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The ^{1}H and ^{13}C NMR of the Tetraphenylcyclopentadienone Dianion

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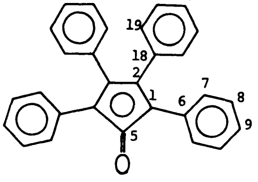
Synopsis. The stable monomer dianion of the title compound was formed by the contact of its tetrahydrofuran-d_8 or 1,2-dimethoxyethane-d_{10} solution with sodium metal at 5 °C and was characterized by means of its ^{1}H and ^{13}C NMR spectra.

It has been known that the alkali metal salts of aromatic ketyls ($A^{\bar{\cdot}}M^{+}$) generated by alkali-metal reduction in an ethereal solvent tend to change competitively to a diamagnetic dimer dianion ($A_2^{2-}2M^{+}$) and a diamagnetic monomer dianion ($A^{2-}2M^{+}$) via a paramagnetic ketyl dimer $(A^{\bar{\cdot}}M^{+})_2$[1)] and that the latter change is dominant in 2-methyltetrahydrofuran, generally causing a pronounced ion pairing with alkali metal.[1a)] Recently, the monomer dianion of fluorenone has been precisely investigated by means of NMR in our laboratory.[2)] We wish to report here on the monomer dianion of sterically hindered tetraphenylcyclopentadienone (**1**).



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Experimental

Compound **1** (Aldrich Co., Ltd.) was used without further purification. Tetrahydrofuran(THF)-d_8 and 1,2-dimethoxyethane(DME)-d_{10} (Canada MSD Co., Ltd.) used as the solvents were dried, degassed, and stored over sodium/potassium in vacuo. 0.2 mol dm^{-3} THF-d_8 and DME-d_{10} solutions of **1** were in contact with a clean sodium mirror in high vacuum at 5 °C in a Pyrex cell fused with an NMR tube. The ^{1}H NMR spectra were measured on JEOL GX-400 (400 MHz) and Varian XL-200 (200 MHz), and the ^{13}C NMR spectra on JEOL FX-90Q (22.5 MHz) and Varian VXR-300 (75 MHz) at room temperature. The ESR and ENDOR spectra were observed on JEOL JES-FE1XG and Varian E-1700, respectively in order to confirm the disappearance of the ketyl radical of **1**. The MO calculation of the charge density was performed on HITAC M-240H at Ibaraki University, the program used for the CNDO calculation being Y4CB04[3)] in the library programs of the University of Tokyo.

Results and Discussion

The contact of **1** with sodium in THF-d_8 or DME-d_{10} gave first a reddish-purple species revealing an ESR and an ENDOR spectra, which can be identified with the radical anion of **1**.[4)] Upon continued contact, it gradually turned orange, the ESR signal of $\mathbf{1}^{\bar{\cdot}}$ disappeared, and a new NMR spectrum developed simultaneously. The ^{1}H and ^{13}C NMR spectra of this new diamagnetic species **1a**, as observed in THF-d_8 after complete reduction, are shown in Figs. 1 and 2 respectively, along with those of **1**. The addition of a reducible aromatic compound, 2-nitroacetophenone, to **1a** led to the ESR spectrum of the radical anion of this compound, while the quenching of **1a** with oxygen gas regenerated **1**. The ^{1}H spectrum of **1a** consists of two sets of AA′BB′C patterns separated from each other; they can be clearly distinguished in terms of the H-H shift correlation 2D NMR, and its spectral center of gravity shifts toward a field higher by 0.29 ppm than that of **1** (Table 1). The observed number of lines in the ^{13}C spectrum of **1a** is equal to that in **1**; furthermore, a line with a particularly weak intensity is included, as in **1**. Its center of gravity was found to shift toward a field higher by 5.73 ppm than that of **1**. The fact that both the ^{1}H and ^{13}C NMR patterns of the orange species produced in THF are completely identical with those in THF-d_8 implies that **1a** does not arise from a possible diamagnetic anion formed by the subtraction of a proton from the solvent. The ^{13}C line with a particularly weak intensity appears at a field much lower than an aliphatic region, although it shifts toward a considerably higher field than that of **1**. These experimental

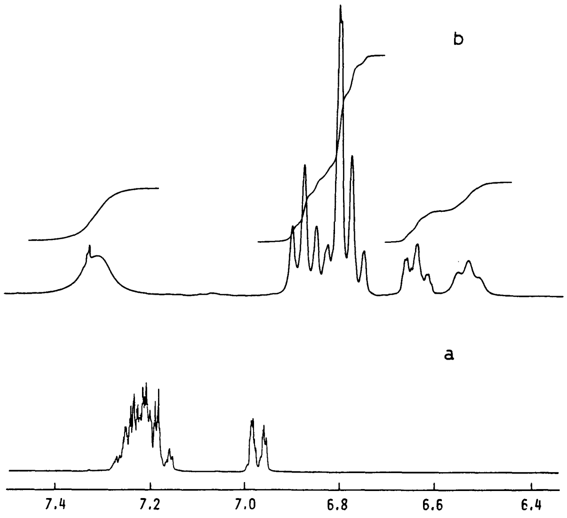

Fig. 1. ^{1}H NMR spectra of **1** (a) (400 MHz) and $\mathbf{1}^{2-}$ (b) (200 MHz) in THF-d_8.

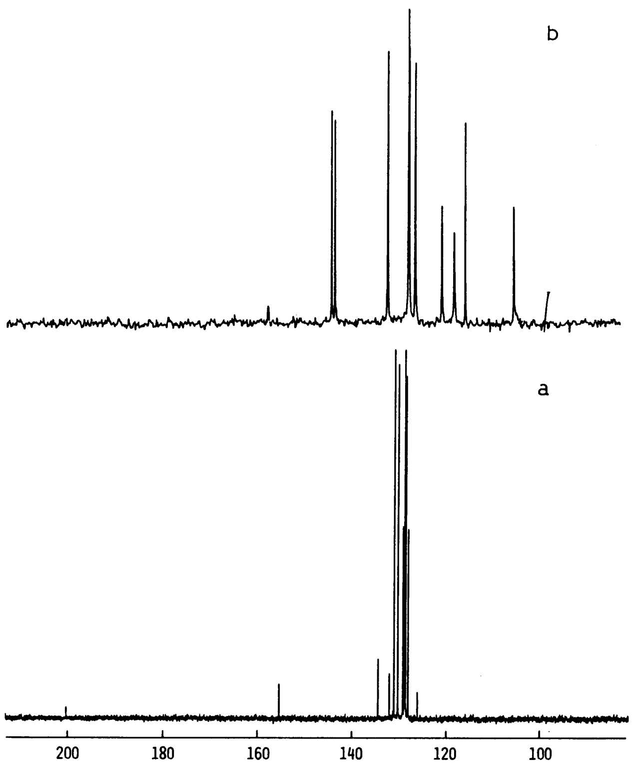

Fig. 2. ^{13}C NMR spectra of **1** (a) (75 MHz) and $\mathbf{1}^{2-}$ (b) (22.5 MHz) in THF-d_8.

Table 1. Chemical Shifts in ppm$^{a)}$

	δ_N	δ_D	$\Delta\delta^{a)}$
H7	7.21±0.05	7.31	−0.01±0.05
8	7.21±0.05	6.88	0.33±0.05
9	7.21±0.05	6.58	0.63±0.05
19	6.98	6.80	0.18
20	7.21±0.05	6.78	0.43±0.05
21	7.21±0.05	6.64	0.57±0.05
C1	126.07	116.16	9.91
2	155.37	105.97	49.40
5	200.20	157.82	42.38
6	134.41	143.68$^{c)}$	−9.27$^{c)}$
7	131.03	128.13	2.90
8	128.59	128.02	0.57
9	129.19	118.54	10.65
18	132.01	144.38$^{c)}$	−12.37$^{c)}$
19	130.21	132.52	−2.31
20	128.83	126.67	2.16
21	128.06	121.09	6.97

a) Relative to TMS. Positive signs denote low-field shifts. δ_N: **1**, δ_D: $\mathbf{1}^{2-}$. b) $\Delta\delta = -(\delta_D - \delta_N)$. c) Assigned tentatively.

results thus show that **1a** can be attributed to a monomer dianion of **1**, $\mathbf{1}^{2-}$, or its disodium salt, $\mathbf{1}^{2-}2Na^+$, and that the formation of a possible pinacolate-type dimer dianion can, therefore, be ruled out.

The higher-field doublet in the ^{1}H NMR of **1** was assigned to H_{19} using lanthanoid-induced shifts due to Eu(fod)$_3$. In the ^{1}H spectrum of $\mathbf{1}^{2-}$ it may be considered that an AA′BB′C group with a much lower-field doublet corresponds to the C_6—C_{11} ring, considering the anisotropic effect of the carbonyl group. The assignment of the ^{13}C spectrum of **1** was that in the literature.$^{5)}$ For $\mathbf{1}^{2-}$, all the tertiary carbons were assigned using the C-H shift correlation 2D NMR combined with proton assignments. C_5 can be distinguished from the other quaternary carbons in terms of its long T_1, as in **1**. The MO calculations by the INDO method$^{6)}$ reveal that most of the excess π-charge densities of $\mathbf{1}^{2-}$ from **1**, Δq_c^π's, occupy the cyclopentadienone moiety; the calculated ^{13}C shifts of $\mathbf{1}^{2-}$ from **1** ($\Delta\delta_c$), estimated using the standard value of k_c, 160 ppm/electron, in $\Delta\delta_c = k_c \cdot \Delta q_c^\pi$, are 19.5, 62.5, and 46.6 ppm for C_1, C_2, and C_5 respectively.$^{7)}$ With the aid of these results, the lines appearing at δ 116.16 and 105.97 were assigned to C_1 and C_2 respectively, while those at δ 144.59 and 143.59 were assigned to C_6 and C_{18}, but C_6 and C_{18} were indistinguishable from each other. Thus, the observed ^{13}C shift pattern of $\mathbf{1}^{2-}$ is, on the whole, consistent with that expected from theoretical considerations.

References

1) a) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964); b) N. Hirota, *ibid.*, **89**, 32 (1967); c) K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *ibid.*, **93**, 6004 (1971); d) T. Takeshita and N. Hirota, *ibid.*, **93**, 6421 (1971).

2) M. Hirayama, H. Suzuki, and H. Ohhata, *Chem. Lett.*, **1987**, 413; M. Hirayama and H. Ohhata, *Bull. Chem. Soc. Jpn.*, **60**, 2751 (1987).

3) This program was prepared on the basis of J. A. Pople, D. C. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968).

4) To be published.

5) L. Knothe and H. Prinzbach, *Liebigs Ann. Chem.*, **1977**, 687.

6) The averaged atomic coordinates from the crystallographic data (J. A. Potenza, R. J. Johnson, R. Chirico, and A. Efraty, *Inorg. Chem.*, **16**, 2354 (1977)) were used.

7) For the phenyl carbons, the pattern of the values of Δδ(calcd) does not correlate well with that of Δδ(obsd). Also, for the ring protons, the values of $\Delta\delta_H$ calculated using k_H=10.7 ppm/electron in $\Delta\delta_H = k_H \cdot \Delta q_c^\pi$ does not correspond well with those of $\Delta\delta_H$(obsd). These results may be accounted for by the fact that the polarization effect of the excess π-charge density at a carbon atom on the ^{1}H or ^{13}C shift does not become predominant over some other contributions to the ^{1}H or ^{13}C shift of the dianion from its neutral precursor, for the excess π-charges in the phenyl rings decrease considerably because of the very weak π-conjugation between the cyclopentadienyl and phenyl rings.