1123. *Preparation and Nuclear Magnetic Resonance Spectra of Some Halogenoquinolines. Nearly Degenerate* ABX *Spectra* *

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The preparation of three new 7-halogeno-2-methylquinolines is described. The proton magnetic resonance spectra of eleven quinolines containing 5- or 7-halogen substituents are presented. The influence of the halogens on the chemical shifts parallels that found in substituted benzenes; the contributory causes are analysed: the small effect on protons *peri* to the halogen seems anomalous. The several protons are affected differently by changes of concentration in carbon disulphide: this phenomenon has been studied in some detail. The easily confused protons 4 and 8 can be distinguished by their different dependence on concentration. Diehl's additive substituent theory of solvent effects is extended, and used to interpret both these concentration effects and also solvent effects on quinoline spectra.

Four of these compounds exhibit partially degenerate ABX spectra. The appearance of such spectra is qualitatively described, and classified by a series of inequalities: these (together with ^{13}C satellites in concentrated solution) are used as aids in the complete analyses.

Modified Skraup reactions with crotonaldehyde and a *m*-halogenoaniline give high yields (cf. ref. 1) of 7- and 5-halogeno-2-methylquinolines. The ratio (7- : 5-) of isomers in these mixtures decreases as the electronegativity of the halogen decreases from fluorine to iodine

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* For previous information see ref. 2.

[1] W. P. Utermohlen, *J. Org. Chem.*, 1943, **8**, 544.

(Table 1), thus paralleling the formation of 5- and 7-halogenoquinolines in the Skraup reaction [2] (an anomalous ratio of the 5-and 7-chloro-2-methylquinolines was reported earlier [2]).

TABLE 1

Quinolines prepared by the Skraup reaction

m-Halogenoaniline		F	Cl	Br	I
Halogeno-2-methylquinolines	(7- : 5-)	72 : 27	55 : 45	52 : 48	46 : 54
,,	B. p. (uncorr.)	236—242°	155—160°/ 25 mm.	150—156°/ 17 mm.	116—124°/ 0·5 mm.
,,	Yield (%)	68	72	72	68

Nuclear Magnetic Resonance Spectra: General Features.—The spectra of the separated 5- and 7-halogeno-2-methylquinolines show a variety of interesting solvent effects and near-degeneracy and have been investigated in some detail. In order to gain greater knowledge of these systems a variety of other 5- and 7-halogenoquinolines were also studied. The spectra of 7-bromo-, 7-bromo-2-methyl- and 5-chloro-2-methyl-quinoline and all of the 5-halogenoquinolines require mathematical analysis, and five of these are discussed below. For the remaining 7-halogeno and 7-halogeno-2-methyl-quinolines the spectra are first-order and the line multiplicity is as expected for compounds of this type, except that in the 7-fluoro-compound the 6-H octet anticipated (by coupling with 5-H, 8-H, and 7-F) is observed as a sextet since $J_{6,F} \approx J_{5,6}$. The results are presented in Tables 2—4.

TABLE 2

Chemical shifts and coupling constants in the 7-halogenoquinolines

	Chemical shifts [a]					Coupling constants			
Substituents	3	4	5	6	8	$J_{3,4}$	$J_{6,5}$	$J_{6,8}$	$J_{4,8}$
7-F, 2-Me [b]	429	475	460	428	448	8·5	8·7	2·6	0·8
7-Cl, 2-Me	430	475	457	438	471·5	8·4	8·6	2·0	1·0
7-Br, 2-Me [c]	431·5	475	452·5	447·5	482	8·5	8·9	2·2	0·8
7-I, 2-Me	431	473·5	443	459	497·5	8·6	8·6	1·7	0·6
7-Br [d]	439	483	457	452	490	8·4	8·9	2·0	0·9
7-F [e]	436	483	464	433	455	8·4	9·1	2·6	0·8

[a] In CS_2 and extrapolated to infinite dilution; c./sec. downfield from tetramethylsilane. [b] ν_F = 110·65 p.p.m. upfield from CCl_3F as internal reference. $J_{5,F}$ = 6·5 c./sec., $J_{6,F}$ = 8·4 c./sec. approx., $J_{8,F}$ = 10·0 c./sec. (from ^1H and ^{19}F spectra). [c] Second-order analysis gives $J_{5,8} \gtrsim 0·4$ c./sec. (see text). [d] ν_2 = 529 c./sec.; $J_{2,3}$ = 4·2 c./sec.; $J_{2,4}$ = 1·9 c./sec.; $J_{5,8}$ = 0·5 c./sec. (cf. note *c*). [e] ν_2 = 528 c./sec.; $J_{2,3}$ = 4·3 c./sec.; $J_{2,4}$ = 1·8 c./sec.; $J_{5,F}$ = 6·5 c./sec.; $J_{6,F}$ = 8·2 c./sec.; $J_{8,F}$ = 10·0 c./sec. (from ^1H spectra).

TABLE 3

meta-Coupling constants (c./sec.) in substituted quinolines [a]

Substituents	None [4]	5-Cl, 2-Me	5-Cl	5-Br	5-I	$5-NO_2$ [4]	$7-NO_2$ [4]	7-Me	$7-CF_3$	7-OMe	$5,7-Cl_2$ [4a]
$J_{6,8}$	1·1	1·9	1·6	1·6	1·1	1·2	2·3	1·5	1·8	2·7	2·0

Substituents	None [4]	6-Me	$8-NO_2$ [4]	$4,6-Me_2$ [3]
$J_{5,7}$	1·5	1·9	1·4	1·8

[a] In CS_2 except where a literature reference is given.

TABLE 4

Chemical shifts in 5-halogenoquinolines [a]

Substituents	2	3	4	6	7	8
5-F [b]	530·5	441	499	(*ca.* 429) [c]	(*ca.* 460) [c]	(*ca.* 470) [c]
5-Cl [d]	530·5	444	507·5	450·5	452	476·5
5-Br [d]	529·5	444	505	463·5	448·5	480·5
5-I	525·5	441	496	*ca.* 480 [c]	439·5	*ca.* 480 [c]
5-Cl, 2-Me [d]	—	436	499·5	444·5	448	469·5

[a] In CS_2 extrapolated to infinite dilution; c./sec. downfield from tetramethylsilane. [b] The specimen contained about 30% 7-fluoroquinoline; peaks, however, could be unambiguously identified. [c] Estimated from incompletely analysed second-order spectrum. [d] Second-order: see text.

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[2] M. H. Palmer, *J.*, 1962, 3645.

Coupling Constants.—These (Table 2) are in overall agreement with those previously reported.[3,4,4a] However, the comparatively large *meta*-coupling constant ($J_{6,8}$), across the 7-halogen-substituent, parallels that found both by us[5] and by others in a variety of other substituted quinolines (Table 3). These figures are generally larger than those for the unsubstituted quinolines. Since in the 5-halogeno-series the *meta*-coupling constants decrease on going from the chloro- to the iodo-compound, the latter being equal to that of the unsubstituted quinoline, it is apparent that a steric effect is unimportant. Furthermore, the 5-nitro-compound also has a low $J_{6,8}$ value, which suggests that these constants are not linearly related to electron withdrawal by the substituent in this series.[6,7]

In *meta*-coupling across a 7-substituent, the constant increases in the order H $<$ Me $<$ CF_3, I $<$ Br, Cl $<$ F, NO_2, OMe; a large coupling constant is apparently associated with an intervening substituent conjugated with the ring, though the quantum-mechanical significance of this is not evident.

Chemical Shifts.—The spectra of these compounds in carbon disulphide were studied in solutions of at least four concentrations, and the dependence of the chemical shift was found to be effectively linear up to at least 4 moles-% ($\sim$ 10% w/v). The shifts, extrapolated to infinite dilution, are presented in Tables 4 and 6.

The halogen substituents have very little effect on protons in the other ring (except 5-Hal on 4-H); but the 2-methyl has a slightly greater effect on the protons of the benzo-ring, particularly 8-H. Thus, in extending Diehl's additive substituent constants[8] to bicyclic systems, cross-ring terms S_{Me} must be included, as has been found for the more strongly perturbing nitro-group.[4,9]

In comparing the halogen-substituent effects, the consistency of varied experimental data can be contrasted with the limited understanding hitherto achieved. Theoretically six main influences may be distinguished, of which four are very familiar.

(*a*) *Internal inductive.* This is a downfield effect for the halogens. If it acted alone, the shift of a given proton in a series of molecules would vary in the order $\tau_i^{\text{F}} < \tau_i^{\text{Cl}} < \tau_i^{\text{Br}} < \tau_i^{\text{I}}$; for brevity, we shall refer to this as an upward trend.

(*b*) *Mesomeric.* This is an upfield effect with a downward trend, acting on *ortho*- and *para*-protons.

(*c*) *Ring current.* The variation of ring currents in a series of unsubstituted condensed benzenoid hydrocarbons[10] suggests that mesomeric substituents might also significantly alter the ring current. This effect would be like (*b*) but would act equally on all the protons of the substituted ring, and, to a smaller extent, of other rings.

(*d*) *Electrostatic field.* This is a downfield effect.[11] The near-equality of the carbon–halogen electrical dipoles (in halogenobenzenes) renders its *comparative* effect negligible, as is confirmed by detailed calculation.

(*e*) *Magnetic anisotropy.* It seems to be generally agreed that for carbon–halogen bonds $\Delta\chi \equiv \chi_{\parallel} - \chi_{\perp} > 0$. (The most cogent single item of evidence * appears to be the very large upfield shift of ^{13}C linked to iodine.[12]) Calculations used the crude dipole approximation,[13] although delocalisation of the halogen $p_{\bar{z}}$ electrons will modify axial symmetry.

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* Note added in proof.—The finding by Traficante and Maciel (*J. Phys. Chem.*, 1965, **69**, 1348) that halogen substitution not only on sp^2-hybridised carbon but also in *linear* acetylenes give *opposite* trends for α- and β-^{13}C shifts cannot be explained by anisotropy alone, and adds a further uncertainty.

[3] (*a*) T. Schaefer, *Canad. J. Chem.*, 1961, **39**, 1864; (*b*) L. W. Reeves and K. O. Strømme, *ibid.*, p. 2318.

[4] P. J. Black and M. L. Heffernan, *Austral. J. Chem.*, 1964, **14**, 558.

[4a] F. A. L. Anet, *J. Chem. Phys.*, 1960, **32**, 1274.

[5] M. H. Palmer and B. Semple, unpublished results.

[6] J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, 1962, **37**, 2594; 1963, **39**, 1722.

[7] P. F. Cox, *J. Amer. Chem. Soc.*, 1963, **85**, 380.

[8] P. Diehl, *Helv. Chim. Acta*, 1961, **44**, 829.

[9] P. R. Wells, *J.*, 1963, 1967.

[10] N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 1962, **36**, 2443.

[11] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

[12] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, (*a*), p. 722; (*b*) p. 731.

[13] H. McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

As has been found by others, the sign of the effect at an *ortho*-proton is indeterminate, the effect of an iodine atom being estimated at +5 to −6 c./sec.* (at 60 Mc./sec.), the other halogens giving correspondingly smaller shifts. At a *meta*- or *para*-proton, the effect is not quite negligible for the heavier halogens, *e.g.*, +3 to 5 c./sec. (upfield) for iodine at both.* At a *peri*-proton on the other hand, the calculated shift with iodine is −10 to −20 c./sec.*, *i.e.*, downfield. But these must only be regarded as probable orders of magnitude, as it is not clear that a magnetic multipole expansion would even converge when the electron clouds actually overlap.

(*f*) *Steric.* Intermolecular Van der Waals' forces are known to affect chemical shifts;[14] such intramolecular effects have received little detailed consideration. Three concepts may be distinguished.[15] (i) At all ranges, London dispersion forces polarise the atoms' electron clouds toward each other (according to an inverse sixth-power law), reducing the diamagnetic term, *i.e.*, shifting the absorption downfield. (ii) For ranges a little above or below the conventional Van der Waals' separation, the repulsive overlap forces produce an opposite effect. (iii) At short range, the major interference of the electron clouds hinders precession and thus now produces a downfield shift. In severely hindered cases, clearly (iii) will predominate; but preliminary calculations[15] suggest there may be some cancellation in only slightly overcrowded situations.

The effect has been observed, particularly in aromatic hydrocarbons;[10,16] and larger steric effects are found in ^{19}F spectra.[17]

Simple geometry shows that a proton *ortho* to any halogen substituent will be somewhat overcrowded, a *peri*-proton distinctly more so; of course this overcrowding will be partially relieved, mostly by in-plane angle-bending.[18] Downfield shifts and a downward trend would thus be expected.

We now turn to the experimental evidence.

para-*Protons.* The small downward trend for 8-H in the 5-halogeno-series closely parallels that of the halogenobenzenes.[12b] It can be ascribed to (*b*) (with *c*), partly cancelled by (*a*) (with *e*).[19]

meta-*Protons.* The distinct upward trend for 5-H and 7-H could naïvely be interpreted in terms of (*a*). But the S_m values (average shift due to a *meta*-substituent) are: F 2 (1), Cl 4 (4), Br 7 (7), and I 14 (13) c./sec.,* all *upfield* of the parent molecule, the pattern again being close to ours. We have obtained the following least-squares fit of Smith's S_m values[20] against Taft's parameters:[21]

$$S_m = -7{\cdot}2\ \sigma_{\mathrm{I}} - 21\ \sigma_{\mathrm{R}} + 0{\cdot}0 \text{ c./sec.}$$

This has a r.m.s. deviation of 5 c./sec. for a three-parameter fit to 16 sets of data, the total range of S_m being 26 c./sec., an unimpressive result. If any significance can be attached to it, the σ_{R} term would be indicative of effect (*c*). But the line joining the four halogen points is approximately *perpendicular* to the best line, the deviation of I being 14 c./sec. This situation is obscure, and contrasts with that for ^{19}F spectra[22] (see also ref. 6).

ortho-*Protons.* The strong downward trend observed in 6-H of the 5-halogeno-compounds (series Ia, total range ~50 c./sec.), and in 8-H (Ib, range 50 c./sec.) and 6-H

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* Assuming $\Delta\chi = 8{\cdot}8 \times 10^{-6}$ cm.^{3} mole^{-1}; the first figure is obtained when the magnetic dipole is placed at the halogen atom, the second when it is at the bond mid-point.

[14] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.

[15] T. W. Marshall and J. A. Pople, *Mol. Phys.*, 1960, **3**, 339.

[16] R. H. Martin, *Tetrahedron*, 1964, **20**, 897, and subsequent Papers.

[17] M. J. S. Dewar, R. C. Fahey, and P. J. Grisdale, *Tetrahedron Letters*, 1963, 343.

[18] C. A. Coulson and D. Stocker, *Mol. Phys.*, 1959, **2**, 397; C. A. Coulson and C. W. Haigh, *Tetrahedron*, 1963, **19**, 527.

[19] R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Amer. Chem. Soc.*, 1959, **81**, 5352.

[20] G. W. Smith, *J. Mol. Spectroscopy*, 1964, **12**, 146.

[21] R. W. Taft, N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, 1958, **9**, 292.

[22] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709.

(II, range 31 c./sec.) of the 7-halogeno-2-methyl compounds again resemble the S_o values: F +14 (+15), Cl −4 (−2), Br −12 (−13), I −23 (−25) c./sec. † [series III, range 37 (40) c./sec.].* Effects (*b*) (with *c*) and (*a*) may well cancel each other at this position to a considerable extent; the positive $S_{o,\mathrm{F}}$ does indicate an important contribution from (*b*) (with *c*) for fluorine. Even if the calculations of (*e*) gave as a minimum value only a quarter of an actual downfield anisotropic effect, we could still not account for the range of shifts in series I. Thus we are led to postulate a contribution from (*f*).‡ Now the ranges in series I, III, and II follow the relevant carbon–carbon bond orders; and steric effects, with their steep dependence on distance, are most likely to be sensitive to small changes in geometry (cf. also ref. 24).§ And it may be relevant that in Smith's S_o–S_m plot (Figure 3 of ref. 20), the only significant || points beside Cl, Br, and I in the anomalous $S_o < 0$, $S_m > 0$ quadrant are the bulky SH, SEt, and Bu^t-groups. Our conclusions agree with those of ref. 26*b*.

peri-*Protons.* On comparing ν_4 in 7- and 5-fluoro-, in 7- and 5-chloro-2-methyl-, and in 7- and 5-bromo-quinoline, we see the net downfield effect on 4-H of the 5-halogeno-substituent (relative to hydrogen) is about 16, 25, and 22 c./sec., respectively.¶ The 4-H in the four 5-halogenoquinolines absorb over a range of only 11·5 c./sec., with no clear trend. Effect (*b*) should here be nil, and (*a*) and (*c*) quite small. Effect (*e*) should give a downfield effect and downward trend, effect (*f*) a downfield effect with an even stronger downward trend than at the *ortho*-position. The marked contradiction with experiment is unexplained.

Dependence of Chemical Shifts on Concentration and Solvent.—The slopes of the concentration–chemical-shift graphs show variable effects of dilution on different protons ** (Table 5); relative gradients within a molecule are more accurately determined than shifts relative to the standard. 7-Bromo-2-methylquinoline was studied up to 11 moles-% in carbon disulphide, and shows very slight deviations from linearity. But the low-melting 7-fluoro- and 7-bromo-quinoline were studied over the whole range 0—100% (Figure 1). There are no less than four cross-over points in the two graphs. No absolute significance can be attached to the curious negative gradients and minima,[28] for we have been using an *internal* standard (of very different shape) in the presence of finite quantities of highly anisotropic molecules.†† In 7-fluoroquinoline, ν_3, which had the largest (upfield) gradient in very dilute solution (Table 5) is less steep than ν_4 or ν_5 in more concentrated solutions;

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* First value in CCl_4 solution; [20] second (in brackets) in cyclohexane.[8]

† Both *ortho* ^{19}F shifts [19] and *ortho* (ring) ^{13}C shifts [12b] show a similar pattern.

‡ Cf. also the marked downfield shift of 8-H (which is both *ortho*- and *peri*-hindered) in 7-halogeno-1-methylnaphthalenes.[23]

§ The chemical shifts of the analogous *cis*-protons of the vinyl halides (in carbon tetrachloride) relative to ethylene are F +58, Cl −11, Br −33 c./sec.,[25] again the same pattern with a scale factor of ~3. The first figure may be due to (*b*) (the charge being spread over fewer atoms). But the fact that the difference between the last two figures is double that of the corresponding interval even in series I could perhaps also be interpreted as largely steric, in view of the much shorter carbon–carbon bond. (See also ref. 26).

|| Taken in CCl_4, derived from more than one compound.

¶ The contribution of effect (*d*) is calculated to be 12, 14, and 15 c./sec., respectively, using Buckingham's parameters.[11]

** For concentration studies in porphyrins see ref. 27.

†† Preliminary experiments [5] with an external standard (and the inaccuracy of bulk susceptibility correction) indicate that 50 ± 6 and 59 ± 2 c./sec. should be subtracted from the frequencies in Figures 1a and b, respectively (for the neat liquids), in order to relate them to tetramethylsilane in pure carbon disulphide. Thus, *apparent* downfield shifts indicate that such protons are less influenced by the averaged intermolecular effects of ring-currents than are those of the internal standard.

[23] R. W. Griffin, J. D. Goss, M. A. Berwick, and R. S. Shulman, *J. Org. Chem.*, 1964, **29**, 2109.

[24] R. H. Martin, J. P. Van Trappen, N. Defay, and J. F. W. McOmie, *Tetrahedron*, 1964, **20**, 2382.

[25] C. N. Banwell and N. Sheppard, *Mol. Phys.*, 1960, **3**, 351.

[26] (*a*) T. Schaefer and T. Yonemoto, *Canad. J. Chem.*, 1964, **42**, 2318; (*b*) T. Schaefer, W. F. Reynolds, and T. Yonemoto, *ibid.*, 1963, **41**, 2969.

[27] G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Amer. Chem. Soc.*, 1963, **85**, 3809.

[28] M. G. Reinecke, H. W. Johnson, and J. F. Sebastian, *Chem. and Ind.*, 1964, 151.

ν_3 in 7-bromoquinoline shows a similar trend to a smaller extent. The effect on 7-chloro-2-methylquinoline of changing the solvent to dimethyl sulphoxide is shown in Table 6 (note the transposition of the 5-H and 8-H absorptions compared with Table 2).

TABLE 5

Dilution shifts of halogenoquinolines in carbon disulphide [a]

Substituents	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_4$	$\Delta\nu_5$	$\Delta\nu_6$	$\Delta\nu_7$	$\Delta\nu_8$
7-F, 2-Me	—	3·0	2·1	2·1	1·5	—	−1·5
7-Cl, 2-Me	—	3·4	4·0	3·9	2·6	—	0·5
7-Br, 2-Me	—	4·0	5·4	4·6	2·7	—	−0·4
7-I, 2-Me	—	4·0	3·5	4·2	3·3	—	−0·4
7-F	1·0	2·7	1·8	2·2	1·6	—	−2·2
7-Br	1·6	3·6	4·0	4·3	2·2	—	−0·4
5-F [b]	(1·0)	(2·8)	(2·5)	—	(1·6)	(2·2)	(−1·6)
5-Cl	0	2·9	2·1	—	1·4	1·4	0
5-Br	1·1	3·6	2·3	—	2·7	2·7	0·2
5-I	0	1·8	2·7	—		1·4	
5-Cl, 2-Me	—	3·3	3·0	—	1·5	1·7	0

[a] Upfield shift from 0 to 5 mole per cent., in c./sec.; estimated accuracy ±0·5 c./sec. [b] See footnotes *b* and *c* to Table 4.

TABLE 6

Chemical shifts for 7-chloro-2-methylquinoline and derivatives [a]

	Proton resonances				
	3	4	5	6	8
Tertiary base	446·5	497·0	479·0	453·0	477·0
1-Oxide	456·0	473·5	487·0	463·0	513·5
Methiodide	488·5	548·0	508·0	483·5	526·0

[a] In dimethyl sulphoxide, extrapolated to infinite dilution; c./sec. downfield from tetramethylsilane.

These results, and those of others on quinolines, may be interpreted using the terminology of Diehl's additive theory of solvent effects in benzene derivatives.[29] He writes:

$$\nu_i^\alpha - \nu_i^0 = \sum_{\mathrm{X}} L_{j,\mathrm{X},\alpha}$$

where ν_i^α is the chemical shift of the *i*'th proton in the solvent system α, and ν_i^0 in the reference solvent hexane; the subscript *j* indicates relative position (*o*, *m*, or *p*); and X is a substituent. Thus, *e.g.*, for 4-nitrotoluene in acetone we have

$$\nu_3^{\mathrm{acetone}} - \nu_3^0 = L_{o,\mathrm{NO_2},\mathrm{acetone}} + L_{m,\mathrm{Me},\mathrm{acetone}}$$

To allow for the overall effect of solvent change on aromatic absorptions, he writes

$$\nu_i^\alpha - \nu_i^0 = L_{\mathrm{H},\alpha} + \sum_{\mathrm{X}} L'_{j,\mathrm{X},\alpha}$$

where $L_{\mathrm{H}}^\alpha \equiv \nu_0^\alpha - \nu_0^0$, the chemical shift difference for benzene. The L' values are found to be reasonably additive and are tabulated. We may extend his notation for the comparison of any two solvent systems,* α and β.

Writing
$$\Delta L_{j,\mathrm{X}} \equiv L_{j,\mathrm{X},\beta} - L_{j,\mathrm{X},\alpha}$$
$$\Delta L'_{j,\mathrm{X}} \equiv L'_{j,\mathrm{X},\beta} - L'_{j,\mathrm{X},\alpha}$$
and
$$\Delta L_{\mathrm{H}} \equiv L_{\mathrm{H},\beta} - L_{\mathrm{H},\alpha} = \nu_0^\beta - \nu_0^\alpha,$$
then
$$\Delta\nu_i \equiv \nu_i^\beta - \nu_i^\alpha = \sum_{\mathrm{X}} \Delta L_{j,\mathrm{X}} = \Delta L_{\mathrm{H}} + \sum_{\mathrm{X}} \Delta L'_{j,\mathrm{X}}$$

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* These need not be pure systems (neat liquids; or infinite dilution); they can also be mixed systems, *e.g.*, finite concentration of solute in solvent.

[29] (*a*) P. Diehl, *Helv. Chim. Acta*, 1962, **45**, 568; (*b*) *J. Chim. phys.*, 1964, 199.

Applying these ideas to bicyclic systems, we may, by subtracting the chemical shifts of quinoline itself in carbon tetrachloride and acetone,[4] obtain a set of $\Delta L_{j,\mathrm{N}}$ values for this pair of solvents, the hetero-atom being regarded as a "substituent." Logically, the reference compound should now be naphthalene; and if we now make a ΔL_{H} allowance of -15 p.p.h.m. for naphthalene-1 protons, and -11 p.p.h.m. for naphthalene-2 protons (all relative to internal tetramethylsilane) [9,20] we obtain the following values: *

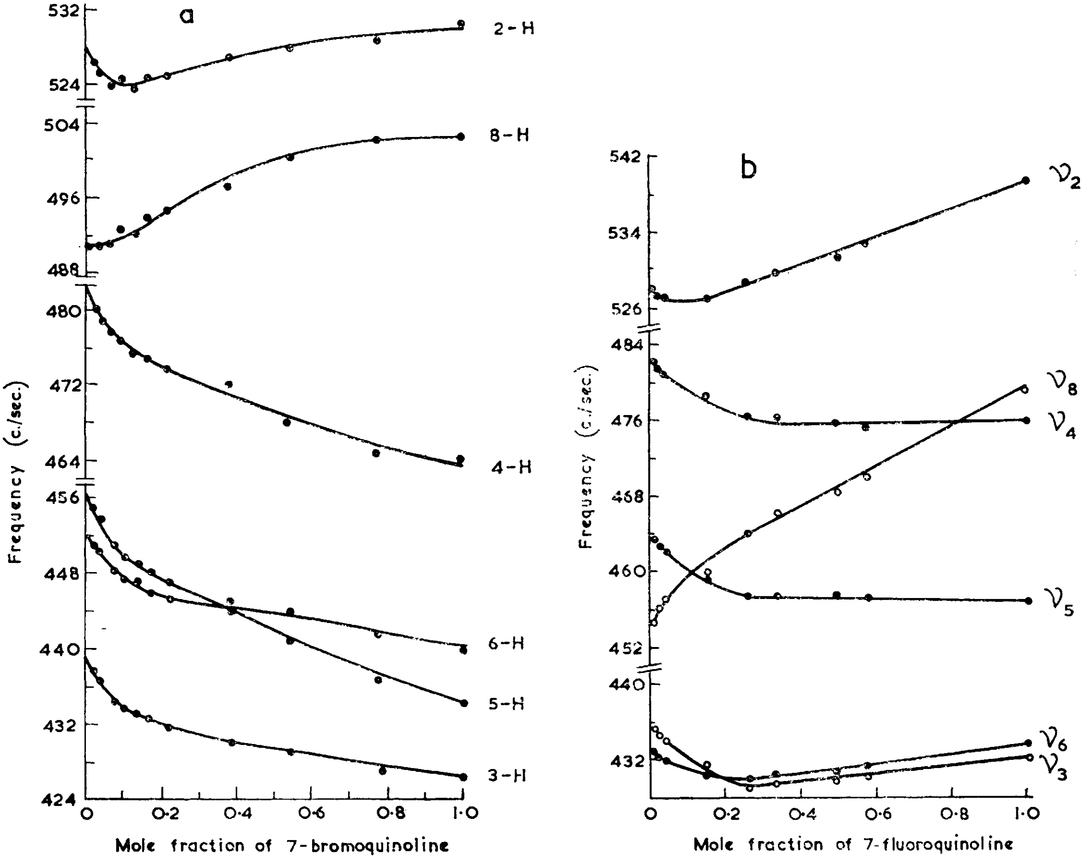

FIGURE 1. Proton chemical shifts in mixtures of carbon disulphide with 7-fluoroquinoline and with 7-bromoquinoline

Proton:	2	3	4	5	6	7	8
$\Delta L_{j,\mathrm{N}}$	-9	-20	-28	-24	-11	-12	-1
$\Delta L'_{j,\mathrm{N}}$	$+2$	-10	-13	-8	0	-1	$+15$

The unit "part per hundred million" (p.p.h.m.) is used in all this section, to facilitate comparison with Diehl. The *o*-, *m*-, and *p*-values can be compared with Diehl's L'^{acetone} values: $\Delta L'_m \approx \Delta L'_p$, and $L'_m \approx L'_p$ in his Table. The large value of $\Delta L'_{peri,\mathrm{N}}$ is striking.

In considering substituted quinolines, we must add suitable terms to the $\Delta L_{j,\mathrm{N}}$ values, *e.g.*, 5-chloro-2-methylquinoline, on changing solvents,

$$\Delta\nu_4 = \Delta L_{p,\mathrm{N}} + \Delta L_{m,\mathrm{Me}} + \Delta L_{peri,\mathrm{Cl}}.$$

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* Less accurate values (40 Mc./sec., graphical presentation) for the same solvent changes with 8-methylquinoline (hetero-ring protons only) are in rough agreement.[3b]

If we compare 7-chloro-2-methylquinoline in carbon disulphide and dimethyl sulphoxide (Tables 2 and 6) we obtain:

Proton:	3	4	5	6	8
$\Delta\nu_i$	−28	−37	−37	−25	−9

The pattern is very similar to that of the previous Table; it is at least consistent with a significant negative value of $\Delta L_{m,\mathrm{Cl}}$ (from ν_5), and small values of $\Delta L_{o,\mathrm{Cl}}$, $\Delta L_{o,\mathrm{Me}}$, and $\Delta L_{m,\mathrm{Me}}$ — agreeing with Diehl's L' values in acetone, a solvent of similar structure and slightly smaller dielectric constant.

If we compare quinoline itself in carbon tetrachloride and as the neat liquid,[4] we find the apparent * values: †

Proton:	2	3	4	5	6	7	8
$\Delta L_{j,\mathrm{N}}$	−21	+17	+17	+10	+8	+2	−38

On comparing the 7-fluoro- and 7-bromo-quinoline in carbon disulphide and as neat liquid (Figure 1), the $\Delta\nu_i$ values * found are:

Proton:	2	3	4	5	6	8
7-Fluoroquinoline	−20	7	22	12	−2	−42
7-Bromoquinoline	−5	21	31	38	20	−20

This particular analogy must not be pressed too far in view of the differences of the systems, but at least the definite positive value of $\Delta L_{m,\mathrm{Br}}$ (again on ν_5) is evident (cf. Diehl's related $L'^{\,\mathrm{benzene}}_{m,\mathrm{Br}}$).

In Table 5, the two solvent systems being compared are infinite dilution in carbon disulphide and 5 moles-% in it: caution must be used in interpreting these much smaller values. The pattern appears to be dominated by the $\Delta L_{j,\mathrm{N}}$ terms; ‡ the $\Delta L_{j,\mathrm{Me}}$ terms are of the order of experimental error. From $\Delta\nu_4$, $\Delta L_{peri,\mathrm{Hal}}$ appears significant and negative. The effects of Cl, Br, and I seem comparable (as are Diehl's $L'^{\,\mathrm{benzene}}_{j,\mathrm{Hal}}$). The smaller overall values of $\Delta\nu_i$ in the fluoro-compounds may not be an additive but a specific effect in this system, stemming from their smaller mutual intermolecular attraction.§

The fact that $\Delta L'_{p,\mathrm{N}}$ and $\Delta L'_{peri,\mathrm{N}}$ are so very different, and (in particular) in Table 5 that $\Delta\nu_4$ is comparatively large and positive whereas $\Delta\nu_8$ is much smaller and often negative, may assist the assignment of the 4-H and 8-H absorptions when criteria of electron density are ambiguous. Thus, in quinoline itself (in acetone solution) the identities of the 4-H and 8-H absorptions were only established by double resonance.[4] This situation, which arises because $J_{3,4} \approx J_{7,8}$, $J_{2,4} \approx J_{6,8}$, and $J_{5,8}$ is not resolved, may occur particularly in 5-monosubstituted quinolines and in 2,6- and 3,7-disubstituted quinolines (with or without an additional 5-substituent). The magnitude of the *meta*-coupling constant may also be of assistance (*vide supra*). In principle, any significant solvent change should show up the difference in $\Delta L'$ values; but its very magnitude may lead to the precise mistake we are seeking to avoid (as in acetone), whereas a concentration effect can be varied at will, within limits.

Another practical point may be made. If it is necessary (for reasons of solubility) to compare the spectra of two compounds in the same polar solvent, regard should be paid to the magnitude of the differential solvent terms $L'_{j,\mathrm{X}}$ before too nice distinctions are drawn.

The scattered analogies we have advanced between solvent studies in quinoline spectra

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* In these three cases, the distinction between internal and external standards is important. When the suggested corrections are applied (*supra*) the $\Delta\nu_i$ values for the unsubstituted ring of the 7-halogenoquinolines are very similar.

† Less accurate values (40 Mc./sec., graphical presentation) for the same solvent changes with 8-methylquinoline (hetero-ring protons only) are in rough agreement.[35]

‡ But preliminary experiments involving diluting solutions in hexane [5] indicate that $\Delta\nu_2$ and $\Delta\nu_8$ are nearer to the other $\Delta\nu_i$ in that system.

§ 7-Trifluoromethylquinoline also has low $\Delta\nu_i$ values.[5] In the monofluoroquinoline series, the boiling points are either similar to, or lower than, those of the parent hydrocarbon,[2,30] and much lower than those of the chloro-analogues.

[30] A. Roe and G. Hawkins, *J. Amer. Chem. Soc.*, 1949, **71**, 1785.

and the work of Diehl are suggestive rather than in any way cogent. It will require the accumulation of much more data before it can be satisfactorily proved that L' values (including $L'_{j,\mathrm{N}}$) are additive in these bicyclic systems.

It must be clearly understood that the interpretation of solvent and concentration effects within the essentially empirical conceptual framework created by Diehl is not to be confused with an understanding of their causes. Only one positive suggestion will here be made. The $\Delta L'_{j,\mathrm{N}}$ values from non-polar carbon tetrachloride to polar acetone (p. 6010) can be qualitatively explained as follows. Let us assume that the dipole term of the multipole expansion of the charge distribution in quinoline lies roughly from 4-H to the nitrogen, with its positive pole shifted slightly towards 3-H. Then, if we take into account the asymmetric position of the dipole and hence its smaller (indirect) effect on the benzo-ring, the reaction-field theory[11] predicts

$$\Delta L'_{4,\mathrm{N}} < \Delta L'_{5,\mathrm{N}} \sim \Delta L'_{3,\mathrm{N}} < \Delta L'_{6,\mathrm{N}} < 0 < \Delta L'_{7,\mathrm{N}} < \Delta L'_{2,\mathrm{N}} \lesssim \Delta L'_{8,\mathrm{N}}.\text{*}$$

Apart from a small discrepancy at 7-H, this is the observed order; indeed, because of the dominance of the $\Delta L'_{j,\mathrm{N}}$, it is very close to the observed order of $\Delta\nu_i$ values in all quinolines studied (comparing non-polar with polar solvents, but excluding aromatics). Thus, within this range of solvent changes, the reaction field is likely to be a major, but certainly not the only, factor; the agreement is qualitative, not even semi-quantitative. But no clear explanation has yet appeared for the fact that aromatic solvents (non-polar benzene and mildly polar quinolines) produce exactly the *reverse* effect; † the order is certainly not, *e.g.*, that of electron densities.[3a] In view of the difficulty in a theoretical understanding,[14] a generalised empirical theory might be of some use for the correlation of results, and has been initiated.[31]

Table 6 also gives the chemical shifts for the corresponding amine oxide and methiodide; apart from the 8-H resonance, the chemical shifts of the amine oxide are more similar to those of the tertiary base than to those of the methiodide. The low-field shift of 3-H and 4-H on quaternisation is similar to that observed in pyridine.[32,33] That the 8-H and 4-H should be almost equally affected is rather surprising, for both the smaller diamagnetic anisotropy of the quaternary nitrogen and the removal of the lone-pair dipole would tend to oppose (in the case of 8-H) the downfield effect of changes in electron density. But as Gil and Murrell point out,[33] several other factors require consideration, not least the solvent.‡

NEARLY DEGENERATE ABX SPECTRA

The spectra to be discussed are examples of concentration-dependent nearly degenerate ABX systems. It is convenient to describe the general types first. The AB part of a quasi-first-order ABX spectrum, for the case $\sigma_\mathrm{B} > \sigma_\mathrm{A}$, $\nu_\mathrm{B} < \nu_\mathrm{A}$, *i.e.*, B absorbing upfield of A, and $J_{\mathrm{A,X}} < J_{\mathrm{B,X}}$ is shown in Figure 2f, the transitions being numbered as in ref. 34. Under circumstances which have been carefully discussed,[35] the AB part appears as a doublet, whose spacing

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* To avoid an awkward notation we have written the number of the proton instead of *j*.

† Note added in proof.—J. N. Murrell and V. M. S. Gil (*Trans. Faraday Soc.*, 1965, **61**, 402) have convincingly explained the benzene solvent effect on pyridines, and confirmed J. V. Hatton and R. E. Richards's explanation (*Mol. Phys.*, 1962, **5**, 153) of shifts in neat pyridines. These ideas extended to quinolines explain the observed trends. For whereas—when reaction field effects predominate—the proton at the positive end of the molecular dipole (4-H) is most shifted to *low* field, when an aromatic solvent is used the loose association leaves 4-H nearest below the centre of the solvent molecule's ring current and hence most shifted to *high* field. The loose quinoline–quinoline association we postulate is like that drawn by these authors, but with the carbocyclic rings *cis* to each other. Ref. 29*b* contains a clear discussion of such questions for substituted benzenes as solutes. Further work is planned in order to clarify these factors.

‡ An ion-pair model (G. Kotowycz, T. Schaefer, and E. Bock, *Canad. J. Chem.*, 1964, **42**, 2451) does qualitatively account for this feature.

[31] C. W. Haigh, unpublished work.

[32] A. R. Katritzky and J. M. Lagowski, *J.*, 1961, 43.

[33] V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, 1964, **60**, 248.

[34] J. A. Pople, W. G. Schneider, and H. J. Bernstein, " High-resolution Nuclear Magnetic Resonance," McGraw-Hill, London, 1959, p. 134.

[35] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.

is $\frac{1}{2}(J_{A,X} + J_{B,X})$: this " deceptively simple " case is shown in Figure 2a. We shall however be concerned with intermediate cases. The following notation will be used: $\delta = \nu_A - \nu_B$; $L = \frac{1}{2}(J_{A,X} - J_{B,X})$. The AB part of an ABX spectrum can be conveniently thought of as two simple AB quartets, namely transitions 1, 3, 5, 7 and 2, 4, 6, 8, each of whose spacings is given by the usual AB formulæ, but with δ replaced by $(\delta \pm L)$, the positive sign referring to the second quartet. For sufficiently small values of δ and L these quartets both effectively degenerate to singlets (Figure 2a). Let us retain the condition $|L| \ll J_{A,B}$ (we have illustrated $L < 0$),

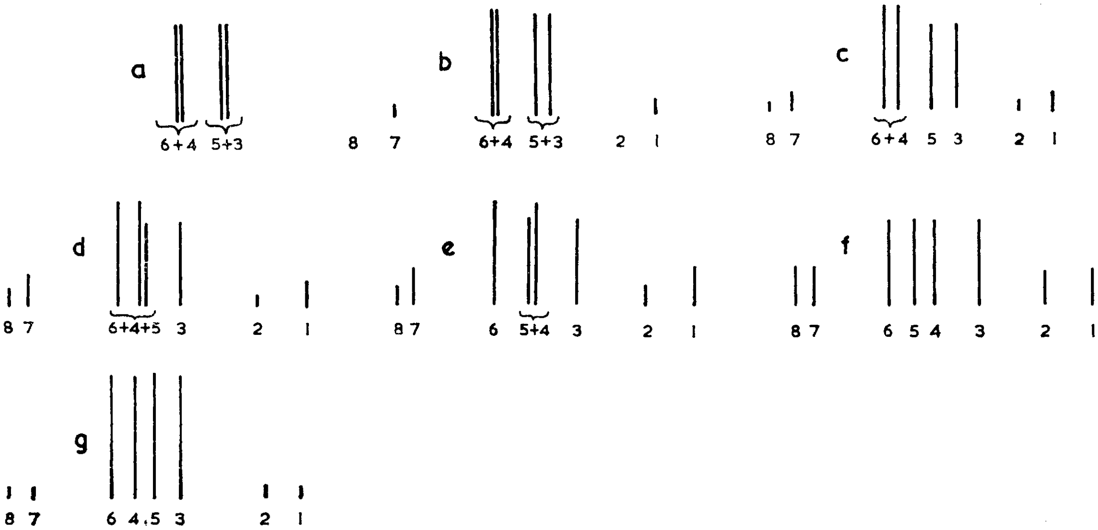


FIGURE 2. Schematic diagrams of AB portions of ABX spectra: (a) degenerate (" deceptively simple "); (b) near-degenerate type (I); (c) type (II); (d) type (III); (e) type (IV); (f) non-overlapping, quasi-first-order; (g) $\nu_A = \nu_B$ but no degeneracy occurs

and allow δ to increase from zero. The transition energies are then conveniently described by the approximate formulæ of Table II in ref. 35. The following types of spectra may be observed (in the order of increasing δ):

(I) Transitions 3 and 5 cannot be resolved though the peak may be broadened, but 1 and 7 are visible, while the other quartet remains degenerate (Figure 2b); six peaks (*i.e.*, including 2 and 8) may be observed at high sensitivity.

(II) Now peaks 3 and 5 are resolved. It is likely that, at the same time, peaks 2 and 8 will appear weakly, and the peak due to transitions 4 and 6 will be broadened (Figure 2c).

(III) Peak 5 is discernible as a shoulder on the 4,6-peak, but for slightly larger δ a single broad (4,5,6)-peak occurs (Figure 2d). The two central peaks have an intensity ratio of 3 : 1 [cf. 2 : 2 for Type (I)].

(IV) The splitting of 4 and 6 is resolved but not 4 and 5 which are crossing each other as δ increases (Figure 2e).

Further increase in δ leads to Figure 2f, with no overlapping of the A and B transitions.

The X peaks, initially a 1 : 2 : 1 triplet for low values of δ, become a quartet as δ increases, whose inner peaks are closer together than indicated by first-order formulæ. Two weak combination bands may be seen in either side of this spectrum.

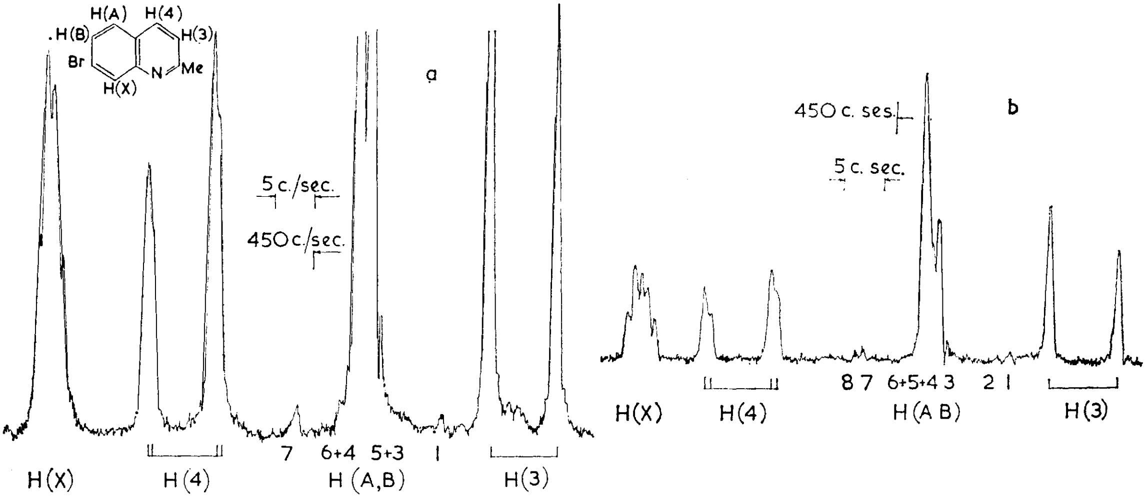
In types (I)—(IV) the overlapping of several transitions, and low intensity of the outer AB peaks limits the accuracy with which δ and the individual coupling constants may be determined.

7-*Bromo*-2-*methylquinoline*.—Here 6-H = B, 5-H = A, and 8-H = X; as the concentration increases the AB part of the spectrum changes from (III) to (II) to (I). Calculations (below) give $J_{A,B} = 8{\cdot}9$, $L = -0{\cdot}9$ c./sec.; a type (III) spectrum at 5·55 moles-% ($\delta = 3{\cdot}0$ c./sec.) becomes type (I) at 10·8 moles-% ($\delta = 1{\cdot}0$ c./sec.).

Figures 3a and c show the type (I) spectrum (10·8 moles-%). Only the appearance of 8-H requires comment: at such a low value of δ as is here indicated, the X part of an ABX system is a 1 : 2 : 1 triplet, with in this case an apparent splitting of $\frac{1}{2}(J_{\mathrm{A,X}} + J_{\mathrm{B,X}}) = 1{\cdot}3$ c./sec.; this is sufficiently near to $J_{4,8}$ (0·8 c./sec.) for the resultant shape to be a 1 : 3 : 3 : 1 quartet. Thus, the spectrum can be analysed as type (I) ABX, plus first-order coupling.

Figures 3b and d (5·55 moles-%) show the characteristics of a type (III) spectrum with transition 5 appearing as a barely discernible shoulder. The X part of an ABX spectrum would now be a quartet whose separations would be 1·0, 0·6, and 1·0 c./sec.; superposition of $J_{4,8}$ (0·8 c./sec.) leads to the observed 1 : 2 : 2 : 2 : 1 quintet. The whole spectrum is downfield relative to Figure 3a, except for 8-H; the reduction in ($\nu_8 - \nu_4$) is clearly evident.

Figure 3e shows the large AB peaks at 2·65 moles-%; these are intermediate between types (III) and (IV), transition 6 appearing as a shoulder.



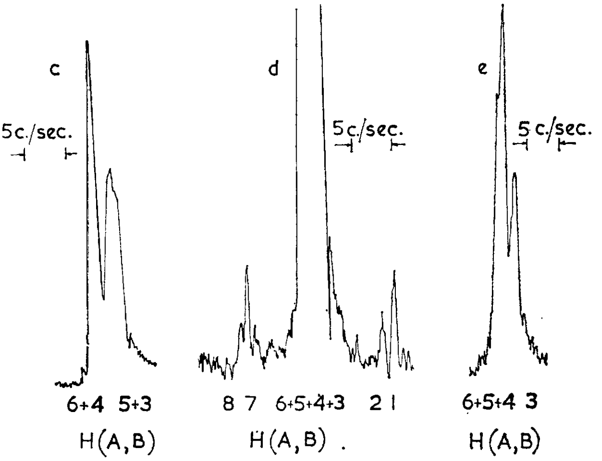


FIGURE 3. Proton magnetic resonance spectra of 7-bromo-2-methylquinoline in CS_2 (the numbering of the ABX transitions used in this and in subsequent figures is described in the text): (a) 10·8 moles-%; (b) 10·8 moles-%, detail at lower sensitivity and higher scale expansion; (c) 5·55 moles-%; (d) 5·55 moles-%, detail at higher sensitivity; (e) 2·65 moles-% detail

The values of $J_{3,4}$ and $\nu_4 - \nu_3$ are such that the true and apparent chemical shifts differ by 0·4 c./sec.; this correction has been incorporated. For several values of δ, 5-H, 6-H, and 8-H were treated as an ABC case: the differences from the ABX transition energies were entirely negligible, and only small intensity changes occurred; in particular the intensity order of the small AB transitions was given by $7 > 1 \gg 2 > 8$, as observed (see Figure 3d). For one value of δ, a full ABCDE spectrum was calculated, which showed no new features of interest.

Spectra were obtained from solutions of ten concentrations in the range 1—10·8 moles-%, and at most concentrations several spectra were taken. Parameters were refined as follows:

assuming that coupling constants would be independent of concentration within the experimental error, those parameters which could be read directly from the spectrum, namely $J_{\text{A,B}}$, $\frac{1}{2}(J_{\text{A,X}} + J_{\text{B,X}})$ and $J_{4,8}$ were measured and a weighted average was taken for all spectra. Those parameters dependent on δ, such as $(2\text{D}_+ + J_{\text{A,B}})$ (in the notation of ref. 34), were plotted graphically against concentration, and hence the best overall value of L obtained; finally δ was calculated for the various concentrations. Extrapolation to infinite dilution gave δ = 5·2 c./sec. Other results are incorporated in Tables 2 and 5.

7-*Bromoquinoline*.—At similar concentrations in carbon disulphide to the above, the spectra duplicate the phenomena discussed, with the addition of proton 2 which has the expected first-order coupling. At 12·8 moles-% (Figures 4a and b) the similarity to Figure 3 is marked, but peak 1 is lost under 3-H absorption. In 10·0 moles-% solution (Figure 4c) the large AB peaks would classify the spectrum as type (I); but higher scale expansion (Figure 4d) resolves peaks 3 and 5, which are separated by 0·6 c./sec. At 7·5 moles-% (Figure 4e) the largest peaks are clearly resolved, and of type (II), whereas at 4 moles-% (Figure 4f), type (II) has nearly become type (III), as it does in more dilute solutions. Figure 4g (from a 2 moles-% solution spectrum) illustrates both the 8-H quintet in dilute solutions and the closeness of the 8-H and 4-H absorptions with the associated intensity effects ($J_{4,8}$ = 0·9 c./sec.). There is a close analogy with the 2-methyl compound up to this point.

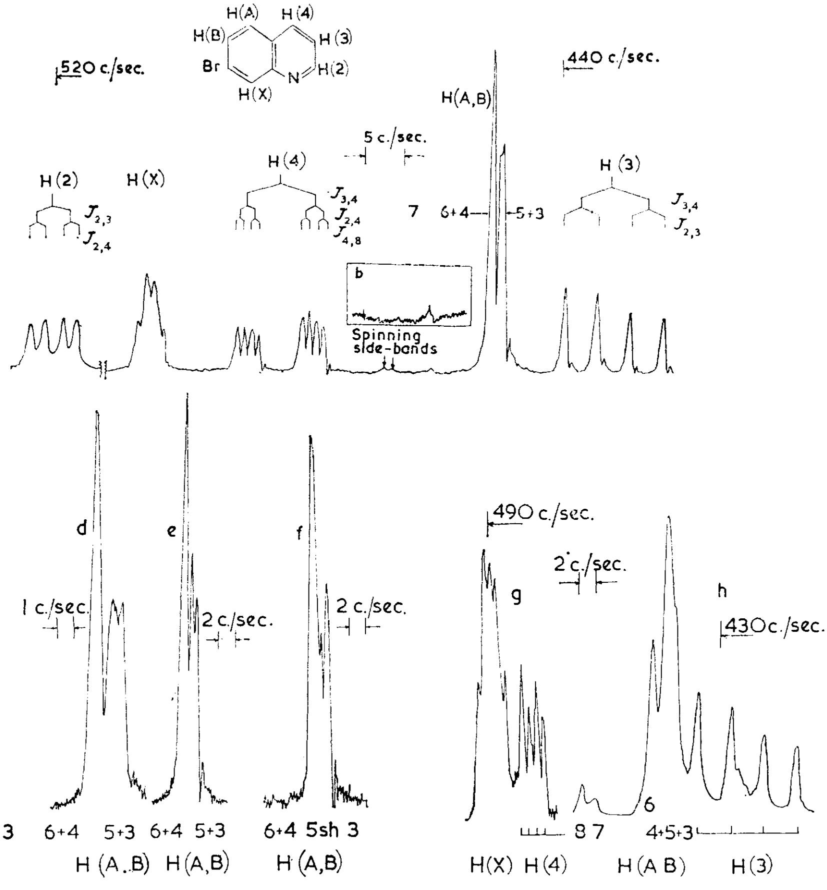


FIGURE 4. Proton magnetic resonance spectra of 7-bromoquinoline in CS_2: (a) 12·8 moles-%; (b) 12·8 moles-% detail; (c) and (d) 10·0 moles-% details; (e) 7·5 moles-% detail; (f) 4 moles-%; (g) 2 moles-% detail; (h) neat liquid, upfield part of spectrum

In very concentrated solutions, however, δ starts decreasing rapidly, passing through the "deceptively simple" phase, and actually changes sign. Thereafter the various types of spectra succeed each other in exactly the reverse order, but with the role of the two quartets interchanged; the X part finally becomes a quintet again. The AB absorption of the neat liquid (Figure 4h) shows the spectrum lies between types (III) and (IV), peaks 8 and 7 are again easily visible with the former as the larger, and peaks 2 and 1 can be observed, but not resolved, near the centre of 3-H. From the neat liquid to the extrapolated infinite dilution, δ has changed from $-5{\cdot}5$ to $+5{\cdot}0$ c./sec. The values of the ABX parameters are $J_{A,B} = 8{\cdot}9$, $\frac{1}{2}(J_{A,X} + J_{B,X}) = 1{\cdot}23$, $L = -0{\cdot}75$ c./sec. (By way of confirmation, dilute solutions in acetone gave a first-order spectrum, and direct measurement gave $J_{5,6} = 8{\cdot}9$, $J_{6,8} = 1{\cdot}7$ c./sec.) The remaining results are incorporated in Tables 2 and 5 and Figure 1.

^{13}C *Satellites of* 7-*Bromoquinoline*.—In very concentrated solution and in the neat liquid the ^{13}C satellites were observed; the $J_{C,H}$ values for protons 2, 4, 5, 6, and 8 are 179, 165, 163, 168, and 168 c./sec., respectively (each ± 2 c./sec.); for proton 3, a more tentative value of 162 c./sec. may be given. The high $J_{C,H}$ for 2-H is expected by analogy with other heterocycles; 6-H and 8-H, in the benzene ring, have higher $J_{C,H}$ values than those in alternant aromatic hydrocarbons.[36]

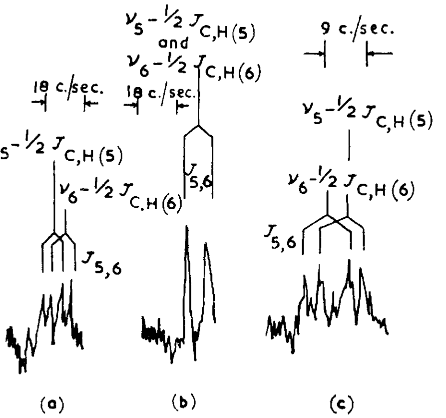


FIGURE 5. Proton magnetic resonance spectra of 7-bromoquinoline in CS_2; upfield ^{13}C satellites of protons 5 and 6: (a) 36 moles-%; (b) 53 moles-%; (c) neat liquid

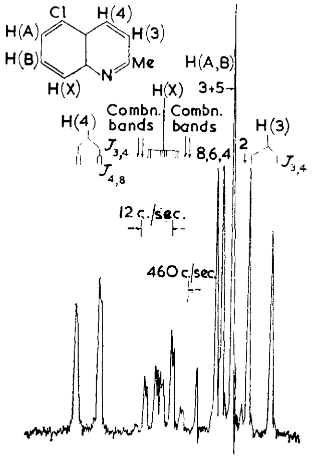


FIGURE 6. Proton magnetic resonance spectrum of 5-chloro-2-methylquinoline in CS_2

The rapid change of δ with concentration produces interesting modifications in the appearance of the (upfield) satellites of 5-H and 6-H. These (being first-order) now appear as nearly identical doublets (*meta* and *para* couplings are not resolved under these conditions). At 36 moles-% solution in carbon disulphide, $\delta = +1{\cdot}2$ c./sec., and as $\frac{1}{2}J_{C,H(6)} - \frac{1}{2}J_{C,H(5)} = 2{\cdot}5$ c./sec., the 6-H satellite is 4 c./sec. upfield of that due to 5-H (Figure 5a). At 53 moles-%, $\delta = -2{\cdot}2$ c./sec., and the two doublets are superimposed (Figure 5b), giving two peaks, each of which is of roughly equal intensity to the 8-H singlet satellite peak. In the neat liquid, however (Figure 5c), $\delta = -5{\cdot}5$ c./sec., so that the doublets are again well separated, with the 6-H absorption now downfield. The change in δ of $6{\cdot}7$ c./sec. from Figure 5a to Figure 5c conveniently confirms that determined indirectly from the ABX analysis. Thus ^{13}C satellites of concentrated solutions and pure liquids may not only be used to establish $J_{H,H}$ values otherwise unobtainable because of symmetry, but also to confirm second-order analyses where these are not well-determined because of near-degeneracy and/or overlapping of peaks.

5-*Chloro*-2-*methylquinoline*.—This compound, at about 6 moles-% in carbon disulphide (Figure 6) provides an interesting variant of a type (II) ABX spectrum; here 7-H = B, 6-H = A, 8-H = X. Because two *ortho* couplings are involved the pattern appears somewhat different, and B is downfield from A ($\delta < 0$). Immediately downfield from the 3-H doublet is the small peak 2 and the rest of the five-peak type (II) AB absorption (*i.e.*, peaks 1 and 7 have negligible intensity). The 4-H doublet with unresolved coupling to 8-H appears at lowest field. All the

[36] P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 1838.

intervening twelve peaks are X absorptions; not only are all the $J_{4,8}$ splittings clearly resolved, giving a central octet, but the two ABX combination bands are also visible and each split by $J_{4,8}$ (=0·8 c./sec.). The transition energies at this concentration fit the ABX formulæ perfectly with $\delta = -2{\cdot}8_5 = L$, $J_{\mathrm{A,B}} = 7{\cdot}5$, $J_{\mathrm{A,X}} = 2{\cdot}1$, $J_{\mathrm{B,X}} = 7{\cdot}8$ c./sec., though the intensities do not. However, an ABC spectrum calculated with these values differed significantly from that observed: an ABC refinement altered the parameters slightly to $\delta = -2{\cdot}9_5 = L$, $J_{\mathrm{A,B}} = 7{\cdot}5$, $J_{\mathrm{A,C}} = 1{\cdot}9$, $J_{\mathrm{B,C}} = 7{\cdot}9$ c./sec., and the true chemical shifts ν_{C} and $\frac{1}{2}(\nu_{\mathrm{A}} + \nu_{\mathrm{B}})$ are actually 1·1 c./sec. closer together than their apparent centres. In more dilute solutions, δ increases very slightly, but $(\nu_8 - \nu_7)$ is sufficiently reduced for the upfield X combination-band frequencies definitely to diverge from ABX formulæ.

5-*Chloroquinoline*.—This compound in carbon disulphide at 4·6 moles-% (Figure 7) is seen to be closely similar to the 2-methyl analogue, but peak 2 is submerged in 3-H absorption. The slightly smaller separation between peaks 4 and 6, and the superposition of the two central peaks in the X spectrum indicates a smaller $|\delta|$. Paradoxically, it is also in agreement with the appearance of peak 7, for now $|\delta| < |L|$, and the 1,3,5,7-quartet is accordingly *less* degenerate (of course, the proximity of 8-H affects intensities). The frequencies do not quite fit the ABX formulæ; an ABC refinement yielded $\delta = -1{\cdot}6$, $L = -3{\cdot}35$, $J_{\mathrm{A,B}} = 8{\cdot}0$, $J_{\mathrm{A,C}} = 1{\cdot}6$, $J_{\mathrm{B,C}} = 8{\cdot}3$ c./sec. Apparently δ is independent of concentration in dilute solution, but again $(\nu_8 - \nu_7)$ decreases slightly as the concentration is reduced.

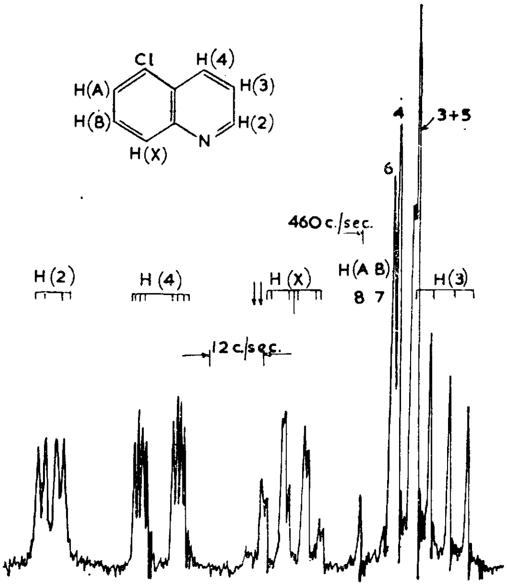


FIGURE 7. Proton magnetic resonance spectrum of 5-chloroquinoline in CS_2

5-*Bromoquinoline*.—The spectrum of this compound is a simple, non-overlapping ABX spectrum (Tables 3 and 4).

Classification of Near-Degeneracy on a Quantitative Basis.—In a simple extension of the arguments of ref. 35, let *i* be the lowest observable intensity, measured on the usual scale, where each peak of a fully resolved strictly first-order spectrum is one unit. Let $\Delta\nu_{\frac{1}{2}}$ be the usual peak breadth at half-height and therefore the assumed minimal peak separation for resolution. Then the following inequalities (valid for $|\delta| \ll J_{\mathrm{A,B}}$, and, as previously specified, $|L| \ll J_{\mathrm{A,B}}$) follow very simply:

A wholly degenerate spectrum changes to type (I); peaks 1 and 7 or 2 and 8 are observable if

$$|\delta| > J_{\mathrm{A,B}} \cdot (2i)^{\frac{1}{2}} - |L| \tag{1}$$

peaks 1 and 7 and 2 and 8 are all observable if

$$|\delta| > J_{\mathrm{A,B}} \cdot (2i)^{\frac{1}{2}} + |L| \tag{1a}$$

type (I) changes to type (II); two of the main four peaks are resolvable if

$$|\delta| > (2J_{A,B} \cdot \Delta\nu_{\frac{1}{2}})^{\frac{1}{2}} - |L| \tag{2}$$

type (II) changes to type (III); peaks 4 and 5 become unresolvable if

$$|\delta| > [J_{A,B}(J_{A,X} + J_{B,X} - 2\Delta\nu_{\frac{1}{2}}) - L^2]^{\frac{1}{2}} \tag{3}$$

Type (III) changes to type (IV); peaks 3 and 5 are resolvable and peaks 4 and 6 are resolvable if

$$|\delta| > (2J_{A,B} \cdot \Delta\nu_{\frac{1}{2}})^{\frac{1}{2}} + |L| \tag{4}$$

Type (IV) changes to a non-overlapping spectrum, and all four main peaks are separately resolvable: a truncated binomial expansion is no longer valid, and the inequality is best derived from the full ABX formulæ. The X absorption of a simple ABX system is a resolved quartet if

$$|\delta| > \tfrac{1}{2}J_{A,B} \cdot \Delta\nu_{\frac{1}{2}}/|L| \tag{5}$$

We have found typical values for $\Delta\nu_{\frac{1}{2}}$ and i to be about 0·5 c./sec. and about 0·02, respectively, on our instrument. As $J_{A,B} < \Delta\nu_{\frac{1}{2}}/i$ the small peaks appear before the large peaks are resolved, *i.e.*, as $|\delta|$ increases from zero, condition (1) is fulfilled before (2) and (1a) before (4). For inequality (4) a rather larger effective value of $\Delta\nu_{\frac{1}{2}}$ has to be used, as peak 6 has to be resolved from the overlapping pair 4 and 5. $\Delta\nu_{\frac{1}{2}}$ and i may be significantly smaller at higher concentrations where greater scale expansion and higher sensitivity may be used; increase in viscosity partly offsets the advantage in $\Delta\nu_{\frac{1}{2}}$.

These inequalities were found invaluable in refining the parameters of 7-bromoquinoline, particularly because peaks 1 and 2 are almost always obscured. For this compound, the inequalities of ref. 35 hold for very small values of $|\delta|$, so that the " deceptively simple " case occurs. However, when $|L|$ is somewhat larger, as in 5-chloro-2-methylquinoline, it is possible when $|\delta| < |L|$ for the AB portion of the spectrum to become less degenerate (cf. the near-ABX case of Figure 7), and we must include the additional inequalities:

peaks 1, 7 and 2, 8 are all observable if

$$|\delta| < -J_{A,B} \cdot (2i)^{\frac{1}{2}} + |L|; \tag{1b}$$

peaks 3, 5 and 4, 6 are resolvable also if

$$|\delta| < -(2J_{A,B} \cdot \Delta\nu_{\frac{1}{2}})^{\frac{1}{2}} + |L|. \tag{4b}$$

When the right-hand sides of both these last inequalities are positive, then for the case $\delta = 0$, what must now be described as the AA′ part of the spectrum will show no degeneracy at all, but will consist of eight symmetrically spaced lines (Figure 2g), whilst the X portion will still be an *exact* triplet (Figure 1b of ref. 35).

In conclusion, not only should solvent effects and concentration effects be taken into account when correlating chemical shifts (this can only be done if concentrations are stated), but also observation of such phenomena may assist in the interpretation of spectra: for example, degeneracy may be partially relieved by change of concentration in the same solvent.

EXPERIMENTAL

5- *and* 7-*Halogeno*-2-*methylquinolines*.—Dropwise addition of crotonaldehyde on to refluxing 70% w/w sulphuric acid containing a *m*-halogenoaniline and *m*-nitrobenzenesulphonic acid gave, after diazotisation to remove unchanged amine and steam-distillation from basic solution, a mixture of 5- and 7-halogeno-2-methylquinolines. Yields and compositions of the mixtures are recorded in Table 1.

Separation of the Isomeric Quinolines.—The 7-halogeno-2-methylquinolines were separated either by several crystallisations of the mixture or as the salt indicated below.

7-Fluoro-2-methylquinoline had b. p. 120°/15 mm., m. p. 38° (hydrate); *nitrate*, m. p. 137° (decomp.) (Found: C, 53·55; H, 3·9; N, 12·75. $C_{10}H_9FN_2O_3$ requires C, 53·55; H, 4·05; N, 12·5%).

7-*Bromo*-2-*methylquinoline* had m. p. 77° (Found: C, 54·1; H, 4·1; N, 6·62. $C_{10}H_8BrN$ requires C, 54·1; H, 3·6; N, 6·3%). The bromo-2-methylquinoline, m. p. 77°, isolated[37]

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[37] K. L. Moudgill, *J. Amer. Chem. Soc.*, 1921, **43**, 2257.

from the interaction of *m*-bromoaniline, paraldehyde, and hydrochloric acid is probably the 7-isomer.

7-*Iodo-2-methylquinoline* had m. p. 81° (Found: C, 44·8; H, 3·1; I, 47·0; N, 7·0. $C_{10}H_8IN$ requires C, 44·6; H, 3·0; I, 47·2; N, 5·2%); *nitrate*, m. p. 135° (decomp.) (Found: C, 36·0; H, 3·4; I, 38·2; N, 9·0. $C_{10}H_9IN_2O_3$ requires C, 36·1; H, 2·7; I, 38·2; N, 8·4%).

Other compounds were either those of an earlier investigation [2] or were purified commercial samples.

Analysis of Mixtures.—The quinoline mixtures were analysed, after distillation of the reaction product to dryness, by quantitative nuclear magnetic resonance, using the separated 7-isomers for identification, and the 2-methyl group as an internal standard. The procedure was checked by analysis of known mixtures.

Proton magnetic resonance spectra were measured on a Perkin-Elmer Spectrometer operating at 60 Mc./sec., with tetramethylsilane as internal reference, and ^{19}F resonance spectra were measured on a Perkin-Elmer Spectrometer operating at 37·46 Mc./sec. All coupling constants are the mean of many measurements.

The authors are indebted to Daphne M. L. Rowe, who carried out the preparations and separations of the 5- and 7-halogeno-2-methylquinolines, to Dr. P. Bladon (University of Strathclyde), for the ^{19}F n.m.r. spectra, to Dr. P. J. Black (Monash University) for his Sirius Autocode programmes,[38] and to Dr. A. L. Porte for his comments on an earlier draft of the Paper.

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[*Received, February* 12*th*, 1965.]

[38] P. J. Black and M. L. Heffernan, *Austral. J. Chem.*, 1963, **16**, 1051.