Dipole Moments and Absorption Spectra of 2-Pyridyl-Phenyl Sulphide and 2-Pyridyl-Phenyl Sulphone

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The electric dipole moments in benzene solution have been measured for the title compounds and analysed in terms of the conformations of these molecules in solution. The origin of the electronic absorptions have been interpreted by means of a theoretical approach (CNDO/S-CI) and, together with the SO_2 stretching vibrations, have been compared with the corresponding spectral features observed for the analogous related diphenyl and di-2-pyridyl compounds.

In earlier papers [1–4], we reported both theoretical and experimental investigations on the stereochemical and physical properties of sulphur bridged molecules of type Ar_2X (X = S, SO_2; Ar = 2-pyridyl-). In the present work our attention has been focused on a comparison of the conformational and spectral aspects in such systems, as they are affected by the replacement of a pyridine group by a phenyl ring. Here we therefore report the results of a dipole moment and u.v. and i.r. spectroscopic study, combined with MO calculations CNDO/S-CI type, of 2-pyridyl-phenyl sulphide and 2-pyridyl-phenyl sulphone. Apart from the u.v. spectrum of the sulphide [5], no physical measurements on these compounds have yet been published.

Experimental

Materials

The 2-pyridyl-phenyl sulphide **1** was obtained according to the literature method [5]. The pale-yellow oil was distilled twice before measurements were made. The 2-pyridyl-phenyl sulphone **2** was prepared by addition of H_2O_2 (30%) to a solution of **1** in acetic acid under reflux (30′). The reaction mixture was poured in cold water and the sulphone **2** was separated. The crude product was recrystallised from acqueous acetic acid to constant m. p. (90 – 1 °C; *lit.* [6]: 87 – 9 °C).

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Physical Measurements

Electric dipole moments of **1** and **2** were measured in benzene soln. at 25 ± 0.01 °C, using apparatus and techniques described in detail elsewhere [7]. The total solute polarization $P_{2\infty}$ was obtained by using the Halverstadt-Kumler method [8]. The experimental molar refraction R_D, measured for the Na_D line, was used in calculating the μ values from the usual Debye's formula.

U.v. absorption spectra were recorded in MeOH soln. using a Perkin Elmer 356 spectrophotometer.

I.r. spectra were recorded on a Perkin Elmer 225 spectrophotometer on KBr disks.

Table 1. Total polarizations ($P_{2\infty}$), molar refractions (R_D), dipole moments (μ) and other parameters for their evaluation, for 2-pyridyl-phenyl sulphide **1** and 2-pyridyl-phenyl sulphone **2** in benzene at 25 °C.

Compound	α [a]	β [b]	$P_{2\infty}$/cm³	R_D/cm³	μ/D
1	5.09	−0.394	220.98	52.9	2.86 (±0.01)
2	14.30	−0.389	638.84	60.1	5.32 (±0.01)

[a] $\alpha = \Sigma(\varepsilon_{12} - \varepsilon_{10})/\Sigma w_2$; [b] $\beta = \Sigma(v_{12} - v_{10})/\Sigma w_2$.

Table 2. Experimental and calculated electronic transitions of sulphide **1** and sulphone **2**.

2-Pyridyl-phenyl sulphide **1**

Theory				Observation	
λ (nm)	f [a]	λ (nm)	f [b]	λ (nm)	log ε [c]
290	0.008	285	0.011	292	3.79
269	0.088	271	0.131	268	3.77
264	0.002	264	0.002		
230	0.272	231	0.197	244	4.04
218	0.026	219	0.053		
213	0.040	213	0.064		
205	0.082	202	0.139	205	4.22
195	0.644	195	0.292		

2-Pyridyl-phenyl sulphone **2**

Theory		Observation	
λ (nm)	f	λ (nm)	log ε [d]
285	0.006		
264	0.093	260	3.69
260	0.010		
226	0.145	228	4.06
215	0.113		
207	0.016	204	4.11
206	0.005		
201	0.011		
197	0.027		

[a] Conformation *N-inside*. [b] Conformation *N-outside*.
[c] In EtOH soln., Ref. [5] and present work.
[d] In MeOH, present work.

Computational Details

The possible conformations of **1** and **2** were denoted by the pair of angles (ω, φ) which are generated by clockwise rotations starting from the planar *N-inside* conformation assumed as (O, O).

The resultant theoretical dipole moments (μ_{calc}) were obtained as a function of the rotation angle φ by a three-dimensional vector addition method of the component moments of pyridine (py), diphenyl sulphide (Ph_2S) and diphenyl sulphone (Ph_2SO_2) moieties. The following experimental moments were thus assumed: $\mu_{py} = 2.20$ D [9]; $\mu_{Ph_2S} = 1.55$ D [10]; $\mu_{Ph_2SO_2} = 5.05$ D [10].

The electronic transition energies were calculated by a CNDO/S-CI treatment [11] restricted to the 30 lowest singly excited states and using the *spd* basis set. The oscillator strengths for the various transitions were determined with the dipole length operator. The parametrisation adopted was reported elsewhere [2]. In the quantum-mechanical calculations the two conformations (36, 36) *(N-inside)* and (36, 216) *(N-outside)* were considered for the sulphide **1**, while only the conformation (90, 90) was taken into account for the sulphone **2**.

Since structural data are lacking, in all computations idealised geometries were considered for the molecules **1** and **2** assuming regular hexagonal rings (C – C and C – N of 0.1400 nm, C – H of 0.1084 nm, all angles 120°) and taking the values of C – S 0.1750 nm, S – O 0.1540 nm, and angle $C\hat{X}C$ of 109.5° (X = S) and 100° (X = SO_2) from similar molecules [12].

Results and Discussion

Molecular Conformations

The energetically preferred conformation for sulphide **1** can be reasonably assumed to be as that found for the analogous diphenyl sulphide and di-2-pyridyl sulphide systems [1–3]. We thus consider for this molecule the two distinct C_{2v} propeller structures (36, 36) and (36, 216), that correspond to the two possible orientations of the pyridine ring with respect to the $C\hat{S}C$ angle, *N-inside* and *N-outside*, respectively. The theoretical dipole moments for these conformations are $\mu_{calc}(36, 36) = 2.31$ D and $\mu_{calc}(36, 216) = 3.62$ D, which, however, are in disagreement with the measured moment of 2.86 D. This experimental value can be thus only interpreted in terms of an equilibrium mixture of the two forms rapidly interconverting, in which the *N-inside* conformation (36, 36) is slightly predominant, namely ca. 61%.

As to sulphone **2**, its "effective" solute conformation can be expected to be strictly similar to that observed for the structurally analogous diphenyl sulphone and di-2-pyridyl sulphone molecules [4]. This view is confirmed by the agreement found between the experimental moment of **2** and the calculated averaged moment $\bar{\mu}_{calc}$ for a quasi-rigid structure in which torsional oscillations occur about C – S bonds in the range (30, 30) – (90, 90).

Electronic Spectra

There is a close correspondence of bands in the spectra of diphenyl sulphide [13, 14], di-2-pyridyl sulphide [2] and 2-pyridyl-phenyl sulphide [5] (present work). By considering the results of the CNDO/S-CI calculations, the nature of the bands of sulphide **1** can be elucidated briefly as follows †. The band at 292 nm is correlated with a nearly pure $n \rightarrow \pi^*$ †† excitation localized on the Py fragment; so far this band appears to be little shifted and enhanced with respect to the corresponding band in pyridine at 288 nm [15] through the lowering of the molecular symmetry and the resultant electron rearrangement. The band emerging at 268 nm consists of two closely situated $\pi \rightarrow \pi^*$ transitions, to the first of which contributes mainly CT from S to Py while to the second mainly CT from S to Ph. The band centred at 244 nm should be attributable to the concomitance of several electronic transitions due to both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations. Finally, the band at 204 nm is predicted to derive from perturbed π (^1L_a) ring transitions. Without attaching a conclusive meaning to it, it is worthwhile noting that conformation *N-inside* provides better reproduction of the observed quantities than conformation *N-outside*.

Comparison of the results obtained by using the *sp* and *spd* basis sets shows that the role played by the S 3d orbitals is unimportant in sulpide **1**. This finding is consistent with current thinking [2, 5, 13, 14, 16] that no expansion of the S valence shell occurs in aryl sulphides and also with *ab-initio* results [17, 18] on representative molecules containing di-coordinated sulphur.

The u.v. spectrum of sulphone **2** bears a close resemblance to those of the related compounds diphenyl sulphone [20] and di-2-pyridyl sulphone [4], so the assignment must be quite similar. In particular (Table 2), the low-energy band stems from two

† It must be, however, stressed that, due to both the inherent limitations of the theoretical method and the molecular size and shape, the present assignments must not be regarded as absolutely conclusive. This point should be considered also on discussing the related sulphone **2**.

†† The σ, π labelling is incorrect, in a strict sense, because of deviation from planarity; it has still been retained in order to give a standard characterisation to the transitions of both molecules.

nearly degenerate transitions of formal "π" character occurring in the Py and Ph rings and with negligible participation of the SO_2 group. The long wavelength tail of this band should obscure the weaker absorption due to a transition of perturbed pyridinic $n \rightarrow \pi^*$ nature. According to the present theoretical results, the different behaviour of this $n \rightarrow \pi^*$ band in the sulphone **2** relative to sulphide **1** is due to the greater bonding character of the n orbital in **2** than in **1**. The 228 nm band is assigned to nearly pure excitations localized in the rings with a modest conjugation transmitted via the S 3d orbitals and no involvement of the O atom. This band is therefore strictly related to the "primary" band of diphenyl sulphone that was classified as due to excitation of the benzene-sulphonyl system [20]. Finally, the band at 204 nm can be ascribed to π transitions associated with electron redistribution inside the aromatic rings and a negligible participation of the SO_2 group and then, in a general sense, can be recognised as a perturbed ^1L_a band.

Along the series of phenyl-pyridyl sulphones the "primary" band shows the trend:

$$220\ (\mathrm{Ar} = \text{2-pyridyl})^3 < 228\ (\mathrm{Ar_1} = \mathrm{Ph},\ \mathrm{Ar_2} = \text{2-pyridyl}) < 235\ \mathrm{nm}\ (\mathrm{Ar} = \mathrm{Ph})$$

which reveals the hypsochromic influence of the Py relative to the Ph group. Unfortunately, the tetrahedral arrangement about the S atom with the two rings lying in perpendicular planes and the complex interplay of mesomeric and inductive effects from the aromatic residues do not allow an easy rationalisation of this evidence.

Unlike the related sulphide **1**, the participation of the S 3d orbitals in the bonding of **2** is found to be quite important, in line with the empirical arguments by Moffitt and Koch [21, 22] and *ab-initio* results by Palmer and Findlay [23] on conjugated sulphones.

SO_2 Stretching Vibrations

The conspicuous strong intensity of the SO_2 stretching bands facilitates their identification in the i.r. spectrum of sulphone **2** at 1304 cm^{-1} (antisymmetric mode) and 1164 cm^{-1} (symmetric mode).

If one considers the average stretching frequency as an index of the strength of the SO bond along the series of phenyl-pyridyl sulphones, then one has the trend:

$$1232\ (\mathrm{Ar} = \mathrm{Ph})^4 < 1234\ (\mathrm{Ar_1} = \mathrm{Ph},\ \mathrm{Ar_2} = \text{2-pyridyl}) < 1239\ \mathrm{cm^{-1}}\ (\mathrm{Ar} = \text{2-pyridyl})^4$$

which nicely parallels the corresponding slight increase in the total bond-order of the SO bond (as calculated within the CNDO/S approach using the rotationally-invariant formula proposed by Ehrenson and Seltzer [23]):

$$1.514\ (\mathrm{Ar} = \mathrm{Ph})^4 < 1.515\ (\mathrm{Ar_1} = \mathrm{Ph},\ \mathrm{Ar_2} = \text{2-pyridyl}) < 1.517\ (\mathrm{Ar} = \text{2-pyridyl})^4.$$

Both these evolutions suggest therefore that the involvement of SO_2 fragment into the molecular bonding increases by progressive replacement of the phenyl rings by pyridine rings.

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