ELECTRONIC SPECTRUM OF THE PENTATHIAZYL CATION

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The electronic spectrum of the pentathiazyl cation (*I*) has been interpreted in terms of a modified π-electronic LCI–SCF method which considers σ-core polarization.

The subject of this note is an attempt to interpret the electronic spectrum of the pentathiazyl cation (*I*) which was prepared recently[1,2]. It is a member of the series of cyclic systems $(SN)_n$. Non-radical species may be neutral (with $n = 2, 4, 6 \ldots$) or (with $n = 3, 5, 7 \ldots$) may be cations (like *I*) or anions.

Molecular-orbital aspects of *I* have been discussed in three papers[3–5] (in ref.[3], S and N atoms were exchanged). X-ray analysis of *I* ($AlCl_4^-$) proved[6,7] an almost planar heart shaped structure with lengths of the N–S bonds in the region of 1·465 to 1·590 Å.

Because of some parametrization problems concerning sulphur in extended methods, we have used the classical LCI–SCF π-electronic version (the PPP method I) and a recently suggested π-electronic LCI–SCF procedure II in which all β^c-integrals are included and which consider the σ-core polarization.

I
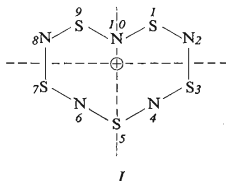
CALCULATIONS, RESULTS AND DISCUSSION

The PPP method has been described elsewhere[8,9] in detail. The following parameters were used (method I): $I_S = 20\cdot27$ eV, $I_N = 14\cdot10$ eV, $A_S = 10\cdot47$ eV, $A_N = 1\cdot80$ eV, $\beta_{NS} = -1\cdot854$ eV; for other expressions used see ref.[9].

In the procedure including the σ-core polarization (method II) the core matrix elements were calculated by means of the following expressions[10]:

$$\beta_{\mu\nu}^c = a \frac{2\alpha_\mu^c \alpha_\nu^c}{\alpha_\mu^c + \alpha_\nu^c} S_{\mu\nu}(b - S_{\mu\nu}) , \qquad (1)$$

where $a = 0.5246$, $b = 2.0$, $S_{\mu\nu}$ are overlap integrals calculated with the Slater AO's

$$\alpha_\mu^c = -I_\mu , \quad I_\mu = a + bZ_\mu + cZ_\mu^2 , \qquad (2), (3)$$

where

$$Z_\mu = Z_\mu^0 + 0.295 \sum \frac{\chi_\mu - \chi_\nu}{\chi_\mu + \chi_\nu} r_{\mu\nu}^{-2} . \qquad (4)$$

Z_μ^0 is the core charge of the atom μ given by the number of electrons which this atom supplies into conjugation. The second term describes a change of the core charge caused by the σ-core polarization. χ's are the Mulliken electronegativities of σ-orbitals, and $r_{\mu\nu}$ interatomic distances. More specific information will be included in ref.[10]. In this type of calculation the ionization potentials and electron affinities due to Hinze and Jaffé[11] were used and electronic repulsion integrals were approximated by the Mataga–Nishimoto formula.

Configuration interaction calculations were performed for 9 to 15 singly excited configurations; in all cases all virtual MO's were included. In Fig. 1 an absorption curve of $S_5N_5^+ AlCl_4^-$ in concentrated (18·3M) sulphuric acid is presented. The solution is stable for about one week. The salt is formed in thionyl chloride solution from a mixture of S_4N_4, $(NSCl)_3$ and $AlCl_3$ $(3 : 1 : 3)^2$.
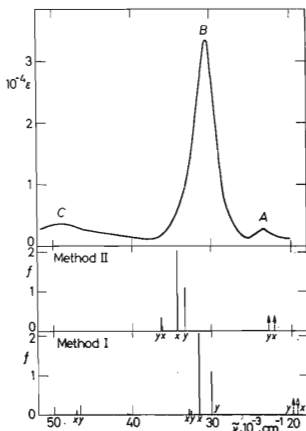

FIG. 1

Electronic Absorption Curve of $S_5N_5^+ AlCl_4^-$ in H_2SO_4 (18·3M) and Results of LCI–SCF Calculation (for methods I and II cf. text)

f Stands for the calculated oscillator strengths and x and y (cf. formula I) denote the polarization directions of transitions. Dotted lines with arrows indicate transitions with f smaller than 0·01.

The configurational interaction data (Fig. 1) suggest that the weak band A in the visible region is due to two weakly allowed transitions and that the strong band B in the region of $28\,000 - 34\,000\ cm^{-1}$ is a composite band due to four transitions (3rd – 6th transitions), the 3rd and 4th being dominant. The data based on method I suggest moreover that the broad weak band C is also due to the species $S_5N_5^+$ although according to method II the respective transition is to be expected only at about $59\,000\ cm^{-1}$.

Since the results for bands A and B (Fig. 1) differ little by the two methods I and II and because the use of a method which allows for the σ-core polarization is more adequate, the nature of the excited states will be discussed only in terms of the latter method. For the four lowest excited states of $S_5N_5^+$ the following CI wave functions were obtained:
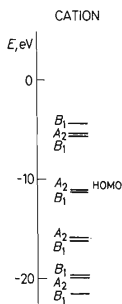

FIG. 2

SCF Orbital Energies (method II) of the Cation I and of the Respective Anion

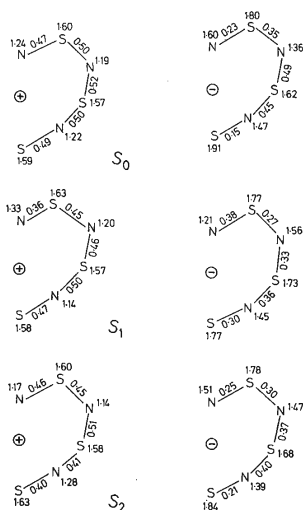   The species of the C_{2v} point group and the highest occupied MO's (HOMO) are indicated.

FIG. 3

Electron Densities and Bond Orders (method I) for the Cation I and the Respective Anion for Three Singlet States (S_0, S_1, and S_2 denote ground and excited states)

$$^S\Psi_1(B_2) = \quad 0\cdot756\Phi_{7\to8} + 0\cdot203\Phi_{7\to10} + 0\cdot619\Phi_{6\to9}$$

$$^S\Psi_2(A_1) = -0\cdot618\Phi_{7\to9} + 0\cdot751\Phi_{6\to8} \ - 0\cdot223\Phi_{6\to10}$$

$$^S\Psi_3(A_1) = \quad 0\cdot683\Phi_{7\to9} + 0\cdot656\Phi_{6\to8} \ + 0\cdot321\Phi_{6\to10}$$

$$^S\Psi_4(B_2) = -0\cdot586\Phi_{7\to8} - 0\cdot208\Phi_{7\to10} + 0\cdot782\Phi_{6\to9}$$

In these expressions symbols $\Phi_{i\to j}$ stand for singly excited configurations.

This result (*i.e.* nearly first order CI) is understandable because the cation *I* is a heteroanalogue of a heart shaped [14]annulene. In Fig. 2 the SCF orbital energies of the cation *I* and of the respective anion are given. The transitions among levels 6, 7, 8 and 9 correspond to those between degenerate frontier orbitals in annulene.

The calculated π-electron densities and bond orders being rather uniform, support the idea that the cation under study is *aromatic* (Fig. 3). This is also true for the first and second excited singlet states. The most remarkable feature of the anion (which is richer by two electrons than the cation *I*) is a very low bond order of the *apex* S—N bonds (*i.e.* at the lower point of the *heart*) which amounts to only 0·15. This represents a serious hindrance to real electron delocalization (*vide infra*). One must not overestimate the significance of bond orders resulting from a π-electronic approximation[5]. However, we have been able recently to show the reliability of the method II[10] in reproducing the experimental values of dipole moments. Apparently (Table I) electron densities based on the method II correspond rather to the total CNDO/2 values than to the π contributions obtained within the framework of the CNDO/2 method. Let us add also that one should not overestimate the CNDO/2 densities because the question of inclusion of *d*-orbitals with systems containing σ-double bonded sulphur remains open.

TABLE 1

SCF Electron Densities in the Cation *I*

| Position | 1 | 2 | 3 | 4 | 5 | 10 |
Atom	S	N	S	N	S	N
Method I	0·48	−0·26	0·49	−0·29	0·51	−0·32
Method II	0·40	−0·19	0·33	−0·22	0·41	−0·24
CNDO/2 $(\pi)^a$	0·43	−0·08	0·14	−0·23	0·67	−0·20
CNDO/2 (total)^a	0·41	−0·17	0·18	−0·15	0·46	−0·07

^{a} Ref.[5].

LCI calculations suggest that an unusually large bathochromic shift of the first absorption band is to be expected when passing from the 14π-electron cation to the radical and anion containing 15 and 16π-electrons, respectively. The reason for this shift is evident even from the scheme of orbital energies for the cation (Fig. 2). For both latter systems the $N \rightarrow V_1$ gap is an *unnatural* one. The reasons for its extremely small value is due to the relationship between I and [14]annulene. Furthermore method I even suggests that the anion should be in a triplet ground state (triplet states, with energies of $-1\cdot28$ and $-0\cdot97$, lie below the first singlet state). It is well known that the standard PPP procedure underestimates the singlet-triplet splitting but at least the prediction, concerning an extremely long wavelength electronic transition, remains valid.

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