

Protonation Equilibria in Water at Several Temperatures of Alcohols, Ethers, Acetone, Dimethyl Sulfide, and Dimethyl Sulfoxide

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Abstract: The protonation equilibria of methanol, ethanol, dimethyl ether, diethyl ether, acetone, dimethyl sulfide, and dimethyl sulfoxide have been measured in aqueous sulfuric acid at 25, 40, 60, and 90 °C. The derived thermodynamic parameters are discussed in terms of structural and solvation effects on basicity.

Considerable progress in the understanding of the behavior of weak bases in moderately concentrated acids has been achieved in the last decade.¹⁻³ It is now clear that each base follows its own acidity function³⁻⁵ and, therefore, that the relative basicities vary with the composition of the aqueous acid solution used.⁶⁻⁸ The acid-base behavior of weak bases must hence be described by two parameters: the pK_{BH^+} value, which refers to the state chosen as standard, usually infinite dilution in water, and a second term which extrapolates the basic properties from the standard state to the more concentrated acid solutions. By using the Bunnett-Olsen equation¹ (eq 1, where $I = c_{BH^+}/c_B$ is the ionization ratio) we have identified this term in the ϕ_e slope parameter, which can be evaluated using eq 1.

$$\log I + H_0 = \phi_e(H_0 + \log c_{H^+}) + pK_{BH^+} \quad (1)$$

Equation 1 solves the practical problem of defining the pK_{BH^+} value even for a base whose acidity function is not known.^{2,6} Let us consider the approach to infinite dilution in water: H_0 approaches $-\log [H^+]$, the first term on the right of eq 1 disappears, and the left side becomes $\log (c_{BH^+}/c_{BH^+})$ for the real reaction at infinite dilution in water, or the thermodynamic pK_{BH^+} . The wide range of ϕ_e values so far reported indicates the considerable differentiation existing between acidity scales and raises a number of questions about the interpretation of divergent behaviors in aqueous acids. These differences have frequently been interpreted,^{9,10} following the work of Taft,¹¹ in terms of the number of possible hydrogen bonding sites available and the number of water molecules involved in the equilibrium. However, on the basis of our work on protonation of dimethyl ether ($\phi_e = 0.82$) and dimethyl sulfide⁷ ($\phi_e = -0.27$), whose conjugate acids obviously have only one hydrogen bonding site, we believe^{3,7,8} that the dominant factor in differentiating acidity scales is the interaction energy between onium ions and water. This depends mainly on the degree of charge localization on the cation, and hence on the size and polarizability of the atom which bonds to the proton. An obvious consequence of more localized charge density is a stronger hydrogen bond with the water molecules. Other things being equal, the effectiveness of charge dispersal will increase with the number of hydrogens linked to the protonation site, because of hydrogen bonding to the solvent. The importance and the meaning of the ϕ_e parameter may be better appreciated if the Bunnett-Olsen equation is rewritten in the general form suggested by Hammett:²

$$H_X + \log c_{H^+} = (1 - \phi_e)(H_0 + \log c_{H^+}) \quad (2)$$

According to the definition of acidity function [$H_X = -\log (a_{H^+}f_X/f_{XH^+})$, where X and XH^+ represent the free and protonated base respectively], eq 2 can be rearranged into

$$\begin{aligned} \log f_{H^+} - \log (f_{XH^+}/f_X) \\ = (1 - \phi_e)[\log f_{H^+} - \log (f_{BH^+}/f_B)] \quad (3) \end{aligned}$$

Equation 3 shows that the slope parameter value depends on the free energy of transfer, from dilute aqueous solutions to concentrated acid, of the species involved in the protonation equilibrium. Positive ϕ_e values are obtained when the energy of solvation of XH^+ is greater than that of the protonated Hammett base, BH^+ , taken as reference. We have discussed this point in detail elsewhere.³

Since eq 1-3 are derived from an empirically found relationship,¹ it seems important to check whether the same type of information can be derived in a different way. Recently Arnett has discussed in detail¹² the derivation of the thermodynamic properties of transferring ammonium ions from gas phase to water. We feel that the application of the same method to the protonation of bases other than amines would offer the data necessary to evaluate in more detail the solvation effects on onium ions, as well as the reliability and limits of eq 3. A fundamental prerequisite for such an analysis is the compilation of a reliable set of thermodynamic quantities for the ionization process in water. We have therefore studied the protonation equilibria of several weak bases, representative of some important functional groups, in aqueous sulfuric acid at several temperatures, and derived the corresponding thermodynamic quantities. These data are reported and discussed in the present paper.

Results

We have chosen as representative substrates methanol (**1**), ethanol (**2**), dimethyl ether (**3**), diethyl ether (**4**), acetone (**5**), dimethyl sulfide (**6**), and dimethyl sulfoxide (**7**). Their protonation has been monitored at 25, 40, 60, and 90 °C by using an NMR technique.^{7,8} This involved the measurement, as a function of the acid concentration, of the chemical shift of the protons nearest to the protonation site, taking the trimethylammonium ion as internal standard ($\Delta\nu = \nu - \nu_{ref}$, in hertz at 90 MHz). By plotting $\Delta\nu$ values as a function of the medium acidity good sigmoid curves were obtained from which the ionization ratios were evaluated at each acid concentration as $I = (\Delta\nu - \Delta\nu_B)/(\Delta\nu_{BH^+} - \Delta\nu)$, where $\Delta\nu_B$ and $\Delta\nu_{BH^+}$ were the chemical shifts of the free base and its conjugate acid, respectively.¹³ In those cases where $\Delta\nu_{BH^+}$ values were not experimentally accessible they were computed as described elsewhere^{7,8} (see also Experimental Section). The $\Delta\nu_B$ and $\Delta\nu_{BH^+}$ values for compounds **1-7** at the four temperatures studied are collected in Table I. Methanol and ethanol undergo reaction with sulfuric acid and this prevents the accurate determination of their chemical shifts at high acid concentration, particularly at 90 °C. The data for compounds **1** and **2** at this temperature are therefore not reliable and have been omitted from the tables.

Table I. Chemical Shifts of Unprotonated ($\Delta\nu_B$) and Protonated ($\Delta\nu_{BH^+}$) Bases in Aqueous Sulfuric Acid^a

Compd	25 °C		40 °C		60 °C		90 °C	
	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$
MeOH	41.7	136.4	41.3	137.5	41.2	135.2		
EtOH	67.8	169.1	67.8	166.0	67.8	173.3		
Me ₂ O	39.6	135.5	39.5	139.7	39.4	125.7	39.2	130.7
Et ₂ O	60.7	153.1	59.4	160.0	59.3	149.5	60.3	145.5
Me ₂ CO	59.7	-16.8	59.8	-13.2	60.4	-13.3	61.1	-5.7
Me ₂ S	71.5	7.0	71.7	6.9	71.4	6.9	71.4	6.9
Me ₂ SO	15.4	-22.8	15.8	-22.9	16.5	-23.0	17.8	-22.9

^a Measured as the difference between the chemical shift of the CH₃ or CH₂ protons nearest to the protonation site and that of the trimethylammonium ion taken as reference, in hertz at 90 MHz.

Table II. Acid-Base Equilibria of Several Weak Bases in Aqueous Sulfuric Acid

Compd	<i>T</i>	$pK_{BH^+}^a$	ϕ_e^a	$(H_0)_{1/2}^b$	<i>m</i> ^b
MeOH	25	-2.05 ± 0.02	0.87 ± 0.002	-8.00 ± 0.20	0.19 ± 0.003
	40	-2.01 ± 0.02	0.87 ± 0.002	-7.71 ± 0.27	0.19 ± 0.005
	60	-2.00 ± 0.01	0.86 ± 0.002	-7.21 ± 0.24	0.21 ± 0.005
EtOH	25	-1.94 ± 0.02	0.86 ± 0.002	-7.20 ± 0.24	0.20 ± 0.005
	40	-1.96 ± 0.02	0.84 ± 0.007	-6.79 ± 0.24	0.22 ± 0.005
	60	-1.97 ± 0.02	0.85 ± 0.003	-6.79 ± 0.19	0.22 ± 0.005
Me ₂ O	25	-2.48 ± 0.04	0.82 ± 0.005	-8.48 ± 0.10	0.22 ± 0.004
	40	-2.53 ± 0.05	0.81 ± 0.01	-8.42 ± 0.20	0.23 ± 0.007
	60	-2.51 ± 0.03	0.78 ± 0.003	-7.37 ± 0.13	0.27 ± 0.005
Et ₂ O	25	-2.39 ± 0.03	0.78 ± 0.005	-6.96 ± 0.15	0.27 ± 0.006
	40	-2.39 ± 0.03	0.79 ± 0.005	-7.16 ± 0.16	0.25 ± 0.006
	60	-2.43 ± 0.01	0.74 ± 0.002	-6.13 ± 0.07	0.32 ± 0.003
Me ₂ CO	25	-2.85 ± 0.05	0.75 ± 0.01	-7.86 ± 0.04	0.29 ± 0.01
	40	-2.87 ± 0.06	0.72 ± 0.01	-7.31 ± 0.18	0.32 ± 0.01
	60	-2.92 ± 0.06	0.69 ± 0.01	-6.92 ± 0.15	0.35 ± 0.01
Me ₂ S	25	-2.94 ± 0.08	0.64 ± 0.02	-6.14 ± 0.20	0.40 ± 0.01
	40	-6.99 ± 0.31	-0.27 ± 0.06	-5.71 ± 0.02	1.26 ± 0.05
	60	-6.82 ± 0.46	-0.30 ± 0.07	-5.48 ± 0.03	1.29 ± 0.09
Me ₂ SO	25	-6.44 ± 0.19	-0.29 ± 0.05	-5.23 ± 0.02	1.27 ± 0.04
	40	-6.12 ± 0.13	-0.35 ± 0.04	-4.81 ± 0.02	1.32 ± 0.03
	60	-1.54 ± 0.01	0.58 ± 0.01	-2.69 ± 0.03	0.52 ± 0.01
	40	-1.49 ± 0.03	0.56 ± 0.01	-2.54 ± 0.09	0.53 ± 0.01
	60	-1.39 ± 0.03	0.57 ± 0.01	-2.34 ± 0.11	0.56 ± 0.01
	90	-1.24 ± 0.03	0.55 ± 0.01	-2.02 ± 0.12	0.58 ± 0.02

^a The pK_{BH^+} and ϕ_e values were obtained, with the listed standard deviations, from the least-squares analysis of $\log I + H_0$ vs. $H_0 + \log c_{H^+}$ plots. ^b The H_0 values at half protonation, $(H_0)_{1/2}$, and the slopes, *m*, reported with the standard deviations, were obtained from the least-squares analysis of $\log I$ vs. $-H_0$ plots.

The $\Delta\nu_B$ values are not changed, within experimental error, in going from 25 to 90 °C. This is also true for the $\Delta\nu_{BH^+}$ values of dimethyl sulfide and dimethyl sulfoxide. In the case of the other compounds studied, different $\Delta\nu_{BH^+}$ values are found on changing the temperature. These being computed values, it is impossible to say whether the differences derive from the method of computation or from some real differences in solvent effects on the oxonium ions. However, we have checked on the influence on the protonation parameters of different choices in $\Delta\nu_{BH^+}$ values. For the compounds studied, this is a minor source of the error (see below).

The ionization ratios, evaluated with the aid of the data in Table I and of the experimental $\Delta\nu$ values, were then used to estimate, through eq 1, the pK_{BH^+} and ϕ_e values reported in Table II. In this table we have also collected the H_0 values at half protonation, $(H_0)_{1/2}$, and the slope (*m*) of the plots $\log I$ vs. $-H_0$. The NMR technique used to evaluate the data reported in Tables I and II suffers from two major sources of error: (1) the use of an internal standard, as the Me₃NH⁺ ion; and (2) the need to compute, in some cases, the $\Delta\nu_{BH^+}$ values. To check on these points we have in a few cases computed the pK_{BH^+} and ϕ_e values: (1) by using the differences of chemical

shift between the CH₃ and CH₂ protons in ethanol and diethyl ether¹⁴ (the pK_{BH^+} and ϕ_e values obtained at 60 °C were respectively -1.99 ± 0.04 , $+0.86 \pm 0.004$, and -2.40 ± 0.04 , $+0.73 \pm 0.006$ for the alcohol and the ether); (2) by varying, in the case of dimethyl ether, the computed $\Delta\nu_{BH^+}$ value by as much as 25% (the pK_{BH^+} and ϕ_e values obtained at 90 °C, for $\Delta\nu_{BH^+} = 160$, were -2.60 ± 0.05 , $+0.80 \pm 0.01$). Comparison with the data in Table II shows that only minor variations were found in the protonation parameters, thus ensuring the reliability of the data in Table II. These data were then used to estimate the thermodynamic parameters for the protonation of the weak bases here studied. ΔG_i° values were obtained from the pK_{BH^+} data at 25 °C, whereas ΔH_i° and ΔS_i° values were obtained from the slope and intercept of $\log K_{BH^+}$ vs. $1/T$ plots. The data are collected in Table III.

Discussion

The derivation of the thermodynamic pK_{BH^+} values from the ionization ratios of weak bases measured in moderately concentrated acid solutions requires the assumption of the validity of the Bunnett-Olsen linear free energy relationship¹ all the way from the acid solutions to the infinite dilution in

Table III. Thermodynamic Parameters for the Protonation in Water at 25 °C of Several Weak Bases^a

Compd (B)	ΔG_i° , kcal/mol	ΔH_i° , kcal/mol	ΔS_i° , cal mol ⁻¹ deg ⁻¹
MeOH	-2.80 ± 0.03	-0.64 ± 0.26	7.2 ± 0.8
EtOH	-2.65 ± 0.03	0.39 ± 0.09	10.2 ± 0.3
Me ₂ O	-3.38 ± 0.05	0.58 ± 0.24	13.3 ± 0.7
Et ₂ O	-3.26 ± 0.04	0.73 ± 0.14	13.3 ± 0.4
Me ₂ CO	-3.89 ± 0.07	0.73 ± 0.12	15.5 ± 0.4
Me ₂ S	-9.53 ± 0.42	-6.87 ± 0.51	9.0 ± 1.6
Me ₂ SO	-2.10 ± 0.01	-2.33 ± 0.20	-0.7 ± 0.6

^a Referred to the process $\text{BH}^+ \rightleftharpoons \text{B} + \text{H}^+$. ΔG_i° values were obtained from $\text{p}K_{\text{BH}^+}$ values at 25 °C, referred to infinite dilution in water as standard state (see Table II); ΔH_i° and ΔS_i° values were obtained, with their standard deviations, from the slope and intercept of $\log K_{\text{BH}^+}$ vs. $(1/T)$ plots.

water. This, and the experimental problems usually found in deriving ionization ratios,^{3,5} led Bunnett and Olsen to estimate the uncertainty in the $\text{p}K_{\text{BH}^+}$ values in the order of 0.2 $\text{p}K_{\text{BH}^+}$ units.¹ Although the absolute values reported in this work may suffer the same uncertainty, the fact that all $\text{p}K_{\text{BH}^+}$ s were measured under identical conditions at each temperature makes it probable that the relative values are subject to a smaller error. We therefore regard the standard deviations reported in Table II as representative of the uncertainty in our data and we will discuss as significant any difference in $\text{p}K_{\text{BH}^+}$ values outside those limits. This conclusion is further supported by the finding that either the change from external to internal reference in the evaluation of $\Delta\nu$ values, or a large variation in the computed $\Delta\nu_{\text{BH}^+}$ values, does not modify the $\text{p}K_{\text{BH}^+}$ or ϕ_e values. Errors in $\text{p}K_{\text{BH}^+}$ values are carried into the derived entropies and enthalpies of ionization. From data in Table III it appears that the error in ΔH_i° values is in the range of 0.1–0.5 kcal/mol and that in ΔS_i° in the range 0.2–1.6 cal mol⁻¹ deg⁻¹. We are aware that more precise results would have been desirable, in particular in the cases of alcohols and dimethyl ether, but the values reported represent the limits of the present techniques.

The detailed interpretation of the thermodynamic parameters for the ionization of the compounds reported in Table III is a matter of some difficulty, since there are not enough data to compare each family of bases. Some trend is evident. For instance, in the comparison of alcohols and ethers it is apparent that the substitution of a hydrogen with an alkyl group has "anomalous" effects on basicity, ethanol and methanol being more basic than the corresponding ethers, as measured both by the ΔG_i° and ΔH_i° values. This represents another instance of the problems which arise when alkyl substitution occurs very close to the acid–base center,¹⁵ the best known example being the sequence of acid strength in methylamines: $\text{Me}_3\text{NH}^+ > \text{MeNH}_3^+ > \text{Me}_2\text{NH}_2^+$.¹⁶ As in that case, and as pointed out in a previous paper,⁷ the higher basicity of alcohols compared to that of ethers must be explained in terms of solvation. The smaller ROH_2^+ cation is much more solvated, and hence stabilized, than the R_2OH^+ ion also because the former oxonium ion has more hydrogen bonding sites for the water molecules than the latter.^{3,7} The difference in solvation between R_2SH^+ can also be used to explain the greater basicity of the oxygen vs. the sulfur compound in dilute aqueous solutions.⁷ According to the treatment we have recently developed^{3,7,8} solvation is measured by the Bunnett and Olsen ϕ_e parameter: the values for methanol, dimethyl ether, and dimethyl sulfide are, in fact, 0.87, 0.82, and -0.27 at 25 °C, respectively. The effect of solvation on the ΔG_i° values prevents any separation in terms of internal and environmental contribution to the total thermodynamic functions.¹⁷

Table IV. Temperature Effect on Activity Coefficient Ratios for Several Bases^a

Compd (X)	$\log (f_{\text{XH}^+}/f_{\text{X}}) - \log (f_{\text{BH}^+}/f_{\text{B}})$		
	25 °C	60 °C	90 °C
MeOH	2.96	2.60	
EtOH	2.93	2.57	
Me ₂ O	2.79	2.36	2.13
Et ₂ O	2.66	2.24	1.91
Me ₂ CO	2.55	2.09	1.77
Me ₂ S	-0.92	-0.88	-0.97
Me ₂ SO	1.98	1.72	1.52
Ar ₃ COH ^b	-5.13	-3.71	-2.12

^a Evaluated, unless otherwise indicated, as $-\phi_e(H_0 + \log c_{\text{H}^+})$, see eq 5, for a sulfuric acid solution 9.17 M; ϕ_e values are taken from Table II. ^b Evaluated as $H_{\text{R}} - H_0$; H_{R} data are taken from ref 21.

The most basic compound appears to be dimethyl sulfoxide. This may be due to the presence of a high electron density on the oxygen atom.¹⁸ On the other hand, the entropy of ionization is outside the range 7–15 cal mol⁻¹ deg⁻¹ found for all the other compounds here studied, as well as for nitroanilines.¹⁹ This suggests that the difference in water structure making ability among the base, its conjugate acid, and the hydronium ion is much smaller in the case of dimethyl sulfoxide than in any other compound so far studied. This is probably linked to the ability of Me₂SO to form ordered structures in water.²⁰

Finally, we must consider the temperature effect on the solvation ability of aqueous sulfuric acid solutions. By rearranging eq 2 we obtain eq 4 which may be rewritten in terms of activity coefficients as in eq 5:

$$H_{\text{X}} - H_0 = -\phi_e(H_0 + \log c_{\text{H}^+}) \quad (4)$$

$$\log (f_{\text{XH}^+}/f_{\text{X}}) - \log (f_{\text{BH}^+}/f_{\text{B}}) = -\phi_e(H_0 + \log c_{\text{H}^+}) \quad (5)$$

Equation 5 offers a way to compute, for a given acid solution and for a given base X, the variation in the activity coefficient ratio $f_{\text{XH}^+}/f_{\text{X}}$ with increasing temperature, as referred to the variation experienced by the Hammett base term $f_{\text{BH}^+}/f_{\text{B}}$. We have collected in Table IV the pertinent data for 60% sulfuric acid solution. The data in Table IV show a leveling of the differences in activity coefficient ratios with an increase of temperature. This is not unexpected, since an increase in temperature should decrease the importance of hydrogen bonding as the way used by the solvent to disperse the positive charge. However, as the comparison of data for dimethyl sulfide and triarylcarbinols suggests, the degree of variation with temperature of the activity coefficient ratios is not a simple function of any structural parameter. Very likely, solvation of the free base is also important in some cases, and direct measurements of activity coefficients at various temperatures would be of great interest.

As a final remark, there is not much advantage in working at 90 °C instead of 25 °C as far as the degree of protonation in a given acid solution is concerned. For instance, half protonation is achieved for dimethyl ether in a sulfuric acid solution 86.4% at 25 °C and 87.6% at 90 °C, whereas for dimethyl sulfide the needed acid concentrations are 69.3 and 69.8% at 25 and 90 °C, respectively.

Experimental Section

Compounds 1–7 were purified by distillation. Acid solutions were made by dilution with water of reagent grade concentrated sulfuric acid and titrated with standard sodium hydroxide. The NMR spectra were recorded on a Bruker HFX-10 spectrometer at 90 MHz equipped with a variable temperature unit. The temperature was checked by measuring the chemical shift of 1,2-ethanediol or of methanol and making reference to appropriate calibration equations;²² the accuracy of this measurement is believed to be ±0.3 °C.²² The computation of

$\Delta\nu_{\text{BH}^+}$ values was made on the basis of eq 1 by expressing $\Delta\nu$ as a function of $\Delta\nu_{\text{B}}$, H_0 , $\log c_{\text{H}^+}$, $\Delta\nu_{\text{BH}^+}$, ϕ_e and pK_{BH^+} . The last three terms were varied by 1% increments until the best fit between calculated and experimental $\Delta\nu$ values was found through the least-squares analysis reported by Sillen.²³ The pK_{BH^+} and ϕ_e values were computed as described elsewhere,^{7,8} using the H_0 data obtained by interpolation of literature values at the appropriate temperature.²⁴ The somewhat larger than usual standard deviations found for $\text{Me}_2\text{S } pK_{\text{BH}^+}$ values probably arise from the narrow range of acidity (about 2 H_0 units) in which protonation of this compound is complete.^{7,8}

References and Notes

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Conformational Properties of *cis,cis*-1,4-Cyclooctadiene. Dynamic Nuclear Magnetic Resonance Spectroscopy and Iterative Strain-Energy Calculations

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Abstract: The ^1H and the natural abundance ^{13}C NMR spectra of *cis,cis*-1,4-cyclooctadiene have been measured from -10 to -180 °C. Dynamic NMR spectroscopy and iterative strain-energy calculations indicate that the compound exists in solution as a mixture of twist-boat (flexible) and boat-chair (relatively rigid) conformations having nearly the same energies. The calculated (strain energy) barrier for the interconversion of these two conformers was calculated to be 9.0 kcal/mol, in good agreement with the experimental (free energy) barrier of 8.0 kcal/mol. The present results are discussed in conjunction with previous experimental and theoretical data on 1,4-cyclooctadiene and related compounds.

In view of the success of dynamic NMR spectroscopy and iterative strain-energy calculations for investigating the conformational properties of *cis,cis*-1,3- and *cis,cis*-1,5-cyclooctadienes,^{1,2} we have carried out corresponding investigations of the remaining *cis,cis*-cyclooctadiene, namely the 1,4 isomer,³ and we now report these results. Dunitz and Waser⁴ have pointed out that Dreiding molecular models of the 1,4-diene can exist as a rigid conformation or as a family of flexible conformations. However, the torsional, angle bending, and nonbonded potential energy contributions of real molecules are poorly reproduced by these molecular models, and therefore deductions based on such models may be misleading. Favini et al.⁵ have published strain-energy calculations on 1,4-cyclooctadiene, but these authors used a simple procedure which does not minimize the energy by allowing the conformations to relax to their optimum geometries. Allinger et al.⁶ have published force-field calculations on 1,4-cyclooctadiene but they did not consider the twist-boat conformation, which, as will be shown in this paper, is the lowest energy conformation of this molecule, nor did they consider conformational interconversion paths.

Although there is presently no published experimental data on the structure or conformational properties of 1,4-cyclooctadiene itself, several papers on dibenzo derivatives of this



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compound and its heterocyclic analogues have appeared recently.⁷⁻⁹

Experimental Section

The *cis,cis*-1,4-cyclooctadiene was synthesized from the 1,3 isomer according to the method described by Moon and Ganz.¹⁰ Its ^1H NMR spectrum in CDCl_3 at room temperature exhibits five absorption bands at δ (ppm) 1.39 (7- CH_2), 2.25 (6,8- CH_2), 2.74 (3- CH_2), 5.31 (1,5- CH), and 5.63 (2,4- CH). Irradiation of the band at δ 2.74 (3- CH_2) caused the quintet at δ 1.39 to become a doublet, and the rough quartet at δ 2.25 to become a doublet of triplets, proving the assignment given above for the olefinic protons. The ^{13}C NMR spectrum in CDCl_3 at room temperature shows five bands at δ (ppm) 23.3 (7- $^{13}\text{CH}_2$), 25.0 (6,8- $^{13}\text{CH}_2$), 29.7 (3- $^{13}\text{CH}_2$), 128.6 (1,5- ^{13}CH), and 130.6 (2,4- ^{13}CH). Selective irradiation with low power at each of the proton chemical shifts was carried out. In each case only a single ^{13}C resonance was observed as a sharp line, the other resonances being multiplets, thus giving directly the assignment shown above.

All NMR spectra were measured on a superconducting solenoid NMR spectrometer operating at 59 kG.^{11,12} The proton noise-de-