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Proton and Carbon-13 NMR Study of Dimer Dianions Produced from 1,1-Diphenylethylene Derivatives

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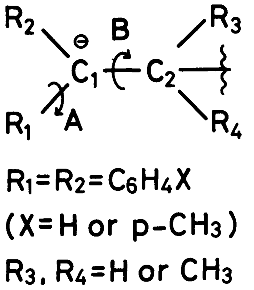
^{1}H and ^{13}C NMR spectra have been observed for the carbanions produced from 1,1-diphenylethylene derivatives. Among five precursors, three have been reduced to corresponding dimer dianions in contact with alkali metal in THF; however, the rest could not be dimerized. Failure in dimerization is controlled by a steric effect of substituents at the 2-position. DNMR measurements were also carried out for 1,1-di-*p*-tolylpropene dimer dianions. The results are discussed in terms of two internal rotations around the bonds between the C_1 and C_2, and the C_1 and C_i atoms.

Many NMR studies have been carried out in order to obtain structural information concerning benzyl-type carbanions which are important in synthetic chemistry. Throughout these studies, NMR parameters have been shown to vary with carbanion structures, cations, solvents and temperatures.[1)]

The dimerization of the radical anions produced from styrene, α-methylstyrene, or 1,1-diphenylethylene has been studied by ESR with dynamic stopped-flow techniques.[2)] The NMR parameters of these dimeric anions have also been partly reported.[3)] The NMR method is especially effective for structural studies of these carbanions since they are unstable when in contact with air or moisture. However, there have not yet been any systematic NMR studies concerning the formations and structures of these dimeric carbanions. This study was aimed at obtaining the NMR parameters of three dimeric carbanions produced from the 1,1-diphenylethylene derivatives. In the measurements of the two dianions at lower temperatures, two phenyl rings were not equivalent because of a hindered rotation around the bond between the C_1 and C_2 atoms. This situation is shown in Scheme 1, where the two restricted internal rotations are differentiated as A and B. Several articles have been written concerning rotations, such as A,[4—11)] but not on those, such as B, in carbanions.



Scheme 1.

Experimental

Five starting materials, 1,1-di-*p*-tolylpropene (**1a**), 1,1-diphenylpropene (**2a**), 1,1-di-*p*-tolylethylene (**3a**), 1,1-dimethyl-2,2-di-*p*-tolylethylene (**5a**), and 1,1-dimethyl-2,2-diphenylethylene (**6a**), were prepared using a conventional method involving reactions of Grignard reagents produced from the corresponding alkyl bromides or iodides with substituted benzophenones. The solvents used for the preparation, THF, THF-d_8, and DME, were refluxed upon sodium metal, distilled, degassed, and finally kept on a sodium–potassium alloy.

An example of the preparation of the carbanions is as follows: 0.95 g of 1,1-diphenylpropene (**2a**) was melted, degassed in vacuum, and dissolved in 10 ml of dried THF. The solution was in contact with a sodium–potassium alloy in vacuum at room temperature. Immediately after contact, the solution became colored dark red. After standing for 24 h, the colored solution was filtered and sealed in an NMR tube and in a stocking glass container with a breakable seal. The concentration of the carbanion solution was about 0.5 or 1 M (1 M=1 mol dm^{-3}).

In order to obtain a chemical evidence, the potassium salt of 1,1-diphenylpropene dimer dianion (**2**) in THF was quenched by water. The quenched product was shown to have a structure consistent with 2,3-dimethyl-1,1,4,4-tetraphenylbutane, based on its ^{1}H NMR parameters ($\delta(CH_3)$= 0.92, δ(2-CH)=2.64, δ(1-CH)=3.91, and $\delta(C_6H_5)$=7.2—7.5 in THF-d_8).

The NMR spectra were measured with a Hitachi R-20B or with a Varian XL-200 FT NMR spectrometer. Variable-temperature spectra were measured in the range from 60 to −110 °C. The ^{1}H and ^{13}C NMR chemical shifts were evaluated from the solvent peak used as an internal reference and then converted to δ_H and δ_C values from TMS, by taking δ_H 1.79 and δ_C 26.4 for THF, δ_H 3.28 and δ_C 58.8 for DME, and δ_H 2.58 and δ_C 37.0 for HMPA.

Results and Discussion

Formation of Dimer Dianions. Typical NMR spectra of the carbanions obtained in this study are given in Figs. 1, 2, and 3, together with spectra of the neutral precursors. From these spectra, each carbanionic sample solution was found to consist of mainly a single species. When the precursors of **1a**, **2a**, and **3a** reacted with alkali metal in THF solutions they produced their dimer dianions, **1**, **2**, and **3**, which were ascertained by their NMR spectra. The same was true

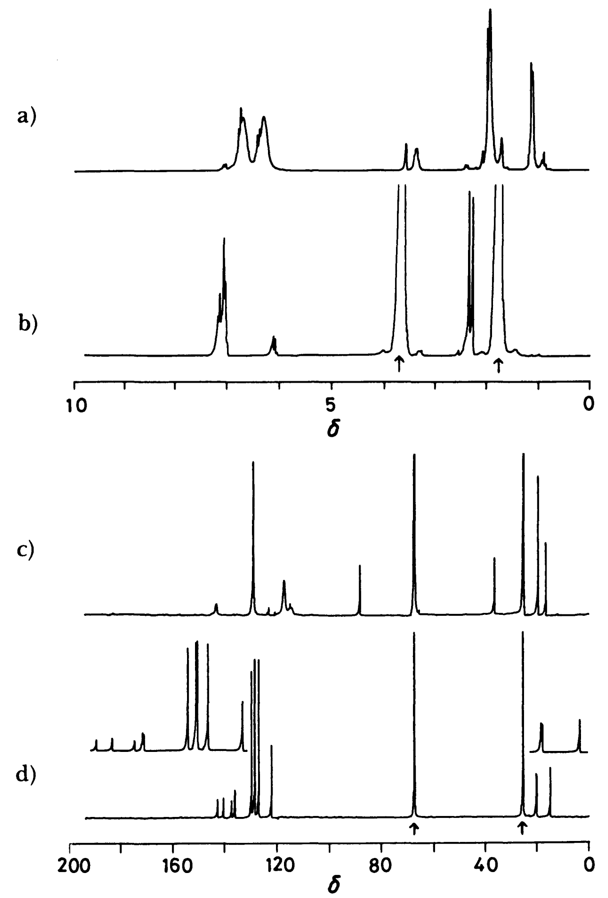


Fig. 1. ^1H and ^{13}C NMR spectra of **1** and **1a**. (a) ^1H spectrum of **1** in THF-d_8, (b) ^1H spectrum of **1a** in THF at 200 MHz and 25 °C, (c) ^{13}C spectrum of **1** in THF, and (d) ^{13}C spectrum of **1a** in THF at 50.3 MHz and 25 °C. The signals of the solvent were denoted by arrows.

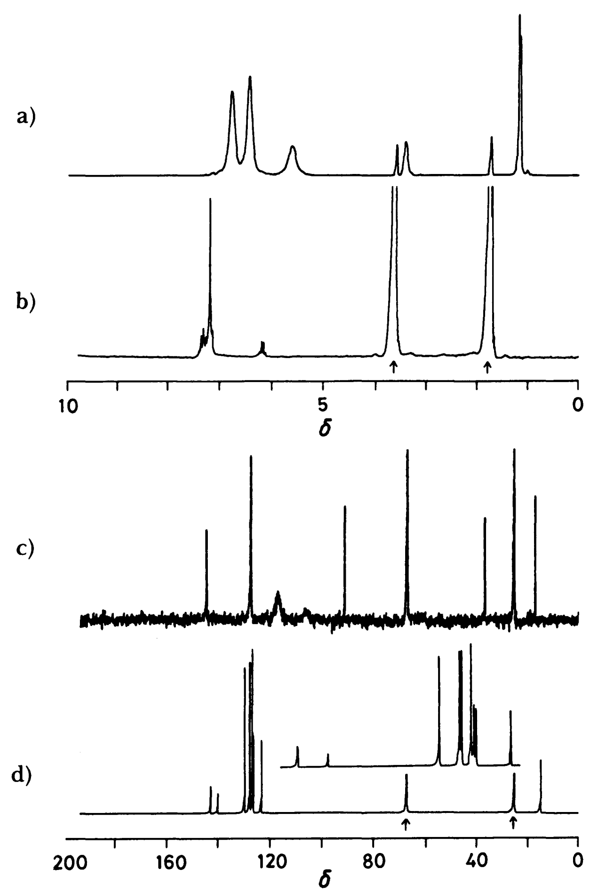


Fig. 2. ^1H and ^{13}C NMR spectra of **2** and **2a**. (a) ^1H spectrum of **2** in THF-d_8, (b) ^1H spectrum of **2a** in THF at 200 MHz and 25 °C, (c) ^{13}C spectrum of **2** in THF, and (d) ^{13}C spectrum of **2a** in THF at 50.3 MHz and 25 °C.

of 1,1-diphenylethylene (**4a**); we have already reported on its dimer dianion **4**.[3] The situation, however, was different for **5a** or **6a** in which the NMR spectrum of a solution treated similarly with metal was complex and its quenched product was multiplex. In every case, an anionic radical species is produced immediately after a precursor is dissolved in THF and comes into contact with metal. The reactant solution changes in color from colorless to dark red. When a C_2 atom of a precursor is substituted by a group, such as a phenyl ring, the radical anion is easily reduced further and becomes a monomeric dianion, as does tetraphenylethylene.[12]

When a substituent at C_2 is a hydrogen or a methyl group, which is not an effective electron-delocalizable group, two-electron reduction does not occur; instead, dimerization occurs between the anion radicals. The latter case has occurred in reactions of **1a**, **2a**, **3a**, and **4a**. In the cases of **5a** and **6a** such dimerization has not occurred. The reason seems to be due to their steric circumstances around the C_2 atoms. The dimerization of the radical anions is known to be an essentially reversible process which can be controlled thermodynamically.[2] The ^1H NMR spectra of the dianions observed in this study show that the anions are stable at room temperature and that their line widths are narrow. In this respect the equilibrium between the dimer dianion and the radical anion is largely shifted to the former.

Further, both the dianions **1** and **2** have two asymmetric carbons in a molecule. Therefore, it is a problem whether they are in either racemic or meso form. In the NMR spectra of several 2,3-disubstituted butanes, the two forms are differentiated in their chemical shifts. For example, the differences in ^{13}C chemical shifts between the two forms of 2,3-dichlorobutanes are reported to be 1.09 and 1.99 ppm for the C_1 and C_2 in the backbone butane skeleton.[13] As shown in Table 2, the C_1 and C_2 chemical shifts of **1** and **2** are attributed to those of a single species. It is therefore estimated that **1** or **2** exists either as the racemic or meso form. This may be controlled sterically. As stated before, dimerization did not occur in the cases of **5a** and **6a**. In other words, two methyl

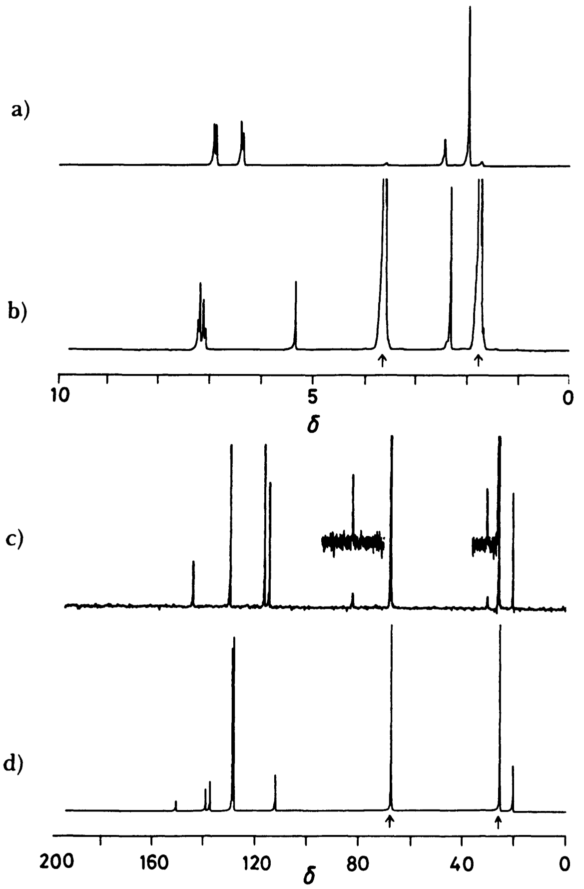


Fig. 3. ^1H and ^{13}C NMR spectra of **3** and **3a**. (a) ^1H spectrum of **3** in THF-d_8, (b) ^1H spectrum of **3a** in THF at 200 MHz and 25 °C, (c) ^{13}C spectrum of **3** in THF, and (d) ^{13}C spectrum of **3a** in THF at 50.3 MHz and 25 °C.

groups at the C_2 of **5a** and **6a** inhibited the dimerization. Therefore, one methyl group at the C_2 of **1a** and **2a** can be said to control the way of dimerization, sterically. This is one reason why only a racemic or meso form of **1** or **2** is prepared. The racemic form is more probable because of a steric reason. However, this is not clear at present and must be studied in the future. Anyhow, it is considered that the anion, **1** or **2**, is in a highly crowded situation.

^1H and ^{13}C NMR Parameters. The NMR parameters obtained for the anions and their precursors are summarized in Tables 1 and 2. All the ^1H chemical shifts of the anions are shielded by about 0.3 to 3.0 ppm, as compared with those of the precursors. This tendency is consistent with that reported previously.[1] However, the protons attached to the C_2 atoms are shifted upfield by about 3 ppm. This large shift is attributed to a hybridization change of the C_2 atom from sp^2 to sp^3, accompanied with dimerization. This fact has also been verified from changes in the ^{13}C NMR parameters. The changes of the chemical shifts of the C_2 are about 82—90 ppm. The values are similar to those observed for triphenyl- and diphenylmethanide ions (92 and 97 ppm).[14] However, a corresponding change of the ^{13}C NMR parameters for the carbons of the anions without hybridization change is about 17 ppm in the case of 1,1,4,4-tetraphenylbutadiene dianion (**7**).[15] Therefore, from the viewpoint of the chemical shift parameters, the C_2 of **1**, **2**, and **3** are considered to be sp^3-hybridized. Additional evidence of hybridization of the C_2 is given by measuring the one-bond J_{CH} coupling constants, which are about 123, 121, and 122 Hz for **1**, **2**, and **3**, respectively. These

Table 1. ^1H NMR Chemical Shifts of Dimer Dianions and Their Precursors

Compd	Solvent	Temp	Assignment					
		°C	ortho	meta	para	2-H	*p*-CH_3	2-CH_3
1	THF-d_8	20	6.68[a]	6.24[a]	—	3.59[a]	1.97	1.15
		−70	6.81	6.36	—	3.39[a]	1.88	1.12
			6.70	6.16			2.02	
2	THF-d_8	23	6.81[a]	6.48[a]	5.65[a]	3.42[a]	—	1.18
3	THF-d_8	23	6.93	6.41	—	2.46	2.00	—
4[b]	THF	31.5	7.01	6.55	5.67	2.48	—	—
1a	THF-d_8	25	7.08	7.03	—	6.10	2.28	1.72
			7.04	7.17			2.35	
	THF	23	7.12	7.06	—	6.14	2.31	c)
			7.07	7.20			2.38	
	DME	25	7.08	7.02	—	6.10	2.27	1.72
			7.04	7.16			2.34	
2a	THF	23	7.4[d]	7.2[d]	7.2[d]	6.22	—	1.75[e]
3a	THF	23	7.25	7.15	—	5.39	2.36	—
4a	THF	23	7.3[d]	7.3[d]	7.3[d]	5.48	—	—
5a	THF	31.5	7.00	7.00	—	—	2.29	c)
	CCl_4	31.5	6.92	6.92	—	—	2.29	1.77
6a	HMPA	23	7.10	7.34	7.22	—	—	1.78
	CCl_4	31.5	7.08	7.08	7.08	—	—	1.78

a) Broad. b) Cited from Ref. 3a. c) Overlapped with large solvent peaks. d) With large uncertainty because of the signal overlapping. e) The value is given for a CCl_4 solution.

Table 2. ^{13}C NMR Chemical Shifts of Dimer Dianions and Those Precursors

Compd	Solvent	Temp	Assignment							
		°C	C_i	C_o	C_m	C_p	C_1	C_2	p-CH_3	2-CH_3
1	THF	25	143.94	117.84[a]	129.84	115.06[a]	89.15	37.67	20.77	17.78
		−70	142.81	117.63	129.06	114.37	88.50	36.43	21.25	17.56
			145.56	118.04	129.81	114.15			20.93	
	DME	25	144.38	117.95[a]	129.68	114.65[a]	88.76	37.31	20.80	18.06
2	THF	23	145.61	118.49[a]	128.87	107.84[a]	92.82	37.79	—	18.05
3	THF	24	144.19	116.43	129.81	114.62	82.90	30.61	20.89	—
4[b]	THF	31.5	145.8	117.5	129.25	108.05	86.9	30.45	—	—
1a	THF-d_8	25	143.36	127.94	129.60	137.11	138.26	123.10	21.36	15.91
			141.38	129.41	130.76	136.93			21.01	
	THF	25	143.48	127.87	129.53	137.04	138.20	123.02	21.30	15.85
			141.31	129.34	130.69	136.86			21.16	
2a	THF	23	143.82	127.94	129.00	127.70	140.97	124.29	—	15.98
			143.74	128.80	130.81	127.50				
3a	THF	23	139.78	128.92	129.56	138.08	151.11	112.94	21.31	—
4a	THF	25	142.45	128.98	128.98	128.47	151.40	114.30	—	—
5a	THF	23	141.57	129.17	130.49	136.13	129.67	129.49	22.64	21.17
6a	HMPA	23	143.57	128.52	130.01	126.74	130.67	137.99	—	22.55

a) Broad signals because of coalescence. b) Cited from Ref. 3c.

Table 3. Comparison of ^{13}C Chemical Shift Changes and Charge Distributions of **1**, **2**, **3**, and **4**[a]

Compd	$\Delta\delta C_i$	$\Delta\delta C_o$	$\Delta\delta C_m$	$\Delta\delta C_p$	$\Delta\delta C_1$	$\Delta\delta C_2$	S_1[b]	S_2[c]
1	−1.55	10.77	0.27	21.89	49.05	85.35	218.23	132.88
	(−0.01)[d]	(0.07)	(0.00)	(0.14)	(0.31)			(0.83)
2	−1.83	9.88	1.04	19.76	48.15	86.50	212.12	125.62
	(−0.01)	(0.06)	(0.01)	(0.12)	(0.30)			(0.79)
3	−4.41	12.49	−0.25	23.46	68.21	82.33	237.60	155.27
	(0.04)	(0.08)	(0.00)	(0.15)	(0.43)			(0.97)
4	−3.35	11.48	−0.27	20.42	64.5	83.85	226.2	142.36
	(−0.02)	(0.07)	(0.00)	(0.13)	(0.40)			(0.89)
7[e]	−2.96	7.11	1.53	15.96	57.82	17.40	135.78	
	(−0.02)	(0.04)	(0.01)	(0.10)	(0.36)	(0.11)	(0.85)	

a) The values for the methyl carbons are not shown in the table because of their small values, but they are included into the evaluation of S_1 and S_2. b) A total sum for a monomer unit. c) $S_2 = S_1 - \Delta\delta C_2$. d) The value in parentheses is the excess electron density on the carbon atom, which was evaluated by a method used in Ref. 18. e) The values are cited from Ref. 15 for the sodium salt.

values are consistent with those of typically sp^3-hybridized carbons.[16] The excess charge distribution of the anions can be evaluated from the differences of the chemical shifts between the anions and the corresponding precursors (Table 3), using an equation proposed by Fraenkel et al.[17] and a factor presented by Spiesecke and Schneider.[18] In a total sum for a monomer unit, S_1 has an uncertainty due to the hybridization change of the C_2 atom of the anion, **1**, **2**, **3**, or **4**. Therefore S_2 is evaluated as a total sum for a monomer unit, except for the difference of the C_2 atom. It is considered that the hybridization of the C_1 atom of the anion does not change from that of the precursor, as disscussed previously.[14] The S_2 values of **3** and **4** are larger than those of **1** and **2**. This is mainly ascribed to the difference of the C_1 chemical shift. This means that **3** or **4** has a larger electron density at the C_1 than **1** and **2** has, suggesting that the counter-cation is nearer to the C_1 for **3** or **4** than for **1** or **2**. This is ascribed to a steric effect of the 2-methyl group for **1** and **2**. The S_2 values are approximately 139 ppm as a mean. This is nearly equal to the S_1 value of **7**. Thus, the excess charge of the dimer dianions is mostly delocalized into the phenyl rings and on the C_1 (or C_4) carbon.

Temperature Dependency of the Chemical Shifts. For three carbanions (**1**, **2**, and **3**), there are two different internal rotations, A and B, as shown in Scheme 1. The ^{1}H NMR signals of the H_o, H_m, and p-CH_3 hydrogens of **1** were broad at 25 °C, as shown in Fig. 1a. When the temperature was lowered, each signal split into two. Similarly, all ^{13}C signals of the phenyl groups of **1** were split into two at −70 °C. Therefore, two geminal phenyl rings of **1** are not magnetically equivalent at this temperature. The chemical shift values at −70 °C are also given in Tables 1 and 2. The values arranged in the same line are those for the protons or carbons belonging to the same phenyl ring.

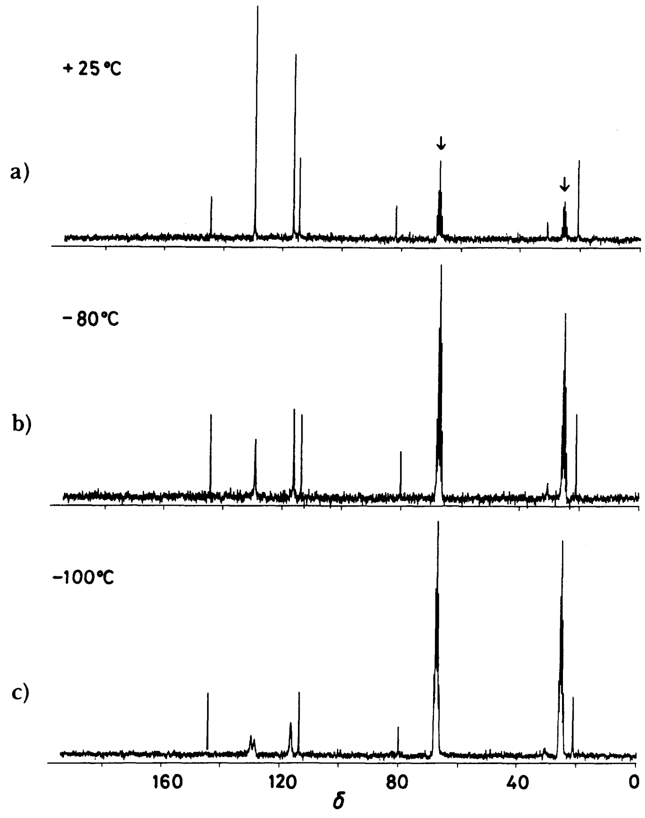


Fig. 4. ^{13}C NMR spectral changes of **3** in THF-d_8 at 50.3 MHz. (a) At 25 °C, (b) at −80 °C, and (c) at −100 °C.

Similarly, the splittings of the signals were also observed at a lower temperature in **2** but not **3**. Therefore, the cause of the nonequivalence is attributed to the presence of a methyl group at the C_2 and to hindered rotation around the bond between the C_1 and C_2 atoms, which is denoted as B in Scheme 1. When the temperature was lowered, **3** showed a broad C_o signal and two broad split C_m signals at −100 °C, as shown in Fig. 4. The peak heights of the C_o and C_m signals are low as compared with those of other carbon signals (C_i and C_p). Therefore, the signal splitting is considered to be caused by the restriction of rotation about the bond between the C_1 and C_i, which is denoted as A in Scheme 1. Even at −110 °C, the C_o signals were not separated into two. Therefore, the thermodynamic parameters of this hindered rotation could not be obtained. The temperature-dependent ^{13}C chemical shifts of **1** are given in Fig. 5. In the figures the vertical line at each temperature shows an approximate line width of each signal. Coalescences were observed for the signals of all carbons in two phenyl rings in the temperature range from −20 to 20 °C, accompanied by signal broadening. This is due to the rotation B. The chemical shift changes of the C_o and C_p carbons of **1** behave in a strange manner. For example, the C_p signals of **1** showed another coalescence phenomenon at −80 °C. This coalescence is quite different from those at higher temperatures. It was not accompanied by broadening of the signals like that as shown at a temperature near 0 °C in Fig. 5. The same is true for the C_o signals. Therefore, this coalescence is explained by temperature-dependent chemical shift changes. However, the origin of this chemical shift change is not clear at present. It seems to be concerned with the active center of the anion: that is, the C_1 atom. Thus, the difference of the chemical shifts is the largest at the C_i which is the nearest carbon from the active center. It must be noted, however, that two C_p atoms have the same chemical shift value at −100 °C, though they have different chemical shifts at −20 °C. The chemical shift differences of the two split signals are about 2.1, 1.0, 0.8, and 1.8 ppm for C_i, C_o, C_m, and C_p atoms at −20 °C, respectively. The difference is larger for the C_i and C_p than for the C_o and C_m. Therefore, the two former carbons are more sensitive to their circumstances than the two latter carbons. This behavior is characteristic in the ^{13}C chemical shifts of monosubstituted benzenes.[19] Another reason for these relative magnitudes is considered to be due to the rotation A, which causes an averaging of the chemical shifts for the C_o and C_m. Thus, the C_p and C_i atoms are on the axis of the rotation A, but the C_o and C_m atoms are not. Further, evidence of the presence of the rotation A in **1** is as follows: the line widths of the C_o and C_m resonances of **1** are about twice those of the C_p and C_i atoms at −70 °C. An effect of the methyl substituent can be evaluated from a comparison of the ^{13}C spectra of **1** and **2**. However, the effect could not be obtained quantitatively. Visually, the signal widths of the ring carbons of **2** are quite larger than those of **1** at about −80 °C. This suggests that a temperature of −80 °C is near the coalescence temperature of **2**, but far from that of **1**. Therefore, the methyl group lowers the potential barrier of the rotation A of **1**, as expected from the electron-donating property of substituent, as reported by Bushweller et al.[8] As a conclusion two internal rotations, A and B, are differentiated for **1**. The former does not stop, even at −100 °C, though the latter stops approximately at −20 °C. The phenomenon observed for **1** at about 0 °C was explained by the restricted rotation B. However, it may be considered to be explained by any other reasons such as the presence of two different aggregation states or two different species (for example, racemic and meso forms). These explanations, however, were denied for the following two reasons. First, two split signals were observed only for the atoms concerning the aromatic rings. Second, they appeared with equal intensity.

Line-Shape Analyses. The temperature-dependent ^{1}H and ^{13}C NMR spectra were analyzed as simple two-site exchanging problems. The line widths were

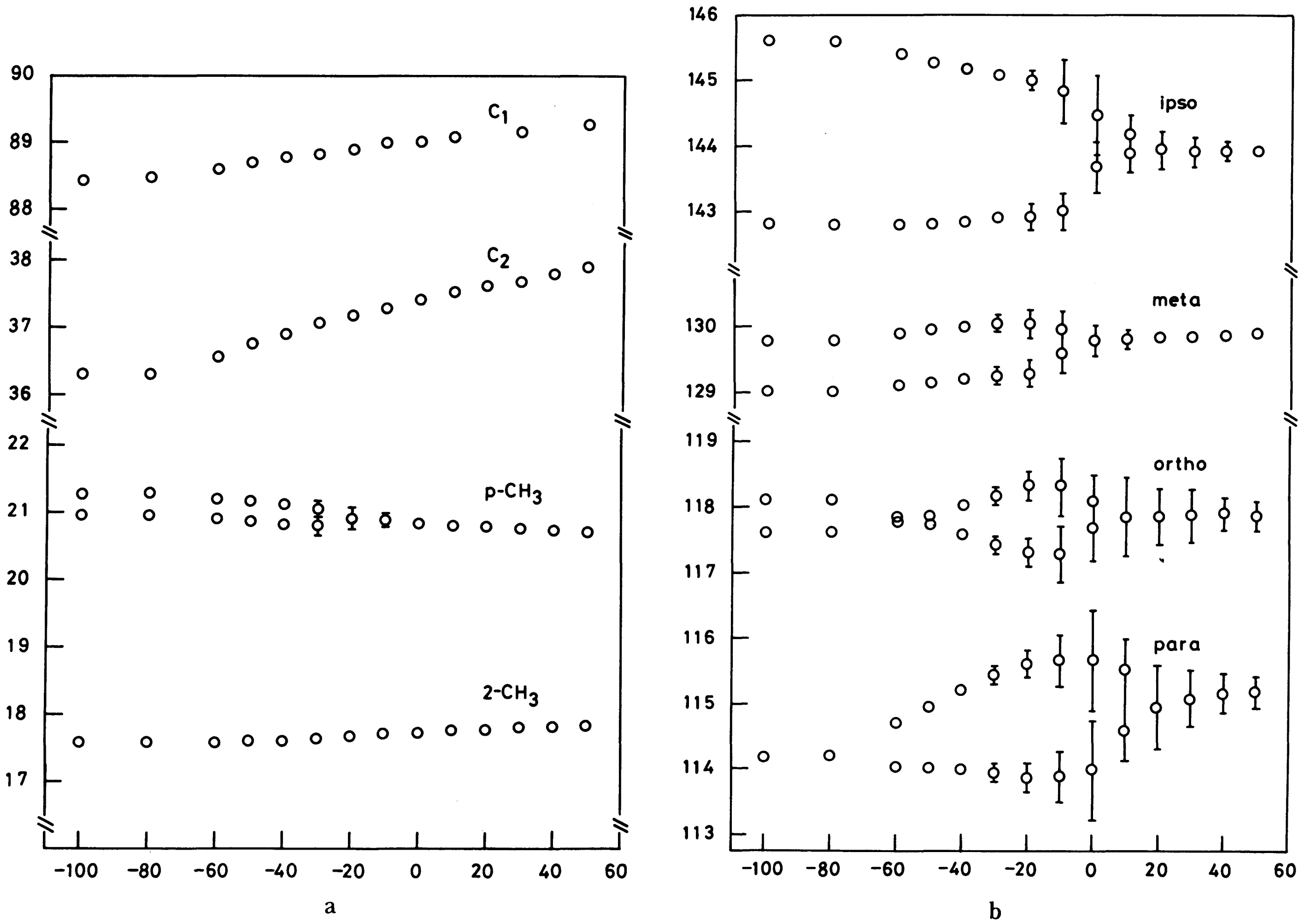


Fig. 5. ^{13}C chemical shifts (ordinate in ppm) of **1** in THF as a function of temperature (abscissa in °C) at 50.3 MHz, (a) Aliphatic and (b) aromatic carbon regions.

Table 4. Thermodynamical Parameters for the Internal Rotation Around the C_1–C_2 Bond of **1** in THF-d_8

E_a/kJ mol^{-1}	$\log A$	ΔH^{*}/kJ mol^{-1}	ΔS^{*}/J K^{-1} mol^{-1}
43.0±0.6	9.8±0.1	40.5±0.6	−66.4±2.1

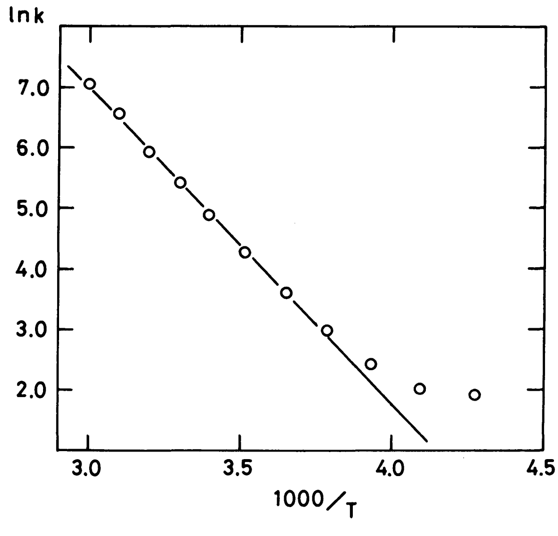


Fig. 6. An Arrhenius plot for the rotation B of **1** in THF.

estimated from the observed spectra. The calculated and experimental line shapes were compared visually. The thermodynamical parameters for the rotation (B) were obtained by Arrhenius and Eyring plots. An example of the analyses is shown in Fig. 6 for an Arrhenius plot of the kinetic parameters obtained for the exchange of the two *p*-CH_3 protons of **1**. However, the plotted points are divergent at the temperatures lower than −20 °C. A reason for this divergence seems to be due to an interaction between the two rotations, A and B, in the molecule. It must also be noted that errors in the DNMR method will become appreciable at two extremes of the range.[20] Therefore, although several trials were carried out, the parameters for other peaks could not be obtained unambiguously, except for the *p*-CH_3 protons. The thermodynamical parameters are given in Table 4, which were obtained for the temperature ranges between −10 and 60 °C concerning the rotation, B. The coalescence temperature can be used to evaluate the change in the free energy of activation for the rotation in the molecule using the following equation:

$$\Delta G_c^{\ddagger} = aT_c[9.972 + \log(T_c/\Delta\nu)],$$

where T_c, $\Delta\nu$, and a are the coalescence temperature, the chemical-shift difference of two exchanging sites, and a constant of 19.14 J mol^{-1} respectively.[21] In the case of **1**, the $\Delta G_c^{\ddagger}$ value is 58.3 kJ mol^{-1} when the values of T_c and $\Delta\nu$ are adopted as ca. 278 K and 28.5 Hz. This value is consisent with that calculated from the parameters given in Table 4.

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