Electron Spin Resonance Studies of the Anion Radicals of Pyridinium Bis(alkoxycarbonyl)methylides [1]

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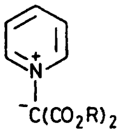
By means of e.s.r. spectroscopy, it was found that short-lived anion radicals of pyridinium bis(alkoxycarbonyl)-methylides have unusual hyperfine splittings and a unique unsymmetrical electronic structure. The hyperfine splitting constants of these anion radicals agree well with the spin densities from MO calculations using the modified Steinberger–Fraenkel method. On the other hand, the hyperfine splitting constants of the cation radicals can be explained by the usual MO calculations.

SINCE cycloimmonium ylides are zwitterions, their electronic properties and reactivities are of interest.[2,3] Catteau and his co-workers calculated the electronic states of the cycloimmonium ylides and discussed their stability.[3] Recently, we reported the trapping of cation radicals of pyridinium bis(alkoxycarbonyl)-methylides by the formation of complexes with diphenylcyclopropenone.[4] We also described the unusual e.s.r. spectrum of the anion radical of pyridinium bis(methoxycarbonyl)methylide (I) with sodium as counterion in tetrahydrofuran (THF), the analysis of which gave evidence for an unsymmetrical electronic structure of the pyridine ring.[1]



(I) R = Me
(II) R = Et

In this paper, we report on the spin densities and formation of the anion radicals of (I) and pyridinium bis(ethoxycarbonyl)methylide (II) with potassium as counterion in 1,2-dimethoxyethane (DME) using e.s.r. spectroscopy.

EXPERIMENTAL

Compounds (I) and (II) were synthesized according to the method of Kobayashi *et al.*[5] Pentadeuteriopyridinium bis(methoxy- and ethoxy-carbonyl)methylides were prepared using pentadeuteriopyridine in a manner similar to that for the preparation of (I) and (II). The purity of the deuteriated compounds was checked by ^{1}H n.m.r. as described in the literature.[6]

Under the condition of a high vacuum, the careful reduction of (I) and (II) with potassium metal in degassed DME at *ca.* −20 to −60 °C immediately produces a short-lived anion radical. The DME solution containing the anion radical was investigated by an X-band e.s.r. spectrometer (JEOL ME-3) with 100 KHz field modulation over the temperature range from 25 to −80 °C. The magnetic field was calibrated by hyperfine splitting (h.f.s.) of the ^{14}N of peroxylamine disulphonate ion. Spectral simulations were carried out with a JEOL spectral computer (model JEC-6). MO Calculations [7] were carried out at the Data Processing Center, Kyoto University (FACOM M-200 computer).

RESULTS AND DISCUSSION

The E.s.r. Spectra of the Anion Radicals of Pyridinium Bis(alkoxycarbonyl)methylides.—An intense well resolved and short-lived e.s.r. spectrum of $(I)^{-\bullet}$ with potassium counterion in DME at room temperature is displayed in Figure 1a (*g* 2.0039). The spectrum consists of several doublets and a large triplet, all of equal intensity, yielding a total of 73 absorption lines. This can be simulated with h.f.s. constants, a_N 0.552 mT for a ring nitrogen and a_H 0.374, 0.326, 0.205, 0.161, and 0.091 mT for five ring protons (Figure 1b), where the experimental error is less than ±0.001 mT. Although the h.f.s. constants have slightly different values from those reported for $(I)^{-\bullet}$ with sodium as counterion in THF,[1] there is the common feature of a significant non-equivalence in the h.f.s. constants of the ring protons (see Table 1).

The e.s.r. spectrum of $(II)^{-\bullet}$ with potassium as counterion in DME at room temperature consists of a total of 85 absorption lines (*g* 2.0039). However, the e.s.r. spectrum, clearly consisting of h.f.s. constants, a_N 0.545 mT due to the ring nitrogen, and a_H 0.372, 0.313, 0.200, 0.160, and 0.096 mT due to the five ring protons as shown in Table 1, is similar to that shown in Figure 1.

Reaction of [$^2H_5$]-(II) with potassium metal in DME produced a short-lived anion radical immediately; its e.s.r. spectrum exhibited a large doublet (1 : 1) of 0.372 mT and also a nitrogen splitting (1 : 1 : 1) of 0.544 mT as shown in Figure 2a (*g* 2.0039). This splitting is quite similar to the largest proton splitting mentioned above. This fact seems to indicate that the γ-deuteron at the active position of the pyridine ring was converted into a proton during the formation of the anion radical.[1] The computer-simulated spectrum was used to obtain the h.f.s. constants: a_N 0.544 mT for a ring nitrogen and a_D 0.052, 0.035, 0.025, and 0.015 mT for four ring deuterons and a_H 0.372 mT for a γ-proton in the ring. Consequently, we were able to observe the e.s.r. spectrum of the anion radical of tetradeuteriopyridium bis(ethoxycarbonyl)methide [$^2H_4$]-(II) shown in Figure 2.

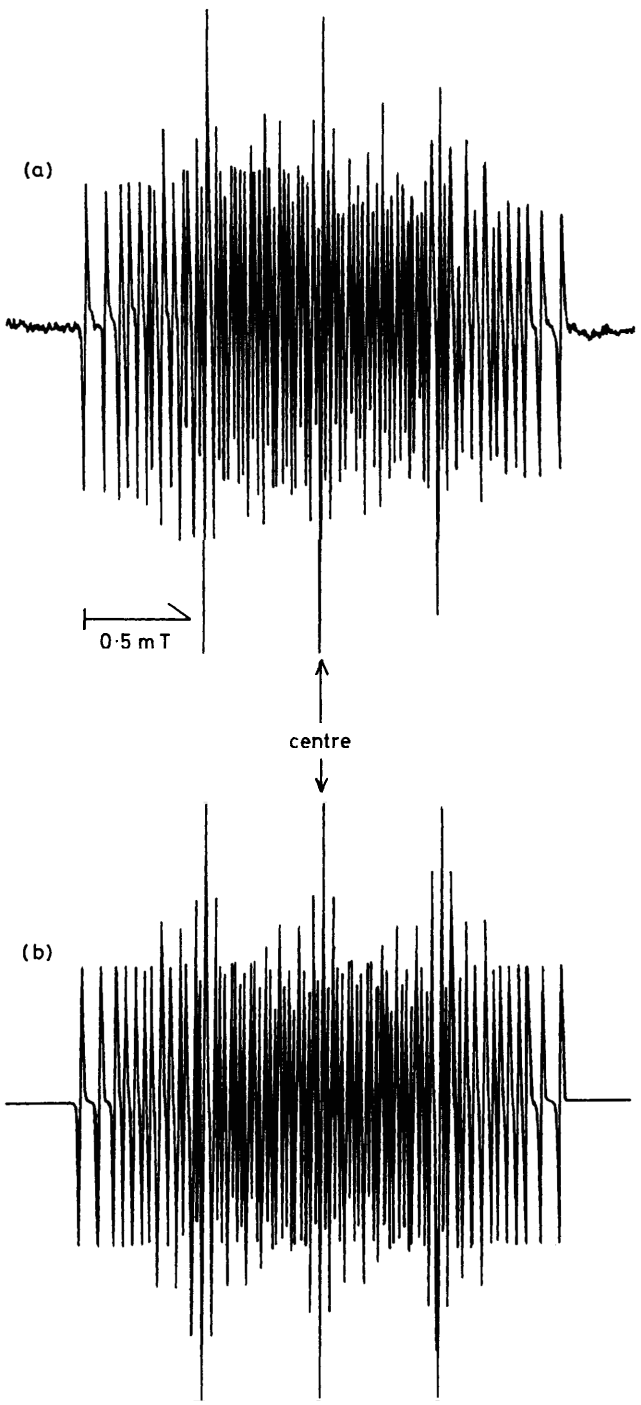


FIGURE 1 E.s.r. spectra of the anion radical of pyridinium bis(methoxycarbonyl)methylide ($I^{-\cdot}$) with K^+ in DME at room temperature (a) and its computer simulation (b) based on the h.f.s. constants listed in Table 1

Since a_H 0.372 mT and the g value in Figure 2 are the same as the values for $(II)^{-\cdot}$, the h.f.s. constant can be assigned to the γ-proton. Also, the ratios a_D/a_H are each *ca.* 0.156, similar to the values of $(I)^{-\cdot}$ and $[^2H_4]$-$(I)^{-\cdot}$ in THF.[1] On the other hand, the reaction of $[^2H_5]$-(I) and $[^2H_5]$-(II) with potassium metal in pure octadeuteriotetrahydrofuran immediately produced a short-lived anion radical; its e.s.r. spectrum was measured and found to exhibit three broad splittings of *ca.* 0.55 mT each, due to nitrogen, since the h.f.s. constants for the deuterium atoms of $[^2H_5]$-(I) and $[^2H_5]$-(II) must overlap each other.

We could not measure the h.f.s. constants of either the alkali metal, even at low temperature, or the protons of the two methoxy- and two ethoxy-groups since they are probably smaller than the computer-simulated linewidth, 0.008 mT. The assignments of the above h.f.s. constants were based on the results of the MO calculations [8—10] summarized in Table 1. Although the e.s.r. spectra at low temperature showed no substantial variation, these spectra demonstrated increased high-field broadening due to anisotropy in the g tensor and in ^{14}N,[11] and small overlap of the h.f.s. linewidths. On the other hand, above room temperature, we could not observe the e.s.r. spectra because the anion radicals decay as soon as they are formed.

However, we were able to conclude that there was no possibility of the formation of radicals other than those mentioned above, as confirmed by a careful and detailed investigation by u.v. and e.s.r. spectroscopy of the reduction of pyridinium bis(alkoxycarbonyl)methylides.[12] Although the ylides have u.v. absorptions of 245 and 430 nm,[5] the anion radicals mentioned above would not have been observed if the absorption of 430 nm had thoroughly decayed upon reduction with alkali-metal at room temperature. The ylides ultimately become other pyridinium neutral radicals (g 2.0030),[12] having u.v. absorptions at 375 and 395 nm, upon continuing the reduction with alkali-metal for a long period even at low temperatures.

Comparison of E.s.r. Data and MO Calculations of $(I)^{-\cdot}$ *and* $(I)^{+\cdot}$.—According to the e.s.r. spectra of $(I)^{-\cdot}$, $(II)^{-\cdot}$, $[^2H_4]$-$(I)^{-\cdot}$, and $[^2H_4]$-$(II)^{-\cdot}$, the unpaired spin densities are widely distributed in the pyridine ring. The h.f.s. constants of the α- and α'-protons and those of the β- and β'-protons of the ring show unequal and widely differing values. To explain this, we looked for precedents of non-equivalent h.f.s. constants in benzene rings.[13] Steinberger and Fraenkel, in the case of benzaldehyde anion radicals, found that the MO calculations gave a coulomb integral value h_C 0.2 for the carbon nearest the oxygen atom of the formyl group and this value agrees well with the experimental data.[14] In our case, using the parameter h_α 0.23 in $(I)^{-\cdot}$, though the spin densities are clearly unequal, the h.f.s. constants of nitrogen and the protons of the ring were larger than the experimental values. In support of this, including the resonance integral,[14,15] $k_{\alpha\ldots s}$ 0.63 for the α-carbon of the pyridine ring and the oxygen of the ester carbonyl group, it should be noted that the MO calculations are an agreement with the experimental results in Table 1. Many other calculations have been attempted by employing various parameters, but good results have not been obtained. According to the MO calculations in Table 1, the spin densities are distributed *ca.* 60.3% in the pyridine ring, *ca.* 3.1% at the ylide carbon, and *ca.* 36.6% in the two methoxycarbonyl groups.

TABLE 1

The spin densities and the h.f.s. constants of the anion radical of pyridinium bis(alkoxycarbonyl)methylides

	Calc. spin densities[b] of $(I)^{-\cdot}$		Calc. h.f.s. constants[c] (mT)	Obs. h.f.s. constants (mT)				
Position[a]	HMO	McLachlan		$(I)^{-\cdot}$ [d]	$(I)^{-\cdot}$ [e]	$[^2H_4]$-$(I)^{-\cdot}$ [f]	$(II)^{-\cdot}$ [g]	$[^2H_4]$-$(II)^{-\cdot}$ [h]
N	0.1955	0.2339	0.545	0.545	0.552	0.544	0.545	0.544
α	0.1275	0.1547	0.325	0.330	0.326	0.052[i]	0.313	0.052[i]
α′	0.0910	0.1011	0.213	0.212	0.205	0.033[i]	0.200	0.035[i]
β	0.0032	−0.0580	0.122	0.151	0.161	0.023[i]	0.160	0.025[i]
β′	0.0248	−0.0191	0.040	0.090	0.091	0.014[i]	0.096	0.015[i]
γ	0.1508	0.1978	0.415	0.361	0.374	0.367	0.372	0.372
C(1)	0.0078	−0.0387						
O(3)	0.0008	−0.0171						
O(3′)	0.0791	0.0685						

[a] The numbering system and structural formula are as shown in Figure 3. [b] The parameters used were h_N 0.8, h_O 2.0, h_α 0.23, $h_{\alpha'} = h_1$ 0.1, $h_5 = h_{5'}$ −0.1, h_{H_3} −0.5, $k_{\alpha \ldots 3}$ 0.63, k_{CN} 0.8, $k_{C=O}$ 1.41, k_{C-O} 0.6, k_{CC} 1.0, $k_{C\equiv H_3}$ 2.5, and λ 1.2. [c] Obtained according to equations, $a_H = Q_H\rho_C$ and $a_N = Q_1\rho_N + Q_1\Sigma\rho_{ON}$; with $Q_H = |2.1|$, $Q_1 = |2.1|$, and $Q_2 = |0.27|$ mT using calculated McLachlan spin densities (ref. 7). [d,f] Values from ref. 1. [e,g,h] With potassium as counterion in DME at room temperature. [i] These are the h.f.s. constants of the deuterium atoms.

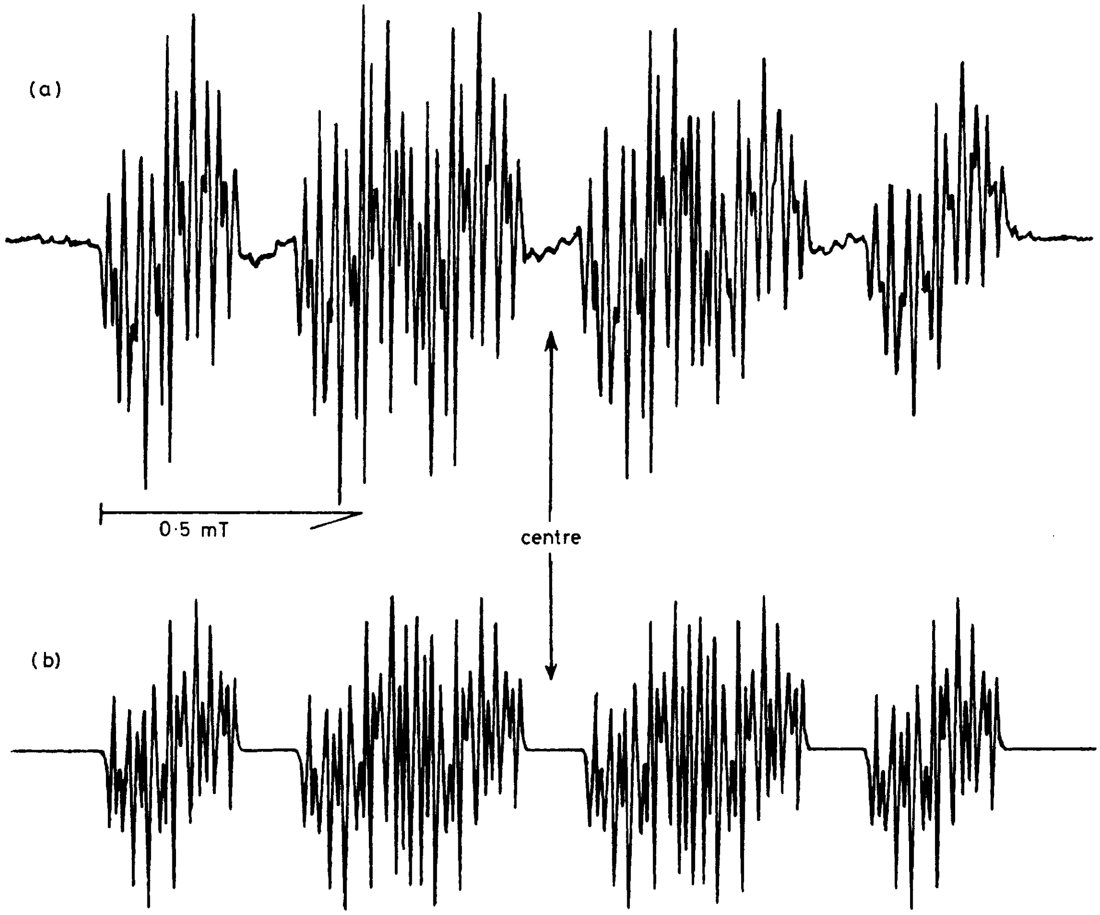


FIGURE 2 E.s.r. spectra of the anion radical of tetradeuteriopyridinium bis(ethoxycarbonyl)methylide $[^2H_4]$-$(II^{-\cdot})$ with K^+ in DME at room temperature (a) and its computer simulation (b) based on the h.f.s. constants listed in Table 1

Upon comparing the h.f.s. constants of $(I)^{-\cdot}$ and $(II)^{-\cdot}$ with those of $(I)^{+\cdot}$ and $(II)^{+\cdot}$, it was found that the h.f.s. constants of the pyridine ring are smaller than those of their anion radicals, the h.f.s. constants of the α- and α′-protons and also the β- and β′-protons of the pyridine ring are equal, and the h.f.s. constants of the methyl and ethyl protons of both alkoxycarbonyl groups could be observed.[4] As shown in Table 2, the usual MO calculations [8—10,16] for $(I)^{+\cdot}$ support the experimental results. The spin density distributions are *ca.* 28.4% in the pyridine ring, *ca.* 39.4% at the ylide carbon, and *ca.* 32.2% in the two methoxycarbonyl groups. In this case, the distribution at the ylide carbon is significant.

It is of interest as to why the anion and cation radicals of pyridinium bis(alkoxycarbonyl)methylides show large differences. In particular, in order to interpret the experimental results for the anion radicals, it may be reasonable to assume that there is an interaction between

TABLE 2

The spin densities and the h.f.s. constants of the cation radical of pyridinium bis(alkoxycarbonyl)methylides

	Calc. spin densities [b] of $(I)^{+\cdot}$		Calc. h.f.s. constants [c]	Obs. h.f.s. constants [d] (mT)	
Position [a]	HMO	McLachlan	(mT)	$(I)^{+\cdot}$	$(II)^{+\cdot}$
N	0.0853	0.0338	0.175	0.26_6	0.168
α,α′	0.0658	0.0711	0.192	0.13_3	0.118
β,β′	0.0099	−0.0180	0.049	0.03_3	0.025
γ	0.1014	0.0928	0.251	0.29_5	0.252
C(1)	0.3332	0.4226			
O(3),O(3′)	0.0759	0.0840			
$H_{(6)},H_{(6')}$	0.0012	0.0009	0.015	0.02_2	0.013 [e]

[a] See Figure 3 for numbering system. [b] The parameters used were h_N 0.8, h_O 2.0, $h_5 = h_{5'}$ −0.1, h_{H_3} −0.5, k_{CN} 0.8, $k_{C=O}$ 1.41, k_{C-O} 0.6, $k_{C\equiv H_3}$ 2.5, k_{CC} 1.0, and λ 0.8. [c] Obtained according to the equations as shown in Table 1; with Q_H |2.7|, Q_1 |2.0|, and Q_2 |0.19| mT using calculated McLachlan spin densities. [d] Values from ref. 4. [e] This is the h.f.s. constant due to the ethylene protons of the ethoxycarbonyl groups.

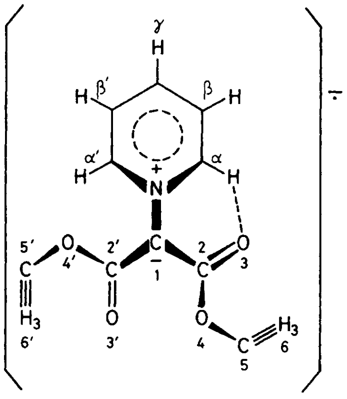


FIGURE 3 Conformation of $(I^{-\cdot})$

the α-proton and the oxygen of the carbonyl group in the anion radical. This situation probably corresponds to the data shown in Table 1, *i.e.* an interaction suggesting the formation of weak intramolecular hydrogen bonding,[17] such as C–H · · · O=C. In this case, the anion radicals form a stable structure,[3] as shown in Figure 3. Also, the results for the charge densities, for example, C_α 0.0308 and O(3) −0.3470, support this interpretation.[18] In conclusion, it may be said that the anion radicals of pyridinium bis(alkoxycarbonyl)methylides have a unique unsymmetrical electronic structure, on the basis of which the MO calculations in Table 1 were made, and these values agree well with the experimental data.

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