

It should be noted that the sum of the S—S bond lengths, 4.70 Å, lies between the sum of the S—S bond lengths in compound (I), 4.72 Å, and the sum of those in compound (II), 4.66 Å.

Furthermore, cf. Fig. 1, the terminal and the central C—S bonds are 1.667 and  $1.719 \pm 0.009$  Å, respectively, as compared with the values, 1.701 and  $1.745 \pm 0.004$  Å, for the corresponding bonds in 2,5-dimethyl-thiothiophthene (I).<sup>3</sup> In 2,5-diphenyl-thiothiophthene (II) the lengths of the terminal C—S bonds are 1.702 and  $1.694 \pm 0.006$  Å, respectively, and the length of the central C—S bond is  $1.743 \pm 0.006$  Å.<sup>6</sup> The terminal C—S bonds in 3,4-diphenyl-thiothiophthene (III) are  $1.664 \pm 0.013$  Å and the central C—S bond there is  $1.749 \pm 0.013$  Å.<sup>9</sup>

The lengths of the terminal and central carbon-carbon bonds in thiothiophthene are 1.368 and  $1.418 \pm 0.010$  Å, respectively. Corresponding bond lengths in compound (I) are 1.363 and  $1.402 \pm 0.004$  Å, corresponding average bond lengths in (II) are 1.381 and  $1.399 \pm 0.008$  Å, and corresponding average bond lengths in (III) are 1.402 and  $1.443 \pm 0.020$  Å, respectively.

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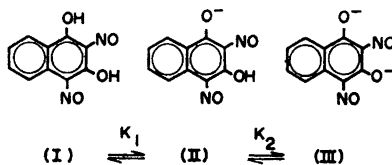
## 2,4-Dinitroso-1,3-dihydroxy-naphthalene as a Metal-Chelating Ligand

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In connection with investigations of the metal chelation properties of nitroso-naphthols, some studies with 2,4-dinitroso-1,3-dihydroxynaphthalene were carried out.

2,4-Dinitroso-1,3-dihydroxynaphthalene is believed to exist in two tautomeric forms (nitrosonaphthol  $\rightleftharpoons$  quinonemonoxime). It is more soluble in water than nitroso-naphthols, and in aqueous solution it behaves as a diprotic acid. The constants of the two dissociation equilibria can be evaluated from absorbances at wavelengths in the region 300–360 nm where the last peaks of the dissociated species are located.



The values of the constants  $K_1 = \frac{[H^+][HL^-]}{[HL]}$  and  $K_2 = \frac{[H^+][L^{2-}]}{[HL^-]}$  were determined in aqueous solutions of varying ionic strength (Table 1). The logarithmic values  $pK_1(I=0.1) = 4.53$  and  $pK_2(I=0.1) = 9.10$  at 25°C were calculated

by means of the corresponding Debye-Hückel equations

$$pK = pK^\circ - 0.509z^2\sqrt{I}/(1 + \alpha\sqrt{I}) + BI$$

The values of  $\alpha$  and  $B$  as well as the thermodynamic  $pK$  values were computed by the method of least squares. These values are also listed in Table 1. Figs. 1 and 2 show the dependence of the  $pK$

Table 1.  $pK_1$  and  $pK_2$  values of 2,4-dinitroso-1,3-dihydroxynaphthalene in aqueous solution at 25°C.

$\sqrt{I}$	$pK_1$ (Obs.)	$pK_1$ (Calc.)	$pK_1^\circ = 4.62$ $\alpha = 1.17$ $B = 0.18$
0.049	4.576	4.571	
0.234	4.434	4.441	
0.452	4.356	4.354	
0.897	4.319	4.318	
1.416	4.437	4.437	
$\sqrt{I}$	$pK_2$ (Obs.)	$pK_2$ (Calc.)	$pK_2^\circ = 9.50$ $\alpha = 1.68$ $B = 0.18$
0.080	9.347	9.357	
0.251	9.151	9.151	
0.450	9.038	9.014	
0.896	8.898	8.917	
1.415	9.015	9.010	

values on ionic strength and the spectra of the various species of 2,4-dinitroso-1,3-dihydroxynaphthalene.

Metal chelates of 2,4-dinitroso-1,3-dihydroxynaphthalene precipitate readily from aqueous solution. It was, however, possible to study absorptiometrically the formation of the first copper(II) chelate in the presence of an excess of copper(II) ions. The data in Table 2 show that the copper(II) chelate  $CuHL^+$  is formed; the logarithmic value 1.19 was obtained for the constant  $K_1 = [H^+][CuHL^+]/[Cu^{2+}][H_2L]$  at ionic strength 0.01. Determinations in the presence of nickel(II) ions were not possible because of precipitation.

Absorption spectra of chelates formed in the presence of divalent cobalt (red, spectral shoulder at 400–450 nm), palladium (brownish-red, shoulder at 400–450 nm), and iron (blue, peak at 650 nm) at pH 4.7 and at a ligand-metal ratio of  $\sim 5$  show that like the (mono)nitrroso-

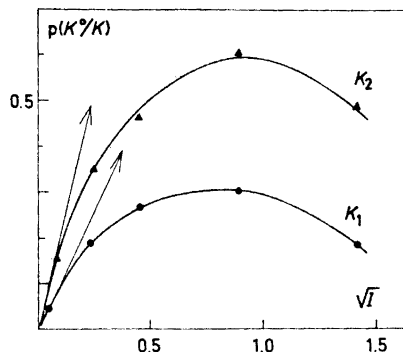


Fig. 1.  $p(K^\circ/K)$  as a function of the square root of ionic strength.

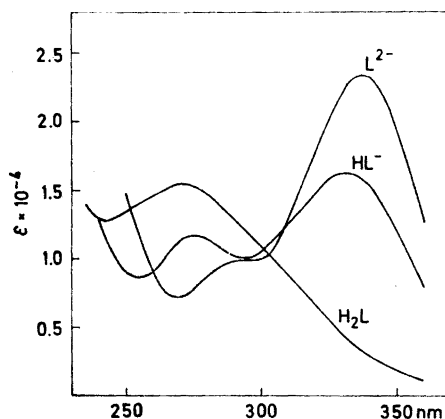


Fig. 2. Electronic spectra of the various forms of 2,4-dinitroso-1,3-dihydroxynaphthalene in aqueous solution.

naphthols, 2,4-dinitroso-1,3-dihydroxynaphthalene forms strong chelates with these metals.

The solid state IR spectrum of 2,4-dinitroso-1,3-dihydroxynaphthalene has peaks at 1690, 1660–1650s, 1590s, 1530w, 1495, 1460s, 1360s, 1305w, 1285w, 1210w, 1160w, 1135, 1090s, 1055, 1035s, 965w, 935s, 885s, 860w, 800w, 780s, 685s, 660, and 550nm (s = strong, w = weak), and resembles the spectrum of 2,4-dinitroso-resorcinol.<sup>1</sup> No hydroxyl-bands seem to

Table 2. Values of the formation constant  $K_I$  of the first copper(II) chelate of 2,4-dinitroso-1,3-dihydroxynaphthalene at 25°C.

$-\log[H^+]$ $\sqrt{I}$	1.59	1.87	1.99	2.29
	0.162	0.121	0.109	0.084
335 nm $\log K_I =$	1.213	1.199	1.198	1.147
340 nm	1.205	1.199	1.196	1.152
345 nm	1.203	1.199	1.197	1.160
350 nm	1.206	1.204	1.182	1.167
355 nm	1.205	1.195	1.191	1.167
360 nm	1.205	1.199	1.191	1.162
365 nm	1.203	1.191	1.190	1.168
$pK_I(\text{mean})$	-1.21	-1.20	-1.19	-1.16

Table 3. Spectral data for 2,4-dinitroso-1,3-dihydroxynaphthalene in aqueous solution at 25°C.

	$\lambda_{\text{max}}$	$\epsilon \times 10^{-3}$	Isosbestic points (nm)
$H_2L$	270	15.5	} 240, 301
$HL^-$	275	11.8	
	332	16.4	} 259, 308
$L^{2-}$	337	23.4	
$CuHL^+$	345	16.5	

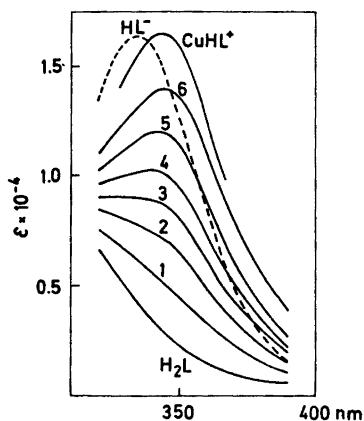


Fig. 3. Spectra showing the formation of the first copper(II) chelate of 2,4-dinitroso-1,3-dihydroxynaphthalene. Curves: at pH 1.34 (1), 1.64 (2), 1.86 (3), 2.04 (4), 2.32 (5) and 2.59 (6).

be present as in the case of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol.<sup>2</sup>

In aqueous solution 2,4-dinitroso-1,3-dihydroxynaphthalene is a much stronger acid than the nitrosonephthols.<sup>3,4</sup> The  $pK^\circ$  values 7.87 and 7.46 have been obtained for 1-nitroso-2-naphthol and 2-nitroso-1-naphthol, respectively.<sup>4</sup>

*Experimental.* 2,4-Dinitroso-1,3-dihydroxynaphthalene crystallizes as a monohydrate from water. (Found: C 50.85; H 3.51; N 11.72. Calc.: C 50.85; H 3.41; N 11.86). A reagent from Eastman Organic Chemicals was used.

The heavy metal salts were perchlorates. Dried potassium chloride was used as neutral salt to adjust the ionic strengths of the solutions.

A Radiometer PHM 4c potentiometer equipped with a Beckman glass electrode and an open-bridge potassium chloride reference calomel electrode was used. Apparent activity coefficient values were taken from a paper of Näsänen *et al.*<sup>5</sup>

The absorption spectra were recorded with a Beckman Model DK 2A recording spectrophotometer and absorbances were measured with a Beckman Model DU monochromator/Gilford photometer apparatus using calibrated 10-mm quartz cells.

IR spectra were recorded on a Perkin-Elmer Model 125 grating spectrometer using KBr pellets.

The methods have been described in detail earlier (see, *e.g.*, Ref. 4).

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