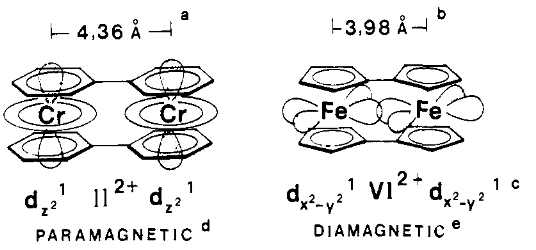

Figure 4. Comparison of the dinuclear species II^{2+} and VI^{2+}. Only the metal contributions to the singly occupied molecular orbitals are shown. ^{a} Estimate from a molecular model. ^{b} Reference 23. ^{c} Reference 24. ^{d} This work. ^{e} Reference 5.

as compared with the bis(arene) complex. Furthermore, metal orbital overlap should be more effective in VI^{2+} (equivalent to 50% σ, 50% π[24]) than in II^{2+} (equivalent to 25% σ, 75% δ; see Figure 4).

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

References and Notes

(1) Metal π Complexes of Benzene Derivatives. 11. Part 10: Ch. Elschenbroich and U. Zenneck, *J. Organomet. Chem.*, **100**, 125 (1978).
(2) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, *10*, 247 (1967).
(3) R. B. King, Ed., *Adv. Chem. Ser.*, **No. 150** (1976).
(4) D. Cowan, C. Le Vanda, J. Park, and F. Kaufman, *Acc. Chem. Res.*, **6**, 1 (1973).
(5) W. H. Morrison, Jr., and D. N. Hendrickson, *Inorg. Chem.*, *14*, 2331 (1975).
(6) C. Le Vanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela, and R. Collins, *J. Am. Chem. Soc.*, **98**, 3181 (1976).
(7) R. F. Kirchner, G. H. Loew, and U. T. Mueller-Westerhoff, *Inorg. Chem.*, **15**, 2665 (1976).
(8) J. C. Smart and B. L. Pinsky, *J. Am. Chem. Soc.*, **99**, 956 (1977).
(9) M. J. Powers and T. J. Meyer, *J. Am. Chem. Soc.*, *100*, 4393 (1978).
(10) The preparation of I has been published previously: Ch. Elschenbroich and J. Heck, *Angew. Chem., Int. Ed. Engl.*, **16**, 479 (1977).
(11) Ch. Elschenbroich, F. Gerson, and F. Stohler, *J. Am. Chem. Soc.*, **95**, 6956 (1973), for leading references.
(12) Chromium vapor (1.88 g, 36 mmol) was cocondensed at −196 °C, 10^{-4} Torr with biphenyl (95 g, 615 mmol). The resulting product was dissolved in 300 mL of O_2-free toluene and unreacted chromium was removed by filtration. The solvent was distilled off and the residue extracted with low boiling petroleum ether, methylcyclohexane, and toluene, each during an 8-h period at reflux temperature. From the toluene fraction, dark brown needles together with amorphous red-brown material precipitated after a few days. The two components can be separated by virtue of their different rates of sedimentation. Analytically pure samples were obtained after repeated recrystallization from toluene (2 × 200 mL): 23 mg of II, yield 0.34% referred to chromium evaporated. Anal. Calcd for $C_{24}H_{20}Cr$: C, 69.90; H 4.89. Found: C, 70.06; H, 4.94. Mass spectrum (field ionization): *m/e* 412 (M^+, 100%). III is contained in the methylcyclohexane fraction and can be isolated via sublimation (180 °C ($<10^{-4}$ Torr)). Mass spectrum (field ionization): *m/e* 572 (M^+, 100%). Complete separation from II has not yet been achieved, however.
(13) D. J. Thoennes, C. L. Wilkins, and W. S. Trahanovsky, *J. Magn. Reson.*, **13**, 18 (1974).
(14) J. Evans an and J. Norton, *Inorg. Chem.*, **13**, 3042 (1974).
(15) D. A. Brown, J. P. Chester, N. J. Fitzpatrick, and I. J. King, *Inorg. Chem.*, **16**, 2497 (1977).
(16) For the spatially crowded ortho protons, van der Waals deshielding also has to be considered. This effect alone, however, does not account for the large shielding difference between ortho and para protons since, in phenanthrene, the van der Waals contribution to shielding of the ortho,ortho′ protons $H_{4,5}$, which bear a similar sterical relationship, amounts to only ≈0.54 ppm: T. B. Cobb and J. D. Memory, *J. Chem. Phys.*, **47**, 2020 (1967).
(17) The diamagnetic shielding effect of a benzene ring on the η^5-cyclopentadienyl protons in phenylferrocene as a function of dihedral angle has been calculated. (a) N. Kamezawa, *J. Magn. Reson.*, **11**, 88 (1973). In this context, it is noteworthy that $\Delta\delta$ for H_o, H_m, and H_p increases with increasing coplanarity of a biphenyl structure as demonstrated by ^1H NMR spectra of biphenyl and 9,10-dihydrophenanthrene. (b) J. Vander Koij, C. Gooijer, and N. H. Velthorst, *Recl. Trav. Chim. Pays-Bas*, **90**, 732 (1971).
(18) We used a 4-mm-outer-diameter two-electrode cell for low-temperature operation equipped with a helical gold spiral working electrode and a concentric platinum wire counterelectrode constructed along the lines of R. D. Allendoerfer, G. A. Martinchek, and S. Bruckenstein, *Anal. Chem.*, **47**, 890 (1975). We are indebted to Dr. H. Ohya-Nishiguchi for helpful suggestions.
(19) Fluid solutions of the dications I^{2+} and II^{2+} do not display ESR signals *if freshly prepared.* However, I^{2+} and II^{2+} gradually cleave off one-half sandwich unit (η-arene)Cr$^+$ yielding mononuclear radical cations. Unaware of this fact, in a previous paper[10] we erroneously attributed biradical character to the species I^{2+}.
(20) The appearance of the spectrum is unaffected by changes in solvent and by dilution down to 10^{-5} M.
(21) N. D. Chasteen and R. L. Belford, *Inorg. Chem.*, **9**, 169 (1970).
(22) Conformation of η-biphenyl in I: fully eclipsed, R(Cr−Cr) = 5.40 Å; fully staggered, R(Cr−Cr) = 4.90 Å; R_{ESR} = 4.68 Å.
(23) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1970 (1969).
(24) The degeneracy of the HOMO of ferrocene (e_{2g}, metal AO contributions Fe d_{xy}, $d_{x^2-y^2}$) is raised upon formation of the dinuclear complex VI.

Ch. Elschenbroich,* J. Heck
Fachbereich Chemie der Philipps-Universität
D-3550 Marburg, West Germany

Received June 11, 1979

Homonuclear and Heteronuclear Coupling in 5′-AMP as Probed by Two-Dimensional Proton Nuclear Magnetic Resonance Spectroscopy

Sir:

We have obtained the two-dimensional, homonuclear, J-resolved, ^1H NMR spectrum[1-3] of 5′-adenosine monophosphate (5′-AMP).[4]

The normal ^1H NMR spectrum of 5′-AMP[5] (Figure 1a) is complicated by strong homonuclear coupling combined with heteronuclear coupling to ^{31}P, which are normally difficult to unravel. Two-dimensional NMR spectroscopy has allowed us to distinguish between homo- and heteronuclear coupling by inspection.

The pulse sequence used (90°-τ-180°-τ-echo) causes transitions which are connected by homonuclear, scalar coupling to be "stretched out" across the second dimension (F_1),[3] whereas heteronuclear coupling causes transitions to appear side by side in the first dimension (F_2), since the heteroatom is unaffected by the pulses.

Figure 2 shows the two-dimensional spectrum of the ribose 3′, 4′, 5′, and 5″ protons. The 3′ proton shows two homonuclear couplings: one to the 2′ proton and one to the 4′ proton. Thus, to first order, the 3′ proton resonates as a doublet of doublets stretched out over F_1. By contrast in the 4′ region we see two pairs of side-by-side transitions. The splitting *within* a pair is caused by long-range, heteronuclear coupling to ^{31}P and the

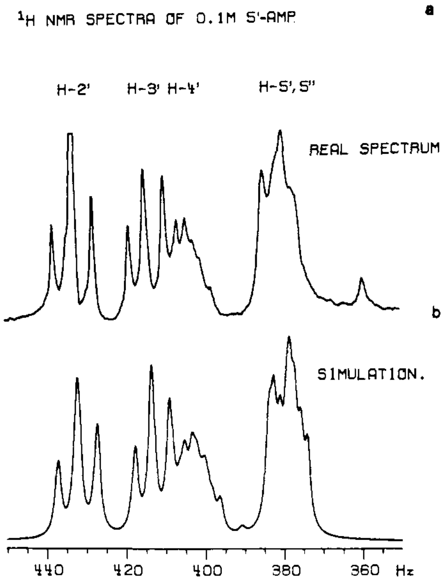

Figure 1. (a) The 90-MHz ^1H NMR spectrum of the higher field ribose protons in 5′-AMP. The central part of the H-2′ multiplet is overlapped by a peak due to HDO. (b) Simulation of the spectrum in Figure 1a using δ and J values obtained from the 2D spectrum.

0002-7863/79/1501-6776$01.00/0

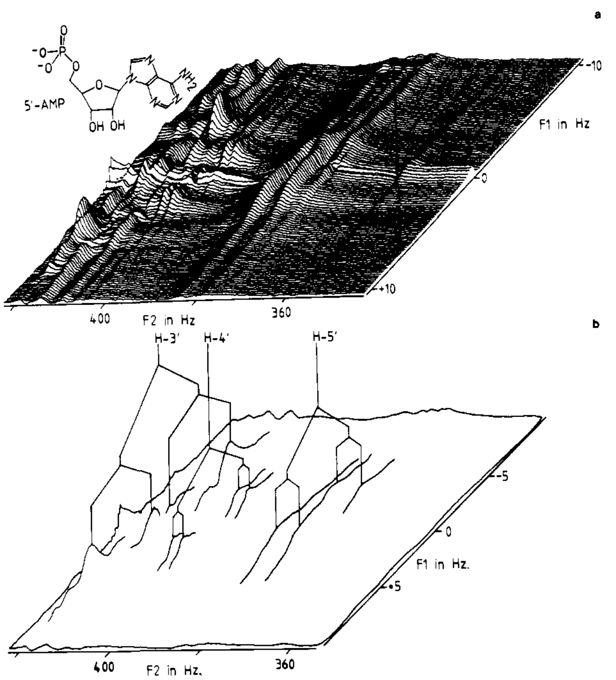

Figure 2. (a) The 2-D, homonuclear, *J*-resolved, ^{1}H NMR spectrum of the H-3′, H-4′, and H-5′,5″ protons in 5′-AMP at ambient temperature. (b) An outline sketch of the main peaks visible in Figure 2a, showing their origins.

Table I

coupling	value in Hz	coupling	value in Hz
$J(1',2')$	5.3	$J(4',P)$	1.9
$J(2',3')$	4.8	$J(5',5'')$	−12.0[a]
$J(3',4')$	4.2	$J(5',P)$	5.3
$J(4',5')$	3.3	$J(5'',P)$	5.3
$J(4',5'')$	3.3		

[a] Reference 5.

splitting *between* pairs is due to homonuclear coupling to the 3′ proton. Each observed 4′ transition is, in fact, the strong, central part of a multiplet due to coupling to the two 5′ protons. Other parts of these multiplets were too weak to be observed. A similar coupling pattern is exhibited by the 5′ protons, except, in this case, the heteronuclear coupling is larger. The signals are also broader due to short T_2's. This makes the determination of the magnitude of the homonuclear coupling to 4′ inaccurate and obscures effects due to the possible nonequivalence of the 5′ protons.

Additional peaks appear in the spectrum along lines of constant F_2 corresponding to transitions in the conventional ^{1}H NMR spectrum. These extra signals are caused by the mixing of the transition at that particular F_2 with other connected transitions. This mixing can be due either to imperfections in the pulse or to strong coupling effects.[3,6] Any peak in the two-dimensional spectrum is associated with two connected transitions in the conventional NMR spectrum. The F_1 frequency of the peak is exactly one half the separation between these transitions in F_2.[3] Using this guide we have been able to assign nearly all the peaks in Figure 2.

Our analysis of the two-dimensional spectrum has enabled us to obtain both the homonuclear coupling constants and the couplings to ^{31}P. The coupling constants are given in Table I. These were then used in a seven-spin, spectral simulation, shown in Figure 1b. The correspondence with the observed spectrum is shown in Figure 1.

In nucleic acids the conformation of the phosphate backbone is extremely important in determining the overall conformation of the molecule.[5,7] Two-dimensional ^{1}H NMR not only allows us to probe these backbone conformations (via the ^{31}P-^{1}H coupling constants) but simultaneously allows the determination of all the homonuclear coupling information.[8]

Acknowledgment. We thank the National Science and Engineering Research Council of Canada for financial support.

References and Notes

(1) W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.*, **64**, 2229–2246 (1976).
(2) K. Nagayama, P. Bachmann, K. Wüthrich, and R. R. Ernst, *J. Magn. Reson.*, **31**, 133–148 (1978).
(3) G. Bodenhausen, R. Freeman, G. A. Morris, and D. L. Turner, *J. Magn. Reson.*, **31**, 75–95 (1978).
(4) 5′-AMP was lyophilized from D_2O and then dissolved in 100% D_2O which contained 0.01 M sodium phosphate buffer (pD 7.0) and 1.0 M sodium chloride. The solution concentration of 5′-AMP was 0.1 M. Spin-echo FID's were accumulated at 90 MHz on a Brucker WH 90 spectrometer equipped with a BNC-12 data system and a NIC-293 I/0 controller; 129 τ values were used at increments of 0.012 s. The data were transferred to and processed on a Nicolet 1180 computer system.
(5) D. B. Davies, *Prog. NMR Spectrosc.*, **12**, 135–226 (1978).
(6) G. Bodenhausen, R. Freeman, R. Niedermeyer, and D. L. Turner, *J. Magn. Reson.*, **26**, 133–164 (1977).
(7) P. H. Bolton and G. Bodenhausen, *J. Am. Chem. Soc.*, **101**, 1080–1084 (1979).
(8) While in press another paper on the distinction between homonuclear and heteronuclear coupling constants by 2-D NMR spectroscopy has appeared: L. D. Hall and S. Sukumar, *J. Am. Chem. Soc.*, **101**, 3120–3121 (1979).
(9) Address correspondence to the Department of Chemistry, Scarborough College, University of Toronto, West Hill, Ontario, Canada M1C1A4.

Jeremy R. Everett, Donald W. Hughes
Alex D. Bain,*[9] Russell A. Bell*
Department of Chemistry, McMaster University
Hamilton, Ontario, Canada L8S 4M1

Received May 21, 1979

An Investigation of the Fluidity of Alkyl Benzenesulfonate Aqueous Micelles by Fluorescence Spectroscopy

Sir:

The influence of supramolecular assemblies on chemical changes has lately become of increasing interest owing to the realization that many important biological processes occur at, or close to, such assemblies (membranes, peptides, nucleic acids) where effects such as charge density and amphipathic environment may be important.[1] Surfactant micelles have been extensively used to model the biological structures. This is justified by the fact that the same forces are responsible for holding biological and micellar aggregates together. Also the lipophilic boundary and hydrophilic regions of micelles find their counterparts in cellular structures. The popularity of the surfactant micelle as an experimental model arises from the ready availability of pure materials and the innate feeling that micelles offer a more tractable problem for quantitative investigation.

The use of fluorescent probes for studying the phenomena of micellization and solubilization has become widespread.[2] Thus, large aromatic hydrocarbons such as methylanthracene, pyrene, etc., have been employed as extrinsic probes to obtain information on rotational diffusion (through fluorescence depolarization)[3,4] and translational diffusion (through the dynamics of excimer formation).[5,6] However, the question must be raised as to whether a micelle which incorporates a relatively large guest residue is the same entity as the micelle without the probe.[7] Here we report some preliminary studies using a variety of alkyl benzenesulfonate isomers which are surfactants having an intrinsic fluorescent probe. These studies

0002-7863/79/1501-6777$01.00/0