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THE NUCLEAR MAGNETIC RESONANCE STUDY OF EXCHANGING SYSTEMS. III[1]. COPE REARRANGEMENT OF CYCLOOCTATETRAENE DIMER BY ^{13}C NMR TOTAL LINE SHAPE ANALYSIS

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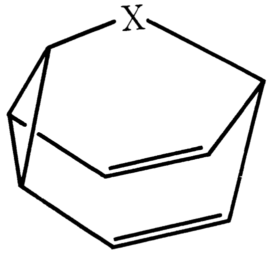
^{13}C NMR spectra of cyclooctatetraene dimer (III) were measured at various temperatures. The complete line shape analysis of temperature dependent spectra was made using the modified Bloch equation method. The activation parameters of the degenerate Cope rearrangement were obtained and were compared with the results obtained by the conventional coalescence temperature method.

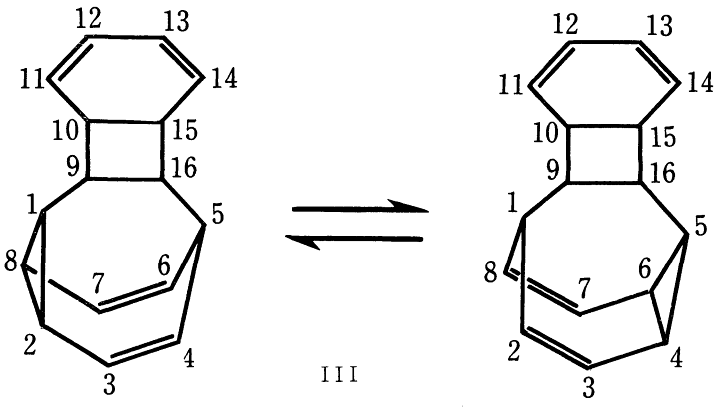
It is well known[2-5] that 3,4-homotropylidene (I) and its bridged derivatives (e.g. II) make a degenerate Cope rearrangement in a thermal process. The kinetics of this process have been investigated mainly by proton magnetic resonance techniques. In general, the compounds which make the rearrangement have a number of hydrogen atoms, and their proton NMR spectra show very complicated patterns because of a variety of spin-spin couplings between the protons included therein. Therefore it is very difficult to analyse the complicated proton spectra of these compounds to extract the kinetic parameters of this process.

Since the proton decoupled ^{13}C magnetic resonance spectra of these compounds show simplified line shapes without complexity due to the spin-spin couplings, it is now possible to make a complete line shape analysis of the spectra using the modified Bloch equation method, even if the number of the exchanging sites is very large[6].



I. X: none
II. X: CH=CH

In this paper, we present the complete line shape analysis of the temperature dependent ^{13}C NMR spectra



III

of a cyclooctatetraene dimer A (III, DACOT) to give the accurate activation parameters of the Cope rearrangement.

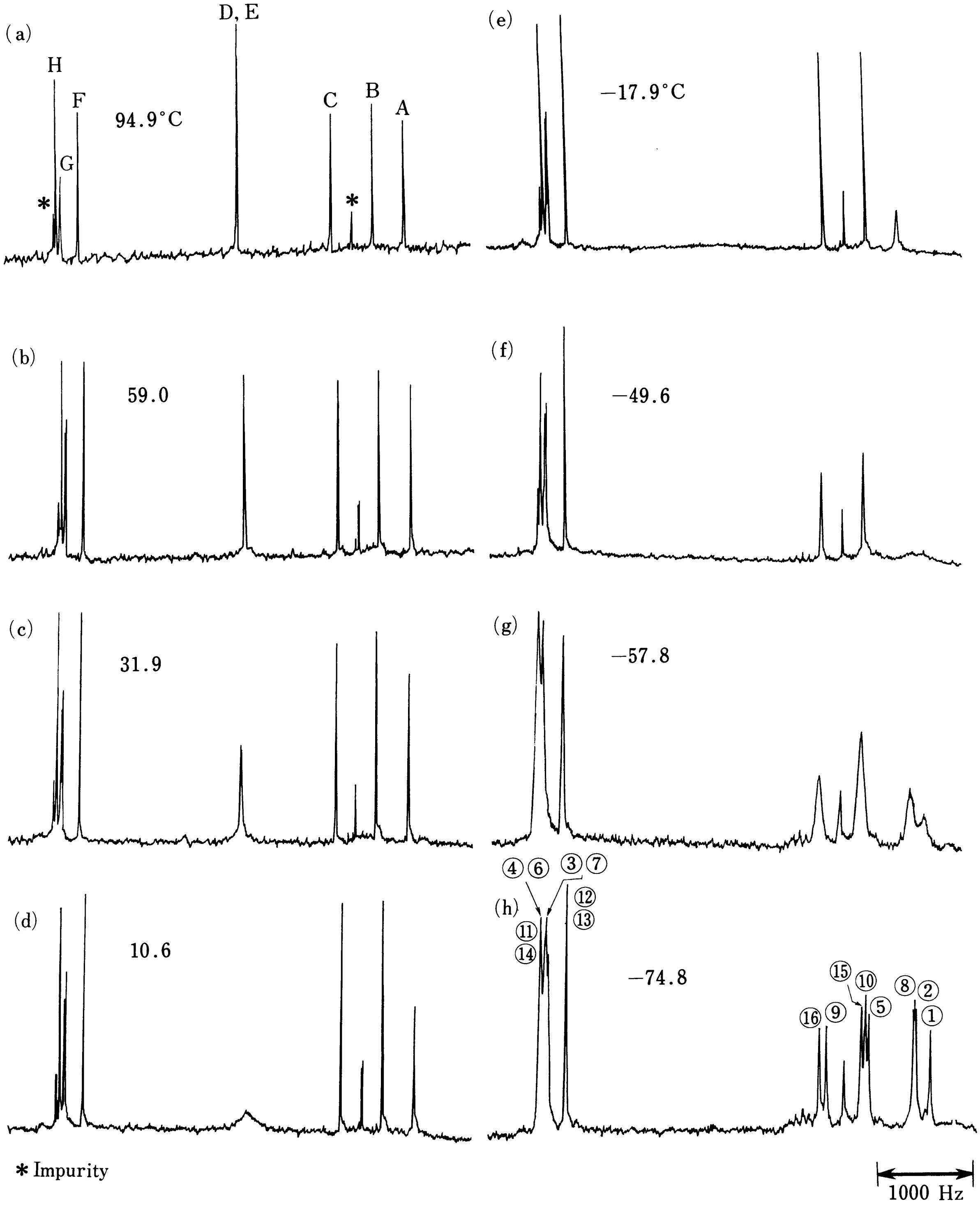
Compound III was prepared by heating freshly distilled cyclooctatetraene at 100°C for 150 hours in a degassed and sealed tube. The crude product was purified by the recrystalization from ether three times. (m.p. 76°C).

^{13}C NMR spectra were measured using a NEVA NV-14 spectrometer with a Varian NV-124 computer system (16K). The solvent was CS_2-CD_2Cl_2, the latter of which provides a deuterium-lock signal. The concentration of the sample was ca. 5 w %. The temperature was determined by a calibrated copper-constantan thermocouple. The complete line shape analysis was made using an EXNMRO computer program$^{6)}$ using the modified Bloch equation method.

Total ^{13}C NMR spectra of DACOT at several temperatures are shown in Fig.I. The rate of the Cope rearrangement of this compound is low enough at about -75°C on the NMR time scale, while at 100°C the exchange is very rapid. The Cope rearrangement of this compound consists of seven exchange processes between two sites as shown above. The exchanging pairs of carbon atoms in this process are C_1-C_5, C_2-C_4, C_6-C_8, C_9-C_{16}, C_{10}-C_{15}, C_{11}-C_{14}, and C_{12}-C_{13}. C_3 and C_7 do not exchange in this process.

The notations of the signals are shown in the spectrum at 94.9°C in Fig.I (a). The intensity of the singlet peak designated as D and E is about twice as strong as the others (A-C,H, and F) at the high temperature (Fig.I(a)), where the rate of exchange is very rapid. Thus, this peak should be assigned to C_2, C_4, C_6, and C_8. This indicates that the average chemical shift of C_2 and C_4 is accidentally coincident with that of C_6 and C_8. The intensities of the two peaks of the signal G

Fig.I. ^{13}C NMR spectra of DACOT at several temperatures.



remain unchanged at all temperatures and are about a half of other peaks (A-C,F, and H). The peak F behaves similarly to the peak G, and its peak height is the same as those of A,B, and C. From these facts, the signal G is assigned to C_3 and C_7 and F is assigned to C_{12} and C_{13}, because the chemical shifts of C_{12} and C_{13} are expected to be approximately the same and the peak F is little influenced by the exchange process due to the long distance from the reaction sites. As the temperature is lowered, the line widths of the peaks A,B,C,D, and E begin to broaden successively, the order of which is D•E > A > C > B > H. The peak H broadens a little. It is well known that the chemical shift of a double bond carbon is at a lower field than that of a four-membered ring carbon, which is in turn at a lower field than that of a three-membered ring carbon. Taking into account the chemical shift tendency, the order of the line broadening of the peaks, and the distances from the exchange sites, all peaks A,B,C,D, and E are reasonably assigned as in Fig.I (h) and Table I.*

Table I. Chemical shifts and chemical shift differences of compound III. (at -74.8°C)

Peak	Carbon	δ	$\Delta\delta$
A	1	21.12	17.42
	5	38.54	
B	10	39.36	1.02
	15	40.38	
C	9	50.17	1.89
	16	52.06	
D	2	25.23	105.29
	4	130.52	
E	6	130.02	104.30
	8	25.72	
F	12,13	123.65	
G	3	128.84	
	7	129.36	
H	11, 14	130.61	

(ppm from TMS)

The outstandingly temperature-dependent peaks are four peaks A,B,C, and D•E. All these peaks consist of a pair of carbons which undergo two site exchange. The chemical shift of each carbon and the chemical shift differences between the pairs of the carbons at a conformationally freezing temperature (-74.8°C) are given in Table I. Using these chemical shift differences, the temperature dependent ^{13}C NMR line shapes were analysed for the four signals of A,B,C, and D•E independently.

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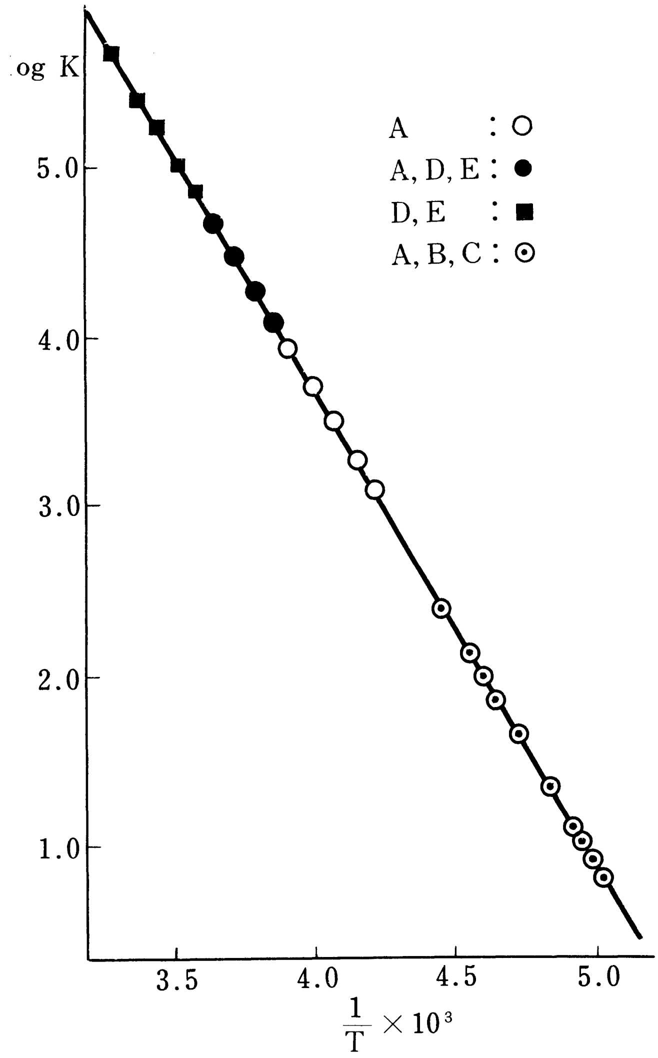
* At the present time, we cannot know which chemical shift between C_2 and C_8 is at a higher field, so we made such an assignment as Table I tentatively. Similar assignments were made to a pair of C_3 and C_7 and to C_4 and C_6.

Fig.II. The Arrhenius plot of log K against 1/T.



The lifetimes of the Cope rearrangement were determined by the visual fitting of the calculated spectra to the observed ones at each temperature. The lifetimes independently obtained in different regions of a spectrum at the same temperature are in good agreement. The Arrhenius plot of the rate constant is shown in Fig.II The relationship between log K and 1/T can be expressed as an almost perfect straight line throughout the whole region of the Cope rearrangement rates. From the Arrhenius plots, the activation parameters of Cope rearrangement of this compound are determined, and these are shown in Table II. The activation parameters obtained independently from the four regions are in close agreement with each other.

Since this process is revealed as a superposition of two site exchanging systems in the ^{13}C NMR spectrum , the free energy of activation ($\Delta G^{\ddagger}_{Tc}$) may be obtained by the coalescence temperature of each exchanging pair. The coalescence temperatures of the signals B and C are determined to be -61.1°C and -59.2°C respectively. However, the coalescence temperatures of the signals A and D•E are not able to determined exactly, because the chemical shift differences of the paired carbons are very large for these signals (Table I), so that the plateau-like line shape at T_c is obscured in the noise. $\Delta G^{\ddagger}_{Tc}$ of B and C parts are shown in Table II. The two $\Delta G^{\ddagger}_{Tc}$ are in good agreement with each other, which are also in excellent agreement with the

Table II. The activation parameters of Cope rearrangement of DACOT.

Part	A	B	C	D,E	Total
Ea(Kcal/mole)	12.8±0.1	12.3±0.6	12.6±0.6	12.3±0.3	12.7±0.2
$\Delta H^{\ddagger}$(Kcal/mole)	12.4±0.1	11.9±0.6	12.2±0.6	11.9±0.3	12.3±0.2
$\Delta S^{\ddagger}$(e.u.)	8.3±0.6	5.9±2.7	7.6±2.8	6.6±1.0	8.2±0.9
$\Delta G^{\ddagger}$(Kcal/mole)	10.6±0.3	10.6±1.0	10.6±1.0	10.5±0.6	10.6±0.4
$\Delta G^{\ddagger}_{Tc}$(Kcal/mole)		10.7	10.6		
at T°C	-60.0	-61.1	-59.2	-60.0	-60.0

values obtained from the complete line shape analysis. Thus, the coalescence temperature method is adequate when the chemical shift difference is not so large. If it is large, however, as is the case of the peaks A and D•E of the compound III, the coalescence temperature method cannot be used and the complete line shape analysis must be adopted.

It is very interesting from the view point of structural chemistry that the activation energy of cyclooctatetraene dimer A (III) (12.7 Kcal/mole) is very near to that of bullvalene (II) (12.8 Kcal/mole) which was obtained by Allerhand et al. from the spin-echo NMR study.⁷⁾

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