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THE STRUCTURE OF SO-CALLED DIAZOHYDROXYAMINOBENZENES

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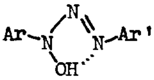
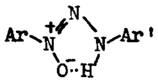
The action of diazonium salts on N-arylhydroxylamines gives rise to compounds which have been assumed to have the structure of 3-hydroxytriazene (I) (1). These compounds have also been formed in good yields by the action of peroxybenzoic acid on diazoaminobenzenes in ether (2); it therefore seems evident that a tautomeric form (II), triazene 1-oxide, is a possible alternative structure. The tautomerism is also reflected in the existence of both O- and N-ethers derived from this type of compounds (3, 4). We now present evidence in favour of the structure of triazene 1-oxide (II).


(I)


(II)

The infrared spectrum of diazohydroxyaminobenzene (III) in carbon tetrachloride exhibits only one band at 3250.6 cm.$^{-1}$ in the 3000-4000 cm.$^{-1}$ region. Whether this band is assigned to an N-H or to an O-H stretching vibration, its lower frequency compared with their normal frequencies indicates the presence of an intramolecular hydrogen-bonding (I or II), in keeping with the result of cryoscopic measurements (5). This intramolecular hydrogen-bonding is also supported by the fact that the band is shifted only slightly to the lower wavelength region when observed in benzene, indicating the absence of an intermolecular interaction due to the hydrogen-bonding to the π-electrons in a molecule of solvent benzene, whereas diazoaminobenzene (IV) shows a much larger shift in benzene (Table 1) owing to this type of interaction.

Table 1

Absorption Bands in 3000-4000 cm.$^{-1}$ Region

Compound	Solvent	ν(cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	A·10^{-3} (l.mole^{-1}cm.$^{-2}$)
III	CCl_4	3250.6	34	7.4
III (^{15}N)	CCl_4	3243.7	34	7.4
III	C_6H_6	3247.6	33	8.4
IV	CCl_4	3326.1	11	4.0
IV	C_6H_6	3305.3	32	9.4
V	CCl_4	3244.8	42	7.8
V (^{15}N)	CCl_4	3237.6	42	7.8

The infrared spectrum of diazohydroxyaminobenzene labelled with ^{15}N at the position remote from the oxygen atom, which was prepared by coupling of N-phenylhydroxylamine with diazotized aniline-^{15}N, showed a band at 3243.7 cm.$^{-1}$, i.e., at the position lower by 6.9 cm.$^{-1}$ than that of the non-labelled compound. Since the shift is quite close to the value of 7.3 cm.$^{-1}$ expected from the Hooke's law treatment of the ^{15}N-isotope effect on the N-H stretching vibration, this result leaves no doubt that the correct or overwhelmingly preponderant structure of diazohydroxyamino-compounds is structure II, rather than structure I, with which such a shift would not be expected to arise.

Similarly, the ^{15}N-labelled p-methoxy derivative (V), the coupling product of N-phenylhydroxylamine with diazotized p-anisidine-^{15}N, absorbs at 3237.6 cm.$^{-1}$, i.e., lower by 7.2 cm.$^{-1}$ than the corresponding non-labelled compound (m.p. 116-117° with decomposition. Found: C, 64.14; H, 5.59; N, 17.34. $C_{13}H_{13}N_3O_2$ requires: C, 64.19; H, 5.39; N, 17.27%), showing that the hydrogen atom is exclusively bonded to the nitrogen atom attached to the p-methoxyphenyl group: p-$MeOC_6H_4\cdot{}^{15}NH\cdot N{:}N^+(O^-)\cdot C_6H_5$. This result seems to indicate that the N-oxide structure (II) is exclusively favoured irrespective of the polar nature of a substituent, because the electron-releasing p-methoxy group has been expected to cause the azo rather than the electron-releasing imino group to be placed adjacent to the p-methoxyphenyl group: p-$MeOC_6H_4N{:}N\cdot N(OH)C_6H_5$. In fact, in the case of diazoaminobenzene, a p-methoxy group favours structure VII, in which the azo group is attached to the p-methoxyphenyl group, over the tautomeric structure (VI) (Table 2). This was shown by comparison of the integrated absorption intensities (A) corresponding to the two N-H absorption bands of forms VI and VII, which were distinguished by ^{15}N-labelling.

The measurements of spectra were carried out as previously described (6), immediately after preparation of solu-

Table 2

Absorption Bands due to Tautomeric Forms of p-Methoxydiazoaminobenzene in Carbon Tetrachloride

$$\underset{\text{(VI)}}{\text{p-MeO}\cdot C_6H_4\cdot{}^{15}NH\cdot N{:}N\cdot C_6H_5} \rightleftharpoons \underset{\text{(VII)}}{\text{p-MeO}\cdot C_6H_4\cdot{}^{15}N{:}N\cdot NH\cdot C_6H_5}$$

		ν_{N-H} (cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$A\cdot10^{-3}$ (l.mole^{-1}cm.$^{-2}$)
^{15}N-labelled Compound	VI	3316.1*	11.8	0.60
	VII	3329.0	11.8	3.10
Non-labelled Compound		3328.6		

* $\nu_{^{15}N-H}$

tions since diazoaminobenzene oxides are relatively unstable in carbon tetrachloride. In tables 1 and 2, $\Delta\nu_{1/2}$ denotes the half band width, and integrated absorption intensities (A) were estimated by Ramsay's method (7).

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