A STUDY OF THE STRUCTURE OF 4-ARYLAZO DERIVATIVES OF 2-PHENYL-5-OXAZOLONE

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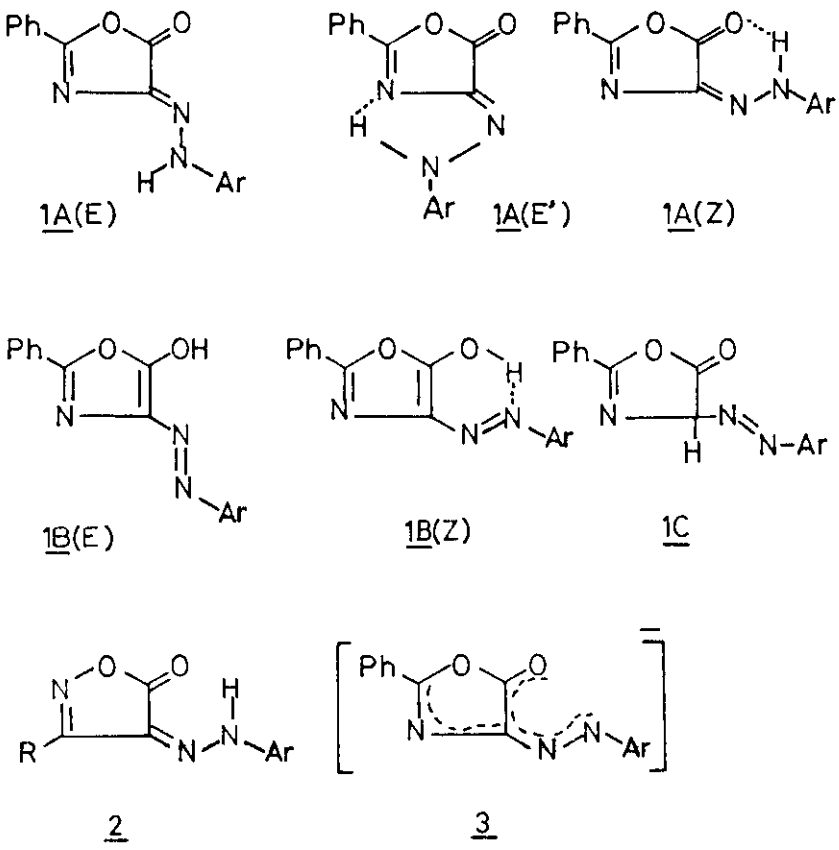
Abstract – Spectroscopic methods (^{1}H NMR and IR) were used to determine the structure of the 4-arylazo derivatives of 2-phenyl-5-oxazolone. The data indicate that such compounds exist in the chelated hydrazone form 1A(z). The ^{15}N isotopomer of compound 1a confirms the hydrazone structure. Also, the HMO method has been used to study tautomerism in such compounds. The results are in full agreement with the spectral data, the hydrazone form 1A(z) being most stable. It is further shown that both the intermolecular and intramolecular hydrogen bonding and electron-withdrawing substituents favor the hydrazone tautomer.

INTRODUCTION

Although the literature cites several reports[1-7] on the reactivity of 2-phenyl-4-arylazo-5-oxazolone, 1a, and its ring-substituted derivatives, no detailed studies have been reported on the tautomeric structure of such compounds. In contrast to this, tautomerism in a group of isomeric compounds – 4-arylazo-3-substituted 5-isoxazolones, 2, has been studied by several investigators.[8-13] In some reports, the arylazo derivatives of 5-oxazolones were formulated as the 5-hydroxy tautomer 1B,[1,3] whereas in some other papers[2,4-7] they were assigned the keto-hydrazone structure 1A (Scheme 1). No such structural assignments were based on spectral evidence. This situation has prompted us to prepare a series of 1 and to examine their tautomeric structure by spectroscopic and theoretical methods. In the present contribution, the results of ^{1}H NMR and IR studies are reported. Also, the relative stabilities of the various tautomeric structures of 1 (Scheme 1) and the effects of hydrogen bonding (intermolecular and intramolecular), interaction with the solvent, and the polarity of substituents in the aromatic ring have been investigated by the Hückel molecular orbital method (HMO).[14]

RESULTS AND DISCUSSION

The diazonium coupling products 1 can possess one of the three tautomeric structures 1A-C shown in Scheme 1. Furthermore, both forms 1A and 1B can exist either in the



Scheme 1

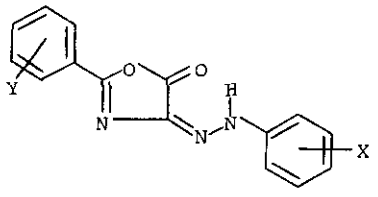
E- or *Z*-configurations. The *Z*-configurations are expected to be stabilized by intramolecular hydrogen bonding. The NMR and IR spectral data of compounds under study, 1a-1m (Table 1) are compatible with the keto-hydrazone structure in the *Z*-configuration, 1A(*Z*) (in chloroform). For example, the NMR spectra of all compounds in chloroform-*d* show, in each case, a downfield signal near 12.50 ppm which can be assigned to a chelated hydrazone NH proton. This is further substantiated by the observation that the ^{15}N-isotopomer of 1a (where the ^{15}N is adjacent to the phenyl ring) in chloroform-*d* exhibits a doublet (J = 95 Hz) in its NMR spectrum centered at 12.50 ppm. The presence of this doublet and the magnitude of the coupling constant indicate the attachment of the proton to the ^{15}N nitrogen atom.[15] The downfield shift of the NH signal in 1 also indicates that such a proton is involved in the formation of an intramolecular chelate ring structure as in 1A(*Z*).[15-17] Although the other structure, 1A(*E'*), might be stabilized by intramolecular hydrogen bonding, it was disregarded on the basis of the IR data discussed below. Furthermore, the absence of a methine proton signal expected for the tautomer 1C excludes this structure.

The IR data obtained for the compounds 1a-1k are also compatible with the assigned structure 1A(*Z*). Thus, each compound exhibits a weak broad band near 3200 cm^{-1} and

Table 1. 2-Aryl-4-arylazo-5-oxazolones 1a-1m[a]

Compd. No.	X	Y	Mp, °C (Mp lit.)	Mol. formula	C, % Calcd (found)	H, % Calcd (found)
1a	H	H	202 (201)[1,4]	$C_{15}H_{11}N_3O_2$	67.91(68.0)	4.17(4.2)
1b	*p*-Me	H	213 (209)[1,4]	$C_{16}H_{13}N_3O_2$	68.80(69.1)	4.69(4.7)
1c	*m*-Me	H	197 (188)[4]	$C_{16}H_{13}N_3O_2$	68.80(68.9)	4.69(4.8)
1d	*p*-OMe	H	205 (203)[4]	$C_{16}H_{13}N_3O_3$	65.07(65.1)	4.43(4.3)
1e	*m*-OMe	H	185	$C_{16}H_{13}N_3O_3$	65.07(64.9)	4.43(4.5)
1f	*p*-Cl	H	240	$C_{15}H_{10}ClN_3O_2$	60.11(60.0)	3.36(3.3)
1g	*m*-Cl	H	225	$C_{15}H_{10}ClN_3O_2$	60.11(60.2)	3.36(3.4)
1h	*m*-Br	H	226	$C_{15}H_{10}BrN_3O_2$	52.34(52.4)	2.92(2.9)
1i	*p*-NO_2	H	317 (317)[1]	$C_{15}H_{10}N_4O_4$	58.06(58.0)	3.24(3.2)
1j	*m*-NO_2	H	255	$C_{15}H_{10}N_4O_4$	58.08(58.1)	3.24(3.3)
1k	H	*p*-Me	231	$C_{16}H_{13}N_3O_2$	68.80(69.0)	4.69(4.8)
1l	H	*p*-Cl	254	$C_{15}H_{10}ClN_3O_2$	60.11(60.1)	3.36(3.4)
1m	H	*p*-OMe	234	$C_{16}H_{13}N_3O_3$	65.07(65.1)	4.43(4.4)

[a]All compounds 1a-1m exhibit $\tilde{\nu}_{CO}$ (1750-1757 cm^{-1}) and $\tilde{\nu}_{NH}$ (3190-3215 cm^{-1}) bands in their IR spectra, and a δ_{NH} (12.4-12.6 ppm) signal in their NMR spectra.



a strong absorption band at 1750 cm^{-1} in its IR spectrum (measured in chloroform). The former band remains unchanged upon dilution. The presence of a CO band suggests that this broad band can be assigned to the hydrazone NH group. In addition, the fact that the CO band of 1 is markedly lower in frequency than that reported for the parent 2-phenyl-5-oxazolone (1820 cm^{-1})[18] excludes the possibility of the CH-azo structure, 1C, and provides support for the chelated hydrazone structure 1A(*z*). In the latter form the lactone is conjugated with the carbon-nitrogen double bond and involved in intramolecular hydrogen bonding. Both these factors were reported[17,19-21] to decrease the force constant of the CO group.

As can be seen from the above spectral data, the most plausible structure of the diazonium coupling products of 2-phenyl-5-oxazolone is the chelated hydrazone form

1A(Z). To cast some light on the stability of this form relative to the other structures 1B-1C, the corresponding bonding energy, BE, of each tautomer was calculated.[22,23] The quantity BE is defined by the equation:

$$BE = E_{\pi} - \Sigma n_i \alpha_i$$

where E_{π} is the total π-electronic energy of the system, n_i is the number of π-electrons contributed by the atom i into the system, and α_i is the Coulomb integral of the atom i. The results of the HMO calculations reveal that the values of the bonding energies of the structures 1A(E), 1A(Z), 1B(E), and 1B(Z) are 24.769, 25.001, 24.546, and 24.672β, respectively. These data indicate that the order of stability of the tautomeric forms is 1A(Z) > 1A(E) > 1B(Z) > 1B(E). The form 1C is expected to be the least stable one because of the interrupted conjugation between the arylazo group and the heterocyclic portion of the molecule. The finding that the form 1A(Z) is the most stable one appears to be in agreement with the spectral data discussed above. It seems worth mentioning that the bonding energy of the chelated structure 1A(E') (24.887β) is lower than that of 1A(Z). From our previous experience,[13] when the difference between the bonding energies per π-electron, ΔBE/n , of the two tautomers is larger than 0.002β, then one tautomer will predominate. On this basis, it is not unreasonable to conclude that the structure 1A(Z) is the predominant form of the compounds 1a-1k.

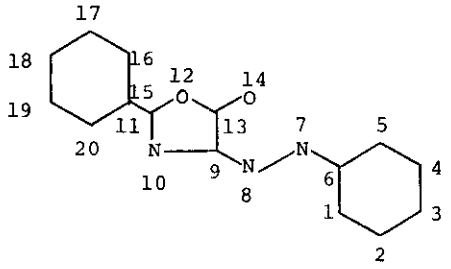
Furthermore, in an alkaline medium, assuming no chemical reaction occurs, the three tautomeric forms 1A-1C are expected to give a common resonance-stabilized anion 3. Using the same method, a value of 24.588β was obtained for the bonding energy of 3. The differences between this value and the bonding energies of the unchelated tautomers 1A(E) and 1B(E) are as follows: ΔBE[1A(E) - 3] = 0.181β and ΔBE[1B(E) - 3] = -0.042β. These values indicate that the acidity of 1B(E) is higher than that of 1A(E). Because in acid-base equilibria of various tautomers the tautomer with higher acidity is considered to be less stable,[22] it seems reasonable to conclude that the hydrazone form 1A is more stable than the azo tautomer 1B. The structure of the anion 3 is intermediate between the hydrazone form 1A(E) and the azo form 1B(E) as seen from the molecular diagrams in Table 2.

Because tautomeric equilibria are solvent dependent, it was worthwhile to examine the effects of the solvent *via* hydrogen bonding upon the relative stabilities of the two forms 1A and 1B. The following results were obtained for the hydrogen bonding of the two forms 1A and 1B with a protic solvent:[24,25]

	1A(E)		1B(E)	
	BE (β)	E(N→V_1) (β)	BE (β)	E(N→V_1) (β)
No H-bond	24.769	0.904	24.546	0.852
Solvent H-bond	24.932	0.870	24.609	0.832

Inspection of these data indicates that, as in the case of intramolecular hydrogen bonding, the intermolecular hydrogen bonding stabilizes both the azo and the hydra-

Table 2. Molecular Diagrams for the Tautomeric Forms and for the Anion of 4-Phenylazo-2-phenyl-5-oxazolone



Position, i	1A(E)	1B(E)	3	Bond, i-j	1A(E)	1B(E)	3
	π-Electron density, q_i				π-Bond order, p_{ij}		
1	1.030	1.000	1.039	1-2	0.672	0.679	0.674
2	0.999	1.000	0.999	1-6	0.642	0.610	0.634
3	1.022	0.999	1.029	2-3	0.663	0.657	0.661
4	0.999	1.000	0.998	3-4	0.663	0.657	0.661
5	1.030	1.000	1.039	4-5	0.672	0.679	0.674
6	0.969	0.989	0.961	5-6	0.642	0.610	0.635
7	1.816	1.166	1.843	6-7	0.260	0.399	0.286
8	1.030	1.053	1.352	7-8	0.343	0.791	0.244
9	0.962	1.106	1.162	8-9	0.809	0.481	0.533
10	1.321	1.304	1.248	9-10	0.317	0.365	0.441
11	0.812	0.870	1.006	9-13	0.417	0.711	0.562
12	1.827	1.810	1.778	10-11	0.798	0.785	0.751
13	0.678	0.822	0.786	11-12	0.306	0.337	0.317
14	1.576	1.912	1.765	11-15	0.392	0.388	0.408
15	1.014	1.012	1.003	12-13	0.364	0.375	0.436
16	0.970	0.983	0.996	13-14	0.310	0.316	0.514
17	1.000	1.000	1.000	15-16	0.611	0.613	0.604
18	0.975	0.987	0.998	15-20	0.611	0.613	0.604
19	1.000	1.000	1.000	16-17	0.678	0.678	0.681
20	0.970	0.983	0.996	17-18	0.658	0.659	0.656
				18-19	0.658	0.659	0.656
				19-20	0.679	0.678	0.681

zone tautomers.

In the present study, the effect of the varying substituent X in the arylazo moiety upon the position of the tautomeric equilibrium was considered. Because of the heterogeneity of the real substituents such as the nitro, methoxy, bromo group, etc., the Coulomb integral α of the *p*-carbon atom in the arylazo moiety was varied, assuming a substituent in the *p*-position of the phenylazo group. The values ranged from $\alpha_{C(X)} = \alpha - 1.5\beta$ (electron-donating) to $\alpha_{C(X)} = \alpha + 1.5\beta$ (electron-withdrawing). This approach has been suggested by Peters[26] and, although it neglects the conjugative effects of the substituent, it is sufficient for the purpose of defining the trends of substituent effects. The results of this investigation are summarized in Table 3. It is obvious that, as the Coulomb integral of the substituent-bearing carbon atom is varied from -1.5β to +1.5β, the stability of the hydrazone tautomer increases.

Table 3. Substituent Effects upon the Bonding Energies, BE, and the Energies of the First Electronic Transitions, $E(N\rightarrow V_1)$, of 4-*p*-Substituted Phenylazo-2-phenyl-5-oxazolones (β units)

$h_{C(X)}$	Tautomer 1A(*E*)		Tautomer 1B(*E*)	
	BE	$E(N\rightarrow V_1)$	BE	$E(N\rightarrow V_1)$
-1.5	25.159	0.715	24.981	0.823
-1.0	24.943	0.790	24.749	0.841
-0.5	24.808	0.859	24.599	0.863
0.0	24.769	0.904	24.546	0.852
+0.5	24.829	0.927	24.597	0.839
+1.0	24.984	0.836	24.745	0.820
+1.5	25.217	0.939	24.976	0.795

EXPERIMENTAL

The IR spectra were obtained in chloroform solutions on a Beckman AccuLab 1 spectrophotometer. The NMR spectra were taken on a Varian EM-360 instrument at 60 MHz in chloroform-*d* solutions, with tetramethylsilane as the internal standard. Melting points were recorded on a Gallenkamp electrothermal melting point apparatus and are uncorrected. Elemental microanalyses were carried out by the Microanalytical Laboratory, University of Cairo, Giza, Egypt.

Synthesis of 4-Arylazo-2-aryl-5-oxazolones 1a-1m

A mixture of N-aroylglycine (0.25 mole) and acetic anhydride (20 ml) was heated until a clear solution was obtained. The resulting solution was cooled and then treated while stirring with a solution of the appropriate diazonium chloride (0.25 mole) containing sodium acetate (3.0 g). After 3 h, the precipitated colored products were collected and crystallized from acetone. The physical properties of

the synthesized compounds are summarized in Table 1.

The ^{15}N isotopomer of 4-phenylazo-2-phenyl-5-oxazolone was prepared by diazotization of ^{15}N-aniline and coupled with 2-phenyl-5-oxazolone following the above procedure. The melting point of the product was the same as that of the ^{14}N compound 1a.

HMO Calculations

The HMO calculations were carried out in the usual way using an IBM 360/65 computer. The values of the empirical parameters adopted in this work (Table 4) are based on those given by Kuder.[27]

Table 4. Heteroatom Parameters Used to Study the Azo-Hydrazone Tautomerism of 4-Phenylazo-2-phenyl-5-oxazolone

$\alpha_X = \alpha - h_X\beta$ $\qquad$ $\beta_{XY} = k_{XY}\beta$

Azo form	Hydrazone form	Anion
$h_N = 0.5$	$h_{NH} = 1.5$	$h_N = 1.75$[a]
$h_O = 2.0$	$h_N = 1.0$	$h_N = 0.5$[b]
$k_{CN} = 0.9$	$k_{C-NH} = 0.7$	$h_{C(N)} = 0.25$
$k_{NN} = 1.0$	$k_{C-N} = 1.1$	$h_O = 1.25$
$k_{CO} = 0.8$	$k_{NN} = 0.7$	$k_{C=N} = 0.8$
	$k_{C-O} = 1.0$	$k_{N=N} = 0.7$
		$k_{C=O} = 0.9$

Hydrogen bonding to the solvent molecule (SH = solvent):

$\alpha_{XH...SH} = \alpha_X - 0.2\beta$ $\qquad$ $\alpha_{Y...HS} = \alpha_Y - 0.2\beta$

Intramolecular hydrogen bonding:

$\alpha_{XH} = \alpha_X - 0.2\beta$ $\qquad$ $\alpha_{Y...H} = \alpha_Y - 0.2\beta$

$\beta_{X(H)Y} = 0.2\beta$

[a] N adjacent to the aryl group and N in the oxazole ring.

[b] N adjacent to the oxazole ring.

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