BENZENOID-QUINONOID TAUTOMERISM IN AZOMETHINES AND THEIR STRUCTURAL ANALOGS

45.* 3-HYDROXY-2-ACETYL-1-METHYLINDOLE IMINES

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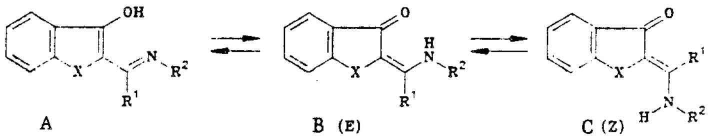
Some 3-hydroxy-2-acetyl-1-methylindole N-aryl- and N-alkylimines have been obtained. According to UV and IR spectroscopy, they exist as the acoplanar E-ketoenamine isomers. Structural relaxation in the excited state results in the formation of flattened, fluorescing forms.

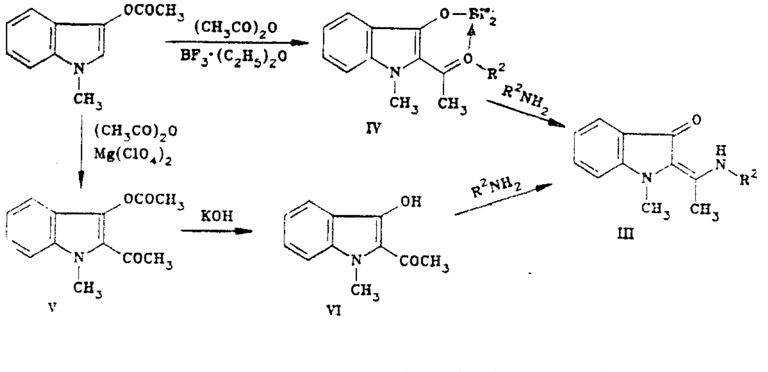
The effect of electronic and steric factors on the position of prototropic equilibrium in (see Diagram), and the spectral luminescent properties of heterocyclic hydroxyaldehyde imines (I) and (II) [2, 3] have been examined. The most stable forms of 3-hydroxy-1-methyl-2-carbaldehyde imine (I) and 3-hydroxy-2-acetylbenzo[b]thiophene imine (II) have the E-ketoenamine structure B (E). Compound (I), which according to X-ray diffraction analysis exists in the planar form [4] held in place by a strong intramolecular hydrogen bond, fluoresces strongly with a small Stokes shift (300 cm^{-1}). The increase in the Stokes shift to 2100 cm^{-1} in the N-arylaminovinyl ketones (II) is due to acoplanarization of the molecule as a result of steric interactions between the groups $R^1 = CH_3$ and $R^2 = Ar$ [3].



(1)

I, III $X=NCH_3$, II X=S; I $R^1=H$, II, III $R^1=CH_3$; I—III R^2=Ar, Alk

In order to examine the effects of a bulky electron-donor substituent in the ring ($X = NCH_3$) and a bulky group at the exocyclic carbon atom ($R^1 = CH_3$) on the structure and spectral luminescent properties of (I) and (II), the 3-hydroxy-2-acetyl-1-methylindole imines (III) were prepared. The latter (Table 1) were obtained by reacting the aryl- and alkylamines with the fluoroborate complex (IV) [5], or with 3-hydroxy-2-acetyl-1-methylindole (VI), obtained by a route which we have developed via the intermediate 3-acetoxy-2-acetyl-1-methylindole (V).



The similarity of the IR and UV spectra of (III) (Table 2) to those of the aminovinyl ketones (II) suggests that the former also have the acoplanar E-ketoenamine structure IIIB

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*For Communication 44, see [1].

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TABLE 1. Properties of (IIIa-e)

Compound	Empirical formula	R^2	Tmp, °C	Yield, % Method A	Yield, % Method B
III a	$C_{17}H_{16}N_2O$	C_6H_5	202...204	72	64
III b	$C_{18}H_{18}N_2O$	p-$CH_3C_6H_4$	238...239	83	68
III c	$C_{18}H_{18}N_2O_2$	p-$CH_3OC_6H_4$	227...229	80	75
III d	$C_{19}H_{18}N_2O_3$	p-$CH_3O_2CC_6H_4$	270...272	27	68
III e	$C_{18}H_{18}N_2O$	$C_6H_5CH_2$	140...142	45	15

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*Method B

TABLE 2. Spectral Properties of (IIIa-e)

Compound	Solvent	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	Fluorescence, λ_{max}, nm	IR spectrum, ν, cm^{-1} (in vaseline grease)
IIIa	Toluene	345 (20,6), 410 (8,0)	500	1550, 1600, 1640
	CH_3CN	342 (24,0), 400 (7,4)		
	2-Propanol	342 (28,4), 405 (8,0)	510	
IIIb	Toluene	345 (21,0), 410 (8,6)	500	1550, 1600, 1635
	CH_3CN	342 (21,6), 405 (6,4)		
	2-Propanol	345 (24,6), 405 (7,6)		
IIIc	Toluene	344 (21,6), 415 (7,8)	515	1550, 1600, 1630
	CH_3CN	342 (23,6), 405 (7,0)		
IIId	CH_3CN	345 (20,0), 410 (5,2)	525	1530, 1580, 1640, 1740
IIIe	Toluene	325 (18,4), 450 (8,8)	485	1500, 1600, 1610
	CH_3CN	330 (18,2), 445 (8,4)		

(E). In fact, the IR spectra of (III) show absorption at 1630-1640 and 1580-1600 cm^{-1} characteristic of stretching vibrations of the conjugated ring carbonyl group and the exocyclic C=C bond [3]. The UV spectra of the aminovinyl ketones (III) (Table 2) show a considerable hypsochromic shift of the long-wavelength band (100-110 nm for R^2 = Ar and 30 nm for R^2 = alkyl), with a concomitant decrease in its extinction as compared with the structurally planar (I). These effects are due to strong steric interactions between the NCH_3 and CCH_3 groups, and between the N-aryl substituent R^2 and the CCH_3 group. The acoplanarization of the (III) molecule prevents effective conjugation of the π-electrons of the aryl ring, and decreases the conjugation in the aminovinyl ketone grouping and the effectiveness of charge transfer from the aminoethylidene region of the molecule to the electron-acceptor carbonyl group. The important part played by steric interactions between the CCH_3 groups and the N aryl substituent R^2 follows from the fact that its replacement by N-alkyl in (IIIe) results in a decrease in the hypsochromic shift as compared with (IIIa-d) (Table 2).

Simultaneously with the increasing acoplanarity in (I), (III) (R^2 = Alk), and (III) (R^2 = Ar), with the consequent hypsochromic shift, there is a decrease in the fluorescence quantum yield in the same sequence, and a considerable increase in the Stokes shift from 330 cm^{-1} in (I) and 1600 cm^{-1} in (IIIe) to 5000 cm^{-1} for the sterically overloaded molecules (IIIa-d). The positions of the fluorescence bands in (IIIa-d) are similar to those in the planar molecule (I). This effect is clearly due to the possibility of adiabatic rearrangement of the structure of (III) involving rotation of the N-aryl groups R^2 around the N—C bond, and flattening of the molecule along the C=C bond in the excited state. The role of such structural relaxation in increasing the Stokes shift has been described [6]. To check this assumption, the spectral and luminescent properties of the aminovinyl ketones (III) were examined in a polymethylmethacrylate (PMMA) matrix, in which structural relaxation is somewhat hindered. The Stokes shift for (IIIa) in PMMA was decreased by 900 cm^{-1} as compared with liquid solutions (Fig. 1, a), whereas for the less strained molecule (IIIe) it was decreased by only 400 cm^{-1} (Fig. 1, b), indicating that rotation of the N-aryl group R^2 makes a substantial contribution to structural relaxation.

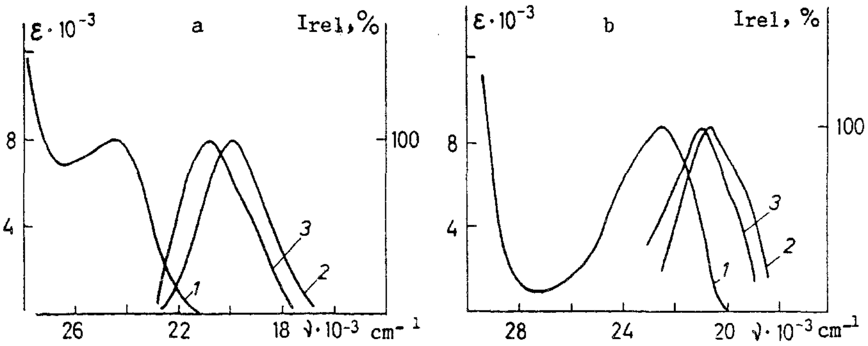

Fig. 1. UV Spectra of (IIIa) (a) and (IIIe) (b). 1) absorption in toluene, 2) fluorescence in toluene, 3) fluorescence in PMMA.

The sterically overloaded 2-(aminoethylidene)-1-methyl-3(2H)-indolones (III) therefore exist in the E-ketoenamine form B (E). Increasing acoplanarity in (1), (III) (R^2 = Alk), and (III) (R^2 = Ar) results in a hypsochromic shift of the long wavelength absorption. Structural relaxation of the molecules of the aminovinyl ketones (III) in the excited state plays an important part in determining their luminescent properties.

EXPERIMENTAL

UV spectra were obtained on a Specord UV-VIS spectrophotometer, and luminescence spectra on a Hitachi 650-60 spectrofluorimeter. IR spectra were obtained on a Specord IR-71 spectrometer. The elemental analyses for (III) and (V) for C, H, and N were in agreement with the calculated values.

4-Methyl-5,6-(N-methylindolo)-2,2-difluoro-1,3,2-dioxaborine (IV) was obtained as described in [5].

3-Acetoxy-2-acetyl-1-methylindole (V, $C_{13}H_{13}NO_3$). To a solution of 0.96 g (5 mmole) of 3-acetoxy-1-methylidole in 7.5 ml of acetaldehyde was added 0.1 g of magnesium perchlorate, and the mixture kept at room temperature for 0.5 h. The solution was then heated to the boil, cooled, and poured into water. The solid was filtered off and crystallized from methanol to give 80-90% of (V), mp 190-191°C. IR spectrum (in vaseline grease): 1660, 1680, 1780 cm^{-1}. UV spectrum (in acetonitrile), λ_{max} ($\varepsilon \cdot 10^{-3}$): 275 (56.4), 320 nm (8.0).

3-Hydroxy-2-acetyl-1-methylindole (VI). To 50 ml of a 20% solution of KOH, cooled to 10°C, was added with stirring 8.8 (45 mmole) of (V) in 5 ml of methanol. The mixture was kept overnight, then 50 ml of water was added, and acidified with HCl solution to pH 4. The solid was filtered off, dried, and crystallized from toluene to give (VI), mp 120-121°C, identical with the product obtained as in [7].

2-(Aminoethylidene)-1-methyl-3(2H)-indolones (III). A. To a solution of 0.24 g (1 mmole) of (IV) in 2 ml of acetonitrile was added 1 mmole of the appropriate amine. The solution was boiled for 0.5-1.5 h, and filtered hot through alumina. The solvent was evaporated, and the residue crystallized from toluene, acetonitrile, or a mixture of the two.

B. To a solution of 0.192 g (1 mmole) of 3-hydroxy-2-acetyl-1-methylindole in 15 ml of toluene were added 0.1 ml of conc. sulfuric acid and 1.5 mmole of the appropriate amine. The mixture was boiled for 1-4 h with a Dean and Stark apparatus, the toluene removed under reduced pressure, and the residue crystallized from toluene or acetonitrile.

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ALKYLATION OF N-(1-ANTHAQUINONYL)UREAS AND THEIR CYCLIZATION TO ANTHRA[1,2-d]IMIDAZOLINONES

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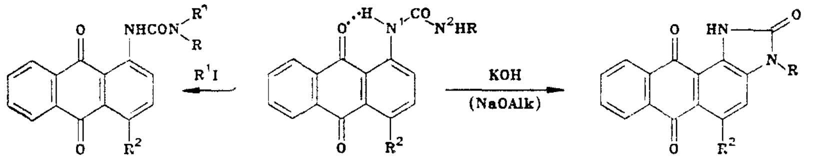
N^1-(1-Anthraquinonyl)-N^2-arylureas in DMSO in the presence of bases form N-anions which cyclize to anthra[1,2-d]imidazolinones, and in the presence of alkyl halides give the N^2-alkyl derivatives. Anions of N^1-(1-anthraquinonyl)-N^2-alkylureas are less stable, and are rapidly converted into 1-aminoanthraquinone.

Anthraquinonylureas are of interest from the practical point of view as dyestuffs [1, 2], pesticides [3], and as additives to lubricating oils which increase their stability to heat and radiation [4]. The chemical properties of these compounds are unknown. The aim of the present investigation was to examine the properties of the newly-synthesized N^1-(1-anthraquinonyl)-N^2-aryl (and alkyl)ureas (Ia-m) [3] in basic media. Ureas are known to behave as mono- or dibasic NH-acids on treatment with bases [5]. Some N-substituted aminoanthraquinones are also known to form N-anions [6, 7].

Addition of an equimolar amount of potassium hydroxide to a solution of the arylureas (Ia-k) in DMSO at 20-25°C results in a considerable deepening of the color of the solution, which remains unchanged in the presence of excess alkali, indicating that the urea is monoionized. In considering the potential for ionization of one of the two NH-acidic centers in the ureas (Ia-k), preference should be given to the HN^2Ar group, since the N^1H grouping is involved in intramolecular hydrogen bonding with the quinone oxygen [3], and is therefore less acidic (cf. [6]). In order to confirm this mode of ionization, we examined the alkylation of the ureas (Ia) and (Ib) in basic media.



II a-e Ia-m IIIa-o

I a–d $R^2=H$, e-h $R^2=OH$, i $R^2=Cl$, j $R^2=4\text{-}OC_6H_4C(CH_3)_3$; a,e,i,j $R=C_6H_5$, b,f $R=3\text{-}ClC_6H_4$, c,g $R=4\text{-}ClC_6H_4$, d R=1-naphthyl h $R=3,4\text{-}Cl_2C_6H_3$; I k $R^2=4\text{-}OC_6H_4C(CH_3)_3$, l,m $R^2=H$; k $R=4\text{-}ClC_6H_4$, l $R=C_4H_9$, m $R=CH_3$

Addition of methyliodide to a solution of the N-anion of urea (Ia) in DMSO resulted even at room temperature in the formation of the N^2-methylurea (IIa). Ureas (Ia) and (Ib) were fully alkylated in dioxane at 60°C in the presence of solid potassium hydroxide to give the N^2-alkylureas (IIa-d) (Table 2). The structures of these products were confirmed spectroscopically, and by the direct synthesis of (IIa) from 1-aminoanthraquinone and N-methyl-N-phenylcarbamoyl chloride.

It would be expected that in the N^2-alylated ureas (Il, m) the acidity of the N^2H group would be reduced as compared with the aryl derivatives (Ia-m) [5, 6], so that either of the NH groups could become ionized. Comparison of the UV spectra of the anthraquinonylureas (Ia, b, l) and (IIb, e) with their anions showed that ionization of the N^2H group (arylureas (Ia, b)) resulted in a shift of the long-wavelength maximum by $\Delta\lambda \simeq 130$ nm (Table 1),

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