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THE STRUCTURE OF ARYLKETOXIMES AND THEIR IMINOXY RADICALS

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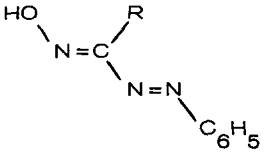
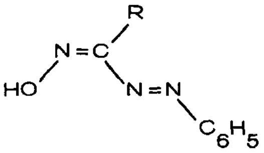
In view of current interest in the hydrogen bonding in oximes,$^{1)}$ the study of the structure of arylazoketoximes appeared desirable. One can conceive of three structures, a linear trans-anti isomer (1), a linear trans-syn isomer (2) and a trans-syn isomer with a strong intramolecular hydrogen bridge (3) in analogy to the red trans-syn isomers of the formazans (4).

1





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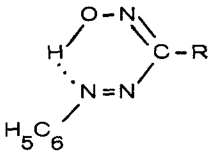

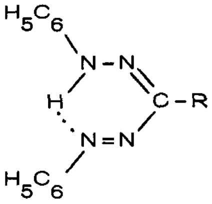

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The IR spectra of 5, 6 and 7 (table 1) in the solid phase show strong bands near 32oo/cm corresponding to the stretching vibrations of strongly associated hydroxy-groups. In 1-3 % carbon tetrachloride solution only bands at 357o/cm are observed, corresponding to the stretching vibration of free hydroxy-groups. These results exclude the structure 3.

Arylazoketoximes associate in the solid phase via strong intermolecular OH • • • N hydrogen bridges and probably give dimers in the form of six-membered rings like simple oximes [2].

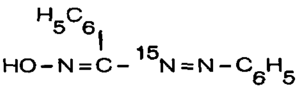
The chemical shift of the OH protons of oximes in dimethyl sulfoxide (DMSO) allows one to distinguish between structure 1 and 2. A larger chemical shift of the OH proton is expected for the trans-anti isomer [3]. As with most oximes, arylazo-aryl-ketoximes are mixtures of 1 and 2: in DMSO two different OH-signals are abtained. 7 (table 1) is a mixture of 1 and 2 in the ratio of 2:1. Surprisingly, phenylazo-formaldoxime (5) and phenylazo-methyl-ketoxime (6) turned out to be pure trans-anti isomers. This assignment is additionally supported in the case of 5 by the difference $\delta_{OH} - \delta_{CH} = 12.66 - 9.38 = 3.28$ [ppm], typical for a cis arrangement of H and OH at $>C=N\diagdown$ [3,4].

Table 1. IR and NMR data

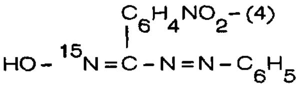
	R	$\nu(OH)_{free}$	$\nu(OH)_{assoc.}$	OH δ [ppm]
5	H [5]	3575/cm	326o/cm	12.66
6	H_3C [6]	3575/cm	32oo/cm	12.58
7	H_5C_6 [6]	357o/cm	331o/cm	12.52, 11.35 (2:1)

The dehydrogenation of these oximes in benzene at 4o°C by di-p-tolylaminyl radical [7] yields iminoxy radicals, which can also be generated by oxidation of the oximes with lead tetra-acetate in methylene dichloride solution in a flow system [8]. The ESR spectra (figure 1 and table 2) show two large nitrogen splittings in the range of 2o and 12 gauss. Surprisingly, the mixture of trans-anti and trans-syn isomers of arylazo-aryl-ketoximes generates only one type of iminoxy radicals. The assignment of the nitrogen splittings has been accomplished by ^{15}N labeling in the oximes 8 and 9.

8



$$\begin{array}{l} \quad\quad\;\; H_5C_6 \\ \quad\quad\quad\;\; | \\ HO-N=C-{}^{15}N=N-C_6H_5 \end{array}$$



$$\begin{array}{l} \quad\quad\quad\quad\;\; C_6H_4NO_2-(4) \\ \quad\quad\quad\quad\;\; | \\ HO-{}^{15}N=C-N=N-C_6H_5 \end{array}$$

9

The iminoxy radical derived from 8 yields the same ESR spectrum obtained from the unlabeled radical. The labeling of the oxime nitrogen in 9 changes the 19.7 gauss ^{14}N-splitting into a 27.2 gauss ^{15}N-splitting; a^{15N}/a^{14N} = 1.38 (gyromagnetic ratio 1.4o). Consequently the smaller 12 gauss nitrogen splitting is due to the azo-nitrogen connected with the aryl group.

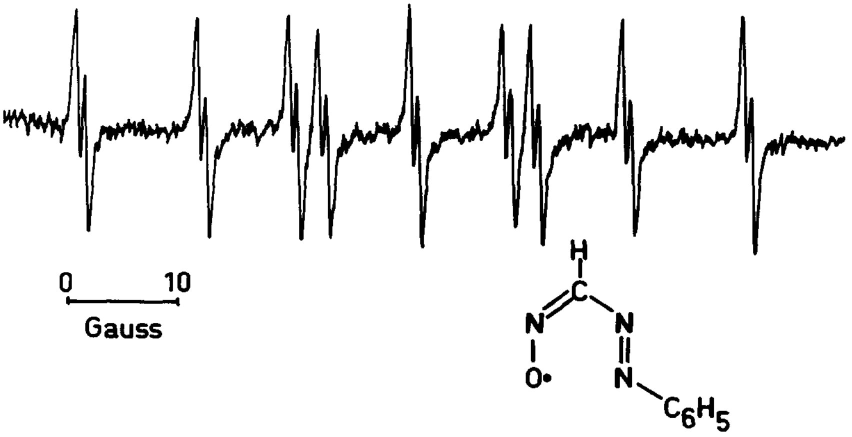
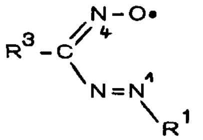


Figure 1. ESR spectrum of the iminoxy radical from phenylazo-formaldoxime (5) generated by the oxidation of the oxime by lead tetra-acetate in CH_2Cl_2 solution.

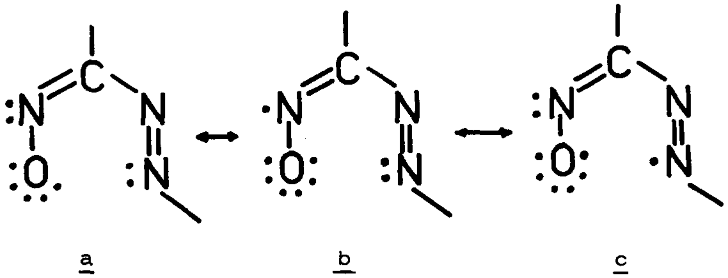
Table 2. ESR data



Solvent	R^1	R^3	a^{N^1}	a^{N^4}	a^H [gauss]
CH_2Cl_2	C_6H_5	H	1o.9	19.3	o.8
C_6H_6	C_6H_5	C_6H_5	11.6	19.8	
C_6H_6	$C_6H_4NO_2$-(4)	C_6H_5	11.6	2o.3	
C_6H_6	$C_6H_4OCH_3$-(4)	C_6H_5	11.4	19.8	
C_6H_6	C_6H_5	$C_6H_4NO_2$-(4)	12.3	19.7	
C_6H_6	C_6H_5	$C_6H_4OCH_3$-(4)	11.9	19.8	

The very high spin density at the nitrogen adjacent to the aryl group excludes linear structures and suggests a cyclic trans-syn conformation for the iminoxy radical species. This cyclic conformation could be the result of a very fast reorientation of linear iminoxy radicals primarily formed. The energeticly prefered cyclic conformation can be represented as a hybrid of the structures 1oa, b and c.

1o



In terms of MO theory, the measured spin densities imply that the unpaired electron is in a σ-orbital, whose main components are orbitals on the O atom and the adjacent N atoms, and which lies in the nodal plane of the π-system.

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