An HMO Study of the Azo-Hydrazone Tautomerism in Diazonium Coupling Products of 5-Isoxazolones

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The HMO method has been used to study tautomerism in 3-substituted 4-arylazo-5-isoxazolones (**2**), the possible tautomeric structures being **2a-2d**. Also the common anions of these tautomers, **6**, have been theoretically studied. In addition to the free molecules, HMO calculations have been carried out for structures with hydrogen bonds to protic solvents, for tautomers with intramolecular hydrogen bonds, and for dimers formed *via* intermolecular hydrogen bonds. In all these situations, the hydrazone form **2a** has been shown to be most stable. Also the inductive effect of electron-donating and electron-withdrawing substituents in the arylazo moiety upon the stability of various tautomers has been investigated. The results obtained on the basis of HMO calculations are in full agreement with the experimental data of Summers and co-workers. Several *m*- and *p*-substituted 4-arylazo-3-methyl-5-isoxazolones have been synthesized and their spectral data and melting points reported.

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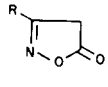
Introduction.

The diazonium coupling products of 3-substituted 5-isoxazolones **1** are of interest because of their use as agricultural fungicides (2,3). These coupling products can exist in four different tautomeric forms **2a-2d**.



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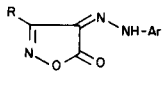
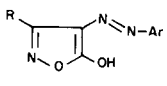
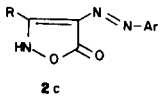


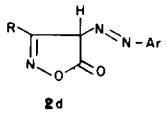
2a



2b

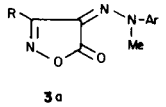


2c

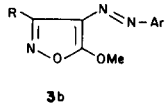


2d

Among the above tautomeric structures, the form **2d** is clearly most unstable because of interrupted conjugation between the arylazo group and the heterocyclic portion of the molecule. The tautomerism of **2** was experimentally studied by two groups of authors who reached different conclusions. Summers and co-workers (4-6) suggest, on the basis of uv, ir, and nmr spectral studies and a comparison of **2** with the methyl derivatives **3a-3c**, that these coupling products exist in the hydrazone form **2a**. On the other hand, Cum and co-workers (7,8) propose the azo-NH form **2c** for such coupling products. Cum and co-workers based their conclusion on a comparative ir and nmr spectral study of the methyl derivatives but they confused one of the methylated derivatives **3c** with an isomeric triazole **4** formed during the reaction (5). As the spectral assignments are somewhat ambiguous in some cases, it seemed



3a



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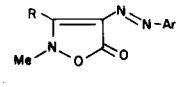
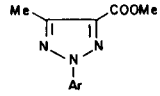


3c



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of interest to re-examine the tautomerism of 4-arylazo derivatives of 5-isoxazolones from a quantum-chemical viewpoint. In our contribution, the relative stabilities of the tautomeric structures **2a-2c** (R = Me, Ph, or H, Ar = Ph) and the effects of hydrogen bonding, solvent interactions, polarity of substituents in the aromatic ring, and dimer formation have been investigated by using the Hückel molecular orbital (HMO) method. In principle, our approach is similar to that employed by Arriau and co-workers (9) to study the tautomerism of phenylazopyrazolones.

Method.

To evaluate the relative stabilities of the tautomeric forms **2a-2c** within the framework of the HMO method, we have used the concept of bonding energy (9,10) defined by Equation (1),

$$BE = E_{\pi} - \Sigma n_i \alpha_i \qquad (1)$$

where BE is the bonding energy, E_{π} is the total π-energy of the system, n_i is the number of π-electrons contributed by the atom i to the system, and α_i is the Coulomb integral of the atom i. The quantity BE appears to be better founded (10-12) than the commonly used delocalization (resonance) energy (13) because of the uncertainty in defining the correct Kekulé structures.

The HMO calculations were carried out in the usual way using an IBM 360/65 computer. The values of the semi-empirical parameters adopted in our work are based on those given by Kuder (14) and are summarized in Table I

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along with those used for the corresponding anion.

The value α_X is the Coulomb integral of the p_z atomic orbital of atom X, α is the same quantity for the $2p_z$ atomic orbital of carbon, β_{XY} is the resonance integral of the XY bond, and β is the same quantity for the C-C bond in planar conjugated hydrocarbons.

The heteroatom, inductive, and conjugation models were used for the 3-methyl group in the 5-isoxazolone ring (Table II) (13,15-17).

The HMO parameters employed for the additional substituents in the aryl ring are given in Table III (18). In our calculations of the relative stabilities of the three major tautomers **2a-2c** hydrogen-bonded to the molecules of the solvent, the Coulomb integrals for the centers XH and Y interacting with hydrogen bonding solvents SH were taken as (19)

$$\alpha_{XH}\ldots SH = \alpha_X - 0.2\beta$$

and

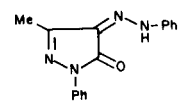
$$\alpha_Y\ldots HS = \alpha_Y + 0.2\beta$$

A similar approach has been used in the treatment of intramolecular hydrogen bonds and hydrogen-bonded dimers (19), where

$$\alpha_{XH} = \alpha_X - 0.2\beta$$
$$\alpha_Y\ldots H = \alpha_Y + 0.2\beta$$
$$\beta_{X(H)Y} = 0.2\beta$$

Results and Discussion.

The values of bonding energies, BE, of the tautomeric structures **2a-2c** for the coupling products of 3-methyl-5-isoxazolone (**1**, R = Me) are summarized in Table IV. These data indicate that, regardless of the HMO model used for the methyl group, the order of stability of the tautomeric forms is **2a** (hydrazone) > **2b** (azo-OH) > **2c** (azo-NH). The form **2d** is expected to be least stable for reasons discussed before. The results appear to be in agreement with the experimental data obtained by Summers and co-workers (4-6), and the order of stability of the various tautomers is analogous to that reported for 4-phenylazo-1-phenyl-3-methyl-5-pyrazolone (**5**) (9).



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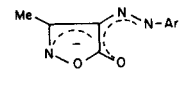


6

In an alkaline medium, the four tautomeric forms **2a-2d** would be expected to give a common resonance stabilized anion **6**. Using the heteroatom model for the 3-methyl group, a value of 14.899β was obtained for the bonding energy of **6**. The differences between this value and the bonding energies of the tautomers **2a-2c** are as follows: $\Delta BE(\mathbf{2a\text{-}6}) = 1.804\beta$, $\Delta BE(\mathbf{2b\text{-}6}) = 1.657\beta$, and $\Delta BE(\mathbf{2c\text{-}6}) = 1.625\beta$. These values indicate that the acidity of the tautomers decreases in the order **2c** > **2b** > **2a**. Because in acid-base equilibria of various tautomers, the tautomer with higher acidity is considered to be less stable (9), it is not unreasonable to conclude that the azo-NH tautomer **2c** is the least stable among the three tautomeric forms **2a-2c**.

The above conclusions are also supported by the values of the bonding energy, BE, calculated for the 4-phenylazo derivatives of 5-isoxazolones and 3-phenyl-5-isoxazolones (**1**, R = H, and **1**, R = Ph), respectively. The results for these compounds are summarized in Table V. In all cases which we have studied, the structure of the anion **6** is intermediate between the hydrazone form **2a** and the azo forms **2b** and **2c** as seen from the molecular diagrams in Table VI.

Because tautomeric equilibria are solvent-dependent, it seemed of interest to examine the effect of interaction with a protic solvent *via* hydrogen bonding upon the relative stabilities of the three major tautomers **2a-2c**. For this purpose, the approach used previously to correlate solvent effects in the esr spectra of semiquinone radicals has been adopted (20,21). The effects of intermolecular hydrogen bonding with a protic solvent upon the stabilities of the three tautomeric structures **2a-2c** (R = Me) are shown below. In addition to the bonding energies BE, the energies of the $N \rightarrow V_1$ transition, $E(N \rightarrow V)_1$, are also given.

Table I

HMO Heteroatom Parameters Used to Study the Azo-Hydrazone Tautomerism of 3-Substituted 4-Arylazo-5-isoxazolones

	$\alpha_X = \alpha + h_X\beta$		$\beta_{XY} = k_{XY}\beta$		
Azo	$h_N = 0.5$	Hydrazone	$h_{NH} = 1.5$	Anion	$h_N = 1.75$ (a)
	$h_O = 2.0$		$h_N = 1.0$		$h_N = 0.5$ (b)
	$k_{CN} = 0.9$		$k_{C\text{-}NH} = 0.7$		$h_{C(N)} = 0.25$
	$k_{NN} = 1.0$		$k_{C=N} = 1.1$		$h_O = 1.25$
	$k_{CO} = 0.8$		$k_{NN} = 0.7$		$k_{C\cdots N} = 0.8$
			$k_{C=O} = 1.0$		$k_{N\cdots N} = 0.7$
					$k_{C\cdots O} = 0.9$

(a) N adjacent to the aryl group and N in the isoxazolone ring. (b) N adjacent to the isoxazolone ring.

Table II

HMO Parameters Used for the Methyl Group

Model	Coulomb Integrals	Resonance Integrals
Heteroatom	$\alpha_{Me} = \alpha + 2\beta$ $\alpha_{C(Me)} = \alpha - 0.2\beta$	$\beta_{C\text{-}Me} = 0.7\beta$
Inductive	$\alpha_{C(Me)} = \alpha - 0.5\beta$	$\beta_{C\text{-}Me} = 0$
Conjugation C-C≡H₃ = C Y-Z	$\alpha_C = \alpha - 0.1\beta$ $\alpha_Y = \alpha$ $\alpha_Z = \alpha - 0.5\beta$	$\beta_{C\text{-}Y} = 0.8\beta$ $\beta_{Y\text{-}Z} = 3.0\beta$

Table III

HMO Parameters for Substituents in the Aryl Group

Substituent	Coulomb Integrals	Resonance Integrals
Cl	$\alpha_{Cl} = \alpha + 2.0\beta$	$\beta_{CCl} = 0.4\beta$
Br	$\alpha_{Br} = \alpha + 1.5\beta$	$\beta_{CBr} = 0.3\beta$
NO_2	$\alpha_N = \alpha + \beta$	$\beta_{CN} = \beta$
	$\alpha_{C(N)} = \alpha + 0.2\beta$	$\beta_{NO} = \beta$
	$\alpha_O = \alpha + 1.5\beta$	

Table IV

Bonding Energies, BE (β units), Obtained for the Tautomers of 4-Phenylazo-3-methyl-5-isoxazolone (**2**, R = Me)

Model of the Methyl Group	Tautomeric Form		
	2a	**2b**	**2c**
Heteroatom	16.703	16.556	16.524
Inductive	16.594	16.447	16.418
Conjugation	22.690	22.549	22.457

Table V

Bonding Energies, BE (β units), Obtained for the Tautomers of 3-Substituted 4-Phenylazo-5-isoxazolones (**2**) and Their Respective Anions (**6**)

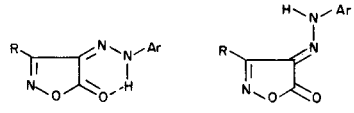
3-Substituent	Tautomeric Form			
	2a	**2b**	**2c**	**6**
None	16.509	16.371	16.241	14.605
Methyl (a)	16.703	16.556	16.524	14.899
Phenyl	24.894	24.747	24.689	23.070

(a) Heteroatom model.

Structure	BE (E(N → V_1))		
	2a	**2b**	**2c**
No H-bond	16.703 (0.902)	16.556 (0.950)	16.524 (0.971)
Solvent H-Bond	16.874 (0.885)	16.616 (0.927)	16.705 (0.985)

The results indicate that intermolecular hydrogen bonding with solvents increases the stability of all tautomeric forms. The stabilization is most pronounced in the case of the azo-NH form **2c**. Also, it seems worth mentioning that solvent interactions decrease the energy of the N → V_1 transition for the hydrazone and azo-OH forms but that there is an increase observed in the case of the azo-NH form.

To cast some light on the configuration of the most stable form **2a**, the effect of intramolecular hydrogen bonding upon its stability has been examined. The tautomeric form **2a** can exist in two possible conformations, *i.e.*:



The treatment developed by Pullman and Pullman for intramolecular hydrogen bonds was used (19). The results of the calculations for **2a** and **2b** (R = Me, Ar = Ph) are as follows:

Structure	BE (E(N → V_1))	
	2a	**2b**
No H-Bond	16.703 (0.902)	16.556 (0.950)
Intramolecular H-Bond	16.943 (0.971)	16.694 (0.994)

It can be seen that intramolecular hydrogen bonding increases the stability of both the hydrazone (**2a**) and the azo (**2b**) forms. However, the stabilization of **2a** is twice larger than that of **2b**. This finding also suggests that the hydrazone form **2a** has the *Z*-conformation rather than the *E*-conformation, in agreement with experimental data.

Finally, the possibility of hydrogen-bonded dimers and higher aggregates in solution has been studied. The three possibilities which we have considered are shown in Fig. 1.

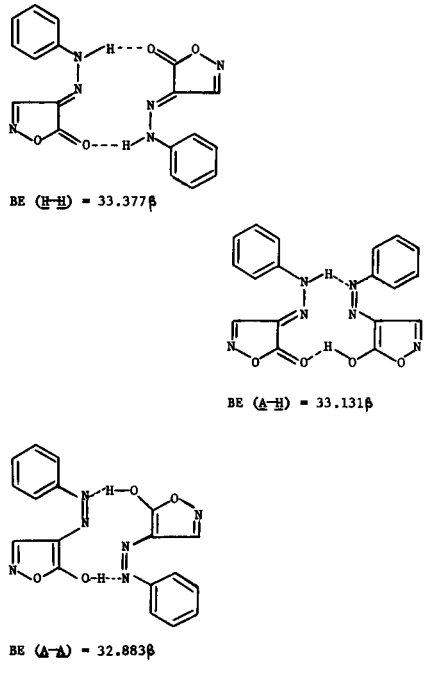
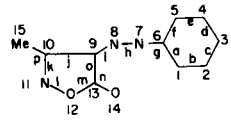


Figure 1. Three hydrogen-bonded dimers of 4-arylazo-5-isoxazolone (**H** hydrazone form; **A** azo-OH form).

Table VI

Molecular Diagrams for 4-Phenylazo-3-methyl-5-isoxazolone (a)



Position r	Electron densities, q_r 2a	2b	2c	6	Bond, rs	Bond orders, p_{rs} 2a	2b	2c	6
1	1.028	0.998	1.000	1.035	a	0.642	0.611	0.612	0.633
2	0.999	1.000	1.000	0.998	b	0.672	0.679	0.679	0.674
3	1.020	0.996	0.998	1.026	c	0.663	0.658	0.658	0.661
4	0.999	1.000	1.000	0.998	d	0.663	0.658	0.658	0.661
5	1.028	0.998	1.000	1.035	e	0.672	0.679	0.679	0.674
6	0.969	0.989	0.989	0.961	f	0.642	0.611	0.612	0.633
7	1.794	1.151	1.160	1.818	g	0.261	0.395	0.395	0.290
8	0.950	1.043	1.042	1.277	h	0.388	0.811	0.808	0.292
9	1.000	1.137	1.150	1.185	i	0.777	0.447	0.451	0.466
10	0.822	0.841	0.647	0.620	j	0.394	0.477	0.622	0.578
11	1.323	1.371	1.820	1.811	k	0.833	0.787	0.463	0.481
12	1.844	1.815	1.859	1.846	l	0.211	0.256	0.116	0.122
13	0.689	0.799	0.734	0.702	m	0.388	0.420	0.393	0.417
14	1.590	1.911	1.680	1.766	n	0.696	0.323	0.621	0.535
15	1.947	1.951	1.923	1.921	o	0.413	0.671	0.524	0.546
					p	0.245	0.236	0.318	0.325

(a) Heteroatom model of the methyl group.

Table VII

Substituent Effect upon the Bonding Energies, BE, of *p*-Substituted 4-Arylazo-3-methyl-5-isoxazolones (R = Me)

$h_{C(X)}$ (a)	Tautomeric Form 2a	2b	2c	6
−1.5	17.096	16.993	16.959	15.290
−1.0	16.879	16.760	16.727	15.072
−0.5	16.743	16.609	16.578	14.937
0	16.703	16.556	16.524	14.899
0.5	16.763	16.606	16.575	14.962
1.0	16.917	16.752	16.722	15.120
1.5	17.149	16.981	16.951	15.356

(a) $\alpha_{C(X)} = \alpha + h_{C(X)}\beta$. This Coulomb integral is for the carbon atom in the *p*-position of the benzene ring and reflects the inductive effect of an electronegative (electron-withdrawing) or electropositive (electron-donating) substituent bonded in this position.

They are the hydrazone-hydrazone dimer (**H-H**; two O . . . HN bonds), the azo-hydrazone dimer (**A-H**; one N . . . HO bond and one O . . . HN bond), and the azo-azo dimer (**A-A**; two N . . . HO bonds). The bonding energies, BE, for these three cases are: **H-H**, 33.377β, **A-H**, 33.131β, and **A-A**, 32.883β. Because the bonding energies of the hydrazone **2a** and azo-OH **2b** tautomers (R = H) are 16.509β and 16.371β, respectively, the extra stabilization due to the dimer formation, if any, should be 0.359β for the **H-H** dimer, 0.251β for the **A-H** dimer, and 0.141β for the **A-A** case. This additional stabilization for the **H-H** dimer is 2.55 times larger than for the **A-A** dimer. Thus, dimerization is expected to favor the hydrazone tautomer. The **A-H** mixed dimer is unlikely because of the steric hindrance due to the presence of two phenyl groups on the same side (14).

We have also decided to explore the possible effect of substituents in the aryl group of 4-arylazo-3-methyl-5-isoxazolones upon the position of the tautomeric equilibrium. As a first-order approach to this problem, the Coulomb integral of the carbon atom to which the substituent is attached has been varied as suggested by Peters (22). Thus, we have, in effect, considered the inductive effect of the hypothetical substituents in our calculations. This approach, although it neglects conjugative effects of the substituents, is considered to be sufficient for the purpose of establishing trends within a given series of compounds. In the present study, we have varied the Coulomb integral of the *p*-carbon atom in the arylazo moiety, assuming a substituent in the *p*-position of the phenyl group. The values were varied from $\alpha_{C(X)} = \alpha - 1.5\beta$ (strongly electron-donating) to $\alpha_{C(X)} = \alpha + 1.5\beta$ (strongly electron-withdrawing). The results are summarized in Table VII and in Figure 2. The data indicate that the stability of the hydrazone tautomer **2a** is increased by electron-withdrawing substituents as compared to the stability of the tautomers **2b** and **2c**. The same effect has

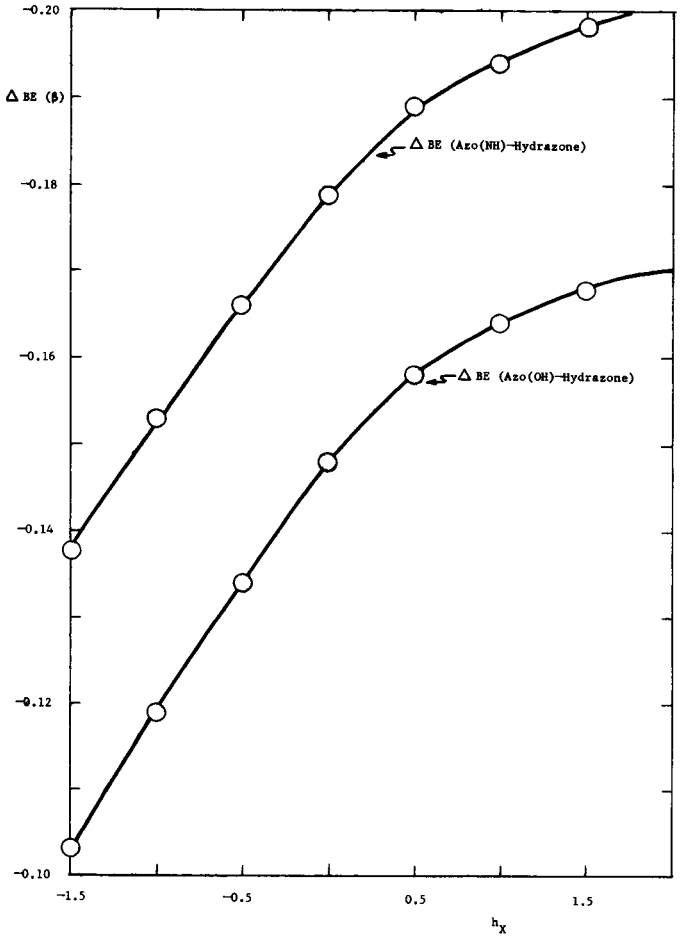


Figure 2. Effect of substituents upon the azo-hydrazone equilibrium in 4-phenylazo-3-methyl-5-isoxazolones.

been observed in the case of 1-arylazo-2-naphthol (14).

The effect of real substituents, *viz.*, *p*-Me, *p*-Cl, *p*-Br, *p*-NO_2, *m*-Cl, and *m*-NO_2, upon the stability of the three tautomers **2a-2c** (R = Me), and their common anion **6** has been studied as well. The results of the calculations are presented in Table VIII. In the tautomers **2a-2c**, both electron-withdrawing and electron-donating substituents are expected to decrease the energy of the N → V_1 transition, i.e., they are expected to cause a bathochromic shift. This does not agree with all available experimental data (Table IX). Our attempts to correlate the theoretical E(N → V_1) values with the experimental wavenumbers of the longest-wavelength absorption bands have proven unsuccessful. This failure is not surprising, however, because of the heterogeneity of the substituents and the possibility of the presence of several tautomers in solution. We know from our previous experience that in cases like this one cannot expect a successful correlation of spectral data.

In conclusion, the results of our theoretical study of 4-arylazo-5-isoxazolones clearly show that the hydrazone form **2a** is the most stable tautomer and that it remains most stable in different situations (intermolecular hydrogen bonding, formation of dimers *via* hydrogen bonds, substituent effects). Thus, our findings are in complete agreement with the experimental evidence obtained by Summers and co-workers (4-6).

EXPERIMENTAL

The ir spectra were obtained for Nujol mulls on a Beckman AccuLab 1 spectrophotometer. The uv absorption spectra were recorded in methanol and in 0.1*N* potassium hydroxide in methanol on a Beckman DK-1 spectrophotometer. The nmr spectra were taken on a Varian EM-360 instrument at 60 MHz for deuteriochloroform solutions, with TMS as internal standard. Melting points are uncorrected.

Synthesis of 4-Arylazo-3-methyl-5-isoxazolones (2).

Substituted anilines were diazotized and coupled with ethyl acetoacetate in ethanol in the presence of sodium acetate as previously described (5,23,24). The ethyl acetylarylazoacetates thus obtained were purified by crystallization from ethanol and were then heated with hydroxylamine hydrochloride and an equivalent amount of sodium acetate in boiling ethanol for 2 hours. Upon cooling, the precipitated 4-arylazo-3-methyl-5-isoxazolones (**2**) were collected and crystallized from ethanol. The melting points and some spectral data for these compounds are summarized in Table IX.

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Table VIII

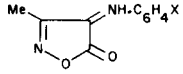
Energy Characteristics of *p*-Substituted 4-Phenylazo-3-methyl-5-isoxazolones (R = Me)

Substituent in the Benzene Ring	Tautomeric Form	BE	HOMO	LUMO	E(N → V_1)
p-Me (a)	**2a**	16.861	0.593	−0.258	0.851
	2b	16.726	0.502	−0.431	0.933
	2c	16.694	0.500	−0.450	0.950
	6	15.056	0.682	−0.012	0.694
None	**2a**	16.703	0.647	−0.255	0.902
	2b	16.556	0.547	−0.403	0.950
	2c	16.524	0.550	−0.421	0.971
	6	14.899	0.819	−0.005	0.824
p-Cl	**2a**	16.751	0.639	−0.256	0.894
	2b	16.606	0.539	−0.408	0.947
	2c	16.574	0.541	−0.426	0.967
	6	14.947	0.788	−0.006	0.794
p-Br	**2a**	16.735	0.640	−0.255	0.895
	2b	16.589	0.540	−0.406	0.946
	2c	16.557	0.542	−0.425	0.967
	6	14.931	0.789	−0.006	0.795
p-NO_2	**2a**	20.601	0.675	−0.131	0.806
	2b	20.447	0.592	−0.092	0.684
	2c	20.417	0.601	−0.096	0.697
	6	18.823	0.924	+0.029	0.895
m-Cl	**2a**	16.752	0.646	−0.255	0.901
	2b	16.605	0.547	−0.403	0.950
	2c	16.573	0.549	−0.421	0.970
	6	14.948	0.813	−0.005	0.818
m-NO_2	**2a**	20.572	0.650	−0.128	0.778
	2b	20.424	0.550	−0.128	0.678
	2c	20.392	0.554	−0.128	0.682
	6	18.768	0.831	−0.005	0.836

(a) Heteroatom model.

Table IX

m- and *p*-Substituted 4-Arylazo-3-methyl-5-isoxazolones (a)



Substituent, X	Molecular Formula	M.p., °C (Ethanol) (Lit.)	δ, ppm (b) (Lit.)	λ max, nm (log ε) (c) (Lit.)	E(N → V_1) (d)
p-Me	$C_{11}H_{11}N_3O_2$	204	2.35, 2.50, 12.40	3.96 (4.24), 3.58 (4.48)	0.851
		(204 (5))	—	—	0.694
None	$C_{10}H_9N_3O_2$	190	2.35, 12.40	381 (4.36), 361 (4.30)	0.902
		(190, 192 (5, 23))	(2.33, 12.80 (5))	(398 (4.31), — (5))	0.824
p-Cl	$C_{10}H_8ClN_3O_2$	—	—	—	0.894
		(186, 192 (5, 23))	—	—	0.794
p-Br	$C_{10}H_8BrN_3O_2$	214	2.35, 12.30	375 (4.32), 365 (4.31)	0.895
		(194 (5))	—	—	0.795
p-NO_2	$C_{10}H_8N_4O_4$	174-175	2.40, 12.60	375 (4.44), 405 (4.42)	0.806
		(176 (5))	—	—	0.895
m-Cl	$C_{10}H_8ClN_3O_2$	—	—	—	0.901
		(162 (5))	(2.38, 12.60 (5))	(392 (4.33), — (5))	0.818
m-NO_2	$C_{10}H_8N_4O_4$	206	2.43, 12.62	368 (4.39), 364 (4.44)	0.778
		(205, 210 (5.23))	—	—	0.836

(a) In the ir region, all compounds exhibit absorption bands at 1700-1720 cm^{-1} ($\tilde{\nu}$CO) and at 3200-3250 cm^{-1} ($\tilde{\nu}$NH) (nujol). (b) In $CDCl_3$ with TMS as internal reference. In addition to the signals shown, all compounds give aromatic proton signals at 7.0-8.5 ppm. The first signal in the table refers to the Me protons, the second signal to the NH proton. (c) The first (longest-wavelength) absorption bands in methanol (first value) and in 0.1*N* in methanol (second value). (d) The first line gives the value for the hydrazone form **2a**, the second line the value for the anion **6**.

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