

titanium dichloride (I) or its zirconium analog (II) has been found. Wilkinson and Birmingham² demonstrated from infrared data that a monomeric π -bonded "sandwich" structure exists for I and II. Sloan and Barber³ reinforced these observations by proton magnetic resonance data on I and II, but no mention has been made of the spatial configuration of the rings.

"Angular" sandwich structures have been postulated for bis-cyclopentadienyl tin and lead on the basis of dipole moments and other measurements,⁴ and X-ray measurements on $(C_5H_5)_2TiCl_2 \cdot Al(C_2H_5)_2$ (III).⁵

We wish to report that the *high* values of the dipole moments obtained, 6.3 and 5.9 *D* for I and II, respectively, indicate that there are four essentially equivalent bond angles and that the structure is similar to the $[(C_5H_5)_2TiCl_2]$ grouping in III, *i.e.*, approaching the tetrahedral configuration as depicted in Fig. A. It is of interest that the structure appears to be independent of the oxidation state.

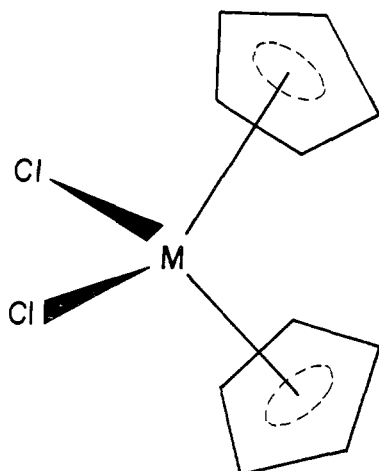


Fig. 1.

The measurements were conducted in benzene using the "dielectric constant-refractive index" method for I and II, and the "dielectric constant-density" method for I. Measurements made both on freshly prepared solutions and on solutions one day old were identical, suggesting that changes in solution, if any, had no effect on the dielectric constant. The results are shown in Table I.

Dielectric constant measurements were made at 30.0° using a heterodyne-beat circuit consisting of two electron coupled oscillators, one controlled with a quartz crystal at 576.5 kc. and the frequency of the other one controlled by the variable capacitance. A Balsbaugh model cell made of Pyrex and monel metal was used. The volume was 50 ml., and the interplate air capacitance was 49.4 μ mf. Refractive index was measured with a Autsch and Lomb Precision Abbe refractometer,

(2) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).

(3) C. L. Sloan and W. A. Barber, *ibid.*, **81**, 1364 (1959).

(4) L. D. Dave, D. F. Evans and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959).

(5) G. Natta, P. Corradini and I. W. Bassi, *J. Am. Chem. Soc.*, **80**, 755 (1958).

TABLE I				
BIS-CYCLOPENTADIENYL TITANIUM DICHLORIDE				
Concn. (wt. fract.)	Dielectric constant ϵ	Density (g./cc.)	η^{20D}	$(\eta_D)^2$
0.000869	2.284	...	1.49440	2.23323
.001929	2.300	...	1.49448	2.23347
.002870	2.313	...	1.49457	2.23374
.00169	2.290	0.8695
.000615	2.279	.8690
.000327	2.269	.8689
Solvent	2.265	.8684
BIS-CYCLOPENTADIENYL ZIRCONIUM DICHLORIDE				
Concn. (wt. fract.)	ϵ	η^{20D}	$(\eta_D)^2$	
0.002978	2.303	1.49459	2.23379	
.001951	2.291	1.49454	2.23365	
.001052	2.276	1.49448	2.23347	
.000472	2.273	1.49440	2.23323	
Solvent	2.265	1.49439	2.23320	

temperature controlled to 0.05°. Densities were measured in a 25 ml. pycnometer.⁶

The data were interpreted by the method of Guggenheim and Prue⁷ and of Halverstadt and Kumler.⁸ A least squares analysis was applied with these results.

	μ (Debyes)	Method
Ti Compound I	6.26 \pm 0.39	Refractive index
	6.22 \pm 0.39	Density
Zr Compound II	5.90 \pm 0.38	Refractive index

The uncertainty given represents the 95% confidence interval of the data.

(6) The dielectric constant, refractive index and density measurements were performed by J. R. Murray of these Laboratories.

(7) E. A. Guggenheim and J. E. Prue, "Physicochemical Calculations," Interscience Publishers, Inc., New York, N. Y., 1953, pp. 106, *et seq.*

(8) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

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THE CONFORMATION OF METAL-ADENOSINE TRIPHOSPHATE COMPLEXES IN SOLUTION

Sir:

The fact that adenosine triphosphate (ATP) forms strong complexes with divalent metal ions is well known and quantitative equilibrium^{1,2} and kinetic studies³ have been carried out by several workers. The most important metal binding sites are undoubtedly the phosphate groups, but the role of the rest of the molecule in forming the metal complex has given rise to much speculation (*cf.* reference 4 for a review of this subject and pertinent literature citations). Solid state infrared studies,

(1) A. E. Martell and G. Schwarzenbach, *Helv. Chim. Acta*, **39**, 653 (1956).

(2) R. A. Alberty and R. M. Smith, *J. Am. Chem. Soc.*, **78**, 2376 (1956).

(3) H. Diebler, M. Eigen and G. G. Hammes, *Z. für Naturforsch.*, **15B**, 554 (1960).

(4) M. R. Atkinson and R. K. Morton in "Comparative Biochemistry," M. Florin and H. S. Mason, ed., **2**, Academic Press, New York, N. Y., 1960, pp. 1-82.

rotary dispersion data and molecular models are consistent with a proposed conformation whereby the phosphate-metal moiety folds back onto the rest of the molecule so as to form a chelate-type structure by binding of the metal ion to the amino group and N-7 of the adenine ring.⁴ Since the nuclear magnetic resonance spectrum of ATP has been determined recently,⁵ it occurred to us that the structure of metal-ATP complexes could be investigated readily utilizing this experimental method. As will be shown, our results indicate that the proposed chelate conformation is extremely unlikely.

Experimental.—Solutions of 0.2 M ATP were prepared in D₂O using the disodium salt obtained from Nutritional Biochemicals Corp. The *pD* of the solution (as measured with a glass electrode) was adjusted with solid Na₂O₂ to about 9.6 so as to insure an uncharged amino group and completely ionized phosphate groups. Solid MgCl₂ or CaCl₂ then was added to a final concentration of 0.1 or 0.2 M MgCl₂ or 0.1 M CaCl₂. Nuclear magnetic resonance spectra were measured with a standard 60 megacycle high resolution spectrometer from Varian Associates (V 4300 B, equipped with a superstabilizer and a field homogeneity control unit) immediately after making up the solutions.

Results and Discussion.—The chemical shifts (in cycles per second) of the C₈, C₂ and C₁' protons with respect to the proton resonance of the residual water are presented in Table I. The standard

TABLE I
PROTON CHEMICAL SHIFTS IN ATP

	H ₈	H ₂	H ₁ '
ATP	-217	-193	-73.2
MgATP	-215	-192	-72.4
CaATP	-215	-191	-71.4

deviation of the many spectra analyzed was about ± 2 cps. Within experimental error, the chemical shifts are identical for all the samples. (The chemical shifts for ATP are also consistent with those obtained by Jardetzky and Jardetzky⁵ if the fact that their spectra were obtained at 40 megacycles rather than 60 megacycles is taken into account.) Since protonation of the pyrimidine ring in ATP results in a shift of the H₂ peak 26 cps. to lower field (at 60 Mc) and protonation of N-7 in guanosine triphosphate shifts the H₈ resonance 54 cps. to lower field (with a corresponding but smaller shift in the H₁' peak),⁵ it seems highly improbable that either Mg⁺⁺ or Ca⁺⁺ is significantly associated with the adenine portion of the ATP molecule. A word of caution should be inserted here: this interpretation assumes implicitly that adding positive charge with Mg⁺⁺ would produce the same general effect as adding a proton to one of the rings. Since the protonic charge is thought to distribute itself throughout the pyrimidine ring in ATP,⁶ Mg⁺⁺ might conceivably form a loose type of complex with the amino group where no charge transfer to the pyrimidine ring occurs;

(5) C. D. Jardetzky and O. Jardetzky, *J. Am. Chem. Soc.*, **82**, 222 (1960).

(6) R. M. Bock in "The Enzymes," (P. D. Boyer, H. Lardy, K. Myrback, ed.), **2**, Academic Press, Inc., New York, N. Y., 1960, pp. 3-38.

thus the chemical shift of the C₂ proton would not be affected. Although such a situation cannot be ruled out, the possibility of forming a stable conformation without some appreciable charge transfer seems slight. A similar situation is also possible for the N-7 site, but it is even more difficult to think of a type of chemical bonding leaving the chemical shift of the C₈ proton unaltered.

These results indicate, therefore, that the structure of the metal-ATP complex in solution is likely to be somewhat extended. This offers the attractive possibility that the amino group and/or N-7 and the metal-phosphate moiety can provide separate binding sites for enzymes. Further experiments are being planned to investigate the effect of an ATP-requiring enzyme on the n.m.r. spectrum.⁷

This research was supported by a grant from the National Institutes of Health (RG-7803).

(7) Since our original manuscript was submitted, a recent communication [K. Hotta, J. Brahm and M. Morales, *J. Am. Chem. Soc.*, **83**, 997 (1961)] has interpreted titration curves of ATP obtained spectrophotometrically in terms of a curled structure involving metal binding at the pyrimidine ring. The presence of Mg⁺⁺ caused a lowering of the apparent *pK* of the amino group (~ 4.5). The n.m.r. spectra at *pD*'s below about 5 are also changed by Mg⁺⁺—a striking feature being the marked broadening of the C₁ and C₃ proton resonances. The lowering of the apparent *pK* by Mg⁺⁺ is similar to that caused by a shortening of the phosphate chain: *cf.* ATP vs. ADP vs. AMP; in the latter two substances a folded structure is not possible. Therefore the observed ultraviolet and n.m.r. spectral changes are probably due to the disturbance of a water bridge structure between the amino and phosphate groups. Since at higher *pD*'s (> 6) the n.m.r. (and apparently ultraviolet) spectra are unchanged by the presence of Mg⁺⁺, the assumption of a folded conformation on the basis of the above mentioned data is not warranted.

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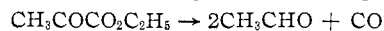
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DIRECT AND SENSITIZED PHOTOLYSIS OF ETHYL PYRUVATE

Sir:

We have observed that irradiation of benzene solutions of ethyl pyruvate leads to photolysis of the α -ketoester. The principal products are carbon monoxide and acetaldehyde, indicating the path



A small amount of carbon dioxide also is produced.

It was of interest to learn whether or not the fragmentation reaction involved a singlet excited state or a long-lived triplet. The latter possibility is suggested by the fact that irradiation of ethyl pyruvate in ether-pentane-alcohol glass at 77° K. gives rise to a weak, blue phosphorescence. In order to establish the decomposition mechanism we used benzophenone as a photosensitizer for the decomposition of the ester. Hammond, *et al.*,¹ and Bäckström and Sandros² have shown independently that excitation of benzophenone in solution is followed by quantitative intersystem crossing; therefore, the chemically significant excited state

(1) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959); G. S. Hammond, W. M. Moore and R. P. Foss, *ibid.*, in press.

(2) H. L. J. Bäckström and K. Sandros, *J. Chem. Phys.*, **23**, 2197 (1955).