Dipole Moment, Spectroscopic, and Theoretical Study of Di-2-pyridyl Sulphones

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The electric dipole moments and u.v. and i.r. spectra of di-2-pyridyl sulphone and of its *p*-nitro- and *p,p'*-dinitro-derivatives have been measured and analysed. Dipole moment data, in conjunction with theoretical calculations of conformational energy (CNDO/2 and EHT), show that these molecules prefer a single conformation in which the pyridine ring planes are perpendicular to the CSC plane and the nitrogen atoms are located *anti* to each other. The main features of the u.v. and i.r. spectra of the compounds examined, together with those of diphenyl sulphone, have been surveyed. The electronic transitions have been interpreted in terms of CNDO/S-CI calculations for the most favoured conformation. Vibrational assignments for the characteristic SO_2 group frequencies are also presented.

IN previous papers [1,2] the molecular solute conformations of di-2-pyridyl sulphide and its *p*-nitro and *p,p'*-dinitro-derivatives were deduced from dipole moments, n.m.r. spectroscopic data, and results of theoretical calculations of conformational energies. The u.v. absorption spectra of these compounds were also presented and interpreted by using a quantum mechanical approach (CNDO/S-CI).[3]

The stereochemistry of sulphur-bridged molecules of type Py_2X ($X = S$ or SO_2) is of interest in view of their increasing application in co-ordination chemistry. The properties of these compounds as ligands were extensively studied and it was established that they normally behave as bidentate ligands.[4-8] However neither experimental nor theoretical investigations are available for di-2-pyridyl sulphone. Previously, the similar diphenyl sulphones were the object of u.v. spectroscopic studies [9,10]

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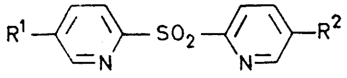
and of dipole moment and molar Kerr constant measurement.[11,12]



(1) $R^1 = R^2 = H$
(2) $R^1 = H$; $R^2 = NO_2$
(3) $R^1 = R^2 = NO_2$

The present paper is concerned with an investigation of physical properties of di-2-pyridyl sulphone and its *p*-nitro- and *p,p'*-dinitro-derivatives. In particular, their electric dipole moments in conjunction with results of theoretical MO calculations (CNDO/2 and EHT) were analysed for conformational information. The electronic spectra of these molecules were measured and surveyed; the spectrum of di-2-pyridyl sulphone, together with that of diphenyl sulphone, was further studied by means of the CNDO/S-CI treatment. Finally, their i.r. spectra were analysed with the main aim of assigning the vibrations of the SO_2 group.

EXPERIMENTAL

Materials.—Di-2-pyridyl sulphone (1), m.p. 216°,[13] 5-nitro-2-pyridyl 2-pyridyl sulphone (2), m.p. 188°,[14] and bis-5-nitro-2-pyridyl sulphone (3), m.p. 227°,[15] were obtained from the corresponding sulphides by oxidation with hydrogen peroxide in acetic acid solution. They were purified by crystallization to constant m.p. and $\varepsilon_{\max}$. The purity grade of each sample was >99.5% by differential scanning calorimetry before determination of dipole moments.

Benzene used as solvent was purified using a literature method [16].

Physical Measurements.—Electric dipole moments were measured in benzene solution at 25 ± 0.01°. Details of apparatus, procedures, symbols, *etc.*, were given in detail previously.[17]

The total solute polarization was obtained by extrapolation at infinite dilution ($P_{2\infty}$) using the Halverstadt–Kumler method.[18] The experimental molar refraction (R_D) measured for the sodium D line was taken as the atomic and electronic polarization ($P_E + P_A$) in calculating dipole moments (μ) from Debye's formula. The estimated error in measured μ values is ±0.01 D for compounds (1) and (2) and ±0.03 D for (3). Results from dipole moment measurements are collected in Table 1.

U.v. absorption spectra were recorded using a Perkin-Elmer 356 spectrophotometer for MeOH solutions.

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

Quantum Mechanical Calculations.—Theoretical calculations of the conformational energy of (1) were carried out by the semi-quantitative CNDO/2 method, using the standard Pople parametrization.[19] Since the Extended Huckel Theory (EHT) [20] has been applied with satisfactory results in conformational analysis,[1,21-23] energy calculations were also performed by this method, using the integrals and parametrization described in ref. 21. In both approaches the sulphur 3*d* orbitals were included in the basis set.

TABLE 1

Polarization data and dipole moments (μ) of di-2-pyridyl sulphones (1)—(3); in benzene solution at 25°

Compound	α	β	γ	$P_{2\infty}$/cm^3	R_D/cm^3	μ/D
(1)	12.21	−0.472	0.312	551.57	56.6	4.92
(2)	7.22	−0.521	0.319	410.73	64.9	4.11
(3)	0.66	−0.505	0.248	97.50	72.4	1.11

The possible conformations of di-2-pyridyl sulphone are defined by the pair of angles ω,ψ which are assumed to be positive for clockwise rotations of the pyridine rings; the convention is used that $\omega,\psi = 0,0$ represents the N,N-inside conformation having the rings coplanar with the CSC plane (Figure 1).

The electronic transition energies of di-2-pyridyl and diphenyl sulphone were calculated by a CNDO/S-CI treatment [24] restricted to the 30 lowest singly excited states. The oscillator strengths for the various transitions were determined with the dipole length operator. The parametrization adopted has been reported elsewhere,[3] the sulphur 3*d* orbitals being included in the calculations. In the present CNDO/S-CI calculations the most probable conformation of the molecules, with the ring planes perpendicular to the CSC plane and, for (1), with the nitrogen atoms *anti* (90,90), was taken into account.

In all the calculations bond lengths and angles were set at values given by an *X*-ray analysis of bis-*p*-bromophenyl sulphone:[25] d(C–S) 1.84; d(S–O) 1.54 Å; $\widehat{CSC}$ 100; $\widehat{OSO}$ 132°; regular hexagonal rings were assumed with d(C–C) = d(C–N) = 1.40; d(C–H) 1.084 Å.

RESULTS AND DISCUSSION

Theoretical Energy Calculations.—Assuming for molecule (1) C_2 molecular symmetry, the potential energy curves were obtained for conrotatory ($\omega = \psi$) and disrotatory ($\omega = -\psi$) twisting mode of the rings. Results of CNDO/2 calculations give a single minimum of energy

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for the 90,90 conformation (see Figure 2), whereas EHT calculations predict two minimum energy conformations denoted by 90,90 and 90,−90. The CNDO/2 method, in general, indicates that energies of all disrotatory forms are considerably larger than those of the conrotatory forms. A non-rigid structure appears compatible with results of EHT calculations which predict small activation energies for interconversion of the 90,90 into the 90,−90 form and *vice versa*; on the contrary, the CNDO/2 calculated barriers are much too large to allow interconversion of the molecule. In conclusion, we see that the two methods of calculation adopted lead to somewhat different predictions for the conformational properties of di-2-pyridyl sulphone. Therefore, integration with complementary experimental data concerning the molecular conformation of this system is crucial for accurate comparison of the theoretical results with each other as well as checking on their relative reliability.

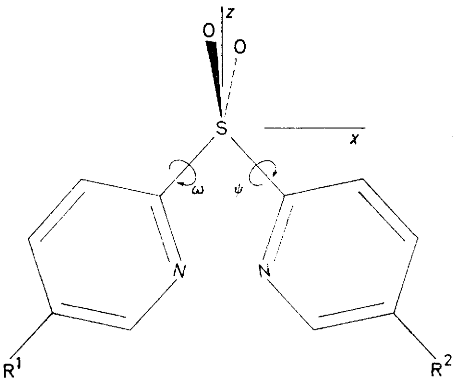

FIGURE 1 Molecular model of di-2-pyridyl sulphones (1)—(3) oriented along the co-ordinate axis. The conformation 0,0 is shown

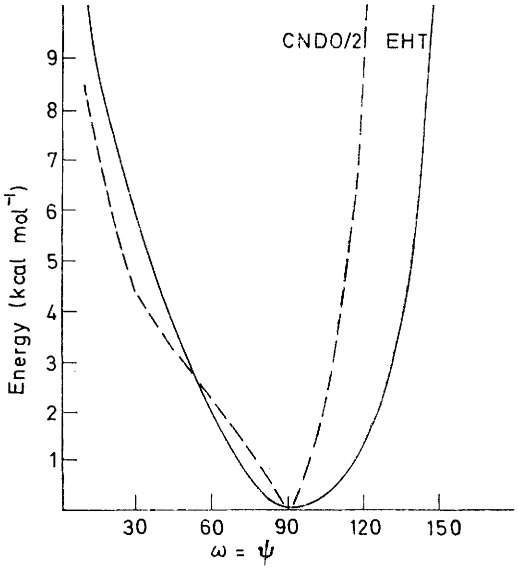

FIGURE 2 CNDO/2 and EHT potential energy curves for conrotatory twisting of the pyridine rings in di-2-pyridyl sulphone. The energy is relative to an arbitrary zero taken as the lowest energy conformation

Dipole Moment Analysis.—The vector addition scheme of group moments, together with a computerized method of calculation,[26] has been used to calculate dipole moments for possible conformations ω,ψ of each molecule examined. Total molecular moments (μ_{calc}) were thus calculated as the resultants of the component moments of diphenyl sulphone (Ph_2SO_2), pyridine (Py), and nitro (NO_2) fragments. The moment of the Ph_2SO_2 moiety as a whole ($\mu_{Ph_2SO_2}$) was taken directly from the experimental moment of this molecule (5.05 D [11]), its direction being along the bisector of the $\widehat{OSO}$ angle with the positive end towards the sulphur atom. The values μ_{Py} 2.20 and μ_{NO_2} 4.01 D were assumed from literature data;[27] the $\widehat{CSC}$ valency angle of 100° used in the calculations was taken from the *X*-ray structure of bis-*p*-bromophenyl sulphone.[25] The accuracy of the whole procedure is at a maximum, owing to the use in the summation of a small number of large fragments which leads to a substantial improvement of the method.[28]

The results obtained for (1) indicate that the experimental moment (μ_{exp}) of 4.92 D cannot be matched with any of the energetically preferred conformations 90,90 and 90,−90, whose μ_{calc} values are 6.45 and 7.50 D, respectively. Since both these μ_{calc} values considerably exceed μ_{exp}, this cannot be interpreted as an average moment $\bar{\mu}$ arising from an equilibrium mixture, in the solution state, of the 90,90 and 90,−90 forms. Finally, a dynamic equilibrium mixture of several forms can be ruled out, because it would involve occurrence of conformations energetically unlikely or sterically forbidden such as the 0,0 one. Therefore the μ_{exp} value of (1) can only be rationalised in terms of concerted torsional oscillations that, under our experimental conditions, take place about C–S bonds in the range $30,30 \leqslant \omega = \psi \leqslant 90,90$. In fact, the condition $\mu_{calc} = \mu_{exp}$ is verified for the C_{2v} fixed structure 60,60 whose μ_{calc} value corresponds, on the other hand, with the averaged moment expected for an equiprobable population of all conformations with twisting angles ranging from 30,30 to 90,90. This result seems more acceptable, in that it is in harmony with the predictions of CNDO/2 calculations and, in particular, with the shape of the corresponding energy curve in Figure 2. This diagram, in fact, is markedly asymmetric about the minimum point and indicates that all conformations in the range 25,25—110,110 differ from the absolute minimum by *ca.* 5 kcal mol^{-1}, *i.e.* by thermodynamic energy barriers that, in solution, are quite easily overcome. The statement that the form 90,90 is the most favoured can be further established by means of the measured moment of (3). In this molecule the conformational preference of (1) is

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retained: however, owing to the presence of the nitro-substituent ($+M$ effect) in the *para*-positions, it is expected *a priori* that the kinetic molecular energy does not exceed the potential barrier to torsion of the rings about the favoured conformation which, as a consequence, will be the most populated one in solution. Actually the sulphone (3) is found to have μ_{exp} 1.11 D in fair agreement with μ_{calc} for the conformation 90,90. Dipole moment analysis for the mononitro-derivative (2) shows that this molecule exists mainly as the conformation 90,90 and indeed this is also in agreement with the above findings. It is noteworthy for (2) that the presence of a single nitro-group is sufficient kinetically to ' freeze ', by electronic effects, the molecule in the most stable conformation.

In conclusion, it is relevant to observe that among the quantum chemical methods adopted, only the CNDO/2 method gives satisfactory results in predicting the conformation of (1). This confirms the ability of the method to handle cases of non-planar molecules and non-bonded interactions which are not attainable by other methods.

Electronic Spectra.—In the u.v. spectrum of diphenyl sulphone the first structured band of medium intensity lies in the low energy part of the spectrum (270—250 nm); the second high intensity band exhibits a maximum absorption at 235 nm; and the third high intensity band occurs below 220 nm with a maximum at 201 nm.[9,10] By analogy with the assignment of bands in the aryl sulphides[29] it was suggested[10] that the ^1L_a benzene absorption at 201 nm is unaffected by oxidation to sulphoxide and sulphone, while the ^1L_b absorption undergoes bathochromic displacement to 265—285 nm (this long wavelength band displays typical ^1L_b benzene fine structure). On the basis of an experimental study of substituent, solvent, and temperature effects, Leandri *et al.*[9] concluded that the ' primary ' 235 nm band of Ph_2SO_2 essentially represents the excitation of the benzenesulphonyl system $\overset{+}{C}_6H_5{=}\overset{-}{S}[O_2]$ with interchange with the other Ph ring; the resonance interaction takes place with the nonbonding orbitals of S and does not involve the S=O bonds, *i.e.* the mechanism is the ' a_1 ' of Moffit and Koch.[30,31] This assignment is corroborated by evidence from dipole moment measurements[11] which indicate a significant flow of electronic charge from the phenyl group to the sulphur $3d$ orbitals in sulphones.

In the u.v. spectrum of (1), two distinct broad absorptions are discernible. One band of medium intensity with three maxima appears in the long wavelength region (245—285 nm) and closely resembles the ^1L_b absorption of pyridine and one band of high intensity lies at shorter wavelengths (235—200 nm) and has the typical shape of a two-component band. In view of its composition, location, and intensity, this latter band can be related to the two short wavelength bands of Ph_2SO_2.

The absorption spectrum of the mononitro-derivative (2) shows a broad intense band at 225—275 nm, with a maximum at 244 nm, and others less pronounced toward lower energies, and a sharp intense band centred at 207 nm. It bears a close resemblance to that of the related *p*-nitro-2-pyridyl phenyl sulphone:[9] the major chromophore responsible can then be recognised to be the nitropyridyl group π^8 (NO_2,Py). On going to the dinitro-derivative (3), the intense broad absorption undergoes a hypsochromic effect and a splitting into two bands, one located at 274 nm and the other less intense at 241 nm. Presumably, this spitting may result from complex mixing of both π–π^* and n–π^* excited states located on the Py rings and also involving the NO_2 groups.

As shown by the results in Table 2, the observed spectrum of Ph_2SO_2 is fairly well reproduced by the CNDO/S-CI calculations. In particular, the long wavelength band is found to arise from two nearly degenerate transitions, one symmetry forbidden and one electric dipole allowed polarized along the x axis (see Figure 1 for the co-ordinate system of axes), both coming from a mixture of excitations involving only the ' π ' † electron framework of the phenyl rings. In a general sense this band can be recognised as a perturbed benzene ^1L_b transition. The band centred at 235 nm is ascribed to a transition, polarized along the y axis, stemming from a nearly pure excitation localized in the phenyl rings with a modest conjugation transmitted *via* the sulphur $3d$ orbitals and no involvement of the oxygen atoms.

TABLE 2

Experimental and calculated electronic transitions of diphenyl and di-2-pyridyl sulphone

Theory			Observation *	
State	λ/nm	f	λ/nm	log ε
	Diphenyl sulphone			
$^1A_2$	260	0	266	3.33
$^1B_1$	259	0.016		
$^1B_2$	222	0.317	235	4.19
$^1B_2$	208	0.003	201	4.58
$^1A_1$	207	0.008		
$^1A_1$	198	0.010		
$^1B_2$	191	0.944		
$^1A_2$	191	0		
	Di-2-pyridyl sulphone			
^1A	282	0.003		
^1B	275	0.043		
^1B	264	0.106	261	3.83
^1A	260	0.038		
^1B	226	0.096	220	3.98
^1B	216	0.114		
^1A	215	0.004		
^1A	208	0.020	206sh	3.89
^1B	207	0.003		
^1A	203	0.003		
^1A	194	0.001		

* From refs. 9 and 10 for diphenyl sulphone.

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† The σ,π labelling is incorrect, in a strict sense, because of deviation from planarity. However, this labelling deduced from the composition of MOs, has been retained in order to give a standard characterisation to the transitions of both molecules.

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This result is in close agreement with the previous band classification by Leandri *et al.*[9] The band with maximum at 201 nm can be attributed to electronic transitions polarized along the (symmetry) *z* axis, arising from several excitations, the most important of which are associated with electron redistribution inside the phenyl rings and with negligible participation of the SO_2 groups. In view of this the band can still be referred to as a ^1L_a perturbed benzene band, in agreement with the assignment by Cumper *et al.*[10]

As for di-2-pyridyl sulphone, the long wavelength band with maximum at 261 nm can be assigned to the two transitions predicted at 264 and 260 nm; the state functions based on CI indicate that these excited states arise from excitation of formal ' π ' character occurring in the pyridine rings and with little participation of the SO_2 group. In addition, theory predicts that there are two transitions, nearly degenerate and of perturbed pyridine ' n–π^* ' character, submerged under the long wavelength tail of the observed band. (Actually, two such transitions should occur because of the presence of two MOs containing the nitrogen lone pairs and of their little splitting stemming from through-bond interaction.) The composite band consisting of a pronounced maximum at 220 nm and an inflection at 206 nm can be attributed to excited states which require for their description just a characterisation similar to that above mentioned for the two short wavelength bands of Ph_2SO_2.

TABLE 3

SO_2 Group frequencies (cm^{-1})

Compound	Antisymmetric stretching	Symmetric stretching	Bending	Wagging	Rocking	Torsion
(1)	1 310s	1 169s	594s	568s	295w	304w
(2)	1 330s	1 177s	606s	569s	297w	307w
(3)	1 340s	1 175s	625s	570s		
Ph_2SO_2 *	1 309s	1 155s	571s	563s	303m	312w
(p-$NO_2C_6H_4)_2SO_2$†		1 165s				

* Refs. 32 and 33. † S. Ghersetti, *Boll. sci. Fac. Chim. ind. Bologna*, 1963, **21**, 232.

In conclusion, it can be remarked that the CNDO/S-CI treatment provides a sound argument in favour of a similar interpretation on the origin of the main bands of Ph_2SO_2 and di-2-pyridyl sulphone.

Infrared Spectra.—The assignment of the SO_2 group frequencies was made by correlation with the results of Uno *et al.*[32] and Nagel *et al.*[33] for the related Ph_2SO_2 molecule. The pyridine ring vibrations were identified and the basis of the assignment proposed by Green *et al.*[34]

As for the SO_2 stretching vibrations of (1), they were easily recognised in view of their strong intensity at 1 310 (antisymmetric mode) and 1 169 cm^{-1} (symmetric mode). In particular, the former band appears as a triplet with two weaker side-bands while the latter is a sharp single band. In the region between 630 and 560 cm^{-1} of (1) three distinct bands of noticeable intensity were found. The ν_{6b} frequency of pyridine (605 cm^{-1}) [34] turns out to be relatively insensitive to substitution (629—613 cm^{-1}); [34,35] since the spectrum of (1) exhibits a medium intensity band at 621 cm^{-1}, this can be identified as a ' pyridine ' band while the remaining two bands at 594 and 568 cm^{-1} can be confidently assigned to the bending and wagging modes, respectively, of the SO_2 group. Weak intensity absorptions observed at 304 and 295 cm^{-1} can be attributed to the SO_2 torsion and rocking vibrations, by analogy with the assignment proposed for Ph_2SO_2.[33] The assignments so far established for (1), Ph_2SO_2, and the nitro-derivatives are collected in Table 3. From these it can be inferred that there are only two SO_2 modes that are significantly affected by replacing phenyl with pyridine rings: they are the symmetric stretching and bending modes. To a first approximation, looking at the average stretching frequency as an index of the strength of the SO bond, the increase occurring on passing from the phenyl (1 232 cm^{-1}) to the pyridine derivative (1 239 cm^{-1}) is diagnostic of more effective participation of the SO_2 group in the molecular bonding of (1) than of Ph_2SO_2. This is consistent with the greater electron-donor power of the pyridine relative to the phenyl ring as manifested by the increase in the total bond order (CNDO/S calculation) of the SO bond: 1.514 (Ph_2SO_2), 1.517 (1).

Nitro-substitution causes a marked raising of the SO_2 antisymmetric stretching vibration as a consequence of an important interaction between the NO_2 and SO_2 groups transmitted *via* the aromatic ring. A similar change is also observed for the band ascribed to the bending mode. The assignment of the bands at 1 531 and 1 539 cm^{-1} in the spectra of (2) and (3), respectively, to the asymmetric stretching of the NO_2 group is straightforward on the basis of their intensity and location. The corresponding symmetric stretching modes are assigned to strong bands, fairly stable in position, appearing at 1 354 and 1 355 cm^{-1}.

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