# Studies on Benzimidazoles. Part VIII.[1] $^1H$ Nuclear Magnetic Resonance Study of Substituted 2-Chloro-1-methylbenzimidazoles

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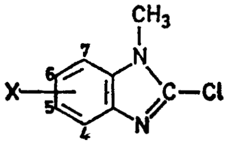
A number of benzo-substituted 2-chloro-1-methylbenzimidazoles has been studied by $^1H$ n.m.r. spectroscopy. It is observed both from the ring and *N*-methyl proton chemical shifts measured in deuteriochloroform and trifluoroacetic acid solution that conjugation effects are present between substituents and the nitrogen atoms of the heterocyclic ring. Proton–proton coupling constants can be rationalized in terms of additive substituent effects when there are no strong mesomeric interactions between substituents and the heterocyclic ring. Charge densities have been calculated for both $\sigma$ and $\pi$-electrons, and the correlations between charges and chemical shifts show that the substituents also perturb the heterocyclic ring through the $\sigma$-skeleton.

THE nucleophilic reactivity of some substituted 2-chloro-1-methylbenzimidazoles[2] and of the corresponding salts[1,3] has been studied previously. The mechanism of the reactions involved and the existence of electronic interactions between the reaction centre (carbon atom in position 2) and the substituents in the homocyclic ring, have also been discussed. The electronic properties of the photo-excited benzimidazoles were also investigated[4] but information concerning the ground state of these molecules is not at present available.

We report here the results of the $^1H$ n.m.r. spectra of several substituted-2-chloro-1-methylbenzimidazoles (1).

(1) 

X = H, 4-OMe, 5-OMe, 6-OMe,
7-OMe, 4-Me, 5-Me, 6-Me,
7-Me, 4-Cl, 5-Cl, 6-Cl, 7-Cl,
4-$NO_2$, 5-$NO_2$, 6-$NO_2$, 7-$NO_2$

To determine the effect of substituents on the electronic characteristics of these molecules and the protonated species in their ground state, the spectra have been recorded in both deuteriochloroform and trifluoroacetic acid solution. In the last solvent our system is almost completely protonated as previously observed.[5]

## RESULTS AND DISCUSSION

For a large number of the spectra recorded in deuteriochloroform solution and some of those in trifluoroacetic acid it has been possible to carry out accurate spectral analysis with the aid of the LAOCN 3 computing program.[6] The chemical shifts and coupling constants obtained in this way should be correct within 0·1 Hz. In the remaining cases the experimental spectrum did not contain a sufficient number of lines for iterative analysis, owing to the small difference in chemical shift between non-equivalent protons: chemical shifts obtained by direct inspection of the spectra are accurate within 1—2 Hz and coupling constants could not be determined. The results are summarized in Tables 1 and 2. For methyl-substituted derivatives the coupling of the methyl group with the aromatic protons could not be resolved and iterative analysis was not possible, except for the 6-methyl derivative in deuteriochloroform solution.

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[1] Part VII, P. Dembech, A. Ricci, G. Seconi, and P. Vivarelli, *J. Chem. Soc.* (*B*), **1971**, **557**.

[2] (*a*) A. Ricci and P. Vivarelli, *Gazzetta*, 1967, **97**, 750; (*b*) A. Ricci and P. Vivarelli, *Gazzetta*, 1967, **97**, 758.

[3] A. Ricci, G. Seconi, and P. Vivarelli, *J. Chem. Soc.* (*B*), 1970, 254.

[4] G. Leandri, A. Mangini, F. Montanari, and R. Passerini, *Gazzetta*, 1955, **85**, 769.

[5] A. Ricci and P. Vivarelli, *J. Chem. Soc.* (*B*), **1968**, **1280**.

[6] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

TABLE 1

Chemical shifts, expressed in p.p.m. from $Me_4Si$, of substituted 2-chloro-1-methylbenzimidazoles (1), measured in 0·5M-$CDCl_3$ solution

| Substituent | $\delta_4$ | $\delta_5$ | $\delta_6$ | $\delta_7$ | $\delta_{N-Me}$ | Other resonances |
|---|---|---|---|---|---|---|
| H | 7·67 | 7·17 | 7·24 | 7·32 | 3·74 | |
| 4-Cl | | 7·22 | 7·18 | 7·12 | 3·77 | |
| 5-Cl | 7·62 | | 7·21 | 7·14 | 3·76 | |
| 6-Cl | 7·60 | 7·23 | | 7·28 | 3·74 | |
| 7-Cl | 7·55 | 7·23 | 7·14 | | 4·09 | |
| 4-$NO_2$ | | 8·12 | 7·41 | 7·64 | 3·94 | |
| 5-$NO_2$ | 8·56 | | 8·24 | 7·39 | 3·94 | |
| 6-$NO_2$ | 7·75 | 8·21 | | 8·30 | 3·94 | |
| 7-$NO_2$ | 7·92 | 7·32 | 7·92 | | 4·00 | |
| 4-Me[a] | | 7·05 | 7·09 | 7·00 | 3·72 | *b* |
| 5-Me[a] | 7·46 | | 7·08 | 7·02 | 3·70 | *c* |
| 6-Me | 7·53 | 7·07 | | 6·98 | 3·65 | *d* |
| 7-Me[a] | 7·40 | 7·13 | 7·13 | | 3·93 | *e* |
| 4-OMe | | 6·68 | 7·18 | 6·84 | 3·70 | *f* |
| 5-OMe | 7·14 | | 6·91 | 7·11 | 3·72 | *g* |
| 6-OMe | 7·52 | 6·89 | | 6·67 | 3·71 | *h* |
| 7-OMe | 7·26 | 7·10 | 6·65 | | 3·95 | *i* |

[a] The chemical shifts of these compounds were obtained by direct inspection of the spectrum and the error should be ±0·02 p.p.m. while in the other cases the values obtained by iterative analysis should be correct within ±0·005 p.p.m. or better. [b] $\delta_{CH_3} = 2{\cdot}60$ ($J_{4\text{-}Me} = 0{\cdot}68$, $J_{5\text{-}Me} = 0{\cdot}33$). [c] $\delta_{Me} = 2{\cdot}43$ ($J_{6\text{-}Me} = 0{\cdot}60$, $J_{4\text{-}Me} = 0{\cdot}75$, $J_{7\text{-}Me} = 0{\cdot}35$). [d] $\delta_{Me} = 2{\cdot}46$ ($J_{5\text{-}Me} = 0{\cdot}53$, $J_{7\text{-}Me} = 0{\cdot}71$, $J_{4\text{-}Me} = 0{\cdot}37$). [e] $\delta_{Me} = 2{\cdot}63$ (unresolved multiplet). [f] $\delta_{OMe} = 3{\cdot}99$. [g] $\delta_{OMe} = 3{\cdot}85$. [h] $\delta_{OMe} = 3{\cdot}89$; [i] $\delta_{OMe} = 3{\cdot}88$.

TABLE 2

Chemical shifts, expressed in p.p.m. from $Me_4Si$, of substituted 2-chloro-1-methylbenzimidazoles (1), measured in 0·5M-$CF_3CO_2H$ solution

| Substituent | $\delta_4$ | $\delta_5$ | $\delta_6$ | $\delta_7$ | $\delta_{N-Me}$ | Other resonances |
|---|---|---|---|---|---|---|
| H[a] | 7·78 | 7·78 | 7·78 | 7·78 | 4·16 | |
| 4-Cl[a] | | 7·70 | 7·70 | 7·70 | 4·22 | |
| 5-Cl[a] | 7·83 | | 7·73 | 7·73 | 4·19 | |
| 6-Cl[a] | 7·78 | 7·72 | | 7·72 | 4·13 | |
| 7-Cl[a] | 7·66 | 7·63 | 7·63 | | 4·45 | |
| 4-$NO_2$ | | 8·64 | 7·99 | 8·28 | 4·30 | |
| 5-$NO_2$ | 8·80 | | 8·64 | 8·00 | 4·30 | |
| 6-$NO_2$ | 8·07 | 8·66 | | 8·84 | 4·31 | |
| 7-$NO_2$ | 8·18 | 7·86 | 8·36 | | 4·32 | |
| 4-Me[a] | | 7·59 | 7·59 | 7·59 | 4·14 | *b* |
| 5-Me[a] | 7·58 | | 7·58 | 7·58 | 4·09 | *c* |
| 6-Me[a] | 7·63 | 7·56 | | 7·63 | 4·05 | *d* |
| 7-Me[a] | 7·72 | 7·60 | 7·60 | | 4·37 | *e* |
| 4-OMe | | 7·17 | 7·68 | 7·31 | 4·12 | |
| 5-OMe | 7·30 | | 7·56 | 7·66 | 4·05 | |
| 6-OMe | 7·70 | 7·39 | | 7·24 | 4·05 | |
| 7-OMe | 7·33 | 7·63 | 7·17 | | 4·40 | |

[a] The chemical shifts of these compounds were obtained by direct inspection of the spectrum and the error should be ±0·02 p.p.m. while in the other cases the values obtained by iterative analysis should be corrected within ±0·005 p.p.m. or better. [b] $\delta_{Me} = 2{\cdot}65$ (unresolved multiplet). [c] $\delta_{Me} = 2{\cdot}57$ (unresolved multiplet). [d] $\delta_{Me} = 2{\cdot}63$ ($J_{5\text{-}Me} = 0{\cdot}60$, $J_{7\text{-}Me} = 0{\cdot}79$, $J_{4\text{-}Me} = 0{\cdot}30$). [e] $\delta_{Me} = 2{\cdot}94$ (unresolved multiplet).

Direct inspection of the results collected in Tables 1 and 2 shows that the substituent effects in compounds (1) and in monosubstituted benzenes are qualitatively similar. The values for the chemical shift differences Δ between substituted-2-chloro-1-methylbenzimidazoles and the unsubstituted compound (1; X = H) for corresponding ring positions parallel the substituent effects in monosubstituted benzenes. The values are reported in Table 3 and are tabulated on the basis of the relative position, *ortho*, *meta*, and *para*, of the proton with respect to the substituent. Larger deviations are found for 7-substituted derivatives. In these compounds the substituent is close to the N–$CH_3$ group and, especially for the nitro- and the methoxy-derivatives, direct through-space effects seem to affect the electronic interaction of these substituents with the aromatic ring. Also the proton chemical shift of the N–$CH_3$ group, which for each kind of substituent differs largely only when dealing with 7-substituted compounds, seem to be affected by this kind of perturbation. Parallel considerations can be made for the results obtained in

TABLE 3

Chemical shift differences Δ (in p.p.m.) between substituted 2-chloro-1-methylbenzimidazoles and the corresponding unsubstituted compound (1: X = H). In the last column the substituent effect Δ for monosubstituted benzenes[a] is reported

| Substituent | Δ-4 | Δ-5 | Δ-6 | Δ-7 | Monosubstituted benzenes |
|---|---|---|---|---|---|
| 4-Cl | | −0·05(*o*) | 0·06(*m*) | 0·20(*p*) | Δ(*o*) = −0·01 |
| 5-Cl | 0·05(*o*) | | −0·03(*o*) | 0·18(*m*) | Δ(*m*) = 0·06 |
| 6-Cl | 0·07(*m*) | −0·06(*o*) | | 0·04(*o*) | Δ(*p*) = 0·12 |
| 7-Cl | 0·12(*p*) | −0·06(*m*) | 0·10(*o*) | | |
| 4-$NO_2$ | | −0·95(*o*) | −0·17(*m*) | −0·32(*p*) | Δ(*o*) = −0·93 |
| 5-$NO_2$ | −0·89(*o*) | | −1·00(*o*) | −0·07(*m*) | Δ(*m*) = −0·26 |
| 6-$NO_2$ | −0·08(*m*) | −1·04(*o*) | | −0·98(*o*) | Δ(*p*) = −0·39 |
| 7-$NO_2$ | −0·25(*p*) | −0·15(*m*) | −0·60(*o*) | | |
| 4-Me | | 0·12(*o*) | 0·15(*m*) | 0·32(*p*) | Δ(*o*) = 0·16 |
| 5-Me | 0·21(*o*) | | 0·16(*o*) | 0·30(*m*) | Δ(*m*) = 0·09 |
| 6-Me | 0·14(*m*) | 0·10(*o*) | | 0·34(*o*) | Δ(*p*) = 0·17 |
| 7-Me | 0·27(*p*) | 0·04(*m*) | 0·11(*o*) | | |
| 4-OMe | | 0·49(*o*) | 0·06(*m*) | 0·48(*p*) | Δ(*o*) = 0·49 |
| 5-OMe | 0·53(*o*) | | 0·33(*o*) | 0·21(*m*) | Δ(*m*) = 0·11 |
| 6-OMe | 0·15(*m*) | 0·28(*o*) | | 0·65(*o*) | Δ(*p*) = 0·44 |
| 7-OMe | 0·41(*p*) | 0·07(*m*) | 0·59(*o*) | | |

The abbreviations (*o*), (*m*), and (*p*) refer to the *ortho*, *meta*, and *para* position of the proton with respect to substituent.

[a] The substituent effects in monosubstituted benzenes were deduced by the following references taking the chemical shift of benzene itself equal to 7·26 p.p.m.: S. Castellano, C. Sun, and R. Kostelnik, ***Tetrahedron Letters***, 1967, 5205; W. Brugel, 'Nuclear Magnetic Resonance Spectra and Chemical Structure,' vol. I, Academic Press, New York, London, 1967.

trifluoroacetic acid solution. Similar kinds of interactions also effect [7] the kinetic behaviour of the reactions of compounds (1) with neutral and anionic nucleophilic reagents. Quantitatively it is not easy to rationalize the complete set of results reported in Table **3** since the deviations of Δ values for compounds (1), with respect to those of substituted benzenes, are in most cases restricted within 0·1—0·3 p.p.m. On the other hand the nucleophilic reactivity [2b] of chlorine in compounds (1) can be correlated to Hammett's substituent constants. For the 5- and 6-$NO_2$ substituted compounds the value of $\sigma^-_{p\text{-NO}_2} = 1{\cdot}27$, which implies a mesomeric interaction between the substituent and the reaction centre [8] through the heterocyclic nitrogens, must be employed. In the case of the $^1H$ chemical shifts reported here, the only means of observing such an effect in the ground state of compounds (1) is through the chemical shift of the $N\text{-}CH_3$ protons. In Figure 1 we have plotted the chemical shift of this group for 5-substituted derivatives against Hammett's σ constants [8] for the *para*-position. It is seen that the δ values measured in $CDCl_3$ solution (plot a) correlate better when $\sigma^-_{p\text{-NO}_2} = 1{\cdot}27$ (full line) is used instead of the normal $\sigma_{p\text{-NO}_2} = 0{\cdot}778$ (dashed line). However, for δ values measured in $CF_3CO_2H$ solution (plot b) the opposite situation holds. This is in agreement with a conjugative interaction (2) between the $NO_2$ and the $N\text{-}CH_3$ group which are *para* to each other, while this is less likely when the heterocyclic ring holds a formal positive charge (3) due to protonation ($CF_3CO_2H$ solution).[9] Furthermore, the slight deviation from linearity of the value for the $OCH_3$ substituent may be due to the mutual inhibition of mesomeric interaction with the $N\text{-}CH_3$ group (both these substituents have $+M$ effect) in the neutral molecule (Figure 1: plot a) and to a favoured conjugation when the heterocyclic ring is positively charged, as in the protonated molecule (Figure 1: plot b). The deviations in the two solvents should be in the opposite way, as is observed. No linearity is observed for the $\delta_{N\text{-}CH_3}$ relative to 6-substituted derivatives employing Hammett's σ constant for the *meta*-position. In this case mesomeric interactions should occur with the unsaturated nitrogen which is now *para* with respect to the substituents.

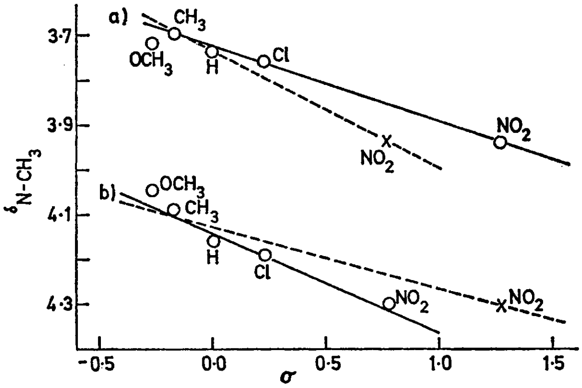
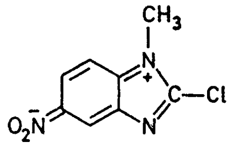
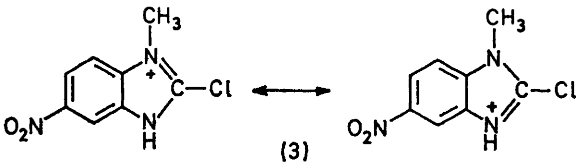


FIGURE 1 $^1H$ Chemical shift of the $N\text{-}CH_3$ group against *para* σ constants for 5-substituted 2-chloro-1-methylbenzimidazoles. Plots (a) and (b) refer to the values measured in $CDCl_3$ and $CF_3CO_2H$ solution respectively



(2)



(3)

The chemical shifts in $CF_3CO_2H$ are always at a lower field of those in $CDCl_3$. For equivalent ring positions the chemical shifts in the two solvents are linearly related. All the values are collected in a single plot (Figure 2), which shows that all the chemical shifts relative to position 4 deviate in the same direction. This is due to the magnetic anisotropy of the unsaturated

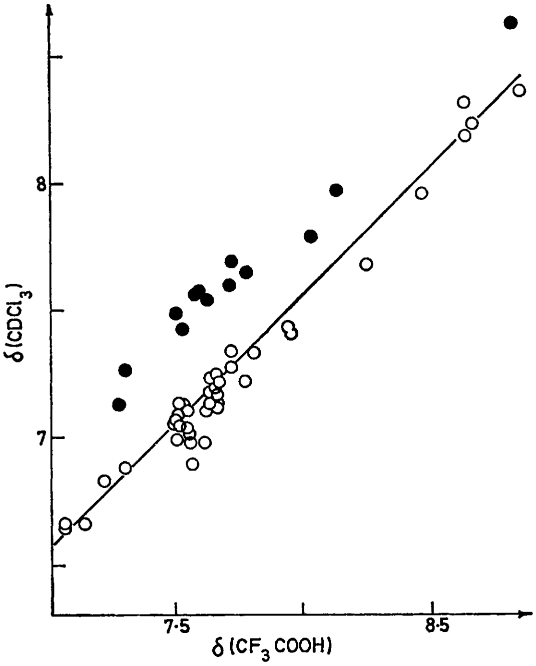


FIGURE 2 Diagram of chemical shifts measured in $CDCl_3$ *vs.* the corresponding values in $CF_3CO_2H$ solution. Full circles correspond to the proton in position 4 for the different substituted compounds (1)

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[7] A. Ricci, G. Seconi, and P. Vivarelli, *Gazzetta*, 1969, **99**, 542.

[8] J. Hine, 'Physical Organic Chemistry,' 2nd edn., McGraw-Hill Book Company, Inc., New York, 1962.

[9] We have previously observed [3] that the kinetic data for the reaction of 2-chloro-1-methyl-5-nitrobenzimidazolium perchlorate with thiophenol in aqueous methanol is compatible with a $\alpha^-_{p\text{-NO}_2} = 1{\cdot}27$. The different electronic interaction of the $NO_2$ with the $N\text{-}CH_3$ group observed in $CF_3CO_2H$ and in $CH_3OH/H_2O$ solutions, may be ascribed to the different abilities of the two solvents to solvate the $-\overset{+}{N}H=$ group.

nitrogen lone pair [10] which is removed when protonation occurs at this nitrogen atom.

The difference of the chemical shifts of the N-$CH_3$ group measured in the two solvents is due mainly to protonation of the unsaturated nitrogen atom. These differences range between 0·32—0·45 p.p.m. and they are not very sensitive to substituent effects.

For the derivatives examined, charge densities have been determined for both $\sigma$ and $\pi$ electrons. The $\sigma$ charge distribution has been determined using a technique previously applied to substituted benzenes,[11] while the HMO method [12] was applied to the $\pi$-electron system. Nitro-substituted derivatives were not included since the method for computing $\sigma$ charge densities does not give good results when the substituent contains $\pi$-electrons.[11]

An approximately linear plot of chemical shifts against charge densities is obtained only when the total charge ($q_C^{tot} = q_C^{\sigma} + q_C^{\pi}$) on the carbon atoms is employed.* In Figure 3 these quantities are reported and it is seen that the chemical shifts measured in trifluoroacetic acid solution (Figure 3: upper plot) give a linear correlation for all the protons. However, for proton H-4, the chemical shift measured in deuteriochloroform solution deviates appreciably. For all substituted derivatives the proton H-4 chemical shift deviates 0·3—0·4 p.p.m. to lower field with respect to the line drawn through the other proton chemical shifts. This fact, as pointed out above, is due to a paramagnetic contribution from the unsaturated nitrogen atom.[10] We have approximately estimated this effect according to Gill and Murrell [10] using the values of $\chi^N$ (components of the molar magnetic susceptibility of nitrogen) given by these authors for pyridine. Standard bond lengths [15] were used to obtain the molecular geometry for 2-chloro-1-methylbenzimidazole. The paramagnetic contribution to the chemical shift of proton H-4 estimated in this way amounts to *ca.* 0·3 p.p.m., as expected.

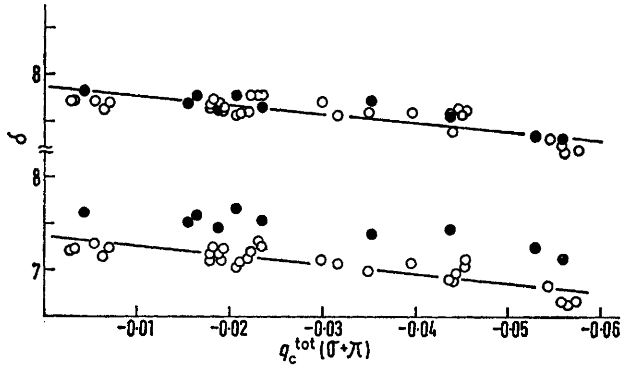

FIGURE 3 Correlation between proton chemical shifts of compounds (1) and the total charge on carbon atoms ($q_C^{tot} = q_C^{\sigma} + q_C^{\pi}$). Upper chemical shifts refer to $CF_3CO_2H$ solution, lower to $CDCl_3$ solution. Full circles refer to chemical shifts of the 4-proton

*Proton–Proton Spin Coupling Constants.*—Spin–spin coupling constants were derived when spectral analysis could be performed and are reported in Table 4. Coupling constants in substituted benzenes have been interpreted in terms of substituent electronegativity and additivity rules have been proposed for disubstituted benzenes.[16,17] According to these authors, provided that no strong mesomeric interactions are present between substituents, coupling constants for disubstituted benzenes can be calculated from those of monosubstituted derivatives, and deviations from the experimental values are restricted within a few tenths of a Hz. This rule is particularly useful when dealing with complex n.m.r. spectra of substituted benzenes since it can provide a trial set of coupling constants to start spectral analysis.

Considering the six-membered ring of compounds (1) as a polysubstituted benzene, the additivity rule for coupling constants can be expressed by equation (1). In disubstituted benzenes proton–proton coupling constants can be obtained from the corresponding coupling constants in benzene plus contributions from each substituent expressed as the difference between coupling constants in monosubstituted benzenes and in benzene itself.[16,17]

$$J_{ab}{}^{R} = 2J_{ab}{}^{A} + J_{ab}{}^{B,R} - 2J_{ab}{}^{C} \qquad (1)$$

In equation (1), a and b represent the coupled protons, A refers to the unsubstituted derivative (1: X = H), B to the monosubstituted benzene with substituent R, and C to benzene itself; $J_{ab}{}^{A}$ has been taken twice since compound (1: X = H) may be formally represented as a disubstituted benzene. As a clarifying example we consider $J_{45}$ in the 7-chloro-substituted compound (1):

$$\begin{aligned} J_{45}{}^{7Cl} &= 2J_{45}{}^{A} + J_{m,p}{}^{Cl} - 2J_{ortho}{}^{benzene} \\ &= 2 \times 7{\cdot}99 + 7{\cdot}46 - 2 \times 7{\cdot}52 = 8{\cdot}40 \end{aligned}$$

The term $J_{m,p}{}^{Cl}$ is the coupling constant between protons *meta* and *para* in chlorobenzene. Coupling constants for monosubstituted benzenes were taken from

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* Although the $\sigma$- and $\pi$-charge densities were computed by different LCAO approximations, these quantities can be added to get a rough total charge density on carbon. They can be in fact made up together to reproduce dipole moments of substituted benzenes [13] and, moreover, total charge densities obtained in this way give a picture of carbon-13 chemical shifts in the same compounds [13] at least as good as that obtained from the more sophisticated approximation represented by the CNDO technique.[14]

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

[11] P. Lazzaretti and F. Taddei, *Tetrahedron Letters*, 1970, 805.

[12] A. Streitwieser, jun., ' Molecular Orbital Theory for Organic Chemists,' John Wiley, Inc., New York, 1961, ch. 2.

[13] P. Lazzaretti and F. Taddei, *Org. Magnetic Resonance*, in the press.

[14] J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, 1968, **72**, 716.

[15] ' Tables of Interatomic Distances and Configuration in Molecules and Ions,' L. E. Sutton Editor, The Chemical Society, London, 1958.

[16] S. Castellano and R. Kostelnik, *Tetrahedron Letters*, 1967, 5221.

[17] K. Hayamizu and O. Yamamoto, *J. Mol. Spectroscopy*, 1968, **25**, 422.

the literature.[16,18] Calculated and experimental spin–spin coupling constants do not differ generally by more than 0·15 Hz (Table 4).

However, for 5- and 6-substituted methoxy- and nitro-derivatives larger deviations are found, which are probably due to conjugative effects between these substituents and the heterocyclic ring as is found in the case of the proton chemical shifts.

We have tried to reproduce *ortho* coupling constants in compounds (1) from HMO bond orders using the equations reported in the literature [19,20] but calculated values deviate appreciably from experimental ones. (The average deviation is of the order of 0·5 Hz). Better reproducibility (average deviation *ca.* 0·3 Hz) is obtained when an alternative equation is derived by a least-square treatment of the values for the compounds (1).

TABLE 4

Coupling constants in Hz for 2-chloro-1-methylbenzimidazoles (1) in $CDCl_3$ solution. Values in parentheses refer to $CF_3CO_2H$ solution. Calculated values were computed by additivity rules

| Subst. | H | 4-Cl | 5-Cl | 6-Cl | 7-Cl | $4-NO_2$ | $5-NO_2$ | $6-NO_2$ | $7-NO_2$ | 4-OMe | 5-OMe | 6-OMe | 7-OMe | 6-Me [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $J_{45}$ exp. | 7·99 | | | 8·90 | 8·34 | | | 8·82 | 8·39 | | | 9·23 | 8·20 | 7·90 |
| | | | | | | | | (9·17) | (8·23) | | | (9·17) | (8·49) | |
| calc. | | | | 8·99 | 8·40 | | | 9·30 | 8·41 | | | 9·23 | 8·29 | |
| $J_{46}$ exp. | 1·16 | | 1·92 | | 0·95 | | 2·05 | | 0·92 | | 2·46 | | 0·80 | |
| | | | | | | | (2·08) | | (0·97) | | (2·30) | | (0·71) | |
| calc. | | | 1·97 | | 0·87 | | 2·09 | | 0·88 | | 2·44 | | 0·72 | |
| $J_{47}$ exp. | 0·67 | | 0·48 | 0·54 | | | 0·49 | 0·45 | | | 0·49 | 0·43 | | 0·56 |
| | | | | | | | (0·54) | (0·52) | | | (0·45) | (0·46) | | |
| calc. | | | 0·48 | 0·48 | | | 0·59 | 0·59 | | | 0·48 | 0·48 | | |
| $J_{56}$ exp. | 7·48 | 7·86 | | | 7·84 | 8·29 | | | 8·24 | 8·22 | | | 8·14 | |
| | | | | | | (8·46) | | | (8·18) | (7·90) | | | (8·34) | |
| calc. | | 7·97 | | | 7·97 | 8·28 | | | 8·28 | 8·21 | | | 8·21 | |
| $J_{57}$ exp. | 1·19 | 1·03 | | 2·08 | | 0·95 | | 2·42 | | 0·76 | | 2·54 | | 1·30 |
| | | | | | | (0·79) | | (2·08) | | (0·60) | | (2·38) | | |
| calc. | | 0·93 | | 2·03 | | 0·93 | | 2·15 | | 0·78 | | 2·50 | | |
| $J_{67}$ exp. | 7·93 | 8·22 | 8·75 | | | 8·30 | 8·98 | | | 8·28 | 8·85 | | | |
| | | | | | | (8·63) | (9·27) | | | (8·14) | (8·90) | | | |
| calc. | | 8·28 | 8·87 | | | 8·29 | 9·18 | | | 8·17 | 9·11 | | | |

[a] Coupling constants relative to methyl derivatives were not computed since $J_{HH}$ values for toluene, at present available are not as accurate as for other monosubstituted benzenes

Therefore, apart from the general validity of such equations, it seems to us that they are always restricted to the system from which they were derived. Consequently, the accuracy of calculated coupling constants for different ring systems is poor compared with the increasing accuracy of the experimental values.

It has been suggested by Günther [21] that the ratio $J_{56}/J_{45}$ is a qualitative measure of π-bond localization. In the case of 2-chloro-1-methylbenzimidazole this ratio is 0·94, very near to complete π-bond equivalence, which indicates that the aromaticity of the benzenoid portion of 1-methylbenzimidazole is high.

## EXPERIMENTAL

*N.m.r. Spectra.*—The samples were 0·5M-solutions in the two solvents containing 3% tetramethylsilane for use as an internal lock signal and reference peak. Spectra were recorded using a JEOL-C60-HL spectrometer at a fixed frequency of 60 MHz, in the internal lock mode. The spectral analysis was carried out using a LAOCN 3 computer program [6] and a CDC 6600 computing system which was also used for charge density calculations.

*Compounds.*—2-Chloro-1-methylbenzimidazole [22] and the corresponding $5-CH_3$ and $5-NO_2$ derivatives were obtained according to known methods.[23,24] The $6-NO_2$, $6-CH_3$, $5-OCH_3$, $6-OCH_3$, 5-Cl, 6-Cl substituted compounds were prepared following our previous report.[2b]

2-*Chloro*-7-*methoxy*-1-*methylbenzimidazole*.—This compound was obtained by chlorination of the corresponding 2-benzimidazolone with $POCl_3$ in the presence of hydrochloric acid, as previously described for the corresponding 6-methoxy-substituted compound.[2b] The product (58% yield) was crystallized from ethanol–water 1 : 2 (v : v), m.p. 89—90° (Found: C, 55·4; H, 4·6; Cl, 18·2; N, 14·4. $C_9H_9ClN_2O$ requires C, 55·0; H, 4·6; Cl, 18·0; N, 14·2%).

7-*Methoxy*-1-*methylbenzimidazol*-2-*one*.—This compound was obtained by cyclization of 3-amino-2-methylamino-anisole hydrochloride [25] (0·1 mole) in the presence of urea (0·11 mole) at 170—175° for 1 hr. The reaction mixture was extracted with boiling aqueous sodium hydroxide solution (10%). The product, m.p. 198—200°, was precipitated from the alkaline solution with hydrochloric acid.

2-*Chloro*-4-*methoxy*-1-*methylbenzimidazole*.—This compound was prepared by methylation of the corresponding 2-chloro-4(7)-methoxybenzimidazole [2a] (0·01 mole) with methyl iodide (0·1 mole) following the procedure previously

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used to obtain 2-chloro-1-methylbenzimidazole.[22] The reaction mixture was eluted from a silica support with cyclohexene–ethyl acetate 70 : 30 (v : v). The compound obtained (30% yield) was crystallized from ethanol–water 1 : 1 (v : v), m.p. 120—121° (Found: C, 55·0; H, 4·6; Cl, 17·9; N, 14·2. $C_9H_9ClN_2O$ requires C, 55·0; H, 4·62; Cl, 18·0; N, 14·2%).

A certain amount of 2-chloro-7-methoxy-1-methylbenzimidazole was also obtained which showed the same chemical and physical properties of the compound obtained by direct synthesis.

The remaining compounds were prepared and purified according to a previous report.[7]

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