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Molecular Interactions Between Arylazopyridines and N-Hydroxyindoles

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Summary. The reaction of isomeric arylazopyridines with 1-hydroxy-2-phenylindole leads to molecular associations between the pyridine derivative and the 1-hydroxy-2-phenylindole itself or its dimer. The role of hydrogen bonding in the formation of the complex is also discussed in the light of conductivity measurements.

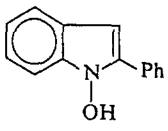
Keywords. Charge-transfer complexes; Hydrogen bond; 1-Hydroxy-2-phenylindole.

Molekulare Wechselwirkungen zwischen Arylazopyridinen und N-Hydroxyindolen

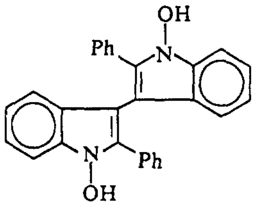
Zusammenfassung. Die Reaktion isomerer Arylazopyridine mit 1-Hydroxy-2-phenylindol führt zu molekularen Associaten zwischen den Pyridin-Derivaten und 1-Hydroxy-2-phenylindol oder seinem Dimer. Die Rolle der Hydrogenbindung bei der Bildung der Komplexverbindung wird mittels Leitfähigkeitsmessungen geprüft.

Introduction

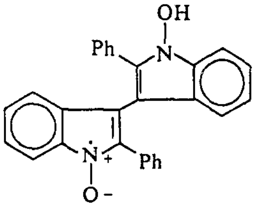
In a previous paper [1] we described the synthesis of solid 1 : 1 molecular complexes (*MC*) between arylazopyridines and 1-hydroxy-2-phenylindole, **I**: X-ray measurements evidenced that hydrogen bonding between the pyridine nitrogen and the hydroxyl group of **I** was the main interaction in the complex. It was also shown that, with pyridine derivatives of lower basicity, e.g. 3-(p-dimethylaminophenyl) or 4-(2,4-dibromophenyl)azopyridine, the 1 : 1 complexes were constituted of one pyridine molecule and the dimer of the donor, 1,1′-dihydroxy-2,2′-diphenyl-3,3′-bi-indole, **II**. In both cases, a molecule of benzene was clathrated in the complex when used as solvent. In an early investigation, Colonna [2] described the formation of a complex between **I** and 4-phenylazopyridine N-oxide that, on the basis of elemental analysis and by analogy with the other examples of the present work, is better characterized as chlatrating a molecule of benzene. Complexes of pyridines and pyridine N-oxides with organic partners have been investigated by several authors [3 a–d]. In this work we describe the interaction of isomeric arylazopyridine N-oxides with **I** and **II** (Scheme 1); in addition, the interaction of arylazopyridines with the same donors are reinvestigated particularly with the aim of checking if different solvent molecules could be clathrated in the cage of the complex. Electrical conductivity data of some indicative complexes are also included.



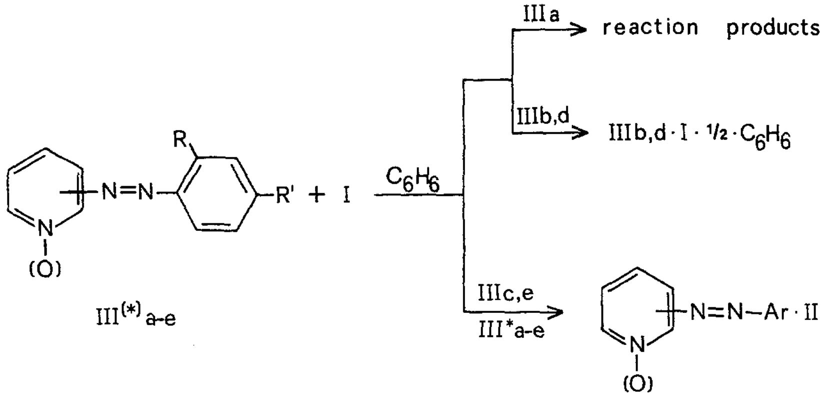
I



II



VII



Compound	R	R'	Isomer
$III^{(*)}a$	H	H	4-
$III^{(*)}b$	"	NMe_2	2-
$III^{(*)}c$	"	"	3-
$III^{(*)}d$	"	"	4-
$III^{(*)}e$	Br	Br	4-

*N-oxide derivative

Scheme 1

Results and Discussion

Table 1 reports analytical data of complexes **IV*a–e**, **V** and **VI**; Table 2 reports UV-Vis solid state determinations on complexes **IV*a–e**, **IIIb,d·I**, **IIIc,e·II**, **V** and **VI**.

As evidenced in Table 2, the *MC* bands range from 550 to 610 nm; no *MC*

Table 1. Analytical data of complexes **IV*a–e**, **V**, and **VI** (calculated values in parantheses)

Compound	Formula	Yield %	M.P. °C	Elemental analysis		
				C%	H%	N%
IV*a	$C_{39}H_{29}N_5O_3 \cdot 1/2C_6H_6$	90	92–94	76.57 (77.05)	5.13 (4.92)	10.70 (10.70)
IV*b	$C_{41}H_{34}N_6O_3 \cdot 1/2C_6H_6$	70	143–146	76.02 (75.73)	5.23 (5.34)	11.91 (12.05)
IV*c	$C_{41}H_{34}N_6O_3 \cdot 1/2C_6H_6$	63	135–138	75.48 (75.73)	5.51 (5.34)	12.14 (12.05)
IV*d	$C_{41}H_{34}N_6O_3 \cdot 1/2C_6H_6$	87	180–181	75.23 (75.73)	5.42 (5.34)	12.21 (12.05)
IV*e	$C_{39}H_{27}N_5O_3Br_2 \cdot 1/2C_6H_6$	56	151–152	62.70 (62.08)	3.61 (3.72)	8.38 (8.62)
V	$C_{27}H_{25}N_5O \cdot 1/2C_7H_8$	72	170–172	76.34 (76.06)	6.07 (6.07)	14.27 (14.54)
VI	$C_{27}H_{25}N_5O \cdot 1/2C_8H_{10}$	60	204–205	75.91 (76.18)	6.28 (6.19)	14.49 (14.33)

interaction can be detected in mixture **IIIa** + **I**, that, as a matter of fact, leads to different reaction products [1].

UV-Vis spectra of compounds **IV*a–e**, in dichloroethane, show no *MC* bands but only insignificant small band shifts compared with the components of the complex, which indicates a high lability of the complex in solution. UV-Vis solid state determinations on the following ground mixtures showed: (i) undetectable interactions in **IIIa,c** + **I**; (ii) absorptions at 488, 598 and 483, 568 nm respectively in **IIIb,d** + **I**; (iii) absorptions at 545, 590 nm in **IIId** + **II**; (iv) no interactions in **III*a** with **I** and **II**.

The above UV-Vis results together with data from Table 2 allow some considerations: (i) all complexes **IV*a–e**, obtained in refluxed benzene, show a higher stability with a *MC* band in the range 588–610 nm (with a λ *MC* depending on the position of the arylazo group in the pyridine ring); (ii) a similar pattern is followed by complexes of pyridines **IIIb-e** with **I**; (iii) the presence of benzene as solvent favours the formation of the complex; (iv) the basicity of the pyridine derivative and the position of the arylazo group in the ring influence the interaction. Pyridines of lower basicity, like **IIIc,e** and **III*a–e** with **I**, undergo a redox reaction before forming a 1 : 1 complex with **II**, while pyridines **IIIb,d** interact directly with **I**: in the latter case the pyridine nitrogen is basic enough to allow a hydrogen bonding with **I** (oxidation potentials of **II** and **I** are 0.41 and 0.55 V respectively [1]); (v) only molecules of aromatic hydrocarbons of the benzene size (benzene, toluene, xylene) are able to be chlatrated in the cage of the complex. Attempts to synthesize complexes of arylazopyridines with **I** in solvents like pyridine or thiophene failed: as a matter of fact, no complex was formed using pyridine as solvent but only starting materials were recovered, while little amounts of **II** and starting

Table 2. UV-Vis of the complexes in solid state

Compound	λ (nm)					Compound	λ (nm)						
III*a													
IV*a		502		584	595								
III*b			541		590	**IIIb**				537		580	
IV*b	472	501	553		610	**IIIb · I**	473	501		550			601
III*c	497	516				**IIIc**	472	501					
IV*c	471	499			594	**IIIc · II**		502		550			
III*d	467	499			591	**IIId**	473	502		542			
IV*d		502		588		**IIId · I**	467		535	568	575		
III*e	473	500				**IIIe**				554			590
IV*e		501			594	**IIIe · II**				551			596
						V		501		547			
						VI			530			584	

arylazopyridine were identified in thiophene; the presence of the heteroatom inhibited the complexation [4] and the reaction stops at the redox phase. In addition, larger aromatic hydrocarbons (naphtalene, diphenyl) did not enter the cell.

FT-IR determinations (nujol) on compounds **IV*a–e**, **IIIb–e + I**, did not show any OH absorption (the OH stretching of **I** is a broad band in the region of 2770 cm^{-1} while that of **II** is a sharp band at 3378 cm^{-1}); a broadening was observed in the region 3100–2550 cm^{-1}. The following results are obtained on some ground selected mixtures: (i) pyridines **IIIb, d** with **I** gave only weak interaction, while **IIIc,e** did none; (ii) pyridines **III*a–e** with **II** evidenced interactions depending on the basicity of the pyridine derivative, with spectroscopic characteristics resembling those of **IV*a–e**; (iii) **IIIa,c,e** did not interact with **II**; (iv) when present, the degree of the interaction appeared much weaker than that showed by products obtained by refluxing the reagents in a solvent (e.g. benzene).

The weak interaction of the complexes was also evidenced by mass spectra that showed no peak of the molecular weight of the complexes, but only the parent peaks of the reagents [5]. We were unable to determine the X-ray structure of complexes **IV*a–e** owing to the impossibility to obtain suitable crystals. Conductivity measurements on some indicative complexes gave σ values ranging from 10^{-10} to 10^{-13} Ohm^{-1} cm^{-1} (for **IIId · I**, **IV*d**, **IV*a**, **IIIe · I** σ values were $5 \cdot 10^{-13}$, $1.4 \cdot 10^{-10}$, $3.8 \cdot 10^{-12}$, $1.5 \cdot 10^{-13}$ Ohm^{-1} cm^{-1} respectively). The influence of the temperature and voltage on σ values, for the complex **IIId · I**, is reported in Fig. 1. As it can be seen, σ increases with the temperature while it is independent from voltage, which means an insulator rather than a semiconductor character of the complex [6].

From the experimental results we can describe the interaction between arylazopyridines N-oxides and **II** as mainly characterized by hydrogen bonding. The disappearance of the OH stretching vibrations of **II** and **I** claims for strong hydrogen bonding between N – OH and the non bonding electrons of pyridine nitrogen or of oxygen in the N – O group. The literature reports considerable investigations on N – – H – O or N – O – – H – O bonding, mainly through IR spectroscopy

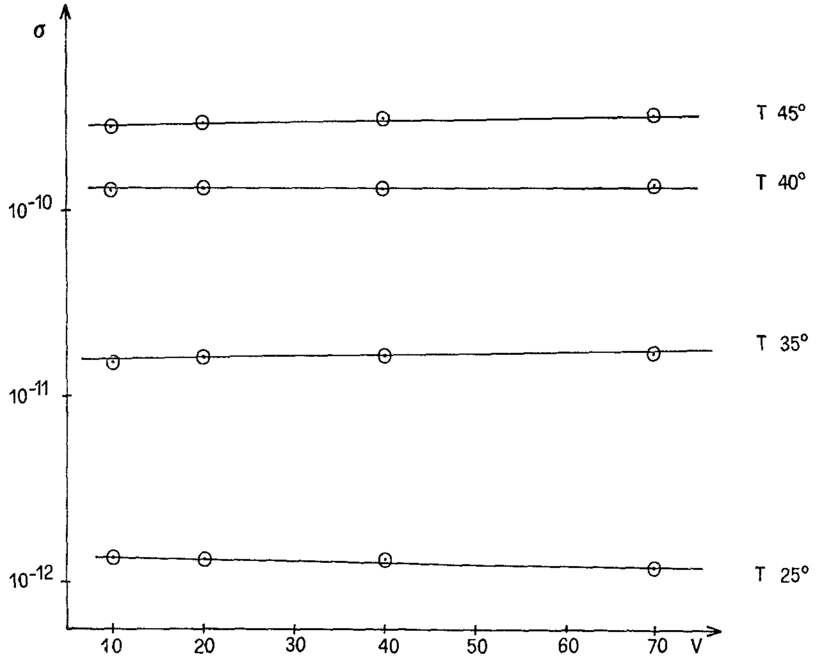


Fig. 1. Dependence of σ (Ohm^{-1} cm^{-1}) from voltage, V (volt), at various temperature values (°C), in the complex **IIId · I**

[7, 8]: in all cases, the disappearence of the OH stretching vibration is replaced by a broadening in the region 2 600–3 000 cm^{-1}. As the analyses show, the interactions give rise to a 1 : 1 : 1/2 complex among the pyridine N-oxide, **II** and the solvent which means, on the contrary, that only one OH of **II** should interact with the N – O group. This is in contrast with the fact that no free OH absorption is observed, which means that both OH groups must be involved in some interaction. It is proved that in pyridine N-oxides the main donor site is the oxygen of the N – O bond (that interacts either with π-acceptors like tetracyanoethylene [3 d], iodine [3 b], hydrogen donors [9]) while the second site, depending on the particular derivative, may be: (a) the azo group (for example, azoalkanes behave as electron donors in *MC* through the azo linkage as well as through the lone pair of each nitrogen center [10, 11], or (b) the dimethylamino nitrogen (as supported by spectroscopic studies on aminoazobenzenes or aminoazopyridines in an earlier report [12]). In both cases, the distance between the two OH groups of **II** does not allow an interaction either with the two different sites of the same pyridine molecule (whatever they may be) or with a singular N – O oxygen. Alternatively, the presence of a weak ESR signal that, on the basis of literature data [13, 14], may be attributed to the presence of a mono-nitroxide radical **VII**, should suggest that the latter molecule is responsible for the complex formation, which is denied by the fact that the radical content in the solid complex is no more than a little percentage. A further hypothesis may be that of an interaction of one of the OH groups of **II** with the amino or the azo linkage of a second molecule of pyridine derivative, as supported by conductance values of some complexes: the value of the complex **IV*b** is in fact 10^2–10^3 times greater than those of complexes **IV*a**,

IIId · I and **IIIe · II**, which could mean a strong intermolecular hydrogen bonding between N−O−H, N−O and $N(CH_3)_2$ groups [15]: in absence of the dimethylamino group (e.g. in donors **III*a** and **IIIe**) or when it disturbs the formation of hydrogen bonds that may be involved in the conduction process [16], the azo linkage may participate in the intermolecular interaction. The already cited impossibility to get crystals suitable for X-ray analysis of such complexes leaves the question of their geometry still open.

Experimental

1-Hydroxy-2-phenylindole (**I**) [17], 1,1′-dihydroxy-2,2′-diphenyl-3,3′-biindole (**II**) [17], arylazopyridines (**IIIa–e**) [18–20], arylazopyridine N-oxides (**III*a–e**) [14, 19], were prepared according to the literature. All solvents were Carlo Erba RP-ACS grade reagents purified and dried following Vogel [21].

UV-Vis spectra were performed on a Perkin Elmer 554 spectrometer equipped with a Perkin Elmer integrating sphere; FT-IR spectra were registered on a Nicolet 20 SX FT-IR spectrometer; ESR spectra were recorded on a Jeol-1PE-1X ESR spectrometer using a deaerated two-leg inverted cell previously described [22].

Electrical Conductivities

Values of σ were determined at various temperatures and 1 min after voltage application, using a thermostatted cell under nitrogen. The pellets of samples, obtained under pressure, had a diameter of 5 mm [23].

Synthesis of Complexes **IV*a–e**

Benzene solutions of equimolar amounts of **I** and pyridines **III*a–e** were refluxed for 7 h under nitrogen. The solutions were cooled and evaporated. The complexes **IV*a–e** were purified by benzene-hexane.

Synthesis of Complexes **V** *and* **VI**

Equimolar amounts (in toluene or xylene) of pyridine **IIId** and **I** were boiled for 7 h under nitrogen. The solutions were cooled and the volume reduced under vacuum. The solid was collected and purified by toluene (complex **V**) or by xylene (complex **VI**).

Attempts of Reaction of **IIId** *with* **I** *in Pyridine or Thiophene*

Pyridine (or thiophene) solutions of equimolar amounts of **IIId** and **I** were refluxed for 7 h under nitrogen. The solutions were cooled and the volume reduced under vacuum. Using pyridine as solvent, only starting materials were recovered, while with thiophene, a little amount of **II** was identified together with starting arylazopyridine.

References

[1] Tosi G., Battistoni P., Bruni P., Cardellini L. (1983) Gazz. Chim. Ital. **113**: 1530

[2] Colonna M., Bruni P. (1967) Gazz. Chim. Ital. **97**: 158

[3] (a) Shine H. J., Goodin R. D. (1970) J. Org. Chem. **35**: 949; (b) Kubota T. (1965) J. Am. Chem. Soc. **87**: 458; (c) Uruska I. (1980) Spectrochim. Acta **6 A**: 639; (d) Bruni P., Tosi G., Cardellini L., Giorgini E., Stipa P. (1989) Spectrochim. Acta **45 A**: 519

[4] Webb N. E., Thompson C. C. (1978) J. Pharm. Sci. **67**: 165
[5] Hutringer O., Jamieson W. D. (1970) Anal. Biochem. **35**: 351
[6] Foster R. (1969) Organic Charge-Transfer Complexes. Academic Press, London; Pagani G. A., Gardini G. (1984) Chimica e Industria **66**: 244
[7] Hadzi D., Kobilazov A. N. (1966) J. Chem. Soc. (A): 439
[8] Detoni S., Hadzi D. (1964) Spectrochim. Acta **20**: 949
[9] Joesten M. D., Schaad L. J. (1974) Hydrogen Bonding. Marcel Dekker, New York
[10] Blackstock S. C., Kochi J. K. (1987) J. Am. Chem. Soc. **109**: 2484
[11] Salvo F. D. (1971) J. Org. Chem. **36**: 3842
[12] Cilento G., Miller E. C., Miller J. A. (1955) J. Am. Chem. Soc. **78**: 1718
[13] Bruni P., Colonna M. (1973) Tetrahedron **29**: 2425
[14] Meier H. (1974) In: Ebel H. F. (ed.) Organic Semiconductors (Monographs in Modern Chemistry, Vol. 2). Verlag Chemie, Weinheim, chapt. 6
[15] Honzl J., Ulbert K., Hadek V., Tlustakova M., Metalova M. (1969) J. Polym. Sci. **C16**: 4465
[16] Colonna M., Bruni P. (1965) Gazz. Chim. Ital. **95**: 1172
[17] Pentimalli L. (1959) Gazz. Chim. Ital. **89**: 1843
[18] Pentimalli L. (1960) Tetrahedron **9**: 194
[19] Colonna M., Risaliti A., Pentimalli L. (1957) Gazz. Chim. Ital. **87**: 923
[20] Colonna M., Bruni P. (1969) Gazz. Chim. Ital. **99**: 885
[21] Vogel A. I. (1988) Textbook of Practical Organic Chemistry, 4th edn. Longmans, London
[22] Russel G. A., Strom E. C. (1964) J. Am. Chem. Soc. **86**: 744
[23] Sandrolini F. (1986) Macromolecole: Scienza e Tecnologica, Vol. 2. Pacini, Pisa

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