Nuclear Magnetic Resonance Conformational Studies of *C*-Substituted Pyrrolecarbaldehydes. Part I. Substituent Effects on Aldehyde Conformations as shown by Long Range Coupling Constants

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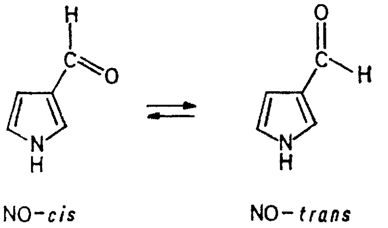
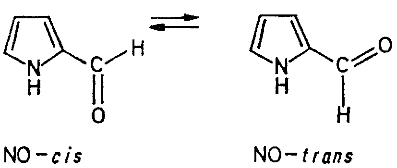
The conformations of the formyl group of the two pyrrolecarbaldehydes and the mono-iodo, -nitro, -ethoxycarbonyl, and -formyl derivatives have been determined by a study of the ^{5}J and ^{4}J long range coupling constants. The results show the influence of the nature and position of the substituent on the relative proportions of the two conformers. The influence of solvent on the value of ^{5}J and ^{4}J is considered for certain cases.

DURING the last few years numerous n.m.r. studies [1-9] have been carried out on the conformation of the formyl group in heterocyclic compounds. The stereospecificity of ^{5}J couplings has been shown and recently the stereospecificity of ^{4}J couplings has also been established.[10,11] These couplings thus allow the conformer proportions to be determined fairly precisely.





Until now research has been essentially concerned with thiophen- and furan-carbaldehydes [1-6] and work on the pyrrole series is relatively rare.[7-9] It thus appeared interesting to study a series of substituted pyrrolecarbaldehydes in order to show the influence of the nature and the position of the substituent.

For pyrrole-2- and -3-carbaldehydes, the formyl group can exist in two conformations, NO-*cis* and NO-*trans*. In all four conformers the requirements for one ^{4}J and one ^{5}J coupling are fulfilled; however N–H exchange is normally fast enough to cause effective decoupling of ^{4}J in the 2-NO-*cis*- and ^{5}J in the 3-NO-*cis*-conformation. It is assumed that all couplings not derived from stereospecific through-bond interactions are zero. When the maximum value of the stereospecific coupling ($^{n}J_{\text{max.}}$) is known, it is thus possible to calculate the population ratio from relationship (I) where $^{n}J_{\text{obs.}}$ is the observed coupling

$$p = 100\ {}^{n}J_{\text{obs.}}/{}^{n}J_{\text{max.}} \qquad \text{(I)}$$

and p the percentage conformer corresponding to the long-range coupling determined.

The values of the coupling constants, and thus the relative conformer populations, are affected by the nature of the solvent; therefore we recorded the spectra of several compounds in different solvents in order to try to relate the conformer populations to the physicochemical characteristics of the solvents.

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[2] M. L. Martin, J.-C. Roze, G. J. Martin, and P. Fournari, *Tetrahedron Letters*, 1970, 3407.
[3] B. Roques, S. Combrisson, C. Riche, and C. Pascard-Billy, *Tetrahedron*, 1970, **26**, 3555.
[4] M. C. Fournie-Zaluski and B. Roques, *Tetrahedron Letters*, 1970, 4909.
[5] B. Roques and M. C. Fournie-Zaluski, *Tetrahedron Letters*, 1971, 145.
[6] B. Roques and M. C. Fournie-Zaluski, *Org. Magnetic Resonance*, 1971, **3**, 305.
[7] L. Arlinger, K.-I. Dahlqvist, and S. Forsén, *Acta Chem. Scand.*, 1970, **24**, 672.
[8] B. Roques, C. Jaureguiberry, M. C. Fournie-Zaluski, and S. Combrisson, *Tetrahedron Letters*, 1971, 2693.
[9] R. A. Jones and P. H. Wright, *Tetrahedron Letters*, 1968, 5495.
[10] M. Farnier and T. Drakenberg, *Tetrahedron Letters*, 1973, 429.
[11] B. P. Roques and S. Combrisson, *Canad. J. Chem.*, 1973, **51**, 573.

RESULTS AND DISCUSSION

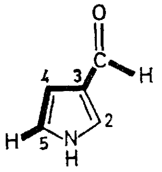
Conformations of Pyrrole-3-carbaldehydes in [$^2H_6$]-*Acetone*.—The ^5J and ^4J couplings obtained for compounds (1)—(9) are shown in Table 1.

TABLE 1

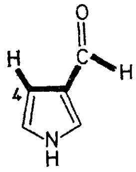
Spin–spin coupling constants and conformational preferences for pyrrole-3-carbaldehydes

3-Aldehyde	Solvent	Coupling constants		%
		^5J/Hz	^4J/Hz	*trans*
Unsubstituted (1)	[$^2H_6$]DMSO	0·79	$^4J_{CHO-H(4)}$ 0·42	95
	[$^2H_6$]Acetone	0·77	$^4J_{CHO-H(4)}$ 0·40	95
2-I (2)	[$^2H_6$]Acetone	0·80	$^4J_{CHO-H(4)}$ 0·40	95
2-NO_2 (3)	[$^2H_6$]Acetone	0·76	$^4J_{CHO-H(4)}$ 0·42	95
2-CO_2Et (4)	[$^2H_6$]Acetone	0·80	$^4J_{CHO-H(4)}$ 0·46	100
5-I (5)	[$^2H_6$]DMSO		$^4J_{CHO-H(4)}$ 0·42	90
	[$^2H_6$]Acetone		$^4J_{CHO-H(4)}$ 0·37	80
5-NO_2 (6)	[$^2H_6$]DMSO		$^4J_{CHO-H(4)}$ 0·26	55
	[$^2H_6$]Acetone		$^4J_{CHO-H(4)}$ ~0·23	50
5-CO_2Et (7)	[$^2H_6$]DMSO		$^4J_{CHO-H(4)}$ 0·32	70
	[$^2H_6$]Acetone		$^4J_{CHO-H(4)}$ ~0·22	50
4-NO_2 (8)	[$2H_6$]DMSO		$^4J_{CHO-H(2)}$ 0·40	0
	[$^2H_6$]Acetone		$^4J_{CHO-H(2)}$ 0·40	
	THF		$^4J_{CHO-H(2)}$ 0·40	
4-I (9)	[$^2H_6$]DMSO	0·52		65
	DMF	0·48		60
	THF	0·36	$^4J_{CHO-H(2)}$ 0·23	45
	[$^2H_6$]Acetone	~0·30	$^4J_{CHO-H(2)} < {}^5J_{CHO-H(5)}$	40

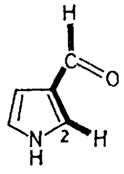
^{5}J *Couplings*. These couplings are observed only for compounds (1)—(4) and (9). The stereospecificity rule predicts a ^5J coupling in the *trans*-conformer (A).



(A)



(B)



(C)

The maximum value (0·80 Hz) of the coupling constant $^5J_{CHO-H(5)}$ was found for 2-iodopyrrole-3-carbaldehyde (2) and for ethyl 3-formylpyrrole-2-carboxylate (4). This maximum value is, moreover, of the same order of magnitude as that observed for the furan [4] (0·75 Hz) and thiophen [4] series (1·00 Hz). The formyl group in compounds (2) and (4) can thus be considered as entirely *trans*, and application of equation (I) shows that pyrrole-3-carbaldehyde (1) and 2-nitropyrrole-3-carbaldehyde are preferentially (95%) in the NO-*trans*-conformation. For 4-iodopyrrole-3-carbaldehyde (9), the $^5J_{CHO-H(5)}$ coupling is *ca.* 0·30 Hz (the error being distinctly $> \pm 0·03$ Hz) which corresponds to *ca.* 40% *trans*-conformer. Finally, for 4-nitropyrrole-3-carbaldehyde (8), no coupling is observed between the aldehyde proton and H(5) indicating that the *cis*-conformer is dominant.

^{4}J *Couplings*. As with ^5J coupling, numerous cases of ^4J coupling are observed. Thus for pyrrole-3-carbaldehyde (1), the formyl proton is coupled with H(4) and H(5) but not with H(2). The study of the ^5J coupling showed that the formyl group is virtually completely in the NO-*trans*-conformation; the ^4J coupling thus imposes a special conformation on the various bonds. [Note that the results obtained for compound (1) differ from those reported by Anderson *et al*; [12] these authors in fact observed no coupling for the formyl proton signal of pyrrole-3-carbaldehyde.]

For 4-substituted aldehydes ^4J coupling with H(2) appears and the stereospecificity of these couplings is represented by conformers (B) and (C).

(a) Pyrrole-3-carbaldehyde (1) and 2-substituted pyrrole-3-carbaldehydes (2)—(4). The maximum value of $^4J_{CHO-H(4)}$ is observed for ethyl 3-formylpyrrole-2-carboxylate (4) (0·46 Hz). This confirms that this compound is essentially entirely in the *trans*-conformation. For the compounds (1)—(3) analysis of the $^4J_{CHO-H(4)}$ values lead to results in good agreement with those determined for $^5J_{CHO-H(5)}$.

(b) 4-Substituted pyrrole-3-carbaldehydes. For 4-nitropyrrole-3-carbaldehyde (8) $^4J_{CHO-H(2)}$ is 0·40 Hz. In order to confirm that this really corresponds to the maximum coupling value we recorded spectra in [$^2H_6$]DMSO and THF. No variation in the coupling constant was observed as expected (see Table 1) when the maximum coupling value is not attained. Given that no $^5J_{CHO-H(5)}$ coupling was apparent and that, in contrast, a $^4J_{CHO-H(2)}$ coupling was found whose value did not vary in solvents of different polarity, the formyl group of 4-nitropyrrole-3-carbaldehyde can be considered as entirely in the NO-*cis*-conformation.

Analysis of the formyl proton signal from 4-iodopyrrole-3-carbaldehyde (9) is difficult. The $^5J_{CHO-H(5)}$ value (*ca.* 0·30 Hz) gives *ca.* 40% *trans*-conformation. The 60% *cis*-conformation should give rise to a $^4J_{CHO-H(2)}$ coupling of *ca.* 0·24 Hz. These two values are too low and similar for the ^4J measurement to be carried out with sufficient accuracy; it is only possible to state that $^4J_{CHO-H(2)}$ is less than $^5J_{CHO-H(5)}$.

(c) 5-Substituted pyrrole-3-carbaldehydes (5)—(7). No $^5J_{CHO-H(5)}$ coupling is apparent and only the $^4J_{CHO-H(4)}$ values permit conformational analysis. When the 5-position is occupied by an iodine atom there is a relatively high proportion of *trans*-conformer (80%), and for a 5-ethoxycarbonyl or -nitro-group the proportions of the conformers are virtually equal. It should be noted that for compounds (6) and (7) the $^5J_{CHO-H(4)}$ values obtained by analysis of the formyl signal are not very accurate; there is probably a $^4J_{CHO-H(2)}$ coupling but its calculated value (*ca.* 0·2 Hz) is too low and similar to that of $^4J_{CHO-H(4)}$ to allow precise analysis.

The results for compounds (1)—(9) suggest the following comments.

(*a*) For pyrrole-3-carbaldehyde the formyl group is predominantly (95%) in the NO-*trans*-conformation. This result is in good agreement with that given by a dipole moment study [13] of this aldehyde. It is noted

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[12] H. J. Anderson and H. Nagy, *Canad. J. Chem.*, 1972, **50**, 1961.

[13] D. M. Bertin, M. Farnier, and H. Lumbroso, *Compt. rend.*, 1972, **274**, 462.

elsewhere that the thiophen and furan isosteres [4] have conformational behaviour analogous to that of pyrrole-3-carbaldehyde.

(*b*) The introduction of a substituent can influence markedly the conformation of the formyl group, this influence varying with the nature and above all the position of the substituent. For 2-substituents the NO-*trans*-conformation is favoured by the presence of NO_2, CO_2Et, or I, though this conformation is already favoured by the unsubstituted aldehyde. For 4-substituents the *cis*-conformer is normally favoured by NO_2 or I either by chelation or by electrostatic repulsion between two oxygen atoms or between the iodine and oxygen atoms. The effect of the nitro-group is particularly marked since in this case the formyl group is entirely in the NO-*cis* conformation. 5-Substituents are far from the formyl group and analysis of the formyl signal shows that the more polar substituents increase the population of the NO-*cis*-conformer. This agrees with the expected effect of dipolar interactions, since in the NO-*cis*-conformation the substituent and the C=O bond moments are almost antiparallel. This explanation can also be used to rationalize the effects of 4-substituents on the conformer ratio.

The discussion is based on the assumption that stereospecific long-range couplings are not affected by substituent. This may not be true but the substituent effect on coupling is probably small enough not to affect the conclusions drawn here.

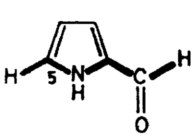
Conformations of Pyrrole-2-carbaldehydes in [$^2H_6$]-*Acetone*.—The values of the coupling constants for the pyrrole-2-carbaldehydes studied are given in Table 2.

TABLE 2

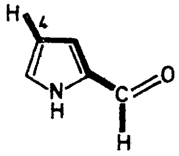
Spin–spin coupling constants and conformational preferences for pyrrole-2-carbaldehydes

2-Aldehyde		Solvent	Coupling constants		%
			^5J/Hz	^4J/Hz	*trans*
Unsubstituted	(10)	[$^2H_6$]Acetone	$^5J_{CHO-H(5)}$ 1·05		5
3-I	(11)	[$^2H_6$]Acetone	$^5J_{CHO-H(5)}$ 1·11		0
3-CO_2Et	(12)	[$^2H_6$]Acetone	$^5J_{CHO-H(5)}$ 0·95		15
3-NO_2	(13)	[$^2H_6$]Acetone	$^5J_{CHO-H(5)}$ 0·88		20
4-I	(14)	[$^2H_6$]Acetone	$^5J_{CHO-H(5)}$ 1·02		8
4-NO_2	(15)	[$^2H_6$]Acetone	$^5J_{CHO-H(5)}$ 1·03		7
5-CO_2Et	(16)	[$^2H_6$]DMSO	$^5J_{CHO-H(4)}$ 0·40—0·45	$^4J_{CHO-H(3)}$ ~ 0·12	45
		[$^2H_6$]Acetone	$^5J_{CHO-H(4)}$ $\leqslant$0·20—0·25		25
5-NO_2	(17)	[$^2H_6$]DMSO	$^5J_{CHO-H(4)}$ 0·45	$^4J_{CHO-H(3)}$ ~ 0·13	50
		DMF	$^5J_{CHO-H(4)}$ 0·32		35—40
		[$^2H_6$]Acetone	$^5J_{CHO-H(4)}$ 0·24		25—30
		THF	$^5J_{CHO-H(4)}$ $\leqslant$0·20		20—25

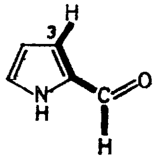
Two types of stereospecific ^5J couplings can arise from conformations (D) and (E). For the unsubstituted aldehyde (10) and for the 3-substituted aldehydes, two ^5J couplings are possible but only $^5J_{CHO-H(5)}$ appears. The maximum value (1·11 Hz) is observed for 3-iodopyrrole-2-carbaldehyde (11), and this compound can be considered to exist only in the NO-*cis*-conformation. The conformer percentages shown in Table 2 for compounds (10)—(15) were determined from equation (I).



(D)



(E)



(F)

^4J Couplings arise from interaction with H(3) when there is an NO-*trans*-conformation [conformer (F)]. Experiments have shown that this coupling is not observed for compounds (10) and (14)—(17).

The results in Table 2 suggest the following comments.

(*a*) The formyl group of pyrrole-2-carbaldehyde (10) is predominantly in the NO-*cis*-form. It should be noted all the same that the coupling value observed by us (1·05 Hz) is consistent with *ca.* 5% *trans*-conformer, and this value is slightly lower than that reported by Roques *et al.*[11] and by Shimokawa *et al.*[14] The existence of the *trans*-conformer was also verified by a low temperature study.[7] The relative intensities of the signals for the two conformers at −70° give *ca.* 5% *trans*-conformer.

(*b*) For 3-substituted aldehydes, the preferred conformation is NO-*cis*. For 3-iodopyrrole-2-carbaldehyde (11), the *cis*-conformation is stabilized by the repulsion between the formyl oxygen and the iodine atom. However, and curiously for 3-NO_2 or -CO_2Et substituents [compounds (12) and (13)] the percentage of the *cis*-conformer tends to decrease.

(*c*) As for the thiophen and furan series,[6] and in contrast to the situation observed for the 5-substituted pyrrole-β-carbaldehydes, the introduction of a substituent at the 4-position [compounds (14) and (15)] hardly influences the formyl group conformation whatever the nature of the group introduced. It is probable that in this case the major effect derives from hydrogen bonding.

(*d*) 5-Nitro- and 5-ethoxycarbonyl-pyrrole-2-carbaldehydes show $^5J_{CHO-H(4)}$ coupling, but in [$^2H_6$]acetone analysis of the signals is difficult (see later). We note, all the same, that the presence of 5-NO_2 or 5-CO_2Et contributes to the suppression of the NO-*cis*-conformer. This is probably due to the fact that hydrogen bonding with nitrogen can affect both the formyl oxygen and one of the oxygen atoms of the group introduced.

*Conformations of Pyrrole-*2,4- *and* -2,5-*dicarbaldehydes.*—*Pyrrole-*2,4-*dicarbaldehyde.* When this compound is dissolved in [$^2H_6$]acetone two couplings are observed: $^5J_{CHO(2)-H(5)}$ 1·05 Hz and $^4J_{CHO(4)-H(3)}$ 0·28 Hz. The conformer percentages are: 2-CHO 5% *trans* and 4-CHO 60% *trans*. These results are in excellent agreement with those reported both for 4-substituted 2-aldehydes and for 5-substituted 3-aldehydes. The introduction of a 4-substituent in pyrrole-2-carbaldehyde does not change the conformer ratio. On the other hand the

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[14] S. Shimokawa, H. Fukui, and J. Sohma, *Mol. Phys.*, 1970, **19**, 695.

presence of a 5-substituent in pyrrole-3-carbaldehyde markedly increases the proportion of NO-*cis*-conformer.

Pyrrole-2,5-*dicarbaldehyde*. The signal of the protons of the two formyl groups shows no coupling in [$^2H_6$]acetone or [$^2H_6$]DMSO, but a certain broadening of the peak suggests that these protons are nonetheless coupled with the ring protons. Thus an accurate determination of the conformations of the formyl groups for this dialdehyde is not possible at room temperature. This compound was studied at low temperature and the results are reported in the following paper.[15]

Solvent Effects.—We were particularly interested in those compounds for which analysis of the spectra in [$^2H_6$]acetone presented some difficulty or led to results with a high margin of error.

4-*Iodopyrrole*-3-*carbaldehyde*. In [$^2H_6$]acetone, the formyl group of 4-iodopyrrole-3-carbaldehyde is *ca.* 40% in the NO-*trans*-conformation. For the thiophen isostere in $CDCl_3$,[4] no coupling of the formyl proton was observed and the compound can be considered as entirely *cis*. This difference in behaviour could be due either to the nature of the heteroatom or the nature of the solvent. We have attempted to estimate the importance of each of these factors. We were not able to compare the conformer proportions of the thiophen and pyrrole isosteres in $CDCl_3$ because of the insolubility of the pyrrole derivative in this solvent. We studied the spectra obtained for 4-iodothiophen-3-carbaldehyde in THF and [$^2H_6$]DMSO (in which the pyrrole isostere is equally soluble) with the following results: [$^2H_6$]DMSO, $^5J_{CHO-H(5)}$ 0·49 Hz, % *trans*-conformation 50; THF, 0·30 Hz, 30. The percentages of the *trans*-conformer were calculated taking into account the fact that the maximum value of $^5J_{CHO-H(5)}$ observed[4] in the thiophen series is 1·00 Hz. Comparison of these values with those shown in Table 1 for the pyrrole isostere shows that the behaviour of the two iodinated aldehydes is very similar. The influence of the solvent is apparent from the results in Table 1. Assuming that the maximum value of the coupling constant is only slightly affected by the solvent, the percentage of *trans*-conformer increases in the order: [$^2H_6$]acetone, THF, DMF, [$^2H_6$]DMSO. One probable explanation is based on the fact that more polar solvents will stabilize the more polar conformer.[16] Summation of bond moments for the two conformers shows that the *trans*-conformer is the more polar.

5-*Substituted pyrrole*-3-*carbaldehydes*. The 5-substituted pyrrole-3-carbaldehydes (5)—(7) were studied in [$^2H_6$]acetone and [$^2H_6$]DMSO. As in the previous case, and for the same reason, the value of $^4J_{CHO-H(4)}$ (and thus the proportion of *trans*-conformer) increases (this time slightly) with increasing polarity of the solvent.

5-*Substituted pyrrole*-2-*carbaldehydes*. As the study of compounds (16) and (17) in [$^2H_6$]acetone does not allow precise conformational analysis, the spectra of these compounds were taken in solution in a variety of solvents. The values of the coupling constants observed are shown in Table 2; we note an increase in $^5J_{CHO-H(4)}$ in the series THF < [$^2H_6$] acetone < DMF < [$^2H_6$]DMSO. In addition, with [$^2H_6$]DMSO a $^4J_{CH-OH(3)}$ coupling appears.

In order to determine accurately the percentages of the *trans*-conformer using $^5J_{CHO-H(4)}$ it was necessary to know the maximum value of this coupling, *i.e.* that given by a pyrrole compound possessing a 2-formyl group entirely in the *trans*-form. Roques *et al.* report that the formyl group of ethyl 2-formylpyrrole-1-carboxylate[8] and 1-acetylpyrrole-2-carbaldehyde[11] should be entirely in the *trans*-form. The value of $^5J_{CHO-H(4)}$ observed for these two compounds is 0·70 Hz.

If we accept this value we deduce that for the nitro-aldehyde (17) in [$^2H_6$]DMSO the percentage of *trans*-conformer is *ca.* 65%. In this case $^4J_{CHO-H(3)}$ is abnormally low compared to $^4J_{CHO-NH}$ 0·31 Hz obtained by Shimokawa *et al.*[14] for pyrrole-2-carbaldehyde and $^4J_{CHO-H(3)}$ 0·37 Hz reported by Roques *et al.*[11] for 1-acetylpyrrole-2-carbaldehyde (values which are moreover close to the maxima observed for ^4J of the pyrrole-3-carbaldehydes). A similar conclusion is drawn from the values obtained for the ester-aldehyde (16) studied in the same solvent.

Thus the choice of a $^5J_{CHO-H(4)}$ maximum value derived from a single examination of pyrrole derivatives seems very dubious. We thought it preferable to make this choice from the results obtained for the furan series; a reliable value for the maximum $^5J_{CHO-H(4)}$ coupling was obtained from the study of furfuraldehyde at low temperature. At −115° the *trans*-conformer signal has $^5J_{CHO-H(4)}$ 0·85 Hz.[3,17] (Dahlqvist and Forsén[17] however made the reserve assignment.) Incidentally the value of $^5J_{CHO-H(5)}$ observed for the *cis*-conformer of furfuraldehyde is of the same order of magnitude as the maximum value of the same coupling constant observed for the pyrrole series. Thus, and as a first approximation, we shall assume that the maximum $^5J_{CHO-H(4)}$ is *ca.* 0·85 Hz. The conformer percentages obtained for compounds (16) and (17) using this value are shown in Table 2. It may be noted that for the ester-aldehyde (16) studied in [$^2H_6$]acetone and the nitro-aldehyde (17) studied in THF a precise value for $^5J_{CHO-H(4)}$ cannot be obtained; we only indicate the upper and lower limits of the conformer percentages. Further, the $^4J_{CHO-H(3)}$ values observed in [$^2H_6$]DMSO for the two aldehydes (16) and (17) are still low compared with the value obtained for this type of coupling in 1-acetylpyrrole-2-carbaldehyde (0·37 Hz), but there is a high margin of error in the determination of ^4J.

Examination of Table 2 shows that the conformer percentages are markedly influenced by the nature of the solvent: the proportion of *trans*-conformer increases

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[15] M. Farnier and T. Drakenberg, following paper.

[16] L. Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

[17] K.-I. Dahlqvist and S. Forsén, *J. Phys. Chem.*, 1965, **69**, 4062.

with increasing polarity of the solvent. For compound (17), however, this conflicts with the rule that the more polar conformer should be stabilized in the more polar solvent. The stabilization of the less polar *trans*-conformer in polar solvents is probably due to the fact that intramolecular hydrogen bonding between NH and C=O is disfavoured relative to intermolecular hydrogen bonding between the nitrogen proton and the polar solvent.

EXPERIMENTAL

Materials.—Compounds (1)—(17) were prepared by methods given in the literature.[18-20] Similarly pyrrole-2,4-dicarbaldehyde,[18] pyrrole-2,5-dicarbaldehyde,[21] and 4-iodothiophen-3-carbaldehyde [22] were prepared as previously described.

N.m.r. Spectra.—The n.m.r. spectra were recorded at 100 MHz on a Varian XL 100 instrument with tetramethylsilane as internal standard: settings, sweep time 2500 and 5000 s; sweep width 25 and 50 Hz; sweep rate $\leqslant 0{\cdot}01$ Hz s^{-1}; concentration $\leqslant 30$ mg per 0·5 ml of solvent. The spectra were analysed as first order and coupling constants were measured directly from the spectra. Chemical shifts are given in the literature.[18,19] For most compounds J values are $\pm 0{\cdot}03$ Hz. For certain compounds, owing in part to the couplings of the ring protons with the nitrogen proton and in part to the presence of the nitrogen atom itself, the signal of the formyl proton alone can be analysed.

Sign of Coupling Constants.—We have not determined the relative signs of the coupling constants; thus in this work, all the coupling constants are given in absolute values. This problem has however been studied by other authors; if the ${}^5J$ constants are positive the ${}^4J$ constants are negative.[11,14]

This study was carried out in the laboratory of Professor S. Forsén, Lund. M. F. thanks Professor S. Forsén for his hospitality and interest.

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[18] P. Fournari, M. Farnier, and C. Fournier, *Bull. Soc. chim. France*, 1972, 283.

[19] M. Farnier and P. Fournari, *Bull. Soc. chim. France*, 1973, 351.

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