Molecular Conformation of Di-2-pyridyl Sulphide. A Dipole Moment, ^1H Nuclear Magnetic Resonance, and CNDO/2 Study

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Di-2-pyridyl sulphide has been prepared and its electric dipole moment measured at 25 and 45° (3.50 D, in benzene solution). The 250 MHz variable temperature pulsed Fourier transform ^1H n.m.r. spectrum has been also measured and analysed. Results of theoretical energy calculations (CNDO/2 type) together with the experimental data have been interpreted in terms of molecular solute conformations. It has been found that the molecule prefers a twisted conformation in which the ring planes are rotated *ca.* 36° out of the CSC plane. A fast interconversion between the three conformers that correspond to the possible relative orientations of the pyridine rings in this structure was found to occur in the solution state.

Our current interest in the study of the relationship between the conformational properties and the chelating ability of sulphur compounds containing pyridine rings [1-5] has prompted us to examine the conformation of di-2-pyridyl sulphide. This molecule has been shown to be a complexing agent for transition metals [6-8] and, more recently, for uranyl ion.[9] In these complexes, di-2-pyridyl sulphide acts as a bidentate ligand, co-ordination occurring only through the two nitrogen atoms. Now if the symmetry and typical linear structure of the UO_2^{2+} systems is considered,[10] it clearly appears that knowledge of the conformational properties of the chelating molecule is a potentially useful tool for the prediction of the stereochemistry of the co-ordination compounds.

Previous investigations of the conformation of the similar diphenyl sulphide molecule have been reported. These used the EHMO approach [11] and experimental

[1] G. C. Pappalardo and G. Ronsisvalle, *J.C.S. Perkin II*, 1973, 701.
[2] G. C. Pappalardo and S. Gruttadauria, *J.C.S. Perkin II*, 1974, 1441.
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[8] M. E. Bridson and W. R. Walker, *Austral. J. Chem.*, 1970, **23**, 1191.
[9] G. C. Pappalardo and A. Seminara, *J. Inorg. Nuclear Chem.*, in the press.
[10] L. Cattalini, U. Croatto, S. Degetto, and E. Tondello, *Inorg. Chim. Acta Rev.*, 1971, 19.
[11] V. Galasso, G. De Alti, and A. Bigotto, *Tetrahedron*, 1971, **27**, 6151.

methods such as dipole moment and molar Kerr constant measurements.[12,13]

Physical measurements as well as conformational information on di-2-pyridyl sulphide, however, are still lacking. We therefore report a comprehensive study of the stereochemistry of this ligand, using the dipole moment method in combination with semi-quantitative MO calculations (CNDO/2 type) of conformational energies, and ^{1}H nuclear magnetic resonance techniques.

EXPERIMENTAL

Materials.—A mixture of 2-mercaptopyridine (11.3 g, 0.1 mol), 2-bromopyridine (15. 8 g, 0.1 mol), potassium carbonate (15 g), and dimethylformamide (25 cm^3) was heated under reflux for 4 h. After cooling, the mixture was filtered and dimethylformamide was removed by evaporation under reduced pressure. The residue crude oil was distilled under vacuum to give di-2-pyridyl sulphide (13.5 g, 72%) as a dense, yellow liquid, b.p. 169—170° at 7 mmHg (lit.,[14] 172—173° at 9 mmHg), n_D 1.647 91 (Found: C, 63.3; H, 4.0; N, 14.9. Calc. for $C_{10}H_8N_2S$: C, 63.8; H, 4.3; N, 14.9%). The purity of the sample used for physical measurements was >99% (g.l.c.).

Benzene used as solvent for dipole moment measurements was purified according to methods described in the literature.[15]

Physical Measurements.—The electric dipole moment of di-2-pyridyl sulphide was measured in benzene solution at 25 ± 0.01° and 45 ± 0.01°, using the apparatus and experimental techniques described in detail elsewhere.[16] The total solute polarization was obtained by extrapolation at infinite dilution ($P_{2\infty}$) with the Halverstadt and Kumler method.[17] The value of the experimental molar refraction (R_D) for the Na_D line (constant at the two temperatures) was the sum of the electronic and atomic polarization (P_e and P_a). The dipole moment (μ) was calculated from Debye's formula.

The Guggenheim method,[18] which does not require precise measurements of solution densities and determination of R_D, was also employed to obtain the dipole moment. The results of both methods are the same within experimental error. The estimated error in μ is ±0.01 at 25 and ±0.03 D at 45°. Duplicate determinations of μ have shown reproducibility of ±0.01 D. The results are summarized in Tables 1 and 2.

^{1}H N.m.r. spectra were recorded at 250 MHz with a CAMECA TSN 250 spectrometer equipped with Fourier transform accessories. The apparatus allowed an acquisition time of 2.719 7 s for a 3 012.048 2 Hz spectral width (resolution 0.367 6 Hz per point). Measurements were made at variable probe temperature from +55° to −80°. The magnetic field homogeneity was readjusted before each recording. Chemical shifts were referred to internal tetramethylsilane for solutions of di-2-pyridyl sulphide (*ca.* 8 wt%) in CS_2, the most reliable solvent for low temperature studies. However, in the quest for the highest possible resolution, solutions of sufficient concentration must be used when ^{1}H n.m.r. spectra are run in the usual mode. This in turn prevents low temperature measurements as the solutes in some cases precipitate from the sample solutions. Therefore in the present work the variable temperature ^{1}H n.m.r. spectra of a dilute solution of di-2-pyridyl sulphide were obtained in pulsed Fourier transform mode. The advantage of this technique is the powerful sensitivity improvement over conventional methods.

Spectral assignments of resonances were easily done on the basis of the observed splitting patterns. Accurate values of chemical shifts and coupling constants for each spectrum have been refined by use of the LAOCOON III program.[19] The root-mean-square deviations for the calculated and experimental lines were *ca.* 0.05 Hz or less. The calculated probable errors for the parameters were usually <0.05 Hz.

The spectral parameters obtained are given in Table 3.

THEORY

SCFMO calculations were performed within the framework of the all-valence electron CNDO/2 approximation,[20] with Pople's original parametrization. A full basis set of orbitals were used, including the 3*d* orbitals of sulphur.

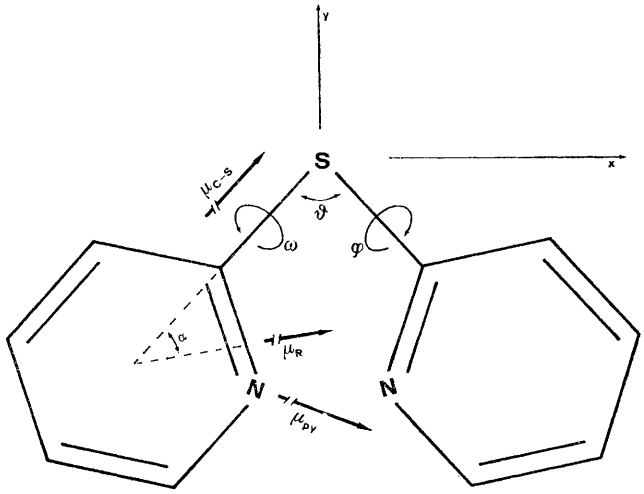

FIGURE 1 Molecular model of di-2-pyridyl sulphide oriented along the co-ordinate axes. The N,N-inside planar conformation, assumed to be the 0,0 one, is outlined

The pyridine rings of di-2-pyridyl sulphide were approximated as regular hexagons with C–C and C–N distances of 1.40 Å, and C–H distances of 1.084 Å. The C–S bond length and $\widehat{CSC}$ angle were assumed to be 1.75 Å and 109°, respectively, as in the case of crystalline di-*p*-tolyl [21] and bis-*p*-bromophenyl sulphide.[22] We assumed that these geometrical parameters did not change owing to internal rotation. Input to the program (run on a CDC 6600 system)

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[14] J. Renault, *Ann. Chim.* (*France*), 1955, **10**, 135.
[15] A. Weissberger and E. S. Proskauer, ' Organic Solvents,' in Techniques of Organic Chemistry,' Interscience, New York, vol. VII, 1961.
[16] G. C. Pappalardo and S. Pistarà, *J. Chem. and Eng. Data*, 1972, **17**, 2.
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[19] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.
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[22] J. Toussaint, *Bull. Soc. chim. belges*, 1945, **54**, 319.

consisted of atomic co-ordinates of the molecule in each possible rotational conformation.

The total energy was thus calculated for the various values of the angles of twist ω,φ in the range 0—360° with intervals 10°. These angles were varied starting with a standard conformation ($\omega = 0$, $\varphi = 0$) where the two rings lie in the CSC plane and the nitrogen atoms point inside the $\widehat{CSC}$ angle (see Figure 1). The angles ω,φ designate the conformation obtained as the two rings rotate in the directions of the arrows shown in Figure 1. A complete contour map of conformational energies as a function of ω,φ is presented in Figure 2.

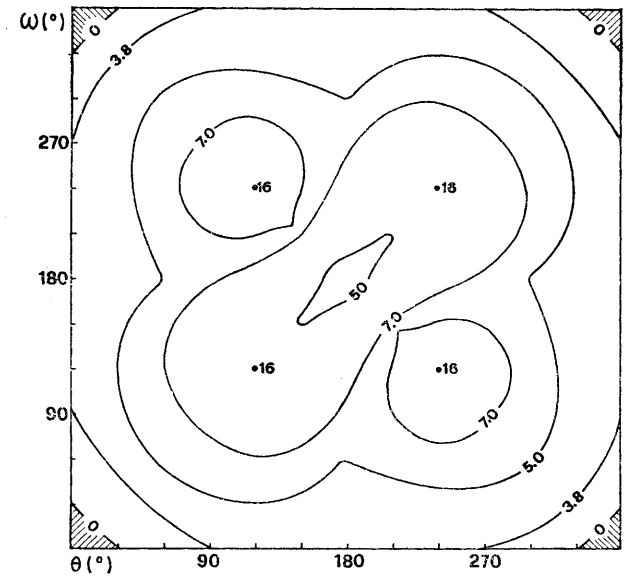


FIGURE 2 CNDO/2 Isoenergy curves for di-2-pyridyl sulphide. The energy scale (kcal mol^{-1}) is referred to the minimum of conformational energy taken as 0

RESULTS AND DISCUSSION

Energy Calculations.—The contour map in Figure 2 shows that the absolute minimum appears at $\omega = \varphi = 0 = 360°$ and represents a planar N,N-inside conformation. A similar all-planar structure is unlikely in the case of diphenyl sulphide because of steric contact between *o*-hydrogen atoms. According to molar Kerr constant studies in benzene,[12,13] diphenyl sulphide has an angle of *ca.* 42—46° between the two phenyl ring planes, in agreement with results of theoretical calculations [11] which predict for the free molecule a value of 48° for this angle. In our opinion, it seems likely that the method adopted overestimates the extent of π–π conjugation compared with the extent of sizable repulsive interactions between the lone pair electrons on the nitrogen atoms which would occur, for di-2-pyridyl sulphide, in the planar N,N-inside conformation. However, Figure 2 appears of interest in that it reveals that small activation energies are required for conversion of a conformation into another along paths lying in the minimum energy area (ranging from 0 to *ca.* 6.5 kcal mol^{-1}). In particular, it can be observed that an energy of *ca.* 4 kcal mol^{-1} is requested for the complete rotation from 0 to 180° of a pyridine ring when keeping the other ring coplanar with the CSC plane. Furthermore, since the peculiar feature of the theoretical potential energy surfaces in Figure 2 is a broad but shallow minimum, it may be argued that several possible conformations, in a wide range about this minimum, can be populated with equal probability in the solution state. A search of the experimental evidence for occurrence of this possibility is thus in order.

Dipole Moment Analysis.—Theoretical moments for the possible fixed conformations ω,φ of di-2-pyridyl sulphide have been calculated through vector addition of bond and group moments in the reference axis system

TABLE 1

Weight fractions of solute (w_2), dielectric constants (ε_{12}) specific volumes (v_{12}), and refractive indices (n_{12}) of solutions of di-2-pyridyl sulphide in benzene

$100\,w_2$	ε_{12}	v_{12}	n_{12}
T 25 °C			
0.284 8	2.293 6	1.141 54	1.497 99
0.394 2	2.301 7	1.141 09	1.498 12
0.627 5	2.319 1	1.140 11	1.498 38
0.785 1	2.330 8	1.139 42	1.498 58
0.900 2	2.339 4	1.138 93	1.498 72
1.136 9	2.357 0	1.137 91	1.499 00
T 45 °C			
0.456 1	2.261 7	1.166 34	1.485 39
0.681 2	0.277 1	1.165 32	1.485 67
0.837 1	2.287 8	1.164 62	1.485 86
0.957 2	2.296 0	1.164 07	1.486 01
0.183 5	2.311 6	1.163 08	1.486 27
1.207 1	2.313 0	1.162 91	1.486 33

outlined in Figure 1. The possible rotational conformations $\omega\varphi$, are defined as described above for the theoretical calculations of conformational energies.

The total moment was calculated by means of the usual relation (1). The component moments along the

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \quad (1)$$

x, y, and z axes for the model shown in Figure 1 can be represented by equations (2)—(4) where the resultant

$$\mu_x = \mu_R \sin\frac{180° - \theta}{2}(\cos\omega - \cos\varphi)\sin\alpha \quad (2)$$

$$\mu_y = 2\mu_R\cos\alpha\sin\frac{180° - \theta}{2}\sin\alpha - \mu_R\cos\frac{180° - \theta}{2}(\cos\omega + \cos\phi)\sin\alpha \quad (3)$$

$$\mu_z = \mu_R(\sin\omega + \sin\varphi)\sin\alpha \quad (4)$$

vector μ_R is given by (5). From simple geometry the

$$\mu_R = (\mu^2_{py} + \mu^2_{C-S} + 2\mu_{py}\mu_{C-S}\cos 60°)^{\frac{1}{2}} \quad (5)$$

angle made by this resultant with C–S axis was obtained as α 38.6°.

The moments μ_{py} 2.20 [23] and μ_{C-S} 1.29 D,[24] with the value $\theta = 109°$ [21,22] for the $\widehat{CSC}$ angle, were used in the

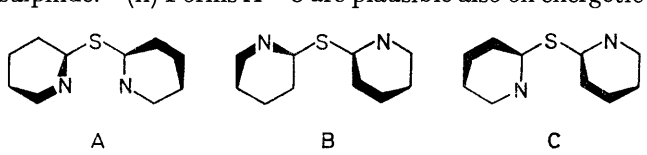
[23] A. L. McClellan, ' Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963.

[24] M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, and H. L. K. The, *Austral. J. Chem.*, 1968, **21**, 281.

computations. As shown previously,[1] the S · · · py resonance interaction effect can be reasonably neglected.

Results of the calculations show that an unequivocal determination of the conformation of di-2-pyridyl sulphide cannot be made on the basis of the dipole moment data, since there are numerous combinations of ω and φ angles for which the calculated dipole moment agrees with the experimental one. In addition to this, the energetic suitability of a single fixed conformation appears improbable when considering the very large minimum zone of conformational energy shown in Figure 2. On the other hand, the alternative possibility of essentially ' free rotation ' about C–S bonds (*i.e.* equiprobable existence of all possible rotational conformers) must be excluded *a priori*. This is because evidence for a barrier to rotation comes from the results of energy calculations as well as from inspection of molecular models. There is, in fact, a maximum energy barrier corresponding to the sterically forbidden conformation ω = φ = 180°.

Consequently, the only remaining possibility is the existence of a mixture of equiprobable rotational conformers. To interpret in a quantitative way the measured dipole moment, we thus assumed as most favoured the possible propeller forms in which the pyridine ring planes are twisted *ca.* 36° with respect to the CSC plane, *i.e.* A (ω = 36, φ = 324°); B (ω = 144, φ = 216°); C (ω = 324, φ = 216°). The choice of conformations A—C was made on the basis of the following criteria. (i) A propeller structure (C_2 symmetry) agrees with the results for the similar diphenyl sulphide. (ii) Forms A—C are plausible also on energetic grounds, since use of molecular models shows that, for twisting angles of *ca.* 36°, the minimum interatomic distance (*ca.* 2 Å) at which repulsive spatial interactions between N—N, N—H, and H–H do not operate can be attained. Also EHT calculations,* carried out using this geometry and the parametrization of ref. 11, predict energy minima corresponding to forms A—C, their relative stability being in the order A (−0.037 0) > C (0.005 5) > B (0.098 1) eV. (iii) The conformational energies as calculated by the CNDO/2 method fall within the minimum zone (3.8, 4.2, and 6.2 kcal mol^{-1} for A, B, and C, respectively).



The averaged dipole moment ($\bar{\mu}$) calculated assuming equal populations of these conformations by means of equation (6), turned out to be 3.70 D, in good agreement with experiment.

$$\bar{\mu} = [\tfrac{1}{3}(\mu_A)^2 + \tfrac{1}{3}(\mu_B)^2 + \tfrac{1}{3}(\mu_C)^2]^{\frac{1}{2}} \qquad (6)$$

TABLE 2

Polarization data and dipole moment (μ) of di-2-pyridyl sulphide in benzene

T/°C	α [a]	ε_{10} [b]	β [c]	v_{10} [d]	γ [e]	$P_{2\infty}$/cm^3	R_D/cm^3	μ/D
25	7.44	2.272 4	−0.426	1.142 77	0.354	303.22	52.1	3.50
45	6.85	2.230 5	−0.453	1.168 41	0.366	291.71	52.1	3.53

[a] $\alpha = \Sigma(\varepsilon_{12} - \varepsilon_{10})/\Sigma w_2$. [b] $\varepsilon_{10} = \lim_{w_2 \to 0} \varepsilon_{12}$. [c] $\beta = \Sigma(v_{12} - v_{10})/\Sigma w_2$. [d] $v_{10} = \lim_{w_2 \to 0} v_{12}$. [e] $\gamma = \Sigma(n^2_{12} - n^2_{10})/\Sigma w_2$.

TABLE 3

^{1}H N.m.r. spectral parameters for di-2-pyridyl sulphide at various temperatures

	δ Values				Coupling constants (J/Hz)					
T/°C	H-3	H-4	H-5	H-6	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
55	7.364	7.458	6.995	8.344	7.967	1.088	0.884	7.407	1.853	4.761
20	7.397	7.513	7.007	8.337	8.012	1.072	0.881	7.361	1.909	4.704
10	7.342	7.460	6.995	8.329	7.784	1.001	0.908	7.510	1.912	4.805
0	7.323	7.452	6.991	8.313	7.929	1.015	0.896	7.380	1.840	4.788
−10	7.328	7.463	7.001	8.320	7.907	1.052	0.958	7.454	1.982	4.807
−30	7.303	7.453	6.996	8.307	8.104	1.089	0.865	7.398	1.806	4.792
−40	7.292	7.453	6.988	8.294	7.884	0.995	0.873	7.456	1.828	4.805
−60	7.297	7.474	7.014	8.299	7.929	1.061	0.888	7.395	1.862	4.760
−80	7.344	7.530	7.074	8.339	7.974	1.036	0.824	7.448	1.944	4.905

^{1}H *Nuclear Magnetic Resonance Spectra.*—Full spectral analysis shows that the observed pattern strictly corresponds to a four-spin ABMX system (Figure 3), and thus there is magnetic equivalence between chemically equivalent protons of the two pyridine rings. This constitutes evidence that the spectral parameters

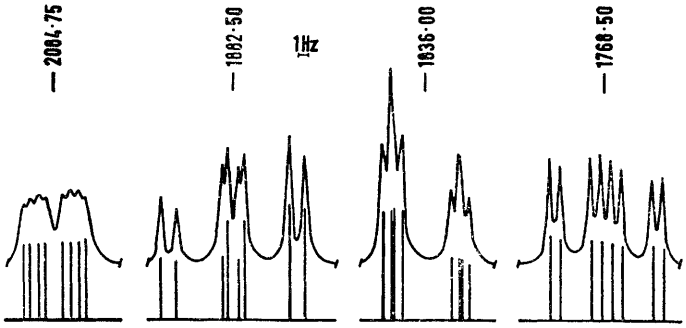


FIGURE 3 250 MHz Pulsed Fourier transform ^{1}H n.m.r. spectrum of di-2-pyridyl sulphide in CS_2 at −80 °C, top; and calculated spectrum, bottom. The signal for 6-H at 2 084.75 Hz is broadened by quadrupolar relaxation of nitrogen

* By V. Galasso, personal communication.

(Table 3) are averages which arise from rapid interconversion (on the n.m.r. time-scale) among the three equally populated twisted conformations. The fact that the observed pattern did not decoalesce in the temperature range +50 to −80°, indicates that even at low temperatures averaging of the proton signals of forms A—C occurs, owing to the rapid rotation of the pyridine rings. Extremely low temperatures, in fact, must be achieved in order to observe slow rotation of these rings.

Concerning possible isomerization pathways between A, B, and C, it is conceivable that the transition state involves in each case a Morino-like structure ($\omega = 0$, $\varphi = 90°$; $\omega = 180$, $\varphi = 90°$), as previously demonstrated by Finocchiaro [25] for diaryl derivatives of type Ar_2X.

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[25] P. Finocchiaro, *Gazzetta*, 1975, **105**, 149 and references therein.