Acenaphthylene thus behaves like azulene in forming a diiron pentacarbonyl complex. The formulation of the deep red azulene complex $C_{10}H_8Fe_2(CO)_5$ prepared by Burton, Pratt, and Wilkinson[21] from azulene and iron pentacarbonyl has been confirmed by mass spectroscopy. However, reaction between azulene and iron pentacarbonyl under slightly different conditions results in a different dark red complex indicated by mass spectroscopy to be $[C_{10}H_8Fe(CO)_2]_2$, apparently closely related to $[C_{10}H_8Mn(CO)_3]_2$[21] and $[C_{10}H_8V(CO)_4]_2$.[22]

A volatile yellow solid, mp 113–115°, obtained from $Fe_2(CO)_{12}$ and allene dimer, C_6H_8 (mixture of ~80% 1,2-dimethylenecyclobutane and ~20% 1,3-dimethylenecyclobutane), has now been shown to be the dicarbonyl $C_{12}H_{16}Fe(CO)_2$ by its mass spectrum. Although infrared and nmr spectra of this unusual, very rare complex are available, an unequivocal decision cannot yet be made between any of several possible structures.

Details of the mass spectra of these olefin complexes of iron carbonyl will be included in future publications on their synthesis and properties.

(21) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

(22) E. O. Fischer, Abstracts of Papers presented at the Symposium on Current Trends in Organometallic Chemistry, Cincinnati, Ohio, June 1963, p 66.

R. B. King
Mellon Institute
Pittsburgh, Pennsylvania 15213
Received February 25, 1966

Nitrogen-15 Nuclear Magnetic Resonance Evidence That Mg^{2+} Does Not Complex with Nitrogen Atoms of Adenosine Triphosphate

Sir:

Because Mg^{2+} cocatalyzes with ATPases, and because ITP and ATP are enzymatically nonequivalent, it is reasonable to guess that Mg^{2+} interacts with the ring moiety of ATP and other nucleoside triphosphates; if so, then, in a solution containing only Mg^{2+} and ATP, an internal chelate (Mg^{2+} interacting simultaneously with ring N atoms and triphosphate O atoms) might result.[1] One of us[2] has previously taken ultraviolet difference spectra to support this idea. Recent studies[3] have concluded, however, that this structure does not form. The most persuasive of these studies have employed nuclear magnetic resonance (nmr), but have thus far been indirect in that the resonances studied were those of protons bonded to C atoms, not those of the N atoms which would be primarily involved. In the present work, by using ^{15}N-substituted ATP, we have succeeded in studying the N resonances, and conclude that Mg^{2+} does not interact with these atoms whereas Zn^{2+} does.

The ^{15}N nmr spectra were obtained at a frequency of about 6.053 Mcps and a magnetic field of 14,025 gauss by the frequency sweep method using a Hewlett Packard Model 5100A frequency synthesizer. A Nuclear Data Model ND-160 Enhancetron was used to enhance signal-to-noise ratios by making repetitive scans of the spectrum.[4] The frequency sweep was derived from the analyzer sweep so that chemical shifts could be measured by counting the frequency synthesizer output frequency at a particular channel containing an nmr peak maximum.

The ATP used for these experiments was 70% enriched in ^{15}N at all nitrogen positions. The nmr samples were 0.5–0.9 *M* in ATP. When samples containing metal ions were prepared, $ZnCl_2$ or $MgCl_2$ was added in amounts needed to give equal metal ion and ATP concentrations. Sample pH was adjusted to about 9.5 with NaOH. Under these conditions the hypothetical metal ion–adenine ring interaction should have been about 90% saturated even for an association constant as low as 1×10^2. Deuterium was usually substituted for exchangeable protons in the sample by lyophilization and solution in D_2O steps. Sample temperature during the measurements was 34°. Chemical shifts did not change noticeably over the pH range 7.0 to 9.6.

Five well-separated nitrogen resonances were observed. These were assigned to particular nitrogen atoms of ATP on the basis of (1) fine structure due to spin–spin coupling interactions, (2) behavior in H_2O and in D_2O solution, and (3) reported values of ^{14}N chemical shifts.

The peak at highest field was assigned to the 6-amino nitrogen.[5] It could only be detected in D_2O solution. Incomplete collapse of the nitrogen–proton spin–spin coupling interaction severely broadened the resonance in H_2O solution. The N-9 resonance could be identified because it was a single line. This nitrogen is not part of a conjugated system and should not couple strongly to nearby protons. The remaining three nitrogen resonances were doublets due to spin–spin coupling to protons on adjacent carbon atoms; N-7 exhibited a 10-cps coupling to H-8 and occurred at lowest field; N-1 and N-3 couple equally to H-2 with $J = 16$ cps. On the basis of Herbison-Evans' and Richards'[6] measurements of ^{14}N chemical shifts in NH_2-substituted pyridine, N-1 should be found at a higher field than N-3. The 10-ppm shift observed between these two nitrogens of ATP is equal to the separation between the heterocyclic nitrogens of *o*- and *p*-amino-substituted pyridines. Chemical shifts for the five nitrogen atoms of ATP are given in Table I. The shifts are also given for ATP in the presence of Mg^{2+} and Zn^{2+} ions.

The results show that there is no significant shift in any nitrogen peak when Mg^{2+} is added to ATP. If Mg^{2+} had coordinated with a nitrogen of the adenine

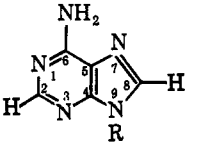
(1) A. Szent-Györgyi, "Enzymes, Units of Biological Structure and Function," O. H. Gaebler, Ed., Academic Press Inc., New York, N. Y., 1956, p 393.

(2) K. Hotta, J. Brahms, and M. Morales, *J. Am. Chem. Soc.*, **83**, 997 (1961).

(3) (a) P. W. Schneider, H. Brintzinger, and H. Erlenmeyer, *Helv. Chim. Acta*, 47, 992 (1964); (b) M. Cohn and T. R. Hughes, Jr., *J. Biol. Chem.*, **237**, 176 (1962); (c) G. G. Hammes, G. E. Maciel, and J. S. Waugh, *J. Am. Chem. Soc.*, **83**, 2394 (1961).

(4) M. P. Klein and G. W. Barton, Jr., *Rev. Sci. Instr.*, **34**, 754 (1963).

(5) The adenine ring portion of ATP is numbered as follows.



(6) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, 7, 19 (1964).

Table I. Chemical Shifts for Nitrogen Atoms in ATP and in Equimolar Metal Ion–ATP Solutions[a]

Sample	Nitrogen atom N-1	N-3	N-7	N-9	NH_2-6
ATP	144.7	135.6	129.5	191.6	282.8
Mg–ATP	144.9	135.0	129.5	191.6	282.3
Zn–ATP	144.4	135.0[b]	132.5[b]	190.1	279.7

[a] Chemical shifts are in parts per million relative to an external $H^{15}NO_3$ reference ($\delta_{^{15}NH_4^+}$ = +340.3 ppm relative to this reference). Except where noted, the uncertainty in chemical shifts was ±0.3 ppm as measured by the scatter of three or more separate measurements. [b] The uncertainty in these values is estimated to be ±0.6 ppm because of a broadening and partial overlap of the peaks.

moiety, either the diamagnetic shielding about that nitrogen or the paramagnetic contribution to its chemical shift should have changed. Since no shifts occurred, it may be concluded that Mg^{2+} does not bind to the adenine ring in the Mg–ATP complex. The chemical shift data in Table I for the Zn–ATP complex indicate that a Mg^{2+}–adenine ring interaction could have been detected if it were present.

The nmr spectrum of the Zn–ATP complex shows that Zn^{2+} ions cause small low-field shifts in the N-9 and 6-amino nitrogen resonances. The shifts are well outside of the experimental uncertainty, which is ±0.3 ppm, and indicate a reduced diamagnetic shielding of these nitrogens in the complex. The N-7 resonance of ATP is shifted to higher field in the Zn–ATP complex.

These shifts are consistent with a model in which Zn^{2+} interacts at both the 6-amino nitrogen and N-7 positions. The high-field shift for N-7 indicates a reduced paramagnetic contribution to its shift due to chelation. The low-field 6-amino nitrogen shift in the presence of Zn^{2+} is the same as that observed when Mg^{2+} ions are added to glycine to form the Mg–glycine complex.[7] In the latter complex, chelation is known to involve the amino group and causes a 3.2 ppm low-field shift in the amino nitrogen nmr.

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(7) J. Happe, unpublished reslts.
(8) Career investigator, American Heart Association.

James A. Happe
Lawrence Radiation Laboratory, University of California
Livermore, California

Manuel Morales[8]
Cardiovascular Research Institute, University of California
San Francisco, California

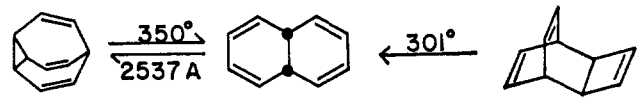
Received February 3, 1966

9,10-Dihydronaphthalene. Formation from Bullvalene and Nenitzescu's Hydrocarbon, Thermal Reorganization, and Photorearrangement to Bullvalene

Sir:

In the final step of a rational synthesis of tricyclo-[3.3.2.$0^{4,6}$]deca-2,7,9-triene (I),[1] acetic acid is eliminated pyrolytically from 9-acetoxytricyclo[3.3.2.$0^{4,6}$]deca-2,7-diene under conditions similar to those reported by Schröder[3] to convert bullvalene (I) to naphthalene. In an effort to maximize the yield in this elimination, the behavior of bullvalene (I) on heating has been reinvestigated. Surprisingly, the first isolable product of the thermal reorganization of bullvalene is 9,10-dihydronaphthalene (II),[4] identified by comparison of nuclear magnetic resonance and ultraviolet spectra with those reported by van Tamelen and Pappas.[5] When I is partially decomposed at 350° in a flow system, II is the only product, while on heating at 400° or at 359° for a longer contact time, three additional major products are produced, at the expense of II. These products, which are themselves stable at 400° and are formed in the approximate ratios 4:2:1, are 1,4-dihydronaphthalene, 1,2-dihydronaphthalene, and naphthalene (each identified by comparison of nuclear magnetic resonance and infrared spectra with those of authentic samples[6,7]). These same products are formed in approximately the same ratios when II itself is heated[8] at 396° and are thus products of the thermal reorganization of 9,10-dihydronaphthalene, not bullvalene.

Although we shall not speculate on the mechanism, the formation of 1,4-dihydronaphthalene cannot be rationalized by any sequence of 1,5-hydrogen shifts and may present a novel mechanistic problem, as indeed may the formation of naphthalene.



I II III

In a second approach to the synthesis of bullvalene, we had conceived a series of thermal reorganizations in which Nenitzescu's hydrocarbon, tricyclo[4.2.2.$0^{2,5}$]-deca-3,7,9-triene (III),[9] might rearrange by way of bicyclo[4.2.2]deca-2,4,7,9-tetraene (IV; by cleavage in III of the cyclobutene ring) and tetracyclo[4.4.0.$0^{3,7}$.-$0^{2,10}$]deca-3,8-diene (V; by intramolecular Diels–Alder reaction in IV) to bullvalene (by homolytic cleavage in V of carbon–carbon bonds 1,2 and 6,7 and formation of carbon–carbon bond 4,7). Although the pyrogenic products at 315° were naphthalene and 1,2-dihydronaphthalene, bullvalene was not formed and the project was abandoned.[10,11]

Reinvestigation in a flow system has given more interesting results. At 301° partial decomposition leads to the formation of 1,2-dihydronaphthalene (ten parts), 9,10-dihydronaphthalene (three parts), and *cis*-1-phenyl-

(1) W. von E. Doering, B. Ferrier, and G. Klumpp, briefly announced in a recent review.[2]
(2) G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem.*, 77, 774 (1965).
(3) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).
(4) W. von E. Doering and G. Klumpp, unpublished results.
(5) E. E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.*, **85**, 3296 (1963).
(6) E. S. Cook and A. J. Hill, *ibid.*, **62**, 1995 (1940).
(7) F. Straus and L. Lemmel, *Ber.*, **54**, 25 (1921).
(8) van Tamelen and Pappas report only naphthalene as the product of heating 9,10-dihydronaphthalene in carbon tetrachloride at 150–200°.[5]
(9) M. Avram, E. Sliam, and C. D. Nenitzescu, *Ann.*, **636**, 184 (1960).
(10) W. von E. Doering and M. Jones, Jr., unpublished results.
(11) In a parallel investigation, Nenitzescu and co-workers[12] heated tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene at 300° for 2 hr and obtained naphthalene (48%), 1,2-dihydronaphthalene (27%), and tetrahydronaphthalene (25%). His hypothetical explanation involves tricyclo-[4.4.0.$0^{2,5}$]deca-3,7,9-triene as an intermediate.
(12) C. D. Nenitzescu, M. Avram, I. I. Pogany, Gh. D. Mateescu, and M. Fărcasiu, *Acad. Rep. Populare Romine Studii Ceretari Chim. (Filiala Bucaresti)*, 11 (1), 7 (1963).