ESR and ENDOR Studies of the 2-Methylbenzophenone Anion Radical: Unusual Spin Density Distribution due to a Sterical Hindrance by Methyl Substitution

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Well-resolved ESR and ENDOR spectra of the 2-methylbenzophenone anion radical were observed at low temperature in DMF. The hyperfine coupling constant values obtained are consistent with each other, and indicate an unusual spin-density distribution in a molecule that is largely different from that of the pristine benzophenone anion radical. The most characteristic is the nonequivalency on the two ortho-positions of the phenyl ring. These findings are also discussed based on a comparison with the case of the 2-methylphenyl phenyl nitroxide, and a lack of a free rotation of the phenyl rings is concluded.

The electron spin resonance (ESR) spectroscopy of an anion radical produced from 2-methylbenzophenone ($\mathbf{1}^{-\bullet}$, Chart 1) was studied as one of the derivatives of benzophenone, and is claimed to be a unique unsymmetrical radical.[1] Grignard reactions were also investigated in this sterically hindered benzophenone.[2] However, only little information concerning the molecular structures of the radical anion or the radical intermediate resulted, due to the lack of a well-resolved hyperfine structure. According to the broad quartet splitting (ca. 1:3:3:1), the ESR spectrum was tentatively analyzed as being due to the three protons at the ortho- and para-positions on the unsubstituted phenyl ring, assuming a large bond twisting of the methylated phenyl ring. The ESR spectra of deuterium compounds also supported this speculation. The localization of the unpaired electron on the unsubstituted phenyl ring of this type was also observed in 2-methylphenyl phenyl nitroxide (**2**, Chart 1), where the bond-twisting angle of the methylated phenyl ring was estimated to be 45—50°.[3] However, a detailed analysis regarding an evaluation of the hyperfine coupling constant (hfcc) values and their assignments was impossible because of the complicated hyperfine structure.

In the case of poorly resolved or complicated ESR spectra, electron nuclear double resonance (ENDOR) spectroscopy is useful for evaluating the hfcc values. This was demonstrated in **2**, for which several small hfccs responsible for its broad spectrum were determined. A discussion concerning the effect of the methyl substitution could thus be successfully made.[4]

From ENDOR observation of $\mathbf{1}^{-\bullet}$ we obtained clearly resolved 7 or 9 different hfccs, and compared the values with those of a benzophenone anion radical ($\mathbf{3}^{-\bullet}$) and **2**. Two characteristics were disclosed: The hfccs at the ortho- and para-positions of the unsubstituted phenyl ring are different and moreover the hfccs at the two ortho-positions are different. The former result is incompatible with that of **2**, and the latter with that of **2** and $\mathbf{3}^{-\bullet}$. Thus, we tried to confirm by ESR experiments these hfccs determined by ENDOR. It turned out that, by reducing the strong alkali-ion pairing in highly polar solvent, such as *N*,*N*-dimethylformamide (DMF), the ESR spectra turned out to be almost perfectly resolved. A computer simulation of the spectrum vindicated an unusual spin-density distribution of $\mathbf{1}^{-\bullet}$. A discussion will be presented on the basis of the experimental results from the view point of a sterical hindrance and a restricted rotation of the phenyl rings of $\mathbf{1}^{-\bullet}$.

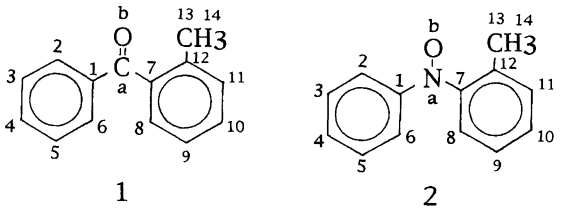

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Chart 1.

Experimental

2-Methylbenzophenone (**1**) was synthesized and recrystallized by a method described in the literature.[5] The anion radical ($\mathbf{1}^{-\bullet}$) was produced by reducing **1** in vacuo with an alkali metal (sodium or potassium). Well purified and dried 1,2-dimethoxyethane (DME) or DMF was used as the solvent. The anion radical in DMF was obtained by replacing the solvent (DME) with DMF after evaporating the solvent.[6]

ESR and ENDOR measurements were carried out using JEOL spectrometers (FE-1X and 3X). The ENDOR device and its cavity (TM_{110} mode type) were previously described in detail.[4] Sample tubing made of a quartz capillary must be used to avoid a large *Q*-value loss by DMF. A computer simulation was carried out using a JEOL computer (JC-6).

Results

The observed ESR spectrum of $\mathbf{1}^{-\bullet}$ with a counter ion Na^+ is shown in Fig. 1 together with its simulated spectrum. The anion radical species is rather of the loose ion-pair type in a DMF solution.[7] The simulation was performed on the basis of the hfcc values determined from the corresponding ENDOR spectrum

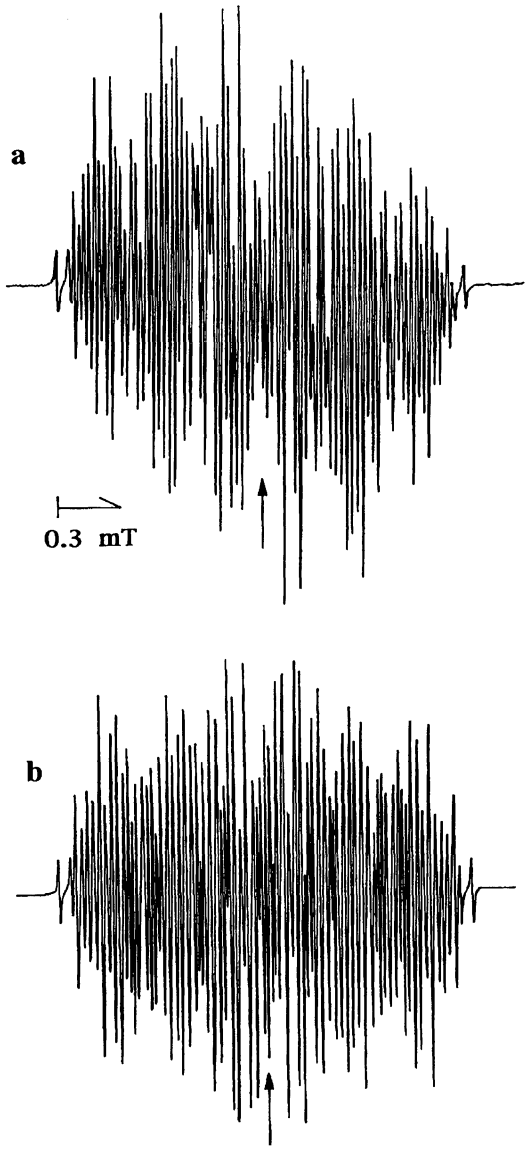

Fig. 1. Observed ESR spectrum (a) of the 2-methylbenzophenone anion radical with a counter ion Na^+ at −60 °C in DMF and its simulated one (b).

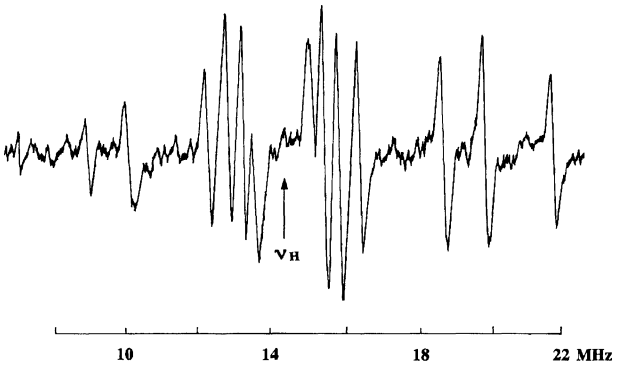

Fig. 2. ENDOR spectrum of the 2-methylbenzophenone anion radical with a counter ion Na^+ at −90 °C in DMF. The symbol ν_H indicates the frequency of the free proton.

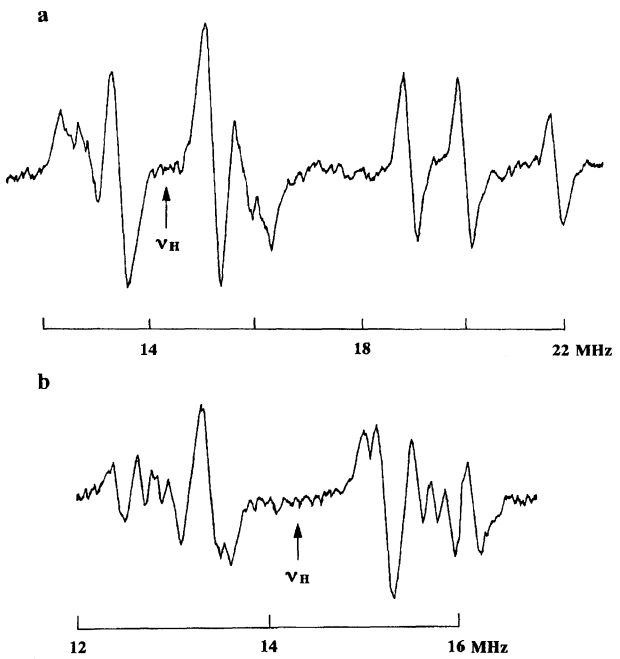

Fig. 3. ENDOR spectrum (a) of the 2-methylbenzophenone anion radical with a counter ion Na^+ at −100 °C in DME, a part of which is enlarged in (b) with higher resolution.

(Fig. 2). The ESR and ENDOR spectra were recorded at −60 and −90 °C, respectively. Figure 3 is the ENDOR spectrum of $\mathbf{1}^{-\bullet}$ with a counter ion Na^+ observed at −100 °C in DME. This spectrum belongs to the tight ion-pair species which causes the broadly resolved ESR spectrum. The ENDOR spectrum of $\mathbf{3}^{-\bullet}$ is also exhibited in Fig. 4 in order to compare these ENDOR spectra and to compare their different characteristics. The analyzed hfccs are summarized later in a discussion concerning a sterically hindered model with less probable free rotation.

Discussion

ESR and ENDOR Spectra. Sterical twisting of the phenyl ring by methyl substitution at the ortho-position is likely to produce small hfccs and, hence, smeared spectra. Besides, the small hfcc due to an alkali ion (Na^+ or K^+) with a large spin quantum number sometimes brings about a broad spectrum. In 2-methylbenzophenone anion radical it turned out that a well-resolved ESR pattern that was different from the previous ones[1,2] was observed in DMF by changing the solvent. This may be due to a loose ion-pair formation in the DMF solvent, in which the alkali cation is solvated.[7] The spectrum shown in Fig. 1a, however, is still difficult to analyze, since there exist a number of nonequivalent protons. A computer simulation (Fig. 1b) was initiated in view of the ENDOR spectrum which resolved (at least) 7 equivalent proton groups, reaching satisfactory reproduction by the slightest modification of the hfcc

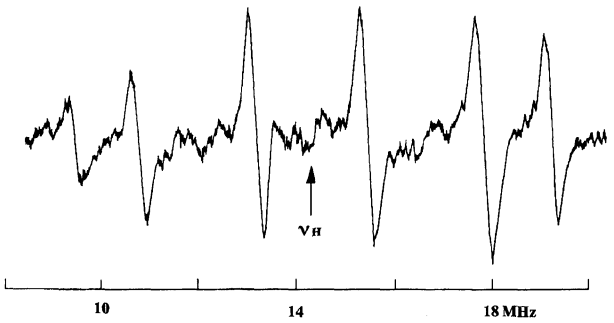

Fig. 4. ENDOR spectrum of the benzophenone anion radical with a counter ion Na^+ at −85 °C in DMF.

values from the ENDOR measurements. A computer simulation like that described in Fig. 1b also ascertains the number of equivalent protons as well. This fact is helpful when the hfccs are assigned to the protons by taking into account the calculated spin-density distributions. The ESR results, thus obtained, are summarized in Table 1.

The ENDOR spectrum of $\mathbf{3}^{-\cdot}$ (Fig. 4) comprises three pairs of absorptions, two large hfcc groups (9.44 and 19.29 MHz doublet for para-protons and 10.87 and 17.83 MHz for ortho-protons) and one small hfcc of meta-protons (13.23 and 15.45 MHz). In the case of $\mathbf{1}^{-\cdot}$, however, three absorptions appear in the frequency range above 18 MHz. This suggests a further splitting of the hfccs of the two ortho-protons in the unsubstituted phenyl ring: 18.64 and 19.79 MHz absorptions.[8] Contradictory to three equivalent protons at the para- and the ortho-positions, speculated from the broad 1 : 3 : 3 : 1 splitting by Maruyama et al.,[1,2] their nonequivalency was unambiguously concluded from the ENDOR measurements. This finding is also remarkable when compared with the almost equivalent hfcc values of the para- and two ortho-protons concluded to exist in the same ortho-methylated system, **2**. The absorption frequencies due to the smaller hfccs were precisely determined to be 15.14, 15.59, 15.81, and 16.34 MHz, two of which belong to the meta-protons in the unsubstituted phenyl ring.[8] The ENDOR data are also compiled in Table 1. As mentioned above, these characteristic properties concerning the hfcc values and number of equivalent protons in $\mathbf{1}^{-\cdot}$ led to a satisfactory ESR simulation; thus, ESR and ENDOR data are both compatible and complimentary. Concerning the hfcc assignment, one comment is necessary: considering the equivalent proton numbers in the simulation, one hfcc in the meta-position (0.108 mT in ESR or 0.106 mT in ENDOR) must be set so as to be equal to one of the nonequivalent protons in the substituted phenyl ring, here in the para-position. In the ENDOR spectrum shown in Fig. 3, the fundamental properties described above are almost the same, but the smaller coupling groups further split, and the hfcc values, themselves, changed slightly (see Table 1), probably because of a tight ion pairing in DME and/or its solvent effect.

Sterically Hindered Structure and Restricted Rotation. Considering the spin-density localization almost exclusively on the unsubstituted phenyl ring and the nonequivalency on the two ortho-protons or the two meta-protons, one has to reckon with a sterically hindered structure and a restricted rotation of the phenyl rings. Here, we take account of a twisting of the methylated phenyl ring around the C_a–C_7 bond, keeping the C_1–C_a–C_7 bond angle and the coplanarity between the carbonyl and the unsubstituted phenyl ring unchanged. Otherwise, the spin density of the LUMO orbital does not concentrate on one phenyl ring. This type of sterical twisting by methyl substitution at the ortho-position was claimed for **2** on the basis of proton as well as nitrogen hfccs.[3,4] Moreover, some kinds of molecular interactions between relatively closely neighboring groups, such as C_6–C_8 and/or O_b–CH_3, must be introduced to make, for instance, the hfcc values of the two ortho-positions of one phenyl ring different. This means, in MO calculations, a slight change in the Coulomb and/or resonance integrals for the concerned atoms. These sophisticated treatments at last produced the comparatively satisfactory results shown in Table 1. In this calculation by the McLachlan method the twisting angle around the C_a–C_7 bond was set to 60° (the resonance integral of 0.5β). This angle works mainly for the localization of the unpaired electron on the unsubstituted phenyl ring and explains the large difference in the hfccs, for example, between the C_6 and C_8 positions. The resonance integral between C_6 and C_8 was set to be 0.12β, and the Coulomb integrals for C_6 and C_2 were changed by 0.05β and -0.05β, respectively. The unsymmetrical changes of the Coulomb and resonance integrals work mainly for the nonequivalency of the two ortho- and meta-positions on each phenyl ring. These treatments can explain the difference between the C_2 and C_6 or C_3 and C_5. The other parameters for C=O and CH_3 are typical ones, which have been described elsewhere.[9] Because of several possibilities to change the MO parameters, we did not attempt a more satisfactory fitting.

In any case, the important points are: 1) a large twisting (60°) of the methylated phenyl group out of π-conjugation, producing a large amount of localization of the unpaired electron on the unsubstituted phenyl group, and 2) an unsymmetrical molecular interaction in the π-conjugated framework, resulting in many nonequivalent spin density distributions. Especially, the latter fact implies the lack of free rotation of the phenyl rings. Even if some kind of molecular interaction on the ortho-positions is taken into account, such a free rotation would average the hfccs between the two ortho- or meta-positions on each phenyl ring, as is the case of $\mathbf{3}^{-\cdot}$. It is, therefore, concluded that 2-methylbenzophenone is a system which shows a specific sterical hindrance and a less probable free rotation of the phenyl rings.

Comparison with 2-Methylphenyl Phenyl

Table 1. Spin Density and hfcc Values of the 2-Methylbenzophenone Anion Radical

Position	Spin density[a]	Calcd hfcc/mT[b]	Obsd hfcc/mT		
			ESR[c]	ENDOR	
				DMF[d]	DME[e]
a	0.458				
b	0.113				
1	−0.017				
2	0.129	0.362	0.308	0.308	0.327
3	−0.043	0.119	0.108	0.106	0.103
4	0.166	0.466	0.532	0.531	0.534
5	−0.051	0.143	0.144	0.144	0.133
6	0.159	0.445	0.390	0.390	0.404
7	−0.005				
8	0.037	0.102	0.054	0.056	0.065
9	−0.008	0.023			0.058
10	0.040	0.113	0.108	0.106	0.103
11	−0.004	0.012			
12	0.024				
13	0.000				
14	0.001	0.068	0.076	0.076	0.093

a) McLachlan method, $\lambda=1.25$. b) McConnell relation was used, $|Q|=2.8$ mT. c) A counter ion Na^+ at −90 °C in DMF. d) A counter ion Na^+ at −60 °C in DMF. e) A counter ion Na^+ at −100 °C in DME. c, d, e) The assignments to, for example, the 2 and 6 or the 3 and 5 positions are tentatively made based on the MO calculation.

Table 2. Comparison of the hfcc Values of the Unsubstituted Phenyl Ring

Compound	Method	hfcc/mT					Comment
		Position 2,6		Position 3,5		Position 4	
$\mathbf{1}^{-\cdot}$	ESR	0.308	0.390	0.108	0.144	0.532	This work
	ENDOR	0.308	0.390	0.106	0.144	0.531	This work
	Calcd	0.362	0.445	0.119	0.143	0.466	This work
2	ESR	0.268		0.083		0.261	Ref. 3,4)
	ENDOR	0.273		0.088		0.273	Ref. 3,4)
	Calcd	0.269		0.123		0.241	Ref. 3,4)
$\mathbf{3}^{-\cdot}$	ESR	0.252		0.082		0.350	Ref. 10)
	ENDOR	0.249		0.079		0.354	This work
	Calcd	0.254		0.083		0.346	Ref. 10)
$\mathbf{4}^{-\cdot}$	ESR	0.339	0.469	0.075	0.131	0.647	Ref. 11)
	Calcd	0.343	0.456	0.089	0.151	0.581	Ref. 11)

Nitroxide, Benzophenone, and Benzaldehyde Anion Radicals. The hfcc values of the unsubstituted phenyl ring for 2-methylphenyl phenyl nitroxide,[3,4] the benzophenone and benzaldehyde anion radicals[10,11] are compared in Table 2 for discussion. The conclusions concerning the exclusive rotation of the methyl-substituted phenyl ring and the twisting angle of 60° are the same as **2**. The remarkable difference, however, is that the para- and two ortho-protons have equivalent spin distributions. In particular, the equivalency on the two ortho-protons in **2** seems to be explained by the free-rotation mechanism which is applied to $\mathbf{3}^{-\cdot}$. A more probable free rotation may result from the fact that **2** is a neutral radical. On the other hand, there exists a counter cation in the vicinity of the molecule and/or $\mathbf{1}^{-\cdot}$ is strongly solvated. Therefore, such a free rotation would be restricted in $\mathbf{1}^{-\cdot}$. Although this situation may also be the case for $\mathbf{3}^{-\cdot}$, the twisted angle is much smaller than $\mathbf{1}^{-\cdot}$ and, therefore, a free rotation is much more probable, even in the anion radical state.

It is interesting to point out that the hfccs of $\mathbf{1}^{-\cdot}$ are similar to those of the benzaldehyde anion radical ($\mathbf{4}^{-\cdot}$).[11] This may suggest a kind of similarity in the molecular structure. The hfcc values of the benzaldehyde anion radical would indicate that the molecule in solution is tumbling as a whole, while maintaining a rigid orientation of the phenyl and formyl groups. This promises unsymmetrical hfccs in the two ortho- and meta-protons. In other words, the phenyl ring is not freely rotating around the bond connecting the two groups. This also seems to be the case concerning $\mathbf{1}^{-\cdot}$.

In conclusion, detailed ESR and ENDOR observa-

tions clarified the complicated sterically hindered structure of 2-methylbenzophenone, and the two unique unsymmetrical characters are disclosed: 1) an exclusive twisting of the 2-methylated phenyl ring out of the π-conjugate, and 2) a restriction of free rotation to prohibit any averaging of the hfccs.

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8) According to the deuterium-substituted experiments,[1] the larger hfcc groups come from the protons on the unsubstituted phenyl ring, indicating that the substituted phenyl ring is considerably tilted out of the π-conjugate of the other half moiety. This is also the case for **2**.[3,4]
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