ESR Studies on Negative Ions of Biphenyl Derivatives. I. Electron Spin Resonance Hyperfine Spectra of 4-Methyl Biphenyl and p, p′-Bitolyl Mononegative Ions

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The electron-spin resonance spectra of biphenyl mononegative ions have been observed by several investigators[1-3], however, those of the derivatives have not yet been studied extensively. In order to study the effect of methyl-group substitution on the spin densities at biphenyl ring carbons, the author synthesized 2-methyl, 3-methyl, 4-methyl, *o, o′*-bitolyl, *m, m′*-bitolyl and *p, p′*-bitolyl and the electron-spin-resonance hyperfine spectra of these mononegative ions were observed. The findings about the ESR spectra of 4-methyl biphenyl and *p, p′*-bitolyl will be presented in this paper.

Experimental

Solvents and Reducing Agents.—Each mononegative ion was made in a solution of either tetrahydrofuran (THF) or dimethoxyethane (DME) by reduction with potassium metal. These solvents were purified by the method described by Deguchi[4].

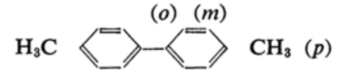
Spectrometer.—The ESR spectrometer employed was a high-resolution apparatus (type JES-3B) constructed by Japan Electron Optics Lab. Co., Ltd; its maximum resolution is about 30 milligauss. The operating frequency of the klystron was about 9470 Mc./sec. The magnetic field was modulated at a frequency of 100 kc./sec. and at a modulation width of about 100 milligauss. An aqueous solution of peroxylamine disulfonate[5] was used as a standard for the *g*-value and the magnetic field.

Overall widths were measured between the points where the resonance signal could just be distinguished from the noise level.

Results

***p, p′*-Bitolyl Mononegative Ion.**—The observed spectra measured in THF and DME are shown in Fig. 1(a) and Fig. 1(b) respectively.

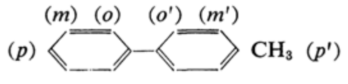
In both cases, the hyperfine structures of these spectra were identical, and the overall width was 46.7 gauss. The *g*-value was 2.0025.



The observed spectra consisted of seventeen groups, each split further into several hyperfine lines. In order to analyze the hyperfine structures of the observed spectrum, we assumed by referring to the spin densities on the carbon atoms of the biphenyl ring as calculated by Hückel's MO treatments (as shown in Fig. 1(d), that the hyperfine splitting coefficients of the six protons in the two methyl groups attached to the para-positions ($\varDelta H_p$), these of four-ring protons at the ortho-positions ($\varDelta H_o$), and those of four-ring protons at the meta-positions ($\varDelta H_m$) were equal to the following values: $\varDelta H_p=5.63$ gauss, $\varDelta H_o=2.66$ gauss, and $\varDelta H_m=0.51$ gauss. Thus, one can explain almost all the hyperfine structures of the observed spectra fairly well. The relative intensities of these hyperfine lines calculated on the basis of this assumption are shown in Fig. 1(c).

The spectra constructed on the basis of calculated spin densities are shown in Fig. 1(d). The observed and calculated spectra were in fairly good agreement in this case.

4-Methyl Biphenyl Mononegative Ion.—The observed spectra measured in THF and DME are shown in Fig. 2(a) and Fig. 2(b) respectively.



Although the shapes of hyperfine structures observed in THF were different from those in DME, inspite of the concentration having been adjusted in a number of ways, the overall width was 33.6 gauss, and the *g*-value was 2.0024 for both samples.

As shown in Fig. 2(a) and Fig. 2(b), the observed spectra consisted of thirteen groups, each of which split alternately into eight or nine hyperfine lines, while the terminal groups split into only a few hyperfine lines.

The line spacing of these hyperfine lines in each group of the spectra was equal to 0.32 gauss. In order to explain the structures of

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[1] E. de Boer, *J. Chem. Phys.*, **25**, 190 (1956).

[2] E. de Boer and S. I. Weissman, *J. Am. Chem, Soc.*, **80**, 4551 (1958).

[3] A. Carrington and J. Dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

[4] Y. Deguchi, *J. Chem. Phys.*, **32**, 1584 (1960).

[5] G. E. Pake, J. Townsend and S. I. Weissman, *Phys. Rev.*, **85**, 682 (1952).

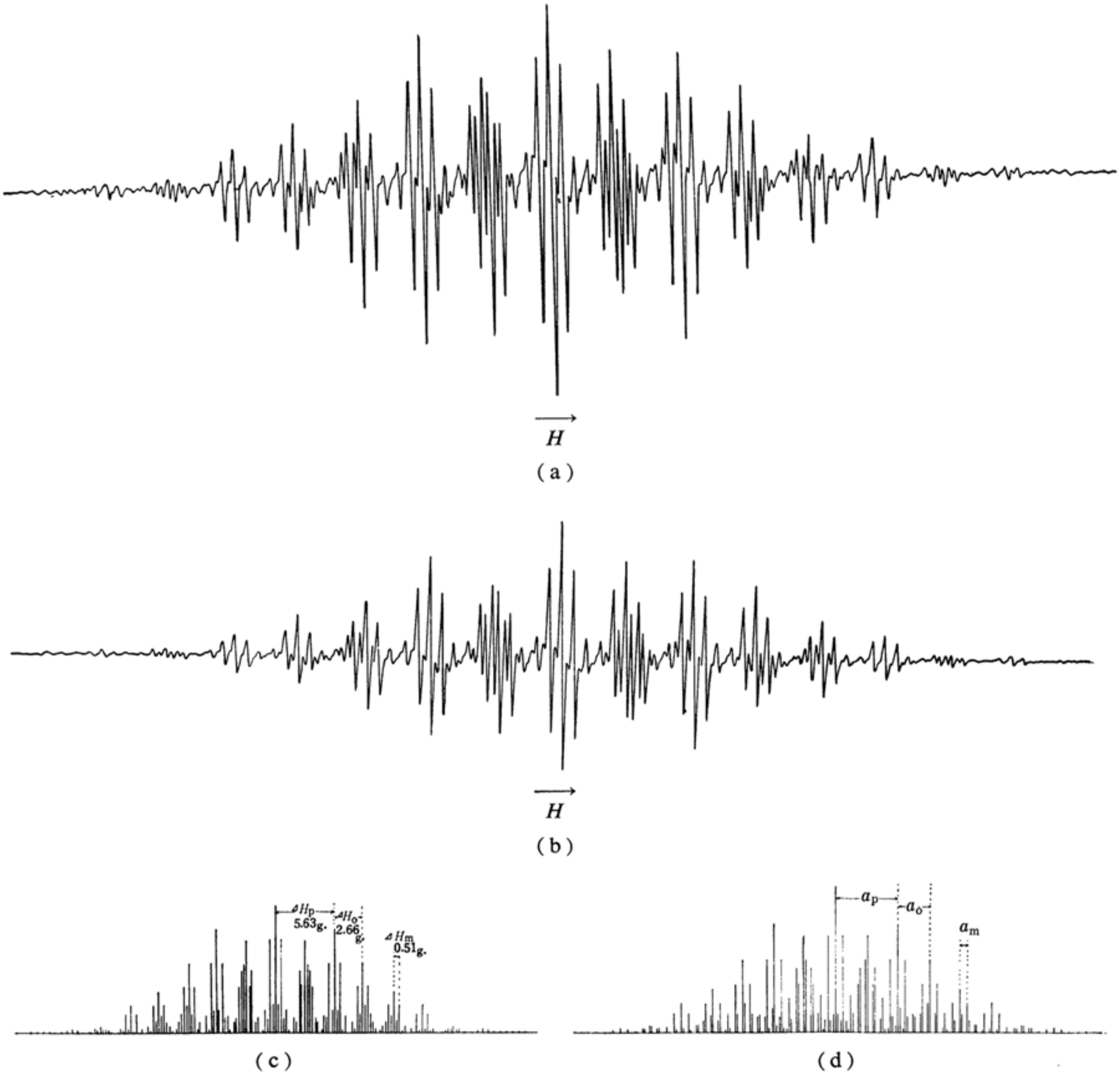
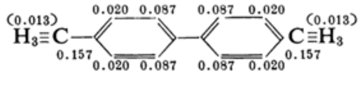


Fig. 1. p, p'-Bitolyl mononegative ion.
(a) and (b) : ESR spectra in THF and DME
(c) and (d) : Intensity diagrams constructed based upon experimentally determined and theoretically calculated spin densities



the observed spectra, the author at first assumed, by referring to the spin densities on the carbon atoms of the biphenyl ring as shown in Fig. 2(d) predicted by Hückel's MO calculations, that the splitting coefficients of each methyl proton and of a ring proton at the para-position (ΔH_p, $\Delta H_p'$) were almost equal, and that the splitting coefficient ratios of methyl protons and of each ring proton at the para-, ortho and meta-positions were nearly equal to 8 : 4 : 1.

Thus, one can explain that the observed spectra consisted of thirteen groups. In this case, however, it was difficult to explain the details of the hyperfine structures of the observed spectra thoroughly. In order to account for the details of the hyperfine structures, the author paid attention to those of the terminal and the next inner groups of the spectrum, since few overlaps of the hyperfine lines would occur among them. Each of the terminal groups and each of the next inner groups in

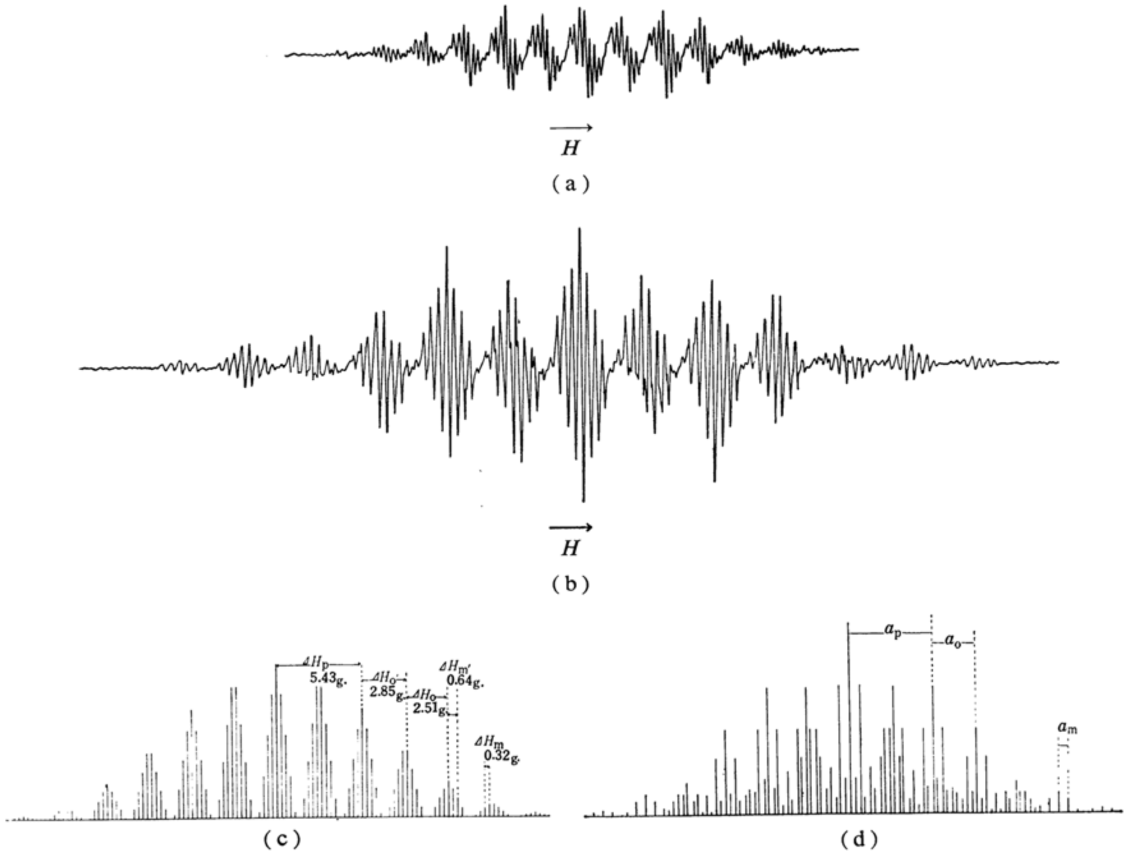
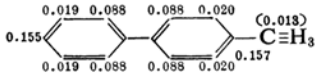


Fig. 2. 4-Methyl biphenyl.
(a) and (b) : ESR spectra in THF and DME
(c) and (d) : Intensity diagrams constructed based upon experimentally determined and theoretically calculated spin densities



the spectra consisted of seven and eight lines respectively, and their relative intensity ratios were 1 : 2 : 3 : 4 : 3 : 2 : 1 and 1 : 3 : 5 : 7 : 7 : 5 : 3 : 1.

On the basis of these relative intensity ratios of the hyperfine lines in the terminal groups, the author assumed that the splitting-coefficient ratio in both pairs of ring protons at the meta-positions ($\Delta H_m' : \Delta H_m$) was equal to 2 : 1. Moreover, since the hyperfine structures of the terminal groups and the next inner groups were different from each other, we assumed finally that the splitting coefficients of both pairs of ring protons at the ortho-position would have different values ($\Delta H_o'$ and ΔH_o) respectively, and that the difference between these values ($\Delta H_o' \sim \Delta H_o$) was equal to 0.32 gauss. Thus one can explain the hyperfine structures of the next inner groups from one end group by considering it as an overlap of two groups of hyperfine lines which have intensity ratios equal to those of the terminal groups.

In this case, one cannot determine which is larger $\Delta H_m'$ or ΔH_m and $\Delta H_o'$ or ΔH_o, but we assumed that $\Delta H_m'$ is larger than ΔH_m, taking into account the results of Hückel's MO calculations, and that $\Delta H_o'$ is larger than ΔH_o, considering the electron inductive effects due to a methyl group.

Putting together these assumptions in the manner described above, the arithmetic ratios of the splitting coefficients, ΔH_s, of each methyl, para, ortho and meta-protons were determined as follows:

$\Delta H_p : \Delta H_o : \Delta H_m' : \Delta H_o : \Delta H_m = 19 : 10 : 9 : 2 : 1$.

The relative intensities of the hyperfine lines thus constructed are shown in Fig. 2(c). The measured values of the splitting coefficients of each proton were as follows:

$\Delta H_p = 5.43$, $\Delta H_o' = 2.85$, $\Delta H_o = 2.51$, $\Delta H_m' = 0.64$, $\Delta H_m = 0.32$ gauss.

On the other hand, the spectrum calculated by Hückel's MO theory is given in Fig. 2(d). The observed and calculated spectra were not in satisfactory agreement with each other in this case.

Summary

The electron spin resonances of 4-methyl biphenyl and p,p'-bitolyl mononegative ions were observed in either dimethoxyethane or tetrahydrofuran, using potassium metal as a reducing agent. Well-resolved proton hyperfine spectra were observed in each case, and the g-value, the overall width, and the hyperfine splitting coefficients due to the methyl protons and ring protons were determined.

The theoretical spectra were constructed according to the spin densities calculated by Hückel's MO treatment, and these results were compared with the observed spectra.

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