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Electron Spin Resonance of Anion Radicals of *N*-Alkyl Phthalimides and Aromatic Acid Anhydrides[1]

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The ESR spectra of anion radicals of *N*-methyl, *N*-ethyl, and *N*-*n*-butyl phthalimides, naphthalic acid anhydride, and pyromellitic acid anhydride were measured in acetonitrile. Both the electrolytic and alkali metal reduction methods were used for the radical generation. The spin densities of these anion radicals were then calculated by McLachlan's method; the calculated results were partly in agreement with the experimental data. Satellite lines due to three kinds of ^{13}C nuclei in the pyromellitic acid anhydride anion radical were observed; one of these splitting constants was assigned to the position 1.

The electron spin resonance of the anion radicals of aromatic esters have previously been studied by the present author.[2] The present investigation was undertaken to study the anion radicals of aromatic compounds with two carbonyl groups bound by an oxygen or a nitrogen atom. It is interesting to consider how much the spin density distribution of the ring is affected by the $O{=}\overset{|}{C}{-}X{-}\overset{|}{C}{=}O$ group (X: O or *N*-alkyl). As the anion radical has a smaller number of protons than the corresponding ester anion, a spectrum with a simple structure may be expected; furthermore, if one takes up a compound in which there are only a few kinds of carbons, it may be easy to observe the satellite lines due to ^{13}C nuclei present in natural abundance. The ^{13}C splittings in the spectra of ^{13}C-enriched radicals have been easily analyzed;[3-8] there have been, however, only a few examples in which the splittings of ^{13}C nuclei present in natural abundance have been entirely analyzed and assigned to the carbon positions without the assistance of ^{13}C enrichment, because these ^{13}C lines have very small intensities and are thus liable to be covered by the proton lines.[9-15] In this investigation, *N*-methyl, *N*-ethyl, and *N*-*n*-butyl phthalimides, naphthalic acid anhydride, and pyromellitic acid anhydride were treated. Three kinds of ^{13}C splittings were observed in the spectrum of the pyromellitic acid anhydride anion radical; one of them could be assigned to the position 1.

Experimental

The radicals were prepared by using both the electrolytic and alkali metal reductions. In the former method, acetonitrile (ACN) was used as the solvent, and tetra-*n*-propylammonium perchlorate, as the supporting electrolyte. Since all the anion radicals studied here were very stable at room temperature, the cell was designed so that the electrolysis could be performed outside the cavity. In the latter method, potassium and sodium metals were used as the reducing agents, and tetrahydrofuran (THF), as the solvent. The ESR measurements were performed at room temperature.

N-*n*-Butyl phthalimide obtained commercially was used without further purification. *N*-Methyl and *N*-ethyl phthalimides were synthesized from potassium salt of phthalimide, and from methyl and ethyl iodides, respectively. Naphthalic acid anhydride was purified by recrystallization from ethanol, while pyromellitic acid anhydride was used after sublimation.

Results

***N*-Alkyl Phthalimides.** *Electrolytic Reduction.* The electrolysis of *N*-methyl, *N*-ethyl, and *N*-*n*-butyl phthalimides yielded yellow-green solutions which gave markedly resolved spectra;

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[2] To be published.

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[10] D. C. Reitz, F. Dravnieks and J. E. Wertz, *J. Chem. Phys.*, **33**, 1880 (1960).

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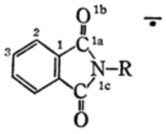
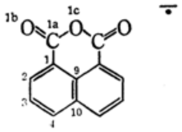
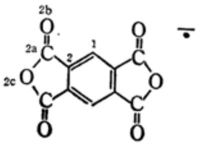
[15] M. R. Das and G. K. Fraenkel, *ibid.*, **42**, 1350 (1965).

TABLE 1. HYPERFINE SPLITTING CONSTANTS

Anion radical		Splitting constant (in gauss)	
	$R = CH_3$	$a_2^H = 0.25$ $a_3^H = 2.41$ $a_{CH_3}^H = 0.91$	$a^N = 2.62$
	$R = C_2H_5$	$a_2^H = 0.24$ $a_3^H = 2.41$ $a_{CH_2}^H = 0.57$	$a^N = 2.55$
	$R = n\text{-}C_4H_9$	$a_2^H = 0.23$ $a_3^H = 2.39$ $a_{CH_2}^H = 0.57$	$a^N = 2.55$
		$a_2^H = 5.22$ $a_3^H = 0.91$ $a_4^H = 5.97$	
		$a_1^H = 0.69$	$a_1^C = 5.51$ $a_{2\ \mathrm{or}\ 2a}^C = 3.57$ $a_{2a\ \mathrm{or}\ 2}^C = 2.49$

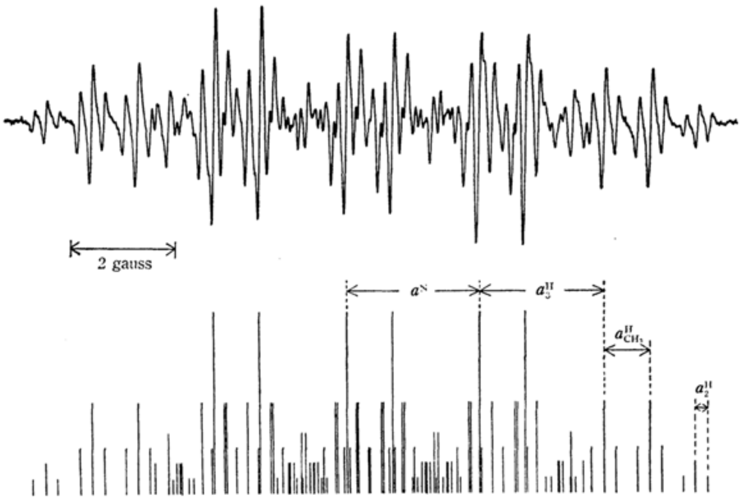


Fig. 1. The ESR spectrum of N-methyl phthalimide anion radical prepared by electrolysis in acetonitrile and the reconstruction.

the radicals thus produced were very stable (the intensities of these ESR signals were unchanged after several days at room temperature). The splitting constants measured are listed in Table 1. The splitting constants common to the three spectra arise from two sets of two equivalent ring protons, while the residual splittings are attributed to the α-protons[*1] of the alkyl groups in each anion. The spectra observed by the electrolysis of N-methyl and N-ethyl phthalimides are shown in Figs. 1 and 2

[*1] The proton position is defined by the notation:

$$\rangle N-\underset{\alpha}{\overset{H_2}{C}}-\underset{\beta}{\overset{H_2}{C}}-$$

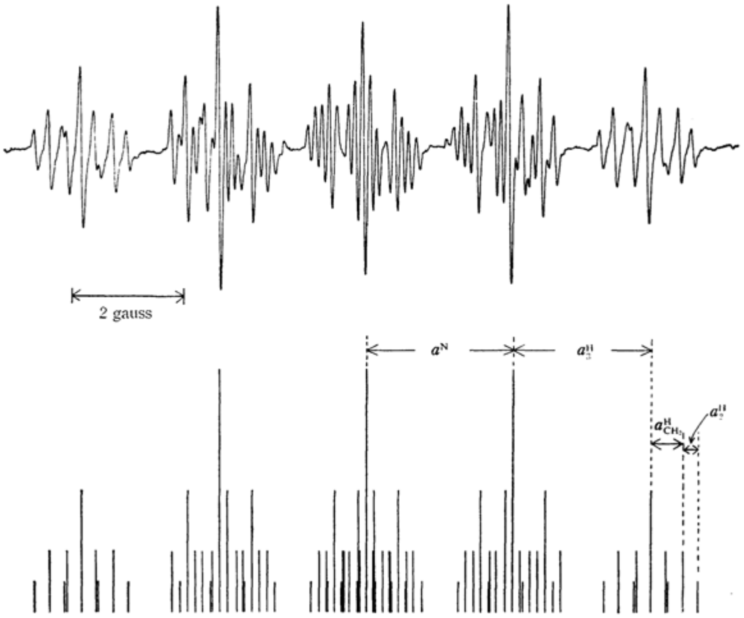


Fig. 2. The ESR spectrum of *N*-ethyl phthalimide anion radical prepared by electrolysis in acetonitrile and the reconstruction.

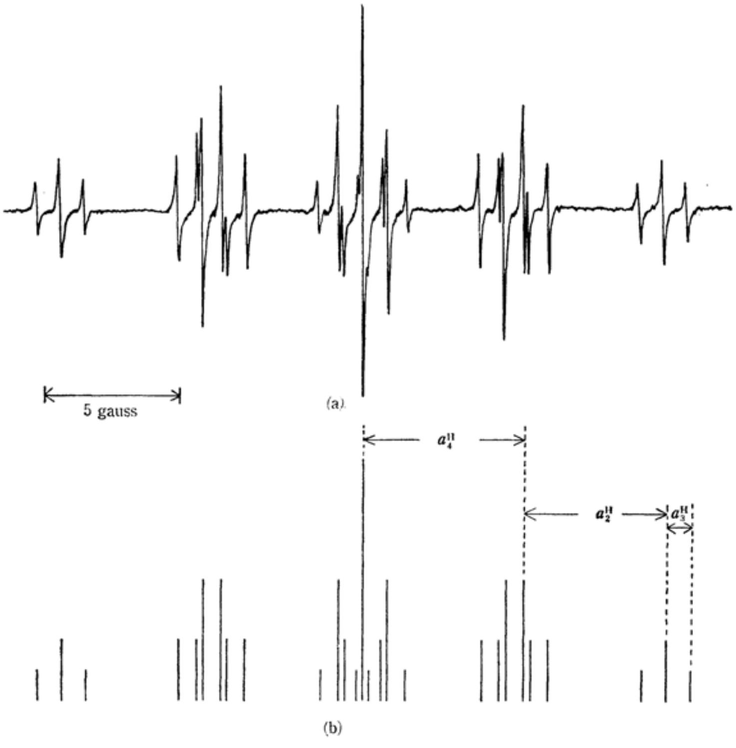


Fig. 3. The ESR spectrum of naphthalic acid anhydride anion radical prepared by electrolysis in acetonitrile and the reconstruction.

respectively, with each reconstruction based on the splitting constants given in Table 1. The assignment to the ring positions at 2 and 3 was made by MO calculations. The average line-widths were

0.08, 0.045, and 0.05 gauss for the spectra of *N*-methyl, *N*-ethyl, and *N*-*n*-butyl phthalimide anions respectively.

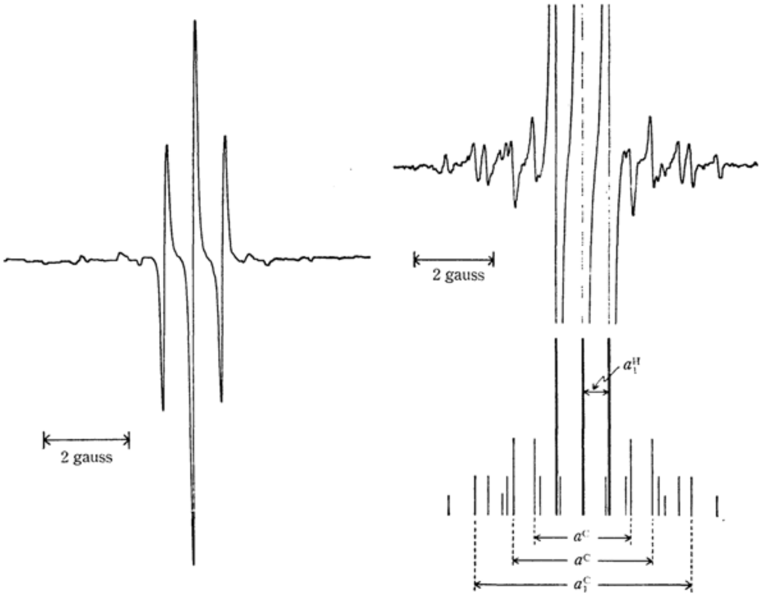
Alkali Metal Reduction. When a THF solution of *N*-methyl phthalimide was in contact with potassium or sodium metal, the surface of the metal turned green. However, the ESR signal could not be observed, because the green substance was insoluble in THF. The contact of THF solutions of *N*-ethyl and *N*-*n*-butyl phthalimides with potassium metal yielded green solutions, which gave poorly-resolved spectra nevertheless very similar to those obtained by the electrolysis of these compounds, while upon contact with sodium metal, only a small change in the spectral pattern was observed. This latter change has not yet been well interpreted, though several possible analyses might be proposed for this spectrum.

Naphthalic Acid Anhydride. The electrolysis of this compound yielded an orange solution, which gave a well-resolved spectrum, shown in Fig. 3 (a), with a large total width (over 24 gauss) and with a line-width of 0.08 gauss. As is shown in the reconstruction on the base of the splitting constants given in Table 1 (Fig. 3 (b)), the spectrum consists of three triplet splittings; it is consistent with that to be expected from the anion radical of this compound. The splitting constants listed in Table 1 were assigned to the ring positions by MO calculations.

In contact with potassium metal, a THF solution of this compound gave a spectrum nearly identical with that obtained by electrolysis, but when it was in contact with sodium metal, no ESR signal was observed.

Pyromellitic Acid Anhydride. The electrolytic reduction of this compound yielded a blue solution which gave a spectrum, shown in Fig. 4 (a), consisting of three lines due to two equivalent protons and several lines of a very low intensity. The triplet splitting is consistent with that to be expected from two equivalent protons of the anion radical of this compound.

The spectrum at high gain presented in the upper half of Fig. 4 (b) indicates that the eight lines of low intensity are observed on either side of the central proton line and, furthermore, that they occur at exactly symmetric positions about the center of the major spectrum. Therefore, a reconstruction was made based on three possible splittings arising from ^{13}C nuclei in this anion radical; this reconstruction was in good agreement with the observed spectrum, as is shown in the lower half of Fig. 4 (b). Therefore, these low intensity lines were interpreted as arising from the splittings caused by the presence of ^{13}C nuclei in natural abundance.



(a) (b)

Fig. 4. The ESR spectrum of pyromellitic acid anhydride anion radical prepared by electrolysis in acetonitrile.
(a) The spectrum measured at low gain.
(b) The spectrum measured at high gain and the reconstruction. The proton hyperfine lines are off scale in the spectrum and are drawn as heavy lines in the reconstruction. The lines of smaller amplitude are ^{13}C satellites.

TABLE 2. CALCULATED AND EXPERIMENTAL SPIN DENSITIES

Anion radical	Position*	Spin density		
		Calculated		Experimental**
		Hückel	McLachlan	
N-Alkyl phthalimide anion	1	0.1111	0.1743	
	2	0.0141	−0.0114	0.010
	3	0.0714	0.0981	0.101
	1a	0.0714	0.1455	
	1b	0.2319	0.1035	
	1c	0.0000	−0.0209	
Naphthalic acid anhydride anion	1	0.0455	0.0085	
	2	0.1480	0.2111	0.218
	3	0.0122	−0.0537	0.038
	4	0.1716	0.2607	0.249
	9	0.0000	−0.0087	
	10	0.0000	−0.0527	
	1a	0.0746	0.0768	
	1b	0.0481	0.0339	
	1c	0.0000	−0.0137	
Pyromellitic acid anhydride anion	1	0.0000	−0.0417	0.029
	2	0.1098	0.1291	
	2a	0.0772	0.0830	
	2b	0.0629	0.0628	
	2c	0.0000	−0.0091	

* See Table 1 for numbering of positions.

** The spin densities calculated by using the relation $a_i^{\mathrm{H}}=Q_{\mathrm{CH}}^{\mathrm{H}}\rho_i^{\pi}$, where $|Q_{\mathrm{CH}}^{\mathrm{H}}|=24.0$ gauss.

The intensity of the satellite lines arising from the ^{13}C nucleus at the position 2 or 2a (see Table 1) should be 4.4 per cent as intense as the corresponding proton line, because there are four equivalent carbon atoms at each of these positions in this anion radical and the natural abundance of ^{13}C is 1.1 per cent. However, this intensity is divided between the two satellites, so that each satellite line must be 2.2 per cent as intense as the corresponding proton line. The intensity of each satellite arising from the ^{13}C nucleus at the position 1 should be 1.1 per cent as intense as the corresponding proton line, since there exist two equivalent carbons at the position 1. The values of experimental ratios obtained from the intensity measurement of low-intensity lines were approximately identical with those predicted above. All the satellite lines expected from the three kinds of ^{13}C nuclei were observed, except for the innermost ones buried beneath the proton lines, as may be seen in Fig. 4 (b). The observed splitting constants are listed in Table 1. The largest one of these three splittings can be assigned to the position 1 because of the smallest intensity of the satellite lines. The same spectrum as that shown in Fig. 4 (b) was also observed by the reduction of a THF solution of this compound with potassium or sodium metal.

Discussion

Molecular Orbital Calculations of Spin Densities. The MO calculations of spin densities were made by the Hückel approximation and by McLachlan's method.[16] The following values of MO parameters were used for the –CO–X–CO– group: $\delta_{\mathrm{N}}=1.5$, $\delta_{\mathrm{O}}=1.5$, $\gamma_{\mathrm{CN}}=1.2$, $\gamma_{\mathrm{CO}}=1.73$, and $\gamma_{\mathrm{CC'}}=1.0$ for the *N*-alkyl phthalimide anions; $\delta_{\mathrm{O(C=O)}}=1.6$, $\delta_{\mathrm{O(C-O)}}=1.5$, $\gamma_{\mathrm{CO(C=O)}}=1.5$, $\gamma_{\mathrm{CO(C-O)}}=1.0$, and $\gamma_{\mathrm{CC'}}=1.2$ for the naphthalic acid anhydride anion, and $\delta_{\mathrm{O(C=O)}}=1.5$, $\delta_{\mathrm{O(C-O)}}=2.0$, $\gamma_{\mathrm{CO(C=O)}}=1.5$, $\gamma_{\mathrm{CO(C-O)}}=1.0$, and $\gamma_{\mathrm{CC'}}=1.0$ for the pyromellitic acid anhydride anion, where $\gamma_{\mathrm{CC'}}$ is the resonance integral parameter for the bond between the carbonyl group and the ring. The Coulomb and resonance integral parameters, δ_x and γ_{xy}, are defined in the two equations, $\delta_x=(\alpha_x-\alpha)/\beta$ and $\gamma_{xy}=\beta_{xy}/\beta$ respectively, where α and β are the Coulomb and resonance integrals for benzene. The calculation results are compared with the experimental spin densities obtained by the equation, $a_i^{\mathrm{H}}=Q_{\mathrm{CH}}^{\mathrm{H}}\rho_i^{\pi}$, where $|Q_{\mathrm{CH}}^{\mathrm{H}}|=24.0$ gauss, in Table 2. The results of McLachlan's calculation are in good agreement with the experimental spin densities for the *N*-alkyl phthalimide and naphthalic acid anhydride anions, but for the

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[16] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

pyromellitic acid anhydride anion, the agreement is not very good.

^{13}C Splittings and Hindered Internal Rotation of Alkyl Groups. According to the theory developed by Karplus and Fraenkel,[17] the splitting constant of ^{13}C at the position 1 was estimated to be -5.074 gauss; this was in relatively good agreement with the experimental value. From the equivalency of the three protons in the methyl group of the *N*-methyl phthalimide anion, it may be determined that the methyl group freely rotates about the N–C bond. On the other hand, the α-proton splitting constants in the *N*-ethyl and *N*-*n*-butyl phthalimide anions are much smaller than the methyl proton splitting in the *N*-methyl phthalimide anion. Therefore, one may consider that these alkyl groups are at least not freely rotating. The ESR measurements of such a hindered internal rotation of alkyl groups have been made for several other radicals.[18–21]

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