 kcal/mol) is, on the other hand, quite different than the experimental observation of essentially no difference in ΔH_f. The excellent agreement in the former comparison leads us to conclude that there must be a serious error in the observed ΔH_f for pyrimidine and that the correct value is about 43 ± 1 kcal/mol.

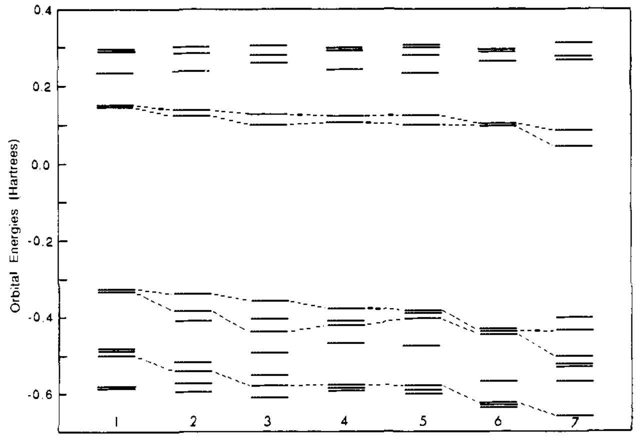

Figure 2. Orbital energies for benzene and the azines. The compounds are numbered as in the text.

Benzene may be obtained via the trimerization of acetylene, and the azines may in principle be obtained via the reaction of three two-heavy-atom molecules. One of the effects of replacing CH groups in benzene by N may be seen in the reverse of these cycloaddition reactions, and they are summarized in Table V. Whereas the dissociation of benzene to acetylene is very endothermic, each nitrogen that is introduced markedly decreases the endothermicity, so that, with s-tetrazine, the reaction becomes exothermic.[30] This is the result of the greater strength of N≡N and C≡N bonds as compared to C≡C.[31]

The dissociation energies cannot be directly compared with the experimental enthalpies because they must be corrected for zero-point energy changes, as well as the change in enthalpy on going from 0 to 298 K. These data require a knowledge of the vibrational frequencies. The experimental vibrational frequencies were used when a satisfactory assignment was available.[32] In the other cases, the zero-point energies and enthalpy changes were estimated using a group equivalent approach.[33] The equations that fit the compounds for which experimental data were available are

$$\mathrm{ZPE} = 17.16n(\mathrm{CH_2}) + 10.16n(\mathrm{CH}) + 10.93n(\mathrm{NH}) + 2.97n(\mathrm{N})$$

$$\text{rms error} = 0.5\ \text{kcal/mol}$$

$$H_T - H_0^\circ = 0.72n(\mathrm{CH_2}) + 0.58n(\mathrm{CH}) + 0.54n(\mathrm{NH}) + 0.51n(\mathrm{N})$$

$$\text{rms error} = 0.08\ \text{kcal/mol}$$

The zero-point energies and values of $\Delta H^\circ_{298} - \Delta H^\circ_0$ are summarized in Table VI, and the corrected energies are compared

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(28) For recent calculations on hexazine, see: Ha, T.-K.; Cimiraglia, R.; Nguyen, M. T. *Chem. Phys. Lett.* **1981**, *83*, 317.

(29) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(30) This leads to thermal instability for tetrazine, cf.: Wiley, P. F. In *The Chemistry of Heterocyclic Compounds*; Wiley: New York, 1978; Vol. 23, p 1099.

(31) Cottrell, T. L. *The Strengths of Chemical Bonds*, Academic Press: New York, 1958.

(32) Vibrational frequencies. Pyridine: Reference 9. Pyrazine: Zarembowitch, J.; Bokobza-Sebaugh, L. *Spectrochim. Acta Part A* **1975**, *A32*, 605. Pyrimidine: Mibini-Nejad, F.; Stidham, H. D. *Ibid.* **1975**, *31A*, 1433. Pyridazine: Stidham, H. D.; Tucci, J. V. *Ibid.* **1967**, *23A*, 2233. s-Triazine: Daunt, S. J.; Shurwell, H. F. *J. Mol. Spectrosc.* **1976**, *62*, 373. s-Tetrazine: Franks, L. A.; Merer, A. J.; Innes, K. K. *Ibid.* **1968**, *26*, 458; Brumbaugh, D. V.; Innes, K. K. *Chem. Phys.* **1981**, *59*, 413. Piperidine: Scott, J. *J. Chem. Thermodyn.* **1971**, *3*, 649. Cyclohexene: Neto, N.; DiLauro, C.; Castellucci, E.; Califano, S. *Spectrochim. Acta, Part A* **1967**, *23A*, 1763. Cyclohexane: Wiberg, K. B.; Walters, V. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 4860. 1,4-Cyclohexadiene: Stidham, H. D. *Spectrochim. Acta, Part A* **1965**, *21A*, 23.

(33) It is known that the enthalpy changes (Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070) and the zero-point energies (Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291) can generally be reproduced by group-equivalent schemes.

Table IV. Enthalpies of Formation and Group Equivalents

Enthalpies of Formation

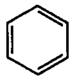
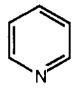
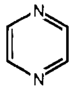
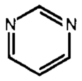
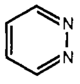
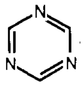
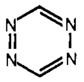
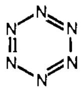
compd	estimated ΔH_f 6-31G* RHF[a]	MP2[b]	MP3[c]	6-31G** RHF[a]	MP2[b]	MP3[b]	ΔH_f obs
benzene	18.6	20.0	19.7	18.6	20.0	19.7	19.8 ± 0.2
pyridine	32.1	32.5	32.5	32.2	32.5	32.8	34.6 ± 0.1
pyrazine	49.2	47.5	47.9	49.1	47.5	47.8	46.9 ± 0.3
pyrimidine[d]	42.6	43.6	43.6	42.6	43.7	43.7	47.0 ± 0.2
pyridazine	69.8	66.6	66.8	69.8	66.5	66.8	66.5 ± 0.3
s-triazine	50.1	53.2	52.8	50.1	53.2	52.8	54.0 ± 0.2
s-tetrazine	123.6	116.8	117.0	123.4	116.5	116.7	(117.)[e]
hexazine	231.9	216.5	217.4	231.5	215.3	216.3	(216.)[3]

Group Equivalents

group	6-31G* RHF	MP2	MP3	6-31G** RHF	MP2	MP3
CH	38.45546	38.58138	38.58611	38.45725	38.58940	38.59462
N	54.46976	54.62523	54.62378	54.46964	54.62490	54.62348

[a] Energies in kilocalories per mole. Rms error = 2.4. [b] Rms error = 0.7 kcal/mol. [c] Rms error = 0.9 kcal/mol. [d] Pyrimidine was not included in the analysis; see text. [e] Estimated ΔH_f based on this analysis.

Table V. Dissociation Energies of Azines (kcal/mol)

reaction	6-31G* RHF	MP2	MP3	ΔH^a calc	6-31G** RHF	MP2	MP3	ΔH^a calc	ΔH obs
 → $3HC\equiv CH$	156.7	164.8	163.2	154.0	155.8	167.0	165.8	153	143
 → $HCN + 2HC\equiv CH$	116.1	123.4	122.6	114.0	115.3	125.1	124.8	117	105
 → $2HCN + HC\equiv CH$	72.0	79.4	79.5	72.0	71.4	80.8	81.3	74	70
 → $2HCN + HC\equiv CH$	78.6	83.4	83.8	76.0	77.9	84.7	85.5	78	70
 → $2HC\equiv CH + N_2$	44.2	58.0	56.5	49.0	43.6	59.1	57.5	50	50
 → $3HCN$	44.1	44.9	46.9	42.0	43.5	45.8	48.1	40	40
 → $2HCN + N_2$	-63.6	-50.0	-49.2	-55.0	-63.9	-49.5	-48.4	-54	-56
 → $3N_2$	-240.3	-212.2	-213.2		-240.3	-212.2	-213.2		-219

[a] Based on MP3 energy changes.

with the available experimental data in Table V. The calculated enthalpy changes are in reasonable agreement with the experimental values, and the inclusion of polarization functions at hydrogen had little effect on the energies.

It was noted above that the relatively constant π–π^* transition energies suggested correspondingly constant π HOMO–LUMO energy differences. This may be examined by reference to Figure 2, which gives the five highest energy filled MO levels and the five lowest energy virtual orbitals. It can be seen that the energies of the π MO's decrease with increasing nitrogen substitution. However, the shifts are about the same for the HOMO's and LUMO's, giving relatively constant differences. The only case where a significant change is found is with *s*-triazine, and the increased HOMO–LUMO gap corresponds to the increased observed transition energy. The general agreement between the trends found in the MO energies and in the electronic spectra implies that the energy changes caused by mixing the appropriate excited-state configurations are rather constant throughout this series of compounds. It may also be noted that the N lone-pair levels are relatively unaffected by nitrogen substitution, and this leads naturally to the remarkable low n–π^* transition energy for *s*-tetrazine, which leads to its red color.[34]

We may now turn to the hydrogenation enthalpies. The structures and energies of a number of partially or completed reduced species were calculated giving the data summarized in Table VII and Figure 3. The energy changes on reduction are shown in Table VIII. In the case of benzene and its reduction

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(34) Spencer, G. H., Jr.; Cross, P. C.; Wiberg, K. B. *J. Chem. Phys.* **1961**, *35*, 1925 and ref 25g.

Table VI. Zero-Point Energies and Enthalpy Changes (298 K)[a]

compd	ZPE	$H_T - H°_0$	sum	compd	ZPE	$H_T - H°_0$	sum
benzene	61.16	3.40	64.56	2,3-dihydropyrazine	60.6	3.6	64.2
pyridine	54.05	3.33	57.38	piperazine	90.5	4.0	94.5
pyrazine	46.64	3.26	49.90	2,5-dihydropyrimidine	60.6	3.6	64.2
pyrimidine	46.27	3.33	49.60	hexahydropyrimidine	90.5	4.0	94.5
pyridazine	46.92	3.28	50.20	1,2-dihydropyridazine	62.5	3.4	65.9
s-triazine	40.23	3.22	43.45	4,5-dihydropyridazine	60.6	3.6	64.2
s-tetrazine	31.42	3.27	34.69	hexahydropyridazine	90.5	4.0	94.5
1,4-cyclohexadiene	74.12	3.93	78.05	1,4-dihydro-s-triazine	54.3	3.4	57.7
1,3-cyclohexadiene	74.1	3.9	78.0	hexahydro-s-triazine	84.3	3.8	88.4
cyclohexene	88.56	4.09	92.65	1,4-dihydro-s-tetrazine	48.1	3.3	51.4
cyclohexane	103.49	4.20	107.69	acetylene	16.18	2.39	18.57
1,4-dihydropyridine	68.7	3.6	72.3	hydrogen cyanide	9.77	2.14	11.91
2,3-dihydropyridine	67.8	3.7	71.5	hydrogen	5.95	2.02	7.97
piperidine	96.72	4.13	100.85	nitrogen	3.33	2.07	5.40
1,4-dihydropyrazine	62.5	3.4	65.9				

[a] Experimental values are given to the nearest 0.01 kcal/mol; estimated values are given to the nearest 0.1 kcal/mol.

Table VII. Energies of Reduced Azines

	6-31G*			6-31G**[a]		
compd	RHF	MP2	MP3	RHF	MP2	MP3
1,4-cyclohexadiene (**9**)	−231.833 57	−232.589 89	−232.635 17	−231.846 98	−232.654 14	−232.703 33
1,3-cyclohexadiene (**10**)	−231.831 90	−232.591 35	−232.635 24	−231.845 22	−232.655 94	−232.703 80
cyclohexene (**11**)	−233.019 65	−233.790 12	−233.840 72	−233.035 44	−233.871 43	−233.927 13
cyclohexane (**12**)	−234.208 00	−234.991 66	−235.047 82	−234.226 24	−235.089 83	−235.152 26
1,4-dihydropyridine (**13**)	−247.823 17	−248.612 94	−248.650 93	−247.837 50	−248.671 12	−248.712 37
2,3-dihydropyridine (**14**)	−247.827 66			−247.838 98	−248.674 30	−248.715 01
piperidine (**15**)	−250.188 71	−251.001 62	−251.052 71	−250.207 43	−251.093 08	−251.149 75
1,4-dihydropyrazine (**16**)	−263.797 74	−264.617 25	−264.650 71	−263.812 75	−264.669 01	−264.704 96
2,3-dihydropyrazine (**17**)	−263.819 13	−264.641 29	−264.672 45	−263.828 52	−264.688 86	−264.723 08
piperazine (**18**)	−266.168 96	−267.011 01	−267.057 14	−266.188 15	−267.095 76	−267.146 78
1,2-dihydropyridazine (**19**)	−263.773 21			−263.787 65	−264.646 17	−264.681 96
4,5-dihydropyridazine (**20**)	−263.794 93			−263.804 53	−264.668 27	−264.702 17
hexahydropyridazine (**21**)	−266.141 15			−266.159 99	−267.070 48	−267.122 15
2,5-dihydropyrimidine (**22**)	−263.827 40			−263.836 86	−264.693 28	−264.728 36
hexahydropyrimidine (**23**)	−266.167 23			−266.186 52	−267.094 12	−267.145 13
1,4-dihydrotriazine (**24**)	−279.833 81			−279.844 06	−280.727 22	−280.752 84
hexahydro-s-triazine (**25**)	−282.143 29			−282.163 23	−283.092 68	−283.138 13
1,4-dihydrotetrazine (**26**)	−295.755 16	−296.641 18	−296.660 87	−295.766 62	−296.675 87	−296.697 17

[a] Calculated using the 6-31G* geometries.

products, the hydrogenation enthalpies are reproduced fairly well using the 6-31G* basis set. On the other hand, the reduction of pyrazine to piperazine is not as well reproduced by the calculations, and here the calculated hydrogenation enthalpy is in error by about 6 kcal/mol. This is not surprising since whereas the electron populations for a hydrogen in H_2 and in the C–H bonds that are formed are almost the same, the electron population for a hydrogen in a N–H bond is markedly different.[35] The hydrogens are not well described using a 6-31G* basis set that includes 15 functions for each carbon and nitrogen but only 2 for each hydrogen. Therefore, the energies were recalculated at the 6-31G* geometries using MP3/6-31G**, which includes a set of p functions at the hydrogens. The use of the 6-31G* structures should be quite satisfactory because the addition of polarization functions at hydrogen has a minor effect on calculated geometries. These data are included in Tables VII and VIII.

It can be seen that the addition of polarization functions at hydrogen has made an improvement in the calculated enthalpy of reduction of pyrazine. In the case of benzene, the calculated enthalpy for the first hydrogenation step is still in good agreement with experiment. The subsequent steps are calculated to be too exothermic by about 3 kcal/mol, and the overall hydrogenation to cyclohexane is in error by 11 kcal/mol. A similar error is found with pyridine (7 kcal/mol).

The net effect of adding polarization functions at hydrogen has been to make the calculated energy changes more exothermic by about 2.5–3.0 kcal/mol per equivalent of hydrogen. It can be seen that the MP2 and MP3 energy differences between the azines are essentially the same, and a similar observation may be made for the dihydro and hexahydro derivatives. Therefore, the problem appears to be related to a proper description of dihydrogen vs the CH and NH bonds in organic compounds. Such problems have previously been noted for other systems.[36]

One way in which to avoid the difficulties with the calculations of hydrogenation enthalpies is to make use of hydrogen-transfer energies. Some of them are given in Table IX. Reactions 1–4 are examples of homoisodesmic processes[37] for which the energy changes are usually fairly reliable. It can be seen that the values are almost independent of basis set or level of correction for electron correlation. Pyridine should have an enthalpy of hydrogenation to the 2,3-dihydro form, which is 2 kcal/mol more exothermic than that for benzene, and using the resonance energy of benzene as defined by the hydrogenation enthalpies (36 kcal/mol), the resonance energy of pyridine becomes 34 kcal/mol. Similar arguments lead to the resonance energies of pyrazine as 32 kcal/mol, pyrimidine as 33 kcal/mol, and pyrimidine as 26 kcal/mol.

Reaction 5 is not a homoisodesmic reaction since the right-hand side has an NH bond whereas the left-hand side does not and is further complicated by the difference in C–H and N–H bond strengths. However, at the MP3/6-31G** level, reactions 1 and 5 differ by only 1 kcal/mol, which seems reasonable. Reaction 6 then suggests that the resonance energy of *s*-triazine is 9 kcal/mol less than that for pyridine, or 25 kcal/mol. Similarly,

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(35) Whereas the electron population at a methane hydrogen is 1.062e, that for a hydrogen of ammonia is only 0.638e.

(36) Ibrahim, M. R.; Fataftah, Z. A.; Schleyer, P. v. R.; Stout, P. D. *J. Comput. Chem.* **1987**, *8*, 1131.

(37) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

Table VIII. Energies of Reduction (kcal/mol)

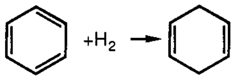
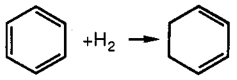
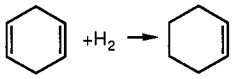
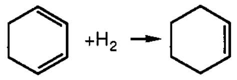
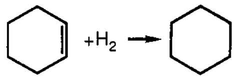
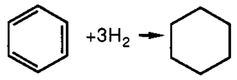
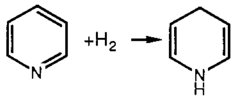
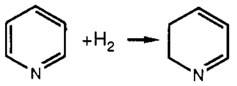
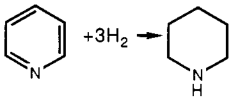
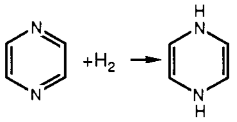
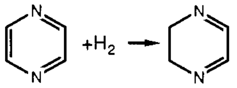
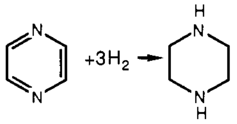
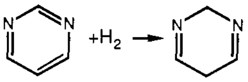
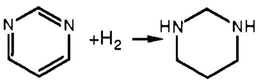
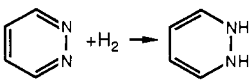
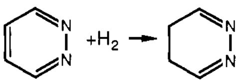
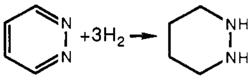
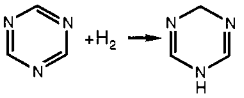
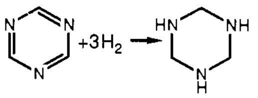
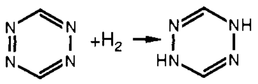
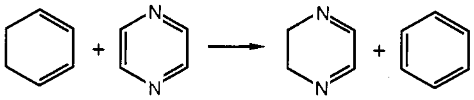
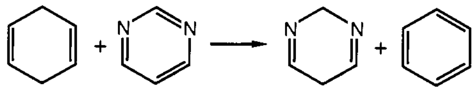
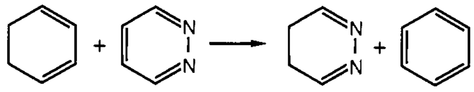
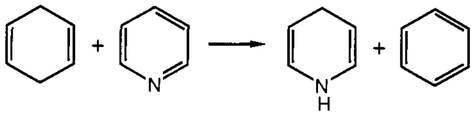
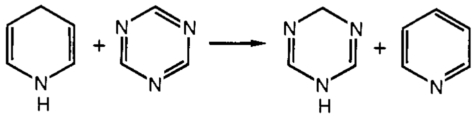
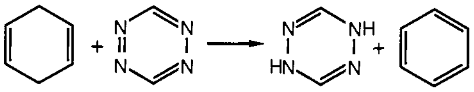
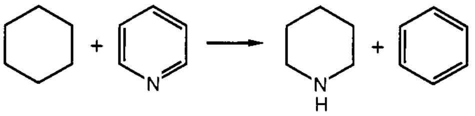
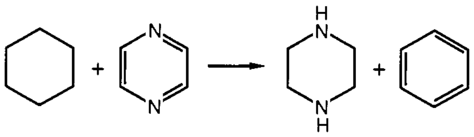
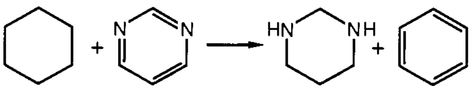
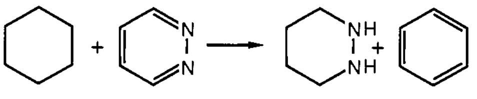
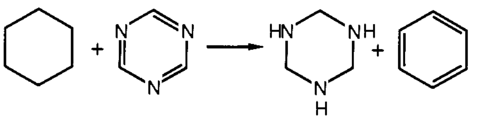
	6-31G*				6-31G**[a]				
reaction	RHF	MP2	MP3	ΔH calc	RHF	MP2	MP3	ΔH calc	ΔH obs
	-2.3	+6.7	-0.5	+5.1	-1.1	+5.1	-2.4	+3.1	+5.4 ± 0.2
	-1.2	+5.8	-0.5	+5.0	0.0	+4.0	-2.7	+2.8	+5.6 ± 0.2
	-37.2	-35.2	-35.3	-28.7	-35.9	-37.4	-38.1	-31.4	-26.6 ± 0.2
	-38.2	-34.3	-35.3	-28.6	-37.0	-36.3	-37.8	-31.1	-26.8 ± 0.2
	-38.6	-36.0	-36.3	-29.2	-37.3	-38.1	-38.9	-31.8	-28.6 ± 0.1
	-78.0	-64.6	-72.1	-52.9	-74.3	-70.5	-79.4	-60.2	-49.6 ± 0.2
	-0.3	+7.2	+0.5	7.4	-1.0	+4.1	-2.9	+4.1	
	-3.1				-1.9	+2.1	-4.5	+1.6	
	-70.5	-55.8	-64.3	-44.8	-68.3	-62.8	-72.6	-53.0	-46.3 ± 0.2
	+7.6	+17.0	+8.9	+17.0	+5.4	+12.7	+4.6	+12.7	
	-5.8	+1.9	-4.7	+1.6	-4.5	+0.3	-6.7	-0.4	
	-66.2	-49.3	-58.8	-38.1	-65.4	-57.2	-67.8	-47.2	-44.3 ± 0.7
	-4.4				-3.3	+1.4	-5.9	+0.8	
	-58.5				-58.8	-52.3	-62.6	-41.6	
	+2.3				+0.5	+8.1	+0.1	+7.8	
	-11.3				-10.1	-5.8	-12.6	-6.6	
	-69.4				-68.4	-60.3	-71.4	-51.0	
	-7.0				-7.5	-7.2	-12.3	-6.0	
	-42.0				-43.0	-38.7	-49.3	-28.3	
	-22.2	-12.3	-19.3	-10.1	-24.4	-15.9	-23.1	-14.4	

Table IX. Hydrogen-Transfer Energies (kcal/mol)

	reaction	6-31G*			6-31G**		
		RHF	MP2	MP3	RHF	MP2	MP3
1		-1.9	-1.8	-1.8	-1.9	-1.8	-1.8
2		-4.6	-3.9	-4.2	-4.5	-3.7	-4.0
3		-2.2			-2.1	-3.7	-3.4
4		-10.1			-10.1	-9.7	-9.9
5		+1.9	+0.5	+0.9	+0.1	-1.0	-0.4
6		-6.7			-6.5	-11.3	-9.4
7		-20.0	-19.0	-18.9	-23.3	-21.0	-20.7
8		+7.5	+8.7	+7.8	+6.0	+7.7	+6.8
9		+11.9	+15.3	+13.3	+8.9	+13.3	+11.6
10		+19.5			+16.5	+18.2	+16.8
11		+8.6			+5.9	+10.2	+8.0
12		+36.0			+31.3	+31.8	+30.1

reaction 7 suggests that *s*-tetrazine has a resonance energy about 20 kcal/mol less than that of benzene, or about 16 kcal/mol.

The differences in conventionally defined resonance energies between benzene, pyridine, pyrazine, and pyrimidine are small despite the significant changes in bond angles and lengths on going from benzene to these azines. It is therefore clear that the thermochemical stabilization associated with a six-electron π-system is not strongly dependent on the structure. In particular, it does not require a regular hexagon, as in benzene, and it can tolerate considerable variation in geometry.

The resonance energies are uniformly smaller than the delocalization energies obtained using the spectroscopic criterion. It is generally recognized that a major part of the difference between the two is the compression energy or the energy required in changing the bond lengths of the reference compounds to those for the delocalized species. They would be expected to be about the same for benzene through pyrimidine, leading to the approximately constant resonance energies. With pyridazine and *s*-tetrazine, the presence of N–N bonds may lead to a significant change in bond energies on reduction and may be the source of the relatively small resonance energies. The origin of the small resonance energy of *s*-triazine is not clear at this time and will require further investigation.

4. Analysis of Wave Functions

We now examine the details of the changes caused by the replacement of CH by N in these compounds via an analysis of the wave functions. We should use a procedure that does not require an a priori model, and therefore we have chosen to use Bader's quantum topology approach.[38] Here a bond is defined in terms of a bond path, which is the path of maximum charge density connecting two bonded atoms in an equilibrium structure.

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(38) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *9*, 18.

Table X. Bond Properties of the Azines[a]

compd	bond	r_e, Å	r_{bp}, Å	r_A, Å	r_B, Å	ρ_c	λ_1	λ_2	λ_3	ϵ	ρ_{ring}
benzene	C–C	1.3861	1.3861	0.6931	0.6931	0.3273	−0.7088	−0.5760	0.2693	0.2305	0.0205
	C–H	1.0755	1.0755	0.6600	0.4156	0.2966	−0.7845	−0.7723	0.4060	0.0158	
pyridine	C–N	1.3209	1.3214	0.8867	0.4347	0.3581	−0.8451	−0.7719	0.8584	0.0949	0.0227
	C_2–C_3	1.3851	1.3851	0.7002	0.6849	0.3313	−0.7305	−0.5856	0.2731	0.2449	
	C_3–C_4	1.3838	1.3838	0.6806	0.7032	0.3288	−0.7116	−0.5824	0.2670	0.2218	
	C_2–H	1.0761	1.0761	0.6684	0.4077	0.3032	−0.8327	−0.8100	0.4255	0.0281	
	C3–H	1.0743	1.0743	0.6614	0.4129	0.2967	−0.7872	−0.7713	0.4059	0.0205	
	C_4–H	1.0754	1.0754	0.6647	0.4107	0.2986	−0.7957	−0.7932	0.4135	0.0031	
pyrazine	N–C	1.3187	1.3191	0.8877	0.4314	0.3576	−0.8464	−0.7610	0.9512	0.1123	0.0249
	C–C	1.3861	1.3862	0.6931	0.6931	0.3343	−0.7504	−0.5989	0.2799	0.2530	
	C–H	1.0748	1.0748	0.6701	0.4047	0.3034	−0.8364	−0.8102	0.4250	0.0323	
pyrimidine	N–C_2	1.3186	1.3195	0.8845	0.4350	0.3645	−0.8875	−0.8072	0.8331	0.0995	0.0252
	N–C_4	1.3209	1.3212	0.8840	0.4373	0.3614	−0.8469	−0.8052	0.7892	0.0517	
	C_4–C_5	1.3821	1.3821	0.7099	0.6722	0.3333	−0.7340	−0.5931	0.2682	0.2376	
	C_2–H	1.0746	1.0746	0.6769	0.3977	0.3103	−0.8816	−0.8504	0.4394	0.0267	
	C_3–H	1.0759	1.0759	0.6731	0.4029	0.3052	−0.8439	−0.8302	0.4317	0.0165	
	C_4–H	1.0729	1.0729	0.6630	0.4099	0.2968	−0.7903	−0.7719	0.4062	0.0238	
pyridazine	N–N	1.3096	1.3112	0.6556	0.6556	0.4145	−0.9564	−0.9207	0.8207	0.0388	0.0238
	N–C_3	1.3101	1.3111	0.8814	0.4297	0.3695	−0.9011	−0.7831	0.9683	0.1508	
	C_3–C_4	1.3940	1.3940	0.6949	0.6992	0.3265	−0.7132	−0.5947	0.2805	0.1993	
	C_4–C_5	1.3673	1.3674	0.6837	0.6837	0.3389	−0.7401	−0.5979	0.2575	0.2378	
	C_3–H	1.0744	1.0744	0.6706	0.4038	0.3040	−0.8381	−0.8134	0.4251	0.0304	
	C_4–H	1.0742	1.0742	0.6668	0.4074	0.2989	−0.7998	−0.7939	0.4137	0.0074	
s-triazine	N–C	1.3180	1.3187	0.8816	0.4371	0.4338	−0.8920	−0.8404	0.7735	0.0613	0.0281
	C–H	1.0747	1.0747	0.6817	0.3930	0.3120	−0.8918	−0.8686	0.4440	0.0267	
s-tetrazine	N–N	1.2908	1.2920	0.6460	0.6460	0.4338	−1.0174	−0.9701	0.8452	0.0488	0.0273
	N–C	1.3183	1.3194	0.8882	0.4312	0.3680	−0.9125	−0.8006	0.9335	0.1398	
	C–H	1.0711	1.0711	0.6822	0.3889	0.3115	−0.8935	−0.8509	0.4361	0.0424	

[a] r_e is the calculated bond length, r_{bp} is the length along the bond path, r_A and r_B are the distances from the atoms to the bond critical point, ρ_c is the charge density at the bond critical point (e/au^3), the λ's are the curvatures in ρ at thee critical point (e/au^5), ϵ is the ellipticity, and ρ_{ring} is the charge density at the ring critical point.

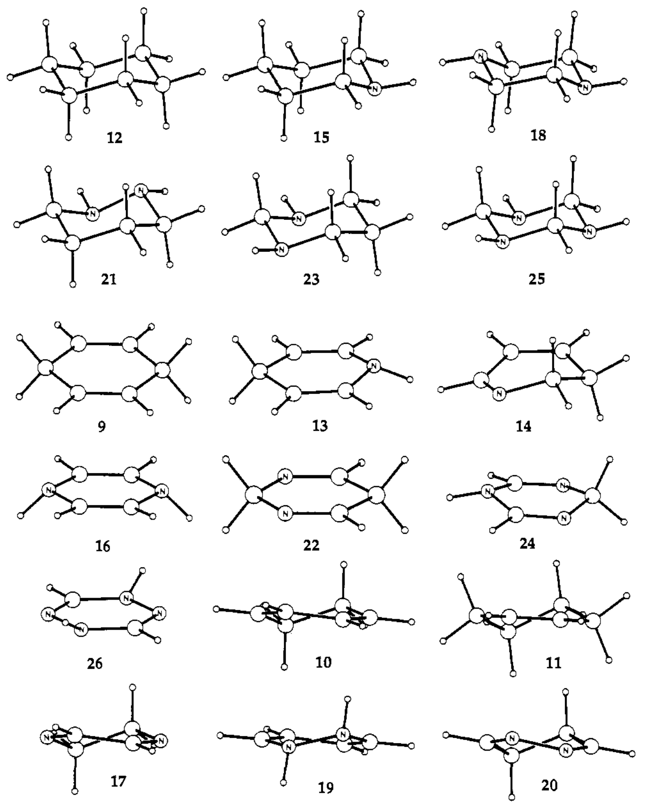

Figure 3. Conformations of reduced azines. The compounds are numbered as in Table VII.

It is characterized by a bond critical point, which is the point of minimum charge density along the bond. In directions perpendicular to the bond path, the band critical point is a maximum in charge density.

The bond properties of the azines as derived from the 6-31G** wave functions are summarized in Table X. The first column gives the calculated bond length, and the second gives the distance along the bond path. If the latter coincides with the line between centers, the two will be equal. However, if the bond path is curved (i.e. the bond is bent), the second will be greater than the first. It can be seen that the C–C bonds are linear but the C–N bonds are somewhat bent. The nature of the bending can be determined by examining the angle between the bond paths at the nitrogen (Table XI). Whereas in pyridine the conventional C–N–C angle is calcd. to be 117.7°, the angle between the bond paths is only 104.5°. As a result, the simplest description of hybridization is that the lone pair occupies an orbital that is largely s, whereas the bonds are formed using essentially p orbitals. In this way it is similar to the nitrogen in ammonia.[39] An examination of Table XI shows that bent bonds at nitrogen are found with all of the azines.

Table XI. Bond Path Angles for the Azines

compd	angle	conv	bond path	Δα
benzene	C-C-C	120.00	121.18	-1.18
pyridine	C-N-C	117.71	104.05	13.67
	N-C-C	123.61	120.69	2.92
	C_2-C_2-C_4	118.22	119.71	-1.49
	C_3-C_4-C_5	118.63	120.58	-1.95
pyrazine	C-N-C	116.61	103.31	13.30
	N-C-C	121.70	119.09	2.61
pyrimidine	C-N-C	116.24	103.09	13.15
	N-C-N	126.88	119.93	6.95
	N-C-C	122.32	120.14	2.18
	C-C-C	116.00	117.97	-1.97
pyridazine	N-C-C	123.29	120.00	3.29
	C-N-N	120.01	102.75	17.26
	C-C-C	116.70	119.07	-2.37
s-triazine	C-N-C	114.38	101.88	12.50
	N-C-C	125.62	119.30	6.32
s-tetrazine	N-C-N	118.43	101.11	17.32
	C-N-N	123.14	117.59	5.55

The distances r_A and r_B are the distances from the nuclei to the bond critical points. In a symmetrical C–C bond, the two will be equal, but for a C–N bond, the higher electronegativity of

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[39] Wiberg, K. B.; Murcko, M. A. *J. Mol. Struct.* **1988**, *169*, 355.

Table XII. Atom Properties of the Azines[a]

compd	atom	n_π	n_T	L	$T = -E$	$-V/T - 1$
benzene	C	0.970	5.9553	0.0003	37.7993	1.000847
	H	0.030	1.0453	0.0001	0.6530	
	sum	6.000	42.0036		230.7138 (230.7139)	
pyridine	N	1.425	8.5815	0.0004	55.3139	1.001066
	C_2	0.761	5.1931	0.0007	37.3358	
	C_3	0.997	5.9621	−0.0002	37.8260	
	C_4	0.915	5.9626	−0.0006	37.8259	
	H_2	0.026	1.0265	0.0001	0.6518	
	H_3	0.032	1.0319	0.0001	0.6459	
	H_4	0.026	1.0277	0.0001	0.6460	
	sum	6.000	41.9990		246.7048 (246.7046)	
pyrazine	N	1.368	8.5432	0.0004	55.3216	1.001281
	C	0.790	5.2185	−0.0023	37.3673	
	H	0.026	1.0120	0.0001	0.6439	
	sum	6.000	42.0084		262.6880 (262.6900)	
pyrimidine	N	1.449	8.6059	−0.0003	55.3630	1.001266
	C_2	0.562	4.4144	−0.0002	36.8443	
	C_4	0.712	5.1871	−0.0006	37.3525	
	C_5	1.019	5.9672	0.0000	37.8515	
	H_2	0.022	0.9969	0.0001	0.6446	
	H_4	0.022	1.0086	0.0001	0.6445	
	H_5	0.032	1.0173	0.0001	0.6383	
	sum	6.000	41.9990		262.6987 (262.7003)	
pyridazine	N	1.240	7.8287	−0.0000	54.8365	1.001303
	C_3	0.769	5.1885	−0.0003	37.3580	
	C_4	0.937	5.9636	−0.0004	37.8530	
	H_3	0.026	1.0078	0.0001	0.6430	
	H_4	0.028	1.0114	0.0001	0.6377	
	sum	6.000	42.0000		262.6564 (262.6571)	
s-triazine	N	1.467	8.6302	0.0008	55.4154	1.001457
	C	0.515	4.3891	0.0032	36.8490	
	H	0.018	0.9785	0.0001	0.6367	
	sum	6.000	41.9982		278.7033 (278.7008)	
s-tetrazine	N	1.178	7.7684	−0.0004	54.8621	1.001671
	C	0.624	4.5071	0.0007	36.9498	
	H	0.020	0.9558	0.0000	0.6239	
	sum	6.000	41.9994		294.5938 (294.5964)	

[a] The table entries are the following: n_π, the π-electron population; n_T, the total electron population; L, the integral of $-\nabla^2\rho$, which would be zero if the integration for the kinetic energy were exact; T, the kinetic energy, which has been corrected for the virial defect by multiplying by $-V/T - 1$; E_T (in parentheses), the negative of the total energy derived from the SCF calculation.

nitrogen leads to a shift of charge density toward the nitrogen and a corresponding shift of the bond critical point away from the nitrogen. It can be seen that r_A and r_B have about a 2:1 ratio for the C–N bonds in these compounds.

An interesting bond property in the present context is the ellipticity.[40] At the bond critical point, as noted above, there is one positive curvature in the charge density (i.e. along the bond, λ_3) and two negative curvatures. One will lie in the plane of the molecule (λ_1) and the other will be perpendicular to the plane (λ_2). If the bond is cylindrically symmetrical, such as the C–C bond in ethane, $\lambda_1 = \lambda_2$. The ellipticity is defined as $\lambda_1/\lambda_2 - 1$ and is zero for ethane. With a C═C bond, on the other hand, λ_1 and λ_2 will be quite different. Here, λ_1 (λ_σ) will have a fairly large negative value, but λ_2 (λ_π), which passes through the p orbital, will be significantly smaller because the p orbital causes the charge density to decrease more slowly in that direction. In this case, the ellipticity is large.

The ellipticity of benzene (0.231) is about half that of ethylene, which seems reasonable for a bond with an order 1.5.[40] The C–C bonds of pyridine and the diazines have similar values, suggesting that the π-bonding is not markedly affected by the introduction of nitrogen. However, an examination of the individual λ-values makes one question the significance of this bonding criterion.[41] The λ_π values for the C–C bonds of benzene and the azines are not much different than that for *cis*-2-butene ($\lambda_\pi = -0.5456$), and the change in ellipticity arises from a decrease in λ_σ as compared to that for *cis*-2-butene (−0.8120). The λ_σ-values tend to decrease with increasing bond length, and so the difference in ellipticity between a normal C═C and a C—C bond in benzene or the azines appears to be mainly due to the increased bond length.

The ellipticity of the C–N bonds is markedly smaller, and that for the N–N is almost negligible with the azines. In the case of *cis*-azomethane, $\lambda_\pi = -1.0400$ and $\lambda_\sigma = -1.2618$. A comparison with the values for pyridazine and *s*-tetrazine shows again that the change is found with λ_σ rather than with λ_π.

The π-electrons are of particular interest in the present context, and therefore we have prepared contour plots for both the total densities and the π-densities. They are shown for each of the azines in Figure 4. It can be seen that the π-density is somewhat concentrated near the nitrogens, but there is not a significant contraction of the π-envelope. There is little evidence of a marked change in the π-electrons on nitrogen substitution.

Starting at a bond critical point, one may develop a surface corresponding to the directions of most rapid decrease in charge density. This is known as a zero-flux surface, and it can be shown that the set of these surfaces provide the appropriate boundary conditions for separating the molecule into quantum mechanically distinct regions of space, one for each atom. Within each of these regions, the usual quantum mechanical properties, such as the virial theorem, apply.[42]

We have carried out numerical integration of the charge density within each of these regions, giving the electron populations for each of the atoms. The kinetic energies of the electrons were obtained at the same time. These data are given in Table XII. The electron populations sum to the total number of electrons with

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(40) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.

(41) For other discussions of the ellipticity, see: Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *57*, 1259. Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909.

(42) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.

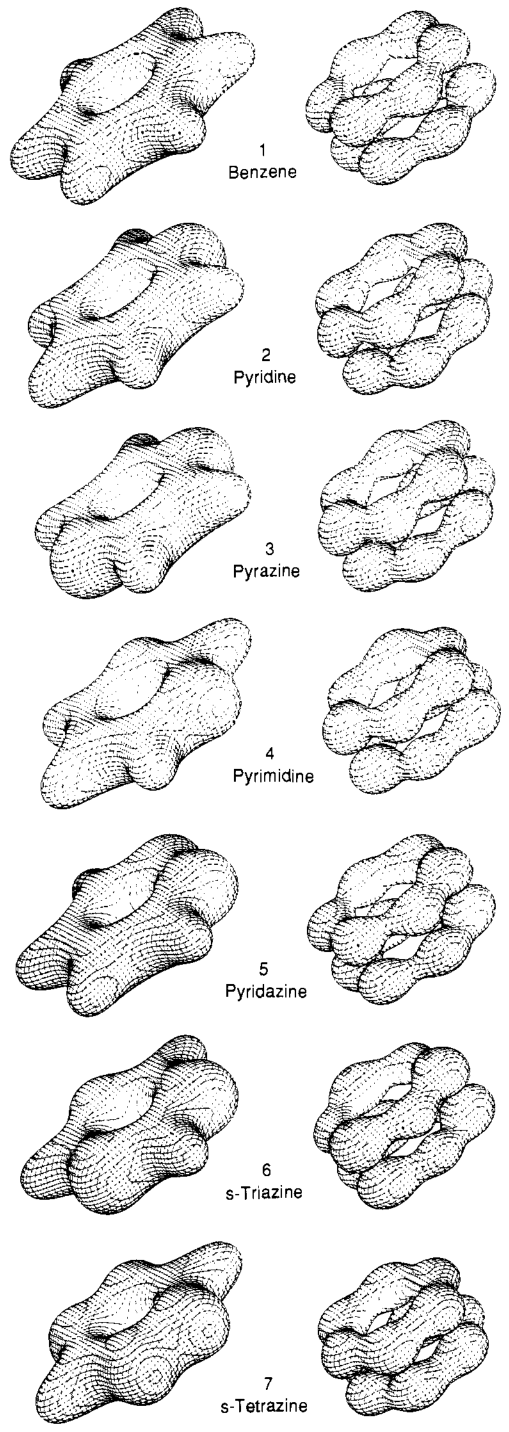

Figure 4. Charge density contours for the azines. The total densities are given at the left, and the π-densities are given at the right. The contour levels were set at 0.1 e/au^3 for the total densities and 0.03 e/au^3 for the π-densities.

little error. Since the virial theorem is satisfied within each atomic subspace, Ω, the kinetic energy of an atom, T_Ω, is related to the potential energy, V_Ω:

$$-V_\Omega = -2T_\Omega$$

The total energy of an atom, E_Ω, is given by the sum of the kinetic and potential energies, and making the above substitution, $E_\Omega = -T_\Omega$. Thus, the calculated kinetic energies are directly related to the total energies of the atoms. Because the SCF calculations used a finite basis set, the virial ratio, $-V/T$, differed slightly from 2.0. The atomic kinetic energies were corrected for the virial defect by multiplying them by $-V/T - 1$. In each case, the sum of the corrected kinetic energies obtained in the numerical integration

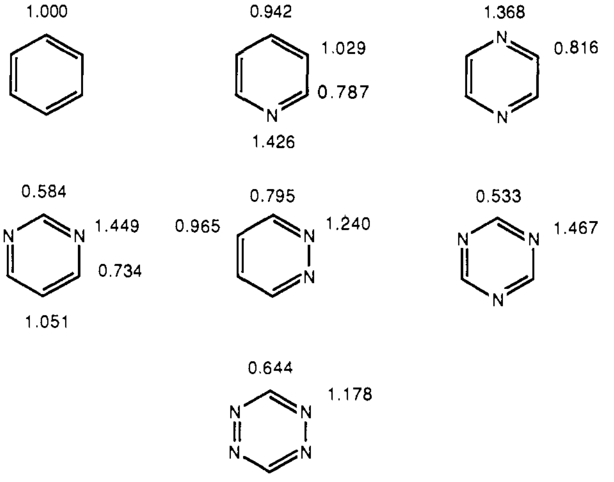

Figure 5. π-Electron populations for benzene and the azines.

agreed with the total energies found in the SCF procedure with an error of about 1 kcal/mol.

In the present context, the π-electron populations are the more interesting quantities. They are given in the third column of Table XII. The small populations at the hydrogens result from the p polarization functions, which were included in the basis set. The π-electron populations for the nitrogens and the CH groups are shown in Figure 5. Let us examine benzene, pyridine, and pyrazine and divide each molecule in half through pairs of symmetrically related C–C bonds. In benzene and pyrazine, both halves contain 3π-electrons by symmetry. In pyridine, no such relationship is required, but the sum of the π-populations is equal for the "benzene" half and the "pyridine" half. This suggests that the π-electrons may be approximately equally distributed with respect to all of the atoms. The larger calculated nitrogen populations in large measure result from the larger volume element associated with the nitrogen because of its greater electronegativity. The same appears to be true with the other compounds. In each case, one may reproduce the calculated π-populations with remarkable accuracy by assuming that a nitrogen will take 0.209e from the adjacent carbons and 0.056e from the *p*-CH groups and donate 0.025e to the *m*-CH groups. Thus, there is a strong similarity between pyridine, pyrazine, and the other azines.

The effects of nitrogen substitution on the charge density distribution for planar molecules such as these are conveniently visualized using the density projection maps pioneered by Streitwieser.[43] Here, the charge density above and below the plane of the molecule at any point is integrated and assigned to that point. Contour diagrams of the values obtained using a 101 × 101 grid for each of the azines are shown in Figure 6. The plots for the total density (left side) clearly show that the volume element associated with the nitrogens is considerably larger than that for the carbons and results in an increased population at the nitrogens. The differences in the π-density (right side) between carbon and nitrogen are considerably smaller and agree with the conclusions drawn from Figure 4. The electron populations and the projection density plots again indicate that there is little difference in the π-charge distribution *per unit volume element* between benzene and the azines.

Finally, the atom energies given in Table XII allow us to examine the origin of the observation by Murdoch that the energy of pyridine is close to the average of that of benzene and pyrazine.[44] This also is found in the calculated energies (Table II). The energy of three CH groups in benzene is −115.3569 hartrees, and that for two CH groups and N in pyrazine is −131.3440 hartrees. The energy of the three "top" carbons of pyridine is −115.4157 hartrees and that of the "bottom" half of the molecule is −131.2891

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(43) Streitwieser, A., Jr.; Collins, J. B.; McKelvey, J. M.; Grier, D.; Sender, J.; Toczko, A. G. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2499.
(44) Murdoch, J. R. *J. Am. Chem. Soc.* **1982**, *194*, 588.

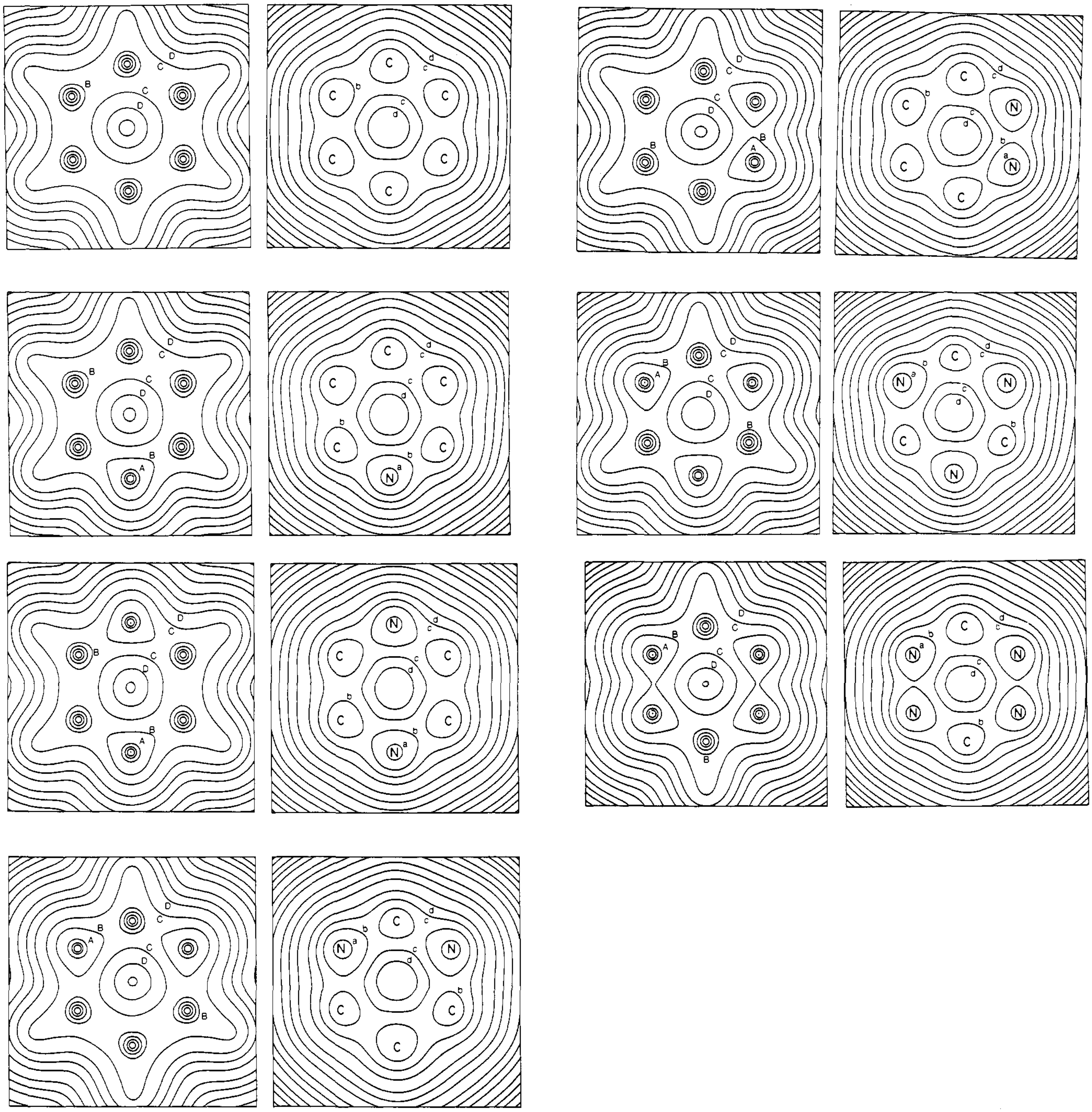

Figure 6. Projection density plots for benzene and the azines. The contour levels are the following: $A = 0.8$, $B = 0.4$, $C = 0.2$, $D = 0.08$ e/au^2; $a = 0.2$, $b = 0.0.08$, $c = 0.04$, $d = 0.02$ e/au^2.

hartrees. The shift in energy of the top carbons of pyridine with respect to benzene is then 36.9 kcal/mol, and that of the bottom half of the molecule with respect to pyrazine is −34.5 kcal/mol. It can be seen that although there are sizable shifts in energy, they are about equal and opposite for the "halves" of pyridine.

5. Conclusions

The π-delocalization energies of the azines were found by the spectroscopic criterion to be essentially equal to that of benzene. In accord with this, the π-density distributions per unit volume element were found to be little affected by replacement of CH by N. Key elements of compounds having π-electron stabilization appear to be a π-electron distribution of 1 per σ-bond in the conjugated framework, which results in reduced π-electron repulsion,[45] and a relatively large HOMO–LUMO gap, which allows the structure of the molecule to be well represented by a single determinant.

On the other hand, the resonance energies as determined from energies of hydrogenation were found to be the following: benzene, 36 kcal/mol; pyridine, 34; pyrazine, 32; pyrimidine, 33; pyridazine, 26; *s*-triazine, 25; *s*-tetrazine, 16. The difference between the π-delocalization energies and the resonance energies is largely the energy change in the σ-system on going from the conjugated system to the reference system (i.e. the compression energy). Another factor that may be responsible for the lower resonance energies of pyridazine and *s*-tetrazine is the difference in bond energies between σ-bonds involving the N–N groups in the azines and in their reduced forms.

Electron populations and energies were obtained via numerical integration within volume elements defined by zero-flux surfaces. The changes in π-electron populations caused by the replacement of CH by N were consistent throughout all of the compounds studied and resulted in large measure from the larger volume

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[45] Dewar, J. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166; *Ibid.* **1960**, *11*, 96.

element associated with the nitrogen. As a result, the total π-electron populations for the "top" and "bottom" halves of pyridine were equal.

The analyses presented herein also led to estimates of the enthalpies of formation of *s*-tetrazine and hexazine. The energies of dissociation to three two-heavy-atom fragments were calculated and were found to become increasingly less endothermic with increasing nitrogen substitution.

In their analysis, Shaik and Hiberty, et al.[7] concluded that "electron delocalization is seldom going to be a driving force in conjugated systems composed of the second row elements C, N and O. These compounds are just about the majority of delocalized species in organic chemistry." It appears to us that electron delocalization is the driving force for the exothermic loss of hydrogen from 1,4-cyclohexadiene to form benzene (in contrast to the strongly endothermic loss of hydrogen from cyclohexene) and for the facile formation of benzene from compounds such as norbornadienone.[46] Many examples of this type could be cited. However, it is also true that some phenomena, which have been explained as resulting from π-electron delocalization, such as the acidity of carboxylic acids,[47] now appear to have other origins.

Calculations. All MO calculations were carried out using GAUSSIAN-82.[48] In most cases, preliminary calculations were carried out using the 3-21G basis set, and for the reduced azines the conformational questions were resolved at this level. The lower energy conformations were then optimized at the 6-31G* level. The geometries of the reduced azines are available as supplementary material. The charge density integrations made use of the PROAIMS package.[49]

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Supplementary Material Available: Tables of the geometries of reduced azines (8 pages). Ordering information is given on any current masthead page.

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A Priori pK_a Calculations and the Hydration of Organic Anions

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Abstract: A novel theoretical procedure is used to obtain a priori estimates of pK_a's for organic compounds in water. The approach features ab initio molecular orbital calculations for the requisite gas-phase acidities and for development of anion–water intermolecular potential functions. Monte Carlo simulations using statistical perturbation theory are then executed to compute differences in free energies of hydration for the anions and for their conjugate acids. Combination in a thermodynamic cycle yields predicted relative pK_a's for the organic acids in water. The procedure is illustrated for methanethiol, methanol, acetonitrile, methylamine, and ethane. The computed pK_a's for acetonitrile (28) and methylamine (33) are consistent with the rough experimental estimates, while the result of 52 ± 2 for ethane falls in the middle of the broad experimental range for this elusive quantity. The hydration of the anions has also been characterized. In each case, there are four to six particularly strong hydrogen bonds between the anions and water molecules in the first solvation layer.

Investigations of the acidity of organic compounds have played a central role in the development of physical organic chemistry and the conceptual understanding of organic reactivity.[1-5] Knowledge of relative acidities is also critical to the daily activities of synthetic and bioorganic chemists as they formulate viable reaction schemes and mechanisms. Although much organic chemistry is carried out in nonaqueous media, it is notable that the acidity of organic compounds is still usually discussed in terms of pK_a's in water.[1-7] However, this is problematic since the acidity of water itself restricts direct equilibrium measurements to acids with pK_a's below ca. 17. Thus, the experimental pK_a's for weaker acids are typically extrapolated from nonaqueous solvents, come from kinetic measurements, and may be complicated by ion-pairing and aggregation effects.[1,3,5,7-11] The resultant uncertainties can be substantial, as reflected in the reported range of aqueous pK_a's for the extreme case of methane and ethane which covers from 40 to 60.[1,7,10,11]

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