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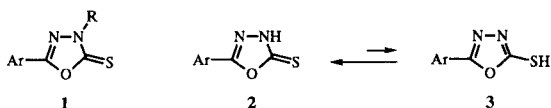
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Twenty four 2-aryl- Δ^2 -1,3,4-oxadiazoline-5-thione derivatives **2** were synthesized and their uv and ir spectra were studied. Correlation between σ -Hammett constants of aryl substituents and the differences in absorption maxima ($\Delta\nu = \nu_1 - \nu_2$ in kK) of the electronic spectra of the deprotonated species were also evaluated. A new method for the synthesis of the 2-(amino)aryl derivatives **2v,w,x** is also reported.

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Introduction.

Δ^2 -1,3,4-oxadiazoline-5-thione derivatives **1** have been reported to show a wide range of biological activities and an increasing variety of uses [1-3]. Many studies have been made on their physical and chemical properties whereas some uv and ir bands of **2** have been reported [4-12]. On the basis of theoretical and spectral data it has been confirmed that among the tautomeric thiono- **2** and thiolo- **3** forms predominantly form **2** exists in solution with the oxadiazole ring in a planar configuration [4,5,10,11].

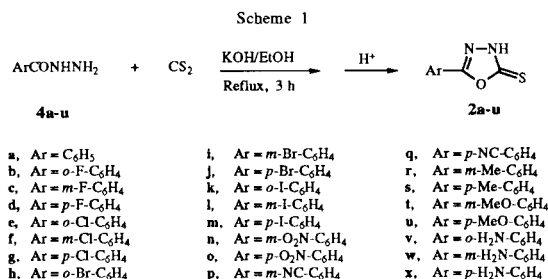


In order to study in a more complete way and more systematically the uv and ir spectra of these compounds and their uv spectral behaviour in different pH conditions, a number of them have been synthesized and the results of this study are now reported.

Results and Discussion.

Compounds **2** were prepared from the reaction of the corresponding benzhydrazides, **4**, and carbon disulfide in the presence of potassium hydroxide [13] and treatment of the resulting anionic form with hydrochloric acid.

For the preparation of the (amino)phenyl derivatives



2v,w,x, the above method gives very poor results, since, under the reaction conditions, carbon disulfide may react with both the hydrazine and the amino group of the aminobenzhydrazide used for this preparation. It was found that these derivatives were prepared more easily and in higher yields by refluxing the corresponding potassium 3-(nitrobenzoyl)dithiocarbazates **5** with hydrazine in absolute ethanol. Under the reaction conditions the nitro group is reduced to the amino group and besides the expected [13] 4-amino-1,2,4-triazole derivative **6** the 2-(amino)phenyloxadiazoline-5-thiones **2v,w,x** were formed in good yields (70-90%).

Potassium 3-(nitrobenzoyl)dithiocarbazates **5** were prepared from the corresponding nitrobenzhydrazides and carbon disulfide in the presence of potassium hydroxide at low temperatures (0-5°).

Electronic Spectra.

The electronic spectra of compounds **2** in ethanol-water (7.5/92.5) solutions in the pH range of nearly 0 to 12

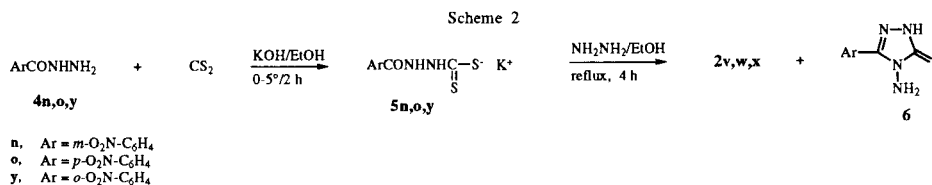


Table 1
Yields, Melting Points, Formulae and Elemental Analyses of the 2-aryl- Δ^2 -1,3,4-oxadiazoline-5-thiones **2** Studied

Compound		Yield %	Mp(°C) (Lit)	Color	Formula	Analysis		
						C%	Calcd./Found H%	N%
2a	H	83	218-220 (218-220) [1] (219-220) [6] (224-225) [20]	wh	C ₈ H ₆ N ₂ OS			
2b	<i>o</i> -F	40	143-145	wh	C ₈ H ₅ N ₂ OSF	48.97 48.70	2.57 2.40	14.28 14.03
2c	<i>m</i> -F	56	106-107	wh	C ₈ H ₅ N ₂ OSF	48.97 48.73	2.57 2.85	14.28 14.19
2d	<i>p</i> -F	75	172-174	l. yel	C ₈ H ₅ N ₂ OSF	48.97 49.10	2.57 2.78	14.28 14.41
2e	<i>o</i> -Cl	35	168-170 (188-190) [20]	wh	C ₈ H ₅ N ₂ OSCl			
2f	<i>m</i> -Cl	52	181-183 (179) [6]	wh	C ₈ H ₅ N ₂ OSCl			
2g	<i>p</i> -Cl	78	170-172 (176-178) [6] (176.5-178) [21]	wh	C ₈ H ₅ N ₂ OSCl			
2h	<i>o</i> -Br	37	192-194	wh	C ₈ H ₅ N ₂ OSBr	37.37 37.47	1.96 1.88	10.90 10.63
2i	<i>m</i> -Br	50	213-215 (212) [6]	wh	C ₈ H ₅ N ₂ OSBr			
2j	<i>p</i> -Br	77	186-187 (189) [6]	wh	C ₈ H ₅ N ₂ OSBr			
2k	<i>o</i> -I	45	152-154	yel	C ₈ H ₅ N ₂ OSI	31.60 31.40	1.66 1.80	9.21 9.05
2l	<i>m</i> -I	54	230-231	l. yel	C ₈ H ₅ N ₂ OSI	31.60 31.62	1.66 1.73	9.21 8.91
2m	<i>p</i> -I	72	196-197	wh	C ₈ H ₅ N ₃ OSI	31.60 31.84	1.66 1.76	9.21 9.29
2n	<i>m</i> -NO ₂	60	164-165 (150) [6]	l. yel	C ₈ H ₅ N ₃ O ₃ S			
2o	<i>p</i> -NO ₂	82	202-204 (202) [6] (207-209) [12] (200-202) [20]	yel	C ₈ H ₅ N ₃ O ₃ S			
2p	<i>m</i> -CN	51	205-206	l. yel	C ₉ H ₅ N ₃ OS	53.19 53.17	2.48 2.44	20.68 20.54
2q	<i>p</i> -CN	70	227-229	yel	C ₉ H ₅ N ₃ OS	53.19 53.04	2.48 2.44	20.68 20.40
2r	<i>m</i> -CH ₃	48	153-154 (158-160) [6]	wh	C ₉ H ₈ N ₂ OS			
2s	<i>p</i> -CH ₃	65	206-208 (223) [6]	wh	C ₉ H ₈ N ₂ OS			
2t	<i>m</i> -CH ₃ O	55	158-160	wh	C ₉ H ₈ N ₂ O ₂ S	51.91 52.00	3.87 3.87	13.45 13.42
2u	<i>p</i> -CH ₃ O	73	198-200 (204-206) [1] (203) [6]	yel	C ₉ H ₈ N ₂ O ₂ S			
2v	<i>o</i> -NH ₂	40	235-236 (235-237) [20]	yel	C ₈ H ₇ N ₃ OS			
2w	<i>m</i> -NH ₂	53	182-183	yel	C ₈ H ₇ N ₃ OS	49.73 49.50	3.65 3.58	21.75 21.83
2x	<i>p</i> -NH ₂	69	228-230 (228-230) [20]	l. yel	C ₈ H ₇ N ₃ OS			

[a] wh = white, yel = yellow, l. yel = light yellow

revealed the existence of three species which correspond to the neutral compound LH **2**, the deprotonated anionic form L⁻ **7** and the protonated cationic form LH₂⁺ **8**.

The electronic spectral data of all three species are listed in Table 2. The $\pi_b \rightarrow \pi_b^*$ transition frequencies (ν_1 , in kK) are due to the phenyl ring and the $\pi_{ox} \rightarrow$

Table 2

ν_{\max} (in kK) of the UV Spectra of 2-Aryl- Δ^2 -1,3,4-oxadiazoline-5-thiones of the Deprotonated (L⁻), Neutral (LH) and Protonated (LH₂⁺) Forms (For ν_1 and ν_2 abbreviations see the text)

Compound		(L ⁻)		(LH)		(LH ₂ ⁺)		
		$\nu_{1\max}$ $\nu_{2\max}$	$\Delta\nu$ log ϵ	$\nu_{1\max}$ $\nu_{2\max}$	log ϵ	$\nu_{1\max}$ $\nu_{2\max}$	log ϵ	
2a	H	44.84	11.17	4.15	40.16	4.00	39.53	4.10
		33.67						
2b	<i>o</i> -F	44.84	11.28	4.20	40.32	4.01	40.00	4.07
		33.56						
2c	<i>m</i> -F	45.05	11.94	4.20	43.48	4.03	43.10	4.06
		33.56						
2d	<i>p</i> -F	44.64	10.84	4.24	39.53	4.14	39.68	4.12
		33.11						
2e	<i>o</i> -Cl	43.48 sh	[a] 9.70	4.27	40.16	4.04	40.16	4.04
		34.36						
2f	<i>m</i> -Cl	44.05	11.26	4.28	40.32	3.99	40.00	4.08
		33.78						
2g	<i>p</i> -Cl	43.10	10.31	4.26	41.15	4.12	39.22	4.11
		32.79						
2h	<i>o</i> -Br	43.86 sh	9.61	4.16	40.00	3.93	39.68	3.90
		32.79						
2i	<i>m</i> -Br	44.05	11.37	4.28	40.00	3.97	40.32	4.04
		34.25						
2j	<i>p</i> -Br	43.10	10.42	4.28	40.32	4.24	39.68	4.21
		32.68						
2k	<i>o</i> -I	46.72	13.93	4.85	40.98	4.10	38.46 sh	4.11
		32.68						
2l	<i>m</i> -I	45.05	12.05	4.45	44.84	4.40	44.84	4.33
		32.79						
2m	<i>p</i> -I	44.05	11.26	4.25	39.53	4.14	38.91	4.14
		32.70						
2n	<i>m</i> -NO ₂	46.30	13.30	4.43	45.87	4.34	39.68 sh	4.16
		32.79						
2o	<i>p</i> -NO ₂	39.68	11.75	4.29	38.91	4.32	38.46	4.43
		33.00						
2p	<i>m</i> -CN	44.14	11.99	4.32	43.86 sh	4.21	39.52 sh	4.10
		27.93						
2q	<i>p</i> -CN	42.02	11.53	4.30	41.32	4.19	41.15	4.20
		32.15						
2r	<i>m</i> -CH ₃	42.92 sh	9.14	4.24	42.74	4.13	42.02	4.09
		30.49						
2s	<i>p</i> -CH ₃	42.55 sh	8.88	4.16	41.67	4.07	39.68	4.11
		33.78						
		33.67		4.22	34.25	4.31	34.81	4.10

Table 2 (Continued)

Compound		(L^-)		(LH)		(LH_2^+)				
		v_{1max}	v_{2max}	Δv	$\log \epsilon$	v_{1max}	v_{2max}	$\log \epsilon$		
2t	m-CH ₃ O	42.55	33.44	9.55	4.12	42.19	39.22	3.99	4.04	
		33.44			4.19	34.01		4.25	34.13	4.12
2u	p-CH ₃ O	41.66	33.11	8.55	4.12	40.00	39.68	4.10	4.09	
		33.11			4.17	33.67		4.40	33.78	4.33
2v	o-NH ₂	35.34	41.32 sh	5.40	3.93	35.09	39.68	3.95	3.98	
		29.94			3.95	29.76		4.01	28.99	3.68
2w	m-NH ₂	41.32 sh	33.11	8.21	4.18	40.16	39.53	4.08	4.12	
		29.94			3.95	29.76		4.01	28.99	3.68
2x	p-NH ₂	40.52	32.26	8.26	3.98	38.91	34.25	3.96	4.20	
		33.11			4.17	34.25		4.07	33.78	4.20
		32.26			4.39	32.26		4.43	34.25	4.17

[a] sh = shoulder.

π_{ox}^* (v_2 , in kK) are due to the oxadiazole ring. A bathochromic shift is observed in $\pi_b \rightarrow \pi_b^*$ transition and a hypsochromic shift in $\pi_{ox} \rightarrow \pi_{ox}^*$ transition in going from L^- to LH_2^+ . A shift to longer wavelengths is also observed in $\pi_b \rightarrow \pi_b^*$ transition from *meta*- to *para*-phenyl substituted derivatives for the LH and L^- species.

Correlation of Δv ($\Delta v = v_1 - v_2$) for the anionic form L^- with σ Hammett constants of the aryl substituents gives the equations (1) and (2), for the *meta* and *para*

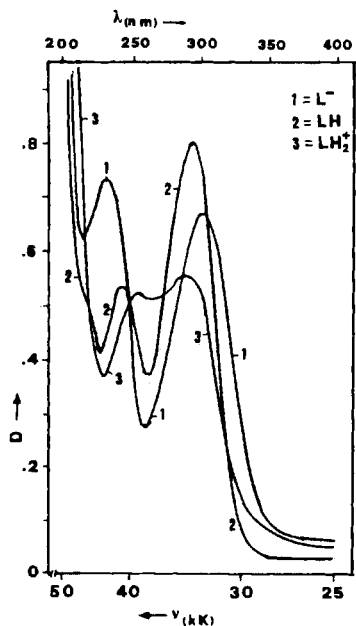


Figure 1. UV spectrum of 2-(*p*-chlorophenyl)- Δ^2 -1,3,4-oxadiazoline-5-thione (2g), $C = 4 \times 10^{-5} M$ in ethanol-water (7.5/92.5 v/v), $I = 1 \times 10^{-2} M$ in potassium chloride and $t = 20^\circ$.

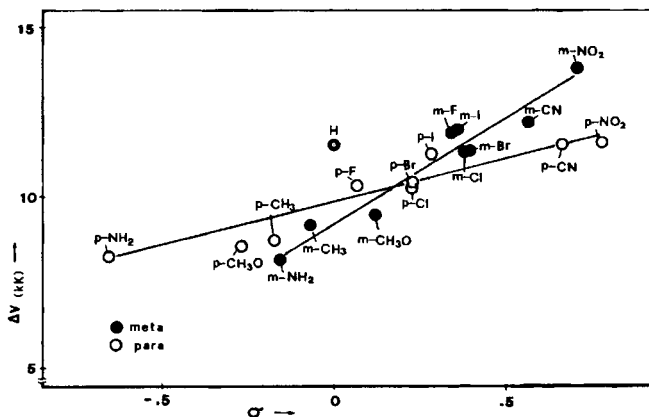


Figure 2. Plot of observed Δv ($\Delta v = v_1 - v_2$) for compounds 2a-x versus σ -Hammett constants.

substituted derivatives of 2 respectively, nine compounds in each case with the exception of the deviated non substituted 2a.

$$\Delta v_{meta} = 9.38 + 5.64\sigma \quad (R=0.970) \quad (1)$$

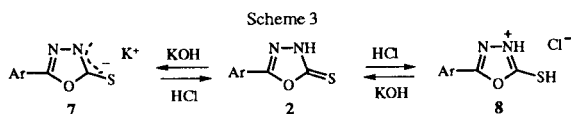
$$\Delta v_{para} = 9.77 + 2.74\sigma \quad (R=0.954) \quad (2)$$

The general meaning of equations (1) and (2) could be that the difference between $\pi_b \rightarrow \pi_b^*$ and $\pi_{ox} \rightarrow \pi_{ox}^*$ transition energies depends on the combined inductive and resonance effect of the substituent of the aryl ring at an increasing order with the increase of electron withdrawal effect of the substituent. It should be noticed however that the ρ value for the *meta*-substituted compounds (equation 1) is more than double compared to that for the *para*-substituted (equation 2), 5.64 versus 2.74 respectively, and this most probably indicates that the inductive is predominating over the resonance effect in this elec-

Table 3
Infrared Absorption Bands of 2-Aryl- Δ^2 -1,3,4-oxadiazoline-5-thiones **2** in Potassium Bromide Pellets

Compound		ν (N-H)	ν (N-H)	ν (N-H)	ν (S-H)	ν (C=N)	[a]	[b]	[c]	[d]	[e]	ν (N-N)
2a	H	3140 m, br	2950 m	2765 w	2560 w	1575 m	1502 s	1350 s	1280 m	1076 s	970 m	945 m
2b	<i>o</i> -F	3180 s, br	2950 w	2745 w	-	1586 m	1467 s	1335 s	1266 m	1072 m	962 s	938 s
2c	<i>m</i> -F	3130 m	2930 m	2760 w	2570 vw	1580 m	1498 s	1340 s	1274 m	1070 m	962 m	948 s
2d	<i>p</i> -F	3090 m	2935 m	2755 w	2575 vw	1584 m	1502 vs	1342 m	1270 m	1070 m	968 m	942 m
2e	<i>o</i> -Cl	3275 m	2920 w	-	-	1565 m	1462 vs	1335 s	1280 m	1070 s	962 s	950 m
2f	<i>m</i> -Cl	3100 m	2920 m	2760 w	2570 vw	1570 m	1503 s	1342 s	1282 m	1075 m	968 m	948 m
2g	<i>p</i> -Cl	3110 m, br	2920 m	2740 w	2550 vw	1565 m	1495 s	1340 s	1280 m	1065 m	975 m	940 m
2h	<i>o</i> -Br	3260 s	2930 w	-	2560 vw	1565 w	1470 s	1335 s	1282 m	1075 m	965 m	955 m
2i	<i>m</i> -Br	3080 m, br	2920 m	2745 m	2550 w	1565 m	1498 s	1340 s	1280 m	1060 m	968 s	945 m
2j	<i>p</i> -Br	3100 m, br	2930 m	2750 w	2560 vw	1562 w	1500 s	1340 s	1280 m	1070 s	975 m	940 m
2k	<i>o</i> -I	3235 s	2920 m	2720 w	-	1555 w	1468 vs	1328 s	1272 m	1060 m	963 m	945 m
2l	<i>m</i> -I	3090 m	2930 m	2760 w	-	1555 m	1500 vs	1340 s	1280 m	1063 m	965 m	945 m
2m	<i>p</i> -I	3110 m, br	2940 m	2755 w	2540 w	1548 w	1505 vs	1340 s	1280 m	1065 s	972 m	938 m
2n	<i>m</i> -NO ₂	3075 m	2925 m	2760 w	2560 vw	1565 w	1500 vs	1336 s	1285 s	1065 m	960 s	945 m
2o	<i>p</i> -NO ₂	3080 m	2920 m	2740 w	2560 w	1567 sh	1500 vs	1340 vs	1277 s	1062 m	960 s	940 m
2p	<i>m</i> -CN	3190 s	2970 s	2760 m	2560 w	1555 w	1482 s	1328 s	1276 s	1075 m	956 m	942 s
2q	<i>p</i> -CN	3200 s	2950 m	2740 w	2550 w	1552 w	1475 vs	1346 s	1272 s	1072 m	954 s	932 m
2r	<i>m</i> -CH ₃	3090 s	2940 s	2765 m	2560 w	1565 m	1500 vs	1336 s	1275 s	1074 s	968 s	945 s
2s	<i>p</i> -CH ₃	3080 s	2930 s	2760 m	2560 w	1562 m	1510 vs	1348 s	1277 s	1070 s	968 s	945 m
2t	<i>m</i> -CH ₃ O	3210 m	2980 m	2770 w	2580 w	1570 m	1502 s	1338 s	1288 m	1078 m	970 m	940 m
2u	<i>p</i> -CH ₃ O	3210 s	2910 m	2770 w	2560 w	1572 m	1520 s	1352 vs	1254 s	1080 m	969 m	936 m
2v	<i>o</i> -NH ₂	3080 m	2930 m	2760 w	2560 w	1570 m	1508 vs	1340 vs	1288 m	1066 m	960 s	940 m
2w	<i>m</i> -NH ₂	3150 m	2910 m	2720 m	2580 m	1580 m	1525 vs	1360 vs	1235 m	1084 s	965 s	945 s
2x	<i>p</i> -NH ₂	3100 s	2950 s	2760 m	2590 w	1570 m	1515 vs	1358 vs	1275 m	1075 m	978 s	937 m

[a] Due to ν (C=S) + ν (C-N) + δ (N-H) (Thioamide I) [b] Due to ν (C=N) contributed by ν (C-O) + ν (N-N). [c] Due to ν (C-N) + ν (C=S) (Thioamide II). [d] Due to ν_{as} (C-O-C). [e] Due to ν (C=S) with contribution of ν (CN) + α (CNN) (Thioamide III). [f] s = strong, m = medium, w = weak, vs = very strong, vw = very weak, br = broad, sh = shoulder.



tronic perturbation of the oxadiazole anionic form, which however has not been observed in the neutral, LH, or the protonated, LH₂⁺ species.

Infrared Spectra.

The ir spectra of compounds **2** taken in potassium bromide pellets are listed in Table 3. The precise frequency value of the bands of ν (N-H), in the range 3275-3080 cm⁻¹, depends to some extent on the position of the substituent in the phenyl ring. Thus in the case of an electron withdrawing substituent the order of increase in frequency is $\nu_{o-} > \nu_{p-} > \nu_{m-}$. The bands at 2980-2910 cm⁻¹ and 2770-2720 cm⁻¹ possibly indicate ν (N-H) with extensive hydrogen bonding [15]. These bands as well as those in the range 3275-3080 cm⁻¹ disappear upon complexation with transition metal ions [16]. In the case of **2v,w,x** derivatives the following absorption bands attributed to the amino group are also observed: ν_{as} (N-H) 3450 m (**2v**), 3340 m (**2w**), 3450 m (**2x**) and ν_{sym} (N-H) 3350 m (**2v**), 3240 m (**2w**), 3350 s (**2x**).

Assignments attributed to the thioamide group -N-C=S, vary in the wide range of 1525 to 954 cm⁻¹

[17], where absorption bands of thioamide I, thioamide II and thioamide III are in the range of 1462-1525, 1266-1288 and 954-978 cm⁻¹ respectively. It is noticeable that in *ortho* halo derivatives thioamide I band possesses the part of the lower frequencies of this range (1470-1462 cm⁻¹), possibly because in *ortho* substitution the two rings deviate significantly from coplanarity resulting to a degree of interruption of the conjugation of the two rings.

The characteristic ir bands of **7** are: at 1945 m due to ν (N-C-S⁻); at 1555s due to ν (C=N); at 1420 s, br due to thioamide I; at 1140 s due to ν (C=S); at 1072 s due to ν_{as} (C-O-C); at 930 s due to ν (N-N). All bands in the range 3095-2760 cm⁻¹ due to ν (N-H) and the band at 2560 cm⁻¹ due to ν (S-H) were disappeared.

The characteristic ir bands of **8** are 3095 m, 2930 s, br and 2760 m all three attributed to ν (N-H) and extensive hydrogen bonding. Also, the band at 2560 m, due to ν (S-H); at 1572 s due to ν (C=N); at 1510 s due mainly to ν (C-S) + ν (C-N) + δ (N-H) (thioamide I); at 1347 s due to ν (C=N) + ν (C-O) + ν (N-N); at 1268 s due mainly to ν (C-N) + ν (C=S) (thioamide II); at 1082 m due to ν_{as} (C-O-C); at 970 m due mainly to ν (C=S) with major contribution of α (CNN); at 945 s due to ν (N-N) and 750 m due to ν (C-S).

The above assignments constitute strong evidence that in the cationic form **8** the protonation takes place in the

sulfur atom, whereas in the anionic form **7** the negative charge is partially delocalised to the group $-N-C-S$ as well as to the aryl ring [14].

EXPERIMENTAL

Melting points were determined with a Buchi apparatus and are uncorrected. The electronic spectra were recorded on a Perkin-Elmer Hitachi 200 spectrophotometer using ethanol-water (7.5/92.5) solutions. The infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer with potassium bromide pellets. The elemental analyses of C, H and N were performed with a Perkin-Elmer 240B CHN Analyser [22].

2-Aryl- Δ^2 -1,3,4-oxadiazoline-5-thiones **2a-u**.

General Procedure.

To a solution of potassium hydroxide (50 mmoles) in absolute ethanol (200 ml), the appropriate benzhydrazide (50 mmoles) was added under stirring. After a few minutes a slight excess of carbon disulfide (70 mmoles) was added and the mixture was held at reflux for *ca* 2-3 hours or until most of the hydrogen sulfide has been evolved. A solid product appeared occasionally during the addition of carbon disulfide, that was usually dissolved upon heating. Evaporation of the solvents by distillation *in vacuo* left a residue, which was dissolved in water, cooled by ice and acidified by hydrochloric acid to give **2** as a solid, which was filtered off, dried and recrystallized from a mixture of ethanol-water (50/50) [1,2].

Potassium 3-(Nitrobenzoyl)dithiocarbazates **5**.

The salts **5** were prepared [18] by treating the corresponding nitrobenzhydrazides **4** (100 mmoles) with carbon disulfide (150 mmoles) in absolute ethanol (200 ml) containing potassium hydroxide (100 mmoles). The mixture was stirred at 0-5° for 3 hours and then was kept overnight in the refrigerator. The precipitated salt **5** was filtered off and washed with cold absolute ethanol and ether.

Compound **5n** had mp 122-126° dec.

Anal. Calcd. for $C_8H_6N_3O_3S_2K$: C, 32.53; H, 2.05; N, 14.22. Found: C, 32.28; H, 1.93; N, 14.16.

Compound **5o** had mp 257-260°.

Anal. Calcd. for $C_8H_6N_3O_3S_2K$: C, 32.53; H, 2.05; N, 14.22. Found: C, 32.37; H, 2.11; N, 14.34.

Compound **5y** had mp 267-270°.

Anal. Calcd. for $C_8H_6N_3O_3S_2K$: C, 32.53; H, 2.05; N, 14.22. Found: C, 32.78; H, 1.91; N, 14.07.

2-(Aminophenyl)- Δ^2 -1,3,4-oxadiazoline-5-thiones **2v,w,x**.

General Procedure.

A mixture of **5** (30 mmoles) and hydrazine hydrate (16 g, 320 mmoles) in absolute ethanol was refluxed for 4 hours. The reaction mixture was then diluted with cold water (200 ml) and acidified by dropwise adding concentrated hydrochloric acid. The precipitate, separated by filtration, was a mixture of **2** with **6** from which compound **2** was separated by successive recrystal-

lization procedures from 1:1 ethanol-water mixtures. Analytical and physical data of all the prepared compounds **2a-x** are given in Table 1.

The potassium and the hydrochloride salts of **2a**, **7** and **8** respectively, were prepared by reacting 20 mmoles of saturated ethanolic solution of **2a** with slight excess of 2*N* solution of either potassium hydroxide or hydrochloric acid. Their mp, yields and elemental analyses are as follows:

Compound **7** was obtained as white plates, mp 297° dec, yield 80%.

Anal. Calcd. for $C_8H_5N_2OSK$: C, 44.43; H, 2.33; N, 12.95. Found: C, 44.76; H, 2.40; N, 12.88.

Compound **8** was obtained as white needles, mp 210-212°, yield 84%.

Anal. Calcd. for $C_8H_7N_2OSCl$: C, 44.76; H, 3.29; N, 13.05. Found: C, 45.24; H, 3.30; N, 13.35.

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