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Spin Density Distributions in Radical Anions of Heterocyclic Amine N-Oxides

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The unrestricted Hartree–Fock (UHF) method of Snyder and Amos is used to calculate, in the π-electron approximation, the spin density distributions in radical anions of heterocyclic amine N-oxides. The computed spin densities are observed to be in good agreement with the experimental values. The computed spin density distribution of the radical anion of pyridine N-oxide is consistent with the greater susceptibility of pyridine N-oxide relative to pyridine to electrophilic nitration. Also, the calculations are consistent with the lower basicity of the N-oxides relative to the parent bases.

Key words: UHF spin densities – Radical anions – Heterocyclic Amine N-oxides – Electrophilic substitution – Basicity.

1. Introduction

As the prototypes of aromatic amine N-oxides, pyridine N-oxide and its derivatives are particularly interesting from the point of view of structure and reactivity. The synthetic potential of these compounds as intermediates in the preparation of substituted pyridines has been recognized since Ochiai [1] and den Hertog [2] observed that pyridine N-oxide is more susceptible to electrophilic attack than pyridine. The 2 and 4 positions are substituted, with the 4-derivatives predominating. These observations are readily explained in terms of the principal resonance forms shown in Fig. 1. Clearly resonance forms 1–5 to 1–7 favour electrophilic substitution at the observed positions. Comparable forms cannot be drawn for pyridine where the surplus negative charge of nitrogen leads to a dipole moment that is substantially greater than that of piperidine the nonaromatic

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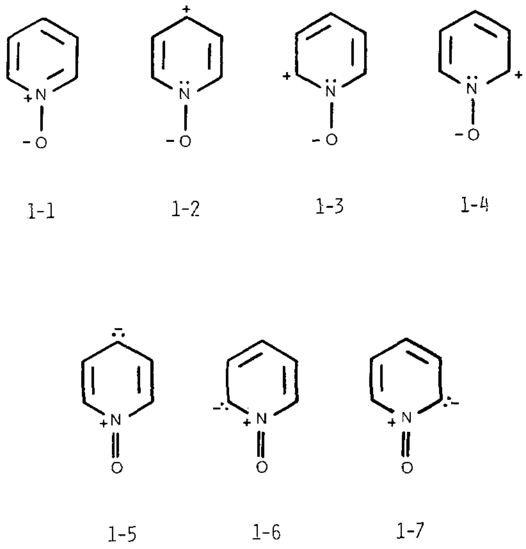

Fig. 1. Principal resonance forms of pyridine N-oxide

analogue. Here it is interesting to note that there appear to be two opposing polarization effects in pyridine N-oxide. Indeed the difference (2.02 D) between the dipole moments [3] of pyridine N-oxide (4.24 D) and pyridine (2.22 D) is less than the difference (4.37 D) between the dipole moments of trimethylamine oxide (5.02 D) and trimethylamine (0.65 D) and, therefore, it may be argued that all seven forms contribute significantly to the structure of pyridine N-oxide. This view is also consistent with the observation of facile nucleophilic substitution at the 2 and 4 positions [4].

Although there is a very large literature dealing with the physico-chemical properties of aromatic amine N-oxides, theoretical studies have been restricted to some early empirical calculations by Kubota [5], Jaffé [6] and Barnes [7]. More recent calculations [8] on the radical anions of heterocyclic amine N-oxides have been stimulated by the availability of electron spin resonance data [4, 9–12]. However, in comparison to the theoretical [13] work on the deoxy analogues, for which extensive experimental data [8, 14] is available, the radical anions of pyridine N-oxide and related compounds have received very little attention. In this paper we report the first unrestricted Hartree–Fock (UHF) calculations on the spin density distributions in the radical anions of aromatic heterocyclic N-oxides.

2. Method of Calculation

The UHF method of Snyder and Amos [15] has been used in the present study. The spin densities and charge densities were obtained after annihilation of the quartet spin component from the UHF wavefunctions. As in our previous work [16] based on the π-electron approximation, two-centre, two-electron repulsion integrals were evaluated by use of Ohno's formula [17], core resonance integrals were approximated by use of Linderberg's formula [18], effective nuclear charges were taken from the work of Mulliken *et al.* [19] and valence state ionization potentials and electron affinities were taken from the tabulations of Hinze and Jaffé [20]. The starting density matrices used for the self-consistent iteration procedure were obtained by use of the following Hückel Coulomb (k) and resonance (β) parameters for the heteroatoms: $k_N = 1.6$, $k_O = 0.7$ and $\beta_{NO} = 0.8$.

Here it should also be noted that in order to obtain better agreement between the results of our calculations and experiment, the nitrogen of the N-oxide functional group has been assumed to have a rather large positive charge. Thus the valence state ionization potential was taken to be 29.16 eV rather than the normal value of 28.16 eV for N^+ [20].

Model geometries were adopted as follows: all molecules were assumed to be planar and the C—C, C—N, N—0 distances were taken to be 1.40, 1.34 and 1.27 Å, respectively.

3. Results and Discussion

The N-oxides of pyridine 1, pyrazine 2, pyridazine 3, quinoline 4, quinoxaline 5, acridine 6 and phenazine 7 were chosen for the present study. The structural formulas and numbering schemes are shown in Fig. 2. The UHF values of the spin densities at the N and C positions of the corresponding radical anions are listed in Table 1. The oxygen spin densities are not included due to the absence of oxygen hyperfine splitting in the electron spin resonance spectra. The charge densities at the C and N positions are also included in Table 1. Of course, the oxygen values

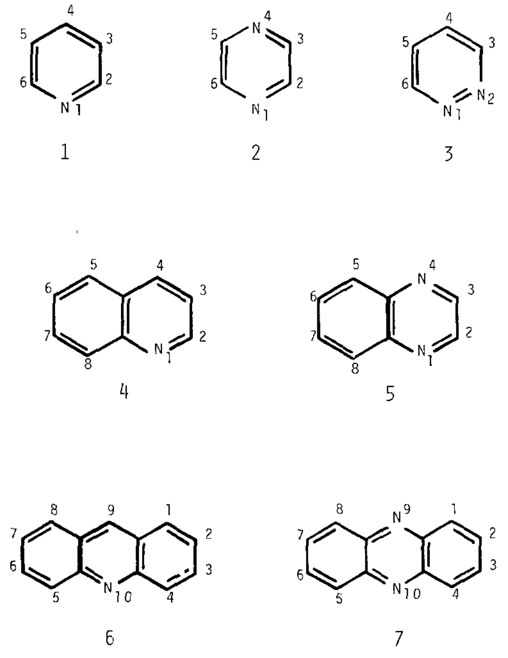

Fig. 2. Structural formulas and numbering schemes of some aromatic heterocyclic compounds

Table 1. Spin densities (ρ_i), electron densities (q_i), nitrogen hyperfine splittings[a] and ring proton splitting constants[b] in the radical anions of some aromatic heterocyclic N-oxides

System	Position[c]	$\langle S^2\rangle_{ba}$	$\langle S^2\rangle_{aa}$	ρ_i	q_i	a_i^M	$\lvert a_i\rvert_{obs}$[d]
1, pyridine N-oxide	1 (N)	0.801	0.750	0.457	1.487	10.05	10.91[e]
	2			0.127	1.198	−3.10	3.01
	3			−0.020	0.987	0.55	0.44
	4			0.213	1.263	−5.04	8.51
2a, pyrazine mono-N-oxide	1 (N)	0.783	0.750	0.508	1.421	11.76	12.09
	2			0.047	0.844	−1.35	2.13
	3			0.043	1.249	−1.03	1.62
	4			0.143	1.570	−3.42	5.54
2b, pyrazine di-N-oxide	1 (N)	0.774	0.751	0.319	1.507	7.02	9.49
	2			0.028	1.070	−0.75	1.37
3, pyridazine mono-N-oxide	1 (N)	0.820	0.751	0.455	1.375	10.10	10.03
	2 (N)			0.167	1.602	3.68	5.26
	3			−0.010	0.796	0.29	0.42
	4			0.065	1.270	−1.52	1.41
	5			0.140	0.986	−3.08	4.58
	6			0.158	1.115	−3.45	5.91
4, quinoline N-oxide	1 (N)	0.821	0.750	0.395	1.491	8.39	6.00
	2			0.125	1.218	−3.03	—
	3			−0.002	0.972	0.06	—
	4			0.211	1.272	−4.98	—
5, quinoxaline mono-N-oxide	1 (N)	0.900	0.751	0.305	1.521	6.71	6.72
	2			0.064	1.081	−1.78	2.44
	5			0.059	0.979	−1.59	1.81
	6			0.044	1.044	−1.18	1.44
6, acridine N-oxide	1	0.839	0.750	0.196	1.129	−4.57	5.34
	2			0.108	0.949	−2.92	2.89
	3			0.084	1.106	−2.27	2.58
	4			0.058	1.103	−1.50	1.43
	9			−0.008	1.012	0.22	0.49
	10 (N)			0.378	1.496	8.36	6.82
7a, phenazine mono-N-oxide	1	0.781	0.751	0.108	0.980	−2.90	3.60
	2			0.062	1.109	−1.68	1.80
	3			0.059	0.940	−1.59	1.65
	4			0.038	1.101	−1.03	1.23
	10 (N)			0.371	1.440	8.34	7.58
7b, phenazine di-N-oxide	1	0.762	0.750	0.600	1.030	−1.62	1.75
	2			0.044	1.005	−1.18	1.36
	9 (N)			0.290	1.511	6.38	5.91

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[a] Nitrogen hyperfine splitting calculated from $a_i = 22\rho_i$ where ρ_i is the spin density on the nitrogen atom at position i.

[b] Ring proton splittings calculated from $a_i = -27\rho_i$ where ρ_i is the spin density on the carbon atom at postion i to which the proton is bonded.

[c] See Fig. 1 for the structural formulas and the numbering scheme.

[d] See Ref. 12.

[e] All hyperfine splittings are expressed in gauss.

may be obtained from the normalization condition. Thus in the radical anion of 1, $q_0 = 9 - 1.487 - 2(1.198) - 2(0.987) - 1.263 = 1.880$. Table 1 includes the theoretical estimates of the nitrogen hyperfine splittings as calculated from Eq. (1) where ρ_i is the spin density on the nitrogen atom

$$a_i^M = 22\rho_i \tag{1}$$

at position i, the theoretical estimates of the ring proton splittings as calculated from Eq. (2)

$$a_i^M = -27\rho_i \tag{2}$$

where ρ_i is the spin density on the ith carbon atom to which the proton is bonded, and the observed hyperfine splittings from the work of Kubota *et al.* [12]. For completeness the expectation values of the S^2 operator before (ba) and after (aa) annihilation of the quartet spin component are listed in Table 1. In agreement with studies on aromatic hydrocarbon radicals [15] and a variety of radical anions [21, 22] we observe that annihilation of the quartet spin component improves the value of $\langle S^2 \rangle$ and also the values of the spin densities.

The ^{14}N and proton hyperfine splittings, calculated by use of the McConnell relation [23], agree well with the observed values listed in Table 1. In contrast to some previous calculations [24] in which the interpretation of ^{14}N hyperfine splittings in terms of the π spin density on nitrogen has not been as successful as the interpretation of hydrocarbon spectra, we note that the agreement between theory and experiment for ^{14}N hyperfine splittings is comparable to the results reported here for proton hyperfine splittings. Furthermore the McConnell relation has been used for both nuclei and the choice of 22 gauss for the proportionality constant Q is precisely the same value that has been shown to be appropriate for the radical anions of aza-aromatics [25]. Here it should be noted that Zeiss and Whitehead [13c] reached a similar conclusion in their study of several relations between spin density and hyperfine splitting in the radical anions of conjugated molecules containing nitrogen. A complete survey of the calculation of ^{14}N hyperfine splittings is beyond the scope of this paper. For brief reviews and additional references the reader is referred to the papers of Black and McDowell [24] and Zeiss and Whitehead [13c].

To conclude we would like to briefly relate our results to the reactivity of heterocyclic amine N-oxides. Electrophilic substitution is favoured at the 2 and 4 positions of pyridine N-oxide [4]. The computed spin density distribution is consistent with this observation since the splitting constants are larger at the 2 and 4 positions than at the 3 position: $a_2 = -3.10$, $a_4 = -5.04$ and $a_3 = -0.55$. Here we should note that our calculations are also consistent with the lower basicity of the heterocyclic amine N-oxides relative to the parent bases. For comparison with the principal resonance forms of pyridine N-oxide shown in Fig. 1, we may draw for pyridine two equivalent Kekulé structures and three zwitterionic forms with a negative charge on nitrogen. The latter three resonance structures favour the basicity of pyridine whereas resonance forms 1–5 to 1–7 of pyridine N-oxide (see Fig. 1) suggest that the N-oxide is very much less basic. The observed pK_a's in aqueous solution support this conclusion: 5.29 for pyridine and 0.79 for pyridine N-oxide [4]. This discussion also supports our decision to raise the valence state ionization potential of nitrogen from the 28.16 eV value used previously [27] to 29.16 eV.

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