Introduction

Of late, the chemistry of bis-mercaptomaleonitrile (mnt) has assumed proportions in the field of inorganic chemistry that make an analysis of its basic electronic structure particularly important. Its ability to form square-planar complexes with a host of transition metal cations marks it as a ligand which will receive increasing attention in the future [8]. In investigating the electronic structure of mnt it was found most convenient to work with the dimethyl thioether. Tetrahedral carbon effectively caps the ends of the π-system without appreciably disturbing the delocalized π-electronic structure. The dimethyl derivative also is more stable chemically than mnt itself.

This paper presents an analysis of the electronic absorption spectra of the dimethyl derivative of mnt and several related molecules in terms of molecular orbital theory.

Results

Two types of calculations were carried out: a set of calculations including the overlap integrals and a set of standard Hückel calculations. In both sets, only the $\pi$-$\pi$ systems were treated, since the filled $\sigma$-orbitals are probably too stable to give rise to electronic transitions in the energy range studied ($< 53,000$ cm$^{-1}$). The molecular orbitals were of the form $\psi = \sum c_i \varphi_i$ where the $c_i$’s are subjected to the usual conditions of normalization and orthogonality.

a) Hückel (HMO) calculations

In this set of calculations, the standard Hückel approximations were assumed ($S_{ij} = \delta_{ij}, \beta_{ij} = 0$ if $|i - j| > 1$). Preliminary values of the molecular parameters

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were chosen from the literature [II] and then adjusted to give the best possible agreement with the experimental results. The following values were found to be consistent with the electronic spectral data:

\[\alpha_C = \alpha\]
\[\alpha_S = \alpha + 4\beta\]
\[\alpha_N = \alpha + 6\beta\]

\[\beta_{C-C} = \beta\]
\[\beta_{C-N} = 1.8\beta\]
\[\beta_{C-S} = 0.6\beta\]
\[\beta_{C-CN} = 0.8\beta.\]

In the Hückel approximation, the electronic population is given by:

\[\text{Pop}_{j\text{th atom}} = \sum_{\text{all occupied levels}} a c_i^2\]
\[a = 1, 2.\]

**b) Calculations including overlap integrals (OMO)**

For this set of calculations, the overlaps were evaluated explicitly and the resonance integrals were assumed to be proportional to overlap integrals.

The overlaps were calculated by the usual procedure [I] using Clementi's [3] double-zeta basis functions and bond lengths obtained from the literature [4, 7]. Both HMO and OMO calculations were performed using programs written for the Columbia IBM-7094 computer. The procedure used for the OMO calculations has been described in detail elsewhere [I, 2].

The resonance integrals were calculated according to the formula

\[H_{ij} = \sqrt{H_{ii}H_{jj}(-F S_{ij})}\]

where the \(S_{ij}\)'s are the overlap integrals and the \(H_{ii}\)'s and \(H_{jj}\)'s are estimated as valence orbital ionization potentials (VOIP). The VOIP have been tabulated [1, 2]. The value \(F = 2.3\) was used for all \(H_{ij}\).

In these calculations the population analysis is given by the formula:

\[\text{Pop}_{j\text{th atom}} = \sum a c_i^2 + \sum a c_i c_i S_{ij}.\]

**Discussion**

We now compare the results of these calculations on various molecules with the spectra given in Tab. 1. The eigenvectors are given in Appendix I.

**Bis-(methylmercapto)maleonitrile** [(CH₃)₂mnt]. The system for this molecule (C₂ᵥ) is labeled as follows:

(5) N
\(\downarrow\) (4) C
\(\downarrow\) (1) C
\(\downarrow\) S
\(\downarrow\) (7) CH₃

(6) N
\(\downarrow\) (3) C
\(\downarrow\) (2) C
\(\downarrow\) S
\(\downarrow\) (8) CH₃

(\(\text{CH}_3\)₂mnt)