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Phosphorus, Sulfur, and Silicon and the Related Elements

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ON THE CAPABILITY OF SULFUR FOR $P\pi$ - $P\pi$ -CONJUGATION IN ISOTHIURONIUM SALTS AND RELATED SYSTEMS

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
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ON THE CAPABILITY OF SULFUR FOR p_{π} - p_{π} -CONJUGATION IN
ISOTHIURONIUM SALTS AND RELATED SYSTEMS

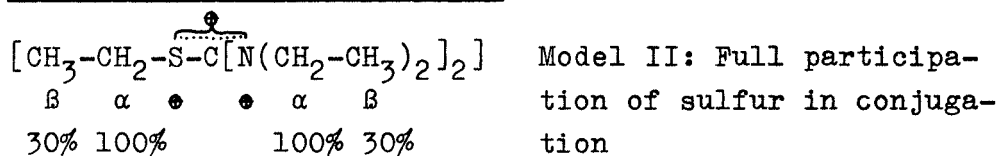
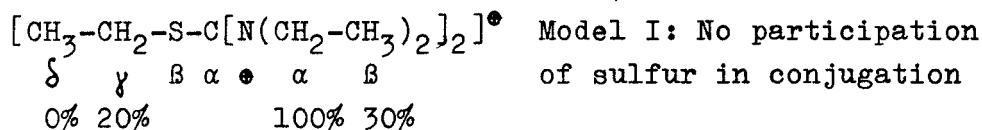
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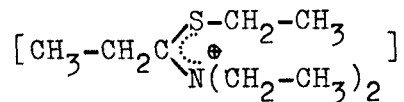
The higher elements such as sulfur are often believed to have a low capability for participation in p_{π} - p_{π} bonding though thiophene is the most "aromatic" compound of the series , X = NH, O, S. In a recent review on sulfur-containing cations, Marino (1) wrote for isothiuronium salts "Clearly,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

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

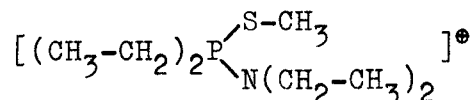
As reported previously (2,3), in ion pairs of organic cations and inorganic and organic anions, the charge centres approach each other as closely as possible. As a consequence, protons in α -position to the onium centre are most sensitive towards the nature of the anion, protons in β - (γ -) position 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):



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



behave similarly, whereas the phosphorus analog



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 $d_{\pi}\text{-p}_{\pi}$ -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.