

placed in Pyrex ampoules and degassed by the freeze-thaw method. The tubes, which were always protected from light, were immersed in a thermostated oil bath at 40°. The individual reactions were removed at the desired intervals and analyzed as above. The results are shown in Table IV.

**The Azobisisobutyronitrile-Initiated Bromination of 1-Bromobutane with NBS.** The reaction mixtures consisted of NBS (2.143 g; 0.0120 mol), 1-bromobutane (6.861 g; 0.0508 mol), and acetonitrile (20 ml) containing 3% AIBN. The solutions were degassed by the freeze-thaw method in the dark, wrapped in silver foil. The tubes were immersed in a thermostated bath at 40° and then removed after varying lengths of time and analyzed as above. The results are shown in Table II.

**Photobromination of 1-Bromobutane in the Presence of Added 1,1-Dibromobutane.** Solutions of 1-bromobutane (0.0067 mol), bromine (0.0016 mol), 1,1-dibromobutane (0.00099 mol), and Freon-113 (0.0010 mol) were degassed in a sealed Pyrex ampoule and irradiated by two 200-W bulbs until colorless. Glpc analysis

was carried out using a 10 ft  $\times$  1/4 in. 5% DEGS column and the product distribution was determined using a calibration curve. The product composition was 1,1-dibromobutane (0.0011 mol), 1,2-dibromobutane (0.0016 mol), 1,3-dibromobutane (0.00020 mol), and 1-bromobutane (0.0050 mol).

**Photobromination of 1-Bromobutane in the Presence of Added 1,3-Dibromobutane.** Solutions of 1-bromobutane (0.0208 mol), bromine (0.0062 mol), 1,3-dibromobutane (0.00366 mol), and Freon-113 (0.00383 mol) were degassed in a Pyrex ampoule and irradiated until colorless and the product distribution was determined using a calibration curve. The product composition was 1-bromobutane (0.0151 mol), 1,2-dibromobutane (0.00557 mol), and 1,3-dibromobutane (0.00433 mol).

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## Tetraazanaphthalene Radical Anions

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**Abstract:** The esr spectra of three tetraazanaphthalene radical anions are reported. Comparison is made among assignments obtained by MO calculations, empirical rules, and experimental methods. The effect of the choice of the  $k_{NN}$  resonance integral upon the calculated spin densities is discussed.

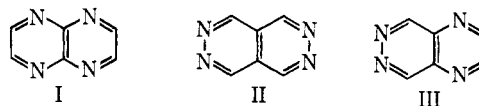
The esr spectra of azanaphthalene radical anions have been investigated by many authors with the purpose of assigning proton and nitrogen hyperfine splittings both experimentally and theoretically.<sup>2-6</sup> In the molecular orbital framework, Coulomb ( $h_N$ ) and resonance ( $k_{CN}$ ) integrals for the nitrogen atom were thus quite well defined<sup>2a, 4-8</sup> and attempts were undertaken to make assignments by using more sophisticated calculations. In some cases they were found, however, to disagree with the results of the standard McLachlan spin densities, but experimental assignment confirmed the correctness of the McLachlan method.<sup>5,6</sup>

Empirical rules were also proposed as a possible alternative in assigning hyperfine splittings<sup>9,10</sup> and they gave satisfactory results when applied to diazanaphthalene radicals.<sup>4,6</sup> In order to verify whether these rules may

be extended to systems with four nitrogen atoms in different ring positions as well as to study the effects of the molecular orbital parameters on the calculated spin densities, three isomeric tetraazanaphthalene radicals were investigated.

### Results and Discussion

The radical anions of three among the possible tetraazanaphthalene isomers, namely the 1,4,5,8-(I), the 2,3,6,7- (II), and the 1,4,6,7- (III) tetraazanaphthalenes,



were obtained and their esr spectra examined. In the experimental conditions employed, the free anions are believed to be obtained since no evidence was detected of splittings due to the counterion and, furthermore, the spectrum of radical I is equal to that obtained by the electrochemical method in formamide solution.<sup>3</sup> The interpretation of the esr spectra is straightforward owing to the symmetry of the molecules involved; the hyperfine splittings of hydrogens and nitrogens are reported in Table I and a sample spectrum is given in Figure 1.

While there is no problem in assigning the splitting constants in the radicals I and II, the assignment of the  $a_H$ 's to the two pairs of hydrogens in III is not straightforward because of the closeness of the two experimental values. On the contrary, the smaller of the two  $a_N$  splittings of III can be assigned to the nitrogens at posi-

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**Table I.** Experimental Hyperfine Splitting Constants and Calculated McLachlan Spin Densities<sup>a</sup>

Radical	Positions	Experimental splittings		Spin densities	
		$a_H$	$a_N$		
I	1,4,5,8		3.40	0.1726	
	2,3,6,7	3.10		0.0998	
II	1,4,5,8	5.50		0.2821	-0.0470
	2,3,6,7		0.45	-0.0075	0.2340
III	1,4		5.54	0.2754	0.2813
	2,3	3.57		0.1280	0.1278
	5,8	3.23		0.1358	0.1259
	6,7		0.63	-0.0055	-0.0036

<sup>a</sup>  $\lambda = 1.2$ ,  $h_N = 0.7$ , and  $k_{CN} = 0.9$ ; for the radicals II and III the additional parameters  $k_{NN} = 1.0$  (fifth column) or  $k_{NN} = 0.75$  (sixth column) were used.

tions 6 and 7 and the greater to those at positions 1 and 4, since, as it appears from the spectra of radicals I and II, nitrogens at positions  $\alpha$  have much greater splittings than those at positions  $\beta$ . This finding is also in agreement with the  $a_N$  values reported at analogous positions in diazanaphthalenes such as phthalazine<sup>2b</sup> and quinoxaline.<sup>4</sup> The spin density distributions of I, II, and III, calculated with the McLachlan method,<sup>11</sup> are in general agreement with the experimental hyperfine splittings (see Table I); for the Coulomb and resonance integrals  $h_N$  and  $k_{CN}$  values which are in the range defined by many authors<sup>2a,4-8</sup> were used, but for the  $k_{NN}$  integral such a well-tested range is not available. In the few cases so far reported<sup>2b</sup> the latter has been equal to  $k_{CC}$ , but the radicals involved had  $a_H$  splittings differing from each other enough not to make the choice of  $k_{NN}$  critical, as it is for the present assignment. Yet, excepting this approximation, the McLachlan spin densities indicate that in radical III  $a_{H-2,H-3}$  is expected to be smaller than  $a_{H-5,H-8}$ .

A second method to make an assignment, based on the empirical evaluation of the perturbation induced by the nitrogen atoms on the  $a_H$  values in respect to those of the parent hydrocarbon (here naphthalene), gave satisfactory results when applied to diazanaphthalenes.<sup>6</sup> Even though such an approach had been proposed<sup>9</sup> and used<sup>10</sup> in the cases of the small perturbations due to substituents such as methyl and chlorine, it worked surprisingly well even when heterocyclic nitrogens were involved.<sup>6</sup> The possibility of applying this method to assign the  $a_H$  values in III has been first tested by evaluating the proton splittings in I and II where there are not problems of assignment; this requires building up the tetraazaphthalenes by using two diazanaphthalenes of appropriate symmetry. The radical I can be built up in three different ways by using twice either the 1,4-,<sup>4</sup> the 1,5-,<sup>4</sup> or the 1,8-diazaphthalene.<sup>12</sup> The  $a_H$  splittings obtained in such a way are, respectively, 2.93, 2.82, and 3.06 G; this shows the internal consistency of the method as well as the good agreement with the experiment (3.10 G). A further test is provided by the radical II which can be built up in two ways using twice either the 2,3- or the 2,6-diazaphthalene;<sup>13</sup> even though the latter of these two cases does not agree as satisfactorily as the former with the experimental result (4.48, 5.62, and 5.50, respectively), the method, as a

(11) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(12)  $a_{H-2} = 4.38$  and  $a_{H-3} = 0.50$  G, according to ref 6.

(13)  $a_{H-1} = 5.02$  and  $a_{H-4} = 4.39$  G, according to ref 6.

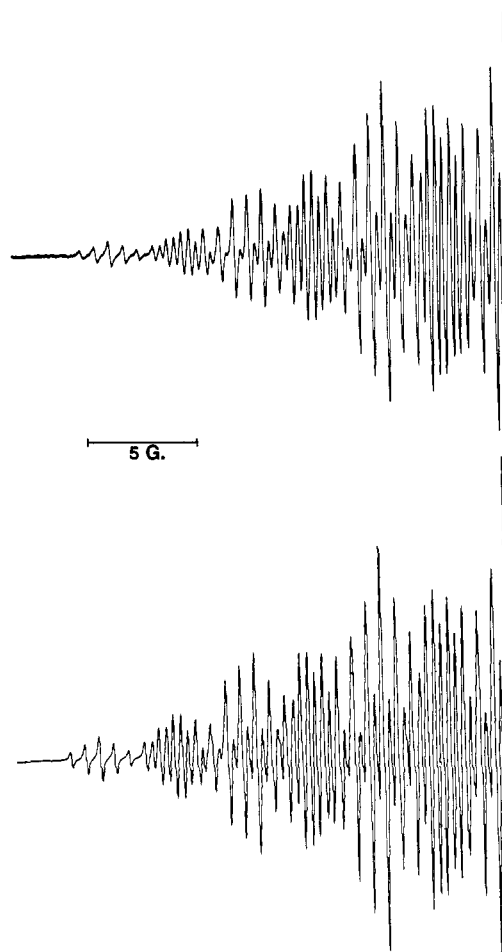


Figure 1. Experimental (upper) and computer-simulated esr half-spectrum of the 1,4,6,7-tetraazaphthalene (III) radical anion.

whole, seems worth careful consideration. As a consequence, the  $a_H$  splittings calculated by building up the tetraazaphthalene III with the 1,4-<sup>4</sup> plus the 2,3-diazaphthalene<sup>2b</sup> are  $a_{H-2,H-3} = 3.63$  and  $a_{H-5,H-8} = 3.32$  G. The values are in good agreement with the experimental splittings but indicate an assignment opposite to that of the McLachlan spin densities. No other diazanaphthalenes of appropriate symmetry and with hyperfine splittings unambiguously assigned are, at present, available for an independent test of this result.

Since the two methods employed lead to opposite conclusions, an experimental determination was attempted to definitely solve the problem. The esr spectrum of a mixture of two 1,4,6,7-tetraazaphthalene radicals, mono- and dideuterated at positions 5 and 8, allowed the determination of the two overall splittings (36.05 and 33.75 G for the mono- and dideuterated radicals, respectively). The overall splittings calculated assuming the spin densities assignment are thus incorrect (35.81 and 33.34 G) while those calculated with the assignment of the additivity rules (36.04 and 33.80 G) agree with the experimental result.<sup>14</sup> Most likely the failure of the MO calculations in predicting the correct assignment depends, as mentioned, on the approximation  $k_{NN} = k_{CC}$ . Indeed, if smaller values are considered for such an integral, the spin densities on C-2 and -3 are almost unaffected while those on C-5 and -8

(14) The  $a_D/a_H$  ratio has been considered, as usual, equal to 0.1535.

