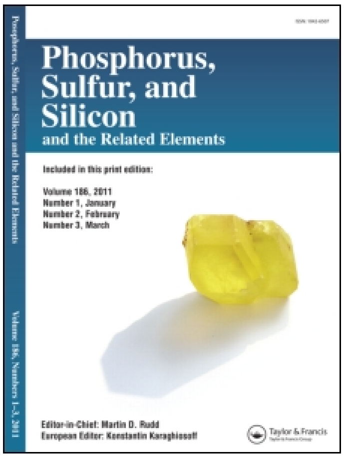


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ON THE CAPABILITY OF SULFUR FOR Pπ-Pπ-CONJUGATION IN ISOTHIURONIUM SALTS AND RELATED SYSTEMS

Günter P. Schiemenz[a]; Matthias Sommerfeld[a]
[a] Institut für Organische Chemie der Universität, Kiel, Federal Republic of Germany

To cite this Article Schiemenz, Günter P. and Sommerfeld, Matthias(1979) 'ON THE CAPABILITY OF SULFUR FOR Pπ-Pπ-CONJUGATION IN ISOTHIURONIUM SALTS AND RELATED SYSTEMS', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 273 — 274

To link to this Article: DOI: 10.1080/03086647908080410

URL: http://dx.doi.org/10.1080/03086647908080410

Phosphorus and Sulfur
1979, Vol. 6, pp. 273–274

ON THE CAPABILITY OF SULFUR FOR p_π-p_π-CONJUGATION IN ISOTHIURONIUM SALTS AND RELATED SYSTEMS

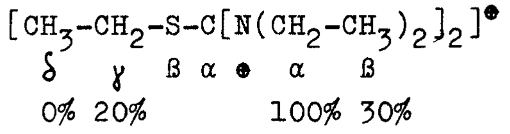
Günter P. Schiemenz and Matthias Sommerfeld

Institut für Organische Chemie der Universität,
Kiel, Federal Republic of Germany

The higher elements such as sulfur are often believed to have a low capability for participation in p_π-p_π bonding though thiophene is the most "aromatic" compound of the series , X = NH, O, S. In a recent review on sulfur-containing cations, Marino (1) wrote for isothiuronium salts "Clearly, the positive charge is distributed over several atoms besides sulfur, which is perhaps the least cationic of the heteroatoms".

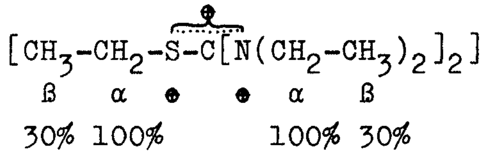
The ^{1}H-NMR spectra of ion pairs of isothiuronium salts do not confirm this view:

As reported previously (2,3), in ion pairs of organic cations and inorganic and organic anions, the charge centres approach each other as closely as possible. As a consequence, protons in α-position to the onium centre are most sensitive towards the nature of the anion, protons in ß- (γ-) position only to about 30% (20%) of the α-effect, and further distant protons almost not at all. In systems with several onium centres such as azolium salts, each of them behaves as a centre of positive charge (3). This allows to discriminate between the different possibilities (models I and II, and charge distribution in between these extremes):



$[CH_3\text{-}CH_2\text{-}S\text{-}C[N(CH_2\text{-}CH_3)_2]_2]^{\oplus}$
δ γ ß α ⊕ α ß
0% 20% 100% 30%

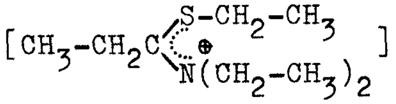
Model I: No participation of sulfur in conjugation



$[CH_3\text{-}CH_2\text{-}\overset{\oplus}{S\text{-}C[N}(CH_2\text{-}CH_3)_2]_2]$
ß α ⊕ ⊕ α ß
30% 100% 100% 30%

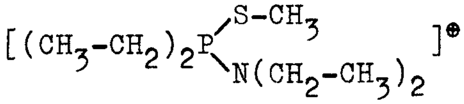
Model II: Full participation of sulfur in conjugation

The results clearly point to model II, i.e. full participation of sulfur in the resonance of the isothiuronium system. Thioimidiumester salts such as



$$\left[CH_3\text{-}CH_2C\begin{smallmatrix} S\text{-}CH_2\text{-}CH_3 \\ \oplus \\ N(CH_2\text{-}CH_3)_2 \end{smallmatrix}\right]$$

behave similarly, whereas the phosphorus analog



$$\left[(CH_3\text{-}CH_2)_2P\begin{smallmatrix} S\text{-}CH_3 \\ \\ N(CH_2\text{-}CH_3)_2 \end{smallmatrix}\right]^{\oplus}$$

turns out to carry the positive charge solely on phosphorus, i.e. it is a true phosphonium salt.

REFERENCES

(1) J.P. Marino, Topics Sulfur Chem. 1, 16 (1976).

(2) G.P. Schiemenz, Sulphur and d_π-p_π-Bonding: New Methods and Results. VIth International Symposium on Organic Sulphur Chemistry, Bangor, Wales, July 5th, 1974.

(3) G.P. Schiemenz and M. Begtrup, The Tetraphenylborate Anion as a Nuclear Magnetic Resonance Shift Reagent for Heterocyclic Onium Cations. Vth International Congress of Heterocyclic Chemistry, Ljubljana (Yougoslavia), July 14th, 1975.