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Evidence for the Formation of π-Dianions of 9-Fluorenone and 10,11-Dihydro-5H-dibenzo[a,d]cyclohepten-5-one from ^{1}H NMR and CNDO Charge Distributions

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It was demonstrated on the basis of reactivity, ^{1}H NMR and CNDO charge distributions that the π-dianions of 9-fluorenone and 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one were formed from the corresponding neutral precursors in contact with sodium or potassium in dimethoxyethane or tetrahydrofuran at low temperature in vacuo.

It has been known that a lot of stable π-dianions of polynuclear aromatic hydrocarbons are formed by the reduction with alkali metal in an aprotic solvent,$^{1)}$ while in the π-systems having hetero atoms, oxygen or nitrogen, or electron withdrawing substituents the detailed investigations on the charge distributions of π-dianions have scarcely been performed due to its instability, although a large number of dianions has been detected as a transient reaction intermediate. Some of these were thought to be stabilized due to the ion-pairing effect with alkali metal ions.$^{2)}$

In this article, we want to demonstrate that the very stable π-dianions were formed from several aromatic ketones in contact with an alkali metal in an aprotic solvent at low temperature in vacuo: 9-fluorenone (**1**) and 10,11-dihydro-5H-dibenzo-[a,d]cyclohepten-5-one (**2**). It is well known that under such a condition the ion-pair of ketyl radical with an alkali metal ion is generally formed. However, the π-dianions of aromatic ketones have not so far been investigated systematically, although a presumed π-dianion of **1** has been utilized as a reaction intermediate.$^{3)}$

In **1** the green solution was obtained via the paramagnetic reddish-yellow one$^{4)}$ in contact with sodium in 1,2-dimethoxyethane (DME) for about 5 days at -10 °C in vacuo and in **2** the purple solution via the paramagnetic blue one$^{5)}$ in DME or tetrahydrofuran (THF) with sodium or potassium for about 10 days at -10 °C in vacuo. These new diamagnetic species were very stable even at room temperature and gave a well-separated ^{1}H NMR spectrum consisting of two doublets and two triplets in the aromatic region, respectively, which appeared on the whole at high-fields from those of the neutral precursor. (Figs. 1 and 2) The ^{1}H shifts relative to those of the neutral molecule are listed in Table 1. When the resulting solution was separated from metal at the stage of one-electron reduction, the color of this radical solution remained further unaltered. This may indicate that a disproportionation equilibrium between the radical anions might not lie considerably to the dianion side even if this equilibrium actually occurred in these solutions.

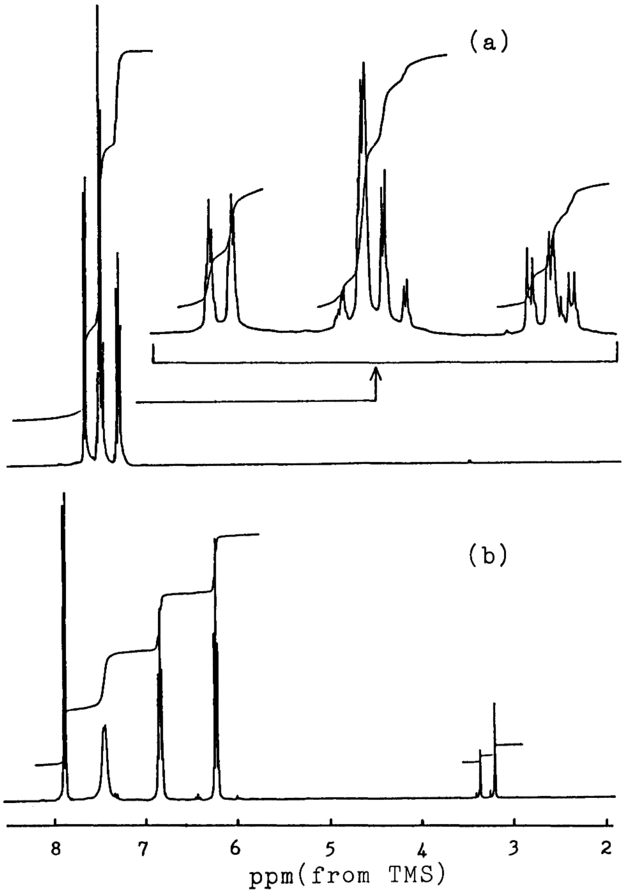


Fig. 1. ^{1}H NMR spectra (300 MHz) of **1** in $CDCl_3$ (a) and of its dianion formed with Na in DME-d_{10} (b). In b, the high-field one of two doublets is considerably broadened by the spin exchange with a slight amount of ketyl radical.

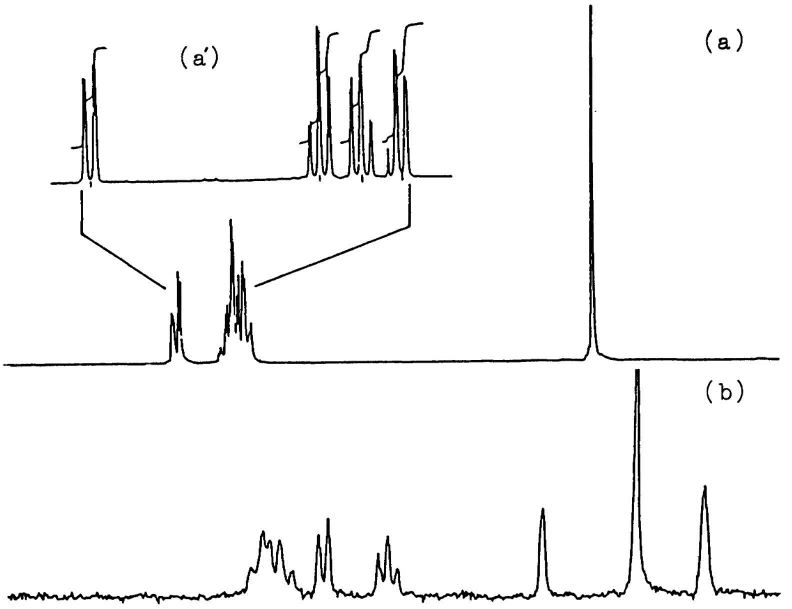
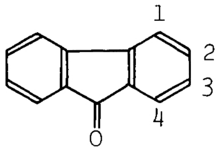
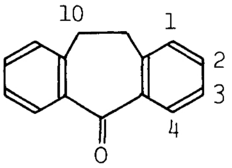


Fig. 2. ^{1}H NMR spectra of **2** in $CDCl_3$ measured at 80 MHz (a) and at 300 MHz (a'), and of its dianion formed with Na in THF-d_8 measured at 80 MHz (b).

Table 1. The changes of ^{1}H shifts and CNDO charge densities from the neutral to dianion molecule

	Position	δ_N [a]	δ_D [a]	$\Delta\delta$ [b]	Δq_{1s} [c]	$\Delta q_{1s}\cdot k_H$
1 	1	7.51	7.89	-0.38	0.0725	1.29
	2	7.49	6.24	1.25	0.0844	1.50
	3	7.29	6.84	0.45	0.0820	1.46
	4	7.66	7.46	0.20	0.0766	1.36
2 	1	7.22	6.20	1.02	0.0740	1.32
	2	7.43	5.45	1.98	0.0747	1.33
	3	7.33	6.69	0.64	0.0468	0.83
	4	8.01	6.95	1.06	0.0893	1.59
	10	3.20	2.57	0.63	0.0516	0.92

a) ^{1}H shifts were measured in ppm at 300 MHz except for the dianion of 2 at 80 MHz. All the shifts were determined relative to TMS. Positive signs denote low-field shift. δ_N are shifts in $CDCl_3$ for the neutral molecule and δ_D for the dianion formed by Na-reduction in DME-d_{10} (1) or THF-d_8 (2). Assignment of the neutral molecule of 1 was made by Ref. 6 and of 2 by the combination of 2D-NMR (the correlation between ^{1}H and ^{13}C shifts) and ^{13}C signals assigned already.7) Assignments of the dianions of 1 and 2 were made using the line broadening in ESR by spin exchange with the corresponding radical anion.

b) $\Delta\delta = \delta_N - \delta_D$.

c) The program Y4CB04 was used, which is one of the library programs collected in the Computer Center of the University of Tokyo and was prepared on the basis of Ref. 8. Atomic coordinates obtained from the X-ray crystallographic data were used after averaged.9,10) $\Delta q_{1s} = q_{1s}(D) - q_{1s}(N)$.

Introduction of oxygen into these new solutions resulted in a perfect recovery of precursor, respectively, while the addition of water in vacuo led to the formation of fluorenol for 1 and also of a corresponding alcohol for 2. These results were confirmed with deuterium oxide. Furthermore, the addition of a reducible aromatic compound, methyl m-nitrobenzoate, in vacuo gave the ESR spectrum of the anion radical of this compound in all the cases studied here. It may be said that if these new species were a pinacolate-type compound (a dimer dianion) such a one-electron reduction should not occur. Thus, a possibility of formation of a dimer dianion can be ruled out on the basis of this experimental result. After the formation of new species in THF or DME, the solvent was removed by distillation, the residue was solved in DME-d_{10} or THF-d_8 and its ^{1}H NMR was measured. No other signals expected from a pure π-dianion were observed in the resulting spectra. It may be reasonable to consider that this fact indicates that a possible abstraction of a proton from the solvent doesn't occur in any case studied here. It may be thus determined that these new diamagnetic species are π-dianions which can be treated as those with two excess π-electrons in its lowest vacant π-MO.

In order to confirm this conclusion, the changes of charge densities on going from the neutral to dianion molecule, Δq, were calculated using the CNDO method.8) The charge-induced ^{1}H shifts were estimated from the excess charge density at the 1s orbital of hydrogen.11) A value of 17.8 ppm/electron obtained simply from the character of a hydrogen 1s orbital was tentatively taken as the proportionarity constant k_H in the relation $\Delta\delta = k_H \cdot \Delta q_{1s}$. As shown in Table 1, in both **1** and **2** the amounts of high-field shifts are fairly larger in most protons than those of experimental ones. As reported in detail previously,5) the spin density distribution of ketyl radical is in general affected considerably by the ion-pairing effect of an alkali metal ion. From the analogy with this effect, it may be anticipated in the present system that a redistribution of charge densities occur due to a strong interaction of sodium ions to the carbonyl group. It is considered that this effect is predominantly responsible for the observed shifts extremely larger than the calculated ones on the overall ring. Thus, the above decision of formation of dianion disodium salts may be supported also by the calculated charge densities. A detailed discussion of the treatment of an alkali metal ion in CNDO calculations is in progress.

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11) Although ^1H shifts have generally been estimated from q_{2pz} at a carbon, which is attached to the proton, using the polarization mechanism,12) it may be considered that its direct estimation from q_{1s} is better than that from q_{2pz}, if the value of q_{1s} is precisely obtained.
Since it is thought that the two excess π-electrons in LUMO (antibonding MO) doesn't contribute to the ring current effect,13) no correction for this effect was made on the observed Δδ values when compared with the theoretical values. Furthermore, a possible difference of bond anisotropy of the carbonyl group between the neutral and dianion molecules was not taken into account on these comparisons.
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