Perhaps the most convincing evidence for the presence of a pentamethylcyclopentadienyl ring in **2a** and its derivatives comes from the mass spectra of **2a** and **4**. The mass spectrum of **4** showed a very strong molecular ion peak (*m/e* 346) and another strong peak at *m/e* 238 ($C_5Me_5Rh^+$). The mass spectrum of **2a** was more difficult to obtain; however, a sample run at 210° gave peaks at *m/e* 237 ($C_5Me_4CH_2Rh^+$, corresponding to loss of HCl from $C_5Me_5RhCl^+$) and 134 ($C_5Me_4CH_2^+$). Peaks at *m/e* 162 ($C_6Me_6^+$) and 147 ($C_6Me_5^+$), both of which are very strong in samples containing hexamethylbenzene, were absent in both spectra.

The parent compounds $[C_5H_5Rh(hal)_2]_x$ have been briefly described by Angelici and Fischer[10] and by Powell and Shaw.[11] The properties of our complexes **2** agree well with those described for $[C_5H_5Rh(hal)_2]_x$.

After completion of this work, our attention was drawn to the recent note by Kasahara, *et al.*,[12] in which they described the conversion of chloro(1,5-cyclooctadiene)rhodium(I) dimer to diiodocyclopentadienylrhodium(III) on treatment with iodine in ether.

While there is an obvious analogy between these reactions we feel that mechanistically they will probably prove quite different since the reaction of Kasahara, *et al.*, was carried out under oxidizing conditions while that described here occurred under reducing conditions.[13] Both reactions, however, testify to the remarkable stability of cyclopentadienylrhodium(III) complexes. Ring-contraction and ring-expansion reactions in organometallic chemistry, while not unknown,[15,16] still remain novel, and none have previously been described which occur so simply and in such high yields as these.

Acknowledgment. We thank the National Research Council of Canada for supporting this work, Johnson, Matthey, and Mallory for the loan of rhodium trichloride, and Dr. W. Schäfer for a gift of Dewar hexamethylbenzene.

[10] R. J. Angelici and E. O. Fischer, *J. Am. Chem. Soc.*, **85**, 3733 (1963).

[11] J. Powell and B. L. Shaw, *Chem. Commun.*, 323 (1966).

[12] A. Kasahara, T. Izumi, and K. Tanaka, *Bull. Chem. Soc. Japan*, **40**, 699 (1967).

[13] The formation of an unstable intermediate, "$RhHCl_2$," by reaction of rhodium trichloride hydrate with hot alcohol has been postulated by a number of authors; *e.g.*,[14] the first step in this reaction (which does not proceed under conditions where "$RhHCl_2$" is not formed) is probably addition of Rh–H to a double bond of Dewar hexamethylbenzene (1). A complex series of rearrangements (which may involve ring-opening and ring-closing steps) must then occur to form the complex 2a with elimination of a "CH_3CH" moiety. Further work to elucidate this mechanism is in progress; however, the "CH_3CH" fragment does not appear as free ethylene.

[14] K. C. Dewhirst, *Inorg. Chem.*, **5**, 319 (1966).

[15] E. O. Fischer and S. Breitschaft, *Chem. Ber.*, **99**, 2213 (1966).

[16] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 3479 (1961).

[17] Fellow of the Alfred P. Sloan Foundation and author to whom inquiries should be addressed.

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Received February 24, 1968

Optically Induced Overhauser Effect in Solution. Nuclear Magnetic Resonance Emission

Sir:

We wish to report the observation of nuclear magnetic resonance (nmr) stimulated emission in the proton nmr spectrum of anthraquinone induced by the optical excitation of this molecule to its lowest lying electronic triplet state. In the experiment, a solution (at 25°) containing 0.005 *M* anthraquinone in perfluorobenzene was irradiated with 3000- to 4000-Å wavelength light using a 3500-W mercury lamp. Under these conditions a steady-state concentration of anthraquinone in the triplet state is obtained.[1,2] Because of the low concentration of the triplet state, only the nmr of the ground state of anthraquinone is observed. Thus the experiment consists of creating a steady-state concentration of triplet-state anthraquinone and looking at the effect on the nmr of the ground state of this molecule.

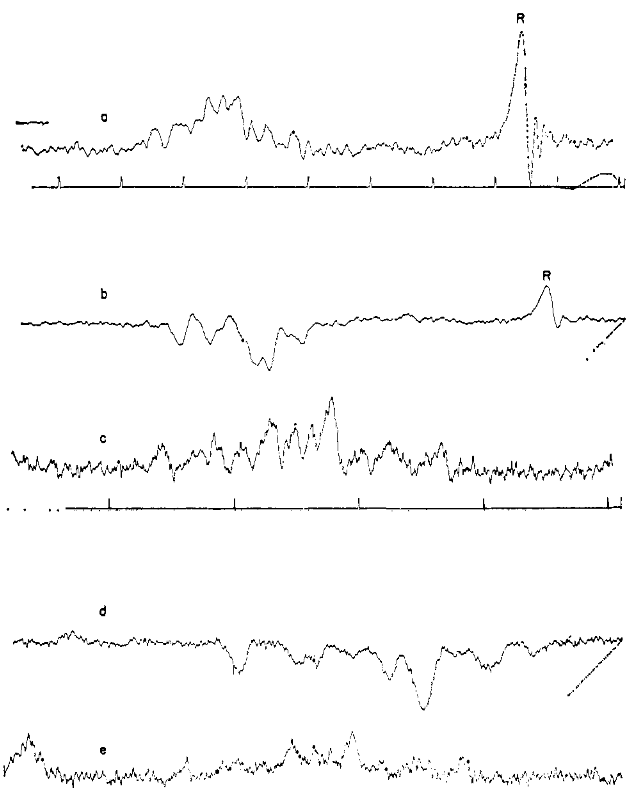

Figure 1. (a) Proton nmr spectrum of 0.005 *M* anthraquinone in perfluorobenzene in the absence of the exciting light. The line labeled "R" is due to benzene which is used as a reference. The other lines which occur at lower field relative to "R" are due to the protons of anthraquinone. This spectrum which is a time-average of 47 passes is not a slow-passage spectrum and the lines are not well resolved. The frequency scale is given below the spectrum. Each marker represents 10.63 Hz. (b) Proton nmr spectrum of the same sample during irradiation. This emission spectrum is a time-average of 12 passes. All other conditions are identical with those used to obtain Figure 1a. The frequency scale for 1b is given in 1a, and the shift of 1b relative to 1a is real. (c) Slow-passage proton nmr spectrum of anthraquinone in the absence of the exciting light. This spectrum is a time-average of 65 passes. The frequency scale is given below the spectrum, and each marker represents 10.63 Hz. This scale also applies to Figures 1d and 1e. (d) Slow-passage proton nmr of anthraquinone during irradiation. This emission spectrum is a time-average of 16 passes. (e) Slow-passage proton nmr of anthraquinone after the sample had been irradiated for 30 min. This spectrum is a time-average of 65 passes.

The nmr emission spectrum which is shown in Figure 1 is the result of an Overhauser effect[3] probably involving

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[1] For anthraquinone, the quantum yield for singlet–triplet crossover is 0.88 in benzene.[2]

[2] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 309.

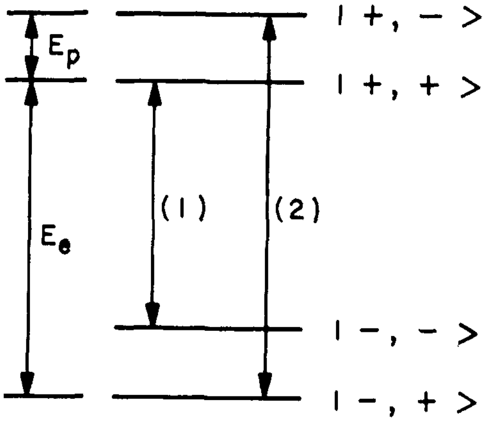

Figure 2. Schematic diagram of a spin system consisting of one proton and one electron in a large magnetic field. Scalar interactions have been neglected. E_p is the energy required for a nuclear spin flip, and E_e is the energy required for an electron spin flip.

the protons and the unpaired electrons of the triplet state. While it seems likely that the triplet-state electrons are involved in the Overhauser effect, the possibility that a free radical is responsible for the observed effect cannot be ruled out completely.[4-6] Before discussing the spectra in Figure 1, it is convenient to present a qualitative description of the Overhauser effect.[7] Consider a system consisting of one electron interacting with one proton. Application of a large magnetic field gives rise to four spin states with relative energies indicated schematically in Figure 2. In this figure the effect of scalar interactions on the energies is neglected, E_p is the energy required for a nuclear spin flip, and E_e is the energy required for an electron spin flip. At thermal equilibrium, the populations for these spin states are given by the Boltzmann distribution.[3] Because of the interaction between the proton and the electron, if the electron spin resonance is saturated (*i.e.*, $N_{-+} = N_{++}$ and $N_{--} = N_{+-}$ where N is the population of the spin state), the nuclear spin populations will change to adjust to this change in the electron spin populations. The large difference between E_e and E_p ($E_e/E_p \approx 660$)[3] makes large changes in the nuclear populations possible. The manner in which the nuclear populations are altered depends upon the nature of the interaction between the electron and the proton. For a direct dipole–dipole interaction, transition 1 in Figure 2 has the highest probability.[3,8] This transition results in an increase in the population of the $|-\rangle$ nuclear spin state, and, if the increase is large enough, nmr emission can occur. A time-dependent scalar interaction results in the predominance of transition 2.[3,9] This transition results in an increase in the population of the $|+\rangle$ nuclear spin state, and enhanced nmr absorption occurs.

With some modification, this qualitative description can be applied to the optical experiment. Instead of one electron and one proton, eight protons and two electrons of triplet anthraquinone are involved.[4] The triplets are formed with the electron spin states having a non-Boltzmann distribution. Relaxation toward a Boltzmann distribution occurs with transitions analogous to transition 1 predominating. This transition increases the population of the $|-\rangle$ nuclear spin state. The nuclear polarization which occurs is retained during the transition of anthraquinone from its triplet state to its ground state. In the ground state, the nuclear spins relax toward a Boltzmann distribution, and stimulated nmr emission occurs. The emission is continuous because triplet-state anthraquinone is being formed continuously.

The occurrence of an Overhauser effect is critically dependent upon the lifetime of the triplet relative to the various electron and nuclear relaxation times in the triplet. If the lifetime of the triplet is short relative to the relaxation time for transition 1 (or transition 2 if it is the dominating transition), no non-Boltzmann nuclear polarization occurs, and no Overhauser effect is observed. If the lifetime of the triplet in long enough to permit the triplet spin system to reach a Boltzmann distribution before returning to the ground state, no Overhauser effect is observed. Thus, the nmr emission of anthraquinone indicates that the lifetime of its triplet lies in between these extremes and that the electron–nuclear interaction in the triplet is predominantly dipolar.

Nmr spectra obtained with and without irradiation of the sample are presented in Figure 1. Figure 1a is the spectrum obtained in the absence of the exciting light. The resonance labeled "R" is due to the protons of benzene which is used as a reference. The other lines are due to the protons of anthraquinone. These lines occur at lower field relative to the benzene line. This spectrum is a time-average of 47 passes[10] since the nmr signals are weak at the concentration employed. In addition, Figure 2a is not a slow-passage spectrum, and the lines due to anthraquinone are not well resolved.

Figure 1b gives the spectrum of the sample during irradiation. This spectrum is a time-average of 12 passes. The lines due to the protons of anthraquinone are inverted, indicating nmr emission. Furthermore, the emission lines are more intense than "R," the benzene line. As mentioned earlier, when the Overhauser effect involves an electron and a proton, an enhancement of the signal (either emission or absorption) is possible.

The high-resolution slow-passage spectra given in Figures 1c, d, and e permit a more detailed examination of the effect on individual lines. Figure 1c is the proton nmr spectrum for anthraquinone before irradiation, and 1d is the spectrum during irradiation. Several points should be made concerning these spectra. First, the emission spectrum is shifted to higher field by about 6 Hz relative to spectrum 1c. In view of the fact that the benzene line in 1b is shifted relative to 1a to the same extent, this shift is probably due to heating of the sample.[11,12] Second, as noted above, the emission

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(3) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961.

(4) This qualification is necessary because (as will be shown later) anthraquinone slowly decomposes, and decomposition *via* a free radical cannot be precluded by the present data. Free-radical formation would affect the spectrum only if the free-radical reconverts to anthraquinone. This conclusion is based on studies of the Overhauser effect involving free radicals produced in chemical reactions.[5,6]

(5) J. Bargon and H Fischer, *Z. Naturforsch.*, 22a, 1551, 1556 (1967).

(6) (a) H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967); (b) R. G. Lawler, *ibid.*, **89**, 5519 (1967).

(7) For a detailed description, see ref 3, p 364.

(8) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

(9) I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956).

(10) The time-averaging was performed using a PDP-8 computer which was interfaced with a modified Varian DP-60 spectrometer by Dr. S. Meiboom and Mr. R. C. Hewitt.

(11) The temperature of the nmr probe was maintained at 25° using nitrogen gas.[12] Apparently, when the sample is irradiated, this gas cannot cool it efficiently.

(12) L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, 47, 1480 (1967).

lines are more intense than the absorption lines; Figure 1c is a time-average of 65 passes whereas Figure 1d required only 16 passes. Third, the lines in the emission spectrum are broader than the lines in the absorption spectrum. This difference in line width cannot be due to a difference in field homogeneity since the line width of the benzene line before irradiation is approximately equal to the line width during irradiation. A triplet-energy-transfer process could be responsible for this broadening.[2,13] Fourth, the nmr emission spectrum is not simply an inversion of the nmr absorption spectrum. Some of the lines in the absorption spectrum are either missing or very weak in the emission spectrum, indicating that all of the protons are not affected equally.

As mentioned earlier,[4] during irradiation anthraquinone slowly decomposes. This can be seen by comparison of Figure 1c with Figure 1e which is the spectrum obtained after the sample had been irradiated for 30 min. Both 1c and 1e were time-averaged over 65 passes. Clearly, the lines in 1c are more intense than the lines in 1e, indicating some of the anthraquinone had decomposed. Whether the mechanism for this decomposition involves a free radical or triplet anthraquinone or both species cannot be decided on the basis of the present data.

In conclusion, the results reported in this communication demonstrate that nmr spectroscopy can be used to study optically excited molecules. Because of the amount of information which can be obtained by means of nmr, this technique is a potentially powerful tool for studying excited molecules.

Acknowledgment. The authors are indebted to Drs. Saul Meiboom and Anthony M. Trozzolo for very informative discussions and helpful suggestions and to Mr. R. C. Hewitt for making the electronic modifications which were necessary in the course of this research.

[13] This possibility is currently being studied using pyrene which exhibits appreciably larger broadening than anthraquinone under these conditions.

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Received April 10, 1968

A Diazotization Leading to the Formation of a Dinitrogen Complex

Sir:

The formation of nitrogen complexes by the decomposition of hydrazine,[1] azide ion,[2] and NH_3,[3] by the capture of N_2 from acyl azides,[4] and by the reaction of elementary N_2 has been described.[5-8] We here report the formation of a nitrogen-containing complex by the reaction of nitrous acid with coordinated ammonia.

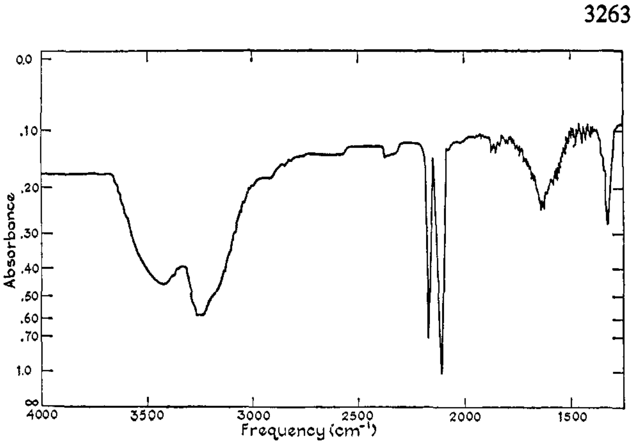

Figure 1. The infrared spectrum of $Os(NH_3)_4(N_2)_2Cl_2$ in the high-frequency range. When the wavelength scale is corrected by calibration, the two bands characteristic of N_2 appear at 2175 and 2120 cm^{-1}.

This reaction is remarkable in its own right, proceeding as it does with great rapidity at room temperature, and is significant also in that it produces the ion $(NH_3)_4Os(N_2)_2^{2+}$, which, to our knowledge, is the first complex containing two coordinated nitrogen molecules for each metal atom to have been characterized.

For the preparation, 1×10^{-3} mole each of $NaNO_2$ and $(NH_3)_5OsN_2Cl_2$, the latter prepared as described by Allen and Stevens,[9,10] was dissolved in 35 ml of water, and the solution was deaerated by using a stream of argon. After *ca.* 30 min, 4 ml of 1 *M* HCl was added slowly, while the reaction solution was stirred vigorously. Up to this point, no reaction was apparent, but when acid was added the solution at once became more deeply yellow and gas was evolved. A sample removed 1 min after the addition of HCl and appropriately diluted showed that the peak characteristic of $(NH_3)_5OsN_2^{2+}$ (208 mμ, log ε 4.4) had disappeared and that a new peak was present at 221 mμ (log ε 4.3). From the spectrophotometric measurements, a yield of *ca.* 34% was determined. Upon the addition of solid alkali halide, an osmium-containing solid is formed. The crude material contains a substantial (*ca.* 25%) admixture of a nitrosyl-containing species. On repeated recrystallization, the intensity of the peak characteristic of the nitrosyl-containing species is greatly diminished, but the characteristic structure (see below) of the nitrogen-containing component is unaltered.

Chloride, bromide, and iodide salts of the refined product were prepared. The infrared spectrum of the chloride salt is shown in Figure 1. It should be noted that the relative intensities of the peaks at 2120 and 2175 cm^{-1} are the same within experimental error for the three preparations, and are, moreover, constant for successive croppings of crystals from a single solution. *Anal.* Calcd for $(NH_3)_4Os(N_2)_2Cl_2$: H, 3.14; N, 29.09; Cl, 18.40. Found: H, 3.22; N, 28.98 Cl, 18.38. Calcd for $(NH_3)_4Os(N_2)_2Br_2$: H, 2.55; N, 23.63; Br, 33.70. Found: H, 2.53; N, 23.43; Br, 33.95. More convincing support of our formulation than the elementary composition, which does not discriminate between ammonia and N≡N, is the gas chro-

[1] A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

[2] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967).

[3] J. Chatt and J. E. Fergusson, *Chem. Commun.*, 126 (1968).

[4] J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966).

[5] A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).

[6] A. Sacco and M. Rossi, *ibid.*, 316 (1967).

[7] A. E. Shilov, A. K. Shilova, and Y. G. Borod'ko, *Kinetika i Kataliz*, 7, 769 (1966).

[8] D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).

[9] A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967).

[10] The preparation of a nitrogen-containing complex of osmium by heating osmium compound with hydrazine has also been reported by Yu. G. Borod'ko, V. S. Burkeev, G. I. Kozub, M. L. Khidekel, and A. E. Shilov, *Zh. Strukt. Khim.*, **8**, 542 (1967).