Alkali Metal Hyperfine Splittings of *o*-Substituted Benzophenone Ketyls

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(Received June 27, 1964)

Aromatic ketyls formed by the reaction of alkali and alkali earth metals with aromatic ketones exist as a contact ion-pair in ethers.[1,2] Their ESR spectra, therefore, show the lines due to splitting by metals as well as by protons. The metal hyperfine splitting of the ketyl generally decreases with an increasing dielectric constant of the solvent, as with other anion-radicals.[3] On the other hand, in a very polar solvent such as *N*, *N*-dimethylformamide, no metal splitting at all has been observed. This variation in the metal splitting can be attributed to charge separation in an ion-pair through solvation.

In the electronic spectrum of the ketyl, the wave number of the maximum absorption peak due to a $\pi \rightarrow \pi^*$ transition shifts towards the red as the radius of the metal cation and the dielectric constant of the solvent increase.[4,5] This spectral shift can be interpreted as a decrease in the cationic effect of a metal on a ketyl anion.[6] Consequently, we expected to find a relationship between the metal splitting, a_M, of the ESR spectra and the wave number, $\bar{\nu}_m$, of the maximum absorption peak of the electronic spectra. Indeed, a close relationship between them was observed; that is, a_M increased with $\bar{\nu}_m$.

In the course of an investigation of the ion-pair structure, we have measured the ESR spectra and the electronic spectra of *o*- and *p*-substituted benzophenone ketyls, such as

TABLE I. METAL HYPERFINE SPLITTING CONSTANTS a_M (GAUSS) AND WAVE NUMBERS $\bar{\nu}_m$ OF MAXIMUM ABSORPTION ($\times 10^3\,\text{cm}^{-1}$) OF KETYLS IN THF AT 18°C

Benzophenone derivative	a_M			$\bar{\nu}_m$		
	Li	Na	K	Li	Na	K
—— (I)	0.32	1.18	0.24	15.3	14.7	14.0
4,4′-Me (II)	0.33	—*	0.25	—**	—**	—**
2,6,2′,6′-Me (III)	0.07	0.16	0.04	14.5	13.4	12.7
2,6,2′,6′-Et (IV)	0.00	0.00	0.00	14.5	13.3	12.8

* Assignment of splittings was not possible because of the broadness of the spectrum.

** No measurement was made.

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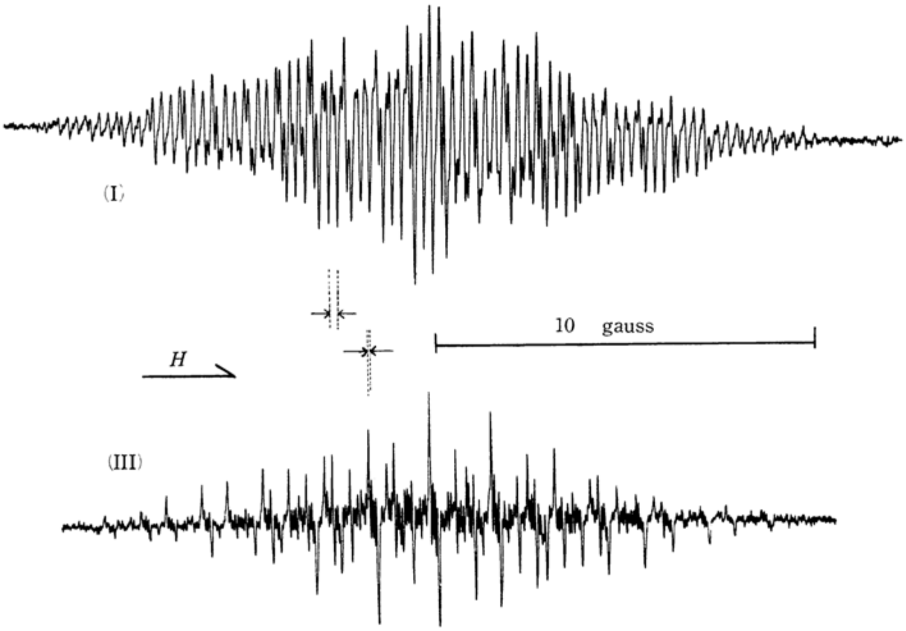

Fig. 1. Potassium splittings of benzophenone (I) and 2, 6, 2′, 6′-tetramethylbenzophenone (III) ketyls in THF at 18°C.

benzophenone (I), 4, 4′-dimethylbenzophenone (II), 2, 6, 2′, 6′-tetramethylbenzophenone (III) and 2, 6, 2′,6′-tetraethylbenzophenone (IV). The preparation of metal ketyls and the method of ESR measurement were described in a previous paper.⁽⁷⁾ The metal hyperfine splittings of ketyls in tetrahydrofuran (THF) are summarized in Table I, while representative spectra are shown in Fig. 1.

In the ketyl ion-pair the cation is mainly localized near the oxygen atom,⁽⁶,⁸⁾ so that the decrease in the metal splitting shown in Table I can only be attributed to the steric effect of the *o*-substituents on the metal cation. Although in the case of the metal ketyl of IV the existence of a contact ion-pair is shown by the fact that the $\bar{\nu}_m$ value shifts regularly with the radius of a metal, no metal splitting is observed in its ESR spectrum. These facts indicate that the magnetic effect of a cation attached to an aromatic negative anion is only effective in rather close contact.

The proton hyperfine splittings of benzophenone ketyls will be discussed in subsequent publications.

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