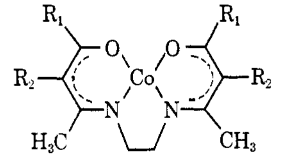
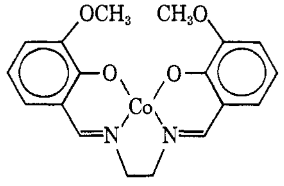
Table I. Spin-Hamiltonian Parameters[a] for Some Co(SB) and Co(SB)py Complexes in Nematic Glass at 77°K



Co(acacen) $R_1 = CH_3$, $R_2 = H$
Co(meacacen) $R_1 = R_2 = CH_3$
Co(benacacen) $R_1 = C_6H_5$, $R_2 = H$



Co(MeOsalen)

Compound	g_x[b]	g_y[b]	g_z	$\lvert a_x^{Co}\rvert$[b,c]	$\lvert a_y^{Co}\rvert$[b,c]	$\lvert a_z^{Co}\rvert$[c]	$\lvert a_z^{N}\rvert$[c]
Co(acacen)	2.928	1.934	2.01	100.3	32.5	32.8	
Co(meacacen)	2.957	1.952	2.031	73.9	30.7	32.0	
Co(benacacen)	3.084	1.937	2.01	104.1	32.0	32.8	
Co(acacen)py	2.435	2.225[d]	2.012	56.2	12.5[f]	92.3	14.7
Co(benacacen)py	2.428	2.22[f]	2.012	55.2	13.5[f]	92.1	14.9
Co(MeOsalen)py	2.40	2.23[f]	2.015	56[e]	10[f]	89.4	14.7

[a] Errors = 1 in the final digit unless indicated differently. [b] The x and y directions are arbitrarily assigned. These directions are in the average Schiff base plane. [c] Units in $cm^{-1} \times 10^4$. [d] Error is ±0.003. [e] Error is ±3. [f] Estimated from computer simulations.

that the unpaired electron occupies the d_{z^2} orbital.[10] The spin-orbit parameters of Co(meacacen), for example, are found to be $b_1 = \lambda/(E_{yz} - E_{z^2}) = -0.159$, $b_2 = \lambda/(E_{xz} - E_{z^2}) = -0.001$; for both SB = meacacen and benacacen, hyperfine parameters are $P \simeq 140$ ($\times 10^{-4}$ cm^{-1}) and $\kappa \simeq 0.1$–0.12. A somewhat larger value of P is required for Co(acacen), and the magnitude of the hyperfine anisotropy ($|A_x| - |A_y|$) is not quite as well reproduced as for the other two complexes.

Comparing b_1 and b_2 shows that the large in-plane g anisotropy arises from a large splitting of the (d_{xz}, d_{yz}) orbitals, with the d_{yz} lying closely below the half-filled d_{z^2} and d_{xz} far lower. Of the other two d orbitals, the in-plane orbital, pointing directly at the ligand atoms (d_{xy} in our coordinates[10]), must be the highest lying empty orbital; the other in-plane orbital ($d_{x^2-y^2}$) must be below d_{z^2} and filled.

The finding that $g_z > g_e > g_y$ for the four-coordinate Co(SB), however, prevents a complete fit to the g factors using a pure d-electron ground-state configuration. An electron in a pure d_{z^2} orbital has no first-order contributions to g_z and second-order corrections ($-3b_1^2$) must tend to decrease g_z below g_e.

It does not appear that mixing of cobalt d orbitals[5] in the low-symmetry environment of the Co(SB) can account for $g_z > g_e$. The Co(SB) probably exhibit an out-of-plane puckering which reduces their overall symmetry to C_2—with twofold rotation about the x axis. In this symmetry d_{z^2}, $d_{x^2-y^2}$ and d_{yz} are all of a symmetry, and it is possible to mix the latter two orbitals with d_{z^2}, forming

$$|z^2\rangle = \alpha(d_{z^2}) + \beta(d_{x^2-y^2}) + \gamma(d_{yz})$$

with $(\alpha^2 + \beta^2 + \gamma^2) = 1$ and where we expect $\alpha^2 \gg \beta^2$ and γ^2. This hybrid orbital has first-order contributions to g_z. However, the contribution from mixing d_{yz} is ($-2\gamma^2 b_2$) which is positive but much too small to counterbalance the negative second-order contribution to g_z.

The contribution to g_z from admixture of $d_{x^2-y^2}$ is ($-8\beta^2 b_3$), where $b_3 = \lambda/(E_{d_{xy}} - E_{d_{z^2}})$. To fit g_z by use of this term would require b_3 to be large and negative, implying that the d_{xy} orbital lies below $|z^2\rangle$ and is doubly occupied and therefore that the unoccupied orbital is $d_{x^2-y^2}$. But this ordering contradicts our above conclusions regarding the placing of these two levels.

A possible simple solution to this contradiction is to postulate the existence of filled predominantly ligand σ orbitals of b (xy) symmetry[6] or, alternatively, filled predominantly ligand π orbitals of b symmetry which could couple, respectively, through the $d_{x^2-y^2}$ or the d_{yz} components of $|z^2\rangle$ to give positive contributions to g_z.

Despite the qualitative difference between resonance spectra of the Co(SB) and Co(SB)py complexes, the results in the latter are also rationalized by placing the odd electron in the d_{z^2} orbital. Complexation by pyridine reduces the splitting between the d_{xz}–d_{yz} orbitals, presumably by reducing the out-of-plane "puckering," and creates the pattern g_x and $g_y > g_z$. The result $g_z > g_e$, however, leads to the same contradictions as in the four-coordinate Co(SB). Cobalt porphyrin complexes also have $g_z > g_e$.[11]

Acknowledgment. This work was supported by the National Institutes of Health and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. B. M. H. wishes to acknowledge Professor R. G. Pearson for a helpful discussion on the symmetry properties of Co(SB).

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(10) We choose the x axis to pass through Co and the center of the C–C bond of the ethylenediamine and the z axis to be normal to the mean SB plane.

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(12) Alfred P. Sloan Foundation Fellow, and recipient of a NIH Career Development Award.

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^{31}P Nuclear Magnetic Resonance Spectrum of Pentamethylcyclopentaphosphine. Evidence for a Large Stereochemical Dependence of the $^1J(PP)$ Spin–Spin Coupling

Sir:

The influence of lone-pair orientation on the nuclear spin–spin coupling constant values has long been

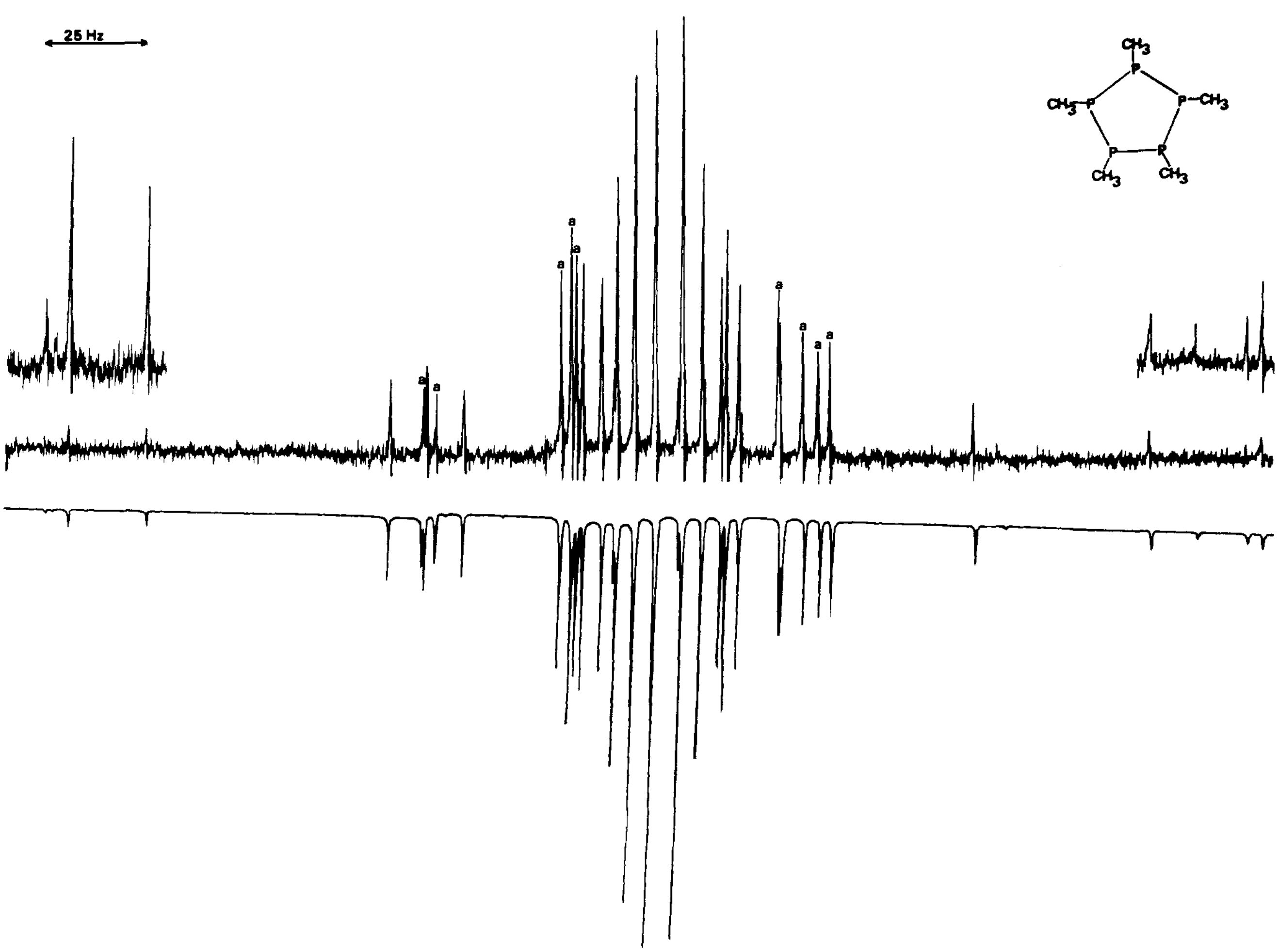

Figure 1. Observed and calculated phosphorus (40 MHz) proton-noise-decoupled spectrum of pentamethylpentacyclophosphine. The a lines are transitions between antisymmetrical eigenstates of the AA'BB'C spin system. In the upper part are shown the weaker experimental lines using a relatively high observing rf field.

recognized.[1] As far as the phosphorus nucleus is concerned, such a stereochemical dependence has been shown for $^1J(P^{13}C)$,[2] $^2J(PC^{13}C)$,[3-5] $^2J(PCH)$,[6] $^2J(PC^{15}N)$,[7] and $^3J(PNCH)$.[8,9] It has also been suggested in the case of the $^3J(POCH)$[10,11] and $^3J(PCCH)$[12,13] couplings.

It has been predicted theoretically that the coupling between the nuclei of a pair of directly bonded phosphorus atoms may vary substantially according to the molecular conformation adopted.[14] Hitherto the experimental indications of such a dependence have been a slight temperature dependence for $^1J(PP)$ in tetrafluorodiphosphine[15] and a larger difference (19 Hz) between the values observed for the two diastereoisomers of the 1,2-dimethyl-1,2-diphenyldiphosphine.[16]

We have now analyzed the proton-noise-decoupled phosphorus nmr spectrum of the pentamethylcyclopentaphosphine $(CH_3P)_5$,[17] and we wish to report here what we believe to be evidence for a large influence of the phosphorus lone-pair spatial relationship on the $^1J(PP)$ spin–spin coupling.

The 40-MHz proton-noise-decoupled phosphorus spectrum of $(CH_3P)_5$ shows a complex AA'BB'C pattern spread over about 300 Hz (Figure 1). Homonuclear tickling experiments were performed on each

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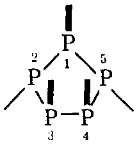
Table I. Phosphorus Chemical Shift and Phosphorus–Phosphorus Coupling Constants in Pentamethylcyclopentaphosphine[a]



$\delta(P_1)$	$\delta(P_2)$ $\delta(P_5)$	$\delta(P_4)$ $\delta(P_3)$	J_{12} J_{15}	J_{14} J_{13}	J_{25}	J_{24} J_{53}	J_{23} J_{54}	J_{43}
−49.8	−49.2	−47.5	−248.6	+23.3	−3.6	−8.1	−236.4	−310.3

[a] The $\delta(P)$ values are in parts per million downfield from external 85% H_3PO_4; the J values are in hertz; a negative sign of $^1J(PP)$ is assumed (see text).

of the phosphorus spectral lines and the results of these triple resonance experiments were used to sketch an experimental energy level diagram (eld). This experimental eld was then compared to the eld of "trial and error" AA′BB′C calculated systems in order to perform iterative calculations with the LAOCOON III program. The best parameters from the analysis are presented in Table I. The error in the coupling constant values is less than 1.2 Hz.

In the molecule under study, $(CH_3P)_5$, the relative orientations of the methyl substituents are unknown. However, X-ray diffraction studies have shown that $(CF_3P)_5$[18] and $(C_6H_5P)_5$[19] exist with two substituents attached to adjacent phosphorus atoms which lie on the same side of the ring. Such a stereochemical relationship which affords the best possible cis–trans alternation of the methyl groups is consistent with the nmr data (the AA′BB′C system and the coupling constant values; see later) and will be assumed here.[20] The assignments of the chemical shifts of phosphorus atoms 2,3 and 4,5 could be reversed (Table I). However, such a labeling would involve two small $^1J(PP)$ values (±23.3 and ∓3.6). Since all the previously reported $^1J(P^{III}P^{III})$ values are larger than 100 Hz, excluding the $^1J(PP)$ = 55 Hz found in the highly strained 1,2,3,4-tetrakis(trifluoromethyl)-3,4-diphosphacyclobutene,[21] this alternate labeling appears to be highly unlikely.

From the spectral analysis only the relative signs of the coupling constants are determined. However, the known directly bonded $^1J(P^{III}P^{III})$ coupling constants range from 100 to 400 Hz in magnitude, excluding the above-mentioned low value. In all this class of coupling constants, those signs which have been determined are negative despite large degrees of variance in the P substituents.[22] As a consequence it seems reasonable to assume that the $^1J(PP)$ values obtained in the phosphorus nmr spectral analysis of the pentamethylcyclopentaphosphine (which are experimentally shown to be of the same sign) are all negative.

The most striking feature of the data in Table I is the large difference observed in the $^1J(PP)$ values (∓248.6, ∓236.4, and ∓310.3 Hz). Small differences in the PPP angles and thus in the hybridization state of the three different kinds of phosphorus atom of $(CH_3P)_5$ in solution are not unexpected,[23] but such small differences cannot be responsible for the large difference here observed in the $^1J(PP)$ values. We suggest that most of this difference is due to the difference in the stereochemical orientation around the coupled nuclei. The largest absolute value (310.3 Hz) would correspond to an approximate cis relationship between the lone pair of the bonded phosphorus atoms.

In assuming negative values of $^1J(PP)$, the experimental order here observed in the $^1J(PP)$ couplings is consistent with the calculation carried out previously.[14]

It must be pointed out that the couplings between nondirectly bonded phosphorus nuclei are different in magnitude and sign. This result is difficult to rationalize in terms of $^2J(PP)$ or $^3J(PP)$ since the observed couplings are simultaneously $^2J(PP)$ and $^3J(PP)$. To our knowledge these are the first $^2J(PPP)$ values reported in the literature.[24]

Clearly a comprehensive understanding of the large stereochemical dependence observed here for the $^1J(PP)$ spin–spin coupling would be of great value for stereochemical study of diphosphines and polyphosphines. Further studies are now in progress on both the experimental and theoretical aspects in order to get more information on this problem.

Acknowledgments. We thank Mr. R. Nardin for his skillful assistance in running the nmr spectra. We are also grateful to Messrs. Taieb and Csakvary for adapting the computer programs to our computer facilities.

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^{13}C CIDNP Effects Associated with the Thermal 1,3 Rearrangement of Oxime Thionocarbamates

Sir:

We have recently reported[1] CIDNP effects in the proton nmr spectra of products **2** and **3** of thermal 1,3

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