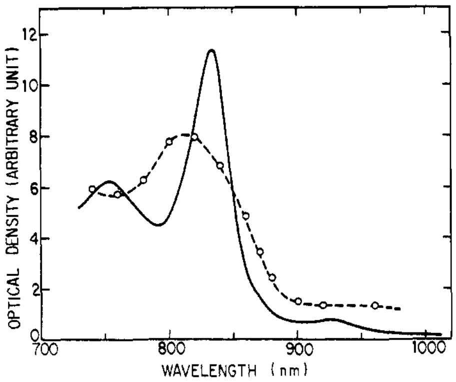

Figure 1. Absorption spectra of Chl a$^+$ formed in the γ-irradiated *sec*-butyl chloride glass at 77°K (—); in the pulse-irradiated benzonitrile solutions at room temperature (- -O).

tion spectrum is concluded to be solely Chl a$^+$ produced by charge transfer from solvent cation *via* biphenyl.[8]

This conclusion is supported by the following experimental results of the charge transfer from Chl a$^+$ to tetramethylbenzidine. When the benzonitrile solution containing Chl a (0.7 m*M*) and benzidine (0.07 m*M*) was pulsed, the absorption due to the Chl a$^+$ was replaced rapidly with the absorption of the benzidine cation which has large peaks at wavelengths above 900 nm[6] and little overlapping with that of Chl a$^+$. Kinetically, both rates of the formation of benzidine cation (determined at 980 nm) and the decay of Chl a$^+$ (determined at 750 nm) were found to be approximately the same. It is extremely difficult to determine the spectrum at 300–450 nm and 600–700 nm because of an intense background absorption of Chl a itself.

The absorption spectrum in the γ-irradiated methyltetrahydrofuran (MTHF) glass containing 7 m*M* Chl a is shown in Figure 2, which is regarded as being due to Chl a anion (Chl a$^-$). In the deaerated MTHF glass, only solute anions are formed since solvent cations are stabilized by rapid ion–molecule reactions with solvent.[6,9] The inset spectrum of Chl a$^-$ was obtained in the irradiated MTHF glass of a much lower concentration of Chl a (0.6 m*M*) after photobleaching the residual absorption band due to the trapped electrons. Although sharp peaks are seen at about 460 and 650 nm (dashed lines), their optical densities are uncertain because of the background absorption of Chl a.

The transient absorption spectrum observed at 20 μsec after pulse for dearated tetrahydrofuran (THF) solutions (Chl a, 0.1–0.2 m*M*) is also shown in Figure 2. The spectrum is assignable to that of Chl a$^-$ on the same basis as for the MTHF glass. When *p*-dinitrobenzene (*p*-DNB) was added to the solution, this absorption was replaced with the absorption of *p*-DNB anion which has a sharp peak at 910 nm.[9] In the THF solution containing Chl a (0.7 m*M*) and *p*-DNB (0.07 m*M*), electron transfer from Chl a$^-$ to *p*-DNB was found to take place. Although the permanent absorption of Chl a in THF solution was reduced after repeated pulse irradiation, it was unchanged in the solution containing *p*-DNB. Since formation of transient Chl a$^-$ was observed in both solutions, it is apparent that Chl a$^-$ is restored completely to the original Chl a by transferring an electron to *p*-DNB. For Chl a$^+$, a similar restoration was confirmed in the presence of benzidine.

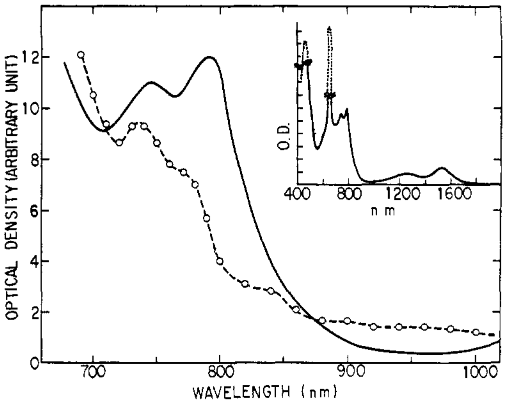

Figure 2. Absorption spectra of Chl a$^-$ formed in the γ-irradiated MTHF glass at 77°K (——) (optical densities of sharp peaks at about 460 nm and 650 nm in the inset (- - - - -) are uncertain); in the pulse-irradiated THF solutions at room temperature (- -O).

Assuming that the radiation chemical yield of the trapped electron in MTHF glass is $G = 2.55$ and all the electrons are scavenged with solutes in the glass,[9] one can calculate the molar extinction coefficient (ϵ) of Chl a$^-$ at 790 nm to be 1.1×10^4 M^{-1} cm^{-1} at 77°K. The $\epsilon_{835\text{ nm}}$ of Chl a$^+$ is roughly estimated to be 7×10^3 M^{-1} cm^{-1} at 77°K. It is noted that the half-lives of these transient ions (about 500 μsec, at room temperature) are much longer than those of radical ions arising from a majority of aromatic hydrocarbons ($\lesssim 20$ μsec[10]). Rapid electron transfer from Chl a$^-$ to vitamin K$_3$, phenazine methosulfate, or flavine mononucleotide was observed by pulse radiolysis for methanol solution. The rate constant is approximately 1×10^9 M^{-1} sec^{-1} for vitamin K$_3$ at room temperature.

The absorption spectra of Chl a$^+$ obtained here are very similar to those prepared by other methods[3,4] at wavelengths above 700 nm. It should be also noted that P-700[11] gives a weak absorption around 800 nm by light irradiation,[12,13] which might be ascribed to Chl a$^+$ or Chl a$^-$. Both Chl a$^+$ and Chl a$^-$ formed in the irradiated glasses show singlet esr spectra with line widths of about 10 G.

Acknowledgment. We thank Drs. K. Shibata, Y. Inoue, and T. Ogawa for their helpful suggestions.

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H. Seki,* S. Arai, T. Shida, M. Imamura
The Institute of Physical and Chemical Research
Wako-Shi, Saitama, 351, Japan
Received February 1, 1973

Effects of Base Strength and Size upon Orientation in Base-Promoted Elimination Reactions

Sir:

The relative importance of base strength and size in determining orientation for olefin-forming elimination reactions has been a subject of controversy for nearly 2

Table I. Relative Olefinic Proportions from Reactions[a] of 2-Iodobutane with Oxyanion Bases in Dimethyl Sulfoxide at 50.0°

System	Base	pK_a of conjugate acid in DMSO	% 1-butene in total butenes	*trans*-2-Butene: *cis*-2-butene
1	Potassium *p*-nitrobenzoate	8.9[b]	5.8 ± 0.1[c]	3.51
2	Potassium benzoate	11.0[b]	7.2 ± 0.2	3.24
3	Potassium *p*-nitrophenoxide	11.0[d]	7.5 ± 0.1	3.58
4	Potassium *o*-nitrophenoxide	11.0[d]	7.5 ± 0.2	3.82
5	Potassium acetate	11.6[b]	7.4 ± 0.1	3.47
6	Potassium *p*-aminobenzoate	12.7[b]	8.0 ± 0.2	3.42
7	Potassium 2,6-di-*tert*-butylphenoxide	15.0[e]	19.2 ± 0.4	3.70
8	Potassium phenoxide	16.4[c]	11.4 ± 0.2	3.34
9	Sodium 2,2,2-trifluoroethoxide	21.6[e]	14.3 ± 0.2	3.32
10	Sodium methoxide	27.0[b]	17.0 ± 0.5	3.14
11	Sodium ethoxide	27.4[b]	17.1 ± 0.4	3.31
12	Sodium *n*-propoxide	28.0[b]	18.5 ± 0.3	3.34
13	Potassium *tert*-butoxide	29.2[b]	20.7 ± 0.4	3.00

[a] [2-BuI] = 0.4 *M*, [base] = 0.5 *M* or saturated solution. [b] C. D. Ritchie in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 230. [c] Standard deviation from repetitive analysis of trapped butene mixture. [d] I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhownik, *J. Amer. Chem. Soc.*, **90**, 23 (1968). [e] Estimated from its heat of deprotonation, ΔH_D, in dimethyl sulfoxide and correlations between ΔH_D and pK_a values in dimethyl sulfoxide. See E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolf, and R. P. Quirk, *J. Amer. Chem. Soc.*, **95**, 1492 (1973). We thank Professor Arnett for providing us with a preprint of this paper.

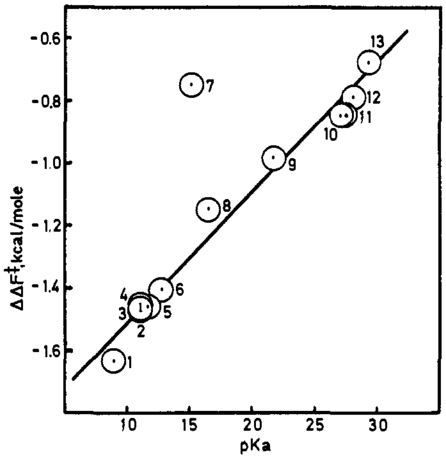

Figure 1. Plot of the free-energy difference for formation of 1-butene and *trans*-2-butene *vs.* the pK_a of the conjugate acid of the base. System numbers refer to Table I.

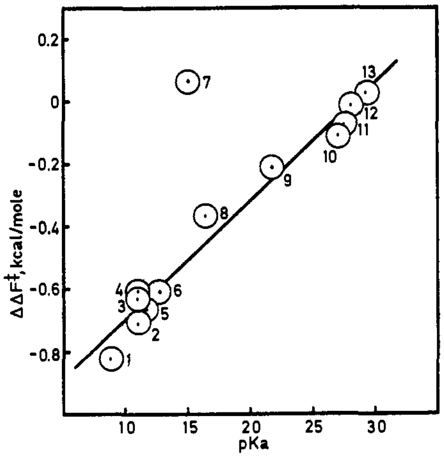

Figure 2. Plot of the free-energy difference for formation of 1-butene and *cis*-2-butene *vs.* the pK_a of the conjugate acid of the base. System numbers refer to Table I.

decades.[1] We now report conclusive evidence of fundamental orientation control by base strength. In addition, the degree of base complexity which is necessary for the onset of base steric effects is demonstrated.

The relative proportions of isomeric butenes which result from reactions of 2-iodobutane with a series of phenoxide, carboxylate, and alkoxide ion bases in dimethyl sulfoxide are recorded in Table I. A nitrogen gas sweep procedure[5] with a 10- or 15-min reaction period was employed to prevent isomerization of the olefinic products. Solvolysis of 2-iodobutane under these conditions produced negligible amounts of butenes when compared to the base-induced reactions.

Dimethyl sulfoxide was chosen as the reaction solvent in order to suppress the complicating effect of base association upon orientation.[6] Also, basicities of a variety of oxyanions in dimethyl sulfoxide are known.

The *trans*-:*cis*-2-butene ratios in Table I are high and essentially constant in the range 3.0–3.8. These results indicate that once base association effects[6] are taken into account, geometrical orientation is insensitive to variation of the base.

Positional orientation is, however, influenced by the identity of base with the relative proportion of the thermodynamically least stable butene being enhanced by base strength increases. Plots of free-energy differences between transition states for formation of terminal and internal olefins, $\Delta\Delta F^{\ddagger}$(1-butene–*trans*-2-butene) and $\Delta\Delta F^{\ddagger}$(1-butene–*cis*-2-butene) *vs.* pK_a values for the conjugate acids of the bases are shown in Figures 1 and 2. Satisfactorily linear relationships extend over a 20-pK unit variation in base strength for 12 of the 13 bases. Significant divergence from the linear free-energy relationships is observed only for potassium 2,6-di-*tert*-butylphenoxide (system 7). For this sterically very hindered base, the proportion of 1-butene is much greater than would be anticipated from its base strength. Such an increase in the amount of terminal olefin is anticipated if steric interactions of a bulky base with α- and β-alkyl groups destabilize the internal olefin-forming transition states.[3]

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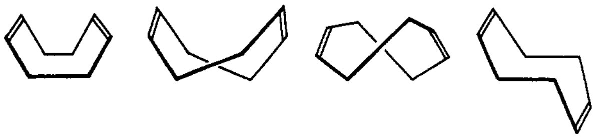
The linear free-energy relationships in Figures 1 and 2 clearly demonstrate a fundamental control of positional orientation by the strength of oxyanion bases. However, for certain outsized bases, such as 2,6-di-*tert*-butylphenoxide (system 7), but not *tert*-butoxide (system 13), steric effects become important in determining positional orientation.

Richard A. Bartsch,* Gerald M. Pruss
Bruce A. Bushaw, Karl E. Wiegers
Department of Chemistry, Washington State University
Pullman, Washington 99163
Received February 27, 1973

Determination of Conformational Barriers in 1,5-Cyclooctadiene by Proton and ^{13}C Nuclear Magnetic Resonance

Sir:

There has been much interest in the conformation of *cis,cis*-1,5-cyclooctadiene (I) and its derivatives, but certain aspects, including the flexibility of this ring system, have remained unclear. The dipole moment of 1,6-dichloro-1,5-cyclooctadiene is consistent with a predominant boat form.[1] An electron diffraction study of I in the gas phase has shown the presence of a twist-boat form (I-*TB*) with possible minor amounts of the chair form (I-*C*).[2] Two recent X-ray studies of derivatives of I have revealed twist-boat conformations,[3] in contrast to dibenzo-1,5-cyclooctadiene which is centrosymmetrical in the crystalline phase and hence must be a chair.[4] Several strain-energy calculations on I have been carried out,[1,5] and the nature of the flexibility of the boat (I-*B*), twist-boat, and skew forms (I-*S*), in contrast to the rigidity of the chair form, has been discussed from a restricted geometric point of view.[6] The 60-MHz ^{1}H nmr spectrum of I has been found to be temperature independent down to −150°, indicating either very low conformational barriers, or possibly very small chemical-shift differences between nonequivalent methylene protons.[7]



I-*B* boat I-*TB* twist boat I-*S* skew I-*C* chair

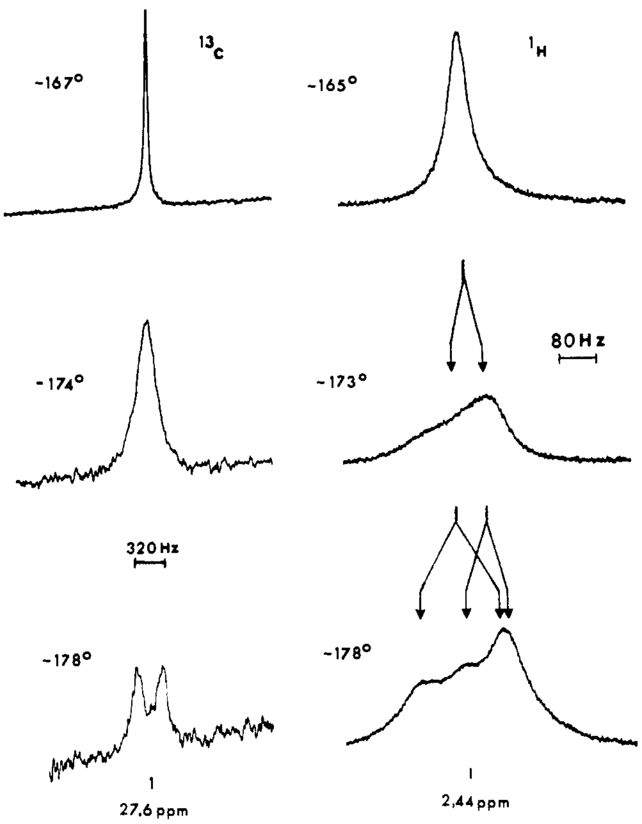


Figure 1. Variable temperature nmr spectra of the methylene groups of *cis,cis*-1,5-cyclooctadiene (*ca.* 3% solution in a 2:3 mixture of $CHCl_2F$ and $CHClF_2$). The ^{13}C spectra (protons decoupled) represent Fourier transforms of free induction decays accumulated after 250 pulses. The ^{1}H spectra were obtained in the frequency sweep mode in single scans. The frequency scale is in ppm downfield from tetramethylsilane nuclei in both cases.

We have now reinvestigated the nmr spectra of I, using temperatures lower than −150°, with both ^{1}H and ^{13}C nmr at a magnetic field of 59 kG.[8] Figure 1 shows that the methylene carbon resonance in the 63.1-MHz cmr spectra of I changes from a single line at high temperatures to a 1:1 doublet below −176°. The olefinic carbon resonance of I broadens at low temperatures, but is not resolved into a doublet, presumably because the chemical-shift difference is too small. The cmr results are consistent with a twist boat of C_2 symmetry, which undergoes a spectral process, labeled A, with a $\Delta G^{\ddagger}$ at −176° of 4.2 ± 0.2 kcal/mol.[9]

Figure 1 also shows 251-MHz pmr spectra of the methylene protons of I at various temperatures. The methylene band, which is relatively sharp at high temperatures, is already quite broad at −165°, and below −168°, it splits into an approximately equal intensity doublet, with the low-field component much broader than the high-field component. At still lower temperatures (*ca.* −175°), each of these resonances splits into two, with the low-field component giving rise to the larger splitting, as shown diagrammatically in Figure 1. The above splittings are of the order of 100 Hz and must result from chemical-shift differences.[10] The

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(8) The spectra were obtained on a superconducting solenoid nmr spectrometer.

(9) The uncertainties in $\Delta G^{\ddagger}$ arise entirely from difficulties in obtaining accurate temperatures in ^{13}C spectra obtained with proton decoupling.

(10) The lowest field proton line at −178° probably originates from the two most inside protons in I-*TB*.