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Synthesis and Spectrophotometric Studies of 2-(5-Carboxy-1,3,4-triazolylazo)-5-diethylamino Aniline

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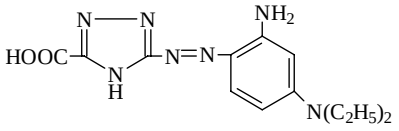
Abstract: In this paper, 2-(5-carboxy-1,3,4-triazolylazo)-5-diethylamino aniline**(CTZAN)** was prepared, the protonation behaviour of this reagent is reported. Its structure was identified .

Keywords: Synthesis, triazolylazo, spectrophotometry, protonation behaviour.

In search for new sensitive and selective organic reagents, triazolylazo and imidazolylazo compounds have not been studied until we reported the synthesis and spectrophotometric studies of some reagents in things like that[1-2]. In this paper, 2-(5-carboxy-1,3,4-triazolylazo)-5-diethylamino aniline **(CTZAN)** was prepared with the structure as:



(CTZAN)

Experimental

To a solution of 3.8 g (0.165 mol) metallic sodium in 30 ml of absolute ethanol, 2-amino-5-carboxy-1,3,4-triazolyl 6.4g (0.050 mol) in 100 ml of anhydrous ether and 18 g (0.154 mol) of isopentyl nitrite were added, and the mixture was refluxed for 6 h. 3-N,N-Diethylamino aniline 7.9g (0.048 mol) in ethanol and hydrochloric acid (1+3) were added at 0-5℃ until the mixture was slightly acidic and deep red color appeared. Crude reddish brown crystals were formed, which were filtered off, washed with ethanol and the crude **CTZAL** was recrystallized from ethanol-water,mp.256-258℃.

Analysis: $C_{13}H_{17}N_7O_2$ found: 51.76%C, 5.83%H, 32.12%N; calc.: 51.48%C,5.65 %H, 32.33%N; IR (KBr, ν /cm^{-1}): 1620 (N=N), 1500 (⬡), 1300 (C-N), 3500 (COOH), 1200-1250 (C_2H_5); ^{1}HNMR ($CDCl_3$, ppm) δ_H: 1.1-1.2 (6H), 1.8-2.1(1H), 3.3-3.4 (4H), 7.4 -7.5 (2H),11.7-12.1(1H).

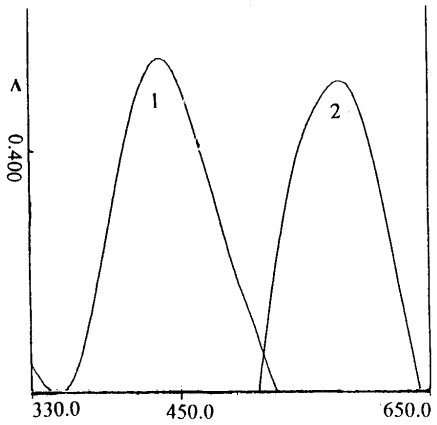
Protonation behaviour of the reagent

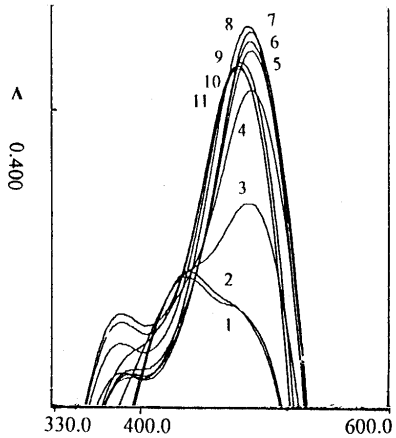
This reagent is soluble in water but insoluble in various organic solvent including ethanol, acetone. The **CTZAN** proton-dissociation constants were determined to be pKa_1= 3.1, pKa_2=7.6 and pKa_3=11.2. The absorption maximum is at 435 nm, that of the cobalt complex is at 580 nm, $\Delta\lambda$ =145 nm, the molar absorptivity increased to 4.06×10^4L.mol^{-1}.cm.$^{-1}$ by addition of mineral acid (1+1), HCl, H_2SO_4, HNO_3 or $HClO_4$. The complexes of other ions were decomposed back to the reagent upon addition of acid. The absorption spectra of the reagent at different pH values are shown in **Figure 1.** The absorption curves of **CTZAN** and its cobalt complex in hydrochloric acid (1+1) are shown in **Figure 2.**

Cobalt was determined as follows : A suitable aliquot of sample solution containing up to 10 μg of cobalt was transferred into a flask and 2.0 ml solution of **CTZAN** 1×10^{-3} mol/L was added, pH was adjusted to 9 with 5 ml **NH_3-NH_4Cl** solution. After 10 min. 2 ml of hydrochloric acid (1+1), or sulfuric acid (1+1) was added. The mixture was diluted to volume. The absorption of the cobalt complex was measured at 580 nm against a reagent blank with 1-cm cells.

Figure 1. CTZAN Absorption spectra at different pH values. **CTZAN** against **H_2O** blank, **[CTZAN]**=4×10^{-5}mol/L, pH: 1, 2.0, 2, 3.0; 3, 4.0, 4, 5.0; 5, 6.0, 6, 7.0, 7, 8.0, 8, 9.0, 9,10.0, 10,11.0, 11,12.0 ,

Figure 2. Absorbance curves of **CTZAN** and its cobalt complex in hydrochloric acid (1+1) **[CTZAN]**=4×10^{-5} mol/L, $[Co^{2+}]=6.79\times10^{-6}$ mol/L. 1),**CTZAN** against **H_2O** blank. 2), Co^{2+} complex against **CTZAN** blank.





References

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