

NON-BONDED INTERACTIONS IN CYCLOBUTANE-THIONES*

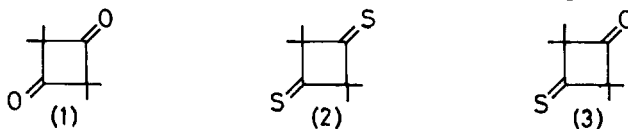
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Abstract : Using UVPEs and electronic spectral data the presence of an interaction between the 1,3-thiocarbonyl groups in 2 has been identified. EHT calculations also predict such an interaction. Presence of weak interaction between 1,3-carbonyl and thiocarbonyl groups in 3 has been inferred from electronic absorption and emission spectra.

Through-bond interaction between the non-bonding orbitals of the carbonyl groups in tetramethylcyclobutane-1,3-dione(1) gives rise to a large n -orbital splitting of 0.7 eV as shown by photoelectron spectroscopy¹; interaction between the π^* orbitals also results in splitting, thus giving rise to four singlet $n\pi^*$ transitions^{2,3}. On the other hand, the reported electronic absorption spectrum for the corresponding tetramethyl-1,3-cyclobutanedithione(2) shows no splitting of $n\pi^*$ absorption band⁴. In order to investigate the non-bonded interaction between the chromophoric groups, we have studied the electronic and uv photoelectron spectra of 2 and tetramethyl-3-thio-1,3-cyclobutanedithione(3) and have carried out calculations based on extended Huckel theory (EHT).



The He-I photoelectron spectrum of 2 shows two sharp bands of the thiocarbonyl group at 8.32 and 8.74 eV indicating an n orbital splitting of 0.42 eV and a band at 10.2 eV due to π orbital. EHT calculations rightly predict an n orbital splitting of 0.37 eV. The splitting is likely to be due to through-bond interaction between the C=S groups. The electronic absorption spectrum of 2 (Fig.1), clearly consists of three band systems due to the C=S group around 500($n\pi^*$), 315($\pi\pi^*$) and 254 nm($n\sigma^*$), with the $n\pi^*$ band showing considerable structure. The $n\pi^*$ band exhibits two distinct bands around 427 and 492 nm in methanol solution (see inset of Fig.1) showing a separation of 0.4 eV probably corresponding to the n -orbital splitting found in UVPEs. The

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$\pi\pi^*$ band shows a splitting of 0.2eV even in cyclohexane solution possibly due to the circum-annular interaction between the π^* orbitals³. If this be so, one should be able to see four $n\pi^*$ transitions in 2 (as in the case of 1) separated from each other by 0.2eV. The peaks in the crystal spectrum of 2 at 440, 472, 510 and 547 nm could indeed correspond to four such $n\pi^*$ transitions, the spacing of 0.2eV being too high to be assigned to any vibrational mode.

UVPEs of 3 shows lone pair bands at 8.48 (C=S) and 9.18 eV (C=O) and the corresponding bands at 10.50 and 11.80 eV. EHT calculations predict the two lone pair orbitals to be separated by 1.0 eV. The electronic absorption spectrum of 3 (Fig.2) shows bands at 525($n\pi^*$;C=S), 324($\pi\pi^*$;C=S), 272($n\pi^*$;C=O) and 244nm($n\pi^*$;C=S). It is interesting to note that the $n\pi^*$ (C=S) band is red shifted with respect to cyclobutanethione (496 nm) while the $n\pi^*$ (C=O) band is blue shifted with respect to cyclobutanone (280 nm) indicating a possible weak interaction between the C=O and C=S groups in 3. Consistent with this

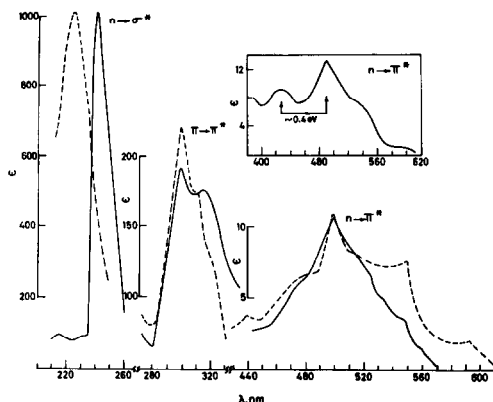


Fig.1. Electronic Absorption Spectrum of Tetramethyl-1,3-cyclobutane dithione. Full line: cyclohexane solution; Broken line: crystal; inset: methanol solution.

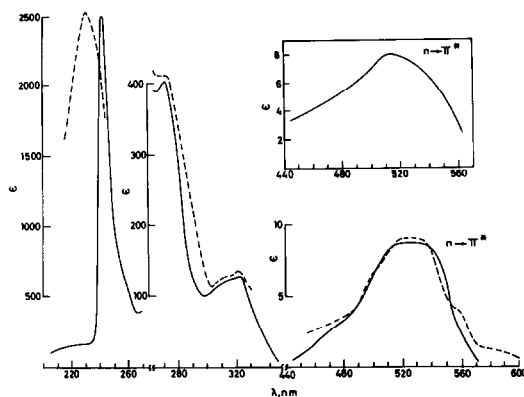


Fig2. Electronic Absorption Spectrum of Tetramethyl-3-thio-1,3-cyclobutanedione. Full line: cyclohexane solution; Broken line: crystal; inset: methanol solution.

observation, 3 shows phosphorescence (595-688 nm; 3MP glass, 77 K) only from the lowest triplet state of the C=S group independent of the excitation band (C=O or C=S chromophore).

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