Calculation of the Ring-current Shifts of Nuclear Magnetic Resonance Signals caused by Aromatic Ligands in Metal Complexes

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Current-loop calculation has been carried out to estimate the n.m.r. ring-current shifts of protons of 1,10-phenanthroline (phen) ligands in $[Co(phen)_m(en)_{3-m}]^{3+}$ (en = 1,2-ethanediamine; m = 1—3). Comparison of the calculated and observed shifts demonstrated that the calculation correctly predicts the upfield shift of an n.m.r. signal of a proton caused by aromatic ligands in a metal complex.

The aromatic ring-current effect in n.m.r. spectroscopy has been used as a useful probe for examining the geometry of a molecule or a molecular aggregate in solution.[1—7] The spacial position of a proton, or the structure of a molecule containing the proton, can be determined from the observed ring-current shift of an n.m.r. signal of the proton,[1—3] if the ring-current shift is correctly predicted by calculation. Such calculations have been done for molecules such as benzene,[8,9] porphyrin,[10] chlorophyll,[11] and phthalocyanine.[12] No full calculation has been carried out for systems of metal complexes containing aromatic ligands, such as phen (1,10-phenanthroline) and bipy (2,2′-bipyridine), although the ring-current effect has been used in many works[4—7] to estimate qualitatively geometries of molecules or aggregates in solution.

In this paper we describe a full calculation of ^1H n.m.r. ring-current shifts for 1,10-phenanthroline (phen) protons in $[Co(phen)_m(en)_{3-m}]^{3+}$ (en = 1,2-ethanediamine; m = 1—3) based on the current-loop model[8,9] and compare the results with the experimental data.[13] The comparison shows that the current-loop calculation correctly predicts the upfield shifts of n.m.r. signals of protons in the neighbourhood of aromatic ligands.

Results and Discussion

Figure 1 shows the numbering of protons on a phen ligand in $[Co(phen)_m(en)_{3-m}]^{3+}$. The observed ^1H chemical shift is caused by several factors including the ring-current effect. The H^2 and H^9 protons of a phen ligand of $[Co(phen)_2(en)]^{3+}$ (Figure 1) should be equivalent in the absence of the effects of the other ligands. Therefore, the difference in the chemical shift between H^2 and H^9 ($\delta_9 - \delta_2$ in ref. 13) must arise from the effects of the other ligands, mainly from the ring-current effect of the other phen ligand, in the same complex. The same argument also applies to the chemical shift differences between H^3 and H^8, H^4 and H^7, and H^5 and H^6. The calculated values for these differences are reasonably close to the observed (with a standard deviation of 0.07), as shown in the Table.

Table. Differences in the upfield shifts between intrinsically equivalent protons of a phen ligand in $[Co(phen)_2(en)]^{3+}$

	Calc.	Obs.*
$\delta_9 - \delta_2$	1.89	1.93
$\delta_8 - \delta_3$	0.86	0.84
$\delta_7 - \delta_4$	0.43	0.44
$\delta_6 - \delta_5$	0.11	0.00

* Ref. 13.

Figure 2 shows a plot of the observed (●) value of the upfield shift of each proton signal of $[Co(phen)_2(en)]^{3+}$ relative to that of the corresponding proton (with an identical locant in Figure 1) of $[Co(phen)(en)_2]^{3+}$ (case 1); a similar plot (○) for the chemical shifts in $[Co(phen)_3]^{3+}$ relative to those in $[Co(phen)_2(en)]^{3+}$ is also shown (case 2). Since the chemical shift changes in each case are related to the increase in the ring-current effect caused by the introduction of an additional phen ligand substituting for an en ligand on the H^2 side (case 1) or the H^9 side (case 2) of the phen ligand(s) in question, the calculation gives an identical series of values for H^2, H^3, $\cdots$, H^9 in case 1 and for H^9, H^8, $\cdots$, H^2 in case 2 (the calculated values are given as crosses in Figure 2). The observed values show a tendency similar to that of the calculated values in each case, although the observed are systematically smaller than the calculated values in both cases. By subtracting 0.26 from the calculated values, values (shown by plus marks in Figure 2) are obtained in good agreement with those observed in case 1 except for H^2 and H^9. In case 2, subtraction of 0.01 gave the best fit with the observed values. In both cases the standard deviation was less than 0.05 except for H^2 and H^9. The systematic deviation (0.26) in case 1 may arise from a shift of the signal position of the internal standard (trimethylsilylpropanesulphonate) in the n.m.r. measurements. The ^1H n.m.r. signal of a sulphonate ion in water is known to shift upfield in the presence of a phen complex because of an association of the ion with the complex ion through hydrophobic interaction.[14] The extent of this association may be large for $[Co(phen)_m(en)_{3-m}]^{2+}$ where m = 3 and 2 but not when m = 1 since the sulphonate ion tends to be

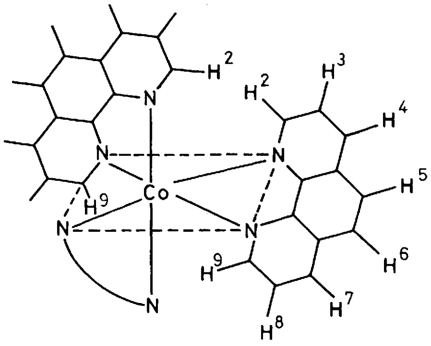

Figure 1. The numbering of protons on the phen ligand in $[Co(phen)_2(en)]^{3+}$

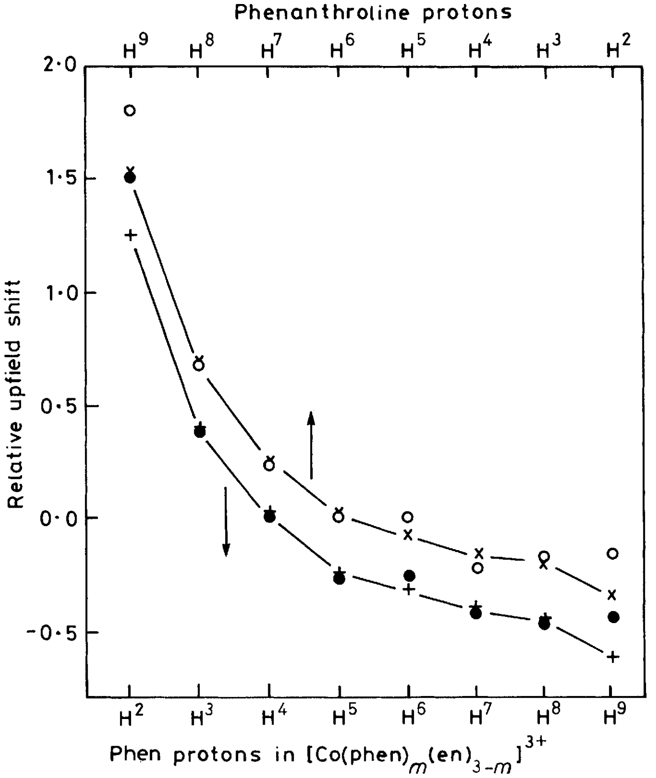

Figure 2. The calculated differences (X) in the ring-current shifts and the observed differences (●, ○) in chemical shifts between protons at the same site of the phen ligand in $[Co(phen)_m(en)_{3-m}]^{3+}$. Upfield shifts of each proton signal in $m = 2$ relative to $m = 1$ (●) and $m = 3$ relative to $m = 2$ (○). The plus (+) marks indicate the calculated value −0.26

located in between two phen ligands in the association complex.[14] Thus the shift of the signal of the internal standard must be large in case 1 but small in case 2.

The calculated shifts deviated considerably (*ca.* 0.2) from the observed for H^2 and H^9 in cases 1 and 2. The deviation for H^2 in case 1 or for H^9 in case 2 is very probably due to the slight difference in the structure of the calculated model from that of the real complex in solution: the ring-current shift of a proton close to an aromatic ring plane is greatly affected by a small change in the distance of the proton from the plane ($\approx$0.25 per 0.1 Å). The reason for the deviation for H^9 in case 1 or for H^2 in case 2 is at present not clear.

Since the simple model used in this paper adequately predicts the upfield shift of an n.m.r. signal of a proton located several angstroms from the aromatic ligands, the method of calculation presented can be used in structural studies, especially for determining the spacial position of a proton from the observed aromatic shift of the proton signal. An application of the method to $[Fe(phen)_3]^{2+}$–arenesulphonate ion pairs to elucidate their geometry in solution has been reported elsewhere.[14]

Experimental

Method of Calculation.—The current-loop model,[8,9] developed to calculate the ring-current shifts of n.m.r. signals of protons in the neighbourhood of a benzene ring, was transferred to metal complexes containing aromatic ligands. A computer program (written in BASIC) to calculate the ring-current and local magnetic anisotropic shifts of ^1H n.m.r. signals at an arbitrary place near aromatic rings is available on request (S. Tachiyashiki, *J. Kagawa Nutr. Coll.*, 1987, **18**, 137).

In calculating the ring-current shifts from π electrons of a six-membered aromatic ring, the radius, *a* (1.39 Å), of the two loops of the π-electron current on both sides of the plane of the aromatic ring and the spacing, *p* (1.28 Å), between the loops were assumed to be the same as the values for benzene.[9] The change in the *p* value in the range of 1.08—1.63 Å affected the calculated values of the shifts considerably, but not the differences in the calculated shifts shown in the Table and Figure 2. The ring-current intensities of the pyridine and benzene moieties in a phen ligand were respectively assumed to be 1.133 and 0.975 times the intensity for benzene.* The ring-current shifts of the n.m.r. signals of phen protons in $[Co(phen)_m(en)_{3-m}]^{3+}$ (m = 1—3) were calculated by simply assuming that the shift is expressed as the sum of the shifts caused by each of the six-membered rings of the phen ligands in the complex ions. A possible pseudo-aromatic ring-current effect of a five-membered chelate ring was disregarded because of a smaller degree of conjugation. (In order to form a closed ring, the metal π orbital must be a $4p_\pi$ orbital which lies high in energy; use of $3d_\pi$ orbitals makes the ring electronically open, because different $3d_\pi$ orbitals, perpendicular to each other, are needed at each end of the π conjugation.) For the calculation, the co-ordinates of the protons of a phen ligand and of the centres of the aromatic rings in $[Co(phen)_m(en)_{3-m}]^{3+}$ were estimated by assuming that the geometrical parameters of the complexes are the same as those obtained for $[Fe(phen)_3]^{2+}$ by single-crystal *X*-ray analysis.[15] Because of the symmetry of the crystal structure there were three sets of co-ordinates for protons of a phen ligand relative to the two neighbouring phen ligands. Thus the calculation was carried out for these three sets and then the calculated shifts were averaged for the three sets.

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* The current intensities were based on those obtained for phenanthrene by molecular orbital calculation (N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 1962, **36**, 2443; C. W. Haigh and R. B. Mallion, *ibid.*, 1982, **76**, 4063; J. Aihara and T. Horikawa, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1853). Calculation assuming the same ring-current intensities as for benzene for the six-membered rings of the phen ligand gave shift values 10% smaller than those obtained in this paper.

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