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Fluorenone Monomer Dianion Studied by ^{1}H and ^{13}C NMR and Charge Density Distribution

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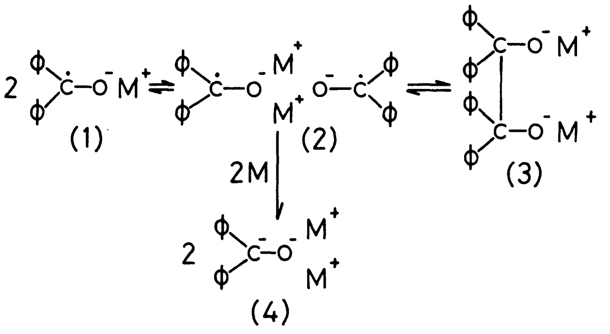
The diamagnetic monomer dianion of fluorenone was prepared from 1,2-dimethoxyethane solution of neutral molecule in contact with excess sodium metal at −5 °C for 5 days and its ^{1}H and ^{13}C NMR spectra were measured. The possibility that a pinacolate-type dimer dianion occurs in an equilibrium system was ruled out from reactivity with oxygen, water, deuterium oxide, and reducible aromatics in addition to the analysis of NMR spectra. The charge density distribution of neutral and dianion molecules was estimated by MO calculations. Comparison between experimental and theoretical ^{13}C shifts suggested a strong interaction of sodium ions with carbonyl group. It is presumed that an anormalous diamagnetic ring current in 14π-peripheral structure is responsible for poor correlation between theoretical and observed ^{1}H shifts.

It was demonstrated by Hirota et al.[1] from ESR and optical measurements that when aromatic ketones (fluorenone, benzophenone, and xanthone) were in contact with alkali metal in a dilute solution, a ketyl monomer (**1**) and a paramagnetic ketyl dimer (**2**) mainly coexisted in equilibrium in an etherial solvent, while in a nonpolar solvent there mainly existed an equilibrium between **2** and a diamagnetic ketyl dimer (**3**). These authors further studied in detail ion-pair structures of **1** and **2** and the equilibrium between **1** and **2**.[2] On the other hand, Herold et al. discussed in detail the substituent effect on the spin density distribution (or hfs patterns) of free anion radical and sodium ketyl of fluorenone by means of ENDOR technique and ESR.[3] Hirota et al. further proposed from optical spectra that when fluorenone of approximately 10^{-2} mol dm^{-3} was in contact with excess sodium in 2-methyltetrahydrofuran (2MTHF) **2** was further reduced into diamagnetic monomer dianion (**4**)[1a] and the concentration of **3** was extremely small.



A direct evidence for the occurrence of **3** and **4** has been required, because their existence was proposed only indirectly by optical measurements. Although the best method to identify a diamagnetic species in solution will be NMR analysis, it seems that NMR measurement of these systems at high-resolution is difficult due to line broadening by fast spin exchange between diamagnetic species and paramagnetic ketyl monomer or dimer. Moreover, it is difficult to discuss the same equilibrium state as that for optical measurements by NMR method, which requires a much higher concentration of species than that in optical measurements.

The present paper demonstrates that a diamagnetic green species formed from fluorenone and excess sodium metal in 0.15 mol dm^{-3} 1,2-dimethoxyethane (DME) solution is ascribed to its monomer dianion (**4**) on the basis of ^{1}H and ^{13}C NMR spectra and calculated electron density distribution.[4]

Experimental

Fluorenone was contacted with sodium metal in DME-d_{10} in high vacuum by standard technique for preparing hydrocarbon anion radicals. Fluorenone (Tokyo Kasei Co. Ltd.) was used without further purification. DME-d_{10} (Canada MSD Co. Ltd.) was dried, degassed, and stored over sodium/potassium alloy in vacuo. 0.6 ml of DME-d_{10} was transferred into an NMR tube containing 10 mg of fluorenone at its bottom and connecting with a high-vacuum line. Sodium mirror was previously made in the upper part of the sample tube, so that the solution could be in contact with metal even after the sample tube was cut off from the vacuum line. The solution was contacted with sodium mirror by turning upside down the sealed tube. ^{1}H and ^{13}C NMR spectra were measured on Varian VXR-300 at 300 MHz on the FT mode. ESR spectra were measured on JEOL JES-FE1XG, in order to confirm the disappearance of anion radical. The MO calculation of charge density was performed on HITAC M-240H at Ibaraki University, the program used for the CNDO calculation being Y4CB04[5] in library programs of the University of Tokyo.

Results and Discussion

The color of fluorenone solution in DME-d_{10} changed to reddish-yellow immediately after contact with sodium at −5 °C. The resulting solution gave a well-resolved ESR spectrum of sodium fluorenide after dilution. The ESR signal gradually disappeared upon continued contact, and the color of the solution turned to green. Several new lines gradually grew up in ^{1}H NMR spectrum. This green species was stable even at room temperature for several days. ^{1}H and ^{13}C NMR spectra observed after 5 days of contact are shown in

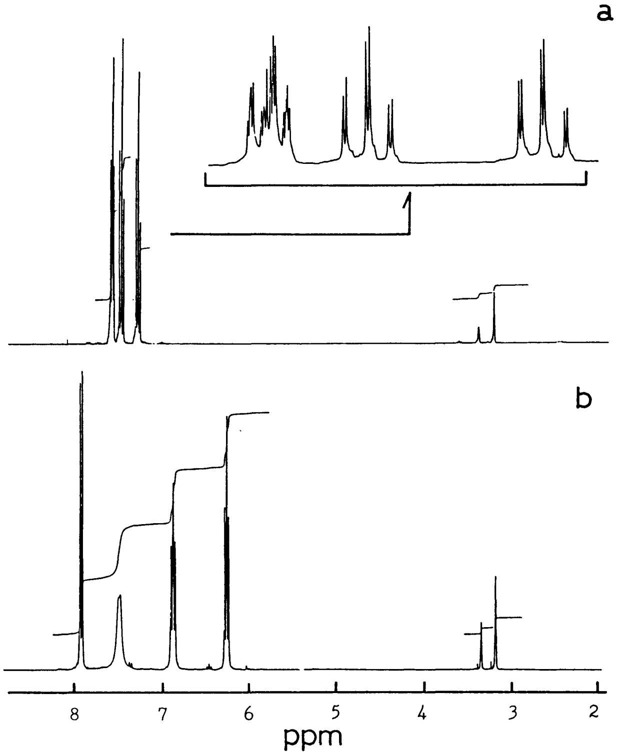


Fig. 1. ^{1}H NMR spectra (300 MHz) of fluorenone in DME-d_{10} (a) and of the diamagnetic green species formed by sodium reduction in DME-d_{10} (b). In (b), the high-field one of two doublets is considerably broadened by the spin exchange with a slight amount of the fluorenone ketyl.

Figs. 1 and 2, respectively, together with that of the precursor. The ^{1}H spectrum consisted of two triplets and two doublets which were separated well. Its center of gravity shifted toward higher field by 0.39 ppm than that of neutral molecule. The pattern of ^{13}C spectrum of this species was identical with that of neutral molecule, suggesting that the spectrum arises from four carbons bonded to a hydrogen and three quaternary carbons, one of which has particularly long T_1. The high-field shift of center of gravity in ^{13}C spectrum was 20.9 ppm relative to that in neutral molecule.

The assignment of ^{1}H and ^{13}C spectra of neutral molecule was made by literature,7) which was confirmed here by the H–C shift correlation 2D NMR (Fig. 3). For the green species, the smallest ^{13}C line was assigned to C_9 by its very large T_1. This is consistent with the intramolecular distribution of calculated excess charge density of a monomer dianion mentioned later. The residual two carbon lines with weak intensity were assigned to C_{10} and C_{11} due to their long T_1 values, the higher-field one being tentatively assigned to C_{10} by the comparison of observed shifts with excess charge density of the dianion. In the ^{1}H spectrum, the line at a higher field of two doublets became much broader than the other in the existence of a small amount of ketyl radical. This is considered to be due to an electron spin exchange between diamagnetic green species and paramagnetic ketyl. From the fact that the hfs constant a_1^{H} is much larger than a_4^{H},3) the higher-field doublet could be assigned to H_1, and the lower-field one to H_4. The lower-field triplet was assigned to H_2 using the same technique. The assignment of four ring carbons was made by combining the above ^{1}H assignment with the 2D correlation NMR between ^{1}H and ^{13}C shifts (Fig. 4). The results are listed in Table 1.

By introducing oxygen into this green solution fluorenone was regenerated. Contacting this solution with a reducible aromatics, methyl *m*-nitrobenzoate, in vacuo, gave ESR of sodium salt of anion radical of this compound. From these experimental results, it may be reasonable to determine that a pinacolate-type compound (diamagnetic ketyl dimer, **3**) is not formed by bonding between ketyl monomers. It was further confirmed by analysing ^{1}H and ^{13}C NMR that addition of water to this species in oxygen-free conditions gave 9-fluorenol and that deuterium oxide treatment gave the corresponding deuterated 9-fluorenol. This result supports the assumption that dimer dianion is not formed. This is also consistent with the fact that C_9 appeared at much lower field than that of pinacol. It can thus be said that an adequate evidence for the formation of diamagnetic monomer dianion (**4**) was obtained. As seen from Figs. 1 and 2, no other diamagnetic species were observed from this green solution and line broadening completely disappeared during contact with sodium metal. Monomer dianion (**4**) is the final product at a high concentration (1.5×10^{-1} mol dm^{-3}) by complete reduction with excess sodium in etherial solvent, similarly as the reduction at a low concentration (4×10^{-2}—5×10^{-3} mol dm^{-3}) in 2MTHF discussed by Hirota et al.1a) A direct formation of **4** from **1** may be expected in the present system in DME in addition to the process through **2**, from larger dissociation constant in $\mathbf{2}\rightleftarrows\mathbf{2}\cdot\mathbf{1}$ in DME than that in 2MTHF.1a) One may expect that monomer dianion observed here is of an ion pair form $A^{=}2M^{+}$ or solvated ion pair $A^{=}2M^{+}(S)_n$, where A and S are fluorenone and solvent, respectively, but not of a solvent-separated ion pair $A^{=}(S)_n2M^{+}$,8) from analogy with the ion pair structures of monomer ketyl proposed by Hirota et al.2a)

Reduction of fluorenone with excess sodium or potassium metal in THF also gave the green species, which was insoluble in THF and precipitated. On the reduction with potassium in DME, paramagnetic reddish-yellow solution initially formed did not change to green even after a long time. These results are consistent with the order of solvation power of solvents for alkali metals, DME>THF. It may be considered that the ionic interaction between ion pairs, $A^{=}2Na^{+}$, is so strong as to overcome solvation of THF to $A^{=}2Na^{+}$, while the ionic interaction between ion pairs $A^{\bar{\cdot}}Na^{+}$ is relatively weaker than solvation power of THF to $A^{\bar{\cdot}}Na^{+}$. The ionic bonding of potassium

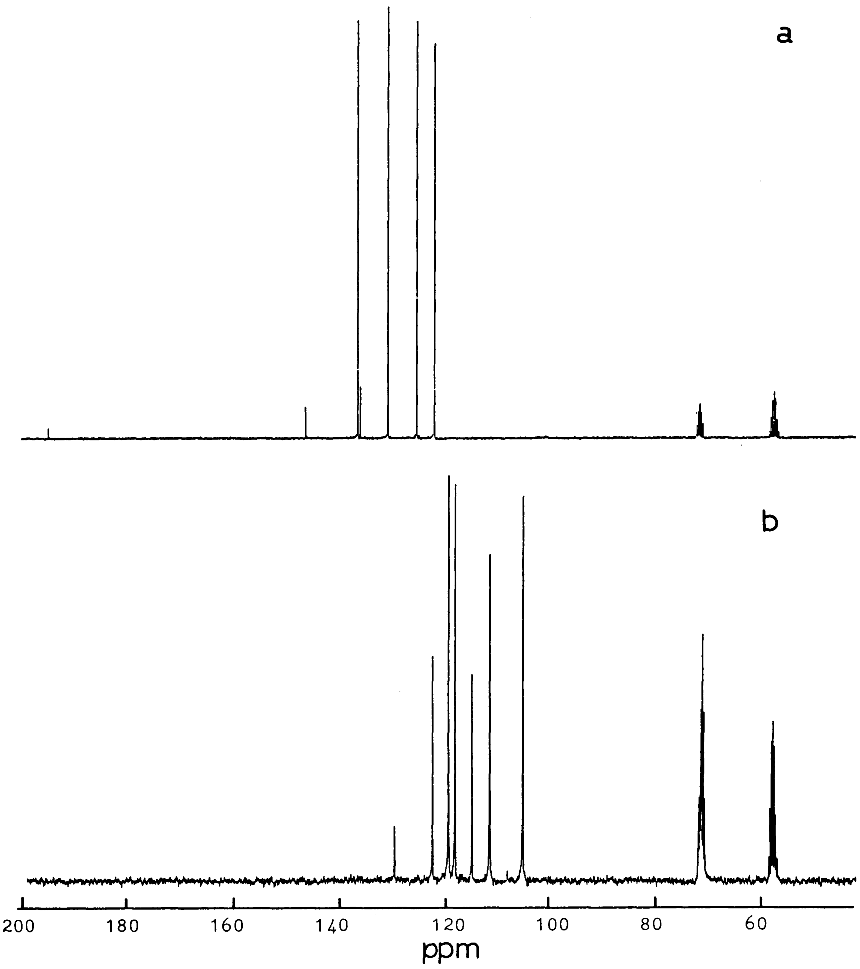


Fig. 2. ^{13}C NMR spectra (75 MHz) of fluorenone in DME-d_{10} (a) and of the diamagnetic green species formed by sodium reduction in DME-d_{10} (b).

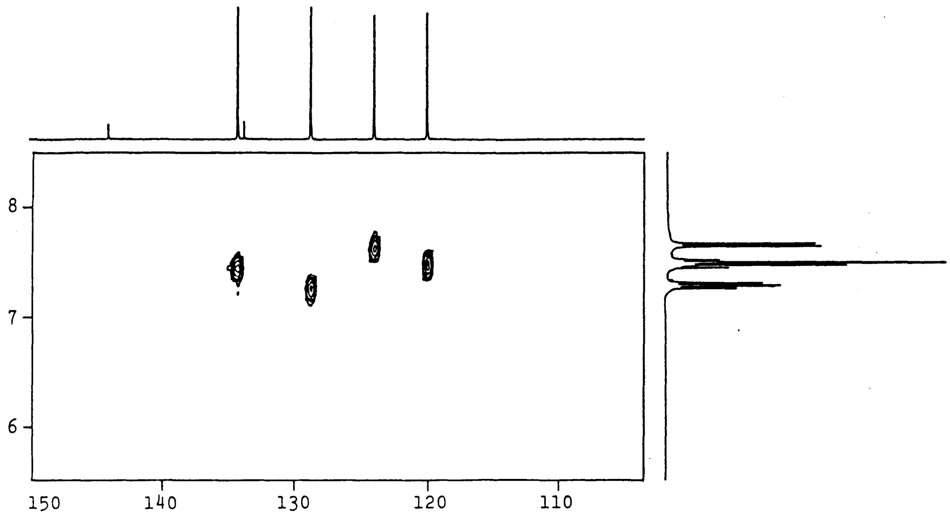


Fig. 3. ^{1}H–^{13}C shift correlation 2D NMR spectrum of fluorenone in CDCl$_3$.

ion to the carbonyl group (perhaps a carbonyl oxygen) is generally considered to be weaker than that of sodium ion owing to the difference in ionic radius. This may explain the experimental result that an ion pair structure $A^{=}2K^{+}$ doesn't exist as a stable species in DME, but exists in THF of which solvation power is weaker than that of DME.

Several workers have previously noted a linear relationship between proton chemical shift $\Delta\delta_H$ and excess local π-charge density at a carbon bonded to proton, Δq_C^{π}, according to the formula,[9] $\Delta\delta_H = k_H \cdot \Delta q_C^{\pi}$. The gradient k_H amounts to 10.7 ppm per unit charge. A

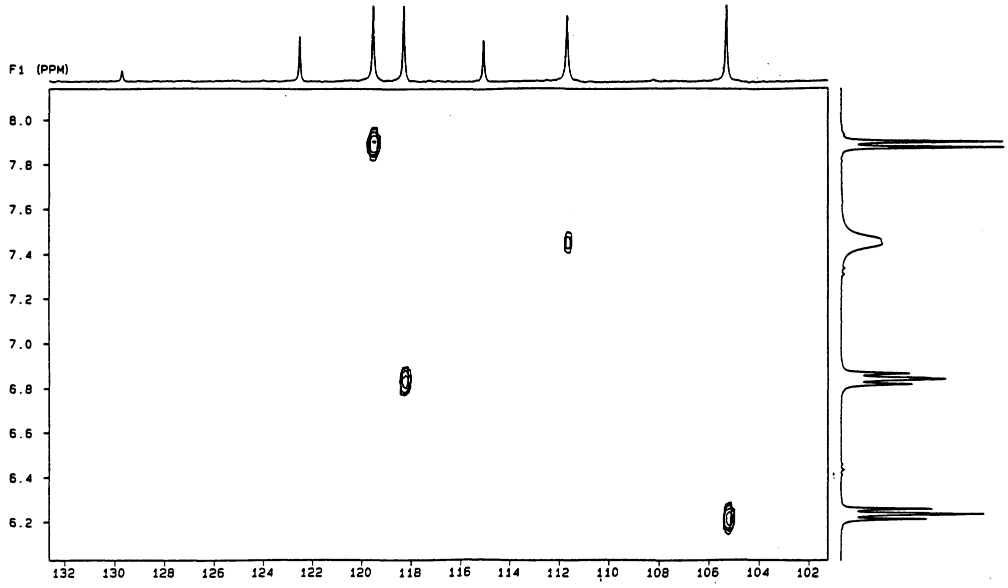
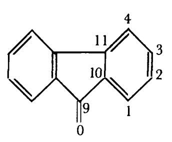


Fig. 4. ^1H–^{13}C shift correlation 2D NMR spectrum of the green species formed by sodium reduction in DME-d_{10}.

Table 1. Observed ^1H and ^{13}C Chemical Shifts

		δ_N [a]	δ_D [a]	$\Delta\delta$ [b]
	H_1	7.60	7.46	0.14
	H_2	7.30	6.84	0.46
	H_3	7.49	6.24	1.25
	H_4	7.59	7.89	−0.30
	C_1	124.53	111.69	12.84
	C_2	129.86	118.29	11.57
	C_3	135.41	105.31	30.10
	C_4	121.25	119.51	1.74
	C_9	193.38	129.70	63.68
	C_{10}	134.90	115.09	19.81
	C_{11}	145.17	122.53	22.64

a) In ppm relative to TMS. All chemical shifts were determined relative to the high-field multiplet of DME. (3.22 ppm from TMS for ^1H and 57.8 ppm from TMS for ^{13}C.) b) Shifts of dianion relative to those of neutral molecule. (Positive signs denote high-field shifts. $\Delta\delta_{obsd} = -(\delta_D - \delta_N)$.)

similar correlation, $\Delta\delta_C = k_C \cdot \Delta q_C^\pi$, was later found for ^{13}C chemical shifts with $k_C \approx 160$ ppm per electron.[10] Although one should be aware that such empirical dependence of δ_H and δ_C on charge density has no firm theoretical foundation, such relations are applicable to the closely related compounds, provided that one accounts for ion pairing, ring current effect, and magnetic anisotropy of neighboring atoms or substituent groups. The neutral precursor was used as a reference of shift (Table 1)[11] for estimating charge-induced shifts ($\Delta\delta_{obsed}$), and these three effects were considered as follows. It has been predicted from theoretical consideration that two excess electrons in the lowest vacant π-orbital of dianion doesn't contribute to the ring current.[12] The ^{13}C chemical shift is particularly insensitive to ring-current effect as long as carbons are within a π-periphery. No correction of the observed shifts for ring current effect was, therefore, applied for comparing the observed shifts with calculated ones. Although the anisotropy of carbonyl bond in dianion is different from that of neutral molecule, the difference may be ignored as a small correction of charge-induced shifts for all the protons and carbons except for C_9. The ^1H and ^{13}C chemical shifts of π-dianion may be affected by ion pairing effect of counter ions, as will be mentioned later.

The charge density on carbon 2pz orbitals, q_{2pz}, was calculated by both the CNDO[6] and semi-empirical SCF π-MO (PPP) methods. The averaged crystallographic data[13] were used for geometric parameters. The changes of π-charge Δq_{2pz} and calculated shift $\Delta\delta$ on going from the neutral molecule to dianion are listed in Table 2 together with the corresponding observed changes of δ_H and δ_C. It is found that the $\Delta\delta$(obsd) pattern of ^{13}C correlates, though roughly, with those of $\Delta\delta$(calcd) estimated by both the CNDO and PPP methods. However, the comparison between observed and theoretical shifts at each position showed very poor agreement: At C_9 $\Delta\delta$(obsd) is extraordinarily larger than $\Delta\delta$(calcd), at C_1 larger, at C_3 slightly smaller, at C_2 very smaller, and at C_4 the comparison was vague, because the theoretical values obtained from CNDO and PPP are widely different. For fluorenone ketyl, the ion-pair effect on electron-spin-density distribution has successfully been explained by INDO calculations.[14] Also for the present dianion, the ionic bonding of sodium ions to carbonyl group may affect largely the shift pattern. Then, in order to make a rough estimate of the change of $\Delta\delta$(calcd) pattern caused by ion pairing, the dependence of Δq_{2pz} on the Coulomb integral parameter of carbonyl oxygen, h_O, was calculated by the Hückel approximation.[15] With

Table 2. Comparisons of Observed and Calculated Differences of ^{1}H and ^{13}C Shifts of Dianion from Those of Neutral Molecule[a)]

	CNDO				PPP		$\Delta\delta_{obsd}$
	Δq_{2pz}[b)]	$\Delta\delta_{calcd}$[c)]	Δq_{1s}[d)]	$\Delta\delta_{calcd}$[e)]	Δq_{2pz}[b)]	$\Delta\delta_{calcd}$[c)]	
H_1		0.34	0.0725	1.21		0.37	0.14
H_2		1.54	0.0844	1.41		2.48	0.46
H_3		2.13	0.0820	1.37		2.16	1.25
H_4		−0.03	0.0766	1.28		0.60	−0.30
C_1	0.0316	5.06			0.0344	5.50	12.84
C_2	0.1441	23.06			0.2321	37.14	11.57
C_3	0.1986	31.78			0.2017	32.27	30.10
C_4	−0.0029	−0.46			0.0564	9.02	1.74
C_9	0.1492	23.87			0.2124	33.98	63.68
C_{10}	0.1262	20.19			0.0717	11.47	19.81
C_{11}	0.1797	28.75			0.1371	21.94	22.64

a) In ppm. See Table 1 for the numbering system. b) Excess charge density at carbon 2pz orbitals in dianion relative to those in neutral molecule. c) Estimated using 10.7 ppm/electron as k_H and 160 ppm/electron as k_C. d) Excess charge density at proton 1s orbitals in dianion relative to those in neutral molecule. e) Estimated using 16.7 ppm/electron as k'_H.

increasing h_O from 1.45, Δq_{2pz} at C_9 considerably increased, at C_1 next largely increased, at C_4 and C_3 slightly increased, at C_2 largely decreased, and at C_{10} and C_{11} almost unchanged. It appears that the result implies the calculated ^{13}C shift pattern changing toward the experimental one and that it suggests formation of strong ionic interaction of sodium ions with carbonyl group. However, the extraordinarily large high-field shift at C_9 will be ascribed to a possible difference of bond anisotropy of carbonyl group in dianion from neutral molecule, in addition to the ion-pair effect. The experimental fact that the shift value of C_9, 129.7 ppm, is much smaller than those of pinacolate-type compounds supports the conclusion that no diamagnetic dimer dianion is formed in the present system. It is generally said that the PPP method explains better the observed ^{13}C shift pattern rather than the CNDO method for hydrocarbon dianions having no hetero atoms or substituents. Since several factors other than charge-induced effect may affect the ^{13}C shift pattern in the present case, it is indefinite which method is more favorable.

As shown in Table 2, ^{1}H $\Delta\delta$(obsd) of dianion is fairly smaller on the overall ring than $\Delta\delta$(calcd) predicted by both methods and its pattern doesn't correlate well with that of ^{13}C $\Delta\delta$(obsd). This allows us to consider that the observed ring proton shifts may contain another effect in addition to the counter ion effect. It may be prossible for polycyclic systems that an anormalous peripheral ring current affects ring proton shifts,[16)] although it doesn't affect the shifts of carbons which are members of the ring itself. One of the most probable structures of fluorenone dianion is that at which one of two excess π-electrons is occupied by C_9. Since this structure has a 14π-periphery, an induced-diamagnetic ring current may be found in the fluorenone dianion. Thus, one may consider that the anormalous ring current is responsible for the decrease in ring proton shifts.

An attempt was made further to calculate $\Delta\delta$ of protons directly from excess charges at proton 1s-orbitals, Δq_{1s}. A value of 16.7 ppm per electron obtained simply from the character of a hydrogen 1s-orbital was used as the proportionality constant k'_H in the relation, $\Delta\delta_H = k_H' \cdot \Delta q_{1s}$. The resulting values of $\Delta\delta_H$ were on the whole larger than $\Delta\delta$(obsd) values as well as those obtained from $\Delta\delta_{2pz}$ and were more uniform through all protons. One must, therefore, depend on the peripheral ring current model.

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15) The CNDO calculation containing sodium atom as a counter ion has tentatively been performed using the atomic parameters of sodium within the Pople's program. However, this attempt resulted in large negative charges on two sodium ions. An attempt is now being made to find some sodium parameters appropriate to explain $\Delta\delta$(obsd).

16) It has been suggested that $4n+2$ polycyclic systems can be treated in terms of their peripheries by considering the cross links as small perturbations.[17] Therefore, the aromatic protons in these systems may undergo an anormalous induced diamagnetic ring current.

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