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THE REACTIVITY AND ELECTRONIC SPECTRA OF PSEUDOAROMATIC SULPHUR COMPOUNDS

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PSEUDOAROMATIC sulphur compounds which we have studied by means of the simple MO-LCAO method can be divided into four groups according to the parent substances from which they can be formally derived by the substitution of the -CH=CH- group by a sulphur atom. The compounds under consideration are analogues of tropylium (I) [thiapyrylium (II), 1,2-dithiylium (III), 1,3-dithiylium (IV)], benzotropylium (V) [1-thianaphtylium (VI), 2-thianaphtylium (VII), benzo-1,3-dithiylium (VIII)], azulene (IX) [thialene (X), isothialene (XI)], tropone (XII) [α- and γ-thiapyrones (XIII,XIV), derivatives of 1,2- and 1,3-dithiylium (XV,XVI; Y=O,S)] and tropolone (XVII) [3-hydroxythiapyrones (XVIII; Y=O,S)] (Fig. 1). Except the compounds nos. XIII-XVI, already known for a longer time, all these substances have been synthesized recently.[1-11] The compounds II and VIII were studied

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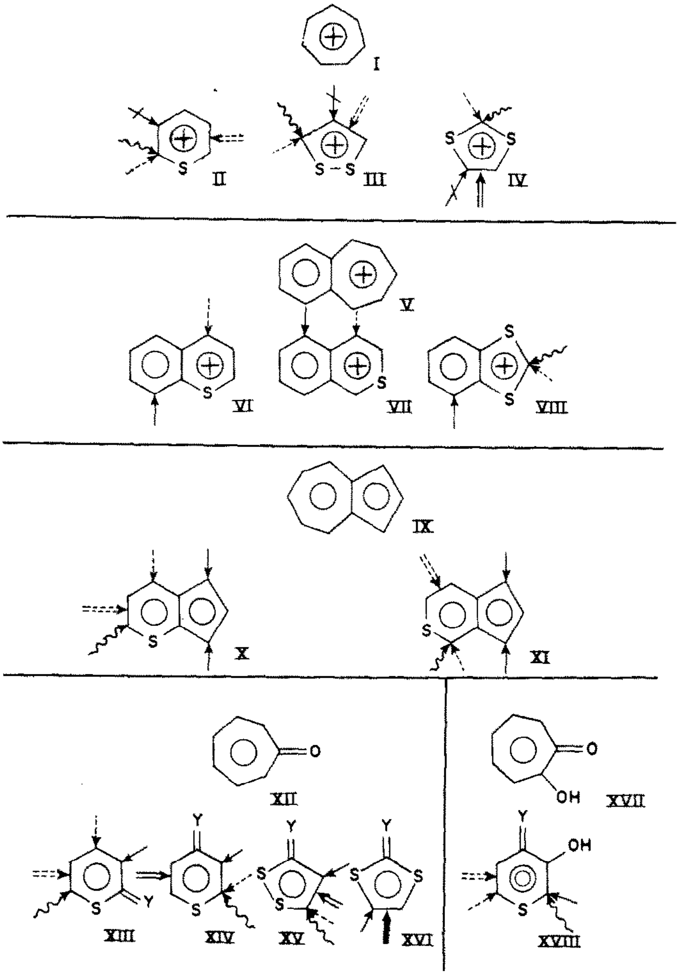

FIG. 1. Survey of the compounds studied together with the data on reactivity centres; for symbols _cf_.text. (Data concerning the compounds X and XI given in paper 8 are from the perturbation calculations; the values presented here result from the secular equations; XVI: model without considering d-orbital.)

theoretically earlier.[12,13] The results of the reactivity calculations based on the Longuet-Higgins model of the hybrid pd^2 sulphur orbitals are summarized in Fig. 1. ($\beta_{CS} = 0.6\ \beta$; exocyclic atoms: $\alpha_O = \alpha_C + 2\beta$, $\alpha_S = \alpha_C + 0.5\beta$, $\beta_{CO} = \sqrt{2}\beta, \beta_{CS} = 0.9\beta$). The predictions are based on the π-electron densities (polar substitutions), free valences (radical substitutions) and bond orders (addition reactions). The information for VI and VII is based on the perturbation calculations; all other data result from the solutions of the secular equations. The theoretical centres of electrophilic, nucleophilic and radical reactivities are marked with arrows (↓, ⇣, ↯, resp.); a double arrow indicates a bond of maximum order (bond order lower than 0.8⇊, 0.8-0.9⇓, higher than 0.9⬇). Should a reaction of certain type be improbable the respective arrow is crossed out. The theoretical data are in agreement with all experimental data hitherto published.[8,9,14-16] The compounds have been studied by means of a model involving the participation of the sulphur d-orbitals; besides this, many compounds have been investigated by means of a model without considering the d-orbitals ($\alpha_S = \alpha_C + \beta$;

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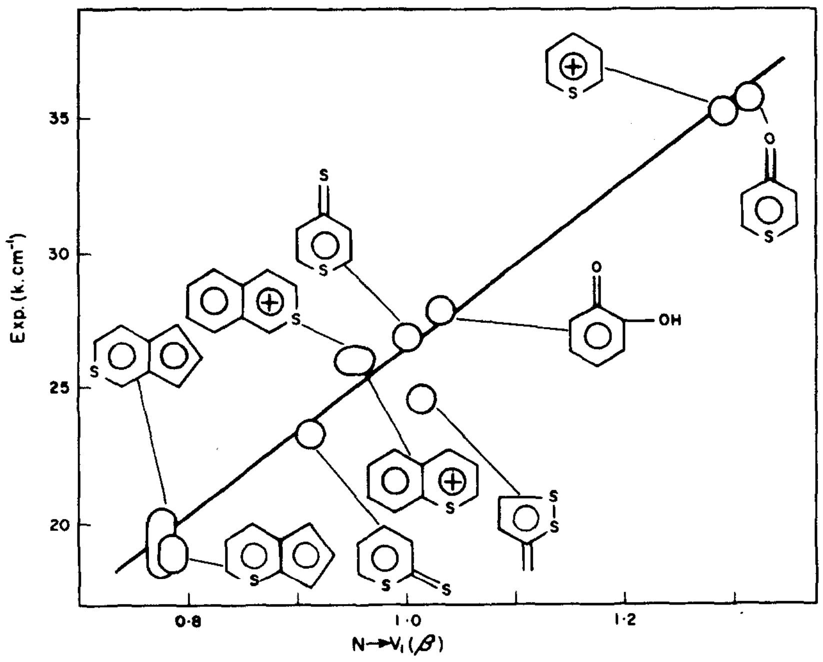

FIG. 2. Energy of the first long-wave absorption maximum of the electronic spectrum plotted against the theoretical value of the N→V$_1$ transition.

β_{CS} = 0.6 β). Contradictory predictions of the position of the maximum reactivity (e.g. for 2-naphtylium) could contribute to the solution of the problem of a suitable model for the sulphur atom orbitals.

Moreover, we have found rather a close linear correlation between the theoretical N→V$_1$ energies and the energies of the first intense absorption maximum in the electronic spectrum (Fig. 2). The slope of this dependence is 30.8 kcm^{-1}/β (βmeans the energy unit of the simple MO method) and is evidently higher than that one for aromatic hydrocarbons where it amounts to 19.5 kcm^{-1}/β.

A more detailed discussion of the reactivity based on static and dynamic indices, the comparison of the models for the sulphur atomic orbitals and the prediction of existence and properties of further pseudoaromatic sulphur compounds will be published in Coll.Czech.Chem.Comm.