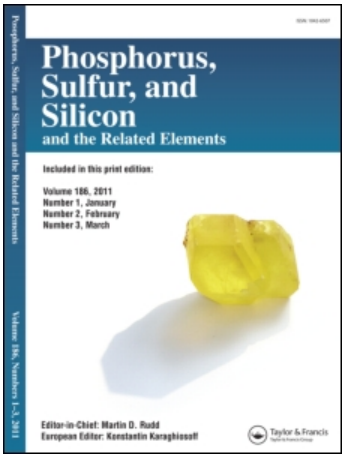


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# A PPP AND CNDO STUDY OF DITHIOCARBONIC ANIONIC DERIVATIVES

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**To cite this Article** Bhasu, V. C. Jyothi and Sathyanarayana, D. N.(1980) 'A PPP AND CNDO STUDY OF DITHIOCARBONIC ANIONIC DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 8: 2, 171 — 175
**To link to this Article: DOI:** 10.1080/03086648008078183
**URL:** http://dx.doi.org/10.1080/03086648008078183

*Phosphorus and Sulfur*, 1980, Vol. 8, pp. 171–176
0308-664X/80/0802-0171$04.50/0



# A PPP AND CNDO STUDY OF DITHIOCARBONIC ANIONIC DERIVATIVES

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(*Received May 15, 1979; in final form August 16, 1979*)

The application of the CNDO and PPP-CI methods to N,N-dimethyl dithiocarbamate, *O*-methyl dithiocarbonate (methyl xanthate) and methyl trithiocarbonate ions for the elucidation of electronic structure and electronic spectra is described. The CNDO/2 calculations have been used to obtain the one centre core integrals of the ionic compounds required in calculating the pi electronic spectra of these molecules using the PPP method. The calculated spectra are in good agreement with the experiment. The atomic charge densities determined for alkyl xanthate, dithiocarbamate and trithiocarbonate ions support the earlier qualitative predictions regarding electronic structure from spectroscopic and other studies.



## INTRODUCTION

The use of alkyl derivatives of thiocarbonic acid in processes of industrial importance and as chelating agents has stimulated much research. There is extensive work on the electronic and vibrational spectroscopy and X-ray crystallographic determinations of the alkali, transition and nontransition metal complexes of xanthic, dithiocarbonic and trithiocarbonic acids to understand qualitatively the physical and chemical properties of these compounds in terms of the electronic and molecular structure; and the subject continues to attract much attention in recent years.[1–14]. There appears to be some controversy in the assignment of the electronic spectral bands in these compounds, however. For example, one of the bands in the ultraviolet region is assigned to a $n \rightarrow \sigma^*$ transition by one group of workers[5,6] while the other group favours it to a $\pi \rightarrow \pi^*$ transition.[7–9] The aim of the present paper was to carry out theoretical calculations on O-methyl dithiocarbonate (methyl xanthate, MXN), N,N-dimethyl dithiocarbamate (DMDTC) and methyl trithiocarbonate (MTTC) ions in order to clarify the electronic spectra and electronic structure using the SCF-MO methods at the PPP and CNDO/2 levels.

Although the PPP pi-electron method has proven to be very successful in computing singlet transition energies, the extension of the method to ionized species has been found to be troublesome. For the ionic species, the changes in the $\sigma$-framework should be taken into account in the pi-electron calculations.[15–18] The technique of determining the core charges via all valence CNDO calculation to develop improved PPP core parameters has been used by Bailey and Bailey,[17] and recently by Gordon and Neumer.[18] The electronic absorption spectra are calculated using these core parameters by the PPP method for MXN, DMDTC and MTTC anions.

## THEORETICAL TREATMENT

The CNDO/2 method in the original form and parametrization suggested by Pople and Segal with a full basis set of valence atomic orbitals including the 3d orbitals of sulfur was employed.[19] The excitation energies and oscillator strengths were calculated by the PPP method with limited configuration interaction.[20,21] The required corrections to the PPP core parameters are obtained by the CNDO/2 results. The valence state ionization potential (VSIP) and the one centre two-electron repulsion integral ($\gamma_{\mu\mu}$) for sulfur were suitably modified (VSIP = $-17.91$ eV, $\gamma_{\mu\mu} = 10.54$ eV). The following standard values[22] for the VSIP and $\gamma_{\mu\mu}$ were employed for the other elements—VSIP: C(1) = $-11.16$, N(2) = $-28.71$, O(2) = $-31.42$ and S(2) = $-23.12$ eV; $\gamma_{\mu\mu}$: C(1) = 11.13, N(2) = 16.75, O(2) = 15.55, and S(2) = 11.14 eV.

TABLE I

Structural parameters[a]

| | | | |
|---|---|---|---|
| | DMDTC | | |
| C—S | 0.1720 | SCN | 120.00 |
| C—N | 0.1344 | $CNC_2$ | 122.80 |
| N—$CH_3$ | 0.1477 | $C_4NC$ | 114.40 |
| C—H | 0.1080 | HCN | 109.47 |
| | | HCH | 109.47 |
| | MXN | | |
| C—$S_1$ | 0.1690 | SCS | 124.00 |
| C—$S_8$ | 0.1670 | SCO | 121.00 |
| C—O | 0.1350 | COC | 116.00 |
| O—$CH_3$ | 0.1480 | HCO | 109.47 |
| C—H | 0.1080 | | |
| | MTTC | | |
| C—S | 0.1680 | $SC_2C_8$ | 115.00 |
| C—$S_3$ | 0.1710 | $S_1CS_3$ | 121.00 |
| S—$C_4$ | 0.1830 | CSC | 101.90 |
| C—H | 0.1080 | HCS | 109.47 |
| | | HCH | 109.47 |

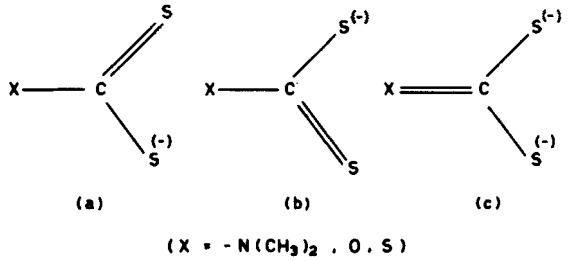
[a] Bond lengths are in nm and angles in degrees; numbering as in Figure 2.

A value of −1.30 eV was used for the resonance integral, $\beta_{CS}$, of the —C(=S)—S group for all the three anions and for $\beta_{CX}$ (X = N, O or S), a value of −2.1 eV was utilized. These values for $\beta$ were found to yield a satisfactory fit between the theory and experiment.

The geometry of the three anions were taken from the X-ray structure determinations.[23–25] The bond angles and bond distances adopted in the calculations are listed in Table I. The calculations were performed on an IBM 360/44 digital computer. The computer programs for the CNDO/2 method were taken from Pople and Beveridge[19] and programs were written to carry out the PPP-CI calculations.

## RESULTS AND DISCUSSIONS

Resonance forms of the type depicted below have been shown to play an important role in influencing the overall structure and properties of these dithio systems. The contribution of each of these different resonance structures has been much discussed qualitatively chiefly from vibrational spectroscopy.




The total sigma and pi electron densities and the net charges on different atomic centres of DMDTC, MXN and MTTC from the CNDO/2 method are presented in Table II. The pi bond orders are shown in Figure 2.

The terminal sulfur atoms in all the three anions carry almost equal and high negative charges. The negative charge of the anion is almost localised on the two sulfur atoms of the $—CS_2$ moiety and is

TABLE II

Electron density population and net charges

| Compound | Electron density/net charge | Atoms[a] $S_1$ | $C_2$ | $X_3$ | $C_4$ | $H_5$ | $H_6$ | $C_8/S_8$ | $H_9$ | $H_{10}$ | $S_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | σ | 4.781 | 3.140 | 3.354 | 2.968 | 0.974 | 1.033 | 2.967 | 0.975 | 1.033 | 4.871 |
| DMDTC | π | 1.721 | 0.678 | 1.716 | 0.956 | | | 0.956 | | | 1.721 |
| | net | −0.592 | 0.182 | −0.070 | 0.076 | 0.026 | −0.033 | 0.077 | 0.025 | −0.033 | −0.592 |
| | σ | 4.930 | 3.051 | 4.324 | 2.904 | 1.040 | 1.007 | 4.918 | | | |
| MXN | π | 1.632 | 0.714 | 1.862 | 0.980 | | | 1.632 | | | |
| | net | −0.562 | 0.235 | −0.186 | 0.116 | −0.040 | −0.007 | −0.550 | | | |
| | σ | 4.941 | 0.097 | 4.244 | 3.098 | 1.019 | 0.984 | 4.928 | | | |
| MTTC | π | 1.511 | 0.785 | 1.906 | 0.969 | | | 1.534 | | | |
| | net | −0.452 | 0.118 | −0.150 | −0.067 | −0.019 | 0.016 | −0.462 | | | |

[a] X = N, O or S; numbering as in Figure 2.

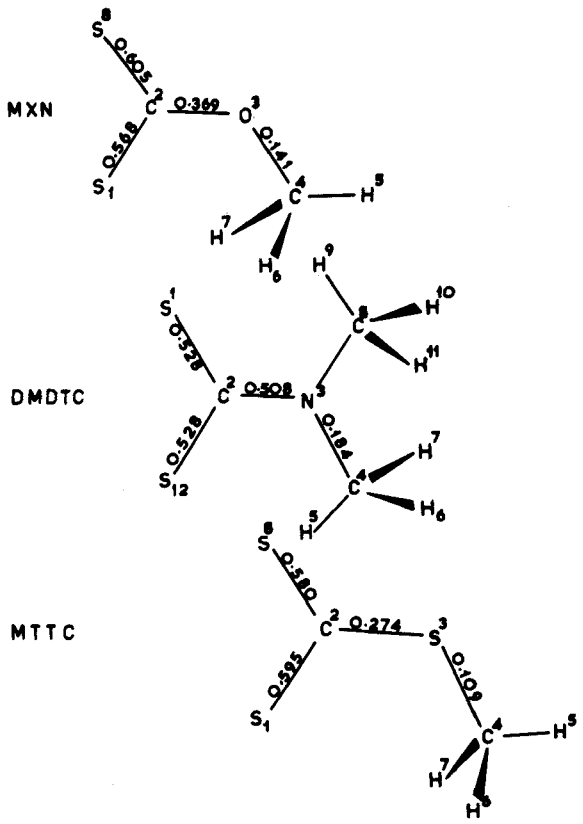



FIGURE 2 Numbering Scheme and pi bond orders.

concentrated on their pi orbitals. The pi electron density clearly shows the strong pi acceptor ability of these sulfur atoms. Further the sulfur atoms are found to be sigma electron donors. Understandably, these dithio compounds coordinate to metal ions easily to produce stable complexes.[2]

The relatively larger pi bond order for the C—N bond (0.508) and the lower pi bond orders for the C=S groups (~0.528) of DMDTC as obtained by the CNDO/2 method indicate that the resonance structure (c) contributes very significantly to a description of bonding in DMDTC. This is in accord with the earlier inferences from a compilation of the dipole moments, infrared spectra and X-ray crystallographic studies of dithiocarbamate complexes.[2,10,12] The C—N bond distances are found[2] to lie at ~1.35 Å which is more towards the double bonded (1.275 Å) rather than single bonded (1.475 Å) CN group. The high double bond character of the C—N bond is also reflected in the force constants[4] and $^1$H NMR spectra of DMDTC complexes.[2]

In contrast to DMDTC, the relatively lesser importance of the resonance form (c) to the total structure of MXN has been suggested by many workers based on C—O—C frequencies in the infrared. The present study also supports this conclusion. The calculated pi bond orders for the two CS groups were distinctly different (Figure 2, $CS_1 = 0.568$, $CS_8 = 0.605$). Thus the pi bond orders show that the two CS bonds have partial double bond character and the bond orders are slightly different for the two bonds. This is also reflected in the X-ray structures of a number of xanthate compounds which have shown significantly different CS bonds.[2] The delocalization of electrons along the C—O—C portion of MXN is evident from the pi bond orders for the $S_2C$—O and $H_3C$—O groups (0.369 and 0.141 respectively). The considerable double bond character of the $S_2C$—O group is also evident from the bond lengths (~1.35 Å) available from the crystal structure analyses of many xanthates.[2,10] The $S_2C$—O distance is some 0.1 Å shorter than the second C—O distance (~1.46 Å). As in MXN, the CNDO/2 results clearly reveal that the C—S bonds of the $-CS_2$ moiety of MTTC have different pi bond orders (Figure 2, $CS_1 = 0.595$, $CS_8 = 0.580$). The $CS_3$ bond has a slightly higher pi bond order (0.274) than $C_4S$ (0.109) (Figure 2). These results clearly suggest the lesser contribution of the canonical structure (c) in MTTC.

A comparison of the charge distributions in DMDTC, MXN and MTTC may now be made. It is clear from Table II that the negative charge on the sulfur atoms of the $-CS_2$ group increases in the order DMDTC > MXN > MTTC in the increasing order of the mesomeric electron releasing abilities, $-SCH_3 < -OCH_3 < -N(CH_3)_2$, The importance of the resonance form (c) decreases in the sequence DMDTC > MXN > MTTC paralleling the decreasing order of the mesomeric electron releasing tendencies of the $-N(CH_3)_2$, $-OCH_3$ and $-SCH_3$ groups. The double bond character of the C=S groups may be predicted to decrease in the order MTTC > MXN > DMDTC. This is clearly borne out from the calculated pi bond orders.

*Electronic Spectra*

Table III contains the calculated singlet transition energies and corresponding oscillator strengths for DMDTC, MXN and MTTC along with the

TABLE III

Calculated and experimental absorption spectra[a]

| Compound | Calculated $\lambda_{max}(f)$ | Experimental $\lambda_{max}(\log \varepsilon)$ |
|---|---|---|
| DMDTC | 240(0.247) | 253(4.12) |
| | 304(0.341) | 287(4.18) |
| | — | 356(1.79) |
| MXN | 225(0.162) | 228(3.97) |
| | 308(0.378) | 304(4.31) |
| | — | 383(1.71) |
| MTTC | 244(0.261) | 235(3.72) |
| | 303(0.339) | 303(4.13) |
| | — | 333(4.22) |

[a] Absorption maxima $\lambda_{max}$ is in nm, $f$ is oscillator strength and $\varepsilon$ is the molar extinction coefficient.

observed spectra of the respective alkali metal salts. As seen from Table III, the calculated values are in good agreement with the experimental data.

There is considerable conflict in the literature in the assignment of the electronic spectral bands of the alkali metal salts of the dithiocarbonic acid derivatives. Janssen[7] examined a variety of dithio-acid compounds and assigned the electronic spectral bands with the aid of simple LCAO–MO Huckel calculations made for the basic structure, X — C(=S)S$^-$ (where X=N, O, S). More recently, Shankaranarayana and Patel[5,6] from this laboratory investigated the spectra of alkyl xanthate, dithiocarbamate and trithiocarbonate compounds and have attributed the high energy band in the spectra of these compounds as arising from $n \rightarrow \sigma^*$ transitions which was favoured by Janssen and his co-workers to a $\pi \rightarrow \pi^*$ transition. Further an additional band in the spectra of DMDTC compounds was simply attributed to the —N—C=S group.[5,6] Simple PPP calculations on some dithiocarbonic esters have been made by Fabian.[14]

The electronic spectrum of the sodium salt of DMDTC in ethanol shows[5,6] two intense absorptions at 287 and 253 nm. The 287 nm band was found to shift to 279 in aqueous solution. The peak at 287 nm may be assigned to a transition arising from a molecular orbital consisting almost completely of the pi orbitals on the sulphur atoms (of the $-CS_2$ group) to one having major contribution from the carbon atom, i.e., $\pi(S) \rightarrow \pi^*$ (1). This assignment agrees with those of Rao *et al.*[8] and Fabian[14] but differs from Shankaranarayana and Patel.[5] The blue shift of the 287 nm band of DMDTC in water compared to its position in ethanol may be due to tighter solvent shell in water causing enhanced stability of the ground state compared to excited state. The band at 253 nm according to the present PPP–CI study can also be attributed to a $\pi \rightarrow \pi^*$ transition originating from a pi molecular orbital having bonding contribution from the $-CS_2$ group to the first antibonding orbital. This assignment is in qualitative agreement with that of the earlier ones.[5–9, 14]

In alkali metal dithiocarbamates the tail end of a strong absorption band is seen around 200 nm, suggesting the presence of an additional band near 200 nm. In fact, the oxidation products of dithiocarbamates, namely, thiuram disulphides have an additional intense band near 220 nm ($\log \varepsilon = 4.2$) besides the two strong bands around 255 and 290 nm. The present PPP–CI calculations in fact suggest a band around 180 nm assignable to a $\pi \rightarrow \pi^*$ transition originating from a pi bonding molecular orbital having major contribution from the nitrogen lone pair to the first antibonding orbital. There is no analogous band in xanthates.

The electronic spectra of the potassium salts of MXN and MTTC show some similarities. The former compound exhibits two intense bands at 228 and 304 nm while the latter compound shows three intense bands at 235, 303 and 333 nm in aqueous medium.[5,6] Both the bands, near 230 and 300 nm, in these two compounds according to the PPP–CI results could be assigned to $\pi \rightarrow \pi^*$ type transitions. The 228 nm band of MXN could be attributed to a transition from a pi molecular orbital which is bonding in the $-CS_2$ region and having significant contribution of the sulfur atoms to the first antibonding molecular orbital. This assignment is compatible with that of Fabian,[14] but differs from Shankaranarayana and Patel,[5,6] who attributed it to a $n \rightarrow \sigma^*$ transition. The 235 nm band of MTTC could be given an identical assignment which is again compatible with Rao *et al.*[8] and Fabian but differs from Shankaranarayana and Patel. The 304 nm band of MXN and the 303 nm band of MTTC can be assigned to a transition from a pi molecular orbital consisting of the orbitals solely located on the sulphur atoms of the $-CS_2$ group to the first antibonding molecular orbital. The 333 nm band of MTTC could not be characterised from the PPP–CI calculations.

The electronic spectra of the alkali metal salts show a less intense band at higher wavelengths, at 456 nm in DMDTC, 387 nm in MXN and 456 nm in MTTC. These bands are easily assigned as arising from a $n \rightarrow \pi^*$ transition and are in accord with the observed solvent effects.[5]

## EXPERIMENTAL

The electronic spectra for the alkali metal salts of DMDTC, MXN and MTTC were taken from the work of Shankaranarayana[5,6] from this laboratory.

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