Analysis of the ESR Hyperfine Coupling in Mono- and Bicyclic Azine Radical Anions by Means of Calculated Spin Densities

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Ab initio studies of the spin density in mono- and bicyclic N hetero-aromatic compounds, and naphthalene are reported. The wave functions were constructed from both minimal and double zeta bases in all cases, and both RHF and UHF formalisms were used together with quartet annihilation. The statistical variations in correlations between spin population density and hyperfine coupling are investigated. After annihilation the MB and DZ wave functions become relatively similar, but do lead to some differences in assignment for the smaller values of a_H. In general the agreement between a_H/a_N and calculated density is improved by two term rather than one term expressions, but there are still a number of experimental hyperfine couplings awaited.

Introduction

Treatment of aromatic and heteroaromatic molecules in solvents, such as 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF), with alkali metals has long been known [1, 2] to yield brightly coloured anion radicals.

$$Ar + M \rightarrow Ar^{\cdot -} + M^{+} \; (M = Li, Na, K).$$

Electrolytic methods, where the radicals are formed on the surface of a pool of mercury (the reducing cathodic electrode) are also used for such radical anion production, and these methods have the advantage that (i) the anion can be produced continuously in an ESR spectrometer cavity, (ii) there is no metallic counter ion (M^+), and hence no additional interaction [2].

In the case of most mono- and bicyclic aromatic radical ions and their aza-analogues, with up to seven non-equivalent hyperfine couplings to hydrogen (a_H, $I = \frac{1}{2}$) and possibly several non-equivalent nitrogen atoms (a_N, $I = 1$), problems of analysis of the complex spectra frequently occur; usually not all the theoretical lines are resolved [2], and even when all are observed there is still the question of assignment of coupling to the appropriate nuclei. The main methods [2] appear to be: (i) extraction of the ^{14}N coupling (1:1:1 triplets) for each N-nucleus; (ii) selective deuteration at known positions, so that ^2H ($I = 1$) splitting with $\gamma_D/\gamma_H = 0.15351$ replaces ^1H splitting [4]; (iii) a study of Me substituted examples of the complex case, with either the assumption that the replacement of H by Me is a weak perturbation, or (iv) attempt to account for the perturbation by the Me group [5]; (v) a study of ^1H NMR line broadening in mixtures of the radical-ion and the neutral molecule, where the broadening is selective and is directly related to the values of a_H [6]. Finally, (vi), by far the most common procedure is to use direct correlations of calculated spin density with hyperfine coupling [2, 4].

For coupling to hydrogen (a_H) in planar aromatic species, the spin density at the H nucleus, which lies in the σ-plane is found to be well represented by π-spin density of the associated C atom [2b]. This relationship (Eq. (1)), usually attributed to McConnell [1, 2], is historically fortunate, since it enabled progress to be made in hyperfine coupling for aromatics at a time when π-electron only calculations were possible

$$a_H = Q_{CH}\, \varrho_C^{\pi}. \qquad (1)$$

Extension of the McConnell relationship to include non-neighbour centres, or contributions from all electrons, does not seem to have provided much additional information; however, this is not the case with hyperfine coupling to nitrogen (a_N). Here the corresponding relationship with ϱ_N^{π} was found to be inadequate, and was extended to include contributions from adjacent atoms X (X = C, N) [2c, 8]:

$$a_N = Q_N\, \varrho_N^{\pi} + \Sigma\, Q_{XN}\, \varrho_X^{\pi}. \qquad (2)$$

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Theoretical justification of these Equations can be found by appropriate simplifications of rigorous equations in a Hartree-Fock framework [9a], but many difficulties remain. Thus, the values of Q_{CH}, Q_{NN}, Q_N vary with the method of calculation of spin density [9b]. For the present and related types of aromatic radicals, numerous empirical [4, 10, 11] and semi-empirical [12–16] electronic wave functions have been utilised. For the $(2N+1)$ electron molecule, obtained by addition of an electron to the $2N$ closed shell system, in principle a $^2\pi$ or $^2\Sigma$ state may be the most stable. For the present series, it seems that $^2\pi$ can be anticipated [2].

In the Hartree-Fock method, and derived semi-empirical methods, the $(2N+1)\,e$ case can be solved either (a) in the Restricted Hartree-Fock (RHF) method, in which all orbitals (Φ_i) except one are doubly occupied:

$$\Psi_{RHF} = |\Phi_0 \bar{\Phi}_0 \ldots \Phi_{N-1} \bar{\Phi}_{N-1} \ldots \Phi_N| \,, \qquad (3)$$

or (b) in the Unrestricted Hartree-Fock method (UHF), with separate orbitals for different spins:

$$\Psi_{UHF} = |\Phi_0 \bar{\Phi}'_0 \ldots \Phi_{N-1} \bar{\Phi}'_{N-1} \ldots \Phi_N| \,. \qquad (4)$$

There are advantages to both methods. The RHF method yields a wave function (Ψ_{RHF}) which is a genuine eigenfuntion of the spin state $\langle S^2 \rangle$ and $\langle S_z \rangle$, whereas the UHF does not give correct values to $\langle S^2 \rangle$ in the general case; this is a direct result of all electrons except one being spin paired in the RHF case. The UHF wave function is said to contain higher spin state contamination [19–21], and procedures are available to eliminate the lowest contaminating component. The annihilation process in the UHF doublet case removes quartet contamination [20, 21]. In some instances, negative spin densities are obtained or inferred from experiment [2]; these can only be obtained from UHF wave functions owing to the dependence on Ψ^2. In cases where degeneracy, or low lying virtual orbitals occur, configuration interaction [22] may be necessary. In the present series (benzene and 1,3,5-triazine excepted) this is not likely to occur.

The present paper is the first *ab initio* study of the azine radical anions (**1**–**18**) and covers several of the theoretical models given above, and with two different basis sets: minimal (atomic orbital) (MB), and double zeta (DZ). All of the molecules were studied at the same geometry as the corresponding neutral compound (where known). For aromatic species this may not be too much of a restriction. For more flexible open chain molecules, geometry optimisation seems to be necessary [9b, 23].

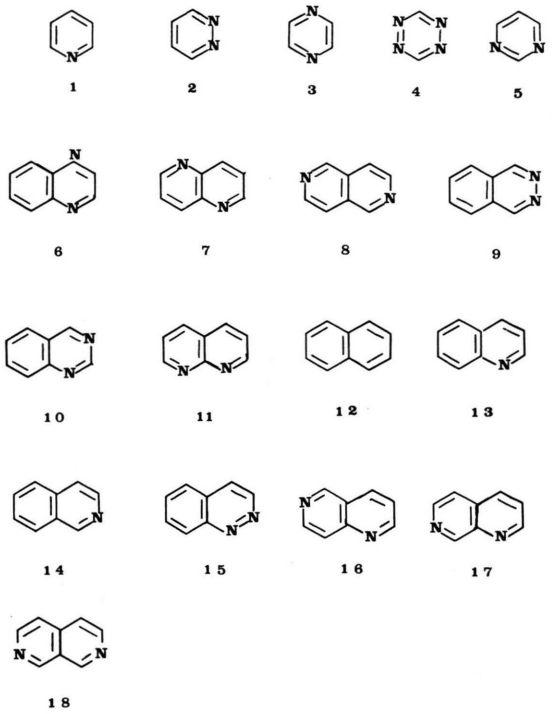
Computational Methods

a) Theoretical Models

The molecules studied were the mono-cyclic azines (**1**–**5**) and their bicyclic analogs (**6**–**18**) including all molecules where ESR data were known for the radical anions. The studies went through a series of stages of refinement: – (i) a minimal basis set (7s 3p/3s) for (C, N/H) and contracted to [2s 1p/1s] was used as previously [24]; (ii) the process was repeated with a (9s 5p/4s) Dunning double zeta basis [27]. The RHF-SCF wave function was obtained for the neutral molecule. The lowest RHF doublet state was computed at the same geometry, then allowed to take up a UHF from, and finally the lowest quartet contaminating state was annihilated from the UHF doublet state. These procedures were followed for all compounds and for both basis sets. The principal energy and spin density results and the value of $\langle S^2 \rangle$ before and after annihilation are shown in Table 1.

b) Molecular Structures

The principal experimental results utilised were: – (i) microwave structures for pyridine (**1**) [28] and pyridazine (**2**) [29]; (ii) electron diffraction for pyrazine (**3**) [30]; (iii) UV-rotational analysis for (**3**) [31] and 1,2,4,5-tetrazine (**4**) [32]; (iv) combined x-ray crystal structure and nematic phase ^{1}H NMR for pyrimidine (**5**) [33, 34], quinoxaline (**6**) [35, 36], 1,5-diazanaphthalene (**7**) [37], and 2,6-diazanaphthalene (**8**) [37]; (v) x-ray diffraction only for phthalazine (**9**) [38], quinazoline (**10**) [39] and 1,8-diazanaphthalene (**11**) [40]; (vi) neutron diffraction for naphthalene (**12**) [41]. There is no experimental data for the remaining molecules, so that we utilised the known consistency of bond lengths in heterocycles [42–45] to construct the cartezian system. Quinoline (**13**) and isoquinoline (**14**) were constructed from **1** and **12**, cinnoline (**15**) from **2** and **12**, and the remaining 1,6- 1,7- and 2,7-diazanaphthalenes (**16**–**18**) from **1**, **12**, **13** and **14**. We note in passing, that the diazanaphthalenes, with one N atom in each ring are alternatively known as naphthyridines.



Results

a) Comparison of Total Energies with Earlier Work

There is an extensive literature on *ab initio* studies of monocyclic azines, and this is cited in Table 1; in contrast, with the exception of naphthalene (**12**) there are no *ab initio* studies of the bicyclic systems, although there are some semi-empirical ones for some members of the series [55, 56]. In general the present results represent the lowest energies yet obtained amongst either minimal bases set or double zeta basis calculations. In the case of the monocyclic azines (**2**, **4**, **5**), the present work gave lower energies than previous studies which used the same basis sets and apparently similar ring skeletons [51]; the C–H parameters were however based upon nematic phase NMR data in the present work, and this probably represents more accurate data than the crystal structure data used in [51]. It is perhaps unwise to attribute too much significance to small differences in total energy among isomers when the geometries of several had not been optimised or obtained from experimental sources; how-

Table 1. Total energies (a. u.) for neutral azines (RHF) and their radical anions (UHF, $^2\pi$).

Molecule	Basis set			
	Minimal		Double zeta	
	Neutral	Anion radical	Neutral	Anion radical
Pyridine (**1**)	−246.0153[a]	−245.9022	−245.6053[a]	−246.5374
Pyridazine (**2**)	−261.8922[b]	−261.8141	−262.5429[b]	−262.5084
Pyrimidine (**5**)	−261.9138[c]	−261.8397	−262.5785[c]	−262.5360
Pyrazine (**3**)	−261.9045[d]	−261.7864	−262.5513[d]	−262.5429
1,2,4,5-tetrazine (**4**)	−293.6675[e]	−293.6540	−294.4516	−294.3401 ($^2\Sigma$)
Naphthalene (**12**)	−382.3704[f]	−382.2907	−383.2322[f]	−383.1775
Quinoline (**13**)	−398.2730	−398.2099	−399.2082	−399.1735
iso-Quinoline (**14**)	−398.2718	−398.2137	−399.2067	−399.1729
Cinnoline (**15**)	−414.1509	−414.1171	−415.1460	−415.1404
Quinazoline (**10**)	−414.1053	−414.0686	−415.1398	−415.1198
Quinoxaline (**6**)	−414.1730	−414.1439	−415.1732	−415.1743
Phthalazine (**9**)	−413.9674	−413.9261	−415.0153	−414.9791
1,5-Naphthyridine (**7**)	−414.1699	−414.1155	−415.1824	−415.1567
1,6-Naphthyridine (**16**)	−414.1722	−414.1318	−415.1814	−415.1682
1,7-Naphthyridine (**17**)	−414.1717	−414.1314	−415.1800	−415.1659
1,8-Naphthyridine (**11**)	−414.0824	−414.0410	−415.1556	−415.0903
2,6-Naphthyridine (**8**)	−414.0248	−413.9729	−415.0585	−415.0462
2,7-Naphthyridine (**18**)	−414.1704	−414.1343	−415.1788	−415.1649

Previous Energies:
[a] Pyridine: −245.765 [24c], −245.622 [46a], −246.327 [48], −246.417 [49], −246.549 a. u. [51].
[b] Pyridazine: −261.685 [24c], −262.313 [49], −262.474 a. u. [51].
[c] Pyrimidine: −261.6787 [24c], −252.361 [49], −262.513 a. u. [51].
[d] Pyrazine: −261.554 [46c], −262.255 [47], −262.352 [49], −262.573 [50], −262.511 [51], −262.513 a. u. [54].
[e] 1,2,4,5-Tetrazine: −293.4748 [24c], −294.150 [49], −294.366 a. u. [51].
[f] Naphthalene: −328.110 [52].

ever, with such a large batch of calculations all performed under standard conditions we note that (i) in the monocyclic series, pyrimidine (**5**) where the N atoms are meta to one another has the lowest energy for both basis sets; (ii) this is not true of the benzo-derivatives where the para-oriented molecule quinoxaline (**6**) is lowest in energy; (iii) generally the energy spread in the diaza-compounds suggests that the molecules (except **6**) with most distant N atoms are the most stable.

Comparison of the total energies of neutral molecule with the anion radical, obtained by the same basis set gives a relative measure of the electron affinity of the species. The values are not absolute since (i) additional diffuse functions are necessary to accommodate the negative charge, (ii) the neutral and ionic species may have different equilibrium geometry and (iii) a configuration interaction study is necessary to fully describe the ion. The last point emerges since the SCF (RHF and UHF give the same energy for closed shells) is a better representation of the ground state than that of the ionised state; i.e. in the CI expansion of $^1A_1$ the SCF function will be more dominant than the corresponding term in $^2\pi$. Recently the gas phase electron affinities of the azines **1**, **2**, **3** and **5** have been estimated from electron transmission spectroscopy to be -0.62, $+0.25$, ± 0.0 and $+0.40$ eV [57]; the present energy differences from Table 1 ($E_{MOL} - E_{ION}$) yield -1.80, -0.94, -1.15 and -0.23 eV respectively, which approximate to the experimental order. In the gas phase, the life-times of the radical anions are extremely short, and near to that of vibration frequencies ($\sim 10^{-14}$ sec); this further substantiates the view that a highly diffuse π-orbital is necessary to obtain realistic values for the electron affinities.

b) The Expectation Value of the $\langle S^2 \rangle$ Operator – effect of basis set and annihilation

In general, although the RHF wave function, by its very nature is an eigen function of $\langle S^2 \rangle$, with eigen values given by $S_Z(S_Z+1)$, this is not true of the corresponding UHF function (above). Thus it can be argued that the divergence of $\langle S^2 \rangle$ from the theoretical value is a measure of quality of the wave function. The values obtained in the present UHF studies (Table 2) should be compared with the theoretical value of 0.75 ($S_Z = 0.5$). First, it is seen that the values before annihilation are very similar

Table 2. Expectation value of the S^2 operator for the radical anions, before (B.A.) and after annihilation (A.A.).

Molecule	Base			
	Minimal		Double zeta	
	$\langle S^2 \rangle$ B.A.	$\langle S^2 \rangle$ A.A.	$\langle S^2 \rangle$ B.A.	$\langle S^2 \rangle$ A.A.
Pyridine	0.8153	0.7510	0.8315	0.7539
Pyridazine	0.8930	0.7629	0.8673	0.7592
Pyrimidine	0.8866	0.7613	0.8678	0.7574
Pyrazine	0.8433	0.7508	0.8361	0.7516
S-tetrazine	0.8895	0.7617	0.7787	0.7506
Naphthalene	0.8392	0.7561	0.8355	0.7555
Quinoline	0.8495	0.7575	0.8678	0.7609
Isoquinoline	0.8832	0.7645	0.8877	0.7649
Cinnoline	1.0095	0.8096	1.0005	0.8019
Quinazoline	0.9732	0.7915	0.9491	0.7851
Quinoxaline	0.8635	0.7579	0.8486	0.7558
Phthalazine	0.8226	0.7539	0.8280	0.7544
1,5-Diazanaphthalene	0.8556	0.7588	0.8539	0.7584
1,6-Diazanaphthalene	0.8866	0.7652	0.8949	0.7653
1,7-Diazanaphthalene	0.8893	0.7656	0.8520	0.7581
1,8-Diazanaphthalene	0.8527	0.7579	0.8734	0.7616
2,6-Diazanaphthalene	1.0652	0.8495	0.9573	0.7905
2,7-Diazanaphthalene	0.8602	0.7592	0.8759	0.7616

for the minimal and double zeta basis, and the similarity is again apparent after annihilation, although (of course) the values are all improved by such a process. Thus for this series of compounds, it is clear that there is little difference between minimal and double zeta bases; since the latter are variationally much superior, and lead to markedly lower energy etc., it seems that $\langle S^2 \rangle$ is probably not a sensitive test of adequacy of wave function. Indeed, it appears that the very poor values (attributed to the basis set) for pentadienyl-, benzyl-, anilino- and phenoxyl-radicals [58, 59], are almost certainly a result of inadequate representation of the molecular structure. The present molecules, with their intrinsically more rigid aromatic and planar structure (the ESR spectra below are not temperature dependent) are probably better represented by their ground state neutral molecule geometries, than the flexible molecules studied by Hinchcliffe [$20_{g,h}$, 58, 59].

Generally the present values (Table 2) of $\langle S^2 \rangle$ are relatively close to the theoretically value of 0.75. Using our previous method [60] of partitioning the total state into doublet (D), quartet (Q) and sextet (S) and using the change in $\langle S^2 \rangle$ to estimate these proportions we arrive at the data of Table 3 for the

Table 3. Estimation of doublet (D), quartet (Q) and sextet (S) composition of the UHF-MB wave functions.

	Wave function				
	Before annihilation			After annihilation	
	D	*Q*	*S*	*D*	*S*
Pyridine	96.6	3.37	0.03	99.99	0.01
Pyridazine	95.32	4.63	0.05	99.85	0.15
Pyrazine	96.90	3.06	0.04	99.99	0.01
s-Tetrazine	95.43	4.52	0.05	99.86	0.14
Quinoline	96.70	3.27	0.03	99.91	0.09
iso-Quinoline	96.72	2.59	0.69	98.05	1.95
Quinoxaline	96.26	3.71	0.03	99.92	0.08
1,5-Naphthyridine	97.57	2.40	0.04	99.96	0.04

worst case, i.e. minimal basis set. This method clearly shows that the value of $\langle S^2 \rangle$ gives a rather exaggerated estimate of the importance of higher states.

c) Experimental Hyperfine Coupling Constants

In this section we are only concerned with assignments to centres (i), where the assignment is based upon experimental information such as internal intensity ratios (e.g. a_N), symmetry (e.g. 2 couplings of same value) or other methods *not* dependent upon spin density.

Overall, the hyperfine couplings (Table 6) obtained by various groups are reasonably consistent with each other, bearing in mind that some radicals are produced by electrochemical processes without a counter-ion (Na^+, K^+ etc.) whilst others have such ions present. A major discrepancy which does occur, is with 2,7-napthyridine (**18**) where Ref. [2] gives data greatly different from Table 6, and apparently is more in line with two determinations for the 2,6-isomer (**8**). Some workers have used Me substitution as an aid to assignment (see below for details), on the apparent assumption that $a_{Me(i)}$ will parallel $a_{H(i)}$. The dangers of this process when a symmetry change, or change of nodal position occurs is shown in Table 6 for the methyl-benzenes. The method has a number of strengths, perhaps exemplified by the H(2) versus H(3) assignments of pyridine by comparison of **1** and its 2,6- and 3,5-dimethyl-derivatives; it is apparent however that a_N is markedly varying in this group, and does not parallel the change at H(2) in *m*-xylene relative to benzene (Table 4); indeed the effect of the Me groups in *m*-xylene is the reverse to that of either of the dimethylpyridines where a_H/a_N are reduced rather than increased (*m*-xylene). The group of pyrazines (Table 6) show parallel changes. We now consider individual assignments for the azines.

(i) Pyrazine (**3**) and 1,2,4,5-Tetrazine (**4**). These assignments are complete and include a_{13_C} [61, 62].

(ii) Pyrimidine (**5**). Differentiation between $a_{H(2)}$ and $a_{H(5)}$ relies upon the 5-methyl derivative single coupling (0.67 gauss) being correlated with 0.72 rather than 1.24 gauss in the parent molecule [63]. The effects of Me substitution above make this uncertain.

(iii) Pyridine (**1**). The instability of this radical has made assignment more complex, although selective deuteration might have been anticipated. Only a_N and $a_{H(4)}$ are totally unambiguous, but the wide difference between the two remaining values probably makes comparison with symmetrical dimethyl derivatives secure [64].

(iv) Pyridazine (**2**). The weak additional splitting of the septet of lines only yields a_N unambiguously [64].

(v) Phthalazine (**9**). Selective deuteration at the 1- and at the 6-positions has made unambiguous all four couplings [61].

(vi) Quinoxaline (**6**). Whilst all the a_N/a_H couplings have been identified, assignment of the latter group has been controversial [62a, b, 65, 67–69]; assignments based upon the pair of dimethylated derivatives are probably secure, and the very low coupling at the β-positions remote from the heterocyclic ring has a parallel in phthalazine (**9**). This molecule is a classic case where the Hückel MO method for spin densities is claimed to yield more accurate results than the more rigorous SCF method [62a, b, 65, 66].

(vii) Quinoline (**13**) and iso-Quinoline (**14**). These are the most complex of the present series. NMR studies of (neutral molecule + ion) radical mixtures show that line broadening leads to assignments at H(4), H(3) and H(2) in **13**, and is supported by non-specific deuteration at positions 5–8 [64]. Similar studies for **14** only yield the assignments for H(1)/H(3). The effect of H replacement by Me in **13** and **14**, together with estimates of the perturbation producted by the replacement [71] does not lead to an unequivocal assignment; further the second largest coupling in **13** [64] becomes the third largest **13** [71] with other smaller re-ordering

Table 4. Calculated spin population densities (ϱ_C^π) and experimental hydrogen HFCC's (a_H) for radical anions.

Molecule		Minimal basis		Double zeta basis		a_H	
		ϱ_μ^π B. A.	ϱ_μ^π A. A.	ϱ_μ^π B. A.	ϱ_μ^π A. A.	Calc.	Expt.
Naphthalene	C1	0.301	0.225	0.301	0.224	5.15	4.84
	C2	0.013	0.044	0.016	0.047	1.95	1.83
Pyridine	C2	0.089	0.062	0.150	0.112	3.13	3.14
	C3	−0.092	0.018	−0.117	−0.004	1.03	0.88
	C4	0.500	0.401	0.537	0.443	9.12	9.10
Pyridazine	C3	−0.255	−0.078	−0.242	−0.075	−0.26	0.16
	C4	0.290	0.218	0.310	0.231	5.28	6.47
Pyrimidine	C2	−0.269	−0.082	−0.152	−0.048	0.23	0.72
	C4	0.379	0.299	0.497	0.384	8.05	9.78
	C5	−0.253	−0.083	−0.341	−0.108	−0.85	1.31
Pyrazine	C2	0.0395	0.024	−0.006	0.040	1.82	2.63
Quinoline	C2	0.029	0.058	0.170	0.131	3.47	3.29
	C3	−0.013	0.035	−0.122	−0.004	1.03	1.26
	C4	0.36	0.274	0.468	0.360	7.62	7.80
	C5	0.249	0.188	0.283	0.181	4.38	3.90
	C6	−0.018	0.034	−0.071	0.001	1.12	1.14
	C7	−0.0005	0.042	0.095	0.068	2.33	2.02
	C8	0.265	0.182	0.432	0.113	3.15	3.46
Isoquinoline	C1	0.268	0.215	0.341	0.264	5.88	5.38
	C3	−0.147	−0.033	−0.118	−0.031	0.54	0.37
	C4	0.339	0.231	0.269	0.181	4.38	3.95
	C5	0.163	0.145	0.087	0.102	2.95	3.26
	C6	0.183	0.139	0.275	0.187	4.48	4.01
	C7	−0.165	−0.034	−0.239	−0.063	−0.04	0.04
	C8	0.381	0.268	0.437	0.295	6.44	6.26
Quinoxaline	C2	−0.005	0.038	0.015	−0.048	0.23	2.36
	C5	0.165	0.110	0.128	0.107	3.04	3.33
	C6	−0.001	0.024	0.007	−0.002	1.06	1.45
1,5-Diazanaphthalene	C2	0.091	0.088	0.117	0.102	2.95	2.95
	C3	−0.065	0.008	−0.057	0.015	1.37	1.69
	C4	0.337	0.245	0.361	0.265	5.90	5.80
Phthalazine	C1	0.266	0.203	0.319	0.247	5.57	5.91
	C5	0.291	0.224	0.279	0.201	4.74	4.64
	C6	0.035	0.058	0.038	0.063	2194	2.14
1,8-Diazanaphthalene	C2	0.020	0.052	0.151	0.113	3.15	3.98
	C3	−0.002	0.037	−0.092	0.003	1.15	0.73
	C4	0.295	0.217	0.391	0.280	6.17	6.39
2,7-Diazanaphthalene	C1	0.229	0.172	0.156	0.122	3.31	3.63
	C3	0.078	0.067	0.107	0.076	2.48	1.97
	C4	0.389	0.289	0.409	0.351	7.45	7.37
Cinnoline	C3	−0.213	−0.063	−0.241	0.074	2.44	–
	C4	0.339	0.223	0.356	0.074	5.46	–
	C5	−0.102	0.001	−0.083	0.0003	1.15	–
	C6	0.304	0.173	0.271	0.152	3.85	–
	C7	−0.295	−0.085	−0.243	−0.071	−0.185	–
	C8	0.423	0.243	0.375	0.210	4.90	–
Quinazoline	C2	−0.127	−0.022	−0.023	0.011	1.30	–
	C4	0.360	0.285	0.515	0.407	8.47	–
	C5	0.408	0.236	0.438	0.240	5.44	–
	C6	−0.289	−0.084	−0.345	−0.104	−0.78	–
	C7	0.309	0.179	0.371	0.208	4.86	–
	C8	−0.077	0.016	−0.192	−0.031	0.54	–
1,6-Diazanaphthalene	C2	0.438	0.314	0.521	0.390	8.16	8.11
	C3	−0.208	−0.047	−0.262	−0.064	−0.06	0.10
	C4	0.234	0.167	0.326	0.227	5.21	5.54

Table 4 (continued)

Molecule		Minimal basis		Double zeta basis		a_H	
		ϱ_μ^π B. A.	ϱ_μ^π A. A.	ϱ_μ^π B. A.	ϱ_μ^π A. A.	Calc.	Expt.
	C5	0.208	0.189	0.159	0.111	3.11	3.04
	C7	−0.079	−0.009	−0.004	0.013	1.34	1.01
	C8	0.260	0.196	0.321	0.219	5.06	5.54
1,7-Diazanaphthalene	C2	0.256	0.207	0.352	0.275	6.08	6.15
	C3	0.173	0.133	0.004	0.099	1.79	2.98
	C4	−0.154	−0.025	−0.035	0.029	1.62	2.09
	C5	0.194	0.163	0.225	0.177	4.30	4.99
	C6	−0.158	−0.038	−0.128	−0.032	0.52	0.24
	C8	0.326	0.211	0.256	0.161	4.01	3.60
2,6-Diazanaphthalene	C1	0.045	0.085	0.111	0.125	3.36	4.39
	C3	−0.317	−0.097	−0.279	−0.088	−0.49	0.45
	C4	0.417	0.249	0.365	0.219	5.06	5.02

changes. The agreement between a_{Me} in substituted quinolines between Refs. [71 and 72] is not good, and generally the complete assignments for **13** and **14** cannot be regarded as secure.

(viii) The Naphthyridines (**7**, **8**, **11**, **16** – **18**). Even those of C_{2v} (**11**, **18**) or C_{2h} symmetry (**7**, **8**) with only 3 independent values for a_H are not assigned with certainty on experimental evidence. Comparison of 1,5-naphthyridine (**7**) with its 3,7-dimethyl-derivative leaves two values (a_N + one a_H) largely unchanged, but a new value closer to one original coupling. Hence the quartet splitting in the derivative [68] leads to an assignment of 0.45 gauss to $a_{H(3)}$ in the parent, but does not assist in the H(2)/H(4) assignment. Comparison of the two sets of couplings in these 1,5-naphthyridines with pyridine and its 3-methyl-derivative [76] suggests that the two compounds are similarly effected by Me substitution, but both are only assigned by recourse to spin density calculations.

d) Correlation between Spin Density and Hyperfine Coupling

(i) π-Spin density at carbon ($\varrho_{C(i)}^\pi$) versus proton hyperfine coupling (a_H)

A correlation between the π-spin density of the double zeta basis set calculations (after annihilation of the quartet component) with the group of hyperfine couplings (a_H) in Table 5 whose values seem likely to be assigned correctly, is shown in Figure 1. A similar correlation occurs with the minimal basis set data, but with more scatter; clearly the correlation is satisfactory for all except pyrimidine (**5**) and quinoxaline (**6**) where some doubt about the experimental assignments still persists. In the latter case, the correlation can be much improved by the reassignment of the two largest couplings (3.33 and 2.38 gauss) to H(5) and H(2) respectively, rather than the reverse, as has been done previously [67–69]. It is interesting to note that all the self-consistent field methods PPP-π [12, 15], and valence shell INDO [14], all give $\varrho_{C(5)}^\pi > \varrho_{C(2)}^\pi$. The previous assignment [67] is based upon H/Me replacements and assumes small perturbations produced by the process. The scale of these perturbations is uncertain, and contrary to the statement in Ref. [67] the study of only the three compounds (**6** and its 2,3- and 6,7-dimethyl-derivatives) does *not* provide a unique assignments to all three spectra. The absence of data

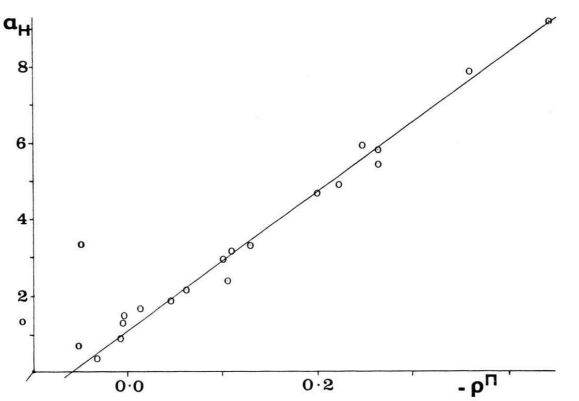


Fig. 1. Correlation of spin densities $\varrho_{C(AA)}^\pi$ with hyperfine coupling (a_H) in conclusively assigned cases.

Table 5. Observed hyperfine coupling constants (gauss) for the azines and related hydrocarbons.

Molecule	a_N	a_H	Ref.
Benzene		3.75	[73]
		3.715 (K^+)	[62a]
Toluene		5.12(2), 5.45(3), 0.59(4)	[73]
p-Xylene		5.34	[73]
o-Xylene		6.93(3), 1.81(4)	[73]
m-Xylene		6.95(2), 1.46(4), 7.72(5)	[73]
Naphthalene		4.90(1), 1.83(2)	[62b]
		4.84, 1.83 (K^+)	[62a]
Pyridine	6.28	9.10(4), 0.88, 3.14	[64]
	6.55	9.70, 0.82, 3.55	[2, 75]
Pyridazine	5.90	6.47, 0.16	[61]
	5.92	5.92	[62a]
Pyrimidine	3.34	9.54(4), 0.72, 1.24	[63]
	3.26	9.78, 0.72, 1.31	[2, 75]
5-Methyl-pyrimidine	3.34	0.26(4), 0.67(2)	[63]
3,5-Dimethyl-pyridine	6.40	8.85(4), 3.18(2)	[76]
	6.21	8.96(4), 3.41(2)	[74]
	7.40	8.98(4), 3.19(2)	[75]
2,6-Dimethyl-pyridine	4.86	9.29(4), 0.71(3)	[76]
Pyrazine	7.18	2.63	[62a,2]
	7.22	2.66	[62b]
	7.213	2.639	[61]
	7.22	2.72	[75]
2,5-Dimethyl-pyrazine	6.67	3.46	[70]
2,6-Dimethyl-pyrazine	6.16, 7.35	2.85	[70]
Tetrazine	5.275	0.212	[61]
Quinoxaline	5.64	3.32, 2.32, 1.00	[62b,2]
	5.72	3.23, 2.42, 1.43	[69]
	5.65	3.31, 2.33, 1.44	[67]
	5.70	3.33, 9.38, 1.45	[62a], [68]
2,3-Dimethyl-quinoxaline	5.13	2.43, 1.40	[67]
	5.21	2.46, 1.38	[68]
6,7-Dimethyl-quinoxaline	4.69	3.25, 2.12	[67]
Phthalazine	0.87	5.78, 4.62, 2.09	[69]
	0.876	5.91(1), 4.64(5), 2.14(6)	[61]
1,5-Naph-thyridine	3.33	2.89, 1.72, 5.70	[69]
	3.37	2.95, 1.69, 5.77	[62a,2]
	3.36	3.01, 1.72, 5.80	[68]
3,7-Methyl-1,5-naph-thyridine	3.25	3.53, 5.58	[68]
1,8-Naph-thyridine	2.39	6.69, 4.38, 0.50	[68]
	2.50	6.39, 3.98, 0.73	[69]
	2.47	6.54, 4.07, 0.70	[2]
2,7-Naph-thyridine	0.36	7.43, 3.68, 2.06	[68]
	0.39	7.37, 3.63, 1.97	[69]
2,6-Naph-thyridine	3.42	5.02, 4.39, 0.45	[68]
	3.29	4.88, 4.37, 0.38	[69]
1,6-Naph-thyridine	3.04, 1.01	8.11, 5.54, 5.54, 3.04, 1.01, 0.10	[68]
	3.04, 2.03	8.11, 5.54, 5.54, 1.01, 1.01, 0.10	[68]
1,7-Naph-thyridine	4.53, 1.80	6.15, 4.99, 3.60, 2.98, 2.09, 0.25	[68]
Quinoline	3.95	3.29(2), 7.80(4), 1.26(3), 3.90, 1.14, 2.02, 3.46	[64]
	3.83	4.40, 8.44, 0.86, 4.06, 0.73, 2.40, 2.73	[71]
	4.46	4.24, 7.54, 0.94, 3.99, 0.83, 2.47, 2.90	[72]
iso-Quinoline	1.92	5.38(1), 0.37(3), 4.01, 3.95, 3.26, 0.04, 6.26	[64]
	2.28	7.16, 0.11, 4.20, 2.53, 4.20, 0.11, 5.16	[71]

for the 5,8-dimethyl-compound is crucial; it would be possible to argue a case based upon spin density at Me (unambiguous) for each of the *four* compounds, and assume the density parallels that of the parent compound. An indicator of the unreliability of intuitive arguments in this group of compounds is seen in a_N; the effect of 6,7-dimethylation is much more marked than 2,3-dimethylation, yet the distance factor is widely different. We return to this point in discussion of the nature of the unpaired orbital (below). In the following discussion we refer to the most rigorous of the present calculated data (double zeta basis, UHF with annihilation) unless otherwise stated.

The principal difficulty of assignment of spin densities to the hyperfine couplings when a_H is unambiguous (Table 4) is in pyrimidine (**5**). If the experimental values are assumed positive, as is usually the case with a_H in this series of compounds, then the values 9.78 and 1.31 gauss do not fit any reasonable correlation line, although all other molecules give a good fit. Previous semi-empirical studies suggested [12] that one coupling is negative (− 1.31 gauss). This certainly leads to a marked improvement in the correlation (Fig. 1, Table 4), but the dilemma with 9.78 gauss remains. The total energy of the present doublet state ($^2A_2$) seems reasonable (Table 1); it does seem possible that a second doublet state ($^2B_1$) may be responsible for the experimental hyperfine coupling. Such a state has the spin density ratios C(5) > C(2) > C(4), and this seems even more improbable in the correlation. There is a clear discrepancy with this compound, and further experimental and theoretical investigations are required.

Table 6. Least squares fits for UHF spin density with hyperfine coupling (a_H, a_N).

Basis set	Nucleus	Annihilation	Equation	Q_i^i	Q_{ij}^i/C	Points	Standard deviations		Overall
							Slope (Q)	Intercept (C)	
DZ	a_H	Yes	(5)	18.00	1.318 (C)	23	0.903	0.173	0.645
DZ	a_H	Yes	(5)	17.38	1.257 (C)	20	0.502	0.093	0.301
DZ	a_H	Yes	(5)	17.59	1.238 (C)	49	0.436	0.078	0.387
DZ	a_H	No	(5)	10.04	2.042 (C)	49	0.544	0.138	0.806
MB	a_H	Yes	(5)	18.45	1.320 (C)	49	1.127	0.183	0.894
MB	a_H	No	(5)	10.47	2.213 (C)	49	0.750	0.171	1.020
DZ (ϱ^{total})	a_N	Yes	(6)	14.49	1.13	12	0.694	0.296	0.555
DZ (ϱ^{π})	a_N	Yes	(6)	14.13	0.721	12	1.761	0.464	0.850
DZ (ϱ_{π})	a_N	Yes	(6)	15.51	0.637	11	0.714	0.182	0.333
DZ (ϱ^{total})	a_N	Yes	(6)	14.64	0.720	11	1.086	0.287	0.529
DZ	a_N	No	(7)	12.23	1.343	6	–	–	0.903
DZ	a_N	Yes	(7)	15.48	2.637	6	–	–	0.876

If pyrimidine is omitted from the correlation (Fig. 1), then a least squares fit (Table 6) of unambiguous data (20 points) to the equation

$$a_H = Q_{CH}^H \varrho_C^{\pi} + C \tag{5}$$

leads to a much reduced overall standard deviation. The present value of the slope Q_{CH}^H is in the range of semi-empirical values, *viz.* 14.1 ~ 15.6 (PPP-π) [12], 18.4 ~ 23.2 (VESCF etc.) [15] and 23.0 (INDO) [14]. The presence of a finite intercept does indicate that a_H is made up of contributions from non-adjacent sources. As in earlier work [14], the McConnell relation between ϱ_C^{π} and the attached $\varrho_H^{1s+1s'}$ does hold well; this relation can be investigated with a full set of theoretical data, irrespective of the state of experimental values.

With respect to comparisons in various methods of calculation reported here, it is interesting to note that $|\varrho_{DZ}| > |\varrho_{MB}|$ before and after annihilation; correlations over all sets of data yield $(\varrho_{DZ})_{BA} = 1.25\ (\varrho_{MB})_{BA} - 0.026$, $(\varrho_{DZ})_{AA} = 1.14\ (\varrho_{MB})_{AA} - 0.015$, with the latter showing much less scatter. The effect of annihilation on either MB or DZ calculations is to reduce the magnitude of ϱ_C^{π} (or ϱ_N^{π}). The relationship between these two (Fig. 2) is nearly linear, and for values of $|\varrho| < 0.3$ yields $\varrho_{AA} = 0.50\ \varrho_{BA} + 0.035$. Annihilation also reduced the scatter between calculated ϱ_C^{π} and a_H (AA is shown in Figure 1).

(ii) Assignment of a_H from present spin density results

Clearly some differences between MB and DZ can be expected both BA and AA. Generally annihilation leads to greater similarity between MB and DZ, as can be expected on intuitive grounds of greater rigor being introduced to both MB and DZ; comparison of AA with BA shows some marked changes in order of a_H; for example, in quinoline (the most complex 7-centre case), ϱ_C^{π} (MB, BA) shows $4 > 8 > 5 \gg$ others; ϱ_C^{π} (MB, AA) has $4 > 5 > 8 >$ others; ϱ_C^{π} (DZ, BA) has $4 > 8 \gg 5 \gg$ others, and finally ϱ_C^{π} (DZ, AA) has $4 \gg 5 > 2 > 8 \gg$ others. On grounds of rigor the (DZ, AA) case must be chosen, experimentally $a_{H(4)} \gg a_{H(2)}$ (Table 4), and two other values lie close to $a_{H(2)}$ both computationally and experimentally. For isoquinoline $a_{H(1)}$ has been shown to be the second largest value (Table 4) [64] of three well spaced values (6.26, 5.38 and 4.01 gauss) with $a_{H(3)}$ very small, although a rather different analysis has also been presented [71]. The present results (DZ, AA) fit in with this general pattern, with $a_{H(8)}$ being indicated as the largest value. Other major discrepancies between the (MB, AA)

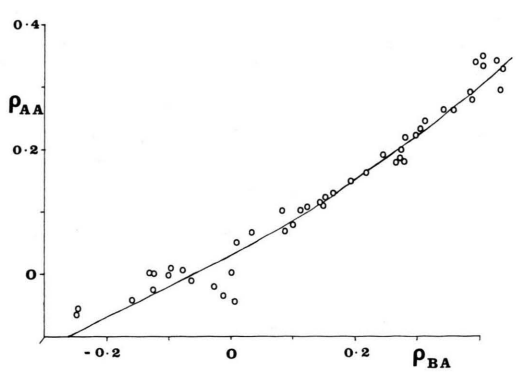


Fig. 2. Correlation of spin densities $\varrho_{C(AA)}^{\pi}$ with $\varrho_{C(BA)}^{\pi}$ double zeta basis.

and (DZ, AA) results are: – for cinnoline (**15**), where no experimental information is available for $a_{H(4)} > a_{H(8)}$ (DZ, AA); 1,7-naphthyridine (**17**) for the three largest couplings $a_{H(2)}$, $a_{H(5)}$, $a_{H(8)}$ where the values are known but not reliably assigned [68].

(iii) Correlation of a_N with Spin Density

For most of the azines (**1**–**11**, **13**–**18**) the assignment of a_N presents few problems owing to the 1:1:1 intensity ratio and relatively large hyperfine interaction. The exceptions are cases with two (or more) nonequivalent N atoms (**10**, **15**, **16**, **17**). The spin population densites and a_N are given in Table 6 and 7. In the first stage a single term fit

$$a_N = Q_N^N \varrho_N^\pi + C\,, \tag{6}$$

analogous to (1) was tried for a_N against ϱ_N^π, using data before and after annihilation and both basis sets. The results (Table 6) show the expected rise in Q_N^N and reduction in A after annihilation, as a result of the general reduction in ϱ_N^π. The standard deviations are little improved by annihilation, but as in the a_H study, the MB and DZ results are now relatively similar. Under similar conditions (DZ, AA), a correlation of a_N with ϱ_N^{total} was poorer than that for ϱ_N^π.

In agreement with the semi-empirical calculations of Zeiss and Whitehead [12], the use of the more complex expression

$$a_N = Q_N^N \varrho_N^\pi + Q_{NX}^N \varrho_X^\pi\,, \tag{7}$$

where the effect of neighbouring carbon atoms (X = C) are included, led to a small statistical improvement (Table 6), but the ratio of the two couplings, self-atom Q_N^N, and neighbour Q_C^N, is such that the former dominates the expression. The replacement of the intercept (C) in (6) by a more clearly defined density term makes the procedure more acceptable; the nature of C is not well defined in (6). Unfortunately there are insufficient experimental data for a meaningful use of (7) in cases, where N-N bonded molecules are included. Given the low proportions of Q_{NC}^N to Q_N^N (Table 6, [2]), it seems that choosing $Q_{NN} = Q_{NC}$ could be a reasonable assumption, and would at least offer some form of allowance for density changes in both neighbours for this small group of molecules (**2**, **4**, **9**, **15**).

(iv) Variation of Spin Density/Hyperfine Coupling with Molecular Structure

The splitting of the lowest pair of unoccupied orbitals (e_{2u}) in benzene when one is occupied by a single electron, has been elegantly described by Carrington [77], in relation to the effects of Me substitution on a_H in benzene. Parallel arguments apply to the monocyclic azine radical anions; the two orbitals in question (e_{2uA}, e_{2uS}) are non-degenerate in the azines. All MO methods lead to conclusions similar to the Hückel theory with respect to e_{2uA} and e_{2uS} (Fig. 3); the latter (symmetrical with respect to two planes, S) has higher density at positions 1 and 4; the higher electronegativity of N over C makes occupation of this orbital more probable in the cases of pyridine (**1**) and pyrazine (**3**) in agreement with the present SCF calculations. In contrast the N atom positions in pyridazine (**2**), pyrimidine (**5**) and 1,2,4,5-tetrazine (**4**) are such that electronegativity differences lead to e_{2uA} (antisymmetric with respect to two planes, A) being occupied, as is found in the SCF calculations. Thus the a_N coupling is expected to be lower in **2**, **4**, **5** than in **1**, **3**, as is observed. The close similarity of a_N for **2** and **4** is as expected, whilst the even lower value for pyrimidine can only be accounted for by the lack of contribution from the neighbouring (C rather than N) centre. This is of course an argument that Q_{CN}^N is smaller than Q_{NN}^N in Equation (7).

The lowest unoccupied pair of orbitals in naphthalene (**12**) are of $2\,b_{2g}$ and $2\,b_{1g}$ symmetry (Fig. 3), and these are nearly degenerate in the SCF calculation. These two correlate directly with e_{2u} of benzene. For $2\,b_{2g}$ the wave function is maximal at the α (1, 4, 5, 8) positions and nodal at the bridge (γ), while in $2\,b_{1g}$ the maxima are at the β (2, 3, 6, 7) and γ (9, 10) positions. Experimentally the hyperfine coupling to ^{13}C is $+7.2$ (α), -1.1 (β), and ± 5.6

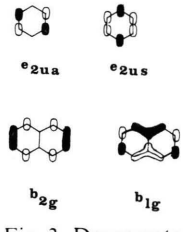


Fig. 3. Degenerate lowest unoccupied orbital (LUMO) of benzene and non-degenerate lowest pair LUMO's for naphthalene.

gauss (γ). The lowest doublet (anion) state corresponds to $^2B_{2g}$ both for naphthalene and its aza-derivatives, in the present work. In an RHF context this leads to zero spin density ($\varrho_C^\pi = 0$) at the bridging (γ) positions, and hence low hyperfine coupling via (8), analogous to (7):

$$a_C = Q_C^C \varrho_C^\pi + \sum_X Q_{CX}^C \varrho_X^\pi . \quad (8)$$

In practice the UHF wave function leads to spin densities ϱ_C^π 0.224 (α), 0.046 (β) and −0.043 (γ) and ϱ_C^{total} 0.258 (α), 0.038 (β) and −0.066 (γ). We have insufficient experimental data in the present series of compounds to evaluate Q_C^C/Q_{CX}^C, but as an initial stage we note that spin densities calculated at ^{13}C, based upon the McConnell Relationship and a_H [2] lead to ϱ values of 0.206 (α), 0.076 (β) and −0.069 (γ), which are close to the present values of ϱ_C^π. If we then adopt the values for Q_C^C and Q_{CC}^C (+35.6 and −13.9 gauss) found for various hydrocarbons by semi-empirical means, we obtain a_C values of +7.93 (α), −2.11 (β) and −7.11 gauss (γ). These fit the experimental values reasonably well provided $a_C(\gamma)$ is negative, and fit rather better than earlier INDO calculations [14] with the same proviso. Thus for naphthalene (**12**), the value of the hyperfine coupling critically depends upon contributions from neighbouring centres via Q_{CC}^C.

For the bicyclic azines (**6**−**11**, **13**−**18**), there is only a_H and a_N data. All the SOMO's are calculated to be of $2\,b_{2g}$ type, i.e. the density is higher at α- than β-positions. The hyperfine coupling above was found to be dominated by the self-atom term (Q_N^N), and it is notable that those compounds (Table 7) with either one α-N, or two α-N's in different rings have generally high a_N (2.5−4.0 gauss); quinoxaline (**6**) is even higher (5.70 gauss) having two N atoms in α-positions, in the same ring. This result is parallel to that of pyrazine (**3**) which is highest of the monocyclic azines (**1**−**5**). Those molecules which have β-N generally have a_N with values below 2.0 gauss, although 2,6-diazanaphthalene (**8**) is exceptional in this group. It is notable that the two compounds with centres of inversion (**7**, **8**) have higher a_N than those of the C_{2v} type (**11**, **18**); the latter have nodal planes through the γ-positions, which contribute less to a_N. In all these cases, the calculated ϱ_N^π follow the variations in a_N reasonably well.

Conclusions

The present paper is the first *ab initio* study of a wide range of aromatic azine radical anions, with more than one basis set, and including RHF/UHF wave functions and annihilation. In general the spin densities give a good account of the variations in hyperfine coupling (a_H and a_N) in these molecules. The lack of experimental data both on ^2H substituted compounds, to give greater reliability in the values for a_H, and ^{13}C labelled compounds to give values for a_C is apparent. Thus this set of molecules

Table 7. Calculated spin population densities (ϱ_N^π) and experimental nitrogen HFCC's (a_N).

Molecule	Spin population density				a_N
	MB, BA	MB, AA	DZ, BA	DZ, AA	Expt
Quinoline	0.356	0.265	0.284	0.219	3.95
Isoquinoline	0.181	0.128	0.149	0.112	1.92
Quinoxaline	0.465	0.360	0.440	0.331	5.70
1,5-Diazanaphthalene	0.269	0.200	0.224	0.165	3.37
Phthalazine	−0.020	0.051	−0.018	−0.025	0.876
1,8-Diazanaphthalene	0.324	0.236	0.198	0.149	2.50
2,7-Diazanaphthalene	−0.061	0.012	−0.095	−0.007	0.36
Pyridine	0.512	0.437	0.397	0.342	6.28
Pyridazine	0.464	0.359	0.432	0.343	5.90
Pyrimidine	0.382	0.282	0.249	0.193	3.34
Pyrazine	0.551	0.451	0.501	0.418	7.21
S-tetrazine	0.391	0.384	0.388	0.293	5.27
2,6-Diazanaphthalene	0.37	0.246	0.319	0.219	3.42
1,6-Diazanaphthalene	0.229	0.182	0.182	0.144	3.04
	0.101	0.083	0.016	0.036	1.01
1,7-Diazanaphthalene	0.416	0.293	0.356	0.268	4.53
	0.179	0.120	0.124	0.088	1.80

has not received adequate attention; even "simple" cases such as pyrimidine and quinoxaline are not well understood. A number of a_H reassignments, particularly in the case of the unsymmetrical bicyclic azines (**13**, **14**, **16** and **17**) are proposed, and others can be regarded as substantiated for the first time. Contrary to some previous work the value of $\langle S^2 \rangle$ is not poor from minimal basis set calculations after annihilation, but the use of the MB spin densities for prediction of the order of hyperfine coupling does not seem to be justified, except on a provisional basis. The largest a_H coupling does seem to be reproduced by MB calculations, and the variations in a_N are well reproduced by both MB and DZ studies. The contribution of neighbouring centres (j) to $a_i (i \neq j)$ seems to be small in all cases, but in view of the sign, can be critical. In all cases the SOMO appears to be of approximate b_{2g} character even when the overall molecular symmetry is only C_s rather than C_{2v}.

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