# **181.** *Studies of Aromaticity by Nuclear Magnetic Resonance Spectroscopy. Part I. 2-Pyridones and Related Systems.*

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Proton chemical shift data have been used in three ways to estimate the aromatic character of the 2-pyridone ring. The results are reasonably consistent and indicate that 2-pyridones have *ca.* 35% of the aromaticity of benzene, as defined by ability to sustain an induced ring current. The formally related 1,2-dihydro-2-methylenepyridine system is not aromatic: this conclusion has bearing on the constitution of adducts from pyridine and 3-picoline with acetylenedicarboxylic ester.

ONE of the best understood mechanisms for proton magnetic shielding is that arising from induced circulations of π-electrons in benzenoid aromatic systems.[1-4] These induced circulations (or ring currents) are responsible for the shielding of protons attached to aromatic rings,[2,3,4] for the paramagnetic shift observed for the protons of a methyl substituent,[3] as in toluene, and for the diamagnetic shielding of the central methylene protons in *p*-polymethylenebenzenes.[4] Calculated magnitudes of these effects agree satisfactorily with the experimental values. Thus there are reliable means of estimating the magnitude of the ring current induced in a closed conjugated system.

Textbooks do not in general attempt succinct definitions of the term "aromatic compound."[5] It is usual to direct attention to the characteristic properties. It emerges that an aromatic compound is always a mono- or poly-cyclic conjugated or cross-conjugated system, but such a system is not of necessity aromatic. The essential feature is a ring of atoms so linked that π-electrons are delocalised right round the ring. *We can define an aromatic compound, therefore, as a compound which will sustain an induced ring current.* The magnitude of the ring current will be a function of the delocalisation of π-electrons around the ring and therefore a measure of aromaticity. Our treatment is confined initially to six-membered monocyclic systems as these can be compared directly with benzene, in which there is full delocalisation of the π-electrons as indicated by the $D_{6h}$ symmetry. Additional computation will be required for the treatment of other than six-membered rings and for fused aromatic ring systems.

Aromatic character in many heterocyclic and in non-benzenoid aromatic compounds is certainly less well defined than for benzenoid hydrocarbons because the usual chemical criteria are essentially qualitative and frequently ambiguous. In principle it is possible to express the aromatic character of all types of system quantitatively in terms of resonance energy, but experimentally it is difficult to obtain meaningful values for borderline, weakly aromatic systems. Arguments based on proton chemical shifts are likely to prove much more definitive and may lead to a quantitative assessment of aromaticity for all types of cyclic system.

We have begun a study of chemically less-defined aromatic systems and herein describe attempts to characterise the aromaticity of 2-pyridones. We conclude that these compounds have only 35% of the aromaticity of benzene.

In order to obtain suitable chemical-shift data for the discussion of aromatic character in the 2-pyridone system, we have determined the line positions (τ values) for protons

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[1] Pople, *J. Chem. Phys.*, 1956, **24**, 1111.

[2] Bernstein, Schneider, and Pople, *Proc. Roy. Soc.*, 1956, *A*, **236**, 515; Pople, *Mol. Phys.*, 1958, **1**, 175; McWeeny, *ibid.*, p. 311.

[3] Johnson and Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

[4] Waugh and Fessenden, *J. Amer. Chem. Soc.*, 1957, **79**, 846.

[5] See, *e.g.*, Cram and Hammond, "Organic Chemistry," McGraw-Hill Book Co. Inc., New York, 1959; Finar, "Organic Chemistry," 3rd edn., Longmans, Green and Co., London, 1959, Vol. I; de la Mare and Ridd, "Aromatic Substitution," Butterworths, London, 1959; Hückel, "Theoretical Principles of Organic Chemistry," Elsevier, Amsterdam, 1955, Vol. I; Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

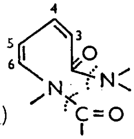
attached directly to the ring and for the protons of substituent methyl groups. From the results, given in Table 1, the shielding contributions arising from a ring current can be assessed provided the line positions in the absence of a ring current can be predicted. This becomes possible from consideration of model structures in which the $\pi$-electrons are regarded as rigidly localised. An alternative approach is given below.

TABLE 1. *Chemical shift data* (*at* 21° *in* $CDCl_3$).

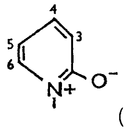
| | | $\tau$ values for ring and subst. group protons at position | | | | |
|---|---|---|---|---|---|---|
| No. | 2-Pyridones | 3 | 4 | 5 | 6(2) | 1 |
| 1 | 1-Me | 3·43 | 2·74 | 3·85 | 2·69 | 6·41 |
| 2 | 1,3-$Me_2$ | 7·85 | 2·88 | 3·93 | 2·75 | 6·47 |
| 3 | 1,5- ,, | 3·49 | 2·80 | 7·92 | 2·89 | 6·48 |
| 4 | 1,6- ,, | 3·56 | 2·78 | 3·96 | 7·64 | 6·46 |
| 5 | 1,4,6-$Me_3$ | 3·74 | 7·90 | 4·09 | 7·68 | 6·49 |
| 6 | 3-Ac-5-$EtO_2C$-1,4,6-$Me_3$ | 7·48(Ac) | 7·88 | 5·68($CH_2$)<br>8·63(Me) | 7·62 | 6·45 |
| | Pyridines | | | | | |
| 7 | (Pyridine [a]) | 3·01 | 2·64 | 3·01 | 1·50 | |
| 8 | 2,4-$Me_2$ | 3·17 | 7·74 | 3·14 | 7·56<br>1·77 | |
| 9 | 2,6- ,, | 3·07 | 2·45 | 3·07 | 7·48 | |
| 10 | 3,5- ,, | 7·74 | 2·83 | 7·74 | 1·88 | |
| 11 | 3,5-$(EtO_2C)_2$-2,6-$Me_2$ | 5·61($CH_2$)<br>8·58(Me) | 1·48 | 5·61<br>8·58 | 7·22 | |
| 12 | 3,5-$(EtO_2C)_2$-2,4,6-$Me_3$ | 5·56($CH_2$)<br>8·61(Me) | 7·70 | 5·56<br>8·61 | 7·45 | |
| | Pyridinium iodides | | | | | |
| 13 | 2,6-$Me_2$-1-Et | 2·06 | 1·59 | 2·06 | 6·95 | 5·26($CH_2$)<br>8·42(Me) |
| 14 | 2,4-$Me_2$-1-Et | 2·15 | 7·35 | 2·15 | 7·03<br>0·74 | 5·15($CH_2$)<br>8·35(Me) |
| 15 | 1,2,4-$Me_3$ [b] | | 7·42 | | 7·06 | |
| 16 | 1,3,5-$Me_3$ | 7·40 | 1·88 | 7·40 | 0·94 | 5·41 |
| 17 | 3,5-$(EtO_2C)_2$-1,2,4,6-$Me_4$ [c] | 5·51($CH_2$)<br>8·58(Me) | 7·56 | 5·51<br>8·58 | 7·14 | 5·69 |
| | Miscellaneous | | | | | |
| 18 | $Et_2$ 1,2-dihydro-2-methylene-1,4,6-trimethylpyridine-3,5-dicarboxylate | | 8·13 | | 7·81(Me)<br>6·45($CH_2$) | 6·96 |
| 19 | Me sorbate | | | | 8·13 | |

[a] Ref. 8, p. 64. [b] The formation of a two-phase system in $CDCl_3$ resulted in serious loss of resolution. [c] Examined as the methosulphate (Me, 6·45).

For 2-pyridone (I), two extreme *non-aromatic* models are (A) and (B),* the latter being the better if aromatic character is fully developed in the 2-pyridone system. We suspect that this zwitterion model (B) is only a partial approximation to a true non-aromatic model because the dipole moment of 1-methyl-2-pyridone, though large (4·15 D



(A)



(B)

in benzene [6]), does not correspond to the complete charge separation in (B) which may be compared with that [7] in glycine zwitterion (15 D). The two models differ appreciably in inductive and mesomeric contributions to the local diamagnetic shielding of the relevant protons. Such effects are particularly serious when ring protons are considered [8] and

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* It is emphasised that (A) and (B) are fixed-bond model structures. Thus (B) is a non-resonating aza-cyclohexatriene, and is not meant to represent a hybrid structure.

[6] Albert, " Heterocyclic Chemistry," Athlone Press, London, 1959, p. 355.

[7] Ref. 6, p. 354.

[8] Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 63.

for this reason we have made use first of the shifts for methyl-protons as these are relatively unaffected. Thus a *m*- or a *p*-nitro-substituent causes a paramagnetic shift of only 0·09 p.p.m. for the methyl protons of toluene.[9] A disadvantage is that the shifts observed for methyl-protons are smaller for a given ring-current density than for ring protons.

Model (A) is not available but the resonance frequencies of protons on methyl substituents at the four positions can be reliably predicted because the major shielding effects will be associated with the magnetic anisotropies of the various multiple bonds. A methyl group at the 3-position has an environment similar to that experienced by an $\alpha$-methyl group in a carotenoid monoester (*e.g.*, compound 38 in ref. 10) and should absorb at $\tau$ 8·06 (in $CDCl_3$). The corresponding amide is not available but the value would be virtually the same (cf. methacrylic ester 8·10 ± 0·02 and methacrylamide[11] 8·06 ± 0·02) and there is little difference from the corresponding aldehydes,[10] which shows that the polarity of the carbonyl group is unimportant. For a 4-methyl group we predict $\tau$ 8·01 by subtracting 0·15 (the frequency difference between " in-chain " and " end-of-chain " methyl-protons in carotenoid esters[10]) from the value (8·16) for the methyl (protons) *trans* to carbonyl in methyl senecioate.[11] A 5-methyl group approximates to the " in-chain " methyl groups of a carotenoid or carotenoid ester (compounds 3, 11, 12, 17, and 25 in ref. 10) and should absorb at 8·03 (for $CDCl_3$ solution). A methyl group at the 6-position is at the end of the conjugated carbon chain and should absorb as in sorbic ester (8·13) (Table 1) except that it will experience a further paramagnetic shift of 0·1 p.p.m. because of the neighbouring nitrogen atom:[12] hence the predicted value for the 6-methyl group protons is 8·03.

In model (B) any *C*-methyl substituent corresponds to an " in-chain " methyl group in carotenoids (8·03), except that when attached at the 6-position it is close to the positive pole on nitrogen and so a paramagnetic correction of 0·63 is required here. The correction comprises 0·1 p.p.m. for the inductive effect of the nitrogen atom and 0·53 p.p.m. for the positive pole, the latter value being the shift for the $\alpha$-methyl groups in the pyridine (no. 9 of Table 1) which results on quaternisation to compound (13).

TABLE 2. *Proton resonance values* ($\tau_{obs.}$) *for* C-*methyl substituents of* 1-*methyl*-2-*pyridones compared with values* ($\tau_{calc.}$) *for the non-aromatic models* (A) *and* (B).

| | | Model (A) | | Model (B) | |
|---|---|---|---|---|---|
| Me position | $\tau_{obs.}$ | $\tau_{calc.}$ | $\tau_{calc.} - \tau_{obs.}$ | $\tau_{calc.}$ | $\tau_{calc.} - \tau_{obs.}$ |
| 3 | 7·85 | 8·06 | 0·21 | 8·03 | 0·18 |
| 4 | 7·89[a] | 8·01 | 0·12 | 8·03 | 0·14 |
| 5 | 7·92 | 8·03 | 0·11 | 8·03 | 0·11 |
| 6 | 7·65[b] | 8·03 | 0·38 | 7·40 | −0·26 |

Average of values (*a*) for compounds (5) and (6) and (*b*) for (4), (5), and (6) in Table 1.

Table 2 allows comparison of these predicted values with the experimental results. The models (A) and (B) give reasonable agreement for ($\tau_{calc.} - \tau_{obs.}$) for all positions of the methyl substituent except the 6-position. This is expected because this position is most affected by the development of the zwitterion on passing from model (A) to (B). It might be argued that the 6-methyl group could seriously distort the planarity of the $sp^2$-hybridised nitrogen atom. That this is not so is shown by the narrow range of absorption of the *N*-methyl group protons (6·41—6·49) in the various 2-pyridones (Table 1).

The average shift ($\tau_{calc.} - \tau_{obs.}$) in Table 2, derived from both models, with neglect of values for the 6-position, is 0·14(5) p.p.m. Because the ring-current contribution to the shielding of the methyl group protons in toluene is 0·40 p.p.m. [being the difference in line position ($\tau$ 7·66) from that of an " in-chain " methyl group in a carotenoid (8·06)], it

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[9] Ref. 8, p. 58.

[10] Barber, Davis, Jackman, and Weedon, *J.*, 1960, 2870.

[11] Jackman and Wiley, *J.*, 1960, 2881.

[12] Ref. 8, p. 53.

follows that the 2-pyridone ring sustains only 36% of the induced ring current of benzene and so has a fractional aromaticity of 0·36.

An alternative method of assessing the ring current involves starting with fully aromatic models and predicting empirically the line positions in the absence of a ring current. To do this we start with the corresponding alkylated pyridines as being related to model (A) and their quaternary salts as being similarly related to (B). It is then assumed that the ring currents in these two systems make the same contribution, 0·4 p.p.m., to the shielding of methyl substituents as does the ring current in toluene. (There is little doubt that pyridine is as fully aromatic as benzene[13].) Data for the appropriate methylpyridines and their quaternary salts, included in Table 1, then allow the computation of the $\tau_{\text{calc.}}$ values listed in Table 3.

The data (in Table 3) derived from the non-aromatic pyridine model overestimate the ring-current contribution ($\tau_{\text{calc.}} - \tau_{\text{obs.}}$) whereas those derived with the non-aromatic pyridinium model as basis underestimate it. A compromise between these two models is required. We therefore compute the line positions directly by taking an appropriate linear combination of the values ($\tau_A$) for an aromatic pyridine and ($\tau_B$) for an aromatic pyridinium model and adjusting a full ring-current contribution of $r = 0{\cdot}4$ p.p.m. for the assumed fractional aromaticity, $x$. Calculated values are then given by the expression (i). The second term in (i) corrects for the partial development of the zwitterion and the third term for the partial loss of ring current. By trial and error it appears that a value of $x = 0{\cdot}31$ gives the best fit between calculated line positions for methyl-protons ($\tau_{\text{calc.}}$) and those experimentally observed ($\tau_{\text{obs.}}$) for 2-pyridones, the results being shown in Table 4.

TABLE 3. *Comparison of proton resonance values* ($\tau_{\text{obs.}}$)[a] *for* C-*methyl substituents of* 1-*methyl*-2-*pyridones with values* ($\tau_{\text{calc.}}$) *for the non-aromatic pyridine and pyridinium models.*

| | Non-aromatic pyridine model | | Non-aromatic pyridinium model | |
|---|---|---|---|---|
| Me position | $\tau_{\text{calc.}}$ | $\tau_{\text{calc.}} - \tau_{\text{obs}}$ | $\tau_{\text{calc.}}$ | $\tau_{\text{calc.}} - \tau_{\text{obs.}}$ |
| 3 | 8·14[b] | 0·29 | 7·80 | −0·05 |
| 4 | 8·12[c] | 0·23 | 7·84[e] | −0·05 |
| 5 | 8·14 | 0·22 | 7·80 | −0·12 |
| 6 | 7·83[d] | 0·18 | 7·44 | −0·21 |

(*a*) As in Table 2. (*b*) Value for compound (10) of Table 1, 7·74, plus 0·4. (*c*) Similarly from average values for (8) and (12). (*d*) for (8), (9), (11), and (12), (*e*) for (14), (15), and (17), and (*f*) for (13), (14), (15), and (17) in Table 1.

$$\tau_{\text{calc.}} = \tau_A - x(\tau_A - \tau_B) + (1 - x)r \qquad . \quad . \quad . \quad . \qquad \text{(i)}$$

TABLE 4. *Proton resonance values* ($\tau_{\text{obs.}}$)[a] *for* C-*methyl substituents of* 1-*methyl*-2-*pyridones compared with values* ($\tau_{\text{calc.}}$) *calculated from eqn.* (i) *with* $x = 0{\cdot}31$.

| Me position | $\tau_A$ | $\tau_B$ | $\tau_{\text{calc.}}$ | $\tau_{\text{calc.}} - \tau_{\text{obs.}}$ |
|---|---|---|---|---|
| 3 | 7·74 | 7·40 | 7·91 | 0·06 |
| 4 | 7·72[b] | 7·44[d] | 7·91 | 0·02 |
| 5 | 7·74 | 7·40 | 7·91 | −0·01 |
| 6 | 7·43[c] | 7·04[e] | 7·59 | −0·06 |

(*a*) As in Table 2. (*b*) Average of values for compounds (8) and (12), (*c*) of those for (8), (9), (11), and (12), (*d*) of those for (14), (15), and (17), and (*e*) of those for (13), (14), (15), and (17) of Table 1.

It is encouraging that this approach and the first give reasonably consistent results, *viz.*, 31% and 36% of aromatic character. Again the agreement between calculated and observed values is poor for the 6-position. The equally poor agreement between the values for the 3-position (Table 4) results from three shielding effects operative at the methyl-protons there which have not been considered. These are a diamagnetic shift resulting from induction by the partial negative charge on the oxygen atom, a paramagnetic shift caused by hydrogen bonding between the 3-methyl group and the negatively

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[13] See, *e.g.*, Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955, p. 106.

charged oxygen, and a paramagnetic shift associated with the diamagnetic anisotropy of the partial carbonyl double bond. It is not feasible to allow precisely for these three effects but it is unlikely that the net correction would exceed 0·1 p.p.m.

We have also attempted an " analysis " of the shifts of the ring protons, using equation (i). We have used the proton line positions for pyridine for $\tau_A$ and have derived values for $(\tau_A - \tau_B)$ from the data for the ring protons in the lutidines (8), (9), and (10) and their quaternary salts listed in Table 1. The value $r$ for the contribution of the ring current to the shielding of the protons in benzene has been taken as 1·55 p.p.m., being the difference between the $\tau$ value for benzene (2·73) and the average of the $\tau$ values for cyclo-octatetraene (4·31) and cyclo-octatriene (4·26).[14] We have also included a correction of $0{\cdot}4x$ p.p.m. to the shift of the 3-proton to allow for the partial negative pole on oxygen, attached at the 2-position.* We find the best fit between calculated and observed proton resonance values is obtained with $x = 0{\cdot}38$ (Table 5). However, the agreement between individual results is much worse than for the methyl-protons. This means that the charge density at the various carbon atoms in the 2-pyridones is certainly very different from that in the corresponding pyridines; for instance it appears that the 4-position has a lower charge density in a pyridone ring than in the pyridine.

The three completed analyses (Tables 2, 4, and 5) are in fair agreement and suggest that the 2-pyridone ring system has 35 ± 5% of the aromatic character of benzene as defined by ability to sustain a ring current.

TABLE 5. *Calculated (on the basis $x = 0{\cdot}38$) and observed ring proton $\tau$ values for 1-methyl-2-pyridone.*

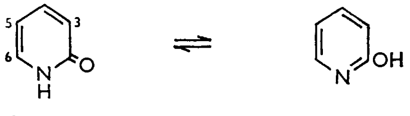
| H position | $\tau_A$ [a] | $(\tau_A - \tau_B)$ [b] | $\tau_{\text{calc.}}$ [c] | $\tau_{\text{obs.}}$ [d] | $\tau_{\text{calc.}} - \tau_{\text{obs.}}$ |
|---|---|---|---|---|---|
| 3 | 3·01 | 1·02 | 3·73 | 3·43 | 0·30 |
| 4 | 2·64 | 0·91 | 3·25 | 2·74 | 0·51 |
| 5 | 3·01 | 1·00 | 3·59 | 3·85 | −0·26 |
| 6 | 1·50 | 0·98 | 2·09 | 2·69 | −0·60 |

[a] Values for compound (7) of Table 1. Average differences between ring proton $\tau$ values in (8), (9), and (10) and their quaternary salts, from Table 1. [c] See text. [d] Values for (1) in Table 1.

The percentage of aromatic character could in principle be calculated from dipole-moment data but there is the difficulty of assigning a moment to model (A). Nevertheless it is reasonable to suppose that the observed figure of 4·12 D could be accounted for by ~35% of aromatic character in 1-methyl-2-pyridone.

In terms of resonance energy, this degree of aromaticity would correspond to a stabilisation of 12~15 kcal. mole$^{-1}$ † which is reflected in the chemical properties of the 2-pyridones. These compounds show well-marked aromatic properties and do not behave as unsaturated lactams, in spite of there being much evidence to indicate that they exist essentially in the 2-pyridone form (I*a*) and not as 2-hydroxypyridines (I*b*).[15] Thus there are no reports of the addition of maleic anhydride across the 3,6-positions, *i.e.*, across the formal diene system of structure (I*a*). Indeed we have tried the Diels–Alder

(I*a*)



(I*b*)

reaction of maleic anhydride with 1-methyl-2-pyridone and its 4,6-dimethyl homologue, and find no evidence of addition under conditions where the corresponding 2-pyrones react

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* The effect (0·4) of the$^{+}$ negative pole in H–C–C–O$^{-}$ is taken as 0·33 of the difference in $\tau$ value between $H_3C{-}N{<}$ and $H_3C{-}N{<\!\!\!-}$.

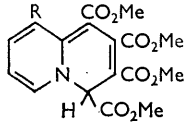
† This value is based on the resonance energy of benzene and on the assumption that there is approximate correspondence between resonance energy and chemical-shift data as measures of aromatic character.

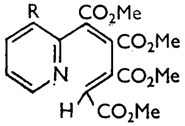
[14] Tiers, personal communication.

[15] Ref. 6, pp. 55—62.

readily. Further, 2-pyridones are not cleaved by alkali, and they and their *N*-alkyl derivatives readily undergo electrophilic substitution in the 3- and the 5-position with a variety of reagents.[16] Whilst the chemical results suggest that 2-pyridones are aromatic, there has hitherto been no simple means of assessing their aromaticity.

(II)





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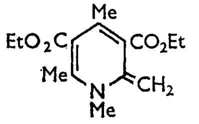
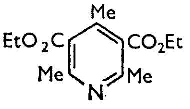


(18)



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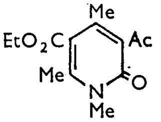

(6)

Recently,[17] it was suggested that nuclear magnetic resonance spectroscopy could not distinguish between the formulations (II) and (III) for adducts of pyridine (R = H) and of 3-picoline (R = Me) with acetylenedicarboxylic ester, because at the time there was no information regarding the magnitude of a possible ring current in (II). Our present results make it clear that the structure (II) could not give rise to a ring current of a sufficient magnitude to account for the observed positions of the ring and methyl-protons. Indeed we have confirmed this by comparing the spectrum of the 1,2-dihydro-2-methylenepyridine (18), which is a very labile compound, with that of the analogous methylpyridine (12). The $\tau$ values for the ring methyl groups in the compound (18) correspond to the virtual absence of a ring current. Presumably systems such as (18) are less aromatic than a corresponding pyridone (6), and perhaps not at all aromatic, because of the lower tendency of carbon than of oxygen to accept a negative charge. To accommodate the chemistry, it is possible to formulate each of the preceding adducts as a mixture of ring-chain tautomers,[18] (II) and (III), in which case the equilibrium must be very rapidly established and must be well towards (III).

*Interpretations of Spectra.*—The spectrum of 1-methyl-2-pyridone (1) contains a complex band around $\tau$ 2·7, a triplet at 3·85, and a doublet at 3·43. The coupling between the 3- and the 5-proton is very small (~1 c.) so that the centres of gravity of the two high-field multiplets will be a good approximation to the chemical shifts. The line positions of the 4- and the 6-proton were then found by using a proton–proton double irradiation technique (developed in these Laboratories by Dr. D. W. Turner) details of which are being described elsewhere.

The 1,3-dimethyl-2-pyridone (2) approximates to an $A_2X$ nuclear-spin system. The 1,5-dimethyl-2-pyridone (3) gives rise to an ABC system, but the chemical shift between the strongly coupled 3- and 4-protons is sufficiently large to allow a first-order analysis. The spectrum of the 1,6-dimethyl-2-pyridone (4) can similarly be analysed because the 4-proton, which is involved in strong coupling with the 3- and the 5-proton, has a line position well removed from the others. The lines in the spectrum of 1,4,6-trimethyl-2-pyridone (5) are assigned on the basis of the chemical-shift data for the preceding pyridones. The assignments for the pyridone (6) follow similarly, the only difficulty then being distinction between the methyl group at the 6-position and that of the 3-acetyl substituent. However, the band at 7·48 is much the sharpest line in the spectrum and therefore is best regarded as arising from the protons of the 3-acetyl group.

The ring protons of the 2,6- and 3,5-lutidines, (9) and (10), and their quaternary salts,

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[16] Rodd, " Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1957, Vol. IVA, pp. 544—546; Elderfield, " Heterocyclic Compounds," Wiley, New York, 1950, Vol. I, pp. 534—537.

[17] Jackman, Johnson, and Tebby, *J.*, 1960, 1579; cf. Acheson and Taylor, *ibid.*, p. 1691.

[18] Cf. van Tamelen, Aldrich, Bender, and Miller, *Proc. Chem. Soc.*, 1959, 309.

(13) and (16), are by symmetry $A_2B$ nuclear-spin systems, and those of 2,4-lutidine (8) and its quaternary salt (14) approximate to the same type.

In the spectrum of the 1,2-dihydro-2-methylenepyridine (18) we have assigned the more deshielded of the two *C*-methyl absorptions to that of the 6-methyl substituent because in the other compounds proximity to the ring-nitrogen results in a paramagnetic shift. The low-field methyl is assigned to that attached to nitrogen. The compound was obtained in the previously described orange and yellow forms[19] but it did not prove possible to obtain distinct spectra corresponding to these supposed 4- and 2-methylene tautomeric forms, even by employing deuterochloroform and Bu$^t$OD, respectively, and examining the solutions as rapidly as possible. In addition to the strong bands listed in Table 1, there were weak bands at 8·02 and 6·87 which could be attributed to methyl and methylene in the 4-methylene system. The spectrum therefore is consistent with the existence of compound (18) as a tautomeric mixture in which the 2-methylene form predominates.

## EXPERIMENTAL

The nuclear magnetic resonance spectra were determined with a Varian 4300 spectrometer with a 56·4 Mc. oscillator. The measurements were made at 21° on 5% solutions in deuterochloroform containing 0·5% of tetramethylsilane as internal reference. The spectra were calibrated by the side-band technique with the aid of a Muirhead-Wigan D-695-A decade oscillator, each of the results which appear in Table 1 being the average of at least four separate determinations. All compounds (see Table) were purified and the spectra were consistent with the compounds' being pure.

| Compound No.[a] | Ref.[b] | M. p., or b. p.; $n_D^t$ | Found (%) | | | Formula | Calc. (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | | C | H | N |
| 1 | 20 | 82°/0·3 mm.<br>$n_D^{20}$ 1·5684 | 65·9 | 6·3 | 12·7 | $C_6H_7NO$ | 66·0 | 6·5 | 12·8 |
| 4 | 21 | 57—58° | 68·2 | 7·4 | 11·5 | $C_7H_9NO$ | 68·3 | 7·4 | 11·4 |
| 5 | 19 | 89° [c] | 69·9 | 7·9 | 10·4 | $C_8H_{11}NO$ | 70·0 | 8·1 | 10·2 |
| 6 | 19 | 91—92° | 62·1 | 6·8 | 5·65 | $C_{13}H_{17}NO_4$ | 62·1 | 6·8 | 5·6 |
| 8 | Com. | 157°<br>$n_D^{22}$ 1·4997 | 78·05 | 8·4 | | $C_7H_9N$ | 78·45 | 8·5 | |
| 9 | ,, | 143°<br>$n_D^{21}$ 1·4983 | 78·3 | 8·4 | | ,, | ,, | ,, | |
| 10 | ,, | 170°<br>$n_D^{24}$ 1·5031 | 78·6 | 8·6 | | ,, | ,, | ,, | |
| 11 | [d] | 73° | 61·9 | 6·7 | 5·9 | $C_{13}H_{17}NO_4$ | 62·1 | 6·8 | 5·6 |
| 12 | [e] | 185°/15 mm.<br>$n_D^{22}$ 1·4938 | 63·4 | 7·2 | 5·3 | $C_{14}H_{19}NO_4$ | 63·4 | 7·2 | 5·3 |
| 15 | 22 | 178° [f] | 38·3 | 4·6 | | $C_8H_{13}IN$ | 38·6 | 4·85 | |
| 16 | 23 | 270° | 38·8 | 4·65 | 5·2 | ,, | ,, | ,, | 5·6 |
| 17 (methosulphate) | 19 | 182° [g] | 49·2 | 6·4 | 3·6 | $C_{16}H_{35}NO_8S$ | 49·1 | 6·4 | 3·6 |
| 18 | 19 | Orange, 69° | 64·4 | 7·5 | | $C_{15}H_{21}NO_4$ | 64·5 | 7·6 | |
| | | Yellow, 74° | 64·6 | 7·6 | 5·3 | ,, | ,, | ,, | 5·0 |
| 19 | 24 | 75°/16 mm.<br>$n_D^{21}$ 1·5020 | 66·4 | 7·75 | | $C_7H_{10}O_2$ | 66·6 | 8·0 | |

[a] As in Table 1. [b] Reference to method of preparation; "Com." signifies commercial origin. Lit., m. p. 84—85°. [d] From the 1,4-dihydro-compound[25] by warming with 2N-nitric acid (7 parts) and concentrated nitric acid (1 part) for 15 min. and then adding an excess of ammonia. [e] By similar oxidation of the 1,4-dihydro-compound.[26] [f] Lit., m. p. 118°. [g] Lit., m. p. 172—174°.

[19] Mumm and Hingst, *Ber.*, 1923, **56**, 2301.
[20] Prill and McElvain, *Org. Synth.*, Coll. Vol. II, p. 419.
[21] Adams and Schrecker, *J. Amer. Chem. Soc.*, 1949, **71**, 1186.
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[24] Posner and Rohde, *Ber.*, 1910, **43**, 2665; Farmer and Morrison-Jones, *J.*, 1940, 1339.
[25] Singer and McElvain, *Org. Synth.*, Coll. Vol. II, 214.
[26] Haley and Maitland, *J.*, 1951, 3155.

1,3-*Dimethyl*-2-*pyridone* (2).—By Adams and Schrecker's methods,[21] 1-amino-3-picoline (7·3 g.) was converted into 3-methyl-2-pyridone (4·5 g.), m. p. 137—139°, and methylated to 1,3-*dimethyl*-2-*pyridone* (4·5 g.) which after fractionation had b. p. 78°/0·5 mm., $n_D^{24}$ 1·5550 (Found: C, 68·3; H, 7·2. $C_7H_9NO$ requires C, 68·3; H, 7·4; N, 11·4%), $\nu_{max.}$ (film) 2911m (C–H), 1649s (C=O), 1595s and 1559m (double bonds) cm.$^{-1}$.

1,5-*Dimethyl*-2-*pyridone* (3).—Similarly, 1-amino-5-picoline (9·3 g.) was transformed into 1,5-dimethyl-2-pyridone (6·3 g.), b. p. 98°/3·5 mm., which after further fractionation had m. p. 40—41° and was very hygroscopic (Found: C, 67·9; H, 7·4; N, 11·1%); it had $\nu_{max.}$ (in $CCl_4$) 2911m (C–H), 1699s (C=O), 1605s and 1528w (double bonds) cm.$^{-1}$.

2,6-*Lutidine Ethiodide* (13).—The components were refluxed together for 10 hr., and the *salt* was crystallised from acetone to give prisms, m. p. 240—242° (Found: C, 41·35; H, 5·55; N, 5·0. $C_9H_{14}IN$ requires C, 41·1; H, 5·4; N, 5·3%).

2,4-*Lutidine Ethiodide* (14).—Prepared by refluxing the components together for 2·5 hr., the *salt* crystallised from t-butyl alcohol as felted needles, m. p. 106° (Found: C, 41·1; H, 5·25%).

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[*Received, July* 11*th*, 1960.]