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Application of Natural Bond Orbital Analysis and Natural Resonance Theory to Delocalization and Aromaticity in Five-Membered Heteroaromatic Compounds

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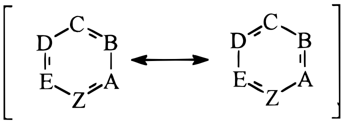
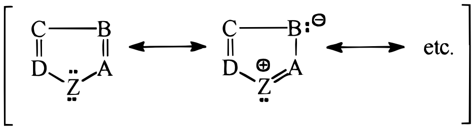
The various measures of delocalization in all of the five-membered nitrogen and oxygen heteroaromatic compounds (azoles and oxoles) were obtained from MO calculations at the HF/6-31G* level and the application of natural bond orbital analysis and natural resonance theory. The hydrogen transfer and aromatic energies of these compounds were also calculated. These were compared to the relative ranking of aromaticity reported by Katritzky from a principal component analysis of other measures of aromaticity. It was concluded that the extent of the transfer of electron density from the p_z orbital of the heteroatom to the rest of the π system is the best measure of delocalization and "aromaticity" of these compounds. This indicated that all of the oxoles are less delocalized than any of the azoles because the electronegativity of the oxygen atom prevents the interaction of its lone pair of electrons with the π system. For this reason the range of delocalization in the oxoles is also much narrower. The degree of delocalization in the π system is the result of the geometry imposed by the σ structure, which in turn is defined by the identity and arrangement of the atoms of the ring.

Introduction

Whereas two equivalent resonance ("Kekulé") structures can be written for many of the six-membered aromatic compounds, only one comparable structure is possible for the five-membered heteroaromatic compounds. Other contributing structures necessarily involve charge separation and consequently are of higher energy. These are the structures that contribute to any double bond character for the bonds involving the heteroatom; a necessary condition for the compound to be aromatic.





In the five-membered heteroaromatic compounds, two of the six π electrons required by the Hückel rule are provided by the "lone pair" of the heteroatom while the remaining four π electrons are provided by the other four atoms of the ring.[1] Unless there is an appreciable contribution by the charge separation structures, the molecule will resemble a diene. If there is not some delocalization of the π bonds, the compound will not be aromatic. The various attempts to quantify aromaticity have generally been related to the energetic, geometric, or magnetic properties of these compounds.[2]

Two often cited methods for estimating empirical resonance energies involve the use of single and double bond energies obtained from Hückel or semiempirical MO calculations for polyenes. Dewar's resonance energy (DRE) is calculated by subtracting bond energies derived from PPP MO calculations from the observed heat of formation.[3] As opposed to Dewar's resonance energy, that of Hess and Schaad (HSRE) is based upon the Hückel MO method and uses eight bond types that depend, in part, upon the number of hydrogens attached to the carbon atoms.[4] The values obtained for the DREs and for the HSREs agreed on the ranking, benzene > pyrrole > furan.

The relative "diene character" or "bond fixation" in the five-membered heteroaromatic compounds may be considered a measure of their lack of aromaticity. For example, the carbon−carbon bond lengths in pyrrole are 1.371 and 1.429 Å while in furan they are 1.354 and 1.440. Thus, furan is less aromatic because there is more "bond fixation" or "diene character". Bird has used the deviation from uniformity of the bond orders in aromatic rings to derive an index of aromaticity, $I_{5\text{ or }6}$.[5] Because

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[1] The heteroatom, N or O, which furnishes the lone pair, will be symbolized in the general case by Z, and the other four ring atoms by A−D. Although most of the compounds contain several heteroatoms, we will use the word heteroatom to refer to the particular heteroatom, N or O, that furnishes the lone pair of electrons to avoid repeating "that furnishes the lone pair" each time.

[2] (a) Cook, M. J.; Linda, P.; Katritzky, A. R. *Adv. Heterocycl. Chem.* **1974**, *17*, 255. (b) Simkin, B. Ya.; Minkin, V. I.; Glukhovtsev, M. N. *Ibid.* **1993**, *56*, 304. (c) Gorelik, M. V. *Uspekhi Khim.* **1990**, *59*, 197 (Eng. 116). (d) Katritzky, A. R.; Karelson, M.; Mallotra, N. *Heterocycles* **1991**, *32*, 127. (e) Jug, K.; Köster, A. M. *J. Phys. Org. Chem.* **1991**, *4*, 163. (f) Zhou, Z. *Int. Rev. Phys. Chem.* **1992**, *11*, 243. (g) Minin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity*; John Wiley and Sons: New York, 1994.

[3] (a) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. (b) Dewar, M. J. S.; Harget, A. J.; Trinajstic, N. *Ibid.* **1969**, *91*, 6321. (c) Dewar, M. J. S.; Trinajstic, N. *Theor. Chim. Acta* **1970**, *17*, 235.

[4] Hess, B. A.; Schaad, L. J.; Holyoke, C. W. *Tetrahedron* **1972**, *28*, 3657.

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Table 1. Selected Data from the Principle Component Analysis of Aromaticity Indices with Scores, t_1, and Loadings, P_1, for Some Heteroaromatic Compounds[a]

	Bird's $I_{(5,6)}$	DRE	HSRE	t_1
benzene	100	3.77	0.065	3.204
pyridine	85.7	3.85	0.058	2.209
pyrazine	88.8	2.85	0.049	2.160
pyrimidine	84.3	3.37	0.050	1.857
pyrazole	73.0		0.055	0.715
imidazole	64.0	2.57	0.042	−0.388
pyrrole	59.0	1.40	0.039	−1.268
isoxazole	47.0			−3.151
oxazole	38.0	2.44	0.007	−4.208
furan	43.0	0.72	0.007	−5.270
P_1	0.386	0.274	0.351	

[a] Data taken from reference 8.

all the bonds in the benzene ring are equivalent, $I_6 = 100$. For furan and pyrrole, I_5 is 43 and 59, respectively.[6]

Based on ab initio MO calculations, Cordell and Boggs have suggested that the lower aromaticity of furan is a result of the contraction of the $2p_z$ orbital of the oxygen atom, which limits the overlap of the lone pair of electrons with the π system of double bonds.[7] Thus furan more closely resembles a diene rather than a closed aromatic system. In pyrrole, however, the nitrogen atom is of optimal size to effectively overlap with the π system so that there is delocalization over the entire system of p_z orbitals.

Recently Katritzky and co-workers have applied principal component analysis to twelve different criteria of aromaticity for sixteen heteroaromatic compounds, including nine five-membered heteroaromatics.[8] The first principal component (the one that gave the best linear relationship among the data) indicated that measures of bond alternation (e.g., Bird's $I_{(5,6)}$ index) and Dewar's (DRE) and Hess and Schaad's resonance energies (HSRE) gave the highest P_1 loadings. That is to say, these indices gave the best correlation with the full data matrix. This first principal component explained 48% of the variance. The various "magnetic criteria" of aromaticity, e.g., molar diamagnetic susceptibility and diamagnetic susceptibility exaltation had very small P_1 loadings but high P_3 loadings (in the third principal component). This indicated that the magnetic indices are "orthogonal" to the "classical aromaticity" indices; i.e., there is a poor correlation between these two classes of indices. It was therefore concluded that these measure different types of aromaticity.[9] The t_1 scores for the heteroaromatic compounds provide an ordering of their relative aromaticities.[10] These scores along with the indices with the highest P_1 loadings are given in Table 1.

As the t_1 scores confirm, the six-membered heteroaromatic compounds appear to be more aromatic than are the five-membered ones. Likewise, among the five-membered heteroaromatics, those with oxygen are less aromatic than those with nitrogen; additional nitrogen atoms tend to increase the aromaticity of both groups of compounds. In later papers, these workers applied PC analysis to an additional 23 heteroaromatic compounds but with a smaller number of aromaticity indices.[11] Thus, they had included 19 of the 20 possible five-membered heteroaromatic compounds; only oxatetrazole was missing. From these studies they concluded that the six-membered heteroaromatic compounds have t_1 scores between +1.2 and +2.7 while for the nitrogen five-membered heteroaromatics (azoles) the t_1 scores range from −1.7 to −0.1. For the oxygen heteroaromatics (oxoles), the t_1 scores lie between −5.1 and −2.8. Exceptions are 2*H*-1,2,3-triazole and 2,5-oxadiazole (compounds that have similar structures) for which the t_1 scores are somewhat higher than for the other members of their families.

Using the experimental bond lengths, Krygowski and Cyranski have calculated geometric indices (similar to Bird's *I* values) and energetic indices for some azoles and oxoles.[12] The energetic indices were derived from the mean value of the bond orders. On the basis of the poor correlation between these two indices, they concluded that they measure different types of aromaticity.

The degree of π delocalization in an aromatic compound is generally considered as providing a measure of its aromaticity. In recent years, the question has been raised as to whether the structure of aromatic compounds, particularly benzene, is the result of the delocalization of the π electrons or is the byproduct of geometric constraints of the σ electron system. Shaik and others have suggested that while the π electrons prefer to be localized (as in the Kekulé structure) it is the σ electrons that prefer bond equalization (as in the D_{6h} structure of benzene).[13] Using a $\sigma-\pi$ separation method, Jug and Köster studied the dependence of the E^σ and E^π as the structures of benzene and several heteroaromatic compounds were distorted from their equilibrium structures.[14] In the case of benzene and the azines, E^π has a maximum while E^σ has a minimum at the equilibrium structure. For five-membered heteroaromatics, including pyrrole and furan, E^π is less for the Kekulé structure than for the equilibrium structure while E^σ is less for the charge-separated structures than for the equilibrium structure. The equilibrium structure is determined by the relative dominance of the σ and π parts. They concluded that although the properties attributed to aromaticity belong to the π delocalization, the origin of the delocalized structure, the geometry, is due to the σ electrons.

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(5) Bird, C. W. *Tetrahedron* **1985**, *41*, 1409; see footnote 26.

(6) Bird has suggested multiplying the I_5 values by 1.235 to agree with the six-membered compounds; however, we will use the original definition as given in footnote 26. Bird, C. W. *Tetrahedron* **1996**, *52*, 9945.

(7) Cordell, F. R.; Boggs, J. E. *J. Mol. Struct. (THEOCHEM)* **1981**, *85*, 163.

(8) Katritzky, A. R.; Barczynski, P.; Musamarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7.

(9) Jug and Köster, ref 2e, have reached a similar conclusion; however, Schleyer et al. have recently questioned the "orthogonality" seen by Katritzky's PC analysis. They found that in a series of five-membered heteroaromatics there was a linear correlation of the stabilization energies and the magnetic susceptibilities; Schleyer, P. von R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337.

(10) The t_1 scores correspond to the distance along the principal component line on which the normalized data points are projected.

(11) (a) Katritzky, A. R.; Feygelman, V.; Musamarra, G.; Barczyski, P.; Szafran, M. *J. Prakt. Chem.* **1990**, *332*, 853. (b) Katritzky, A. R.; Barczynski, P. *J. Prakt. Chem.* **1990**, *332*, 885.

(12) Krygowski, T. M.; Cyranski, M. (a) *Tetrahedron* **1996**, *52*, 1713. (b) *Ibid.* **1996**, *52*, 10255.

(13) (a) Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657. (b) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (c) Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. (d) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Phys. Chem.* **1988**, *92*, 5086. (e) Hiberty, P. C.; Ohanessian, G.; Shaik, S. S.; Flament, J. P. *Pure Appl. Chem.* **1993**, *65*, 35.

(14) Jug, K.; Köster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772.

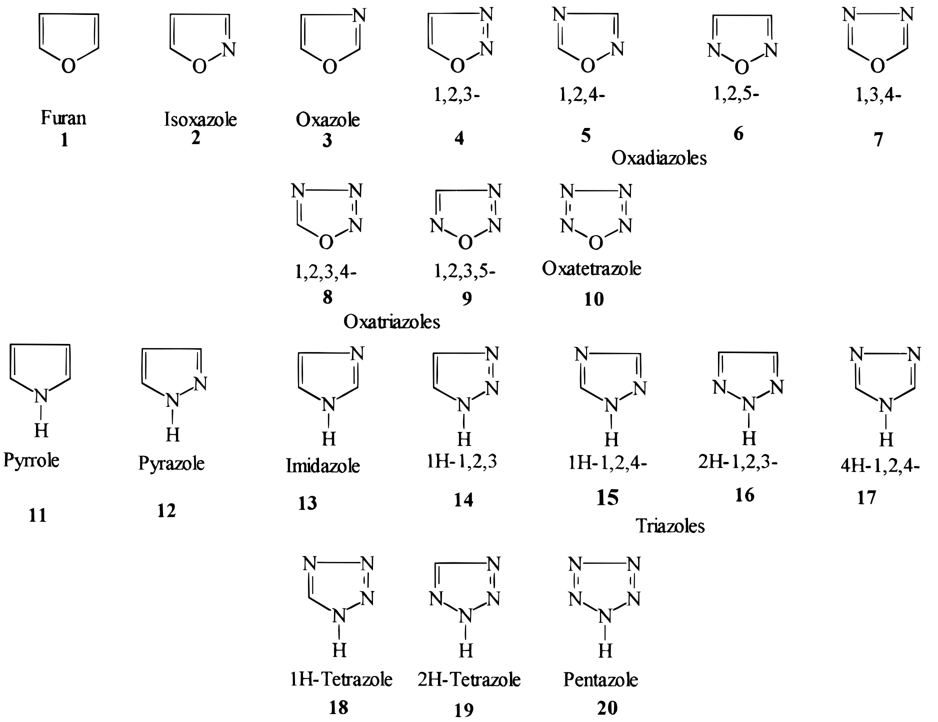

Figure 1. Five-membered heteroaromatic compounds used in this study.

It was of interest to apply the recently developed natural bond orbital (NBO) analysis[15] and natural resonance theory (NRT)[16] to the five-membered heteroaromatic compounds to provide an insight into their relative degree of π delocalization and its relationship to their structure and to compare this with the geometric and energetic indices.[17]

Computational Methods

All the possible five-membered heteroaromatic compounds containing nitrogen (azoles) and/or oxygen (oxoles) were included in the study, **1**−**20** (Figure 1). (Some of the compounds are unknown.) Ab initio SCF wave functions for each compound were calculated using the polarized split-valence 6-31G* basis set and with their geometries fully optimized but with at least C_s symmetry (planar).[18−20] The total Hartree−Fock energies, heats of formation, and selected bond lengths and angles are listed in Table 2. For these compounds, the heats of formation were calculated from the isodesmic methane transfer reactions where the products are ethane, ethene, methylamine, methyleneimine, and/or methanol. The heats of formation were also calculated by the recently developed CBS-4 method, which is reported to give heats of formation within 2 kcal/mol of the experimental values.[21] The heats of formation calculated by the methane transfer reactions and the CBS-4 method for compounds **1**−**20** are given in Table 3. The average deviation of the heats of formation calculated by these two methods is only 3.7 ± 3.5 kcal/mol. Thus, the heats of formation calculated from the methane transfer reactions seem to be quite reasonable.[22] In the Natural Bond Orbital (NBO) analysis, the full density matrix is partitioned into localized one center (core and lone pair) and two center orbitals (the NBOs) describing a Lewis type structure. Carrying out the NBO analysis on the density matrix gives not only the total charge on each atom but also separates the s- and p-electron densities. Electron delocalization is indicated by depleted bonding orbitals and the partial occupancy of "non-Lewis antibonding" NBOs. The percentage of electron density transferred to the antibonding orbitals is designated as "% non-Lewis". The energy of delocalization can be determined by deleting the occupancy of all or some the antibonding orbitals and rediagonalizing the matrix. Deletion of the excited-state orbitals involved in the double bonds of the "classical" Kekulé structure gives the π delocalization energy, $E_\pi^{(\mathrm{deloc})}$. As Streitwieser et al. have reported, in the case of benzene deletion of

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[15] (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735, 1736.

[16] Glendening, E. D., Ph.D. Thesis, University of Wisconsin at Madison, 1991.

[17] In 1994, a reference was given in Chemical Abstracts (*120*, 7601) to a paper in Chinese entitled "Studies on molecular aromaticity by using natural bond orbitals" by L. Shan and L. Li that appeared in *Gaodeng Xuexiao Huaxue Xuehao* **1993**, *14*, 836. However the abstract did not give sufficient details as to how the "pseudo-delocalization energy" from the NBO analysis was made or how the results were interpreted.

[18] (a) Gaussian 92, Revision C, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1992. (b) NBO 4.0, Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 1994.

[19] Full optimization of several of the heteroaromatic compounds that have adjacent lone pair of electrons, e.g., 1,2,3-oxadiazole, still gave the planar, C_s, symmetry. Frequencies were calculated for some, but not all, of the compounds; all of the frequencies were real.

[20] MP2/6-31G* calculations are reported to give geometries closer to the experimental values for the oxoles and azoles than do those at the HF/6-31G* level. (a) Kassimi, N. El-B.; Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem.* **1995**, *99*, 12790. (b) *Ibid.* **1996**, *100*, 8752, and references therein. However, as discussed later, the actual geometry of the oxoles and azoles has little effect upon delocalization.

[21] (a) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299. (b) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. *J. Chem. Phys.* **1996**, *104*, 2598. (c) Gaussian 94, Revision C.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, Raghavachari, J. A. K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

[22] The heats of formation were not corrected for the zero point energies.

Table 2. Energies, Heats of Formation, and Bond Lengths and Angles of the Five-Membered Heteroaromatics[a–c]

	furan **1**	isoxazole **2**[d]	oxazole **3**	pyrrole **11**	pyrazole **12**	imidazole **13**[e]
energy	−228.62521	−244.58850	−244.63297	−208.80785	−224.79349	−224.81444
ΔH_{form}	−2.3 (−8.3)	21.0 (18.8)	−6.9 (−3.7)	32.8 (25.9)	42.1 (43.3)	29.0 (30.6)
d(1−2)	1.3437 (1.362)	1.3606 (1.399)	1.3289 (1.357)	1.3628 (1.370)	1.3300 (1.349)	1.3493 (1.364)
d(2−3)	1.3391 (1.361)	1.2814 (1.309)	1.2686 (1.293)	1.3577 (1.382)	1.3024 (1.331)	1.2890 (1.314)
d(3−4)	1.4409 (1.430)	1.4277 (1.425)	1.3883 (1.395)	1.4266 (1.417)	1.4131 (1.416)	1.3715 (1.382)
d(4−5)	1.3391 (1.361)	1.3398 (1.356)	1.3331 (1.353)	1.3577 (1.382)	1.3630 (1.373)	1.3503 (1.364)
d(1−5)	1.3437 (1.362)	1.3209 (1.344)	1.3549 (1.370)	1.3628 (1.370)	1.3411 (1.359)	1.3718 (1.377)
A−Z−D	107.1 (106.5)	109.4 (108.8)	104.6 (103.9)	109.5 (109.8)	112.8 (113.1)	106.8 (106.9)

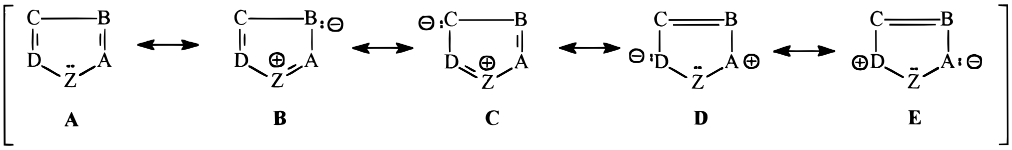
	1,2,3-oxadiazole **4**	1,2,4-oxadiazole **5**	1,2,5-oxadiazole **6**	1,3,4-oxadiazole **7**
energy	−260.56645	−260.60127	−260.54739	−260.61273
ΔH_{form}	43.7	21.8	55.6	14.6
d(1−2)	1.3568	1.3732 (1.418)	1.3329 (1.380)	1.3363 (1.348)
d(2−3)	1.2306	1.2763 (1.303)	1.2751 (1.300)	1.2630 (1.297)
d(3−4)	1.3761	1.3697 (1.380)	1.4287 (1.421)	1.3841 (1.399)
d(4−5)	1.3345	1.2745 (−)	1.2751 (1.300)	1.2630 (1.297)
d(1−5)	1.3206	1.3070 (−)	1.3327 (1.380)	1.3363 (1.348)
A−Z−D	107.6	106.6 (114.2?)	111.6 (110.4)	102.1 (102.0)

	1*H*-1,2,3-triazole **14**[f]	1*H*-1,2,4-triazole **15**[g]	2*H*-1,2,3-triazole **16**[f]	4*H*-1,2,4-triazole **17**
energy	−240.76902	−240.80415	−240.77687	−240.79298
ΔH_{form}	66.3	44.2	61.4	51.3
d(1−2)	1.3177 (1.355)	1.3409 (1.359)	1.3031 (1.323)	1.3555
d(2−3)	1.2665 (1.309)	1.2941 (1.323)	1.3079 (1.346)	1.2809
d(3−4)	1.3555 (1.356)	1.3549 (1.359)	1.4034 (1.405)	1.3649
d(4−5)	1.3563 (1.370)	1.2974 (1.324)	1.3079 (1.346)	1.2809
d(1−5)	1.3429 (1.378)	1.3294 (1.331)	1.3031 (1.323)	1.3555
A−Z−D	111.3	109.9 (110.2)	116.2 (117.1)	104.0

	1,2,3,4-oxatriazole **8**	1,2,3,5-oxatriazole **9**	oxatetrazole **10**	1*H*-tetrazole **18**	2*H*-tetrazole **19**	pentazole **20**
energy	−276.55337	−276.52975	−292.48916	−256.75408	−256.75704	−272.71368
ΔH_{form}	60.7	75.5	101.2	84.4	82.6	110.1
d(1−2)	1.3642	1.3242	1.3242	1.3261 (1.347?)	1.2906 (1.324)	1.2949
d(2−3)	1.2221	1.2302	1.2200	1.2522 (1.283?)	1.2760 (1.284)	1.2613
d(3−4)	1.3631	1.3762	1.3718	1.3412 (1.345?)	1.3438 (1.351)	1.3257
d(4−5)	1.2698	1.2686	1.2200	1.2893 (1.290?)	1.2998 (1.310)	1.2613
d(1−5)	1.3056	1.3341	1.3242	1.3302 (1.351?)	1.3075 (1.334)	1.2949
A−Z−D	104.8	109.7	107.6	108.0 (105.3?)	114.3	112.0

[a] HF/6-31G* energies are given in hartrees and bond lengths in Å. [b] Heats of formation, in kcal/mol, are from isodesmic methane transfer reactions. See text. [c] Figures in parentheses are experimental values; unless otherwise indicated, bond lengths and angles are from *Handbook of Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Pergamon Press: Oxford, 1985. [d] Stiefvater, O. L., *J. Chem. Phys.*, **1975**, *63*, 2560. [e] Christen, D.; Griffiths, J. H.; Sheridan, J. *Z. Naturforsch.* **1981**, *36A*, 1378. [f] Begtrup, M.; Nielsen, C. J.; Nygaard, L.; Samdal, S.; Sjøgren, C. E.; Sorensen, G. O. *Acta Chem. Scand.* **1988**, *42A*, 500. [g] Bolton, K.; Brown, R. D.; Burden, F. R.; Mishra, A. J. *Chem. Commun.* **1971**, 873.

Scheme 1



the excited states for the three Kekulé double bonds gives an $E_{\pi}^{(\text{deloc})}$ of 147 kcal/mol. This value is much higher than the usually assumed value of 36 kcal/mol but is similar to that obtained from the lowest π−π* transition in the UV spectrum of benzene.[23] The values for $E_{\pi}^{(\text{deloc})}$ obtained by deleting the occupancy of the 2−3 and 4−5 π* bonds in each of the heteroaromatic compounds are given in Table 3 along with the total percentage of the electrons in the "antibonding" orbitals; "% non-Lewis".

Natural resonance theory (NRT) furnishes the weight of each of the contributing Lewis structures to the ab initio wave function. Application of NRT to the six-membered aromatic compounds, benzene, pyridine, etc., results in two equivalent structures, each having a resonance weight of 35−46%, in agreement with the Kekulé picture for these compounds. The remaining structures involve charge separation. For the five-membered heteroaromatic compounds, the single principal, or Kekulé, structure **A**, accounts for as much as 70% (Scheme 1).

One might expect that the percentage of the "non-Kekulé" or charge-separated structures, e.g., **B**−**E**, should increase with the aromaticity of these compounds. The total of the resonance weights of all the "non-Kekulé" or delocalized structures is given as "NRT % Delocalization" in Table 3.[24,25] Natural bond orbital analysis and the natural resonance theory calculations (HF/6-31G*) were also made for optimized,

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[23] Glendening, E. D.; Faust, R.; Streitwieser, A.; Volhardt, K. P. C.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, *115*, 10952.

[24] Structures B−E account for 70−83% of the "NRT % Delocalization" while the remainder includes the small contributions from 30 to 50 other possible resonance structures.

[25] The NBO and NRT measures of delocalization for **1**−**20** were also calculated using the geometry obtained by optimization at the MP2/6-31G* level (reference 20). Although the various measures of delocalization were somewhat greater, their ordering was the same as that obtained using the HF/6-31G* geometry. For the purpose of consistency, the HF/6-31G* level calculations are used in this paper.

Table 3. NBO and NRT Results for Five-Membered Heteroaromatics

	one and two heteroatoms						oxadiazoles			
	furan **1**	isoxazole **2**	oxazole **3**	pyrrole **11**	pyrazole **12**	imidazole **13**	1,2,3-oxadiazole **4**	1,2,4-oxadiazole **5**	1,2,5-oxadiazole **6**	1,3,4-oxadiazole **7**
lone pair environment	C−O−C	C−O−N	C−O−C	C−N−C	C−N−N	C−N−C	C−O−N	C−O−N	N−O−N	C−O−C
charge on Z	−0.542	−0.389	−0.553	−0.612	−0.405	−0.636	−0.397	−0.404	−0.217	−0.564
occupancy of p_z orbital	1.7586	1.7569	1.7521	1.6426	1.6068	1.6383	1.7363	1.7485	1.7673	1.7538
n to π^* transfer	0.228	0.230	0.234	0.338	0.373	0.342	0.250	0.238	0.224	0.232
% non-Lewis	1.455	1.528	1.493	1.941	2.140	1.941	1.697	1.579	1.0.512	1.429
NRT % delocalization	27.5	28.8	28.4	36.6	50.6	48.5	31.9	30.1	28.4	27.3
Bird's I_5[a]	43	47	38	59	73	64		39	43	50
I_5^{AM1}[b]	35	48	38	67	74	68	31	49	75	49
I_5'	42	47	38	63	77	60	39	45	51	40
Katritzky's t_1 score[b]	−5.27	−3.15	−4.21	−1.27	0.72	−0.39	−4.20	−3.14	0.14	−2.82
ΔH_{form} (methane transfer)[c]	−2.3	21.0	−6.9	32.8	42.1	29.0	43.7	21.8	55.6	14.6
ΔH_{form} (CBS-4)[d]	−8.3	22.3	−1.9	24.1	42.1	30.8	40.1	26.3	54.5	20.3
hydrogen transfer energy	−20.5	−1.2	−19.9	−11.9	3.2	−11.2	−6.8	−1.2	15.7	−12.8
aromatic energy	13.0	17.2	20.6	20.6	25.1	17.7	24.6	26.9	21.4	26.0
HOMO−LUMO gap (au)	0.4978	0.5197	0.5168	0.5007	0.5280	0.5159	0.5202	0.5559	0.5543	0.5582
$E_\pi^{(\mathrm{deloc})}$ (kcal/mol)	92	94	96	118	130	123	101	101	86	93

	1*H*-1,2,3-triazole **14**	1*H*-1,2,4-triazole **15**	2*H*-1,2,3-triazole **16**	4*H*-1,2,4-triazole **17**	1,2,3,4-oxatriazole **8**	1,2,3,5-oxatriazole **9**	oxa-tetrazole **10**	1*H*-tetrazole **18**	2*H*-tetrazole **19**	pentazole **20**
lone pair environment	C−N−N	C−N−N	N−N−N	C−N−C	C−O−N	N−O−N	N−O−N	C−N−N	N−N−N	N−N−N
charge on Z atom	−0.409	−0.437	−0.185	−0.667	−0.411	−0.224	−0.232	−0.450	−0.194	−0.220
occupancy of p_z orbital	1.5758	1.6070	1.5525	1.6461	1.7399	1.7412	1.7365	1.5946	1.5227	1.5191
n to π^* transfer	0.404	0.374	0.428	0.335	0.246	0.247	0.251	0.386	0.457	0.461
% non-Lewis	2.299	2.126	2.379	1.818	1.639	1.674	1.736	2.148	2.525	2.525
NRT % delocalization	50.8	53.9	44.8	34.6	31.0	31.5	32.6	52.2	68.4	57.6
Bird's I_5	73	81	88	66				72	82	89
I_5^{AM1}	57	75	96	76	46	41	49	69	59	71
I_5'	71	75	94	61	40	43	38	72	84	81
Katritzky's t_1 score	−0.19	0.95	3.07	0.32	−3.05	−3.28		1.13	−0.31	1.62
ΔH_{form} (methane transfer)	66.3	44.2	61.4	51.3	60.7	75.5	101.2	84.4	82.6	110.1
ΔH_{form}(CBS-4)	63.1	47.5	59.9	53.9	59.0	71.3	103.3	82.9	79.2	112.4
hydrogen transfer energy	−1.4	1.7	23.3	−5.2	−1.5	10.4	11.5	2.7	21.3	18.3
aromatic energy	27.5	31.2	37.8	19.4	25.0	21.8	32.0	24.6	34.1	40.1
HOMO−LUMO gap	0.5287	0.5513	0.5397	0.5552	0.5754	0.5609	0.6082	0.5755	0.5606	0.6013
$E_\pi^{(\mathrm{deloc})}$	144	135	142	120	100	95	95	139	158	161

[a] Reference 5. [b] Taken from references 11a,b. [c] From isodesmic methane transfer reactions. [d] CBS-4 values.

but planar, structures of the open-chain analogues of the heteroaromatic compounds, CH═D−Z−A═BH **1a**−**20a**. These results are tabulated in Table 4.

Results and Discussion

A. Geometric Indices. Because Katritzky's analysis indicated that Bird's I_5 index of aromaticity gave the best correlation, an analogous index, I_5', was calculated for each of the compounds using Bird's method and the bond lengths obtained from the ab initio MO calculations.[26] (The A═B and C═D bond lengths obtained from the HF/6-31G* calculations tend to be shorter, i.e., they have more double bond character than the experimental bond lengths.) In most cases these were in fair agreement ($r^2 = 0.92$) with the sixteen I_5 values calculated by Bird for those compounds for which experimental bond lengths were available.[27] As was found for many other indices, the range of the I_5 and I_5' values for the oxoles is much narrower than that found in the azoles; vide infra. In a similar manner, Katritzky used the bond lengths from the semiempirical AM1 MO calculations with Bird's method to derive one of the variables used in the PC analysis. We include these in Table 3 as I_5^{AM1}. There is a poorer correlation of these values with either the I_5 or I_5' values ($r^2 = 0.46$ and 0.58). The I_5, I_5^{AM1}, and I_5' values are included in Table 3. It is significant that all of the I_5, I_5^{AM1}, and I_5' values for the azoles are greater than any of those for the oxoles.

B. Energetic Indices. 1. Heats of Formation. It has been suggested that the heat of formation may be considered as a measure of aromaticity. This is fallacious because the heat of formation depends on the specific elements and, at least in part, upon the particular order of the bonds in the molecule. As the data in Table 3 demonstrates, the heats of formation of the heteroaromatic compounds increase with the successive replacement of CH units by pyridine-like N atoms. Therefore, only the relative stability of isomeric compounds, e.g., **2**/**3**, **4**/**7**, **8**/**9**, **12**/**13**, etc., should be compared. It can be seen that the more stable isomers are not necessarily the more aromatic. For example, in the isomeric pair, pyrazole **12** and imidazole **13**, both the experimental and calculated heats of formation are considerably less for **13**, i.e., **13** is the more stable. However, all of the aromaticity indices indicate that **12** is the more aromatic compound. A similar situation exists for the isomeric isoxazole **2** and

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(26) Bird's I values were calculated according to reference **5**. For the five-membered compounds, $I_5 = 100(1 - V/35)$ where $V = (100/N_o)(\Sigma(N - N_o)^2/5)^{1/2}$. N_o is the arithmetic mean of the bond orders, N. For the I_5' values, bond orders were calculated from the HF/6-31G* bond lengths, R, where $N = a/R^2 - b$, and a and b are constants, depending upon the atoms of the bond.

(27) For **14**, **16**, **19**, and **20**, the experimental bond lengths were for substituted compounds rather than the parent molecules themselves.

Table 4. NBO and NRT Results for the Open Chain Analogues of the Five-Membered Heteroaromatic Compounds, CH═D−Z−A═BH[a]

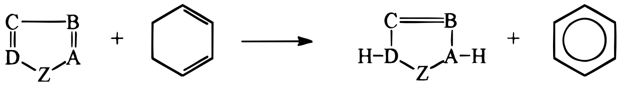
	1a	**2a**	**3a**	**11a**	**12a**	**13a**	**4a**	**5a**	**6a**	**7a**
bond lengths										
Z−A	1.3520	1.3671	1.3378	1.3796	1.3408	1.3650	1.3517	1.3716	1.3644	1.3445
A═B	1.3140	1.2497	1.2415	1.3229	1.2543	1.2552	1.2020	1.2492	1.2498	1.2392
C═D	1.3140	1.3138	1.3126	1.3229	1.3225	1.3208	1.3122	1.2412	1.2498	1.2392
Z−D	1.3520	0.3579	1.3586	1.3796	1.3779	1.3843	1.3638	1.3458	1.3644	1.3445
charge on Z	−0.597	−0.465	−0.597	−0.690	−0.496	−0.705	−0.454	−0.468	−0.336	−0.599
occupancy of p_z orbital	1.8429	1.8698	1.8290	1.7666	1.7749	1.7487	1.8474	1.8553	1.8944	1.8170
n to π^* transfer	0.146	0.122	0.159	0.219	0.211	0.236	0.143	0.135	0.098	0.171
% non-Lewis	0.721	0.621	0.871	0.926	0.944	1.053	0.712	0.767	0.559	1.018
NRT % delocalization	14.8	13.1	17.8	18.9	19.1	21.5	14.9	15.9	12.0	20.8
energy (au)	−229.76071	−245.71726	−245.77029	−209.94226	−225.90961	−225.95633	−261.69736	−261.72853	−261.66934	−261.77751
ΔH_{form} calculated	−3.8 (−3.2)	31.3 (34.5)	−2.0	39.6 (35.7)	60.3 (63.5)	31.0	52.6	33.0	70.0 (71.1)	2.3
HOMO−LUMO gap (au)	0.5093	0.4960	0.5300	0.4688	0.4628	0.4888	0.4969	0.5401	0.5389	0.5719
$E_{\pi}^{(\mathrm{deloc})}$	48.7	38.9	53.9	65.4	60.7	71.5	45.0	43.9	30.1	58.5

	8a	**9a**	**10a**	**18a**	**19a**	**20a**	**14a**	**15a**	**16a**	**17a**
bond lengths										
Z−A	1.3586	1.3540	1.3605	1.3315	1.3234	1.3298	1.3257	1.3444	1.3345	1.3704
A═B	1.2003	1.2021	1.2003	1.2181	1.2207	1.2175	1.2213	1.2530	1.2542	1.2522
C═D	1.2389	1.2494	1.2003	1.2511	1.2531	1.2175	1.3200	1.2544	1.2542	1.2522
Z−D	1.3521	1.3692	1.3605	1.3715	1.3386	1.3298	1.3834	1.3651	1.3345	1.3704
charge on Z	−0.458	−0.330	−0.324	−0.518	−0.318	−0.329	−0.496	−0.514	−0.312	−0.722
occupancy of p_z orbital	1.8360	1.8741	1.8565	1.7300	1.7482	1.7263	1.7385	1.7591	1.7802	1.7350
n to π^* transfer	0.154	0.118	0.135	0.255	0.237	0.258	0.247	0.226	0.206	0.250
% non-Lewis	0.855	0.632	0.706	1.100	1.041	1.053	1.007	1.058	1.001	1.166
NRT % delocalization	17.6	13.3	14.7	22.6	21.3	21.6	20.7	21.7	20.4	23.8
energy (au)	−277.70603	−277.65155	−293.63082	−257.90742	−257.85925	−273.84219	−241.89528	−241.92464	−241.87271	−241.96812
ΔH_{form} calculated	47.4 (52.7)	81.6 (86.0)	94.9 (102.2)	70.7 (78.6)	101.0 (106.1)	111.9	78.1	59.7	92.2 (93.0)	32.4
HOMO−LUMO gap (au)	0.5497	0.5540	0.5748	0.5056	0.4889	0.5067	0.4696	0.4930	0.4756	0.5200
$E_{\pi}^{(\mathrm{deloc})}$	49.4	35.7	40.6	74.1	65.5	71.7	70.1	66.2	57.1	76.7

[a] Values in parentheses are CBS-4 values for the heats of formation. See footnote 33.

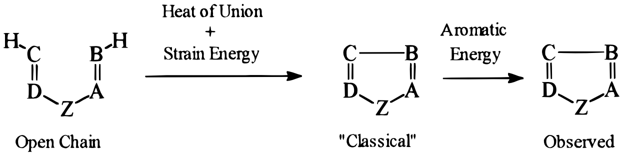
oxazole **3**.[28] Therefore the heats of formation are a measure of thermodynamic stability but not of aromaticity.

2. Hydrogen Transfer and Aromatic Energies. Instead of considering the heats of formation, it is the resonance energy that should be an energetic measure of aromaticity. Wiberg has suggested that the energy of hydrogen transfer between aromatic compounds can be used to give their relative resonance energies.[29] The energy of hydrogen transfer to the five-membered heteroaromatics compounds was calculated by the following general reaction.[30]



The hydrogen transfer energies are included in Table 3. For the azoles, the hydrogen transfer energies agree quite well with the I_5' values ($r^2 = 0.93$) while, as we shall see for other indices, the oxoles give a much poorer agreement ($r^2 = 0.23$). The hydrogen transfer energies for both the oxoles and azoles group themselves according to the environment about the heteroatom; D−Z−A.[31]

Rather than adding hydrogen in a "1,4-manner" to give the dihydroheterocycles, Dewar has derived a set of "aromatic energies" by the "2,3-addition" of hydrogen to give the open chain compounds with release of the "heat of union" and ring strain.[32]



Dewar estimated the heat of union for the C−C bond as 3.5 kcal/mol from the experimental ΔH_{form} of a series of molecules such as the uniting of two molecules of ethene (2 × 12.5) to form butadiene (28.5). For the C−N and N−N bonds, it was necessary to resort to the heats of formation calculated by the AM1 method. By comparing the heats of formation of cyclopentadiene and 1,4-pentadiene, the ring strain in the five-membered rings was estimated as 3.4 kcal/mol. Using the experimental heats of formation for vinyl ether and furan, he calculated an aromatic energy (AE) of 12.1 kcal/mol. From the experimental ΔH_{form} of pyrrole and an estimated value for divinylamine, he arrived at an AE of 22.5 kcal/mol. We have calculated AE's for the azoles and oxoles using the heats of formation of the open chain analogues, CH═D−Z−A═BH **1a**−**20a**. Table 4.[33] We used Dewar's value of 3.5 kcal/mol for the heat of union of the C−C bond but calculated the values for C−N and N−N bonds as 12.3 and 34.9 kcal/mol from the CBS-4 values of 23.4 kcal/mol for $CH_2{=}NH$ and 48.2 and 81.7 kcal/mol for $CH_2{=}CH{-}N{=}CH_2$ and $CH_2{=}N{-}N{=}CH_2$ respectively. The calculated AE's are given in Table 3. The aromatic energies of the azoles tend to parallel the hydrogen transfer energies ($r^2 = 0.86$) but do not cluster as do the hydrogen transfer energies. The agreement for the oxoles is much poorer ($r^2 = 0.22$). It appears that among the energetic indices, the hydrogen transfer energies are only slightly better than the aromatic energies as a measure of relative aromaticities relative to Katritzky's t_1 scores ($r^2 = 0.44$ versus 0.36) while there is slightly better correlation of the I_5' values with the aromatic energies ($r^2 = 0.34$ versus 0.31). Again the poor overall correlation of the energetic indices with the I_5' values is primarily due to the oxoles ($r^2 < 0.23$) while the azoles give a much better correlation ($r^2 > 0.81$). The poor correlation between the geometric (I_5 and I_5' values) and the energetic indices (hydrogen transfer and aromatic energies) appear to be similar to that found by Krygowski and Cyranski.[12] Contrary to what is found for most other indices, the hydrogen transfer energies and the aromatic energies for the oxoles and azoles overlap, and the range of values for each family are similar.

3. HOMO−LUMO Gap. It has been suggested that the HOMO−LUMO energy separation may serve as an index of aromaticity because a larger energy gap should increase the tendency to "retain its type"; that is, to retain aromaticity by substitution rather than addition reactions.[34] There is, however, little correlation of the HOMO−LUMO energy gap with any of the geometric, energetic, or delocalization measures; $r^2 < 0.38$.

C. Delocalization Indices. Every compound, **1**−**20**, contains 36 electrons. In the NBO analysis, about 98% of the electrons are assigned to the core orbitals, the two center bonds, or the lone pairs in the Lewis structure. The remaining 1.62 to 2.86% ("% non-Lewis") is delocalized in the "non-Lewis" antibonding orbitals. About 30% of this delocalization is due to the transfer of π electrons from the two double bonds of the Lewis structure to the two π^* orbitals, "π to π^*".[35] For the oxoles, the transfer of electron density from the lone pair in the p_z orbital of the oxygen atom to the two π^* orbitals, "n to π^*", accounts for about 40% of the total delocalization, while for the azoles this is about 50%.[36] Thus the two π^* orbitals are assigned about 70−80% of the delocalized electron density, this having come from the two π bonds and the lone pair of the heteroatom. The remaining 20−30% is due to small contributions from electron transfer from the various σ bonds to σ^* orbitals. Table 3 includes the "% non-Lewis" or total percent of electron transfer to the

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[28] Calculations at HF/6-31G* level for the model compounds $Z{-}CH{=}NH$ and $Z{-}N{=}CH_2$ (Z = HO and NH_2), where the bond angles and distances are kept equal, indicate that the Z−C═N bonding, as in oxazole and imidazole, has the lower heat of formation (i.e., is more stable). Also the π electrons in the Z−CH═NH system are more delocalized. This is opposite to what is found for the cyclic compounds in which there is greater π delocalization for those with the Z−N═C bonding.

[29] Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178.

[30] Because some of the dihydro compounds can exist as geometric or conformational isomers, the isomer with the lower energy was used to calculate the hydrogen transfer energy.

[31] The energy of transfer of 2 mol of hydrogen to the heteroaromatics to give the tetrahydro compounds was also calculated. However, these energies gave a poorer correlation with other indices than did the hydrogen transfer energies from the dihydroheteraromatics. The heats of formation of the tetrahydro products more closely correlate with the ΔH_{form} of the heteroaromatics themselves.

[32] Dewar, M. J. S.; Holder, A. J. *Heterocycles* **1989**, *28*, 1135.

[33] The ΔH_{form} of 10 of the open-chain analogues were also calculated by the CBS-4 ab initio method, and the values were an average of 4.3 ± 2.3 kcal/mol higher than those obtained from the HF energies (Table 4).

[34] (a) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423. (b) Zhou, Z.; Parr, R. G.; Garst, J. F. *Tetrahedron Lett.* **1988**, *29*, 4843. (c) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371.

[35] In the five-membered heteroaromatic compounds, the electron density from the $\pi_{(2-3)}$ orbital is transferred to the $\pi^*_{(4-5)}$ orbital and conversely from the $\pi_{(4-5)}$ orbital to the $\pi^*_{(2-3)}$.

[36] We define the magnitude of n to π^* electron transfer as the amount of electron density returned to the lone pair on heteroatom on deletion of the excited-state orbitals involved in the two double bonds of the classical Kekulé structure.

Table 5. Delocalization Data for the Heteroaromatics Organized According to Amount of n to π* Transfer in the Azoles

Azoles

	C=D	D−N−A	A=B	n to π* transfer	$E_\pi^{(\mathrm{deloc})}$	% non-Lewis	NRT % delocalization	charge	H transfer energy	aromatic energy	t_1 score
4*H*-1,2,4-triazole **17**	N=C	C−N−C	C=N	0.335	120	1.82	34.6	−0.667	−5.2	19.4	0.32
pyrrole **11**	C=C	C−N−C	C=C	0.338	118	1.94	36.6	−0.612	−11.9	20.6	−1.27
imidazole **13**	C=C	C−N−C	C=N	0.342	123	1.94	48.5	−0.636	−11.2	17.7	−0.39
pyrazole **12**	C=C	C−N−N	N=C	0.372	130	2.14	50.6	−0.405	3.2	25.1	0.72
1*H*-1,2,4-triazole **15**	N=C	C−N−N	N=C	0.375	135	2.13	52.9	−0.437	1.7	31.2	0.95
1*H*-tetrazole **18**	N=C	C−N−N	N=N	0.386	139	2.15	52.2	−0.450	2.7	24.6	1.13
1*H*-1,2,3-triazole **14**	C=C	C−N−N	N=N	0.404	144	2.30	50.8	−0.409	−1.4	27.5	−0.19
2*H*-1,2,3-triazole **16**	C=N	N−N−N	N=C	0.428	142	2.38	44.8	−0.185	16.8	37.8	3.07
2*H*-tetrazole **19**	C=N	N−N−N	N=N	0.457	158	2.58	68.5	−0.194	10.9	34.1	−0.31
pentazole **20**	N=N	N−N−N	N=N	0.461	161	2.53	57.6	−0.220	10.3	40.1	1.62
range of values				0.126	43	0.76	33.9	0.482	28.1	22.4	4.34

Oxoles

	C=D	D−O−A	A=B	n to π* transfer	$E_\pi^{(\mathrm{deloc})}$	% non-Lewis	NRT % delocalization	charge	H transfer energy	aromatic energy	t_1 score
1,3,4-oxadiazole **7**	N=C	C−O−C	C=N	0.232	93	1.43	27.3	−0.564	−12.8	26.0	−2.82
furan **1**	C=C	C−O−C	C=C	0.228	92	1.46	27.5	−0.542	−20.5	13.0	−5.27
oxazole **3**	C=C	C−O−C	C=N	0.234	96	1.49	28.4	−0.553	−19.9	20.6	−4.21
isoxazole **2**	C=C	C−O−N	N=C	0.230	94	1.53	28.8	−0.389	−1.2	17.2	−3.15
1,2,4-oxadiazole **5**	N=C	C−O−N	N=C	0.238	100	1.58	30.1	−0.404	−2.3	26.9	−3.14
1,2,3,4-oxatriazole **8**	N=C	C−O−N	N=N	0.246	100	1.64	31.0	−0.411	−1.5	25.0	−3.05
1,2,3-oxadiazole **4**	C=C	C−O−N	N=N	0.250	101	1.70	31.9	−0.397	−6.8	24.6	−4.20
1,2,5-oxadiazole **6**	C=N	N−O−N	N=C	0.224	86	1.51	28.4	−0.217	15.3	21.4	0.14
1,2,3,5-oxatriazole **9**	C=N	N−O−N	N=N	0.247	95	1.67	31.5	−0.224	9.8	21.8	−3.28
oxatetrazole **10**	N=N	N−O−N	N=N	0.251	95	1.74	32.6	−0.232	10.4	32.0	
range of values				0.027	15	0.31	5.3	0.347	35.8	19.0	5.41

antibonding orbitals, and the specific amount of electron density transferred from the lone pair of the heteroatom to the two π* orbitals, "n to π*".

The relative amount of electron transfer from the two π bonds to the π* orbitals is about the same for each pair of nitrogen and oxygen compounds with the same structure, e.g., **1** and **11**, **2** and **12**, etc.[37] Therefore the amount of electron transfer from π to π* depends primarily upon the A=B−C=D structure and is almost independent of the heteroatom. The situation is quite different for the transfer of electron density from the lone pair of the heteroatom to the π* orbitals. The range of values for the n to π* transfer in the azoles is 5.5 times greater than that in the oxoles. (Also the range of the other measures of delocalization, $E_\pi^{(\mathrm{deloc})}$, % non-Lewis, and NRT % delocalization, is much larger for the azoles.) For the azoles the other measures of delocalization, e.g., $E_\pi^{(\mathrm{deloc})}$, % non-Lewis, etc., correlate with the transfer of electron density from the nitrogen lone pair to the π* orbitals; $r^2 > 0.95$. In the oxoles, however, the other measures of delocalization do not agree as well with the n to π* transfer; $r^2 > 0.82$. Also contrary to what is found for the azoles, the presence of two adjacent nitrogen atoms decreases, rather than increases, the transfer of electrons from the oxygen p_z orbital to the π system. This is particularly true for 1,2,5-oxadiazole **6** where the n to π* transfer is actually the lowest of any oxole although some other indices, such as the t_1 score and hydrogen transfer energy, indicate a high aromaticity. For the various measures of delocalization, e.g., $E_\pi^{(\mathrm{deloc})}$, NRT % delocalization, % non-Lewis, n to π*, etc., the values for the oxoles have a much small range than found for the azoles. Because the range of the values for π to π* transfer is about equal in the two families while the range of the n to π* transfer is about five times smaller for the oxoles; it appears that it is the greater electronegativity of the oxygen atom that is responsible for reducing the ability of the lone pair in the p_z orbital of the heteroatom to be delocalized into the π system of the other atoms of the ring. Thus, as suggested by Cordell and Boggs,[7] it is the electronegativity of the heteroatom that has the major effect in defining the aromaticity of the five-membered heteroaromatic compounds.

D. Comparison of the Aromaticity−Delocalization Indices. Examination of the data in Table 3 indicates that for both heteroatom families the measures of delocalization, $E_\pi^{(\mathrm{deloc})}$, NRT % delocalization, % non-Lewis occupancy, and n to π* transfer, depend on the environment about the heteroatom. The identity of the atoms, C or N, next to the heteroatom, particularly in the azoles, separates the charge on the heteroatom along with the hydrogen transfer energies. These quantities are essentially constant for a given pair of atoms next to the heteroatom.[38] In Table 5 these quantities, along with Katritzky's t_1 scores, are organized for each heteroatom, first according to the environment about the lone pair and then, within each set, by their n to π* transfer values. The order is the same as that for the $E_\pi^{(\mathrm{deloc})}$ values.

It is important to note in Table 5 that the structures of the oxygen and nitrogen compounds are in exactly the

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(37) A plot of π to π* electron transfer for oxygen versus nitrogen compounds has a slope of 1.0. Therefore the range of π to π* transfer is the same for both families of compounds while the amount of π to π* electron transfer for each oxygen compound is 0.032 less than in the analogous nitrogen compound.

(38) The NBO analysis is able to separate the occupancy of the 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals and, because the heterocycles are planar, the separate σ and π charges on each atom can be calculated. As Table 3 indicates, the occupancy of the p_z orbital of the heteroatom, or π charge, is fairly constant but it is the σ charge, particularly the p_x and p_y charges, that is primarily responsible for the grouping of the total charges. These in turn depend on the electronegativity of the adjacent atoms, A and D, which are either nitrogen or carbon. In the oxoles, the σ charges on A and D are consistently 0.16 ± 0.02 more positive than in the analogous azoles, but there is little difference for atoms B and C. The same situation exists for the open chain analogues, **1a**−**20a**, even though there is no B−C bond. The electronegativity of Z shifts the σ charges on A and D by a constant amount, but the variation in charges depends on the particular atoms of the A=B−C=D system.

same order when they are arranged according to the environment about the heteroatom and the amount of n to π^* transfer. Thus, as was found for the π to π^* transfer, the particular arrangement of the atoms within the ring has the same relative effect on the indices in either family. There is a somewhat poorer correlation of the delocalization indices with Katritzky's t_1 scores.[39] For the azoles, increasing the number of pyridine-like nitrogen atoms adjacent to the heteroatom increases the delocalization as indicated by $E_\pi^{(\mathrm{deloc})}$, NRT % delocalization, % non-Lewis, and n to π^* transfer. There is a good correlation ($r^2 = 0.96$) between the $E_\pi^{(\mathrm{deloc})}$ values and the n to π^* transfer. Also the correlation with the aromatic and hydrogen transfer energies, % non-Lewis, and I_5' values is greater than 0.84. As noted before, in the case of the oxoles, the range of values for both the $E_\pi^{(\mathrm{deloc})}$, the NRT % delocalization, % non-Lewis, and n to π^* transfer is much narrower than is found for the hydrogen transfer energies and t_1 scores. Contrary to what is found for the azoles, the presence of nitrogen atoms on both sides of the heteroatom in the oxoles decreases the measures of delocalization, particularly the amount of n to π^* transfer and $E_\pi^{(\mathrm{deloc})}$, relative to when only one nitrogen atom is next to the oxygen atom.

With the exception of those oxoles with two adjacent nitrogen atoms, within each family there is fair agreement among the n to π^* transfer, $E_\pi^{(\mathrm{deloc})}$, and the NRT % delocalization; $r^2 > 0.78$. The aromatic energies agree best with the measures of delocalization while the hydrogen transfer energies agree better with Katritzky's t_1 scores. One must therefore decide whether it is the hydrogen transfer energies or the n to π^* transfer that is the better measure of "aromaticity". The narrow range of the measures of delocalization found in the oxoles is not reflected in the hydrogen transfer energies, the aromatic energies, or the t_1 scores. Thus, we conclude that the amount of n to π^* transfer should be a more valid measure of delocalization, and the data in Table 5 were organized accordingly.

E. Rational for the Ordering of Delocalization. If we assume that the amount of n to π^* electron transfer is the best measure of delocalization, it is necessary to examine what factors are responsible for any anomalies in the t_1 scores, hydrogen transfer and aromatic energies, and/or other measures of delocalization of some of the compounds. In general there is quite good agreement between the various geometric, energetic, and delocalization indices for the azoles; $r^2 > 0.83$. For the oxoles there is much poorer agreement which may be due in part to the narrower range of values for the delocalization indices. In Table 5, the most noticeable deviation is for 1,2,5-oxadiazole **6** where the environment about the heteroatom, N−O−N, predicts that it should have a higher delocalization. In contrast to its having the highest hydrogen transfer energy, I_5', and t_1 score among the oxoles, it has the lowest values for n to π^* transfer and $E_\pi^{(\mathrm{deloc})}$. The % non-Lewis and NRT % delocalization are also much lower than found for either **9** or **10**, the other oxoles having the N−O−N system. Also for its nitrogen analogue, 2*H*-1,2,3-triazole **16**, the values of the $E_\pi^{(\mathrm{deloc})}$ and NRT % delocalization are somewhat lower than expected while the n to π^* transfer and % non-Lewis values are in the proper order relative to its hydrogen transfer and aromatic energies, and its high t_1 score.[40] These two compounds have the lowest bond polarizations in each family because there is a smaller difference in electronegativity between the atoms in the C═N−Z−N═C system.[41] For this reason, the charge on the heteroatom in compounds **6** and **16** is the lowest in each family. Compound **6** also has the lowest π charge on oxygen of the oxoles; however, in the azoles both **19** and **20** have lower π charges on nitrogen than does **16**. In compounds **6** and **16**, there is less of a difference in σ charges on the heteroatom and the adjacent N atoms, but the π charge on oxygen is low because there is little transfer of π electron density to the diene system. In **16**, there is more transfer of π electron density and thus a greater positive π charge on the heteroatom. We conclude from the delocalization data that, in spite the high "aromaticity" indicated by the t_1 score, the I_5' value, and hydrogen transfer energy, 1,2,5-oxadiazole **6** has the lower aromaticity indicated by the low n to π^* transfer of electron density, $E_\pi^{(\mathrm{deloc})}$, and NRT % delocalization.[42]

These anomalies appear to be a result of the arrangement of atoms in the A═B−C═D system and their interaction with the heteroatom and not the particular geometry (bond lengths) whose effect on delocalization is rather minimal. Calculations using a fixed geometry (that of furan or pyrrole) for the isomeric oxadiazoles **4**−**7**, or triazoles **14**−**17**, give the same order, although of lower magnitude, for n to π^* transfer, $E_\pi^{(\mathrm{deloc})}$, and % non-Lewis as found for the optimized structures. However if the A═B and C═D bond lengths of **1**, **6**, **7**, **10**, **11**, **16**, **17**, or **20** (those having C_{2v} symmetry) are increased slightly and the geometry reoptimized (which results in shorter Z−A, Z−D, and B−C bonds) the measures of delocalization, e.g., n to π^* transfer, % non-Lewis, and $E_\pi^{(\mathrm{deloc})}$, are increased although the stability decreases. The lowering of the bond order of the formal double bonds and increasing the bond order of the formal single bonds increase the delocalization; i.e., less bond alternation increases the delocalization. This is consistent with recent work by Katritzky and co-workers. From calculations using a "self-consistent reaction field" model with the AM1 and ab initio MO programs, they found that increasing the dielectric constant of the medium surrounding the azoles **11**, **12**, **13**, and **15** produces a structure with shorter formal single bonds (Z−A, Z−D, and B−C) while the formal double bonds (A═B and C═D) are lengthened.[43] This decrease in bond alternation results in an increase in the aromaticity as indicated by

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[39] Any linear correlation between the indices should be coincidental although a correlation in their relative order may be expected. For a number of indices there are however surprisingly good correlations. The correlation coefficients, r^2, for the linear relationships between the charge on the heteroatom, hydrogen transfer energy and Katritzky's t_1 value for the oxoles versus the azoles having the similar structure are 0.996, 0.994, and 0.897, respectively.

[40] Katritzky has noted that the t_1 scores for **6** and **16** were considerably higher than expected. The high t_1 score found for **6** was due at least in part to a large contribution of the I_5^{AM1} value which is considerably greater that that of I_5 or I_5'. Table 3 and ref 11b.

[41] The average value of the A−Z and D−Z bond dipoles for the oxygen and nitrogen compounds having the same structure are in the same order and have a correlation coefficient of $r^2 = 0.954$. Again it is the arrangement of the A═B−C═D system that defines the electron distribution.

[42] Based on the ${}^1J({}^{13}\mathrm{C},{}^{13}\mathrm{C})$ coupling constants in a series of oxoles and azoles, Witanowski and Biedrzycha have arrived at an ordering of their aromaticity as **6** < **3** < **1** < **2** and **13** < **11** < **14** < **12** < **16**. Thus these magnetic criteria agree that within the oxoles, **6** has a low aromaticity, but in the azoles, **16** is much more aromatic. Witanowski, M.; Biedrzycha, *Z. Magn. Reson. Chem.* **1994**, *32*, 62.

[43] Katritzky, A. R.; Karelson, M.; Wells, A. P. *J. Org. Chem.* **1996**, *61*, 1619.

Bird's I_5 values, which are a measure of bond order uniformity. These results agree with the conclusions of Jug and Köster that the geometry of the five-membered heteroaromatics depends on a balance between the σ and π structures.[14] When the σ structure is perturbed by decreasing the bond alternation, the total energy of the system is increased, but the π structure, which is responsible for the delocalization, becomes more stabilized. Decreasing the bond alternation results in a greater contribution from the charge separated (delocalized) structures.[44] However, the major differences in the delocalization are due not to the geometry of the molecule but rather the arrangement of the atoms in the azoles and oxoles which defines the relative order of delocalization.

For the 1,2,3,5-oxatriazole **9**/2*H*-tetrazole **19** pair, the t_1 scores suggest a lower delocalization than that indicated by the NBO measures of delocalization or the hydrogen transfer or aromatic energies. It is the t_1 scores for the **9**/**19** pair that are obviously out of line and are too negative as compared to the other compounds. On the other hand, it appears that the t_1 scores for the 1,3,4-oxadiazole **7**/4*H*-1,2,4-triazole **17** pair are somewhat too positive. In contrast to the Z—N=C system in **6** and **16**, the Z—C=N system in the **7**/**17** pair has the largest charge separation, bond polarization, of any of the compounds. The presence of carbon atoms adjacent to the heteroatom increases the charge separation in the A—Z—D system and is responsible for the C—Z—C < C—Z—N < N—Z—N order of increasing delocalization.

Conclusions

According to the geometric indices and the various measures of delocalization obtained from the natural bond orbital analysis and natural resonance theory, all the oxoles are less aromatic, or delocalized, than any of the azoles. With the exception of 1,2,5-oxadiazole **6**, this is also true for the t_1 scores obtained by Katritzky's principal component analysis of a series of aromaticity indices. For the energetic indices, however, there is considerable overlap of the hydrogen transfer and aromatic energies for the oxoles and azoles. Thus, the amount of π delocalization is considered to be a better indication of their aromaticity.

For the azoles, the amount of transfer of electrons from the lone pair in the π orbital of the heteroatom to the rest of the π system of the ring (designated as n to π^* transfer) agrees well with the "energy of delocalization", $E_\pi^{(\mathrm{deloc})}$, and percentage of the electrons assigned to non-Lewis structures, % non-Lewis; ($r^2 > 0.96$). The agreement with the aromatic and hydrogen transfer energies are somewhat poorer ($r^2 > 0.82$). The n to π^* transfer, $E_\pi^{(\mathrm{deloc})}$, and % non-Lewis for the azoles generally follow the t_1 scores obtained by Katritzky. The most noticeable deviations are for 2*H*-1,2,3-triazole **16**, where the t_1 score seems too large, while those of 1*H*-1,2,3-triazole **14** and 2*H*-tetrazole **19** seem too small. The delocalization indices of the azoles group themselves according to the environment about the heteroatom: C—N—C, **17** < **11** < **13**; C—N—N, **12** < **15** < **18** < **14**; and N—N—N, **16** < **19** < **20**. The pyridine-like nitrogen atoms adjacent to the heteroatom increase the delocalization, presumably by reducing the charge separation due to the smaller differences in electronegativity than when carbon atoms are adjacent to the heteroatom.

The oxoles are not only less delocalized but also their degree of delocalization is fairly insensitive to the structure. The range of values for the various indices of delocalization, in addition to the geometric index, I_5, is much narrower for the oxoles than is found for the azoles. Both of these effects appears to be due to the oxygen atom being too electronegative to allow the lone pair of electrons in the p_z orbital to interact effectively with the rest of the π electron system of the ring. Those oxoles in which two nitrogen atoms flank the oxygen atom appear to be less delocalized than the other oxoles; opposite to what is found for the azoles. This is particularly true for 1,2,5-oxadiazole **6** which has the lowest π delocalization of any oxole. When grouped according to the environment about the heteroatom, the order of n to π^* transfer is the same for the azoles and oxoles that have the same arrangement of the other atoms of the ring. Therefore, the particular arrangement of the atoms has a similar ordering effect on the indices within both family of compounds.

Forcing the five-membered heteroaromatic compounds to have less bond length alternation increases the delocalization of the π electrons, although the total energies are raised slightly. This supports the view of Jug and Köster that when the σ structure of such compounds is distorted by decreasing the bond alternation, the π structure becomes more delocalized, or stabilized. Thus the σ framework, whose structure depends on the identity of the five atoms of the ring, defines the π delocalization.

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[44] Not surprisingly, when a regular pentagonal geometry is used for furan, no bond length alternation, the energy is 9 kcal/mol higher but the n to π^* (0.234), $E_\pi^{(\mathrm{deloc})}$ (100.3 kcal/mol), NRT % delocalization (30.6%), and % non-Lewis (1.626%) are considerably greater than for the optimized structure.