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An NMR Study of the Carbanions Produced from Triphenylethylene and Its Methyl-Substituted Derivatives[1,2)]

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The triphenylethylene dianion, which was produced by reducing triphenylethylene with metallic potassium in THF, was characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H spectrum was assigned by making spectral comparisons with those of dianions having methylphenyl groups. The ^{1}H and ^{13}C NMR data showed that two geminal phenyl rings were magnetically equivalent. This result indicated that a rapid rotation exists around the $C^{\ominus}$–$C^{\ominus}$ bond at room temperature. Extra charge distributions in the dianion were estimated; these are discussed together with the data for the other carbanions.

The reaction of substituted ethylenes with alkali metals has been known to produce metal compounds.[3,4)] The type of the compound produced varies from metal to metal (Li, Na, K, etc.) and from substituent to substituent. We have reported on the NMR spectra of the compounds—dianions or dimer dianions—produced from several phenylethylene derivative.[5—7)] According to those studies for stable anion formation from ethylenic compounds, it is necessarily attached by one or two phenyl groups in the ethylenic skeleton. Recently, a direct NMR observation of the stilbene dianion was reported.[8)]

In the present study, the formation of a dianion from triphenylethylene was attempted. As described in a previous paper,[9)] even-carbon carbanions are more difficult to prepare than the odd-carbon type. Therefore, no NMR spectra of triphenylethylene dianion (**1**) have been reported. The dianion has two different ethylenic carbons in a molecule, as shown in Fig. 1. In this dianion molecule one of the ethylenic carbons is attached to two phenyl rings (A-ring, diphenylmethanide ion moiety), whereas the other ethylenic carbon is attached to one phenyl ring (B-ring, benzyl ion moiety).

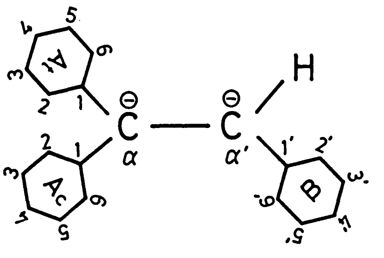

Fig. 1. Numbering of the phenyl rings and atoms in the triphenylethylene dianion, **1**.

Table 1. The ^{1}H Chemical Shifts of the Starting Materials and the Quenched Hydrocarbons in ppm in CCl_4[a)]

Compound	Bp/mmHg or Mp	Phenyl A-ring	Phenyl B-ring	CH=	CH	CH_2	CH_3
1a	m.69	7.20	7.00	6.89	—	—	—
2a	175/5.5	7.00	7.10	6.84	—	—	2.37
		7.21					2.40
3a	194/7	7.20	6.83	6.68	—	—	2.15
		7.33	6.98				2.38
			7.03				
4a	172/3	6.90	6.73	6.64	—	—	2.05
		7.23	6.96				2.23
			6.98				2.33
							2.38
1b		7.13	7.0	—	4.17	3.30	—
2b		6.94	6.94	—	4.07	3.23	2.24
3b		7.09	6.52	—	4.10	3.20	2.00
			6.71				2.11
			6.82				
4b		6.93	6.55	—	4.03	3.15	2.00
			6.68				2.12
			6.82				2.26

a) Referred to TMS.

Its ^{1}H and ^{13}C NMR data were observed and compared with those of other related carbanions reported previously.[5–8)]

Experimental

The experimental procedures were almost identical to those described in previous reports.[5–7)] The starting material dissolved in THF or THF-d_8 was allowed to come into contact with alkali metal in a vacuum at room temperature for one or two days. The obtained colored solutions were filtered, concentrated as much as possible, and then sealed into 5-mm or 10-mm o.d. NMR sample tubes. Four compounds were used as starting materials for preparing the carbanions. They were triphenylethylene (**1a**; hereafter the precursor of the carbanion **1** will be shown as **1a** and so on), 1,1-bis(4-methylphenyl)-2-phenyl-(**2a**), 1,1-diphenyl-2-(2,5-dimethylphenyl)-(**3a**), and 1,1-bis(4-methylphenyl)-2-(2,5-dimethylphenyl)ethylene(**4a**). Table 1 shows the melting or boiling points as well as the ^{1}H chemical shifts of the starting materials. The table also includes the ^{1}H chemical shifts of the hydrocarbons which were obtained by the reactions of the carbanions with water (hereafter these hydrocarbons are represented as **1b** and so on). Quantitative analyses showed that the carbanions formed with potassium contains two metal counterions in a molecule. However, in other cases, such as sodium or lithium, the carbanions have less than two of metal counterions in a molecule. In such cases, the ^{1}H signals of the carbanions are so broad that they cannot be easily assigned. This broadening may be due to contamination of a small amount of the radical anions in the solution. Therefore, in this study we only discuss those carbanions with potassium as counterions. The ^{1}H NMR spectra were measured mostly with a Hitachi R-20 spectrometer at 60 MHz, but partly with a Varian HR-220 spectrometer at 220 MHz. The ^{13}C spectra were measured with a Bruker HX-270 at 67.9 MHz or a Varian XL-200 spectrometer at 50.3 MHz. The ^{1}H or ^{13}C chemical shifts of the carbanions were measured relative to the more shielded peak of the solvent, THF, which was taken as being 1.79 or 26.4 ppm with respect to TMS, respectively. The MNDO MO calculation was carried out using a HITAC M680 and a library program (MOPAC) at the Computer Center, Institute of Molecular Science in Okazaki.

Results and Discussion

^{1}H Spectra. The ^{1}H chemical shifts of the studied carbanions are given in Table 2. Some unassigned and missing signals are represented as blank spaces in Table 2. The spectra obtained in THF solutions did not allow a complete assignment, due to overlapping with large solvent peaks. A complete assignment of the spectrum of **1** was obtained by making measurements in a THF-d_8 solution at 220 MHz. A typical spectrum of **1** is shown in Fig. 2. Two strong peaks can be seen at 6.55 ppm; other complex multiplet signals appear at 6.14, 5.89, and 5.61 ppm. The spectra of **2**, **3**, and **4** are useful for assigning **1**. Multiplet patterns and intensities of the signals are also convenient for their analysis. The chemical shifts of **1** were thus assigned as given in

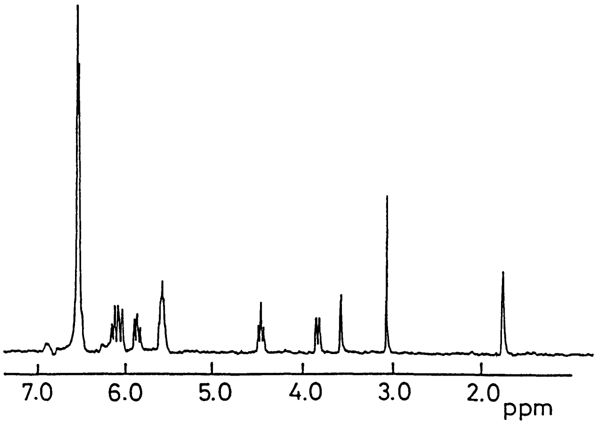

Fig. 2. ^{1}H NMR spectrum of **1**, measured at 220 MHz in THF-d_8.

Table 2. ^{1}H Chemical Shifts of Triphenylethylene Dianions and Several Related Carbanions in THF in ppm at 60 MHz[a,b)]

Anion	H-2 (H-6)	H-3 (H-5)	H-4	H-2′ (H-6′)	H-3′ (H-5′)	H-4′	Others	Ref.
1[c)]	6.55	6.55	5.61	6.08 (3.83)	5.89 (6.14)	4.48	3.05 (=CH)	
2	6.47	6.47	—[d)]	e	e	4.43	f	
3	ca. 6.6[g)]	ca. 6.6[g)]	5.66	— (4.11)	6.06 —	4.61	f	
4	6.60[h)]	6.43[h)]	—	— (4.04)	6.04 —	4.57	f	
5	—	—	—	5.38[h)] (4.80[h)])	5.89[h)] (6.01[h)])	4.20	1.32 (CH_3)	6
6	7.01	6.55	5.67	—	—	—	2.48 (CH_2)	5
7	7.01	6.57	5.66	—	—	—	—	7

a) Referred to TMS. b) Potassium as counterions. c) Measured at 220 MHz. The values are referred to the more shielded residual peak of THF-d_8 which is taken as 1.75 ppm with respect to TMS. d) The mark (—) shows the lack of hydrogen indicated. e) Not fully determined. f) The signals of the methyl protons were masked by large solvent peaks. g) Complex multiplets. h) Tentative assignment which is exchangeable.

Table 2. Several chemical shifts previously reported are also included in Table 2 for a comparison: those for the α-methylstyrene dimer dianion (**5**),[6] the 1,1-diphenylethylene dimer dianion (**6**),[5] and the tetraphenylethylene dianion (**7**).[7] In Fig. 2, the H-4 resonance of **1** has a quintet-like pattern, while the H-2 and H-3 resonances produce a strong doublet. In this spectrum the chemical shifts of H-2 and H-3 are incidentally overlapped with each other. The spectral pattern is therefore considered to be that of an $A_2A'_2X$ system. Separation of two strong peaks in the $A_2A'_2$ portion would be $(J_{AX}+J_{A'X})/2$. Its experimental separation (about 4.5 Hz at 220 MHz) is well coincident with a value of 4.6 Hz averaged from the data concerning twenty monosubstituted benzenes ($J_{23}+J_{24}$=9.52—9.06 Hz).[10] By introducing methyl groups into the A- and/or B-rings, the chemical shifts of H-2 and H-3 (or H-5 and H-6) in an A-ring separate each other; an AB-type quartet pattern was observed in the case of **4**. Two signals at 3.83 and 6.08 ppm of **1** can be assigned in two ways: as either H-2′ and H-6′ or vice versa. Carbanions **3** and **4** have signals at 4.11 and 4.04 ppm, respectively, which can be ascribed to the signals of either H-2′ or H-6′. From a steric consideration, however, two methyl groups in the B-ring of **3** and **4** would prefer to take the 2′- and 5′- positions, rather than 3′ and 6′. Therefore, two signals at 4.11 and 4.04 ppm seem to come from 6′-H. In comparison with these two signals (**3** and **4**) the signal at 3.83 ppm of **1** is assigned as that of H-6′. A decoupling experiment of this H-6′ signal showed the assignment of H-5′ to be correct. The assignments of the remaining H-2′ and H-3′ signals thus become certain. Several characteristics ^{1}H spectral features can be pointed out, and summarized as follows: (1) A substituent effect of the methyl group can be seen in the chemical shifts of **2** and **4**, compared with those of **1** and **3**. This tendency is also seen in the chemical shifts of **2a**, **2b**, **4a**, and **4b**, as compared with those of **1a**, **1b**, **3a**, and **3b**, respectively. (2) The H-2 of **1**, **2**, **3**, and **4** are more shielded than the corresponding protons of **6** and **7**. (3) The H-4 chemical shifts of **1**, **3**, **6**, and **7** are almost similar. (4) The H-4′ of **1** and **2** are more shielded than those of **3** and **4**. (5) The H-6′ of **1**, **3**, and **4** are appreciably more shielded than that of **5**. However, the H-2′ of **1** is less shielded than that of **5**. (6) NOE of the H-α′ signal was observed in the intensities of H-2′(15%) and H-2 (or H-3, 3%) signals.

^{13}C Spectra. The ^{13}C chemical shifts of **1** and several related carbanions are given in Table 3. The spectrum of **1** has 12 signals, as shown in Fig. 3. Four strong peaks, which appeared at 108.3, 119.65, 129.1, and 140.7 ppm, were assigned to those of C-4, C-6, C-5, and C-1, respectively, based on a consideration of their intensities and chemical shifts. Among the eight remaining signals, two at 139.9 and 88.9 ppm have longer T_1 than do the others. These are therefore assigned to the signals of C-1′ and C-α, respectively. The assignment of the

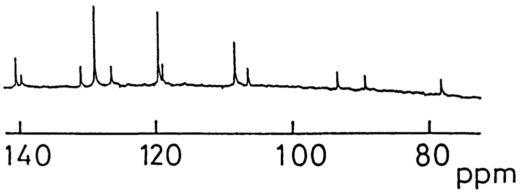

Fig. 3. ^{13}C NMR spectrum of **1**, averaged for 180 scans at 67.9 MHz in THF. Solvent peaks in the lower frequency are not shown.

Table 3. Carbon Chemical Shifts of Triphenylethylene Dianion and Related Compounds, in ppm with Respect to TMS

Compound	**1**[a]	**5**[a,b]	**6**[a,b]	**7**[a]	**1a**	**1b**
C-1	140.7	—	145.8	148.6	138.38 144.36[c]	145.65
C-2,C-6	119.65	—	117.5	117.5	130.35 128.90	128.95[d]
C-3,C-5	129.1	—	129.25	128.6	129.45 128.90	128.85[d]
C-4	108.3	—	108.05	106.9	128.20 127.48	126.8
C-α	88.9	—	86.9	96.6	141.49	54.1
C-1′	139.9	137.5	—	—	143.52	141.3
C-2′	106.25	103.3[d]	—	—	131.20	129.85[d]
C-3′	126.7	129.6[d]	—	—	128.33	128.75[d]
C-4′	92.95	88.0	—	—	128.20	126.5
C-5′	131.15	131.5[d]	—	—	128.33	128.75[d]
C-6′	119.0	107.9[d]	—	—	131.20	129.85[d]
C-α′	77.65	78.4	—	—	128.64	42.8
Others	—	33.65 (CH_2) 19.15 (CH_3)	30.45 (CH_2)	—	—	—

a) Potassium as couterions. b) Ref. 14. c) The upper or lower value is that of A_t or A_c ring, respectively. See Table 5. d) Tentative assignment which is exchangeable.

remaining signals was mostly achieved using a low-power, single-frequency decoupling of the adjacent proton signal, the assignment of which was already mentioned in the preceding section. The ^{13}C spectrum of **1a** gave at least 12 signals. The spectrum was previously measured in $CDCl_3$, and discussed by Proulx and Smith.[11] The chemical shifts of **1a** or **1b** can be used as reference compounds for estimating the effect of the extra charge on the ^{13}C spectrum of **1**. The ^{13}C chemical shifts of **1a** and **1b** in THF are included in Table 3. They are almost consistent with those measured in $CDCl_3$.[11]

Internal Rotation. Three internal rotations can be considered around the bonds of C-1 to C-α, C-α to C-α', and C-α' to C-1$'$ for **1**. The ^{1}H and ^{13}C spectra of **1** observed at room temperature show that two ortho-positions in the B-ring can be differentiated; those in the A-rings, however, can not be differentiated. One can therefore conclude that an internal rotation does exist around the bond of C-1 to C-α, but does not exist around the bond of C-1$'$ to C-α'. Both the ^{1}H and ^{13}C spectra show that the two A-rings of **1** can not be differentiated. However, the ^{13}C spectra of **1a** give four signals, which are assigned for carbons having no proton. The two A-rings of **1a** can therefore be differentiated by a C-13 NMR measurement. These facts show that an internal rotation around the bond of C-α to C-α' does exist in **1** at room temperature.

Ring Current Effect. As can be seen in Table 2, the H-4 and H-3 chemical shifts of **1** are almost equal to those of **6** and **7**. However, the H-2 chemical shift of **1** is upfield by about 0.4 ppm, compared with that of **6** or **7**. This upfield shift of H-2 can be explained by a ring current effect of the neighboring phenyl ring (B-ring). However, the situation of **1** is rather crowded. The H-6$'$ of **1** is upfield by about 1.0 ppm, compared with that of **5**. This upfield shift will also be explained by the ring current effect of the neighboring phenyl rings (A rings). To obtain a quantitative explanation of the chemical shifts, the ^{13}C and ^{1}H chemical shifts were correlated as shown in Fig. 4. In Fig. 4, the H-6$'$ shift seems to be out of range. A correlated straight line is therefore drawn from eight values, except for that of H-6$'$, with a correlation coefficient of 0.90. From Fig. 4, an upfield shift by 2.1 ppm of the H-6$'$ signal is attributed to the ring current effect of two neighboring A rings. The same is true for the H-α' signal, by about 0.5 ppm.

Extra Charge Effect. The extra charge seems to have a large effect on the H-α' signal of **1**. The signal appeared most upfield at 3.05 ppm. This signal should be compared with that of **1a**, which appeared near 7.0 ppm. Thus, the H-α' showed about a 4.0 ppm upfield shift. Based on this value and the discussion in the previous section, about 0.2 unit of extra negative charge

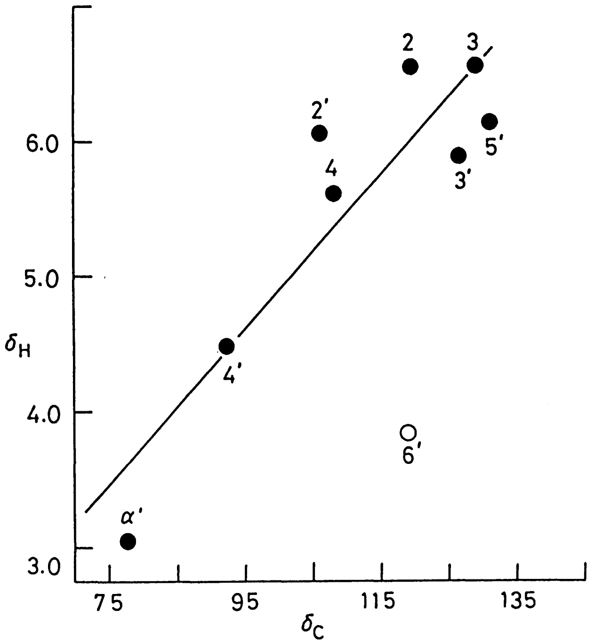

Fig. 4. Correlation between ^{13}C and ^{1}H chemical shifts of **1** in ppm.

Table 4. Comparison of Extra Charge Distributions in Triphenylethylene Dianion in Units of the Absolute Value of the Charge of an Electron

Position	From ^{13}C NMR	From ^{1}H NMR	From MNDO MO
1	−0.004	—	0.132[a)]
2(6)	−0.062	−0.061	−0.149[a)]
3(5)	0.000	−0.061	−0.041[a)]
4	−0.122	−0.149	−0.231[a)]
α	−0.329	—	−0.254
1$'$	−0.023	—	0.074
2$'$	−0.156	−0.086	−0.246
3$'$	−0.010	−0.104	0.013
4$'$	−0.220	−0.236	−0.353
5$'$	0.018	−0.080	−0.002
6$'$	−0.076	−0.100[b)]	−0.195
α'	−0.319	−0.312[b)]	−0.216

a) Average value for two or four similar carbons in A_c and A_t rings. See Table 5. b) Ring current effect is taken into consideration, as stated in the text.

Table 5. Structures of **1** and **1a** Optimized by MNDO MO Method

Bond length/Å	C_{α}–$C_{\alpha'}$	C_{α}–C_{1}	$C_{\alpha'}$–$C_{1'}$	$C_{\alpha'}$–$H_{\alpha'}$
1	1.480	1.433 (1.438$^{a)}$)	1.376	1.101
1a	1.355	1.494 (1.491)	1.479	1.098
Bond angle/degree	C_{1}–C_{α}–$C_{\alpha'}$(A_c)	C_{1}–C_{α}–$C_{\alpha'}$(A_t)	$C_{1'}$–$C_{\alpha'}$–C_{α}	$C_{\alpha'}$–$C_{\alpha'}$–C_{α}
1	118.3	117.5	131.4	111.7
1a	124.3	120.1	128.3	119.3
Dihedral angle$^{b)}$/degree		A_c	A_t	B
1		31.4	30.0	0.0
1a		79.5	83.1	75.6

a) As the MO calculations were carried out for a rigid optimized model, two A rings are differentiated as A_t and A_c which are trans and cis against to the B ring. The values in parentheses are those for the A_c ring. b) The dihedral angles are measured with respect to the plane formed from three atoms C_{α}–$C_{\alpha'}$–$H_{\alpha'}$ around the C_2 axis of each ring through two atoms of C_{ipso} and C_{para}.

would be located on C-α' (using an equation proposed first by Fraenkel et al.[12]). As far as the charge densities are concerned, however, an estimation based on the ^{13}C chemical shifts is more reliable than that from the ^{1}H chemical shifts. For estimating the charge densities on the carbon atoms from the ^{13}C spectrum of **1**, it is necessary to select a suitable compound as a reference. Since **1a** seems to be suitable as a reference, its ^{13}C spectrum has been almost completely assigned in $CDCl_3$.[11] We can therefore take **1a** as a reference. The aromatic carbons of **1** are more shielded than those of **1a**. This fact is ascribed to the extra negative charge effect. The extra negative charge distribution can be estimated for **1** (Table 4), for the charge densities are estimated using an equation proposed by Fraenkel et al.[12] and factors presented by Schneider et al. (160 and 10.7 ppm/electron for ^{13}C and ^{1}H, respectively).[13] It must be noted that the charges estimated from the ^{1}H and ^{13}C chemical shifts are almost parallel, except for those at the meta-positions. The inconsistency at the meta-positions has previously been pointed out for similar systems.[14–16]

The electron densities of **1** were also calculated by using a semiempirical MNDO MO method. The total calculated charge densities on the carbon atoms of **1** are given in Table 4. The calculated densities are almost parallel to the observed ^{13}C NMR chemical shifts. The correlation between the two is good, with a correlation coefficient of 0.97, except for the two ethylenic carbons, which seem to be different from other aromatic carbons.

Geometrical Optimization of 1 by the MNDO MO Method. The geometry of **1** was optimized by using the MNDO MO method. The typical structures for **1** and **1a** are given in Table 5. A characteristic point which appeared in two phenyl rings (A and B) of **1**, represents the bond lengths between the phenyl ring and ethylenic carbons. They are 1.438 and 1.376 Å for the A and B rings, respectively. This is especially concerned with the conjugation between the p-orbitals of the ethylenic carbon and the phenyl ring. Another point of interest regarding **1** and **1a** is the bond lengths between C-α and C-α'. They are 1.480 and 1.355 Å, respectively. The former reflects the existence of an internal rapid rotation around the C-α and C-α' bond at room temperature. The dihedral angles shown in Table 5 are more controlled by the sterically crowded nature of **1a** than in the case **1**. The heats of formation were calculated to be 87.88 and 119.21 kcal mol^{-1} for the optimized structures of **1a** and **1** (Table 5), respectively.

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