phosphorus bond distance in **1** is much shorter than the reported average values in $(C_6H_5P)_5$ [2.217 (6) Å][16] and $(C_6H_5P)_6$ [2.237 (3) Å][17] in spite of the strong steric hindrance in **1**, indicating that the bond in the diphosphene has considerably double bond character. All intermolecular approaches correspond to the van der Waals interactions.

Reaction of **1** in carbon tetrachloride with chlorine gas at room temperature gave (2,4,6-tri-*tert*-butylphenyl)phosphonic dichloride almost quantitatively after treatment with water. The same result was obtained in the presence of methanol.

The compound **1** is the first isolated phosphobenzene with a localized P=P bond in contrast to [(trifluoromethyl)phosphinidene]tributylphosphorane[18] with a delocalized P=P bond. Compound **1** may serve as a good model for theoretical studies as well as studies in organic and inorganic chemistry. Further investigation of the chemical properties and reactions of **1** is now in progress.

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Supplementary Material Available: Table of atomic positional and thermal parameters for **1** (2 pages). Ordering information is given on any current masthead page.

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^{183}W NMR Spectroscopy: $^2J_{W-W}$ Coupling. Structural Application to 1-12 Heteropolytungstates

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Iso- and heteropolytungstates are well-known compounds,[1] but only a few X-ray structures have been published. Very recently, Acerete et al.[2,3] and Gansow et al.[4] have used tungsten NMR spectroscopy (^{183}W: spin $^1/_2$, 14.27% natural abundance, sensitivity 5.8×10^{-2} compared to ^{13}C) to delineate some trends in the electronic structure of chosen heteropolytungstates via chemical shift studies. In fact, tungsten-183 is characterized by a huge chemical range (±3000 ppm/Na_2WO_4), and any subtle change in tungsten chemical environment will be reflected on its chemical shift. Moreover, a tungsten NMR experiment is performed on solution, which allows the chemist to study time-dependent systems, as it will be shown in this communication, and the structural indications obtained through such an experiment can nicely complement an X-ray structure.[2,4,5]

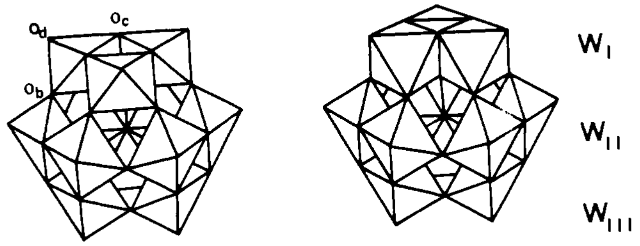

Figure 1. α and β isomerism in Keggin structure (oxygen O_a which are bound to three W are not indicated in the figure).

Heteropolytungstates belonging to 1-12 series are represented by the general formula $X^nW_{12}O_{40}^{(8-n)-}$ (X = H_2, P, B, Si, etc.). The more symmetrical structure (α type, ideal symmetry T_d) is shown in Figure 1.[6,7] In this arrangement, four W_3O_{13} moieties are clearly seen, which result in the 12 octahedrons sharing corners and linking via edges. The four O_a-type[8] oxygens define a tetrahedral cavity where the X heteroelement is found. By rotating one W_3O_{13} group by 60°, a less symmetrical β-type structure[7] (Figure 1) is derived from the α one (ideal symmetry C_{3v}). These two kinds of structures are easily discriminated in tungsten NMR spectroscopy: α structure, one singlet (12 equivalent tungsten atoms); β structure, 3 peaks in the ratio 1:2:1.

$H_2W_{12}FO_{39}{}^{5-}$[9] (I) belongs to the α-type series,[10] but the fluorine atom introduces a C_{3v} symmetry. Its tungsten NMR spectrum shows three types of tungsten resonances in a 1:2:1 ratio: a doublet (δ -94.3 ± 0.1, J_{W-F} = 32 ± 1 Hz) and two singlets (δ -104.1 ± 0.1, -108.6 ± 0.1). This result confirms nicely the proposed structure[11] in which the fluorine atom, bound to three tungsten atoms, replaces an O_a-type oxygen (Figure 1).

The magnetic nonequivalence of the three tungsten groups allows, for the first time, homonuclear $^2J_{W-W}$ coupling to be resolved (Figure 2). These coupling constants fall into two well-defined classes: coupling between two tungsten atoms within the same W_3O_{13} moiety (W-O_c-W bond), 5 ± 1 Hz and coupling between one tungsten atom in a W_3O_{13} group and one tungsten atom in a $W_3O_{12}F$ group (W-O_b-W bond), 22 ± 1 Hz. To these two very different coupling constant values do correspond two different kinds of bonding scheme with characteristic bond angles and W-W distances (Table I).

The β-$SiW_{12}O_{40}H_4$[15,16] molecule possesses the same symmetry as I. Its ^{183}W NMR spectrum shows[17], again, three types of tungsten atoms (δ -109.7 ± 0.1, -114.7 ± -129.8 ± 0.1; ratio 1:2:1) corresponding to the W_I, W_{II}, W_{III} peaks in Figure 1, the more intense resonance (δ -114.7) being attributed to the six central tungsten atoms (W_{II}). $^1J_{W-W}$ homonuclear couplings are

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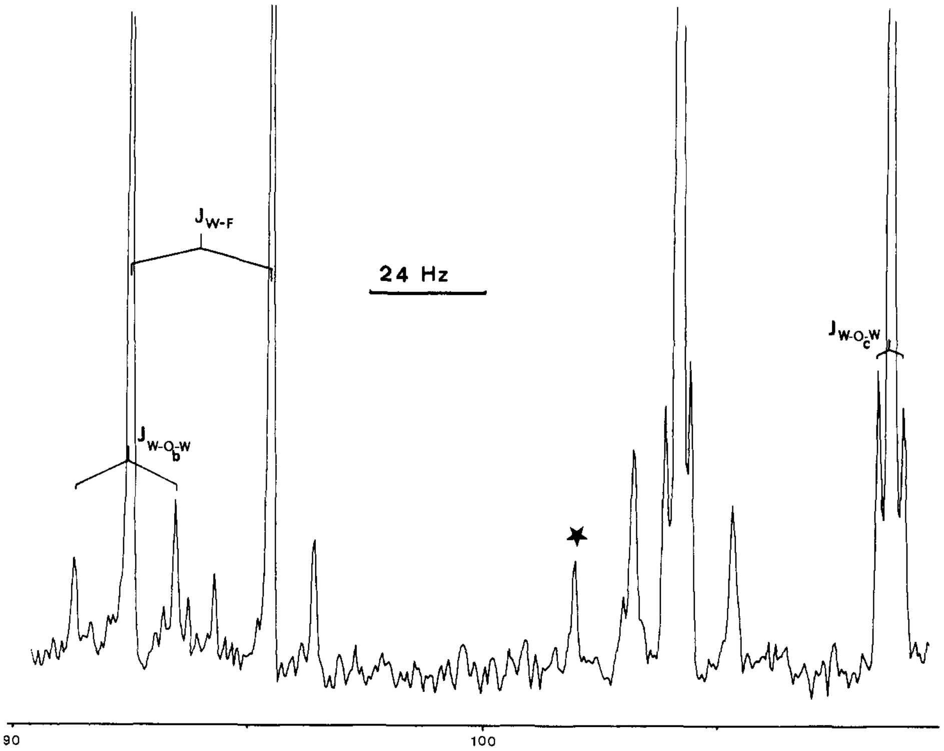

Figure 2. ^{183}W spectrum of $H_2W_{12}FO_{39}^{5-}$ showing $^2J_{W-W}$ coupling constants. Note the AB pattern for these homonuclear couplings (24 000 scans).

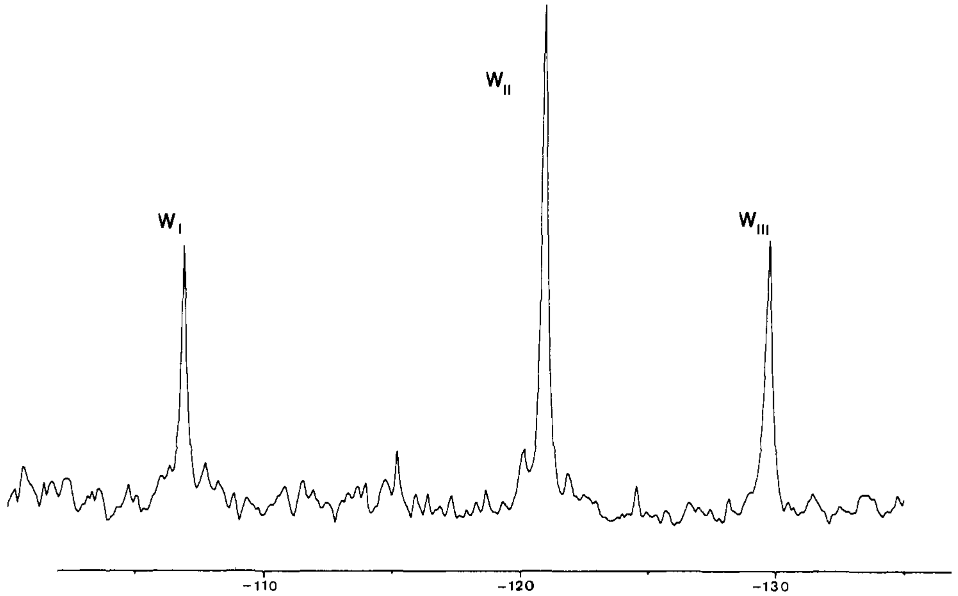

Figure 3. ^{183}W spectrum of Tungstate X; 24 000 scans. Partial $\beta \rightarrow \alpha$ (metatungstate ion) conversion can be detected (δ −117.5 peak).

Table I. Average of W–W Distances and W–O–W Angles in Known 1-12 Structures[a]

anions	ref	d_{W-W}, Å, intra	∠W–O_c–W, deg	d'_{W-W}, Å, intra	∠W–O_c'–W, deg	d_{W-W}, Å, extra	∠W–O_b–W, deg	d'_{W-W}, Å, extra	∠W–O_b'–W, deg
$H_3W_{12}O_{40}^{5-}$	12	3.31	118			3.69	147		
α $SiW_{12}O_{40}^{4-}$	13	3.35	123			3.69	153		
$PW_{12}O_{40}^{3-}$	14	3.40	125			3.68	151		
β $SiW_{12}O_{40}^{4-}$	15	3.34	121	3.35	118°	3.73	147	3.65	146
		$^2J_{W-W} \sim 8$ Hz						$^2J_{W-W} \sim 20$ Hz	

[a] The prime indicates the values for the W_3O_{13} group which has been rotated by 60° in β-$SiW_{12}O_{40}^{4-}$.

again present in the spectrum, amounting, respectively, to 8 ± 1 and 20 ± 1 Hz. The first coupling (8 Hz) should then represent an *intragroup* coupling pathway (W_{II}–O_c–W_{III}); the second one (20 Hz) is characteristic of an *extra-group* coupling between one tungsten of the rotated (β) W_3O_{13} group and one central W_{II}. This analysis unambiguously assigns the δ −109.7 resonance to the W_I tungstens and the δ −129.8 one to the W_{III} type.

Contrary to β-$SiW_{12}O_{40}H_4$, the so-called "tungstate X"[18] has never been characterized clearly, but a wealth of indirect proofs favors a β-type structure of the metatungstate ion for this compound.[19] Despite its low stability in aqueous solutions,[20] we succeeded in recording its ^{183}W (Figure 3) spectrum which is comparable to the β-$SiW_{12}O_{40}H_4$ one, i.e., 3 singlets (1:2:1) at δ -107.2 ± 0.1, -120.9 ± 0.1, and -130.6 ± 0.1. This result confirms definitely a β-type structure. Nevertheless, an overnight accumulation gives much broader lines (6-8 Hz, half-width) than with any other heteropolytungstate, this broadening coming either from very temperature-dependent chemical shift or from some exchange process with another intermediate of very low concentration. This broadening process does not allow the determination of the intragroup ^2J coupling, but an extra-group coupling (19 ± 1 Hz) is easily detected on the δ -107.2 (W_I) and -120.9 (W_{II}) lines.

These above examples show how useful can be the determination of $^2J_{W-W}$ couplings. The method will be of particular interest when dealing with multiline ^{183}W NMR spectra one finds, for example, in the 1-11 series. Finally, from Table I[12-15] it is clear that $^2J_{W-W}$ couplings are dependent on the W-O-W angles, but a definite correlation will be forseen only when enough ^2J values are available. We are actually tackling such a project.

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Rotational Diffusion of Rose Bengal in Aqueous Micelles: Evidence for Extensive Exposure of the Hydrocarbon Chains

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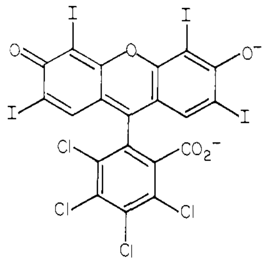
Organization of surfactants in micelles and the extent of water to hydrocarbon contact therein are important and much debated problems. At different times, water was believed to penetrate the micelle completely[1] or not at all[2-4] or reach to any intermediate depth.[5] The classical Hartley model, describing micelles as "oil-droplets in ionic coats",[6] cannot be reconciled with any appreciable water-to-hydrocarbon contact. Three different micellar models have been proposed recently to account for the experimental data. The Menger model describes micelles as porous clusters of surfactants which provide opportunities for considerable water penetration.[7] Fromherz rationalized micellar structures in terms of a surfactant block model which allows wetting the entire hydrocarbon chain in the time average.[8] Dill and Flory discussed molecular organization of surfactants in terms of a statistical theory by using lattice models.[9] This approach provides a substantial probability for methylene groups, even in the middle of the chain, to be in the outer layer of the lattice and predicts a few alkyl chains to lie entirely on the surface of the micelle.[9] Results of kinetic,[10] ^{13}C NMR,[11] and ORD[12] spectroscopic investigations were marshalled in support of the porous micelle model. Interpretation of these results, however, has been questioned.[3] Data are presented in this communication on the rotational diffusion of rose bengal in aqueous micellar hexadecyltrimethylammonium bromide (CTABr) and sodium dodecyl sulfate (SDS) which strongly supports the extensive exposure of surfactant methylene groups to water.



rose bengal

Rose bengal was chosen as a probe since it is a large rigid molecule (a prolate ellipsoid with semiaxes of 2 and 7 Å[13] and a solvated volume of 1670 Å^3 in EtOH[14]) whose absorption and fluorescence spectra, fluorescence lifetime, and anisotropy are extremely sensitive to solvent viscosity and hydrogen bond strength.[14-18]

Rose bengal was purified as described in the literature.[15,19] Its absorption maximum changed from 548 nm in water at neutral pH gradually with increasing amounts of CTABr and SDS to 562 and 558 nm. These data provide evidence for the efficient binding of rose bengal to micelles and allow the assessment of the binding constants, $K_{CTABr} \geq 10^4$ M^{-1}, $K_{SDS} \geq 10^2$ M^{-1}. Fluorescence lifetimes, determined by time-correlated single photon counting using picosecond laser pulses as the excitation source,[20] are given

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(20) A Spectra-Physics cavity dumped rhodamine 6G dye laser, synchronously pumped by a mode-locked argon ion laser (No. 171), was used to provide tunable 15-ps pulses at 400 kHz. Rose bengal samples were excited at 575 nm. The emission, viewed at 90°, was passed through an ultraviolet polacoat polarizer (3M type, 105 UV WRMR) set at 54.7° for lifetime and 0 or 90° for anisotropy measurements. Following the polarizer, the emitted light passed through a Jarrell-Ash 25-cm monochromator, set at 610 nm for rose bengal, onto a RCA 8850 PM tube. The "start" signal for the Ortec 457 TAC was obtained from a portion of the laser pulses via a Texas Instruments TIED 56 silicon avalanche photodiode and an Ortec 437-MHz discriminator. Photon counting and data treatment by the Marquardt algorithm have been previously described.[21] Lack of any instrumental artifact was demonstrated by reproducing the published lifetimes and rotational anisotropies in different solvents (see Table I and ref 25). *G* values (eq 1) were obtained by measuring the fluorescence intensity of rapidly rotating rose bengal in MeOH at 0 and 90°.

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