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The electronic structure of sulfonamidyl radicals. An ESR spectroscopic and ab-initio MO study of sulfonamidyl and some carboxamidyl radicals

Teeninga, Hermannus

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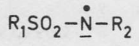
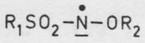
SUMMARY

This thesis describes an investigation of the electronic structure of sulfonamidyl radicals ($R_1SO_2\dot{N}R_2$) and some structurally related carboxamidyl radicals ($R_1C(O)\dot{N}R_2$). Both types of radicals have been invoked as intermediates in several chemical reactions. The present work originates from our interest in the influence of the sulfonyl group on a nitrogen-free radical center in comparison with that of the carbonyl group.



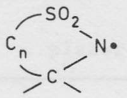
$R_1SO_2-\dot{\underline{N}}-R_2$

1



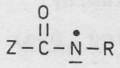
$R_1SO_2-\dot{\underline{N}}-OR_2$

2



n = 1,2

3

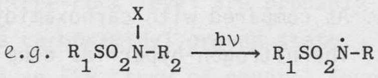


$Z-\overset{\overset{O}{\|}}{C}-\dot{\underline{N}}-R$

Z = R_1R_2N-, R_1O-

4

Therefore, a large variety of amidyl radicals of the types 1 - 4 have been generated and studied by ESR spectroscopy. These rather short-lived amidyl radicals were produced by photolysis of carefully degassed solutions of the corresponding N-bromo compounds (or, in some cases, the N-chloro compounds) in inert solvents, such as trichlorofluoromethane, directly in the cavity of the ESR spectrometer at low temperatures. In the Table the ESR results for 1 - 4 have been summarized together with some literature data for normal N-alkylcarboxamidyls (from the work of Ingold *et al*).



$$e.g.\ R_1SO_2\overset{X}{\overset{|}{N}}-R_2 \xrightarrow{h\nu} R_1SO_2\dot{N}-R$$

X = Br, Cl

Furthermore, *ab-initio* MO calculations have been carried out on model systems for sulfon- and carboxamidyls. The open-shell restricted Hartree-Fock (RHF) calculations have been performed mainly by using the "double zeta" basis of Roos and Siegbahn.

Chapter 1 contains an introduction and survey of the literature, with particular emphasis on aminyls ($R_1\dot{N}R_2$) and carboxamidyls. The discussion is mainly

TABLE: Observed nitrogen hfsc's and g values for different types of sulfon- and carboxamidyls.

radical	A_N (gauss)	g value
1 (15d - 29d)	12.9 - 13.5	*ca* 2.0044
2 (34d - 49d)	11.2 - 11.8	*ca* 2.0050
3 (55d - 65d)	12.4 - 13.4	*ca* 2.0045
4 ($Z = R_1R_2N$-, 78d - 82d)	14.9	*ca* 2.0047
4 ($Z = R_1O$, 85d - 87d)	14.0 - 15.6	2.0046 - 2.0053
acyclic carboxamidyls[a] ($R_1C(O)\dot{N}R_2$)	14 - 16[b]	2.0044 - 2.0055[b]
cyclic carboxamidyl[a] (5-membered ring, 59d)	11.2	2.0063

[a] Taken from literature data. [b] Depending on the bulk of R_2.

centered on the question how information about *configuration* and *conformation* of free radicals can be deduced from ESR-spectral data. In addition, the prerequisites for the ESR-spectroscopic detection of free radicals of low *persistence* are outlined.

In *Chapter 2* a detailed study of N-alkylsulfonamidyls 1 is presented. In fact, this study is an extension of the work of Zomer and Engberts on N-*t*-butylsulfonamidyl radicals. As compared with carboxamidyls, sulfonamidyls are somewhat more persistent. The nitrogen-hyperfine coupling constants (hfsc's) and g values (Table) are characteristic for a π_N *electronic ground state*, in which the odd electron resides in an N-2p orbital perpendicular to the SNC plane. Substituent effects on the A_N values are small and suggest little or no spin delocalization onto the sulfonyl group. The temperature dependence of the A_{H_β} parameter of several $R_1SO_2\dot{N}CH_2R_2$ and $R_1SO_2\dot{N}CHMe_2$ radicals has also been measured.

Chapter 3 contains an ESR study of N-alkoxysulfonamidyl radicals 2. The ESR data (Table) provide further support for a π_N electronic ground state of sulfonamidyls. The somewhat reduced A_N values (*ca* 2 G) suggest spin delocalization onto the alkoxy group. Again, variation of R_1 exerts very little influence on the ESR parameters: the SO_2 moiety serves as an electronic blocking group. From some preliminary quantitative photochemical experiments it is con-

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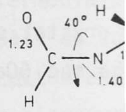

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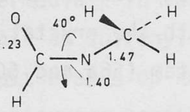
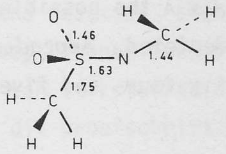
Chapter 6 contains
carbamidyls (4, Z = R_1

cluded that N-alkoxysulfonamidyls are sufficiently *stabilized* that they survive long enough in solution to form dimers. However, these dimers are so unstable that complicated reaction mixtures are often obtained.

Chapter 4 records the results of the quantum mechanical calculations. Geometry optimizations have predominantly been performed on different states (π and Σ) of N-methylformamidyl (<u>53d</u>) and N-methylmethanesulfonamidyl (<u>15d</u>) radicals. The following optimized structures have been obtained:



twisted "π_N", ∠ CNC = 120°



planar π_N, ∠ SNC = 115°

The computational results present evidence for interaction between the π and Σ states of carboxamidyls. On the other hand, it is shown that the ground state of sulfonamidyls can be described adequately as a π_N state. These results offer a rationale for the unexpectedly high A_N values of carboxamidyls as compared with those of sulfonamidyls. Accordingly, the molecular orbital containing the odd electron in the carboxamidyls will have a higher s character, mainly as a result of a contribution of a bent Σ_N state. Such a contribution would necessarily occur in twisted conformations. It is argued that further calculations even beyond the Hartree-Fock level are probably required to obtain a reliable description of the carboxamidyl ground state.

Chapter 5 deals with an ESR study of several four- and five-membered ring sulfonamidyls <u>3</u>. The ESR parameters (Table) of <u>3</u> almost equal those of acyclic sulfonamidyls <u>1</u>. This observation definitely rules out the possibility of an sp-hybridized nitrogen atom in sulfonamidyls. Further evidence for a planar geometry around nitrogen is obtained from an analysis of the experimental A_{H_β} values using the Heller-McConnell equation. Largely based on these results, the ESR-spectral data for acyclic and cyclic carboxamidyls are discussed.

In addition, interesting Hofmann-Löffler rearrangements have been found for N-bromo-3,3-di-*n*-propyl and N-bromo-3,3-di-*n*-butyl benzyl sultams (<u>63b</u> and <u>65b</u>). The reactions have been performed under photolytic and thermal conditions.

Chapter 6 contains a preliminary ESR study of ureyls (<u>4</u>, Z = R_1R_2N-) and carbamidyls (<u>4</u>, Z = R_1O). The ESR parameters (Table) again suggest a π_N type ground state for these species. The small differences with N-alkylcarboxamidyls can be rationalized in terms of twisting around the C(O)N bond rather than in terms of spin delocalization.

Finally, to obtain an unambiguous structural assignment of the proposed sulfonamidyls, the ESR parameters of several corresponding sulfonyl nitroxides have been determined. At the same time, sulfonyl nitroxides constitute an interesting class of free radicals. Their ESR spectral properties are discussed in Chapters 2 and 5.

In *Appendix* A the possible electronic states of carbox- and sulfonamidyl radicals are depicted. *Appendices* B en C deal with the crystal structure determination of a four- and five-membered ring sultam (56a and 60a).

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1

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