never been reproduced by other workers.[3a,8] In view of our results, low-temperature proton bombardment should prove generally useful as a technique for the preparation of thermally unstable compounds. Gas phase irradiations should be of particular value in the synthesis of products less volatile than the reactants.

Acknowledgments.—We are indebted to Messrs. W. J. Brown, R. Smol, and particularly W. D. Riel for their assistance with the experimental work.

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[8] F. Schreiner, J. G. Malm, and J. C. Hindman, *J. Am. Chem. Soc.*, **87**, 25 (1965).

Correspondence

Remarks on the Electronic Spectrum of Dibenzenechromium(I) Ion

Sir:

In their discussion of the spectrum of dibenzenechromium(I) iodide, $Cr(bz)_2I$, Yamada, *et al.*,[1,2] reported four intense bands in the ultraviolet and visible spectral region in addition to other weaker bands at longer wavelengths. The spectrum of $Cr(bz)_2I$ in aqueous solution is shown in Figure 1a. The band notation is that used by Yamada, *et al.*[1] On the basis of intensity, polarization, and solvent shift, the above-mentioned authors suggested that band IV is due to a $\pi-\pi^*$ transition within the benzene rings, whereas the other bands were assumed to correspond to transitions involving metal orbitals.

Berry[3a] approached this subject in a more theoretical way. This author supported Yamada's assignment of band IV with some theoretical evidence, attributing this band to the ${}^1E_{1u} \leftarrow {}^1A_{1g}$ $\pi-\pi^*$ benzene transition, shifted toward higher wavelengths because of the interaction between ring and chromium electrons.

Independently, Feltham[4] reported an electronic absorption spectrum of $Cr(bz)_2^+$ ion quite similar to Yamada's $Cr(bz)_2I$ spectrum.

While studying the photochemistry of some metal sandwich compounds, we examined the photochemical decomposition of $Cr(bz)_2I$ in aqueous solution. The spectral changes during irradiation suggested that band IV was not concerned with the $Cr(bz)_2^+$ ion. In fact it can easily be shown that *band IV corresponds to the well-known absorption band of the I^- ion*[5] (Figure 1b). As a matter of fact, the spectrum of $Cr(bz)_2OH$[6] does not exhibit such a band (Figure 1c). *This spectrum must be considered the real spectrum of $Cr(bz)_2^+$ cation.*[7]

In order to verify the assignment of $Cr(bz)_2I$ band IV to the I^- ion, we have compared the spectra of I^- ion in water and in ethanol. The maxima were found at 225 and 221 mμ, respectively, showing a red shift as observed by Yamada, *et al.*,[1] in the case of $Cr(bz)_2I$ band IV.

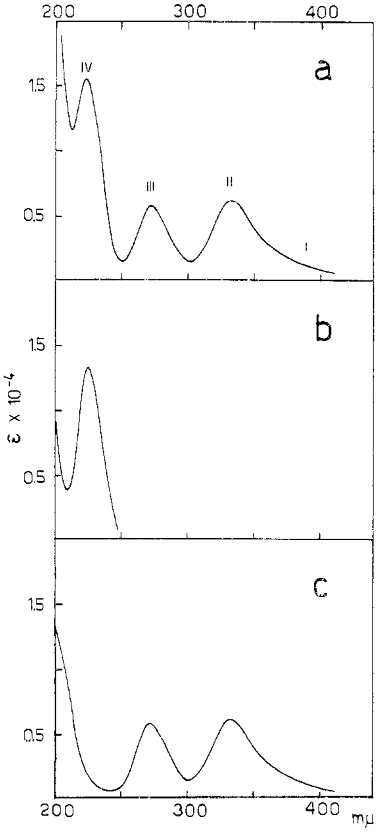

Figure 1.—(a) Spectrum of $Cr(bz)_2I$. (b) Spectrum of I^- ion. (c) Spectrum of $Cr(bz)_2OH$.

All the spectra of chromium–arene compounds agree with the above-stated considerations. In fact, all the cationic species (whose spectra were evidently recorded as iodide salts) show a band at about 225 mμ,[4] whereas the neutral complexes obviously do not exhibit such a band.[3b,4] It can also be noted that the band below 200 mμ reported by Feltham[4] as a band of chromium–arene cations very likely corresponds to the iodide absorption band at ~195 mμ.[5]

It must be noted that the erroneous assignment of band IV to a $\pi-\pi^*$ benzene transition has been taken as proof of considerable localization of π electrons in benzene rings.[1,3a] Actually, the fact that benzene bands are not substantially shifted toward higher

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[1] S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **30**, 647 (1957).

[2] S. Yamada, H. Yamazaki, H. Nishikawa, and R. Tsuchida, *ibid.*, **33**, 481 (1960).

[3] (a) R. S. Berry, *J. Chem. Phys.*, **35**, 29 (1961); (b) R. S. Berry, *ibid.*, **35**, 2025 (1961).

[4] R. D. Feltham, *J. Inorg. Nucl. Chem.*, **16**, 197 (1961).

[5] (a) J. Franck and G. Scheiber, *Z. Physik. Chem.*, **A139**, 22 (1928); (b) L. E. Orgel, *Quart. Rev.* (London), **8**, 422 (1954).

[6] This compound was obtained from $Cr(bz)_2I$ by precipitating I^- with fresh Ag_2O.

[7] The absorbance of OH^- ion is negligible at wavelengths higher than 210 mμ.[5b]

wavelengths suggests that in dibenzenechromium the rings retain considerable benzenoid character.[8]

Acknowledgment.—The authors wish to thank Dr. S. Valcher, who kindly provided a sample of $Cr(bz)_2I$.

(8) Regarding the symmetry of dibenzenechromium compounds, two alternative molecular point groups have been proposed: D_{3d}[9a] or D_{6h}.[9b] Our finding that the $\pi-\pi^*$ transition is not far from being benzenoid is in accordance with the D_{6h} symmetry.

(9) (a) H. P. Fritz and W. Lüttke, Proceedings of the 5th International Conference on Coordination Chemistry, London, Special Publication No. 13, The Chemical Society, London, 1959, p 123; F. Jellinek, *Nature*, **187**, 871 (1960); F. Jellinek, *J. Organometal. Chem.*, **1**, 43 (1963); (b) H. P. Fritz, W. Lüttke, H. Stammreich, and R. Forneris, *Chem. Ber.*, **92**, 3246 (1959); F. A. Cotton, W. A. Dollase, and J. S. Wood, *J. Am. Chem. Soc.*, **85**, 1543 (1963); A. Haaland, *Acta Chem. Scand.*, **19**, 41 (1965).

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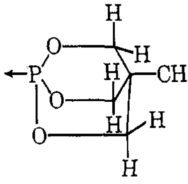
Nuclear Magnetic Resonance Spectra of Symmetrical Spin Systems Containing Phosphorus

Sir:

During the past 2 years, several papers[1-6] have appeared describing briefly the proton magnetic resonance spectra of symmetrical spin systems for inorganic compounds containing two or more phosphorus nuclei. These spectra seem to have caused some mystification, the features which could not be explained on a "first-order" basis being attributed to "phosphorus–phosphorus or long-range coupling." In certain cases attempts have been made to treat the spectrum using a simplified nuclear spin system. Verkade, *et al.*,[6] for instance, studied the spectra of metal carbonyl complexes of the type $M(CO)_mL_2$, where M = Ni, Fe, Cr, Mo, and W, and L is the 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ligand (I). For each compound the spectrum of the methylene protons of the two ligand groups was examined and treated as the X part of an $AA'X_2$ subsystem, where A and A′ are the two phosphorus nuclei (one in each ligand L), and the long-range coupling J'_{AX} is assumed to be zero. These authors gave no proof of the validity of their approach, but such a proof is desirable in view of the fact that, in general, it is *not* possible to use a nonsymmetrical spin system as a model for a more complex symmetrical case. In principle, the compounds investigated constitute a 20-spin system since there are 18 protons and two phosphorus nuclei. However, the methyl protons are only coupled to other nuclei to a slight extent, and they may therefore be neglected from the analysis. Moreover, all six methylene protons in one ligand are demonstrably chemically equivalent and are equally coupled to every other magnetic nucleus, provided that we consider long-range (H, H) coupling between the ligands to be zero, and they are therefore also effectively magnetically equivalent. Thus, the nuclear spin system that needs to be considered is $X_6AA'X'_6$, with $J_{XX'} = 0$. Explicit expressions for the X transitions of the $X_nAA'X'_n$ case have now been given,[7] so simplification of the spin system is not necessary. However, it can readily be shown that the X transitions for an $X_nAA'X'_n$ system with $J_{XX'} = 0$ are identical with those for an $X_{2n}AA'$ system. Therefore, the compounds examined by Verkade, *et al.*,[6] could be treated as comprising $X_{12}AA'$ spin systems. The reduction by these authors to X_2AA' spin systems is not, however, valid, as can be seen from the explicit expressions given by Harris[7] for the equivalent $X_nAA'X'_n$ cases. It is true that all of the X lines of the X_2AA' (or $XAA'X'$) system are contained in the $X_{12}AA'$ (or $X_6AA'X'_6$) case, but the latter has many additional lines. In particular, when $J_{AA'} \gg |J_{AX} - J'_{AX}|$ and the X spectrum is "deceptively simple," giving approximately a triplet,[8] the extra lines of the full spin system give added width to the central band of the triplet. This fact makes the quantitative use of line widths to obtain values of J_{PP} dubious, and it may be said that the results listed by Verkade, *et al.*,[6] as crude values for J_{PP} are minimum values (which are still, of course, of some interest).



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It is worth stressing that the "odd" appearance of spectra in these symmetrical cases[1-6] is due entirely to their symmetry. The apparent triplet appearance for the X spectrum[6,8] only occurs for strongly coupled cases, $|J_{AA'}| \gg |J_{AX} - J'_{AX}|$, and departure from it must be considered as *normal*. The opposite extreme (a simple doublet[7]) is obtained[6,9] when $|J_{AA'}| \ll |J_{AX} - J'_{AX}|$ and $J'_{AX} \approx 0$. The sharp outer pair of lines in the X spectrum will always be present when there is a spin system with two groups of chemically equivalent nuclei of the type $X_nX'_nX''_n \ldots AA'A'' \ldots$. Spectra of such cases for phosphonitrilic compounds $(NPX_2)_r$ were illustrated by Allen, *et al.*[5] The sharp X doublet lines arise from A spin states with the maximum (all spins α) and minimum (all spins β) values of $F_z(AA\ldots)$. The separation of the doublet is given by

(1) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **4**, 419 (1965).

(2) R. G. Hayter, *ibid.*, **3**, 711 (1964), and other papers in this series.

(3) R. B. King, *ibid.*, **2**, 936 (1963), and other papers in this series.

(4) D. S. Payne, H. Nöth, and G. Henniger, *Chem. Commun.* (London), 327 (1965).

(5) G. Allen, D. J. Oldfield, N. L. Paddock, F. Rallo, J. Serregi, and S. M. Todd, *Chem. Ind.* (London), 1032 (1965).

(6) J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).

(7) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

(8) R. J. Abraham and H. J. Bernstein, *ibid.*, **39**, 216 (1961).

(9) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).