Conformations of Furan-, Pyrrole-, and Pyridine-carbaldehydes: an *ab initio* Molecular Orbital Study

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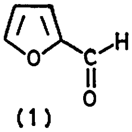
Ab initio molecular orbital theory with the minimal STO-3G basis set was used to study the conformational preferences of furan-2-, furan-3-, pyrrole-2-, pyrrole-3-, pyridine-2-, pyridine-3-, and pyridine-4-carbaldehydes. The calculations yielded conformational energies, potential functions for internal rotation, rotational barriers, stabilisation energies, charge distributions, electric dipole moments, and π-overlap populations. Results were compared with available experimental data, and analysed to identify the main intramolecular factors determining the favoured conformations of these molecules.

MUCH effort has been directed recently towards determining the conformational preferences of simple heteroaromatic aldehydes, and a wide variety of physical methods has been applied to problems of this nature. We have previously reported and analysed infinite-dilution electric dipole moments and molar Kerr constants for several such molecules (pyridine-,[1] pyrrole-,[2] furan-, and thiophen-carbaldehydes [3]) and many other aromatic carbonyl compounds as solutes in non-dipolar solvents. It is now recognised, however, that the position of equilibrium between alternative rotational isomers of a particular molecule can be markedly medium-dependent. For example, in the much-studied case of furan-2-carbaldehyde,[4] the *trans*-form (2) is preponderant in the vapour phase, but the *cis*-isomer (1) is undoubtedly the more abundant in dipolar solvents. Such effects, which occur in dense media because of preferential solvation and/or reaction-field stabilisation of one isomer relative to the other,[5,6] are likely to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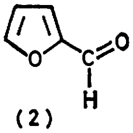
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[1] C. L. Cheng and G. L. D. Ritchie, *J.C.S. Perkin II*, 1973, 1461.

[2] C. L. Cheng, I. G. John, G. L. D. Ritchie, and P. H. Gore, *J.C.S. Perkin II*, 1974, 1318.

[3] C. L. Cheng, I. G. John, G. L. D. Ritchie, P. H. Gore, and L. Farnell, *J.C.S. Perkin II*, 1975, 744.

[4] See ref. 3 for a summary up to 1973 of the main references to studies of furan-2-carbaldehyde.

[5] R. J. Abraham and T. M. Siverns, *Tetrahedron*, 1972, **28**, 3015.

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obscure the fundamental intramolecular features determining the relative stabilities of the possible stereostructures.

In order to establish the preferred conformations of the free molecules, we applied *ab initio* molecular orbital theory to the heteroaromatic aldehydes mentioned above. The calculations also yielded rotational barriers, stabilisation energies, charge distributions, electric dipole moments, and π-overlap populations. Semiempirical calculations for some of these molecules have been reported previously,[7] but only furan-2-carbaldehyde[8] and pyridine-2-carbaldehyde[9] have been studied by using *ab initio* molecular orbital theory.

METHOD AND RESULTS

Standard LCAO SCF molecular orbital theory was used with the Gaussian 70 series of programs[10] and the minimal STO-3G basis set,[11] which has previously been used successfully in a variety of conformational studies.[12,13]

TABLE 1

Calculated total and relative energies for parent ring systems and for stable conformations of derived carbaldehydes

Molecule	Conformation	Total energy[a] (hartree)	Relative energy (kJ mol^{-1})
Benzene		−227.890 06[b]	
Furan		−225.749 75	
Pyrrole		−206.223 82	
Pyridine		−243.637 79	
Benzaldehyde	CCCO planar	−339.115 40[b]	0
Furan-2-carbaldehyde	OCCO *cis*	(−336.976 20)	3.45
	OCCO *trans*	−336.977 52	0
Furan-3-carbaldehyde	C(2)CCO *cis*	−336.976 06	0
	C(2)CCO *trans*	(−336.975 83)	0.62
Pyrrole-2-carbaldehyde	NCCO *cis*	−317.455 58	0
	NCCO *trans*	(−317.452 64)	7.75
Pyrrole-3-carbaldehyde	C(2)CCO *cis*	−317.452 59	0
	C(2)CCO *trans*	(−317.452 01)	1.55
Pyridine-2-carbaldehyde	NCCO *cis*	(−354.858 92)	10.23
	NCCO *trans*	−354.862 80	0
Pyridine-3-carbaldehyde	C(2)CCO *cis*	(−354.861 91)	1.53
	C(2)CCO *trans*	−354.862 48	0
Pyridine-4-carbaldehyde	CCCO planar	−354.861 57	0

[a] Energy of less stable rotational isomer in parentheses. [b] From ref. 13.

The microwave structures (furan,[14] pyrrole,[15] and pyridine[16]) for the heteroaromatic rings were used as the basis for constructing molecular geometries, with standard[17] bond lengths and bond angles being adopted for the carbaldehyde group. Conformations are defined by the dihedral angle, ϕ, between the planes of the heteroaromatic ring and the carbaldehyde group, with $\phi = 0°$ corresponding to the structure having the carbonyl group *cis* to the heteroatom. Computations were performed for dihedral angles of 0, 60, 90, 120, and 180°.

Calculated total and relative energies for the parent ring systems and for the stable conformations of the derived aldehydes are listed in Table 1, which also includes previously reported results for benzene and benzaldehyde.[13] The energy values for $\phi = 0$, 60, 120, and 180° allowed the potential function $V(\phi)$ for internal rotation to be fitted by a truncated Fourier expansion (1).[18] The potential

$$V(\phi) = \tfrac{1}{2}V_1(1 - \cos\phi) + \tfrac{1}{2}V_2(1 - \cos 2\phi) + \tfrac{1}{2}V_3(1 - \cos 3\phi) \quad (1)$$

constants V_i, in turn, enabled the prediction of the conformational angle, $\phi_{\text{max.}}$, corresponding to the maximum $V(\phi_{\text{max.}})$ in the potential function. Values of $\phi_{\text{max.}}$, of the barriers $V(\phi_{\text{max.}})$ to interconversion from *cis* to *trans*, and of the potential constants V_1, V_2, and V_3 are summarised in Table 2. The rotational barrier is largely determined by V_2, which reflects the tendency of the molecule to adopt a uniplanar conformation in order to maximise conjugative stability. The V_1 component encompasses the effects of

TABLE 2

Calculated potential constants, rotational barriers, and conformational angles for potential energy maxima for (hetero)aromatic carbaldehydes

	Calculated potential constants (kJ mol^{-1})				
Molecule	V_1	V_2	V_3	Barrier (kJ mol^{-1})	$\phi_{\text{max.}}$ (°)
Benzaldehyde	0	27.61	0	27.6	90
Furan-2-carbaldehyde	−3.41	28.03	−0.04	26.3	88
Furan-3-carbaldehyde	1.07	24.15	−0.46	24.5	91
Pyrrole-2-carbaldehyde	6.37	35.29	1.38	39.2	91
Pyrrole-3-carbaldehyde	1.81	27.17	−0.26	28.0	91
Pyridine-2-carbaldehyde	−9.35	23.70	−0.87	18.7	86
Pyridine-3-carbaldehyde	−1.27	25.87	−0.26	25.1	90
Pyridine-4-carbaldehyde	0	25.26	0	25.3	90

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[7] See references to theoretical studies listed in refs. 1—3 and also the following: V. N. Sheinker, O. A. Osipov, V. I. Minkin, E. G. Derecha, R. M. Minyaev, V. A. Troilina, A. S. Kuzharov, and N. N. Magdesieva, *Zhur. obshchei Khim.*, 1974, **44**, 1314; R. M. Minyaev, V. I. Minkin, and V. N. Sheinker, *Zhur. org. Khim.*, 1975, **11**, 1950; D. Kloepper and T. Weller, *Z. Chem.*, 1974, **14**, 62; B. Klabuhn, E. Clausen, and H. Goetz, *Tetrahedron*, 1973, **29**, 1153; H. Lumbroso and G. C. Pappalardo, *J. chim. Phys.*, 1974, **71**, 3; V. Galasso, *Mol. Phys.*, 1973, **26**, 81.

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[17] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253.

[18] L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 2371

intramolecular dipole alignments, steric hindrance, and other non-bonded interactions. Although smaller than the V_2 term, it is clearly the decisive factor in determining the relative stabilities of the *cis*- and *trans*-conformations. The V_3 contribution is small and relatively unimportant for the molecules treated in this paper.

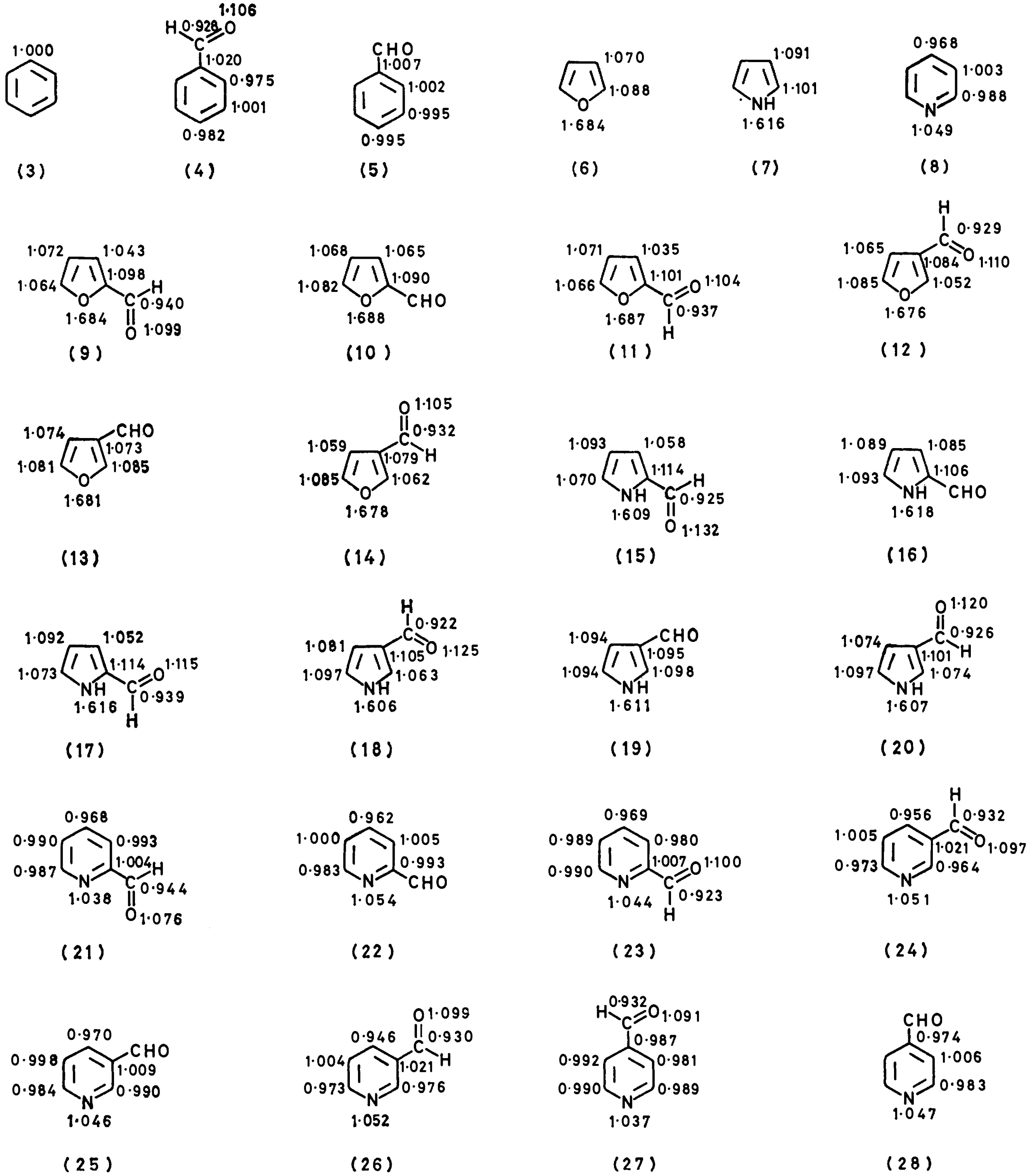


FIGURE π-Electron charge distributions for *cis*-, orthogonal, and *trans*-conformations of heteroaromatic carbaldehydes

Certain derived quantities are useful in interpreting the conformational observations. Among these are stabilisation energies relative to benzene, given as the energy changes, ΔE_{SE}, for reactions such as (i). Values of ΔE_{SE} (Table 3) provide a comparison of the interaction of the carbaldehyde group with the heterocyclic ring and its corresponding interaction with benzene. A positive value for ΔE_{SE} implies larger stabilisation in the heteroaromatic system. Charge distributions obtained by the Mulliken approach[19] are also of interest. Calculated π-electron populations are displayed in the Figure, which also assigns structure numbers used for reference in the discussion which follows. The three structures shown for each heteroaromatic carbaldehyde are, in sequence, the *cis*- ($\phi = 0°$), orthogonal ($\phi = 90°$), and *trans*- ($\phi = 180°$) forms. Mulliken π-overlap populations (π_{CC}) and directly calculated molecular dipole moments are also included in Table 3. Dipole moments obtained by using the STO-3G basis set are consistently lower than experimental values, but trends within groups of related molecules are reproducible. The π-overlap populations reflect the double-bond character in the bond linking the carbaldehyde group to the heteroaromatic system.

(i)

TABLE 3

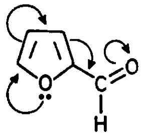
Relative stabilisation energies, dipole moments, and π-overlap populations for C_{ar}–C bond for conformations of (hetero)aromatic carbaldehydes

	ϕ (°)	Stabilisation energy (kJ mol^{-1})	Dipole moment (10^{-30} C m)	π_{CC}
Benzaldehyde	0	0	6.34	0.047
	90		5.94	0.014
Furan-2-carbaldehyde	0		7.77	0.050
	90		5.80	0.014
	180	6.4	6.17	0.051
Furan-3-carbaldehyde	0	2.6	6.14	0.047
	90		5.17	0.013
	180		5.10	0.046
Pyrrole-2-carbaldehyde	0	16.9	3.24	0.056
	90		7.24	0.016
	180		10.47	0.056
Pyrrole-3-carbaldehyde	0	9.0	10.41	0.050
	90		10.87	0.014
	180		13.41	0.049
Pyridine-2-carbaldehyde	0		12.41	0.043
	90		10.17	0.013
	180	−0.9	7.97	0.044
Pyridine-3-carbaldehyde	0		10.21	0.046
	90		7.51	0.014
	180	−1.7	2.20	0.046
Pyridine-4-carbaldehyde	0	−4.1	4.94	0.045
	90		5.54	0.013
Furan			1.43	
Pyrrole			6.34	
Pyridine			6.84	

DISCUSSION

Furan-2- and -3-carbaldehydes.—Table 1 shows that the *trans*- ($\phi = 180°$) form (11) of furan-2-carbaldehyde is energetically favoured, with the *cis*- (ϕ 0°) conformer (9) lying higher in energy by 3.5 kJ mol^{-1} (*i.e.* $\Delta E_{c-t} = E_{cis} - E_{trans} = 3.5$ kJ mol^{-1}). The barrier to internal rotation from the *cis*-conformation, $\Delta E^{\ddagger}_{c\rightarrow t}$, is calculated to be 26.3 kJ mol^{-1}. Such predictions are in good agreement with results from two experimental studies of furan-2-carbaldehyde in the vapour-phase: microwave and far-i.r. spectroscopy (Mönnig *et al.*,[20] $\Delta E_{c-t} = 3.1$ kJ mol^{-1}, $\Delta E^{\ddagger}_{c\rightarrow t} = 36$ kJ mol^{-1}); far-i.r. spectroscopy (Miller *et al.*,[21] $\Delta E_{c-t} = 8.5$ kJ mol^{-1}, $\Delta E^{\ddagger}_{c\rightarrow t} = 25$ kJ mol^{-1}). The relatively large value of V_2, from the Fourier expansion of $V(\phi)$ shown in Table 2, confirms that strong conjugative interaction between the carbaldehyde and heterocyclic groups stabilises the planar conformations, while intramolecular dipole–dipole and/or steric interactions, as measured by V_1, cause the *trans*-form to have the lower energy.

The π-electron distribution in the *trans*-conformation (11) reflects electron reorganisation as in (29), with changes from the distribution in furan (6) being explicable in terms of the valence structures (30) and (31). The stabilisation energies, ΔE_{SE}, in Table 3 show that the carbaldehyde group interacts more strongly with the 2-position of furan than with benzene, because of reinforcement (29) of the normal electronic effect (32) in furan.



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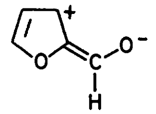

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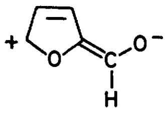

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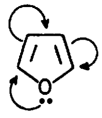

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For reasons already mentioned, the *cis*-conformer becomes favoured in media of high relative permittivity ($\varepsilon_r >$ *ca.* 3). The literature describing such conformational studies has been summarised;[3] additional relevant work is detailed in ref. 22.

In the case of furan-3-carbaldehyde the calculations indicate a slight preference for the uniplanar *cis*-conformation (12) rather than the corresponding *trans*-structure (14) ($\Delta E_{c-t} = -0.6$ kJ mol^{-1}). Such a result is unexpected since the mutual orientation of the furan and carbaldehyde group dipole moments is energetically more favourable in (14) than in (12). Because of the very small energy difference predicted, additional more refined calculations were performed in which an STO-3G optimized geometry was used for the furan ring, and all parameters in the CHO substituents were optimized separately for (12) and (14). These yielded the data shown in (33) and (34), and an energy difference, ΔE_{c-t}, of −0.2 kJ mol^{-1}. It seems, therefore, that the

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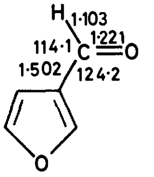
[21] F. A. Miller, W. G. Fateley, and R. E. Witkowski, *Spectrochim. Acta*, 1967, **23A**, 891.

[22] O. A. Osipov, V. N. Sheinker, A. S. Kuzharov, Z. N. Nazarova, E. G. Derecha, and S. B. Bulgarevich, *Zhur. obshchei Khim.*, 1974, **44**, 393; C. G. Andrieu, C. Chatain-Cathaud, and M. Fournié-Zaluski, *J. Mol. Structure*, 1974, **22**, 433; E. G. Merinova, V. N. Sheinker, M. E. Perel'son, and O. A. Osipov, *Zhur. org. Khim.*, 1976, **12**, 597; J. Fernández Bertran and M. Rodriguez, *Org. Magnetic Resonance*, 1974, **6**, 525; B. P. Roques, S. Combrisson, and F. Wehrli, *Tetrahedron Letters*, 1975, 1047; D. J. Chadwick, *J.C.S. Perkin II*, 1976, 451.

cis- and *trans*-isomers of furan-3-carbaldehyde are of approximately equal energy. The barrier to internal rotation ($\Delta E^{\ddagger}_{c\rightarrow t}$ = 24.5 kJ mol^{-1}) is slightly lower than in furan-2-carbaldehyde, indicative of reduced conjugative interaction between the furan ring and the carbaldehyde group.



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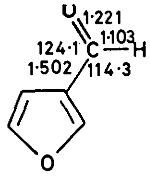

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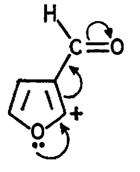
Unfortunately there are no gas-phase experimental data on record with which the theoretical predictions can be compared. However, ^{1}H n.m.r.[23] and i.r.[24] spectra of furan-3-carbaldehyde in various dipolar and non-dipolar solvents were interpreted as indicating the presence of the *trans*-conformer (14) alone; dipole-moment measurements [25] were inconclusive. If the *cis*- and *trans*-isomers of furan-3-carbaldehyde are virtually equi-energetic in the gas phase, as our calculations suggest, the inferences drawn from the spectroscopic investigations of solutions are surprising, since solvents of high relative permittivity would be expected to stabilise the more strongly dipolar *cis*-form (12).

The calculated charge distribution suggests electron delocalisation as in (35) and an increased contribution relative to furan from valence structures such as (36).



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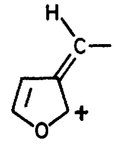

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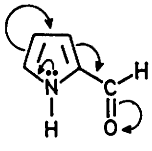
A comparison of the stabilisation energies and π-overlap populations (Table 3) of furan-2- and -3-carbaldehyde provides further indications of the weaker conjugative interaction of a carbaldehyde group at the 3-position than at the 2-position of furan. Strong experimental evidence supporting this prediction was drawn from ^{1}H n.m.r. studies of furan carbaldehydes by Gronowitz *et al.*[26]

Pyrrole-2- *and* -3-*carbaldehydes*.—For pyrrole-2-carbaldehyde, we find that the planar *cis*-conformation (15) is much more stable than the *trans*-structure (17) (ΔE_{c-t} = −7.8 kJ mol^{-1}), and that these two conformers are separated by a large energy barrier ($\Delta E^{\ddagger}_{c\rightarrow t}$ = 39.2 kJ mol^{-1}). The values of both $\Delta E^{\ddagger}_{c\rightarrow t}$ and V_2 (Table 2) indicate the very strong conjugative interaction known to occur between the 2-pyrrolyl and carbaldehyde groups. The parameter V_1, which is also relatively large, originates in the stabilising intramolecular dipole–dipole interaction in (15), and perhaps also reflects intramolecular hydrogen bonding in this conformation.

The only relevant structural investigation of pyrrole-2-carbaldehyde in the vapour phase is a microwave spectral study [27] which confirmed that (15) is the preferred conformation. In addition it has been shown by a variety of physical methods that (15) is also strongly favoured in dense media. Literature up to 1973 has already been summarised,[2] and additional studies have been reported (dipole moments,[28] i.r. and Raman spectra,[29] and ^{1}H n.m.r. spectra [30]).

The charge distribution indicates electron rearrangement (37) and enhanced contributions relative to pyrrole of the valence structures (38) and (39). There is a stabilising interaction between the carbaldehyde and 2-pyrrolyl groups, as evidenced by the large positive value of ΔE_{SE}. As with the furans, this is consistent with a reinforcement (37) of the delocalisation in pyrrole itself (40). The value of ΔE_{SE} is larger for pyrrole-2-carbaldehyde than for furan-2-carbaldehyde, and this can be attributed to the greater π-electron donating ability of the heteroatom in pyrrole as compared with furan, as manifested by the charge distributions in (6) and (7).



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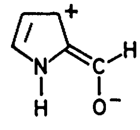

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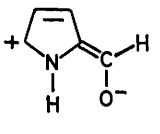

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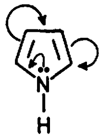

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In pyrrole-3-carbaldehyde the energy difference between the uniplanar *cis*- (18) and *trans*- (20) conformers is considerably reduced (ΔE_{c-t} = −1.6 kJ mol^{-1}) but a slight preference for the *cis*-structure is again evident. The barrier to internal rotation in pyrrole-3-carbaldehyde ($\Delta E^{\ddagger}_{c\rightarrow t}$ = 28.0 kJ mol^{-1}) is smaller than that found in pyrrole-2-carbaldehyde, implying a weaker conjugative interaction of the carbaldehyde group with the 3-position

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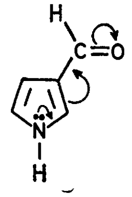
[30] M. Farnier and T. Drakenberg, *J.C.S. Perkin II*, 1975, 333.

of pyrrole. Such predictions are of particular interest since the vapour phase conformational preference of pyrrole-3-carbaldehyde has not yet been established experimentally. However, studies[31] of pyrrole-3-carbaldehyde and many substituted derivatives in various solvents through measurements of n.m.r. spectra and dipole moments have established that the *trans*-conformer (20) is preferred in solution. The conformational situation for pyrrole-3-carbaldehyde is therefore analogous to that described above for furan-2-carbaldehyde: the less dipolar *cis*-structure is intrinsically the more stable but solvation and reaction-field effects cause a strong preference for the *trans*-conformer in dense media.

The π-electron distribution in this molecule reflects electron delocalisation (41) with an increased contribution (relative to pyrrole) of the valence structure (42). The stabilisation energy is again relatively large, for reasons similar to those already detailed for furan-2-carbaldehyde and pyrrole-2-carbaldehyde.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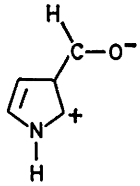
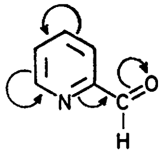

(42)

Pyridine-2-, -3-, and -4-carbaldehydes.—Table 1 shows, not unexpectedly, that for pyridine-2-carbaldehyde the uniplanar *trans*-structure (23) is much more stable than the *cis*-form (21) (ΔE_{c-t} = 10.2 kJ mol^{-1}). The corresponding energy barrier ($\Delta E^{\ddagger}_{c\rightarrow t}$ = 18.7 kJ mol^{-1}) and the potential constant V_2 are smaller than those found for benzaldehyde and the furan- and pyrrole-carbaldehydes, and indicate reduced mesomeric interaction between the 2-pyridyl and carbaldehyde groups. However V_1 is exceptionally large, as would be expected because of the proximity of the two strongly dipolar groups. Previous STO-3G calculations[9] for this molecule were based on a slightly different geometric model, but gave results in substantial agreement with ours. An analysis of the microwave spectrum[32] of pyridine-2-carbaldehyde established that the *trans*-conformation (23) is favoured in the vapour state and several studies have demonstrated the same preference for (23) in dense media (see ref. 1 for summary of literature up to 1972; also recent confirmatory ^{1}H and ^{13}C n.m.r. studies[9,33,34]).

The charge distribution in (23) is explicable through electron delocalisation (43), with increasing contributions from valence structures (44)—(46). Examination of the π-charge arrangement in pyridine itself (8) shows accumulation of negative charge on nitrogen resulting from electron donation from the 2-, 4-, and 6-positions. The electron reorganisation in (23) is therefore the reverse of that normally favoured by pyridine. Hence it is not surprising that the relative stabilisation energy for pyridine-2-carbaldehyde (and in fact for pyridine-3- and -4-carbaldehydes also) is negative, indicating a destabilising interaction.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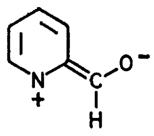
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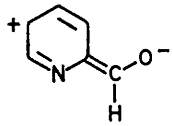
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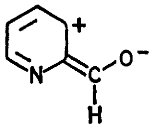
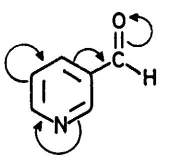

(46)

Pyridine-3-carbaldehyde shows a similar preference for the uniplanar *trans*-conformer (26). The energy difference between (26) and (24) (ΔE_{c-t} = 1.5 kJ mol^{-1}) is however much smaller than for the corresponding structures of pyridine-2-carbaldehyde, although the barrier to interconversion is greater ($\Delta E^{\ddagger}_{c\rightarrow t}$ = 25.1 kJ mol^{-1}). The parameter V_1 is also much reduced because of the increased distance between the dipolar groups. Experimental evidence concerning the conformational preference of pyridine-3-carbaldehyde is available only for the solution state, where the less dipolar form (26) is well established[1] as the more abundant isomer, as predicted for the vapour phase.

The charge distribution (26) corresponding to (47) shows electron donation (relative to pyridine) at the 2-, 4-, and 6-positions [(48)—(50)]. Once again the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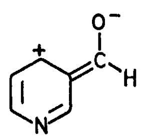
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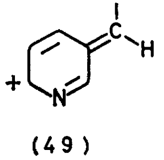
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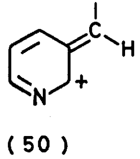
(50)

π-electron-accepting carbaldehyde group opposes the natural π-acceptance by the pyridine nitrogen and a relative destabilising interaction is found.

The two equivalent uniplanar structures of pyridine-

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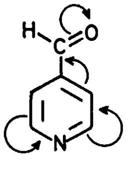
[31] See papers cited as refs. 3 and 11—13 in ref. 2, and also the following: C. Jaureguiberry, L. Lacombe, and B. Roques, *Tetrahedron Letters*, 1973, **42**, 4181; M. C. Fournié-Zaluski, C. Jaureguiberry, and B. Roques, *ibid.*, p. 4177.

[32] Y. Kawashima, M. Suzuki, and K. Kozima, *Bull. Chem. Soc. Japan*, 1975, **48**, 2009.

[33] W. Danchura, T. Schaefer, J. B. Rowbotham, and D. J. Wood, *Canad. J. Chem.*, 1974, **52**, 3986.

[34] T. Drakenberg, *J.C.S. Perkin II*, 1976, 147.

4-carbaldehyde are separated by an energy barrier ($\Delta E^{\ddagger} = 25.3$ kJ mol^{-1}) which is slightly smaller than that in benzaldehyde. The charge distribution in (27) reflects π-electron delocalisation (51) with electron donation (relative to pyridine) from the 1-, 3-, and 5-positions of the pyridine ring [(52)—(54)], and the interaction is destabilising. Our Kerr-effect study[1] confirmed that pyridine-4-carbaldehyde has the uniplanar conformation in the dissolved state, but the vapour-state structure has not yet been determined by experiment.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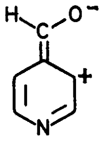
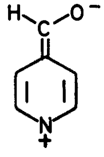

(52)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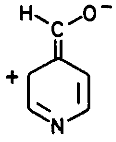
(54)

General Conclusions.—The present application of *ab initio* molecular orbital theory to heteroaromatic aldehydes has identified the main intramolecular features governing the conformational preferences of such molecules in the vapour state. In all cases except furan-3-carbaldehyde, where there is no significant preference, the choice between the uniplanar, resonance-stabilised *cis* and *trans* alternatives is resolved in favour of the form in which group dipole interactions are minimised. The direction of the dipole moments of furan and pyridine is the reverse of that for pyrrole; in the latter the moment acts along the H–N bond towards the ring, with H constituting the positive end of the dipole. In consequence the *trans*-structures of furan-2-, pyridine-2-, and pyridine-3-carbaldehydes are favoured, whereas the *cis*-forms of pyrrole-2- and pyrrole-3-carbaldehydes predominate. The near-zero energy difference between the *cis*- and *trans*-conformers of furan-3-carbaldehyde can be rationalised in terms of two factors: (i) the small difference between the magnitudes of the dipole moments of these conformers (Table 3); and (ii) the relatively large distance between the two main interacting group moments within the molecule. The effect of (ii) is clear from the data for pyridine-3-carbaldehyde where, despite a large difference between the moments calculated for the two planar conformations, the energy difference is predicted to be small ($\Delta E_{c-t} = 1.5$ kJ mol^{-1}), presumably because of the large separation between the component moments. For furan-3-carbaldehyde the difference between the dipole moments of (12) and (14) is much smaller, and it is not surprising that ΔE_{c-t} is correspondingly lower.

For several of the molecules studied here the energy difference between the *cis*- and *trans*-isomers is known to be markedly solvent-dependent, and the gas-phase conformational preference can be reversed in media of high relative permittivity (strongly dipolar solvents, *e.g.* acetone, chloroform, and dimethyl sulphoxide). Solvent effects of this type would be expected to be more pronounced for molecules having a relatively small gas-phase energy difference between the rotational isomers: furan-2-, furan-3-, pyrrole-3-, and pyridine-3-carbaldehydes.

Fourier decomposition of the potential function for internal rotation leads to potential constants V_1, V_2, and V_3 for each molecule. The V_1 term reflects the energy difference between the uniplanar *cis*- and *trans*-structures, and usually may be taken as a measure of the dipole–dipole interaction energy. It is specially noteworthy that for each of the heterocycles (furan, pyrrole, and pyridine) V_1 is considerably larger when the carbaldehyde group is at the 2- rather than the 3-position. Such a result emphasises the importance, already mentioned, of the effective separation between intramolecular group moments. The V_2 contribution indicates the energy difference between planar and orthogonal structures. In this sense it measures the electron delocalisation in the planar structures, and should correlate with the π_{CC} overlap populations. Although the correlation is not perfect it can be seen that molecules with the highest values of V_2 (pyrrole-2- and furan-2-carbaldehydes) have the highest values of π_{CC}, whereas those with the lowest values of V_2 (pyridine-2-, furan-3-, and pyridine-4-carbaldehydes) have the lowest.

The stabilisation energies may be rationalised by noting initially that the carbaldehyde group is a π-electron acceptor. The heteroatoms in the furan and pyrrole rings are π-electron donors, the interaction is co-operative, and ΔE_{SE} is positive. On the other hand the heteroatom in pyridine acts as a π-electron acceptor, the interaction is competitive, and there is a relative destabilisation.

The conjugative abilities, relative to benzene, of the five- and six-membered heterocycles are of fundamental importance in determining the preferred conformations of ketones in which both a phenyl and a heterocyclic group are attached directly to the carbonyl group, *e.g.* phenyl 2-pyrrolyl ketone. The furyl, pyrrolyl, and thienyl groups, in notable contrast with the pyridyl group, conjugate much more effectively than a phenyl ring with the carbonyl group. In consequence,[1-3] the five-membered heterocycle retains the uniplanar *cis*- or *trans*-arrangement with the carbonyl group, and steric interactions are accommodated by rotation of the phenyl group from this plane. A contrary argument would be expected to apply to, *e.g.* phenyl 2-pyridyl ketone and related molecules.

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