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).

Tetraazanaphthalene Radical Anions

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Contribution from the Laboratorio dei Composti del Carbonio Contenenti Eteroatomi, C. N. R., Ozzano Emilia, Italy, and the Institute of Organic and Industrial Chemistry, University of Bologna, 40136 Bologna, Italy. Received January 28, 1971

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.[2–6] In the molecular orbital framework, Coulomb (h_N) and resonance (k_{CN}) integrals for the nitrogen atom were thus quite well defined[2a,4–8] 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.[5,6]

Empirical rules were also proposed as a possible alternative in assigning hyperfine splittings[9,10] and they gave satisfactory results when applied to diazanaphthalene radicals.[4,6] 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,
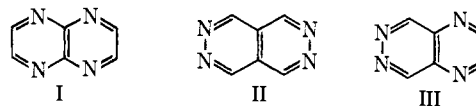
were obtained and their esr spectra examined. In the experimental conditions employed, the free anions are believed to be obtained since no evidence was detected of splittings due to the counterion and, furthermore, the spectrum of radical 1 is equal to that obtained by the electrochemical method in formamide solution.[3] 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[a]

Radical	Positions	Experimental splittings a_H	a_N	Spin densities	
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

[a] $\lambda = 1.2$, $h_N = 0.7$, 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 α have much greater splittings than those at positions β. This finding is also in agreement with the a_N values reported at analogous positions in diazanaphthalenes such as phtalazine[2b] and quinoxaline.[4] The spin density distributions of I, II, and III, calculated with the McLachlan method,[11] 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[2a,4-8] were used, but for the k_{NN} integral such a well-tested range is not available. In the few cases so far reported[2b] 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.[6] Even though such an approach had been proposed[9] and used[10] 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.[6] 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 tetraazanaphthalenes 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-,[4] the 1,5-,[4] or the 1,8-diazanaphthalene.[12] 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-diazanaphthalene;[13] 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.
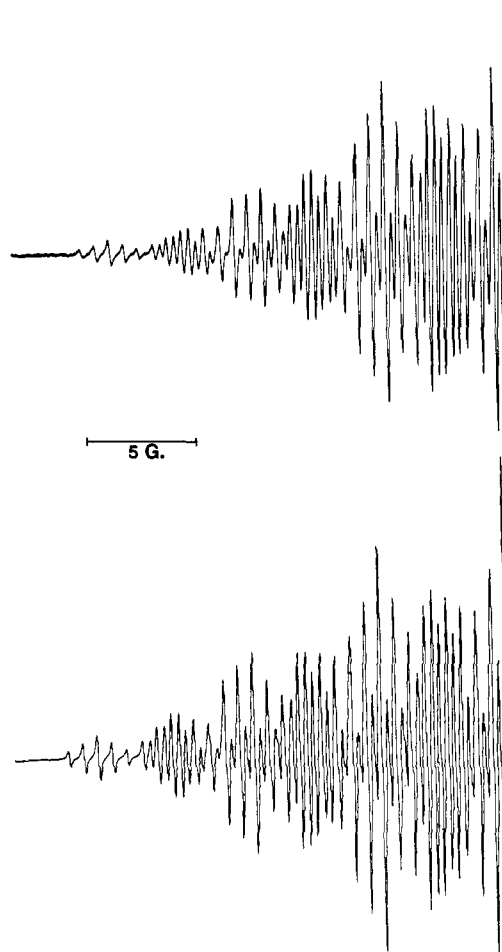(13) $a_{H-1} = 5.02$ and $a_{H-4} = 4.39$ G, according to ref 6.

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

whole, seems worth careful consideration. As a consequence, the a_H splittings calculated by building up the tetraazanaphthalene III with the 1,4-[4] plus the 2,3-diazanaphthalene[2b] 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-tetraazanaphthalene radicals, mono- and dideuterated at positions 5 and 8, allowed the determination of the two overall splittings (36.0$_5$ and 33.7$_5$ 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 (36.0$_4$ and 33.8$_0$ G) agree with the experimental result.[14] 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.

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decrease and eventually, for $k_{NN} = 0.75$, become smaller than those of C-2 and -3. This value still leads to qualitative agreement with the trend of a_H splittings reported in the literature for other radicals containing the NN bond; however, it cannot be used in the radical II since, owing to the orbital crossing effect,[15] its first antibonding orbital becomes symmetric instead of antisymmetric for $k_{NN} < 0.9$, and the carbon and nitrogen spin densities are thus reversed (see Table I).

Experimental Section

The radicals were obtained by allowing solutions of I, II, and III in hexamethylphosphorictriamide (HMPTA) to react with a potassium mirror in a vacuum sealed tube; the solvent was dried on barium oxide and distilled immediately before use.

The 1,4,5,8-tetraazanaphthalene (I) was obtained by the reaction of 2,3-diaminopyrazine with glyoxal;[16] the nmr spectrum (in

HMPTA) shows a single peak at 9.7_0 ppm. The 2,3,6,7-tetraazanaphthalene (II) resulted from the reduction of ethyl pyridazine-4,5-dicarboxylate with $LiAlH_4$, followed by condensation with hydrazine.[17] The 1,4,6,7-tetraazanaphthalene (III) was obtained by condensation of 4,5-diaminopyridazine with glyoxal;[18] the nmr spectrum (in $CDCl_3$) shows two peaks of equal intensity at 9.2_5 and $10._0$ ppm, which are shifted, in HMPTA, at 10.1 and 10.4. The deuterated derivatives of III were obtained by flowing gaseous deuterium into a CH_3OD solution of the corresponding 5,8-dichloro derivative,[18] using palladium-on-carbon as a catalyst. The nmr spectrum of the resulting compound has two peaks in the same positions of III but with a 5:1 intensity ratio, thus indicating a noncomplete deuteration at the 5 and 8 positions. The esr spectrum of the corresponding radical is in fact a 60–40% mixture, respectively, of the di- and monodeuterated tetraazanaphthalene (III) at positions 5 and 8.

The esr spectra were recorded on Varian 4502 spectrometer (100 kHz, modulation) and the simulated spectra were plotted on a IBM 7094 computer by assuming a Lorentzian line shape with a 0.12-G width.

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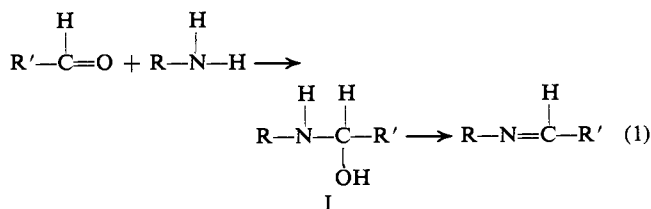(18) N. T. Patel and N. Eastle, *J. Heterocycl. Chem.*, **3**, 512 (1966).

The Reaction of Amines with Pyridoxal Azomethines. The Question of Transaldimation and Its Role in the Mechanism of Vitamin B₆ Enzymes[1]
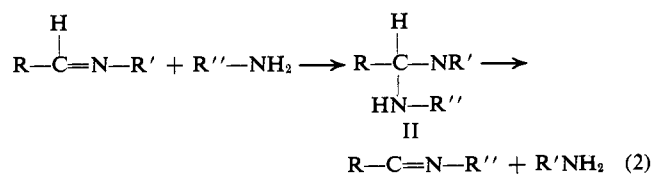
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Abstract: The nuclear magnetic resonance (nmr) spectra of D_2O solutions of pyridoxal with 2,3-diaminopropionic acid, 2,4-diaminobutyric acid, ornithine, and lysine are discussed. In all systems, two Schiff bases are observed, both of which contain one amino acid and one pyridoxal moiety. No evidence is found for the intraconversion of these Schiff bases (transaldimation) *via* a geminal diamine species such as has been proposed to arise from the condensation of the free amino group with the azomethine linkage. In the 2,3-diaminopropionic acid, 2,4-diaminobutyric acid, and ornithine cases, slow appearance of the internal geminal diamines is observed; however, their formation is much slower than are Schiff base formation and dissociation. Schiff bases containing one pyridoxal and one amino acid moiety are observed in the ornithine and lysine cases. Evidence is reported indicating that one of the Schiff bases in the 2,3-diaminopropionic acid–pyridoxal system is in rapid equilibrium with another species. Various possibilities are considered and it is concluded that the second species is a carbinolamine. The relevance of these reactions to the initial steps of substrate–vitamin B₆ enzyme interactions is discussed.

Jencks and Cordes[3] and Koehler, *et al.*,[4] found by kinetic analysis that the reaction of certain Schiff bases with amines to form a second Schiff base (transaldimation) was too rapid to proceed through dissociation to the aldehyde and amine. These authors[5] had previously demonstrated the importance of carbinolamines as intermediates in the Schiff base formation reaction 1. They therefore suggested that the trans-

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$$R'-\overset{\overset{H}{|}}{C}=O + R-\overset{\overset{H}{|}}{N}-H \longrightarrow$$

$$R-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{N}}-\overset{\overset{H}{|}}{C}-R' \longrightarrow R-N=\overset{\overset{H}{|}}{C}-R' \quad (1)$$

$$I$$

aldimation reaction passes through a geminal diamine type structure II analogous to the carbinolamine (I) as represented in eq 2.

$$R-\overset{\overset{H}{|}}{C}=N-R' + R''-NH_2 \longrightarrow R-\overset{\overset{H}{|}}{\underset{\underset{HN-R''}{|}}{C}}-NR' \longrightarrow$$

$$II$$

$$R-C=N-R'' + R'NH_2 \quad (2)$$