

Nematic Phase Nuclear Magnetic Resonance Studies of Some Disubstituted Pyridines

Molecular Geometry of 2,6-Difluoropyridine

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The n.m.r. spectra of 2,6-difluoropyridine, 2,6-dichloropyridine and 3,5-dichloropyridine oriented in a nematic phase have been analysed and the average orientations of these molecules discussed and compared with other pyridines. The geometry of 2,6-difluoropyridine has been derived and indicates ring distortion in the vicinity of the fluorine substituents. Absolute signs of the major indirect coupling constants have been deduced.

Pyridine and its derivatives have been studied by the n.m.r. technique in both thermotropic and lyotropic nematic solvents by several groups.¹⁻⁹ Apart from accurate structural data on pyridine^{1, 6-8} and pentafluoropyridine³ conformational data have also been obtained for γ -picoline⁴ and pyridine-2,6-dicarbaldehyde.⁹ Direct comparison of the geometry of the pyridine molecule derived from n.m.r. data with the recently revised microwave data¹⁰ shows satisfactory agreement between the two methods. The primary aim of the present study was to obtain accurate structural information on 2,6-difluoropyridine in view of a possible substituent effect on the pyridine ring similar to that observed in fluorobenzene.¹¹ We have also measured nematic phase n.m.r. spectra of 2,6- and 3,5-dichloropyridine and attempted to correlate the orientations of various pyridines in liquid crystal solvents.

THEORY

The observed n.m.r. spectra of all the spin systems in question can be described by the Hamiltonian

$$\hat{\mathcal{H}} = -\frac{h}{2\pi} \sum_i \gamma_i B_0 (1 - \sigma_i) \hat{I}_{zi} + h \sum_{i < j} [(J_{ij} + D_{ij}) \hat{I}_{zi} \hat{I}_{zj} + \frac{1}{4} (\hat{I}_i^+ \hat{I}_j^- + \hat{I}_i^- \hat{I}_j^+) (2J_{ij} - D_{ij})] \quad (1)$$

where the first term represents the Zeeman energy of the magnetic nuclei and the second term describes the isotropic indirect coupling (J_{ij}) and direct dipole-dipole (D_{ij}) magnetic interactions between the nuclei. As the coupling constants, J_{ij} , are essentially solvent independent they are accurately measured from the isotropic spectra of the solute molecules and used as constants in the Hamiltonian (1). The n.m.r. spectrum of an oriented system then yields screening constants σ_i and direct couplings, D_{ij} . The former parameters are usually predominantly isotropic, but occasionally contain large anisotropic components. The latter parameters depend on internuclear distances, r , and angles, θ , between r and the magnetic flux density, B , in the following manner,

$$D_{ij} = -\frac{h\gamma_i\gamma_j}{2\pi^2 r_{ij}^3} S_{ij} \quad (2)$$

where

$$S_{ij} = \frac{1}{2} \langle 3 \cos^2 \theta_{ij} - \delta_{ij} \rangle \quad (3)$$

with the brackets denoting motional averaging of the solute molecules in the nematic medium. For a rigid molecule all S_{ij} values can be expressed by the elements of a symmetrical and traceless matrix $\{S\}$,¹² describing the average orientation of the molecules. The number of independent elements of this matrix is a function of molecular symmetry and the whole matrix depends on the choice of the Cartesian coordinate system associated with the molecule and its average orientation.

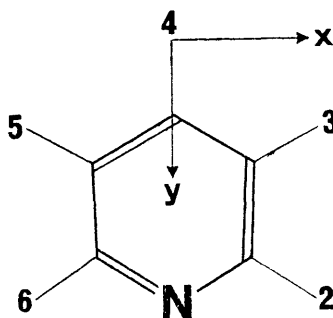


FIG. 1.—Numbering of magnetic nuclei and designation of coordinate system.

Fig. 1 shows the numbering of magnetic nuclei in the pyridine ring systems studied and the orientation of the coordinate system. All the molecules studied possess C_{2v} symmetry and therefore two S values define their average orientation. 2,6- and 3,5-Dichloropyridines are examples of AB_2 spin systems with two direct coupling constants. If the geometries of the molecules are known, their orientations can be derived. Frequencies and intensities of the nine observable lines can be expressed analytically and are tabulated by Englert and Saupe.¹³ 2,6-Difluoropyridine represents an $ABB'XX'$ spin system. Six different D values characterise this molecule and, as there are five unknowns, two S values and three relative coordinates, the system is over-determined and analysis of the spectrum yields full geometrical information.

In the present work it was found useful to define a parameter, S'_x ,

$$S'_x = \frac{S_{yy} - S_{xx}}{3S_{zz}} = -\frac{c_{x^2-y^2}}{\sqrt{3c_{3z^2-r^2}}} \quad (4)$$

describing the relative anisotropy of orientation in the x,y -plane. This parameter can be related to the theory of liquid crystal ordering in a manner analogous to that used by Gilson *et al.*¹⁴ for the parameter S_{xx}/S_{yy} . We prefer the choice of S'_x because it provides a clear physical interpretation. It can be shown, using the methods of Gilson *et al.* that $-1 \leq S'_x \leq 1$, provided that the z -axis represents the direction of smallest molecular dimension. If, for example, the x -axis of the molecule were held parallel to the magnetic field and the only degree of freedom were translational movements and rotations about the x -axis, then S'_x would equal one. In contrast, for a molecule such as benzene, S'_x equals zero since there is no anisotropy in the x,y -plane. Furthermore, the parameter is also symmetrised such that an interchange of x and y coordinates simply changes the sign and not the absolute value of S'_x .

It follows from the transformational properties of the matrix $\{S\}$ that rotation of

the coordinate system through an angle α about the z -axis leads to a new value of S'_x , namely,

$$S'_x = S'_x (\cos^2 \alpha - \sin^2 \alpha). \quad (5)$$

EXPERIMENTAL

Liquid crystal, Phase IV, which is a eutectic mixture of the two isomers of 4-methoxy-4'-n-butylazoxybenzene was obtained from E. Merck. 2,6-Difluoropyridine was obtained from Cambrian Chemicals Ltd., and the dichloropyridines from Ralph N. Emanuel Ltd. The solutions studied contained 10-20 mole % of solute in nematic solvent.

The majority of n.m.r. spectra were recorded on a JEOL MH-100 spectrometer equipped with a wide sweep unit NM-WS1 and standard variable temperature accessory. 4 kHz modulation side-bands were used for frequency calibration. Experiments requiring the highest precision were carried out on a Bruker HX90E FT spectrometer, operating at 90 MHz for ^1H resonance and 84.68 MHz for ^{19}F resonance and a Varian HR 220 CW spectrometer. No field-frequency lock was used to avoid introducing an external capillary reference to the sample with consequent deterioration in degree of ordering. The FT technique was found particularly suitable for this type of work. 16 pulses were generally sufficient to obtain satisfactory S/N ratios. This required a data acquisition time of only *ca.* 10 s and thus effects of magnetic field instabilities were minimized. Differences in line positions between two consecutive runs were less than 1 Hz. With 2,6-difluoropyridine the sample was not removed from the probe or disturbed in any way between running the ^1H and ^{19}F spectra. The use of the HR 220 spectrometer with its superconductive magnet had the advantages of better resolution and S/N ratio because the sample tube could be spun without destroying the solute orientation. However, the time required for accurate measurements of line positions by the CW technique was approximately two orders of magnitude greater than that taken for the FT spectra resulting in somewhat lower overall accuracy. Also, the ^{19}F spectrum could not be obtained in this case.

RESULTS AND DISCUSSION

Table 1 lists the isotropic J values taken from the literature for the three di-substituted pyridines. Fig. 2 shows a typical AB_2 spectrum. Numbering of the transitions corresponds to that given by Englert and Saupe.¹³ There are four possible

TABLE 1.—SELECTED VALUES OF INDIRECT COUPLING CONSTANTS^a FOR DISUBSTITUTED PYRIDINES

compound	J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}
3,5-dichloropyridine	—	2.0	—	—	—	—
2,6-dichloropyridine	—	—	—	—	7.8	—
2,6-difluoropyridine ¹⁵	(-)-2.5	8.0	1.2	(-)-12.2	7.9	0.55

^a All values in Hz.

solutions of this spin problem, corresponding to four different assignments of lines which predict very similar line intensities. For 3,5-dichloropyridine these are,

$$(a) D_{24} = 52.5 \text{ Hz}, D_{26} = 327.0 \text{ Hz}, S_{xx} = -0.189, S_{zz} = 0.179$$

$$(b) D_{24} = -55.0 \text{ Hz}, D_{26} = -326.0 \text{ Hz}, S_{xx} = 0.189, S_{zz} = -0.181$$

$$(c) D_{24} = 49.5 \text{ Hz}, D_{26} = -328.0 \text{ Hz}, S_{xx} = 0.190, S_{zz} = -0.091$$

$$(d) D_{24} = -51.0 \text{ Hz}, D_{26} = 327.5 \text{ Hz}, S_{xx} = -0.189, S_{zz} = 0.090$$

Solution (a) can be discarded as it produces a very unlikely orientation of the molecule with a large, positive S_{zz} value. Examination of the energy level diagram shows that it is possible to distinguish between the cases of like and unlike signs of

D values by the INDOR technique. For example, if the intensity of line 7 (fig. 2) is monitored a response is expected from lines three and eight in the case of like signs of D values or from lines one and six in the case of unlike signs of D values. By this

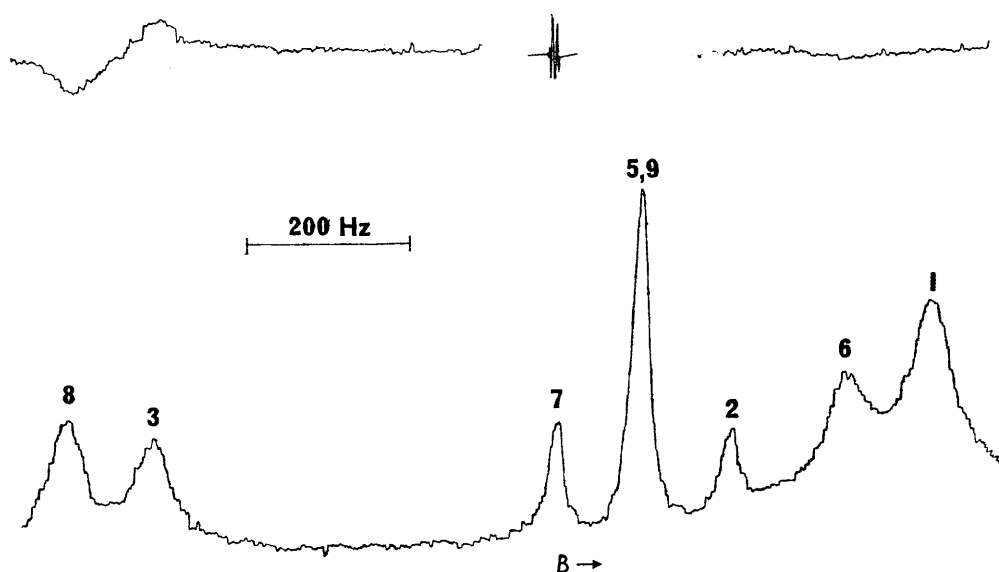


FIG. 2.—Spectrum of 3,5-dichloropyridine in Phase IV liquid crystal. Upper trace shows the INDOR response of line 7.

technique it was possible to eliminate solutions (c) and (d). Table 2 summarises the results for dichloropyridines. No meaningful error analysis was possible since the exact geometry of the molecules is not known and the S values in table 2 were computed on the basis of pyridine geometry. It can be seen that parameter S'_x defined

TABLE 2.—CHEMICAL SHIFT AND ORIENTATION PARAMETERS FOR DICHLOROPYRIDINES ORIENTED IN PHASE IV

compound	concentration mole %	approx. temp./K	$\delta_{AB}/\text{p.p.m.}$	S_{xx}	S_{yy}	S'_z
3,5-dichloropyridine	10	289	1.82 ^a	0.209	−0.197	0.37
	10	298	1.74 ^a	0.189	−0.181	0.36
	10	308	1.55 ^a	0.166	−0.161	0.35
	20	290	1.47 ^a	0.132	−0.130	0.34
2,6-dichloropyridine	10	298	0.26	0.133	−0.177	0.17
	15	298	0.26	0.095	−0.131	0.15

^a Isotropic component, $\delta_{\text{isotropic}} = 0.94 \text{ p.p.m.}$

by eqn (4) changes comparatively slowly with temperature and concentration and is thus a characteristic of a given solute molecule and its solvent. Both pyridines orient preferentially along the x -axis, the 3,5-isomer considerably more so than the 2,6-isomer. This is in marked contrast to the orientation of pyridine itself.

In the spectrum of 3,5-dichloropyridine (fig. 2) the outer pairs of lines are significantly broader than the remaining lines. Their widths decrease from *ca.* 70 Hz at

308 K to *ca.* 50 Hz at 289 K and are almost certainly due to nitrogen quadrupolar relaxation for the following reason. It can be shown that in any AB_2 oriented spin system when the coupling $D_{BB} \gg D_{AB}$ and δ_{AB} , then the mixed wavefunctions associated with $F_z = \pm \frac{1}{2}$ become essentially the basic product functions and the transitions associated with the outer pairs of lines in the spectrum become essentially B transitions. Thus, in fig. 2 the spectral lines 1, 3, 6 and 8 arising primarily from the hydrogen atoms adjacent to the nitrogen strongly reflect this quadrupolar influence. It should also be noted for 3,5-dichloropyridine that the chemical shift difference is very anisotropic whereas for the 2,6-isomer it is virtually isotropic (see table 2).

Fig. 3 shows the 1H and ^{19}F spectra of 2,6-difluoropyridine. 43 lines were assigned and used as data for the iterative program LAOCNOR which computed the chemical shifts and direct coupling constants satisfying the Hamiltonian (1) with minimum r.m.s. error between experimental and theoretical line frequencies. Results of iteration on all chemical shifts and direct couplings are given in table 3. The r.m.s. errors for the FT and CW spectra were 0.85 and 1.13 Hz respectively, indicating consistency within the experimental error in line position measurements. No single difference between experimental and computed frequency exceeded 2 Hz.

The subject of error analysis has been frequently discussed. In this work "probable errors of parameter sets" given in the program output were divided by the factor 0.6745 to obtain r.m.s. errors of parameter sets. These were then compared with "standard errors" also given by the program and the larger value chosen in each case. Two facts seem to justify this approach. First, the system is sufficiently overdetermined in terms of the ratio of the number of lines to the number of unknowns

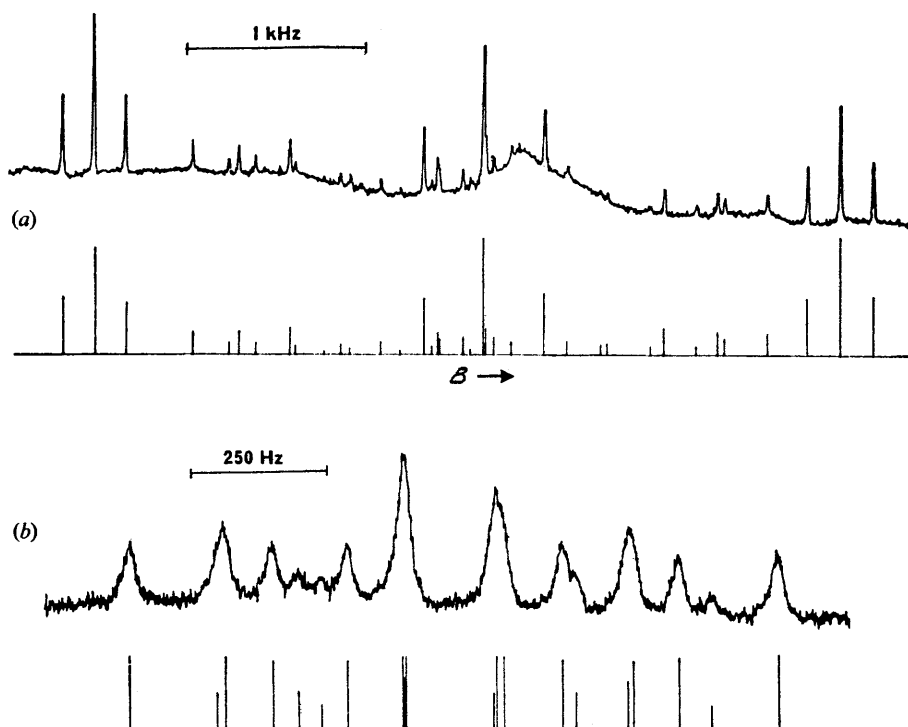


FIG. 3.—FT n.m.r. spectra of 2,6-difluoropyridine. (a) 90 MHz 1H spectrum, (b) 84.68 MHz ^{19}F spectrum. Theoretical spectra are shown below the experimental traces.

that the errors in experimental line positions are adequately taken into account. Secondly, the diagonal terms in the matrix of error vectors dominate over off-diagonal terms showing that all parameter sets can be determined more or less independently. We thus believe that in the present case, the error treatment in the program, originally developed by Castellano and Bothner-By,¹⁶ is sufficiently rigorous.

TABLE 3.—EXPERIMENTAL PARAMETERS OF THE SPECTRA OF 2,6-DIFLUOROPYRIDINE IN PHASE IV

	set A ^a	set B ^b
D_{23}^c/Hz	-365.47 ± 0.42	-374.27 ± 0.56
D_{24}/Hz	-143.74 ± 0.45	-136.05 ± 0.58
D_{25}/Hz	-191.68 ± 0.38	-174.85 ± 0.54
D_{26}/Hz	-338.14 ± 0.51	-304.90 ± 1.36
D_{34}/Hz	-1687.79 ± 0.23	-1536.05 ± 0.31
D_{35}/Hz	-419.35 ± 0.62	-378.02 ± 0.81
$\delta_{AB}/\text{p.p.m.}$	0.988 ± 0.005	0.992 ± 0.003

^a Values based on 90 MHz ¹H spectrum and 84.68 MHz ¹⁹F spectrum; 10 mole % solution; temperature 300 K. ^b Values based on 220 MHz ¹H spectrum; 15 mole % solution; temperature 294 K. ^c D values defined according to Snyder.¹⁹

The results of table 3 were then used as input for the iterative program SHAPE¹⁷ to find the best values of $\{S\}$ and relative geometry to satisfy the experimental D values and C_{2v} symmetry. The resulting relative geometry is given in table 4. Computed D values for this geometry agreed with the experimental D values within the errors given in table 3. The two independent experiments agreed within the computed errors supporting the above method of error analysis. The value of r_{35} was kept constant during the iteration and was chosen on the basis of microwave data for 2-fluoropyridine.¹⁸ Comparison of this geometry with that of pyridine,¹⁰ shows that H(3) is only slightly, (*ca.* 1 pm), shifted towards H(4) along the y -axis. If the ring remained undistorted, the NCF angle would need to increase by *ca.* 1° compared with

TABLE 4.—COMPUTED GEOMETRY OF 2,6-DIFLUOROPYRIDINE

	set A	set B
S_{xx}	0.140	0.126
S_{zz}	-0.167	-0.154
x_2^a	222.08 ± 0.15	222.09 ± 0.36
x_3	215.32	215.32
x_4	0.00	0.00
y_2	-383.86 ± 0.56	-383.30 ± 0.89
y_3	-127.61 ± 0.16	-127.52 ± 0.24
y_4	0.00	0.00
r_{23}	256.35	255.86
r_{24}	443.48	442.99
r_{25}	506.94	506.70
r_{26}	444.16	444.18
r_{34}	250.30	250.25
r_{35}	430.64^b	430.64^b

^a Coordinates and distances in pm. ^b r_{35} was kept constant during iteration.

the corresponding NCH angle in pyridine, and the C—F bond length would have to become 127 pm. While the former situation is quite possible, this C—F bond length seems unrealistically short and therefore some ring distortion appears highly likely.

The computed geometry (table 4) can be explained by "pushing in" the C(2) atom towards the centre of the ring with corresponding shrinkage of the C—N and C(2)—C(3) bonds. The exact amount of displacement depends on the assumed length of the C—F bond, but is probably at least 4 pm (for $r_{\text{C-F}} = 131$ pm). Similar effects were observed in fluorobenzene¹¹ and 2-fluoropyridine.¹⁸

An attempt was made to determine absolute signs of the largest isotropic coupling constants, J_{24} , J_{26} and J_{34} . This required iterative computations for the eight possible permutations of signs of the J values. The resulting r.m.s. errors are given in table 5. Cases with the same r.m.s. error differed only in the value of D_{24} indicating that J_{24} and D_{24} cannot be determined independently in this experiment. Cases 3-8 can be rejected by virtue of their much higher errors, some individual discrepancies between line frequencies being as high as 10 Hz. The set of D values corresponding to case 2 was found to be incompatible with C_{2v} symmetry and could only be satisfied by lowering the molecular symmetry to C_s . This was checked by the program SHAPE when

TABLE 5.—R.M.S. ERRORS BETWEEN OBSERVED AND CALCULATED LINE POSITIONS FOR VARIOUS SIGN COMBINATIONS OF INDIRECT COUPLING CONSTANTS IN 2,6-DIFLUOROPYRIDINE

case	J_{24}	signs of J_{26}	J_{34}	r.m.s. error/Hz
1	+	—	+	0.85
2	—	—	+	0.85
3	+	+	+	5.53
4	—	+	+	5.53
5	+	+	—	5.91
6	—	+	—	5.91
7	+	—	—	2.13
8	—	—	—	2.13

it was found that the resulting discrepancies in D values exceeded the experimental errors by a factor of 10. We thus conclude that J_{24} is positive, J_{26} negative and J_{34} positive, provided that the D values are negative. On the other hand, if we assume that J_{34} is known to be positive then this determines the absolute signs of J_{24} , J_{26} and the D values. The attempt to determine the sign of J_{23} by the same method was unsuccessful, because sign reversal did not produce any increase in errors. If, contrary to the expectations of Thomas and Griffin,¹⁵ J_{23} were positive, the following corrections would have to be made to the geometry :

$$\Delta x_2 = +0.02 \text{ pm}, \quad \Delta y_2 = -0.73 \text{ pm}, \quad \Delta y_3 = -0.18 \text{ pm}.$$

The question of the possible anisotropy in J_{FF} deserves some comment. It has been suggested³ that this can be measured by comparing the ratio D_{26}/D_{35} for different orientations. However, we feel that this method is rather insensitive in assessing anisotropic contributions. For the method to be applicable, it is necessary (a) that the ratio D_{26}/D_{35} be measured for grossly different orientations of solute molecules which is often difficult to achieve in practice and (b) that the accuracy of determination of this ratio be appreciably higher than changes in its value caused by the presence of D_{26} (indirect). In the present work, despite high accuracy in computed D values, it was felt that these conditions were not satisfied and thus no firm conclusions have been drawn regarding the magnitude of D_{26} (indirect). We accordingly are somewhat doubtful about the validity of the conclusions reached by Emsley *et al.*,³ that for pentafluoropyridine, all D_{FF} (indirect) values are negligibly small. In the present work we would only comment that the "best fit" D values from the SHAPE program differ by <0.5 Hz from the experimental D values (table 3) and thus appear to be

self-consistent. As the system is overdetermined this implies no appreciable D_{26} (indirect) contribution.

Table 6 provides a complete list of the pyridine-type systems investigated to date in thermotropic nematic solvents. Comparison of the orientation anisotropies in the xy plane is most easily made with the S'_x parameter defined earlier. The values for pyridine and 3,5-dichloropyridine suggest that this parameter is essentially solvent independent. The most notable variation in the parameter is its change of sign on going from pyridine and γ -substituted pyridine systems to perfluoropyridine and symmetrically disubstituted pyridines. This reflects a change in the principal axis of polarisability from the $C_2(y)$ axis in the former group of molecules to the x -axis direction in the latter group. However, in the absence of polarisability data for the majority of these molecules no quantitative interpretation of this S'_x variation can be given.

TABLE 6.—ORIENTATIONS OF PYRIDINES IN THERMOTROPIC NEMATIC SOLVENTS

compound	solvent	experimental S'_x	estimated S'_x	reference
pyridine	A	-0.10		1
pyridine	B	-0.12		7
pyridine-bromine complex	Phase IV	-0.18		6
γ -picoline	EBBA + C	-0.49	-0.49 ^a	4
pyridine-2,6-dicarbaldehyde	Phase IV	0.33		9
3,5-dichloropyridine	Phase IV	0.35	0.21 ^b	this work
3,5-dichloropyridine	MBBA	0.32	0.21 ^b	5
2,6-dichloropyridine	Phase IV	0.16	0.21 ^b	this work
2,6-dibromopyridine	D	0.21	0.23 ^c	2
2,6-difluoropyridine	Phase IV	0.22	0.11 ^d	this work
pentafluoropyridine	Phase IV	0.14	0.11 ^d	3

A = anisole-*p*-azophenyl-*n*-capronate; B = $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{OCOPr} + \text{C}_5\text{H}_{11}\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_4$; C = *O*-carbobotoxy-4-oxybenzoic acid ethoxyphenyl ester; D = 4,4'-di-*n*-hexyloxyazoxybenzene.

^a Value based on $S'_x = -0.38$ for toluene.²¹ ^b Value based on $S'_x = -0.63$ for *p*-dichlorobenzene.²⁰ ^c Value based on $S'_x = -0.67$ for *p*-dibromobenzene.²⁰ ^d Value based on $S'_x = -0.44$ for *p*-difluorobenzene.²⁰

An attempt has been made to compare these S'_x values with values based on substituted benzenes for which there are orientation data available. The S'_x values in the fourth column of table 6 were calculated using a simple additive model and the available data for mono- and di-substituted benzenes (see footnote table 6). The angular transformation [eqn (5)] was also applied where necessary. With certain notable exceptions the agreement between experimental and estimated S'_x values is quite good. In 2,6-difluoropyridine the discrepancy may be due to a specific solute-solvent interaction involving the F atoms. In 2,6- and 3,5-dichloropyridine, the experimental S'_x values are notably different. The simple additive method used here cannot distinguish between these two molecular shapes, but it is perhaps noteworthy that the estimated S'_x value is roughly the mean of the two experimental values.

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