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A Proton Magnetic Resonance Study of Dialkyl Terephthalate Dianions

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NMR spectra were observed for green solutions formed from dimethyl, diethyl, and diisopropyl terephthalates in contact with sodium metal in THF-d_8 *in vacuo* at ambient probe temperature. A comparison of proton chemical shifts with excess charge densities calculated by the CNDO MO method supports that the green species are disodium salts of π-dianions.

It has been demonstrated by observation of NMR spectra that several unsubstituted aromatic compounds are reduced into their dianions by alkali metal *in vacuo* in aprotic solvent.[1] However, for aromatic compounds containing N- or O-hetero atom and electron-withdrawing substituents, the formation of their dianions has not so far been ascertained, probably because of their instability in solution.

Dimethyl terephthalate (DMTP), when brought into contact with Na metal in THF *in vacuo*, is at first converted into its purple-red anion radical[2] and then into a diamagnetic green species (G-species) within several minutes even if kept separated from Na metal; this species is stable for several months at room temperature even with a high concentration of starting substance of *ca.* 0.5 mol dm^{-3}. Kowata and Koizumi[3] interpreted this phenomenon in terms of UV investigation as follows: The G-species is the disodium salt Na$^+$DMTP^{2-}Na$^+$ of DMTP dianion formed from the sodium salt DMTP$^-$-Na$^+$ of DMTP anion radical by the disproportionation

$$2(\mathrm{DMTP^-\,Na^+}) \rightleftharpoons \mathrm{Na^+\,DMTP^{2-}\,Na^+} + \mathrm{DMTP}.$$

Their interpretation was supported by an experimental result that the G-species has a powerful agency capable of reducing aromatic compounds such as trinitrobenzene stronger in electron affinity than DMTP. We now report ^{1}H NMR spectra successfully observed for this system.

Experimental

DMTP and diethyl terephthalate (DETP) obtained from Tokyo Kasei Kogyo Co. were used after recrystallization from benzene, and diisopropyl tetrephthalate (DPTP) was synthesized from DMTP by the exchange reaction of ester groups. THF-d_8 (Merck Sharp and Dohm Canada Ltd.) was purified by vacuum distillation after contact with Na–K alloy *in vacuo*. ^{1}H NMR spectra were measured on a Hitachi R-20A spectrometer at ambient probe temperature (34 °C) at 60 MHz in a frequency-swept mode. MO calculations were performed on HITAC-8250 at the Computer Center of Ibaraki University and on Hitachi M-200H at the Computer Center of the University of Tokyo. The program used for CNDO MO calculations is Y4CB04[4] from the library programs collected in the Computer Center of the University of Tokyo.

Results and Discussion

A 0.3 mol dm^{-3} THF-d_8 solution of DMTP was kept in contact with Na metal for 10 min *in vacuo* at room temperature and 24 h after separation from the Na metal an NMR spectrum was measured for the resulting green solution, which is shown in Fig. 1a. New resonance lines A′ and B′ appeared at higher-fields of corresponding ring (A) and methyl proton peaks (B) of unreduced DMTP, respectively, and furthermore, the intensity ratio A′/B′ was nearly equal to A/B, hence A′/A≈B′/B. On introducing air into the sample tube, the solution was caused to turn light yellow with formation of a white precipitate and the lines A and B disappeared. When methyl *p*-nitrobenzoate was introduced into the sample tube containing the G-species *in vacuo*, the formation of sodium salt of the anion radical of this ester was confirmed by observation of ESR. Also in the spectra obtained from DETP and DPTP in contact with Na in THF-d_8, the expected higher-field lines corresponding to the neutral molecule were observed and the intensity ratios A′/A, B′/B, and C′/C for ring,

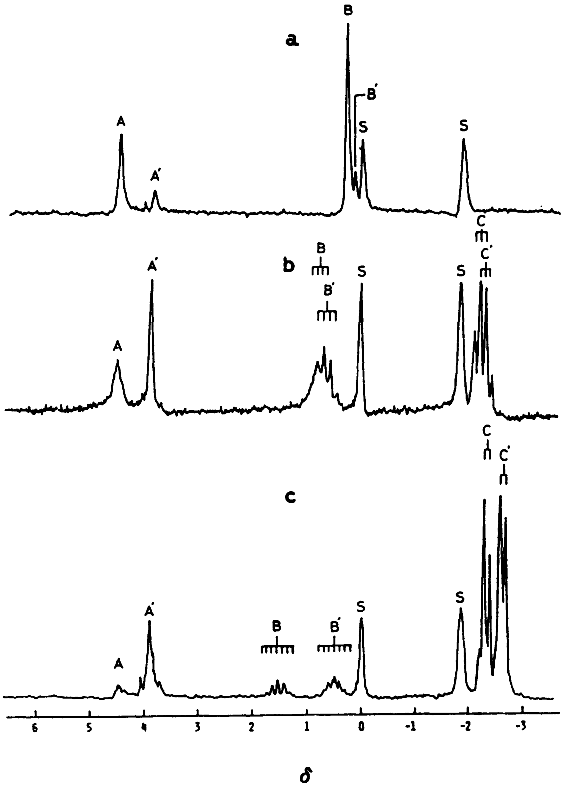

Fig. 1. NMR spectra of the dianion disodium salts of dialkyl terephthalates accompanied by the unreduced neutral molecule in THF-d_8 at 60 MHz and 34 °C. (a) DMTP, (b) DETP, (c) DPTP. The shifts are measured from the lower-shielding peak of THF. A: Ring-H, B: α-H, C: β-H, S: the solvent as an isotopic impurity. The prime letters indicate the dianion peaks.

α-, and β-protons, respectively,[5] were nearly equal to one another for both the systems, except that the intensity of A for DPTP is too small (Figs. 1b and 1c).

With all the samples, for several minutes after separation from Na metal an extensive line broadening was observed only for the peak A and then the line width became gradually sharper, while for the other protons line broadening was negligible due to smaller hfs constants than those of ring protons. These results may suggest that electron spin rapidly exchanges between the neutral molecule and the anion radical sodium salt still remaining owing to slow disproportionation. On the other hand, the line A′ remained sharp under the same conditions and this may then be considered to be ascribed to a very slow exchange of electron spin between the anion radical sodium salt and the G-species in solution.

These features of NMR spectra together with the interpretation of this reaction system based on UV spectra[3] indicate that all the lines denoted by prime letter in Fig. 1 result from dianion disodium salts. This is supported also by the fact that the lines B′ and C′ assume the same coupling patterns as those of B and C, respectively. The magnitude of $J_{\alpha\beta}$ is unchanged on going from the neutral to dianion molecule.

It has previously been decided from an ESR investigation[2] that the ester groups in the terephthalate anion radicals are fixed on the benzene plane, and this situation should also be applied to the dianion molecules. Actually, the line A′ is composed of several lines, though not completely resolved, as seen from Fig. 1 and this should be a superposition of two slightly different AA′BB′ patterns arising from *cis* and *trans* rotational isomers (Fig. 2). The center of these superposed lines is taken as the average shift of the ring protons of dianion. The shift values measured from the lower-shielding methylene peak of THF as an isotopic impurity are listed in Table 1.

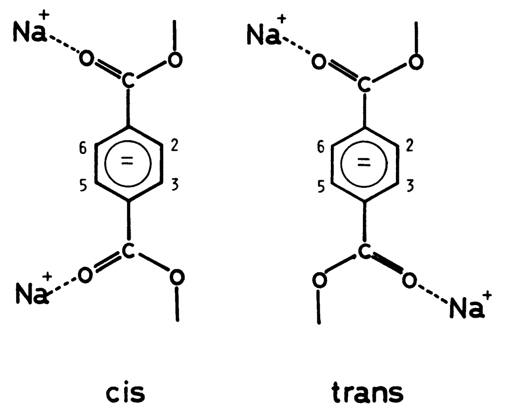

Fig. 2. The proposed structures of disodium salts of dianions of dialkyl terephthalates.

Table 1. The observed ^{1}H shifts of dianions

Compound		Ring-H	α-H	β-H
DMTP	Neutral[a]	4.45	0.30	
	Dianion[a]	3.84	0.16	
	$\Delta\delta_H$(obsd)[b]	−0.61	−0.14	
DETP	Neutral	4.52	0.76	−2.23
	Dianion	3.90	0.65	−2.33
	$\Delta\delta_H$(obsd)	−0.62	−0.11	−0.10
DPTP	Neutral	4.54	1.55	−2.35
	Dianion	3.89	0.53	−2.64
	$\Delta\delta_H$(obsd)	−0.65	−1.02	−0.29

a) Measured in ppm from the lower-shielding methylene peak of THF as an isotopic impurity. Negative sign denotes high-field shift. b) Shift of the dianion relative to its corresponding neutral molecule.

It has previously been established[1c,6,7] that, in simple aromatic systems, the proton chemical shift ($\Delta\delta_H$) is directly proportional to the excess π-electron density (Δq) on the carbon atom to which the proton is bonded. This may be empirically expressed by the simple linear relationship

$$\Delta\delta_H = k\,\Delta q,$$

where the constant k has been experimentally found to have a value of 10 to 11 ppm per electron.[1c,6,7] Then, proton chemical shifts provide reliable information about charge density distributions, provided that there exists no interfering effect such as the magnetic anisotropy of neighboring atoms or substituent groups. It has been predicted from theoretical consideration that the two excess electrons in the lowest vacant π-orbital of the dianion do not contribute to the ring current.[8] Therefore, no correction of the observed shift for the ring current effect is required for comparing the observed with calculated shifts. Although the anisotropy of C=O and C–O bonds for the dianion is considered to be different in magnitude from that for the neutral molecule, this effect may be neglected since these bonds are remote from the ring protons.

Thus, the π-charge densities on the carbon 2p orbitals, ρ^{π}_{2p}, were calculated by using both the CNDO and semiempirical SCF π-MO (ppp) methods. Several geometric parameters used were taken from the literature.[9] MO calculations were made for the *cis* and *trans* rotational conformers for the ester groups (Fig. 2) and ρ^{π}_{2p} was averaged over positions 2 and 6 and over the two conformers. The increase in the resulting average ρ^{π}_{2p} on going from the neutral to dianion molecule is taken as the excess charge, $\Delta\rho^{\pi}_{2p}$. The increases in the ring proton shifts corresponding to $\Delta\rho^{\pi}_{2p}$, $\Delta\delta_H$, were then calculated from $\Delta\rho^{\pi}_{2p}$ by using 10.7 ppm as k and are compared with the observed ones

Table 2. Comparison of observed shifts ($\Delta\delta_H$(obsd)) with those predicted from MO calculations ($\Delta\delta_H$(calcd)) for dimethyl terephthalate dianion[a]

		Ring-H	α-H
$\Delta\delta_H$(obsd)		−0.61	−0.14
$\Delta\delta_H$(calcd)	CNDO	−1.14(0.106)[b]	
	PPP	−1.29(0.121)[c]	
	CNDO	−1.6(0.095)[d]	−0.8(0.05)[d]

a) In ppm relative to the corresponding neutral molecule. Negative sign denotes high-field shift. b) The figure in parentheses is $\Delta\rho^{\pi}_{2p}$ (CNDO) (see text). c) The figure in parentheses is $\Delta\rho^{\pi}_{2p}$ (ppp) (see text). d) The figure in parentheses is $\Delta\rho^{H}_{1s}$ (CNDO) (see text).

($\Delta\delta_{\rm H}$(obsd)) in Table 2. The result shows that $\Delta\delta_{\rm H}$(calcd) is about twice as much as $\Delta\delta_{\rm H}$(obsd) for both the cases using the MO methods.

On the other hand, it has been predicted theoretically that a 6% increment of electron density on a hydrogen 1s orbital ($\rho^{\rm H}_{1s}$) corresponds to 1 ppm high-field shift of the hydrogen. Using this relation, an attempt was made to estimate, though roughly, $\Delta\delta_{\rm H}$ of ring protons from the excess charge on its 1s orbital estimated by the CNDO method, $\Delta\rho^{\rm H}_{1s}$. $\rho^{\rm H}_{1s}$ was obtained from the averaging mentioned above. As shown in Table 2, the result indicates a further larger high-field shift than $\Delta\delta_{\rm H}$(obsd). The same process was applied to the α-protons of methyl group but resulted in too large high-field shift.[10]

It may be resonable to consider that the counter ion effect of Na ions is responsible for this discrepancy: The hfs patterns in ESR spectra of terephthalate anion radicals have excellently been interpreted in terms of MO calculations performed on the ion pair model based on the interaction of Na ion with a carbonyl oxygen of one ester group.[2] By analogy with anion radicals, one may expect that the two Na ions bind to each of the two carbonyl oxygens of ester groups in the dianion disodium salt (Fig. 2). In this model, the bonding of Na ion to the carbonyl oxygen may increase the π-densities on the ester groups and hence may decrease those on the ring. This model is thus possibly effective for elucidation of the above discrepancy for the ring protons. However, the much larger value of CNDO $\Delta\rho^{\rm H}_{1s}$ for the methyl protons than expected is difficult to be explained from this consideration and appears to be associated with the change in the anisotropy of C=O and C–O bonds on going from the neutral to dianion molecule. $\Delta\delta_{\rm H}$(obsd) of the α-protons for DPTP is much larger than those for the other two compounds and this may suggest that the C–H bond of the isopropyl group in this dianion trends to be perpendicular to the molecular plane, in contrast to the case of the anion radical of this compound where this bond has been determined to be fixed on the benzene plane.[2]

It is known that for actual charged molecules the excess charge trends to be somewhat more uniformly distributed over the molecule than indicated by simple MO calculations.[1b] This effect is in competition with the trend of electron localization toward the ester groups by the bonding of Na ion. Another possible explanation for such discrepancy between the observed and calculated $\Delta\delta_{\rm H}$ is related to the formation of π-π dimer dianion proposed on the basis of much larger concentrations of the starting aromatic compound than that suitable for the observation of ESR. This model is attractive since this might lead to about half $\Delta\rho$(calcd).

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$$\mathrm{O{=}\underset{|}{C}{-}O{-}\underset{\alpha}{CH_2}{-}\underset{\beta}{CH_3}}.$$

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10) CNDO calculations were made for two rotational conformers for methyl groups in which one C–H bond is perpendicular and coplanar to the benzene plane. The excess $\rho^{\rm H}_{1s}$ for the dianion, $\Delta\rho^{\rm H}_{1s}$, was estimated through the averaging of $\rho^{\rm H}_{1s}$ over the three methyl protons in each conformer.