

Preparation and some spectral properties of substituted *N*-phenyl-5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximides

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The preparation of substituted *N*-phenyl-5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximides and of the starting 5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboxylic anhydride is described. The prepared imides have shown the linear dependence between $\nu_{\text{as}}(\text{C}=\text{O})$ and Hammett σ constants. It has been found that the substituent on the phenyl residue has but slight effect upon the λ_{max} of the electronic spectrum.

N-Substituted 1,4-dithiine-2,3-dicarboximides and substituted 5,6-dihydro-1,4-dithiine-2,3-dicarboximides have become known only in the last decade. This readily available class of substances, as a result of their colour and pharmacological properties, is of importance in the investigation of new dyes and drugs [1–4]. Since the substituted *N*-phenyl-5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximides have not yet been prepared we have explored the possibilities of preparing these substances and investigated their spectral properties.

Experimental

Infrared spectra were recorded with a UR-20 (Zeiss, Jena) spectrometer. The concentration of chloroform solutions was adjusted so that the maximum absorption in the region 1900–1600 cm^{-1} was $\sim 75\%$. The measurements were done in 0.1-cm cells. Calibration was performed using a standard polystyrene foil. The reading accuracy was $\pm 0.5 \text{ cm}^{-1}$.

Electronic spectra at 215–750 nm for solutions in dry methanol (10^{-3} – 10^{-4} M) were measured with a Perkin–Elmer 450 instrument.

The p.m.r. spectra were measured at 80 MHz on a Tesla BS-487A spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal standard.

The purity of the products was determined by thin-layer chromatography on silica gel-coated commercially available aluminum foils (Silufol, Lachema, Brno) with benzene–cyclohexane–ethyl acetate (1 : 1 : 2). The observed R_F values are in Table 1.

2,3-Dicyano-5-methyl-5,6-dihydro-1,4-dithiine (I)

Disodium 2,3-dimercaptomaleinnitrile (10.24 g; 0.051 mole) [1] was dissolved with heating ($\sim 50^\circ\text{C}$) in a mixture of *N,N*-dimethylformamide (30 ml) and dioxan (100 ml) contained in a flask equipped with a reflux condenser, stirrer, dropping funnel, and

Table 1

N-(X-Phenyl)-5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximides

Com- pound	X	Formula	<i>M</i>	Calculated/found				Yield [%]	M.p. Solvent	λ_{\max} [nm] ϵ	<i>R_F</i>
				% C	% H	% N	% S				
<i>IV</i>	4-OH	C ₁₃ H ₁₁ NO ₃ S ₂	293.36	53.22 53.51	3.69 3.82	4.78 4.95	21.86 21.96	76	178—180 Chloroform	416 2240	0.410
<i>V</i>	4-OCH ₃	C ₁₄ H ₁₃ NO ₃ S ₂	307.91	54.70 54.97	4.26 4.25	4.56 4.67	20.86 20.80	95	123 Ethanol	416 2210	0.490
<i>VI</i>	4-OC ₂ H ₅	C ₁₅ H ₁₅ NO ₃ S ₂	321.42	56.05 56.35	4.70 4.74	4.36 4.49	19.95 20.06	94	146 Ethanol	416 2220	0.530
<i>VII</i>	4-CH ₃	C ₁₄ H ₁₃ NO ₂ S ₂	291.39	57.71 57.65	4.93 4.61	4.81 4.76	22.01 21.90	83	183—184 Ethanol	416 2280	0.560
<i>VIII</i>	3-NH ₂	C ₁₃ H ₁₂ N ₂ O ₂ S ₂	292.38	53.40 55.68	4.14 4.27	9.58 9.91	21.93 21.68	52	210—212 Chloroform	416 2100	0.315
<i>IX</i>	H	C ₁₃ H ₁₁ NO ₂ S ₂	277.37	56.29 56.09	4.00 3.98	5.05 5.09	23.12 23.14	85	184—185 Ethanol	415 2240	0.520
<i>X</i>	4-Cl	C ₁₃ H ₁₀ ClNO ₂ S ₂	311.81	51.25	3.23	4.49	20.57 20.53	83	131—132 Ethanol	417 2600	0.570
<i>XI</i>	4-Br	C ₁₃ H ₁₀ BrNO ₂ S ₂	356.27	43.83 43.65	2.83 2.87	3.93 3.98	18.00 18.10	90	122 Ethanol	417 2560	0.610
<i>XII</i>	3-NO ₂	C ₁₃ H ₁₀ N ₂ O ₄ S ₂	322.36	49.00 48.86	3.16 3.11	8.79 8.79	20.12 19.56	73	141—143 Acetic acid	416 2850	0.485
<i>XIII</i>	4-NO ₂	C ₁₃ H ₁₀ N ₂ O ₄ S ₂	322.36	49.00 48.83	3.16 3.19	8.79 8.77	20.12 19.96	70	195—196 Acetic acid	416 2600	0.490
<i>XIV</i>	3-Cl	C ₁₃ H ₁₀ ClNO ₂ S ₂	311.81	51.25	3.23	4.49	20.57 20.61	74	106 Ethanol	415 2480	0.540
<i>XV</i>	3-OH	C ₁₃ H ₁₁ NO ₃ S ₂	293.36	53.22 52.01	3.69 3.68	4.78 4.87	21.86 21.25	94	207 Chloroform	415 2320	0.460
<i>XVI</i>	3-CH ₃	C ₁₄ H ₁₃ NO ₃ S ₂	291.39	57.71 58.28	4.93 4.51	4.81 4.87	22.01 22.05	79	108 Ethanol	415 2280	0.550
<i>XVII</i>	2-NH ₂	C ₁₃ H ₁₂ N ₂ O ₂ S ₂	292.38	53.40 53.21	4.14 4.18	9.58 9.58	21.93 21.94	89	322—324 Chloroform	409 2600	0.370

a thermometer. A solution of 1,2-dibromopropane (10.1 g; 0.05 mole) in dioxan (10 ml) was added dropwise during 50 min and the temperature of the mixture was kept at 75–80°C for 2 hrs. The reaction mixture was cooled, the separated sodium bromide removed, and the solution concentrated to 40 ml and poured onto crushed ice (200 g). The precipitated crude product was crystallized from 90% ethanol. Yield 7.9–8.3 g (87–91%), m.p. 87–88°C which value is in agreement with the data given in the literature [5].

5-Methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboxylic anhydride (II)

Water (440 ml) was added dropwise during 50 min at the maximum temperature of 110°C to a solution of 2,3-dihydro-5-methyl-1,4-dithiine (83 g; 0.455 mole) in concentrated sulfuric acid (880 g) contained in a flask equipped with a stirrer, a reflux condenser, and a thermometer. After cooling to 80°C the reaction mixture was poured onto ice (2500 g) and let stand for 1–2 days during which time the separated oily product solidified. The collected solid material was thoroughly washed with cold water and dried, followed by heating with a solution of sodium hydroxide (40 g) in water (170 ml) to remove the present imide. The solution was treated with charcoal, filtered, and acidified to pH 1 at 5°C. Compound *II* separated as oil which solidified on standing for 3–4 hrs. Yield 84 g (98%), m.p. 65–66°C (from ether).

For $C_7H_6O_3S_2$ (202.3) calculated: 41.57% C, 2.99% H, 31.71% S; found: 41.75% C, 2.88% H, 31.65% S.

$\nu(C=O)$ 1776, 1885, $\nu(C=C)$ 1565. The p.m.r. data (δ , p.p.m.): CH_3-C (1.55), $S-CH_2-C$ (3.20), CH (3.70).

5-Methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximide (III)

Crystalline ammonium acetate (43.20 g; 0.3 mole) was added to compound *II* (20.23 g; 0.1 mole) dissolved with heating in 99% ethanol (400 ml) and the mixture was heated under reflux for 2 hrs. Concentrated ammonium hydroxide (22 ml) was added during 1 hr and the mixture was heated for an additional 1 hr after which time the solvents were removed, the crude product was washed with water and crystallized from ethanol. Yield 17 g (85%), m.p. 182°C.

For $C_7H_7NO_2$ (201.3) calculated: 41.77% C, 3.51% H, 6.96% N, 31.86% S; found: 42.08% C, 3.70% H, 6.83% N, 31.82% S.

$\nu(C=O)$ 1730, 1776, $\nu(NH)$ 3436, $\nu(C-N)$ 1338, $\nu(C=C)$ 1556.

N-(X-Phenyl)-5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximides (IV–XVII)

Compound *II* (0.01 mole) was dissolved in warm ethanol (10 ml) followed by addition of a few drops of acetic acid and a solution of the substituted aniline (0.01 mole) in ethanol (5 ml). The reaction mixture was refluxed for half an hour and cooled below the freezing point. The separated product was recrystallized. For proper crystallization solvents and analytical figures see Table 1.

N,N-Phenylene-bis(5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximides)
(XVIII and XIX)

A mixture of *II* (2.02 g; 0.01 mole) and *m*- or *p*-phenylenediamine (0.005 mole) in glacial acetic acid (15 ml) was heated under reflux for 3 hrs. The solution was cooled, the

separated product washed with ethanol and crystallized from *N,N*-dimethylformamide. Yields *XVIII*: 1.8 g (75%), *XIX*: 1.7 g (71%).

N,N-*m*-Phenylene-bis(5-methyl-1,4-dithiine-2,3-dicarboximide) (*XVIII*) melted at 263–265°C.

For $C_{20}H_{16}N_2O_4S_4$ (476.62) calculated: 50.40% C, 3.38% H, 5.88% N, 26.91% S; found: 50.69% C, 3.44% H, 6.15% N, 26.55% S.

$\nu(C=O)$ 1719, 1776.

N,N-*p*-Phenylene-bis(5-methyl-1,4-dithiine-2,3-dicarboximide) (*XIX*) melted at 232–234°C.

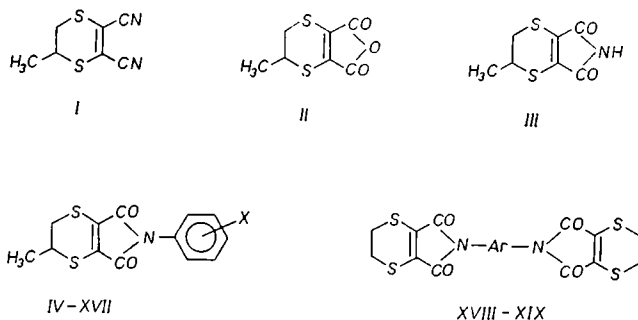
Found: 49.98% C, 3.48% H, 6.07% N, 26.55% S.

$\nu(C=O)$ 1720, 1774.

Results and discussion

The starting compound for the preparation of *N*-X-phenyl-5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximides (*IV–XVII*), namely 5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboxylic anhydride (*II*) has not been described so far. We synthesized this substance by a procedure analogous to the one recommended for the preparation of 5,6-dihydro-1,4-dithiine-2,3-dicarboxylic anhydride [1] under suitably altered conditions.

The procedure for making *II* involved preparation of 2,3-dicyano-5-methyl-5,6-dihydro-1,4-dithiine (*I*) from disodium 2,3-mercaptomaleinnitrile and 1,2-dibromopropane. Although the substance *I* was described [3, 4], no experimental details were given in the quoted works. The dicyano compound *I* was consecutively hydrolyzed under acidic and alkaline conditions to give, under the conditions given in the Experimental section, nearly quantitatively the wanted substance *II*. It is worth mentioning that compound *I* is directly converted to the anhydride *II* even under 100-fold dilution. The anhydride *II* is not hydrolyzed to the corresponding dibasic acid either when boiled in water for several hours or in the presence of hydrochloric acid. It reacts, however, readily with ammonia to give the imide *III* and with primary aromatic amines to give almost quantitatively the *N*-substituted imides *IV–XVII*.



Ar = *m*-phenylene,
p-phenylene.

Scheme 1

The yields, as can be seen in Table 1, are markedly affected by the substituents on the aromatic ring. When the reaction was carried out with *m*-phenylenediamine, bis-derivative *XVIII* was obtained besides the monoderivative *XIII*. The bis-derivative *XVIII* was the main product of this reaction when the process was carried out with a twofold excess of *II*. The reaction of *II* with *p*-phenylenediamine afforded exclusively the bis-derivative *XIX* (Scheme 1).

Benzene and chloroform solutions of *II* and *III* and of some *N*-X-phenyl imides *IV*–*XVII* showed strong fluorescent effects. As can be seen from the data given in Table 1, the intensity of the band in the electronic spectrum in the visible region is low and the region where this band appears is only slightly affected by the nature of substituents. It therefore appears unlikely that these substances will find application as dyes.

Infrared spectra of the imides *IV*–*XVII* showed intense bands at 1550–1560 cm^{-1} corresponding to the double bond of the 5-methyl-5,6-dihydro-1,4-dithiine ring. This band is located at higher values (by 15–20 cm^{-1}) than in the case of imides belonging to the 5,6-dihydro-1,4-dithiine type of substances [1]. Similar shift to higher values was observed for the anhydride *II* when compared with 5,6-dihydro-1,4-dithiine-2,3-dicarboxylic anhydride. In the region of the C=O stretching vibrations the imides *IV*–*XVII* showed two absorption bands. The more intense band, appearing at lower wavenumber (1722–1713 cm^{-1}), corresponds to the asymmetric vibrations and the less intense one, appearing at higher wavenumber (1777–1772 cm^{-1}), belongs to the symmetric vibrations of the dicarbonyl system [6]. The wavenumbers of asymmetric and symmetric vibrations are given in Table 2. In the series of the compounds under investigation, similarly to other five-membered cyclic imides [7, 8], a linear correlation between the wavenumber ν_{as} and Hammett σ constants can be found:

Table 2

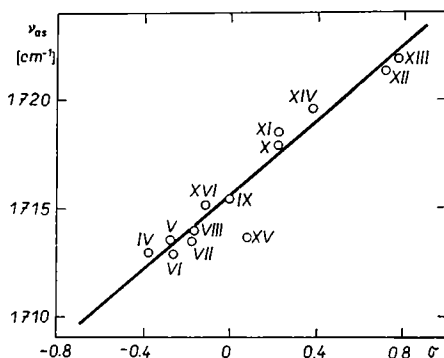
Wavenumbers of the C=O stretching vibrations in cm^{-1} and σ constants of the substituents for some *N*-(X-phenyl)-5-methyl-5,6-dihydro-1,4-dithiine-2,3-dicarboximides

Compound	X			
<i>IV</i>	4-OH	1713.0	1775.0	–0.37
<i>V</i>	4-OCH ₃	1713.5	1773.0	–0.27
<i>VI</i>	4-OC ₂ H ₅	1713.0	1772.0	–0.25 ^b
<i>VII</i>	4-CH ₃	1713.5	1776.0	–0.17
<i>VIII</i>	3-NH ₂	1714.0	1774.0	–0.16
<i>IX</i>	H	1715.5	1776.0	0.00
<i>X</i>	4-Cl	1718.5	1775.5	0.23
<i>XI</i>	4-Br	1718.0	1774.0	0.23
<i>XII</i>	3-NO ₂	1721.5	1776.5	0.71
<i>XIII</i>	4-NO ₂	1722.0	1777.0	0.78
<i>XIV</i>	3-Cl	1720.0	1776.0	0.37
<i>XV</i>	3-OH	1714.0	1776.0	0.09
<i>XVI</i>	3-CH ₃	1715.0	1776.0	–0.07

a) Taken from [9].

b) Taken from [10].

Fig. 1. Dependence of $\nu_{\text{as}}(\text{C}=\text{O})$ on σ constants for N -(X-phenyl)-5-methyl-5,6-dihydro-1,4-dithiine-2,3-carboximides.



$$\nu_{\text{as}} = 8.5(\pm 0.4) \sigma + 1716.7 \pm (0.1),$$

$$r = 0.987, \quad s = 0.5$$

where r is the correlation coefficient and s the standard deviation.

The relatively high value of the slope of linear dependence, 8.5 (Fig. 1), indicates that the free electron pair present here plays an important role in the transfer of the effects of the substituent onto the carbonyl groups.

No correlation has been made in the case of compound *XV* since here the observed ν_{as} value does not fulfil the condition for linear dependence. Compound *XVII* showed ν_{as} and ν_{s} identical with the values observed for compound *VIII*.

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