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- ESR and ENDOR Study of 2,3-Dihydro-1-oxo- $1\lambda^4$,2,3,5-thiatriazol-3-yl Radicals

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Dehydrogenation of 2,5-dihydro-1,2,3,5-thiatriazole 1-oxides with thermally formed bis(4-methylphenyl)aminyl generated 2,3-dihydro-1-oxo-1 λ^4 ,2,3,5-thiatriazol-3-yl radicals. ESR, ENDOR and triple resonance studies in combination with ¹⁵N labelling yielded the magnitude and assignment of all ¹H and ¹⁴N hyperfine coupling (HFC) constants. The radicals have a basic five- π -electron amidrazon-2-yl structure with the highest spin density at N-2.

KEY WORDS ESR Nitrogen-centred radicals 2,3-Dihydro-1-oxo-1/4,2,3,5thiatriazol-3-yl radicals

INTRODUCTION

We have recently reported¹ studies of 2,5dihydro-1,2,3,5-thiatriazol-5-yl radicals (1), which combine the basic structural features of 1,2,3,5-dithiadiazolyl and tetrazolinyl radicals, i.e. the thioaminyl and the hydrazyl molety, in a five-membered cyclic π -electron system. S-Oxidation should have a pronounced effect on the properties of these radicals. Replacement of —S— by —SO— is expected to disconnect the cyclic conjugation and may lead to a five- π -electron amidrazon-2-yl molety as the basic structural element. Related radicals are known, e.g. the stable 4,5-dihydro-1H-1,2,4-triazolyl radicals (2).²

Hydrogen abstraction from the parent 2,5-dihydro-1,2,3,5-thiatriazole 1-oxides (3) should lead to the formation of 2,3-dihydro-1-oxo-1 λ^4 ,2,3,5-thiatriazol-3-yl radicals (4).

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RESULTS AND DISCUSSION

Reaction of 3a-e with thermally formed bis(4-methylphenyl)aminyl generated the radicals 4a-e. Only radicals with aryl substituents in positions 2 and 4 are persistent. Attempts to detect radicals with alkyl groups in these positions by ESR in the liquid phase were not successful.

ENDOR studies of 4a and d (Fig. 1) clearly revealed all ¹H HFC constants and the largest ¹⁴N splitting and, in addition, general triple experiments³ provided the relative signs. The multiplicities of different sets of equivalent protons were derived from the ESR spectra, which were sufficiently resolved and are all well simulated using the data given in Table 1. Examples are shown in Figs. 2 and 3.

¹⁵N labelling gave an unambiguous assign-

ment of all N HFC constants. The simulation of the 300 K ESR spectra of 4d and e yielded $a(^{15}N-3) = 6.2$ and $a(^{15}N-5) = 3.44$ G. Consequently the large nitrogen splitting of ca. 8 G must stem from N-2. a(N-2) and a(N-3) clearly decrease with decreasing temperature (see Table 1). All ¹⁴N HFC constants are considered to be positive as for 1^1 and 2^2 A comparison of the proton HFC data of 4c with those of 4d reveals that the larger 'H splittings [4c (230 K): -2.58 (1H), -2.29 (2H) and +0.74 G (2H)] belong to the 2phenyl protons. Their further assignment to specific positions is based on the relative signs and the number of equivalent protons. This pattern corresponds to that found for the N-phenyl protons in 1 [2,5-dihydro-2,4diphenyl-1,2,3,5-thiatriazol-5-yl, ENDOR, dimethoxyethane, 220 K : a(N-2) = 7.61. a(N-2) = 7.61. 3) = 4.12, a(N-5) = 5.08, a(H-2',4',6') = -1.79

Reference Data



Figure 1. ENDOR spectrum of 2,3-dihydro-2,4-diphenyl-1-oxo-114,2,3,5-thiatriazol-3-yl (4a) in toluene at 230 K.

Table 1. Hyperfine coupling constants of the 2,3-dihydro-1-oxo-124,2,3,5-thiatriazol-3-yl radicals 4a-e in toluene										
Compound	Method	7 (K)	8(N-2) (G)	a(N-3) (G)	a(N-5) (G)	a(H-2',6') (G)	a(H-3',5') (G)	a(H-4') (G)	a(H-2",4",6") (G)	a(H-3",5") (G)
4a	ESR	230	8.19	4.03	2,35	2.33	0.79	2.48	0.56	
	ENDOR	230	8.18			-2.29	+0.75	-2.58	-0.54	+0.13
4b	ESR	300	8.45	4.45	2.40					
4c	ESR	300	8.45	4.43	2.44	2.20	0.81	2.42		
	ESR	230	8.15	3.99	2.32	2.29	0.74	2.58		
4d	ESR	300	8.44	6.21	2.45	2.20	0.82	2.43	0.44	
	ESR	230	8.17	5.80	2.43	2.31	0.79	2.51	0.65	
	ENDOR	230	8.19			-2.29	+0.74	-2.58	-0.54	+0.13
4 0	ESR	300	8.46	6.19	3.44	2.18	0.80	2.45	0.45	



Figure 2. ESR spectrum of 4c in toluene at 300 K, together with a simulation using the data in Table 1.

Reference Data



Figure 3. ESR spectrum of 4d in toluene at 300 K, together with a simulation using the data in Table 1.

and a(H-3',5') = +0.61 G] and 2 [4,5-dihydro -1,3,5,5-tetraphenyl - 1*H* - 1,2,4-triazolyl,² ENDOR, toluene, 230 K: a(N-1) = 7.58, a(N-2) = 6.44, a(N-4) = 3.95, a(H-2',4',6') = -1.96and a(H-3',5') = +0.69 G]. Small HFC constants were found for the protons of the 4phenyl moiety, 4a (230 K): a(H-2'',4'',6'') = -0.54 and a(H-3'',5'') = +0.13 G. The *g* values of 4a-e were determined to be 2.0031.

The ESR-ENDOR results for the 2,3dihydro-1-oxo-1 λ^4 ,2,3,5-thiatriazol-3-y1 radicals (4a-e) indicate a π -SOMO which is mainly localized on N-2, N-3 and N-5, with the highest spin density at N-2. Delocalization of the unpaired electron into the sulphinyl link is negligible as indicated by the low g value of 2.0031. This value corresponds well with the g values for N-centred radicals with a triply coordinated (tetravalent) sulphur atom directly bonded to nitrogen, e.g. N-sulphinylaminyls, g = 2.0034.⁴ The π -SOMO of 4 is in accordance with a basic amidrazon-2-yl structure similar to that of 2.

EXPERIMENTAL

Compounds 3a-e were available in this laboratory.¹ Samples of toluene solutions containing 0.002 M 3 and 0.002 M tetrakis(4-methylphenyl)hydrazine were degassed by several freeze-pump-thaw cycles, sealed and heated at 90 °C for about 10 s to generate the radicals.

ESR and ENDOR spectra were recorded on a Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system. g Values were determined using an NMR gaussmeter and a Hewlett-Packard Model 5342A frequency counter; this was calibrated with the perylene radical cation. Hyperfine coupling constants measured in megahertz (ENDOR) were converted into gauss using 1 MHz = 0.7145/g G.

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