

THE UV SPECTRA OF ETHYLENE-1,2-BISDITHIOCARBAMATES

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ABSTRACT

In the uv spectra of ethylene-1,2-bisdithiocarbamates (EDTC) three very intensive bands at about 207, 260 and 285 nm, and one of low intensity at about 340 nm are found. All of them show blue shift with increasing of the solvent polarity. The 340 nm band is ascribed to an $\pi^* \leftarrow n$ transition, while the bands at about 260 and 285 nm are attributed to $\pi^* \leftarrow \pi$ transitions.

INTRODUCTION

The properties and structure of dithiocarbamates have been the subject of extensive studies (ref. 1,2). In these studies the electronic spectra of dithiocarbamates have been also studied extensively. However, the assignments of some of the uv bands have been a controversial subject for a long time.

In this paper the main concern is the origin of the most intensive uv bands in the spectrum of ethylene-1,2-bisdithiocarbamates (EDTC).

EXPERIMENTAL

Disodium-EDTC was prepared from ethylenediamine, carbon disulphide and 15% solution of sodium hydroxide as described by Engst and Schnaak (ref. 3). Dipotassium-EDTC was obtained by neutralization of ethylene-1,2-bisdithiocarbamic acid with potassium hydroxide in medium of acetone. Our analysis has shown that the first compound crystallizes with six molecules of water and the second with two.

The uv spectra were recorded on Pye Unicam SP 1800 B spectrophotometer, the pH's of the solutions were measured with Radiometer PHM 28.

RESULTS AND DISCUSSION

In the uv spectra of EDTC three very intensive bands between 200 and 300 nm (see Fig. 1), and one of low intensity between 340 and 350 nm, are found. All of them show a blue shift with increasing of the solvent polarity. In the spectrum of $\text{Na}_2\text{EDTC}\cdot 6\text{H}_2\text{O}$, which is completely identical with that of $\text{K}_2\text{EDTC}\cdot 2\text{H}_2\text{O}$, recorded in methanol, the bands appear with λ^{max} at 212 ($\epsilon = 1940 \text{ m}^2\text{mol}^{-1}$), 261 ($\epsilon = 2140 \text{ m}^2\text{mol}^{-1}$), 290 ($\epsilon = 2800 \text{ m}^2\text{mol}^{-1}$) and 348 nm ($\epsilon = 17 \text{ m}^2\text{mol}^{-1}$) which in solution of water are shifted to 207, 260, 285 and 341 nm, respectively.

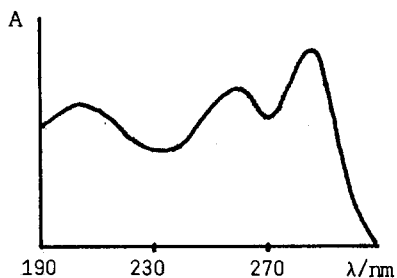


Fig. 1, uv spectrum of EDTC (solvent water)

The band of low intensity at about 340 nm can be unambiguously attributed, as in other dithiocarbamates (ref. 1,2) to an $\Pi^* \leftarrow n$ transition.

The strongest among the observed bands in the spectrum, which appears at about 285 nm, as mentioned above, shows the blue shift with increasing of the solvent polarity. A band of similar behaviour in the region between 260 and 300 nm is found in all dithiocarbamates. It is supposed that

origin of this band might belong to an $\sigma^* \leftarrow n$ transition (ref. 2). A similar band of remarkable high intensity occurs at about 270 nm in the spectra of thioamides. This band shows slightly blue shift too. At first, it has led to the presumption that it might be due to an $\sigma^* \leftarrow n$ transition (ref. 4,5). Later on however, Sandström (ref. 5) showed by MO calculation that the 270 nm band of thioacetamide should be red shifted in thiobenzamide by conjugation, as it is indeed experimentally found. These facts have evidently shown that the 270 nm band of thioamides arises from a $\Pi^* \leftarrow \Pi$ transition. The second band in the uv spectra of thioamides, which appears between 230 and 260 nm, Hosoya et al (ref. 6) have attributed to a second $\Pi^* \leftarrow \Pi$ transition.

On the supposition that if the band at about 285 nm of EDTC is indeed due to an $\sigma^* \leftarrow n$ transition, it should be not so much affected by conjugation (ref. 5), whereas if it is due to a $\Pi^* \leftarrow \Pi$ transition it should be markedly red shifted. We have therefore examined the behaviour of this band as a function of pH. We have found that at pH 1 this band appears at 271 nm, while at pH 4 it is shifted to 285 nm. On the further increasing of pH, it moves no more. The si-

milar behaviour shows the 260 nm band. At pH 1 it occurs at 240 nm, while at pH 7 it is shifted to 260 nm.

The behaviour of the band maxima with increase of the pH values can be explained as follows: it is supposed that in strongly acidic solution EDTC is protonated, whereas at higher pH it is in ionic form.

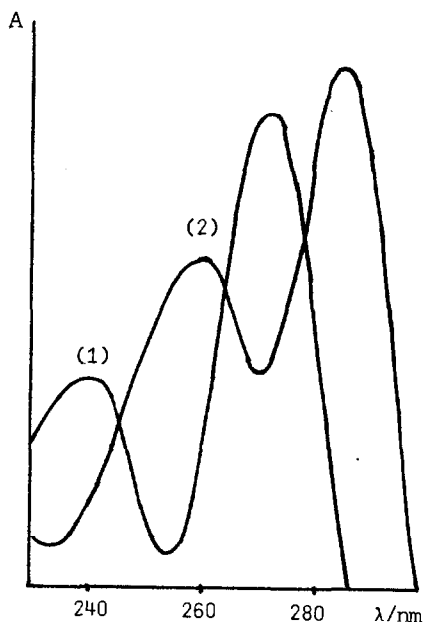
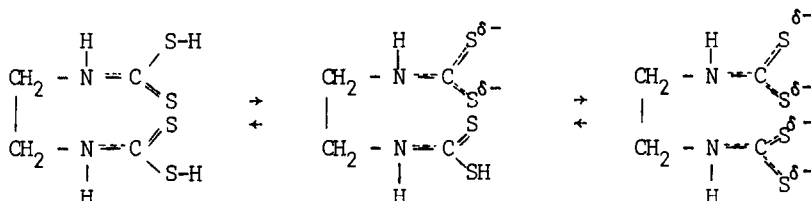


Fig. 2, uv spectrum of EDTC
(1) at pH 1, (2) at pH 7

In ionic form, by extending the conjugative system, the electron density is delocalized over both $C=S$ bonds, which consequently results in red shift. These results indicate that the intensive bands at about 285 nm and 260 nm might be due to $\pi^* \leftarrow \pi$ transitions.

The opposite behaviour (blue shift) of the 260 and 285 nm bands with increasing of the solvent polarity could be explained as follows: the solvent interaction is a kind of partial bond formation (ref. 7) between the polar part of the ions $N=C=S\delta^-$ and the polar solvent. Due to this, the polar part should be in some way fixed, and the unpolar part probably rotates around partially double $N=C$ bond and conjugation decreases which results in blue shift.

ACKNOWLEDGEMENT

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