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

This thesis describes an investigation of the electronic structure of sulfonamidyl radicals (\(R_1SO_2NR_2\)) and some structurally related carboxamidyl radicals (\(R_1C(0)NR_2\)). 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.

\[
\begin{align*}
R_1SO_2^+N-R_2 & \quad R_1SO_2^-N-OR_2 \\
C_n^+SO_2^-N^* & \quad Z-C-N-R \\
Z=R_1R_2N-R_10^-
\end{align*}
\]

\(n=1,2\)

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.).

Furthermore, \(\textit{ab-initio}\) 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 (\(R_1\hat{N}R_2\)) and carboxamidyls. The discussion is mainly

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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-buty1sulfonamidyl 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 \( \pi_N \) electronic ground state, in which the odd electron resides in a 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 \( A_{\text{H}} \) parameter of several \( \text{R}_1\text{SO}_2\text{NCH}_2\text{R}_2 \) and \( \text{R}_1\text{SO}_2\text{NCHMe}_2 \) 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 \( \pi_N \) electronic ground state of sulfonamidyls. The somewhat reduced \( A_N \) values (ca 2 G) suggest spin delocalization onto the alkoxy group. Again, variation of \( \text{R}_2 \) exerts very little influence on the ESR parameters: the \( \text{SO}_2 \) moiety serves as an electronic blocking group. From some preliminary quantitative photochemical experiments it is concluded that N-alkoxysulfonamidyls are long enough in solution to be stable that complicated symmetry optimizations have been performed on the odd electron in these radicals as a result of a contribution necessary occur in twisted conformations even beyond the H Complete description of the computer results of carboxamidyls and of sulfonamidyls can be derived with those of sulfonamidyls 1.

The computational results for sulfonamidyl 3. The ESR spectra of sulfonamidyls 1. This orbital sp-hybridization nitrogen hyperfine coupling constants around nitrogen and \( A \) and \( g \) values using the Hessenberg's ESR-spectral data for a.

In addition, interest is devoted to N-bromo-3,3-di-n-Pt

Chapter 6 contains a detailed discussion of carboxamidyls (4, Z = R₁C(O)N).
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 (\(\pi\) and \(\Sigma\)) of N-methylformamidyl (53d) and N-methylmethanesulfonamidyl (15d) radicals. The following optimized structures have been obtained:

\[
\text{twisted } \pi^*, \quad L_{\text{N-C}} = 120^\circ \\
\text{planar } \pi^*, \quad L_{\text{N-C}} = 115^\circ
\]

The computational results present evidence for interaction between the \(\pi\) and \(\Sigma\) states of carboxamidyls. On the other hand, it is shown that the ground state of sulfonamidyls can be described adequately as a \(\pi^*_N\) 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 \(\Sigma^*_N\) 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 3. The ESR parameters (Table) of 3 almost equal those of acyclic sulfonamidyls 1. 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 \(A_{HB}\) 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-\(\alpha\)-propyl and N-bromo-3,3-di-\(\alpha\)-butyl benzyl sulfamates (63b and 65b). The reactions have been performed under photolytic and thermal conditions.

Chapter 6 contains a preliminary ESR study of ureyls (4, \(Z = R_1R_2\)) and carbamidyls (4, \(Z = R_1D\)). The ESR parameters (Table) again suggest a \(\pi^*_N\) type
ground state for these species. The small differences with N-alkylcarboxamidyls can be rationalized in terms of twisting around the C(0)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 and C deal with the crystal structure determination of a four- and five-membered ring sultam (56a and 60a).