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Proton and Carbon-13 NMR Study of 1,1,4,4-Tetraphenyl- and 1,4-Diphenyl-1,3-butadiene Dianions in Solution. The Charge Distributions, Structural Features and Rotational Barriers of Phenyl Groups

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The dicarbanions (**1** and **2**) produced from 1,1,4,4-tetraphenyl- and 1,4-diphenylbutadienes (**1a** and **2a**) were investigated by means of the ^1H and ^{13}C NMR techniques. Large upfield shifts of the proton and carbon signals caused by the conversion of the hydrocarbons into the dianions were observed. Such shifts were used for evaluating the excess charge distributions in the dianions. From the coupling constants obtained it is concluded that the configuration of the central bond of the anion is the trans one for **1** but the cis one for **2**. Thermodynamical parameters were obtained for the restricted rotation of the phenyl group of the lithium salt of **2**.

Butadiene is the simplest hydrocarbon among the acyclic unsaturated conjugate ones. The dianions derived from the butadienes are, therefore, one of the interesting objectives from their electronic and structural view points. There have been many NMR studies concerning carbanions with odd carbon skeletons, such as allyl, pentadienyl, or heptatrienyl carbanions.[1] Little work, however, has been reported on the NMR parameters of the acyclic carbanions with even carbon skeletons. A ^1H NMR study of 1,1,4,4-tetraphenylbutadiene dianion (**1**) was reported in our previous paper.[2] Recently, we have observed the NMR spectra of the dianions (**2**) produced from 1,4-diphenylbutadiene.[3] We therefore wish to report on the structures and behaviors of these dianions, evaluated from their ^1H and ^{13}C NMR data.

Experimental

The starting materials, **1a** and **2a**, were commercially available and were used without further purification. The solvents used for the preparation of the anionic sample solutions, THF, THF-d_8, and DME, were refluxed upon sodium metal, distilled, degassed, and finally kept on a sodium–potassium alloy. The starting hydrocarbon, **1a** or **2a**, was sublimed, degassed under vacuum, and then dissolved in dried and degassed solvents. The solution was in contact with freshly cut alkali metal flakes (lithium, sodium, or potassium) at room temperature in a hand-made reaction container under vacuum. Immediately after contact, the solution showed a deep-purple color. This colored solution sometimes did not give any narrow ^1H NMR signals, except for very broad ones which were ascribed to a contamination of some anionic radical species. Consequently, the solution was kept in its vessel with stirring for a day or two longer at room temperature so that the reaction would come to completion. Then, the resulting solution was filtered and sealed in an NMR tube and a glass ampule with a breakable seal. All NMR samples were prepared to be 0.1—0.3 mol dm^{-3} solutions sealed in 5 or 10 mm o.d. NMR tubes.

All of the NMR spectra were measured on a Varian XL-200 Fourier transform NMR spectrometer. Variable-temperature spectra were measured in the range from +50 to −95 °C. The proton and carbon-13 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 (1.75) and δ_C 26.4 (25.4) for THF (THF-d_8), and δ_H 3.28 and δ_C 58.8 for DME.

In order to obtain chemical evidence that the anionic species are dicarbanions, the sodium salt of **2** in THF was quenched by deuterium oxide. The quenched products consist of two isomers. A major component was shown to have a structure consistent with *cis*-1,4-dideutero-1,4-diphenyl-2-butene, C_6H_5–CHD–CH=CH–CHD–C_6H_5; yield ca. 80%; its NMR data were δ_C(CHD)=33.2, $^1J_{CD}$=19.5, δ_H(CHD)=3.48 broad, δ_H(CH)=5.70, doublet (J=5.1 and $J_{\beta\beta'}$=11.4). Another minor component was shown to have a structure consistent with *trans*-3,4-dideutero-1,4-diphenyl-1-butene, C_6H_5–CH=CH–CHD–CHD–C_6H_5: yield ca. 20%; its NMR data were $\delta_H(C_1H)$=6.41, doublet (J=15.9); $\delta_H(C_2H)$=6.23, d–d (J=15.9, 6.6); $\delta_H(C_3HD)$=2.49, d–d (J= 6.6, 8) broad; $\delta_H(C_4HD)$=2.75, doublet (J=8 broad).

Results and Discussion

NMR Chemical Shifts and Excess Charge Distributions. The NMR parameters obtained for the anionic species and their precursors are summarized in Tables 1 and 2. Typical examples of the ^{13}C NMR spectra are also shown in Figs. 1 and 2.

All of the ^1H chemical shifts of the dianions are shielded by about 0.2 to 3.4 ppm, as compared with those of the corresponding precursors. This tendency of the upfield shift changes is consistent with the general trend observed in other carbanions.[1] However, it should be pointed out here that the β-proton-chemical-shift change of **2** is significantly large and characteristic. For example, the upfield shift changes of the lithium salt of **2** are about 3.4 and 1.7 ppm for α- and β-protons. While those of pentadienyllithium (as a typical odd-carbon carbanion) are about 2.0, 0.0, and 1.9 ppm for α-, β-, and γ-protons respectively.[4] The upfield shift changes are clearly alternative for the example of odd-carbon carbanions. **2** (as an example of even-carbon

Table 1. Proton NMR Data of The Carbanions and Their Precursors at 200 MHz and 23 °C

Compd/metal/solvent	Chemical shifts δ/ppm					Couplings/Hz	
	H_o	H_m	H_p	H_α	H_β	$J_{\alpha\beta}$	$J_{\beta\beta'}$
1/Na/THF-d_8	7.23	6.70	5.96	—	5.99	—	15.4$^{a)}$
2/Li/THF-d_8	6.03$^{b)}$	6.38$^{b)}$	5.33	3.61	4.95	12.2	7.7
2/Li/THF-$d_8$$^{c)}$	5.92 5.96	6.21 6.38	5.22	3.66	4.91	d)	d)
2/Na/THF-d_8	5.94 5.96	6.18 6.37	5.18	3.79	4.96	11.6	9.4
1a/THF	(7.43	—	7.08)	—	6.79	—	d)
1a/$CDCl_3$	(7.45	—	7.15)	—	6.79	—	11.1$^{a)}$
2a/THF	7.44	7.28	7.17	7.01	6.68	15.5	10.6
2a/$CDCl_3$	7.41	7.30	7.21	6.92	6.64	15.7	10.3

a) Measured from the ^{13}C satellite spectrum at 300 MHz. b) Broad. c) Measured at −60 °C. d) Not available.

Table 2. C-13 Chemical Shifts (δ) of the Carbanions and Their Precursors in ppm

Compd/metal/solvent	Assignment$^{a)}$					
	C_i	C_o	C_m	C_p	C_α	C_β
1/Na/THF	145.12	121.94(152)	128.67(151)	112.33(158)	87.31	109.21(139)
2/Li/THF	146.65	118.53(149) 110.60(149)	128.45(149)	104.86(157)	65.74(146)	97.42(146)
2/Na/THF	146.03	118.32(153) 109.69(149)	129.56(146) 128.00(148)	103.01(157)	67.73(b)	98.06(146)
2/K/DME	144.50	118.23(b) 108.60(b)	130.05(b) 128.07(b)	103.10(b)	b)	100.59(b)
1a/THF	143.40 140.91	129.74(160$^{b)}$) 128.36(158$^{b)}$)	131.47(159$^{b)}$) 128.93(160$^{b)}$)	128.4$^{b)}$(158$^{b)}$) 128.17(160$^{b)}$)	145.13	126.61(154)
2a/THF	138.51	127.18(158$^{b)}$)	129.35(159$^{b)}$)	128.21(160)	130.22(158$^{b)}$)	133.66(156)
2a/DME	138.43	127.15(b)	129.36(160)	128.23(161)	130.12(b)	133.66(156)

a) The values in parentheses are the $^1J_{CH}$ in Hz. b) With large error or not available because of overlapping or low intensity of the signal.

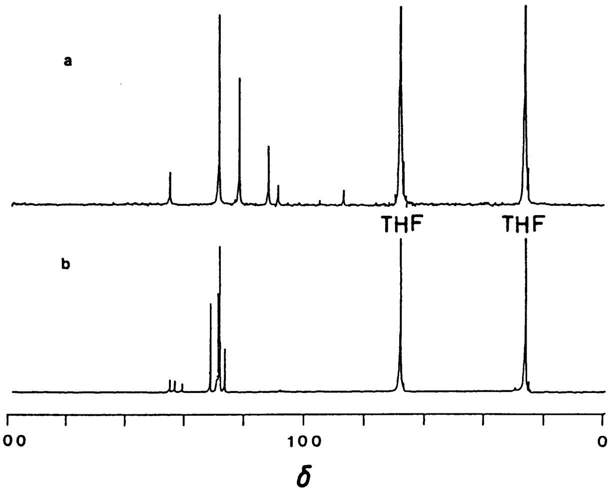


Fig. 1. ^{13}C NMR spectra of **1** and **1a** in THF. (a) The sodium salt of **1** and (b) **1a**.

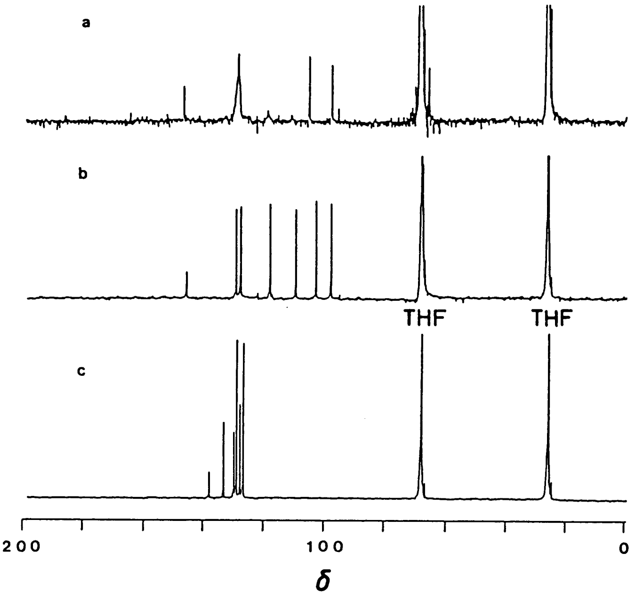
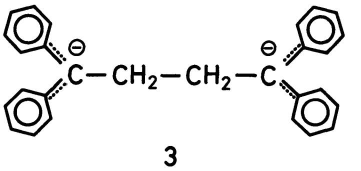


Fig. 2. ^{13}C NMR spectra of **2** and **2a** in THF. (a) The lithium salt of **2**, (b) the sodium salt of **2**, and (c) **2a**.

carbanions), however, cannot have such alternation of the shift changes because of its symmetrical even-carbon skeleton. It is also noted that the aromatic proton shifts of **2** are in order of meta, ortho, and para positions from low to high field in the same manner as phenylmethanide ion,$^{5)}$ while those of **1** are in the order of ortho, meta, and para positions as well as those of 1,1,4,4-tetraphenylbutane-1,4-diide (**3**) and 1,1,2,2-tetraphenylethanediide ions (**4**).$^{6)}$ This distinc-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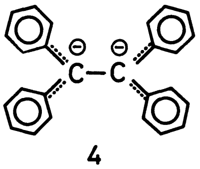
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tion between the two casses can be explained in terms of several reasons. One is due to the number of phenyl groups available to delocalization of excess charge, as is pointed out before.[6c] This is because the former dianion has one phenyl group, but the latter has two phenyl groups on the α-carbon, which is an anionic center.

The large upfield shifts of the carbon signals caused by the conversion of hydrocarbons into dianions as well as those of the proton signals are transpired from the data given in Table 2. It is well-known that for delocalized carbanions, carbon-13 shift changes have been used as empirical guides to the distribution of electron densities within the carbanions.[1,7] Because the change are much larger in magnitude than those observed in the ^{1}H chemical shifts and are less sensitive to other effects than to changes in the electron density. The excess charges on carbons in the carbanions are obtained from a comparison of the chemical shifts between the carbanions and their neutral precursors. The differences of the chemical shifts are extremely large, for example 58—64 ppm at α-carbon, 17—36 ppm at β-carbon, and 30—47 ppm at the total sum of the phenyl carbons, as shown in Table 2. An estimation of the charges on the carbon atoms is made by using an empirical equation proposed by Fraenkel et al.[8] and a factor (160 ppm/electron) presented by Spiesecke and Schneider.[9] The experimentally evaluated values are presented in Table 3. As for the dianion **2**, in comparison with the total excess charges on a phenyl ring, the value of the lithium salt (0.265) is smaller than the values of the sodium and potassium salts (0.283 and 0.296 respectively). However, the excess charge of **1** is estimated to be 0.189 per phenyl ring. This value is smaller than even the smallest one of **2** (0.265). On the other hand, the excess charges on the α- and β-carbon atoms increase from potassium to lithium salts. Furthermore, excess charge on the β-carbon is estimated to be 0.207—0.227 for **2**, though for **1** it is almost one half of **2**. These facts can be explained on the basis of the following: the relative decrease of the charge on the α- of β-carbon atom is consistent with a large delocalization of the charge into phenyl rings. Therefore, the total excess charges on the carbon atoms of dianions **1** and **2** are evaluated to be about 1.7—1.8e from Table 3. It must be pointed out here that the excess charges on the β-carbon of **2** is the second largest next to the α-carbon of **2**. This is one of the characteristic points of the dianion of **2**. This situation will be related to the structural features described later.

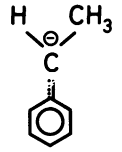
Structural Features of the Dianions in Solution. As shown in Table 1, the values of $J_{\alpha\beta}$ and $J_{\beta\beta'}$ of the neutral precursor (**2a**) agree with the previous data reported by Bothner-By and Harris.[10] Consequently, this confirms that **2a** has a certain configuration of trans, trans geometry. Further, the values of $J_{\beta\beta'}$ of **1a** and **2a** have an approximately average value between the typical magnitudes of the s-trans geometries with respect to the rotation about the central bond. In the dianions, on the other hand, $J_{\beta\beta'}$ of **1** and **2** were about 15 and 8 Hz, respectively. These values suggest that the configuration around the central bond of the anion is trans for **1**, but cis for **2**. The situations are quite different for the two carbanions, **1** and **2**. This can be explained as follows: Two phenyl groups attached to the C_α of **1** will have a greater repulsion than the α-carbon moiety of **2** due to steric effects. Another fact must be noted, that the $J_{\beta\beta'}$ value of the sodium salt of **2** is almost similar to that of the lithium salt. Therefore, the cis configuration of **2** is one of its characteristic structural features. The results obtained here regarding the THF solution are consistent with a theoretical prediction[11] and an X-ray analysis of the dianion in the solid state.[12] The *cis*-butene-like skeleton of **2**, thus determined, can surround the counter-cations. This situation is related to the fact that the excess charge is concentrated, especially on both the α- and β-carbons in the dianion **2**, as stated in the former section. From the large excess charge on C_α and C_β it is considered that the two carbons are expected to be in the proximity of the counter cations. As described in the experimental section, the main quenched product of **2** has the cis configuration in the central bond, which is assigned from its coupling constant of 11.4 Hz, as compared with the value of 2-butene.[13] Therefore, it is concluded that the configuration of **2** is held as it is when it is quenched by D_2O.

Table 3. Comparison of Charge Distributions of **1** and **2** in Unit of the Absolute Value of the Charge of an Electron

Anion/metal/solvent	q_i	q_o	q_m	q_p	q_{ring}	q_α	q_β
1/Na/THF	−0.019	0.044	0.010	0.100	0.189	0.361	0.109
2/Li/THF	−0.051	0.079[a]	0.006	0.146	0.265	0.403	0.227
2/Na/THF	−0.047	0.082[a]	0.004[a]	0.158	0.283	0.391	0.223
2/K/DME	−0.037	0.086[a]	0.002[a]	0.157	0.296	b)	0.207

a) Average values of two positions. b) Not available.

Equivalency or Nonequivalency of Ortho or Meta Positions in the Phenyl Groups of the Dianions. The chemical shifts of two ortho or meta carbons in a phenyl ring of **1** are equivalent, but those of **2** are nonequivalent, as is shown in Figs. 1a and 2b. Additionally, coalescence of meta carbon lines and broadening of ortho carbon resonances were observed for the lithium salt of **2** at room temperature, as shown in Fig. 2a. The appearance of the nonequivalency in the sodium and potassium salts was attributed to the higher rotational barrier about the C_α and C_i bond, as compared with the case of lithium salt (Figs. 2a and 2b). This fact can be interpreted on the basis of the effect of the counter cations.[14] The nonequivalency was caused by a conjugative interaction between C_i and C_α. This situation is similar to the nonequivalency observed in 1-phenylethanide (**5**) and 2,5-diphenylhexane 2,5-diide (**6**) ions.[6c,14,15] This is due to the fact that both a phenyl ring and a butadiene skeleton prefer to take their positions on a plane because of a strong $p\pi$–$p\pi$ interaction. However, in the neutral molecule **2a** there is a free rotation around the bond between the phenyl ring and its adjacent carbon; however, in the case of **2** the rotation is restricted in its NMR time scale. On the other hand, the two phenyl rings connected to the α-carbon of **1** cannot be coplanar due to their steric hindrance as well as those of the neutral precursor **1a**.[15] As is shown in Fig. 1, however, the ^{13}C spectra of **1** showed an equivalency of the four ortho or meta carbons in the two geminal phenyl rings, while there are two C_i, C_o, C_m, and C_p signals in **1a**. These facts suggest that there is a free rotation about the C_i and C_α bond in **1** and **1a**, while the rotation around the bond between the C_α and C_β atoms is forbidden in **1a** but allowded in **1** at room temperature.



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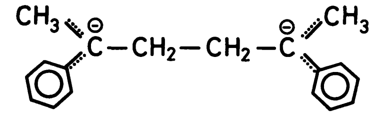

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Temperature Dependency of the Chemical Shifts of 2. It was pointed out before that in the ^{13}C NMR spectrum of the lithium salt of **2** (Fig. 2a) coalescence of the C_m signals and broadening of the C_o signals were observed at room temperature. These phenomena can be explained by the restricted rotation of the phenyl group around the C_i–C_α bond. The temperature-dependent ^{13}C chemical shifts are shown in Figs. 3a and 3b. As shown in the figures the C_m and C_β shifts are almost constant in the temperature range studied, while the C_i, C_o, and C_p shifts move towards a lower field by about 1—2 ppm in magnitude when the temperature is raised; the C_α shift, however, moves towards a higher field by about 2 ppm. This tendency can be explained by an excess charge on the C_α which increases with increasing temperature. This means that the $p\pi$–$p\pi$ interaction between the C_α and C_i decreases with increasing temperature. This is consistent with the fact that the phenyl ring can rotate at higher temperature, faster than that of the NMR time scale. In the sodium salt of **2**, on the other hand, the spectrum does not change its line shape in the temperature range from −70 to 60 °C. Therefore, the activation free-energy change will be larger than 68 kJ mol^{-1} by using an equation given by Sandström[16] and the chemical-shift difference of 78.5 Hz. Therefore, it must be said that the barrier of phenyl rotation of **2** is strongly affected by a counterion whose tendency is similar to that stated by Worsfold and Brownstein.[14]

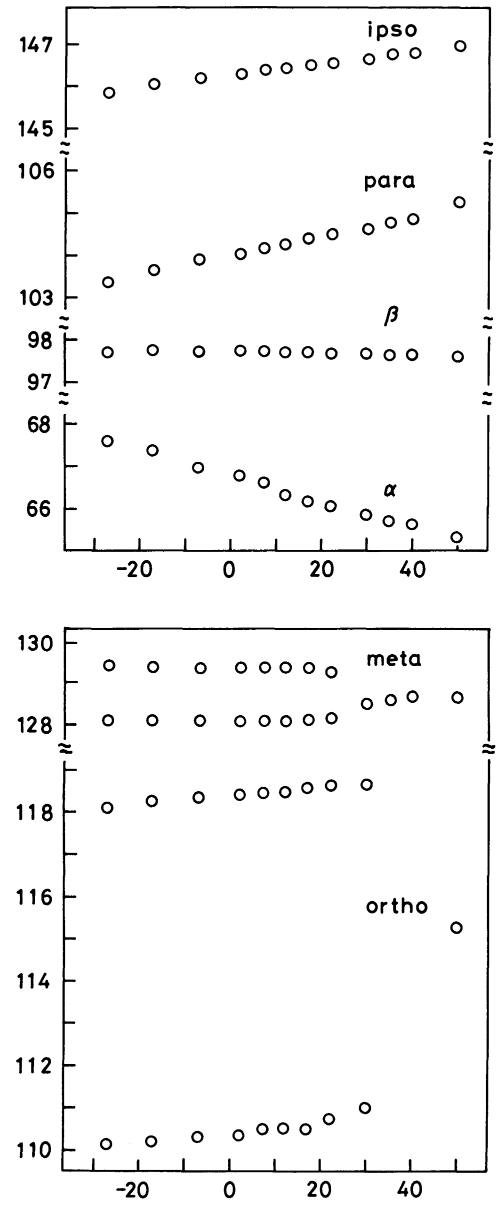

Fig. 3. ^{13}C chemical shifts (ordinate in ppm) of **2** in THF-d_8 as a function of temperature (abscissa in °C) at 50.3 MHz.

Table 4. Thermodynamical Parameters for the Hindered Rotation of the Phenyl Group of the Lithium Salt of **2**

Site	E_a/kJ mol^{-1}	log A	ΔH^{*}/kJ mol^{-1}	ΔS^{*}/J K^{-1} mol^{-1}
Ortho	62.7±1.2	13.0±0.3	60.3±1.1	−3.0±4.0
Meta	61.6±1.4	12.7±0.3	59.2±1.4	−10.0±5.0

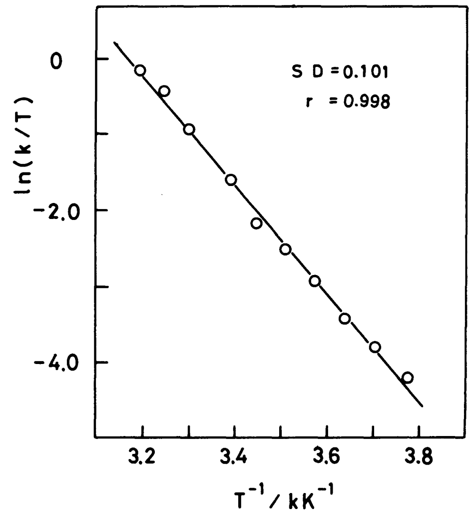

Fig. 4. An Eyring plot for the rotation of phenyl groups of the lithium salt of **2** in THF-d_8.

In the lithium salt of **2**, ^{13}C NMR analyses were carried out for both the ortho and meta carbon signals as an AX-spin system. The parameters used for the DNMR analyses are $\Delta\delta$ (ortho)=405; $\Delta\delta$ (meta)=64.3 Hz; T_2^{*}=0.134 s. The kinetic parameters have been determined by visual fittings of the calculated line shapes with the experimental ones. The thermodynamic parameters were obtained by the Arrhenius and Eyring plots of the rate constants with inverse temperatures, one of which is shown in Fig. 4. The parameters, thus determined, are given in Table 4. The parameters independently obtained for both the ortho and meta carbons are consistent with each other within the experimental errors. The values are compared with those reported for similar substituted phenylmethanide ions.[14,17-20] The barrier of the phenyl rotation of **2** is larger than those observed for diphenylmethanide ions.[21,22]

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