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Behavior of Triphenylethylene Dianion in Diethyl Ether Solution

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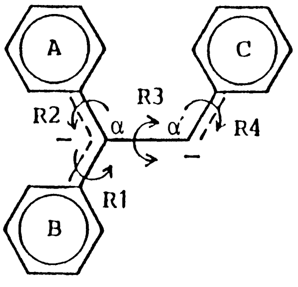
The temperature-dependent ^{13}C NMR spectra have been observed for triphenylethylene dianion in diethyl ether. The analyses of spectral changes with temperatures reveal that the geminal phenyl rotations have differential rates and that the rotations are affected by rotational motion about the ethylenic C_{α}-C_{α}' bond in the solution.

The molecular structure and dynamic behavior of π-conjugated carbanions have been the subject of extensive investigation. Problems which concern the structure and behavior of these species include the charge distribution and the various types of ion-pairs involved. Further, many of these anions are not rigid, but undergo rotation about partial double bonds at rates within the NMR time scale.

Recently, we have succeeded in the NMR observation of dilithium salt of triphenylethylene in ether. This report describes ^{13}C dynamic NMR evidence for differential rates of geminal phenyl rotations and for rotational motion about the ethylenic C_{α}-C_{α}' bond of triphenylethylene dianion in the solution. The preparation of the dianion and procedures employed in this study are similar to those described in the previous reports.[1a,c] Spectral assignments were confirmed by CH-COSY method.

As for the carbanion, there are four different internal rotations R1, R2, R3, and R4, as shown in Scheme 1. Although ^{13}C NMR signals of ipso carbons were broad at 27.0 ℃, the two geminal phenyl rings of the dianion are magnetically equivalent at this temperature, as shown in Fig. 1a.



Scheme 1.

The carbon chemical shifts of two ortho and meta positions of the phenyl ring C are nonequivalent, indicating that the rotation R4 is restricted even at room temperature. Several articles

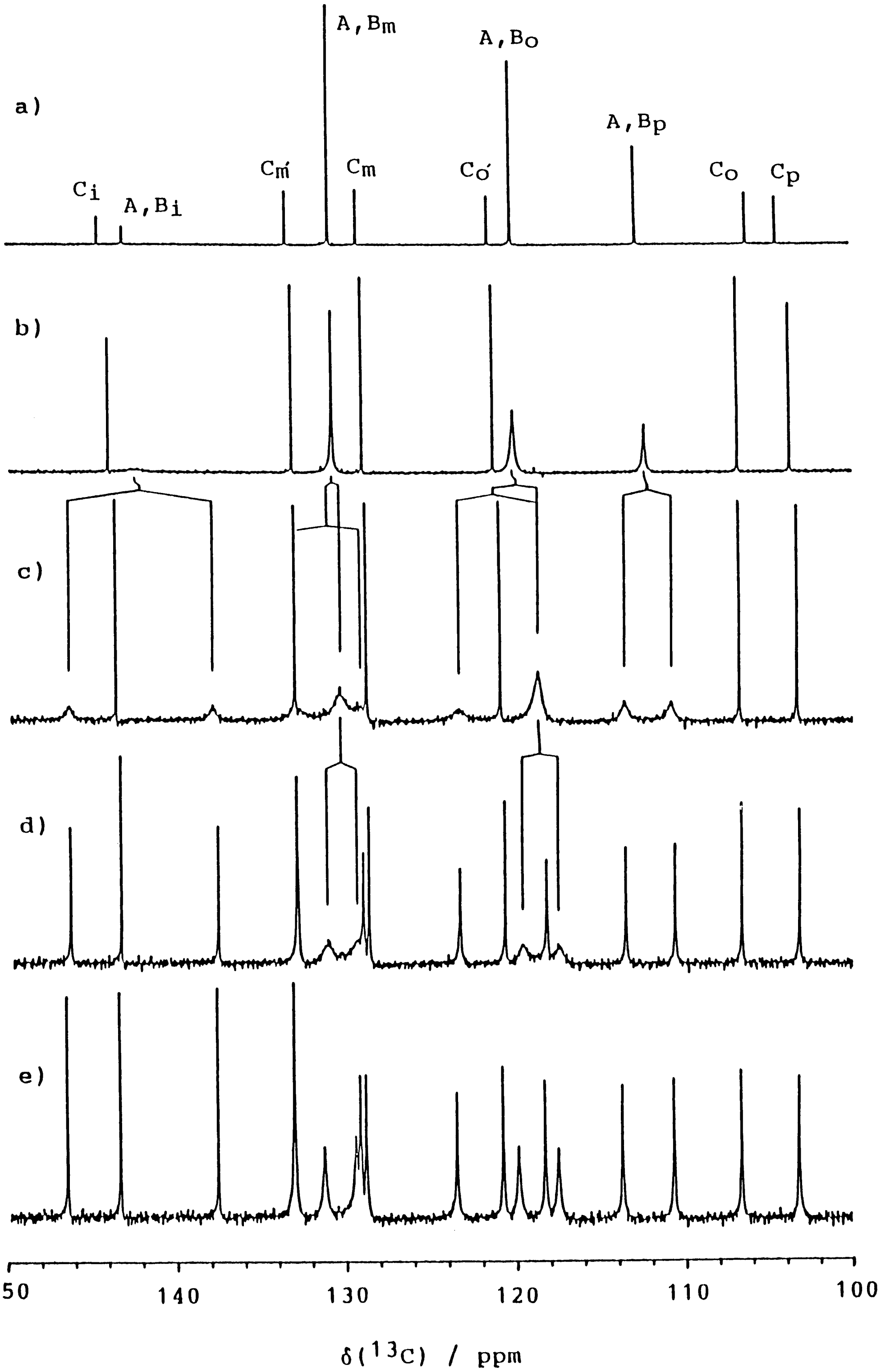


Fig. 1. ^{13}C NMR spectral changes of triphenylethylene dianion in diethyl ether at 100 MHz. (a) At 27.0 ℃, (b) at -30.0 ℃, (c) at -70.3 ℃, (d) at -90.3 ℃, (e) at -100.3 ℃.

Table 1. ^{13}C Chemical Shifts of Triphenylethylene Dianion at 100 MHz[a)]

Temp.	A and B[b)]					C[b)]				
℃	ipso	ortho	meta	para	α	ipso	ortho	meta	para	α'
27.0	143.17	120.27	131.01	112.95	75.67	144.68	106.46 121.64	129.39 133.53	104.69	60.95
-100.3	137.57	118.32 123.49	129.15 133.01	110.69	75.96	143.28	106.69 120.79	128.79 133.01	103.22	60.67
	146.42	117.54 119.89	129.43 131.29	113.74						

a) The chemical shifts were measured for ca. 0.3 mol dm^{-3} solution in diethyl ether relative to the more shielded residual solvent peak, which is taken as 17.10 ppm from TMS. b) See Scheme 1.

have been reported concerning rotations about a benzylic carbon-to-phenyl bond, such as R4 in carbanions.[1)]

When the temperature was lowered, each signal of ring A and B split into two or four, as shown in Fig. 1c-e. The chemical shifts obtained at 27 ℃ and -100.3 ℃ are given in Table 1. These spectral changes are explained by the rotational motions R1, R2 and R3.

^{13}C signals of the geminal phenyl rings, A and B split into two at ca. -60 ℃. Simultaneously, the signals of ortho and meta in one of the geminal phenyl rings (say ring A) split into two. However, those of the ring B remained broad single lines, indicating that the ring was rotating. Therefore, below -60 ℃ two geminal phenyl rings are not magnetically equivalent and have different rotational rates. The cause of the nonequivalence is attributed to the presence of the phenyl ring C and to the hindered rotation about the C_{α}-$C_{\alpha'}$ bond, which is denoted as R3 in Scheme 1.

The signals of ortho and meta carbons in the ring B split into two each at ca. -85 ℃. Although all carbon signals of three phenyl rings were observed as expected for a frozen conformer, those of ortho and meta in the ring B were slightly broad, and the intensities were small as compared with those of other signals at -100.3 ℃ in Fig. 1e. Thus, the ring B may still rotate very slowly even at -100.3 ℃.

The temperature-dependent ^{13}C NMR spectra were analyzed as a simple two-site exchange problem.[1c,2)] The thermodynamic parameters determined for the motion R3 are E_a = 41.7 ± 0.4 kJ mol^{-1}, log A = 29.8 ± 0.2, $\Delta H^{\ddagger}$ =

39.9 ± 0.4 kJ mol^{-1}, and $\Delta S^{\ddagger} = -3.1 \pm 2.0$ J K^{-1} mol^{-1}. While, the rotational barriers $\Delta G_c^{\ddagger}$ for the motions R1, R2, and R3 were estimated from the coalescence temperatures and measured values of the difference of chemical shifts in Hz; they are 36, 39, and 40 kJ mol^{-1}, respectively. The barriers of the geminal phenyl rotation is smaller than those observed for tetraphenylethylene dianion3) and diphenylmethanide ions,4) but larger than those for 1,1-di-p-tolylethylene dimer dianion.5) The activation parameters of internal motion about the C_{α}-$C_{\alpha'}$ bond such as R3, has never been determined by NMR spectroscopy in dianions which were produced from stilbenes.1a,b,3) It is pointed out that the barrier to R3 is similar to that to the restricted rotation about the sp^2-sp^3 bond in 1,1-di-p-tolylpropene dimer dianion, although frequency factor and activation entropy are much different.5)

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2) The activation parameters for the rotational motion R3 were obtained by Arrhenius and Eyring Plots which based on total line-shape analysis. Those of R1 and R2 could not be done rigorously due to signal overlapping.

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