Bonding in thiirene dioxides
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CHAPTER 1

AIM AND SURVEY

Thiirene dioxides \( \mathcal{Z} \) and thiirane dioxides \( \mathcal{Z} \) have been known for more than ten years as likely intermediates in the Ramberg-Beclklund rearrangement\(^1\) of \( \alpha \)-halo sulfoxes \( \mathcal{I} \) to alkenes and alkynes.

\[
\begin{align*}
R-CHX-SO_2-CHX-R & \xrightarrow{\text{base}} \text{R-CH}X-SO_2-CHX-R \\
R-CH_3-SO_2-CX_2-R & \xrightarrow{\text{base}} \text{R-CH}_3-SO_2-CX_2-R \\
& \xrightarrow{-SO_2} \text{RC}\equiv\text{CR}
\end{align*}
\]

Support for the intermediacy of three-membered rings was found in the isolation of 2,3-diphenylthiirene-1,1-dioxide \( \mathcal{S} \) by Carpino \textit{et al.}\(^6,\) using triethylamine as a base and an aprotic solvent like dichloromethane.

\[
\begin{align*}
\text{Ph-CHBr-SO}_2-\text{CHBr-Ph} & \xrightarrow{\text{Et}_3\text{N}} \text{Ph-CH}Br-SO_2-\text{CHBr-Ph} \\
\text{Et}_3\text{N} & \xrightarrow{\text{CH}_2\text{Cl}_2} \text{Ph-CH}Br-SO_2-\text{CHBr-Ph}
\end{align*}
\]

Although several attempts have been made\(^4,\)\(^7,\)\(^8\), thiirene dioxide itself has hitherto not been isolated. The simplest known stable derivatives are the methyl substituted compounds \( \mathcal{G} \) and \( \mathcal{H} \), also first synthesized by Carpino \textit{et al.}\(^7,\)\(^9\).

\[
\begin{align*}
\text{O} & \xrightarrow{\text{H}} \text{O} \\
\text{CH}_3 & \xrightarrow{\text{H}} \text{CH}_3
\end{align*}
\]
A great similarity in reactions is observed for the cyclic unsaturated ketones, sulfoxides and sulfones. The three-membered rings 8 are relatively unstable, losing CO$_{10}$, SO$_{11}$ or SO$_2$ easily, whereas the five-membered rings 9 are highly reactive and very prone to undergo Diels-Alder dimerization$^{12-14}$. The sulfones are more reactive than the corresponding sulfoxides.

\[ \text{R} - \text{Ct} \rightarrow \text{RC} = \text{CR} + \text{X} \quad \text{X} = \text{CO}, \text{SO}, \text{SO}_2 \]

\[ \text{2} \rightarrow \text{X} \quad \text{X} - \text{H}_2 \rightarrow \text{C} + \text{X} \]

In spite of this similarity there are different electronic interactions in thiirene dioxides and cyclopropenones. Carpino et al.$^7$ noticed that the polarity of the ketones varied much more than that of the analogous sulfones. From dipole moments they concluded that mesomeric structure 10a constitutes an important contribution to the charge distribution in cyclopropenone, whereas the analogous structure 11a was unimportant in thiirene dioxide.

\[ 10 \quad \rightarrow \quad 10^a \]
\[ 11 \quad \rightarrow \quad 11^a \quad \rightarrow \quad 11b \quad \rightarrow \quad \text{etc.} \]
On the other hand, the very low IR SO stretching frequencies for thiirene dioxides point to important contributions of structures like \textit{11a}. This study was intended to shed some light on these seemingly contradictory observations.

In a hydrogen bonding study on thiophene dioxides De Jong and Janssen \cite{15} showed that mesomeric structures analogous to \textit{11b} were important, whereas mesomers analogous to \textit{11a} were not. We studied some substituted thiirene dioxides and thiophene dioxides on the one hand, and diphenylcyclopropenone and tetraphenylcyclopentadienone on the other hand by their hydrogen bonding abilities. The results have been presented in a short paper \cite{16} and are discussed more comprehensively in Chapter 3. The synthesis of para-substituted 2,3-diphenylthiirene-1,1-dioxides \cite{17} \textit{12} used in the hydrogen bonding experiments is discussed in Chapter 2, along with our attempts to synthesize the elusive cyclic systems thiirene-1-imine \textit{13}, and thiirene-1-ox-1-imine \textit{14}, nitrogen analogs of thiirene dioxides.

![Diagram](image)

The photoelectron spectra and the data obtained from CNDO calculations published by Solouki et al. \cite{18,19} and by Schweig et al. \cite{20-22} show the effects of inductive and conjugative interactions on the energies of the molecular orbitals. We have tried to show how these interactions affect the charge distribution and the bond strengths in thiirene dioxides and related sulfones. An explanation is presented for the weak SO bond (as judged from IR stretch frequencies) and the relatively small charge separation (as judged from dipole moments and hy-
drogen bonding abilities) in thienene dioxides. The con-
jugative and inductive effects are discussed in terms of
simple HOMO-LUMO interactions of Hückel$^{23}$ and Möbius$^{24}$
type, obtained from CNDO/2 and ab-initio SCF MO calcula-
tions.

Our second aim was to see whether any relationship
existed between the differences in the population of the
sulfur 3d-orbitals and the different conjugative and in-
ductive interactions in the various sulfones studied. In
fact, we were expecting the d-orbital populations to dif-
fer mainly because of conjugative interactions in the $\sigma_{CS}$
and the $\sigma_{SO}$ bonds. Electron density difference plots were
used to obtain detailed information about the electron
density rearrangements due to inclusion of sulfur d-orbi-
tals in LCAO SCF-MO calculations. The final results of
this investigation, presented in Chapter 4, give a clear
insight into the factors which govern d-orbital popula-
tion in sulfones and sulfides, and, in a generalization,
other molecules of second-row elements. The argument
given, clearly demonstrates why carbonions adjacent to a
sulfur atom$^{25-29}$ (regardless of its oxidation state) are
even less stabilized than the neutral parent compounds.

The relation between the charge density on the oxy-
gen atoms of the sulfonyl and the carbonyl group, and the
experimentally determined hydrogen bond strengths$^{15,16}$,
is further investigated in Chapter 5. The results of
CNDO/2 and ab-initio calculations on sulfones can be used
to construct simple electrostatic models for the predic-
tion of hydrogen bond strengths. A very simple model is
presented, which can account for the observed trends in
hydrogen bonding abilities of sulfones and ketones. A
more sophisticated method given by Bonaccorsi et al.$^{30}$
was also tested. Making use of the full spatial electron
density distribution, obtained from ab-initio calcula-
tions, electrostatic potential energy-surfaces were com-
puted. These energy-surfaces may be used to predict the
strengths and the geometries of hydrogen bonds towards
The appendices contain information about the computer programs, the basis sets and the molecular geometries used. A short description is given of the computer programs written to obtain the Mulliken population analyses\textsuperscript{31} from symmetry adapted molecular orbitals\textsuperscript{52}, the electron density plots\textsuperscript{33}, and the electrostatic potential energy-surface plots\textsuperscript{30}.