# Utilization of (n,$\pi^*$) Excitation Bands in the Formation of Radicals. II. Thiobenzophenone Anion Radical[1]

**Hanan C. Heller**

*Contribution from the Scientific Laboratory, Ford Motor Company, Dearborn, Michigan 48121.* *Received March 30, 1967*

**Abstract:** Selective formation of the thiobenzophenone anion radical is accomplished by light excitation (5770 A) of thiobenzophenone within its (n,$\pi^*$) band. Excitation with 3660-A light results in the formation of both benzophenone and thiobenzophenone anion radicals. By analogy with the carbonyl group, and for several other reasons, the sulfur atom is assumed to participate in the $\pi$ bond of the thiocarbonyl group *via* an electron in a 3p orbital, rather than in a pd$^2$ orbital. Experimental spin densities are determined for the *ortho*, *meta*, and *para* positions of the radical from its proton hyperfine couplings, using McConnell's relationship. It is found, however, that matching only these experimental values with spin densities obtained by a McLachlan-type calculation does not yield a unique choice of Coulomb and resonance integrals for the thiocarbonyl group. An estimate of the spin density on the sulfur atom, $\rho_S$, is obtained from the measured $g$ value of the radical. The inclusion of this estimated $\rho_S$ in the matching process yields integrals for sulfur which, as expected, are smaller than those of oxygen. A similar approach gives reasonable integral values for the carbonyl group in the benzophenone radical. As for photochemical properties, thiobenzophenone is shown to be capable of *photosensitizing* the oxidation of acyloins to $\alpha,\beta$-diketone anion radicals, as previously found for benzophenone. This is believed to occur *via* the scavenging of a hydrogen (or electron) by the triplet state of thiobenzophenone.

Several studies in recent years have utilized light excitation in the formation of radicals in solution. These have included the formation of anion (*e.g.*, $\alpha,\beta$-diketone[1] and benzophenone[1-3]), neutral (*e.g.*, tri-*t*-butylanilino and phenoxy[4]), and cation radicals (*e.g.*, hexamethylbenzene[5]). Most of these studies employed unfiltered mercury light, or at best light energies corresponding to *any* of the absorption bands of the parent molecules. However, from a practical viewpoint, it has been found best to utilize excitations in the (n,$\pi^*$) bands of these polyatomic molecules.[1] The reasons for this are twofold. First, in many heteroatom-containing molecules, the (n,$\pi^*$) bands are well separated from the ($\pi,\pi^*$) bands in the same molecule, as well as from (n,$\pi^*$) and ($\pi,\pi^*$) bands in different molecules. Utilization of (n,$\pi^*$) bands allows therefore the selective excitation of such a molecule in the presence of other molecules acting as hosts or impurities. A particular demonstration of this is given in the present report. Moreover, the different locations of (n,$\pi^*$) bands in different molecules can facilitate photosensitization studies, as demonstrated earlier in the photosensitized formation of $\alpha,\beta$-diketone (acylil) anion radicals.[1] Secondly, the relatively small molar extinction coefficients associated with (n,$\pi^*$) bands ($\epsilon \simeq 10$–$100$) allow for a homogeneous excitation throughout the solution or solid in which the radical is to be generated. The ensuing radicals are therefore well distributed and exhibit, in many cases, sharp, well-resolved esr spectra.

In the present work, (n,$\pi^*$) excitation is employed for the selective formation of a radical which has not been studied to date, *i.e.*, the thiobenzophenone anion radical.[6] The structure of the radical and the spin-density distribution in it are discussed and compared to those of the benzophenone radical. In addition, the photosensitizing capability of thiobenzophenone is demonstrated.

## Experimental Section

Thiobenzophenone was prepared by treatment of an ethanolic solution of benzophenone with $H_2S$ in the presence of HCl.[7] The recrystallized solid was dark blue, but turned white on prolonged exposure to air, presumably due to conversion to benzophenone. Because of this instability, radical formation was carried out within a short time after the preparation of thiobenzophenone. Solutions consisting of the compound ($\sim$0.5 *M*) and NaOH ($\sim$0.3 *M*) in 70:30 ethanol–water were used. Solutions were transferred to an esr sample holder, made of Pyrex tubing (3-mm o.d.), and no attempt was made to exclude air during the transfer. The esr cavity was cylindrical, operating in the $TE_{011}$ mode; a small hole was drilled in the cylinder wall for light entrance. Selective light excitation was performed with a Bausch & Lomb monochromator equipped with a 200-w mercury source. Corning glass filters were used when elimination of second-order lines was necessary (see below). A similar lamp was employed for unfiltered irradiation.

The magnetic field was monitored with a proton probe and a Hewlett-Packard 524C frequency counter. Spectroscopic $g$ values were measured by comparison with the position of the center line of the *p*-benzosemiquinone anion radical in *n*-butyl alcohol, which was utilized as a secondary standard. The $g$ value of the *p*-benzosemiquinone ion was taken as 2.00468 at room temperature.[8] The error in measurement is estimated to be $\pm$0.0001.

Optical spectra were recorded on a Cary Model 14 spectrophotometer.

## Results and Discussion

### 1. Formation and Identification of the Thiobenzophenone Anion Radical.

Irradiation of the thiobenzophenone solution for several minutes with 3660-A light gives rise to an esr signal. However, while some of the initial esr lines increase in intensity during the

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[1] H. C. Heller, *J. Am. Chem. Soc.*, **86**, 5346 (1964). Part I of this series.

[2] P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963).

[3] R. Wilson, *Can. J. Chem.*, **44**, 551 (1966).

[4] N. M. Atherton, E. J. Land, and G. Porter, *Trans. Faraday Soc.*, **59**, 818 (1963).

[5] R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1120 (1965).

[6] While this report was in preparation, a preliminary communication appeared in which the esr spectrum of the anion radical of a derivative of thiobenzophenone, *p*-$CH_3OC_6H_4CSC_6H_4OCH_3$-*p*, was reported: E. G. Janzen and C. M. Dubose, Jr., *J. Phys. Chem.*, **70**, 3372 (1966). This radical, prepared by the action of alkali metals in tetrahydrofuran, possesses some hf splittings and a $g$ value similar to those reported here.

[7] B. F. Gofton and E. A. Braude, "Organic Syntheses," N. Rabjohn, Ed., Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 927.

[8] B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

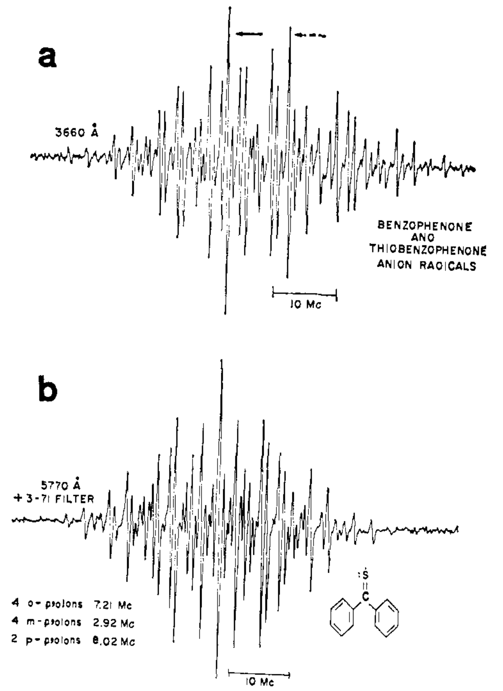

Figure 1. (a) Esr spectrum of thiobenzophenone and benzophenone anion radicals formed by 3660-A excitation of a basic alcoholic solution of thiobenzophenone. The dashed and solid arrows point to the centers of the benzophenone and thiobenzophenone radicals, respectively. (b) Esr spectrum of thiobenzophenone anion radical alone formed by 5770-A excitation of a basic alcoholic solution of thiobenzophenone.

irradiation, additional new lines rapidly appear. In fact, these new lines, which are intermixed with the initial set of lines, are already quite prominent by the time the first field scan is completed, several minutes after initiation of the irradiation. A typical spectrum obtained after 10 min of irradiation is shown in Figure 1a. A similar spectrum was obtained during irradiation of the solution with unfiltered mercury lamp light.

It is clear from the asymmetric line distribution in Figure 1a that the irradiated solution contains more than one radical species. Inasmuch as benzophenone was the starting material for the synthesis of thiobenzophenone, and that it may also be a photoproduct of the latter,[9] it was assumed that one of the radicals in solution is the benzophenone anion radical. This radical forms readily in a basic solution which is exposed, for example, to benzophenone's $(n,\pi^*)$ band at 3660 A.[1-3] A thiobenzophenone solution containing added amounts of benzophenone and exposed to 3660-A light gave a spectrum identical with Figure 1a, except for a slight increase in the relative intensity of some of the lines. The most prominent increase occurred for the line marked with a broken arrow, strongly suggesting that it is the center of the spectrum of the benzophenone radical.

Assuming that Figure 1a consists of lines due to only two species and knowing the hyperfine (hf) splittings of the benzophenone radical, it is possible, in principle, to extract the spectrum of the second species. This may be done by computer techniques or, perhaps more simply, by subtraction of the recorded spectrum of the benzophenone radical from the composite spectrum stored in a multichannel analyzer, such as the Varian CAT 1024.[10] It is the purpose of the present work, however, to demonstrate the *selective* formation of this second radical species by purely photochemical means.

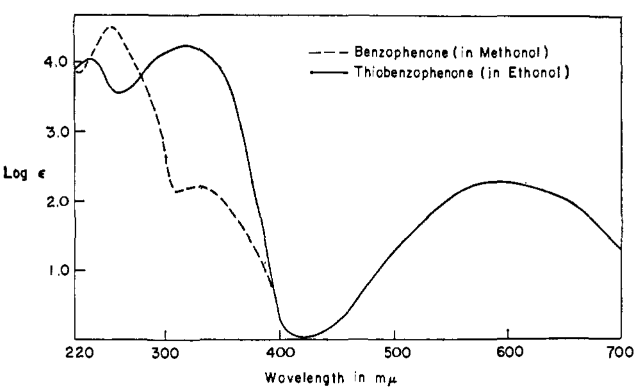

Figure 2. Electronic absorption spectra of benzophenone and thiobenzophenone in alcoholic solution. The spectrum of thiobenzophenone is taken from the work of Korver, *et al.*[11]

The electronic spectra of benzophenone (as recorded in the present work) and of thiobenzophenone (recorded by Korver, *et al.*[11]) in alcoholic solutions are shown in Figure 2. For benzophenone it is well established by now that the band centered at 3350 A is due to a $(n,\pi^*)$ transition, while the one at 2500 A is due to a $(\pi,\pi^*)$ transition.[12,13] Although no detailed study of the various bands of thiobenzophenone has yet been reported, the similarity of its spectrum to that of benzophenone suggests that the band centered at 5900 A is due to an $(n,\pi^*)$ excitation,[14] while the bands below 4000 A are due to $(\pi,\pi^*)$ excitations. The shift of the $(n,\pi^*)$ band of thiobenzophenone relative to that of benzophenone is to be expected, since the energy of the band is related to the ionization potential of the atom on which it is centered. The ionization potential of oxygen is 13.6 ev, whereas that of sulfur is 10.4 ev,[15] in accord with the red shift of the thiobenzophenone band. The extinction coefficients of the main bands of thiobenzophenone also support the above assignment, *i.e.*, $\log \epsilon \simeq 2$ for the "forbidden" $(n,\pi^*)$ band and $\log \epsilon \simeq 4$ for the allowed $(\pi,\pi^*)$ band.

It is clear from Figure 2 that unfiltered mercury or 3660-A light would excite both thiobenzophenone and benzophenone in solution. On the other hand, 5770-A light would result in the direct excitation of the thiobenzophenone only. The photochemical generation experiment was repeated, therefore, employing the 5770-A band of mercury. A 3-71 Corning filter was used in conjunction with the Bausch & Lomb (grating) monochromator to eliminate second-order lines at ~2875 A.

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[9] G. Oster, L. Citarel, and M. Goodman, *J. Am. Chem. Soc.*, **84**, 703 (1962).

[10] A striking example of the second approach is provided by the identification of a second radical, in addition to the 5-thymyl radical, in X-irradiated 5,6-dihydrothymine: H. C. Geller, S. Schlick, and T. Cole, *J. Phys. Chem.*, 71, 97 (1967).

[11] O. Korver, J. U. Veenland, and Th. J. de Boer, *Rec. Trav. Chim.*, **84**, 289 (1965).

[12] See, for example, S. F. Mason, *Quart. Rev.* (London), **15**, 287 (1961).

[13] In this discussion on the spectral features of benzophenone and thiobenzophenone, we are neglecting small spectral shifts, especially for the $(n,\pi^*)$ bands, due to the basicity of the solutions employed for irradiation.

[14] H. M. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[15] J. N. Murrell, "Theory of the Electronic Spectra of Organic Molecules," Methuen & Co., London, 1963, p 174.

**Table I.** Experimental and Calculated (McLachlan) Spin Densities

| | | Experimental[d] | | Calculated[d] | | | |
|---|---|---|---|---|---|---|---|
| Anion radical | Position | | | (1) | (2) | (3) | (4) |
| (1) Thiobenzophenone[a,f] | *ortho* | 0.1086 | (0.0954) | 0.1137 | 0.1102 | 0.1109 | (0.0988) |
| | *meta* | 0.0440 | (0.0386) | −0.0415 | −0.0401 | −0.0396 | (−0.0364) |
| | *para* | 0.1209 | (0.1061) | 0.1148 | 0.1108 | 0.1158 | (0.0999) |
| | Sulfur | ≃0.20[e] | | 0.0564 | 0.1810 | 0.1724 | (0.1803) |
| | Carbon(1)[c] | ... | | 0.5037 | 0.3909 | 0.3681 | (0.4389) |
| | Carbon(2)[c] | ... | | −0.0392 | −0.0370 | −0.0286 | (−0.0344) |
| (2) Benzophenone[a,g] | *ortho* | 0.1181 | (0.1037) | 0.1174 | 0.1200 | 0.1120 | (0.1051) |
| | *meta* | 0.0434 | (0.0381) | −0.0402 | −0.0414 | −0.0385 | (−0.0362) |
| | *para* | 0.1460 | (0.1282) | 0.1332 | 0.1332 | 0.1284 | (0.1245) |
| | Oxygen | ≃0.15–0.25[e] | | 0.1051 | 0.0909 | 0.1449 | (0.1937) |
| | Carbon(1)[c] | ... | | 0.3406 | 0.3596 | 0.3194 | (0.2824) |
| | Carbon(2)[c] | ... | | −0.0104 | −0.0156 | −0.0077 | (−0.0004) |
| (3) Benzophenone[b,h] | *ortho* | 0.1063 | | 0.0979 | | | |
| | *meta* | 0.0346 | | −0.0319 | | | |
| | *para* | 0.1477 | | 0.1330 | | | |
| | Oxygen | ... | | 0.1453 | | | |
| | Carbon(1)[c] | ... | | 0.2703 | | | |
| | Carbon(2)[c] | ... | | 0.0272 | | | |

[a] Radicals produced by light excitation of basic ethanol–water solutions (70:30). [b] Radical prepared by Rieger and Fraenkel[21] by electrolytic reduction in N,N-dimethylformamide. [c] Carbon(1) is the carbonyl (thiocarbonyl) carbon and carbon(2) is the ring carbon directly bonded to carbon(1). [d] Data in parentheses pertain to $Q = -75.6$ Mc; the rest of the data pertain to $Q = -66.4$ Mc. [e] Estimate of spin density based on experimental $g$ value. [f] Spin densities calculated with (1) $h = 2.0$, $k = 1.0$, $\gamma = 0.9$; (2) $h = 0.6$, $k = 0.6$, $\gamma = 1.0$; (3) $h = 0.8$, $k = 0.8$, $\gamma = 1{,}0$; (4) $h = 0.6$, $k = 0.6$, $\gamma = 0.9$. [g] Spin densities calculated with (1) $h = 1.8$, $k = 1.4$, $\gamma = 1.0$; (2) $h = 2.0$, $k = 1.4$, $\gamma = 1.0$; (3) $h = 1.3$, $k = 1.25$, $\gamma = 1.0$; (4) $h = 1.0$, $k = 1.2$, $\gamma = 1.0$. [h] Spin densities calculated by Rieger and Fraenkel[21] with $h = 1.5$, $k = 1.6$, and $\gamma = 0.9$.

The spectrum obtained under these conditions is shown in Figure 1b. This spectrum, which is due to only one species, arises from the interaction of the odd electron with two groups of four protons each, and one group of two protons, and is assigned to the thiobenzophenone anion radical. The hf couplings are 8.02 Mc for the two *para* protons, 2.92 Mc for the four *meta* protons, and 7.21 Mc for the four *ortho* protons. The latter two assignments are based on comparison with spin densities calculated by the McLachlan procedure.[16] A careful examination of Figure 1a shows that it is a composite of Figure 1b and of the spectrum of the benzophenone radical. Confirmation for the presence of a sulfur atom, instead of an oxygen atom, in the radical exhibiting the spectrum of Figure 1b is provided by the measured $g$ values. The $g$ value of the thiobenzophenone radical is 2.0054, while that of benzophenone is measured at 2.0033. This difference in $g$ value, which in large measure reflects the different spin–orbit couplings for sulfur ($\zeta_S = -382$ cm$^{-1}$) and oxygen ($\zeta_O = -152$ cm$^{-1}$),[17] is readily apparent from the positions of the central lines of the two radicals in Figure 1a (solid and dashed arrows).

**2. Spin Densities in the Thiobenzophenone and Benzophenone Radicals.** Experimental spin densities are readily obtained from measured hf splittings *via* McConnell's relationship[18]

$$a_{H(i)} = Q\rho_{C(i)} \qquad (1)$$

where $a_{H(i)}$ is the hf coupling of proton $i$, and $\rho_{C(i)}$ is the spin density of the uncoupled $\pi$ electron on carbon $i$, which is directly attached to proton $i$. $Q$ is a constant, for which many investigations have employed the value of −66.4 Mc (23.7 gauss).[19] Recently, some investigators have found that a value of $Q = -75.6$ Mc (−27 gauss) is more suited for some compounds, such as semiquinones.[20] In the present work, spin densities were calculated using both values of $Q$, but most of the ensuing discussion will concentrate on densities calculated with $Q = -66.4$ Mc. Experimental spin densities calculated with these values of $Q$ for the thiobenzophenone and benzophenone anion radicals are given in Table I. For comparison purposes, Table I also contains experimental spin densities determined by Rieger and Fraenkel[21] for the benzophenone radical formed by electrolytic reduction of benzophenone in dimethylformamide.

The experimental spin densities were compared with calculated values obtained by employing (1) Hückel LCAO molecular orbitals and (2) McLachlan's[16] procedure. The following parameters were varied for calculation purposes.

(1) $\alpha_S$ (or $\alpha_O$) $= \alpha_C + h\beta_{CC}$, where $\alpha_S$ ($\alpha_O$) is the Coulomb integral for the 3p-sulfur (2p-oxygen) orbital, $\alpha_C$ is the integral of the 2p-carbon orbital, $\beta_{CC}$ is the resonance integral for the 2p orbitals on two neighboring carbon atoms, and $h$ is a variable parameter. It was varied from 0.0 to 2.0 in 0.2 unit.[22]

(2) $\beta_{CS}$ (or $\beta_{CO}$) $= k\beta_{CC}$, where $\beta_{CS}$ ($\beta_{CO}$) is the resonance integral between sulfur (oxygen) and carbon p orbitals, and $k$ is a variable parameter. It was varied from 0.4 to 2.0 in 0.2 unit.[22]

(3) $\beta_{C-CS}$ (or $\beta_{CCO}$) $= \gamma\beta_{C-C}$, where $\beta_{C-CS}$ ($\beta_{C-CO}$) is the resonance integral between the thiocarbonyl (carbonyl) carbon and the ring carbon adjacent to it, and $\gamma$ is a variable parameter. It was varied between 0.8 and 1.0 in 0.1 unit.

The choice of limits for the above three parameters is rationalized as follows. The lower limit of $h \simeq 0$ is suggested by the electronegativity of sulfur,[23] which

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

(17) D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952); **17**, 905 (1949).

(18) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(19) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

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

(21) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2811 (1962).

(22) Smaller units, such as 0.1 and 0.05, were used for some calculations where initial results suggested the use of a finer variation.

(23) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 117.

is close to that of carbon; hence $\alpha_S \simeq \alpha_C$. The upper limit for $h$ is somewhat arbitrary and was selected as $h = 2.0$ for comparison of results with benzophenone, where $h$ is expected to be between 1.0 and 2.0.[23] The longer C–S bond, as compared with C–C bond lengths, dictates a choice of $k < 1$. The upper limit of $k$ was again chosen for comparison with benzophenone.[23] Parameter $\gamma$ was varied between 0.8 and 1.0 to allow for possible nonplanarity of the radicals.

Note that the electron of the sulfur participating in the $\pi$-electron network of the radical is assumed to be in a 3p orbital. Attempts have been made in the past to explain the properties of aromatic systems containing sulfur (*e.g.*, thiophene) by assigning the $\pi$ electrons of sulfur to pd$^2$ hybrid orbitals.[24] Although this approach may be useful in the case of aromatic rings or thiol groups where two sulfur electrons participate in the $\pi$ network, there appears little justification for applying it to the orbitals of the thiocarbonyl sulfur in the thiobenzophenone molecule. In the later case only one sulfur electron is expected to be involved in the $\pi$ network, and configurational mixing of 3d orbitals will not be compensated for by substantial increase in resonance energy. Moreover, the similarity of the electronic spectra of the carbonyl and thiocarbonyl chromophores strongly suggests a disposition of electrons in the latter similar to that of the former, *i.e.*, two 3p unshared electrons in a nonbonding orbital, one 3p electron participating in the $\sigma$ bond to the thiocarbonyl's carbon, and one 3p electron involved in the $\pi$ network. The extra electron in the radical is then situated in the lowest unoccupied $\pi$ orbital.

None of the Hückel molecular orbitals calculated with the above three parameters yielded spin densities compatible with those determined experimentally for thiobenzophenone or benzophenone, with either $Q = -66.4$ or $-75.6$ Mc. The calculated spin densities for the *ortho* and *para* positions were, in general, quite smaller than the experimental values. In addition, the calculated values for the *meta* positions were close to zero. Similar results were found by Rieger and Fraenkel for the benzophenone case.[21] The results suggest a high probability of *negative* spin densities[18] for the *meta* positions. It is fairly well established by now that, for radicals possessing negative spin densities, better agreement between calculated and experimental spin densities is achieved by employing McLachlan's approach.[16] Spin densities were therefore calculated[25] by employing the following expressions

$$\rho_r^\pi = c_{r0}^2 - \lambda\sum_s \pi_{rs}c_{s0}^2 \qquad (2)$$

and

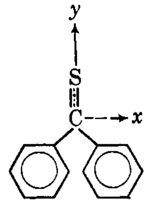
$$\pi_{rs} = -4\sum_i^{\text{occ}}\sum_j^{\text{vac}}(c_{ri}c_{sj}c_{si}c_{rj})/(E_j - E_i) \qquad (3)$$

where $i$ is summed over all occupied, and $j$ over all unoccupied orbitals. In these expressions, $\rho_r^\pi$ is the $\pi$-electron spin density on carbon $r$, $c_{r0}^2$ is the Hückel spin density, $\pi_{rs}$ is the atom–atom polarizability between carbons $r$ and $s$, $c_{ij}$'s are the coefficients of the atomic wave functions in the molecular orbitals, $E_i$'s are the energies of the Hückel molecular orbitals, and $\lambda$ is a constant taken to be 1.2 $\beta$.

**a. Thiobenzophenone.** The spin densities calculated by this procedure for the *ortho*, *meta*, and *para* positions of the thiobenzophenone radical were closest (within $\pm 6\%$ tolerance) to the experimental values ($Q = -66.4$ Mc) when $h = 2.0$, $k = 1.0$, and $\gamma = 0.9$. The densities calculated with these parameters are shown in Table I. However, an increase in tolerance to $\pm 10\%$, which in view of the approximations entailed in the McLachlan approach is more realistic, resulted in 21 sets of values for $h$, $k$, and $\gamma$ giving densities in accord with experiment. All of these calculated spin densities were quite sensitive to the choice of $\gamma$ ($\gamma = 0.9$ or 1.0 only), suggesting that the radical is planar or nearly so. The calculated spin densities, however, were quite insensitive to the choice of $k$ ($k$ ranging between 0.6 and 1.2) and extremely insensitive to the choice of $h$ ($h$ between 0.6 and 2.0).

It is clear from these results that the experimental value of the densities on the *ortho*, *meta*, and *para* positions do not provide sufficient data for a unique characterization of the molecular orbitals of the radical. In fact, in the case of the 1,4-benzosemiquinone ion it has been shown that parameters chosen to yield calculated values in agreement with only the experimentally available spin densities (*e.g.*, $\rho_{C(2)}$ in benzosemiquinone) may give wrong densities for "blind" centers in the molecule (*e.g.*, $\rho_{C(1)}$ and $\rho_O$ in benzosemiquinone).[20] A closer examination of the calculated spin densities of the thiobenzophenone radical revealed that the densities of the thiocarbonyl's sulfur and carbon are considerably more sensitive to the choice of $h$ and $k$. This is not surprising, inasmuch as these parameters characterize the thiocarbonyl group and are apt to affect it most radically. Since C$^{13}$ signals arising from the natural abundance of C$^{13}$ in the thiocarbonyl's carbon could not be readily discerned in the spectra, an attempt was made to extract an estimate of the spin density on the sulfur, $\rho_S$, from the measured $g$ value of the radical.

Consider the following representation



in which the radical is assumed to be planar, or nearly so, with its $\pi$ network above and below the plane of the paper along the $z$ direction. The nonbonding electrons of the sulfur are then in the $p_x$ orbital of this atom. Because of the symmetry of the molecule, the spectroscopic $g$ tensor is expected to be diagonalized along the Cartesian axes chosen.[26] The isotropic (experimental) $g$ value is then given by

$$g_i = {}^1/_3(g_x + g_y + g_z) \qquad (4)$$

Studies with oriented radicals in single crystals have firmly established that $g_z$ has a value close to the $g$ value

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(24) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

(25) Computations were performed on a Philco 212 computer, utilizing the Jacobi method for diagonalization purposes.

(26) The $g$ value results of several oriented radicals indicate that this is indeed so. For a compilation of experimental $g$ tensors see J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

of a free electron, *i.e.*, 2.0023.[27] Therefore

$$g_i \simeq 2.0023 + {}^1/_3(\Delta g_y' + \Delta g_y'' + \Delta g_x) \qquad (5)$$

where $\Delta g_x = g_x - 2.0023$, etc., and the contribution along the $y$ axis has been divided into two parts. By far the most important contribution, $\Delta g_y'$, is due to the virtual admixture by spin–orbit coupling of the $(\mathrm{n},\pi^*)$ state with the ground state of the radical. This contribution is given by

$$\Delta g_y' = \frac{2\zeta_\mathrm{S}\rho_\mathrm{S}}{\Delta E(\mathrm{n},\pi^*)} \qquad (6)$$

In this expression,[28] $\zeta_\mathrm{S}$ $(= -382\ \mathrm{cm}^{-1})$ is the spin–orbit coupling parameter for sulfur, and $\Delta E(\mathrm{n},\pi^*)$ is the energy separation between the $(\mathrm{n},\pi^*)$ excited state and the ground state. The other contributions, *i.e.*, $\Delta g_y''$ and $\Delta g_x$, are expected to be much smaller, since they arise from admixture of $(\pi,\sigma^*)$ states, which have considerably larger $\Delta E$. These admixtures are also nullified to a considerable extent by admixture of $(\sigma,\pi^*)$ states. Moreover, these other contributions involve mostly carbon centers with $\zeta_\mathrm{C} = -28\ \mathrm{cm}^{-1}$, which is much smaller than $\zeta_\mathrm{S}$. Therefore, $\Delta g_y'' \simeq \Delta g_x \simeq 0$, and

$$2.0054 \simeq 2.0023 + \frac{2}{3}\left(\frac{\zeta_\mathrm{S}\rho_\mathrm{S}}{\Delta E(\mathrm{n},\pi^*)}\right) \qquad (7)$$

In other words, the $g$ tensor for the sulfur-containing radical is expected to be axially symmetric, or nearly so.[29] Note, however, that this conclusion is reached as a result of the particular bonding scheme assumed for the sulfur. If a different bonding scheme is assumed, such as is necessary in alkyl sulfide radicals, a completely anisotropic $g$ tensor may result.[30]

In the absence of an experimental value for $\Delta E(\mathrm{n},\pi^*)$ for the thiobenzophenone radical, the value of 16,950 cm$^{-1}$ measured for the thiobenzophenone molecule was utilized. The difference between the two values is expected to be small and should not materially change the present results. The value thus obtained for the spin density on sulfur is $\rho_\mathrm{S} = 0.2$.

The inclusion of this value for $\rho_\mathrm{S}$ greatly reduces the choice of values for $h$ and $k$. Of the 21 sets of values mentioned above only two sets yield calculated $\rho_\mathrm{S}$ close to 0.2, while the other 19 sets give $\rho_\mathrm{S} < 0.13$.[31] These two "good" sets are (1) $h = 0.6$, $k = 0.6$, $\gamma = 1.0$, and (2) $h = 0.8$, $k = 0.8$, and $\gamma = 1.0$, with a $\rho_\mathrm{S}$ value of $\simeq 0.18$. The spin densities calculated with these parameters are tabulated in Table I. Note, however, that a slight deviation from the axial symmetry assumed for the $g$ tensor of the radical would yield $\rho_\mathrm{S} < 0.2$.

Similar results were obtained with $Q = -75.6$ Mc, although calculations with this parameter were not quite as extensive as with $Q = -66.4$ Mc. Only sets with $0.6 \leq h \leq 1.0$ and $0.6 \leq k \leq 1.0$ gave spin densities in agreement with experimental values. Most of the "good" sets had values of $\gamma = 0.9$, suggesting a slight nonplanarity for the radical. Sets with $h$ and $k$ greater than 1.0 gave, in general, poor values for $\rho_\mathrm{S}$. The results obtained with one typical "good" set for $Q = -75.6$ Mc are tabulated in Table I.

**b. Benzophenone.** It is of interest to compare the results for the thiobenzophenone radical with those found for the related benzophenone radical. For the latter, only two sets of values for $h$, $k$, and $\gamma$ gave calculated spin densities for the *ortho*, *meta*, and *para* positions within a ±10% tolerance of the experimental values. These are (1) $h = 1.8$, $k = 1.4$, $\gamma = 1.0$, and (2) $h = 2.0$, $k = 1.4$, and $\gamma = 1.0$. Both sets yield $\rho_\mathrm{O} \simeq 0.1$. Experimental spin densities as well as those calculated with the two sets of parameters are tabulated in Table I.

A difficulty arises in trying to estimate an experimental value for $\rho_\mathrm{O}$. If one assumes a nearly axially symmetric $g$ tensor, as was done for the thiobenzophenone radical, and utilizes the $\Delta E(\mathrm{n},\pi^*)$ found for benzophenone molecule, *i.e.*, $\simeq$29,800 cm$^{-1}$, one obtains $\rho_\mathrm{O} \simeq 0.29$. However, since $\zeta_\mathrm{O}$ $(= -152\ \mathrm{cm}^{-1})$ is much smaller than $\zeta_\mathrm{S}$ $(= -382\ \mathrm{cm}^{-1})$, and $\Delta E(\mathrm{n},\pi^*)$ for benzophenone is considerably larger than that of thiobenzophenone, considerable deviation from axial symmetry is to be expected for the $g$ tensor of the benzophenone radical. Although this deviation cannot be estimated from available experimental data, a lower limit may be set on $\rho_\mathrm{O}$ by making the (probably drastic) assumption that $\Delta g_y'' \simeq \Delta g_x \simeq \Delta g_y'$. In this case $\rho_\mathrm{O}$ would be $\simeq$0.1.

A more realistic estimate of $\Delta g_y'$ for the benzophenone radical may be obtained by comparison with radicals containing carbonyl or carbonyl-like groups in which the value of $\rho_\mathrm{O}$ has been firmly established. One such radical is the *p*-benzosemiquinone anion radical, for which $\rho_\mathrm{O}$ has been found to be 0.14.[20,32] The isotropic $g$ value for this radical is 2.0047. Recalling that $\Delta E(\mathrm{n},\pi^*)$ for this radical is[33] $\simeq$20,000 cm$^{-1}$ and that it comprises two carbonyl groups, one finds that $\Delta g_y'$ constitutes about 60% of the $g$-tensor anisotropy.[34] If a similar relative contribution is assumed for $\Delta g_y'$ in the benzophenone radical, $\rho_\mathrm{O} \simeq 0.18$. In the same vein, a qualitative comparison with the $g$ tensor of the carbonyl-like radical di-*t*-butyl nitroxide suggests a $\rho_\mathrm{O}$ of 0.15–0.25.[35]

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[27] H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Am. Chem. Soc.*, **82,** 766 (1960); see also ref 26.

[28] H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

[29] Some experimental evidence for this conclusion is provided by the esr study of the phenylsulfenyl radical obtained by pyrolyzing diphenyl disulfide: P. J. Zandstra and J. D. Michaelson, *J. Chem. Phys.*, **39**, 933 (1963). This radical, in which the sulfur atom is assumed to be bonded in a similar way to the sulfur in thiobenzophenone, exhibits $g$ components of 2.0, 2.0, and 2.1246.

[30] An example is the $\mathrm{HOOC{-}CH(NH_2){-}CH_2{-}S\cdot}$ radical produced in irradiated cystine dihydrochloride: Y. Kurita and W. Gordy, *J. Chem. Phys.*, **34**, 282 (1961).

[31] The "best" set ($h = 2.0$, $k = 1.0$, $\gamma = 0.9$), which gave calculated spin densities for *ortho*, *meta*, and *para* positions within ±6% of experimental values, turns out to be a very "poor" set since it predicts $\rho_\mathrm{S}$ to be 0.056.

[32] W. M. Gulick, Jr., and D. H. Geske, *J. Am. Chem. Soc.*, **88**, 4119 (1966).

[33] The value of $\Delta E(\mathrm{n},\pi^*)$ for neutral *p*-benzoquinone is $\simeq$22,200 cm$^{-1}$ (see ref 15), and Y. Harada and H. Inokuchi (*Mol. Phys.*, 8, 265 (1964)) suggest that for the radical $\Delta E(\mathrm{n},\pi^*)$ is between 18,200 and 22,200 cm$^{-1}$.

[34] The $g$-value variation is assumed to arise almost totally from two carbonyl groups, the contributions of the four ring carbons being very small. For each carbonyl group $\Delta g_y'$ is then approximately 60%.

[35] O. H. Griffith, D. W. Cornell, and H. M. McConnell (*J. Chem. Phys.*, **43**, 2909 (1965)) have determined the components of the $g$ tensor of di-*t*-butyl nitroxide, $\mathrm{(CH_3)_3NO(CH_3)_3}$, oriented in a host crystal of tetramethyl-1,3-cyclobutanedione. This neutral radical is isoelectronic with a carbonyl anion radical and may serve as a rough model for it. Assuming the N–O direction is along the $y$ axis (present notation), then $g_x = 2.0061$, $g_y = 2.0089$, and $g_z = 2.0027$. Since the spin density of the uncoupled electron is distributed almost exclusively on the nitrogen and oxygen centers, $g_y$ is almost totally due to admixture of $(\mathrm{n},\pi^*)$ state, and $g_x$ to admixture of $(\pi,\sigma^*)$ states, with the ground state. Here,

These conclusions, in spite of their qualitative nature, suggest that the "best" values of $h$ (1.8 or 2.0) yield $\rho_O$ which is probably too low. It is interesting to note that with a tolerance of $\pm 12\%$ one obtains $\rho_O = 0.145$ for $h = 1.3$, $k = 1.25$, and $\gamma = 1.0$. Moreover, if one accepts larger tolerances, values of $\rho_O$ closer to 0.2 may be calculated. All of these require $h$ values of 1.0 to 1.4. It appears, therefore, that a set of values of $h = 1.3$, $k = 1.25$, and $\gamma = 1.0$ (rather than the two "best" set listed before) may be more realistic for the characterization of the benzophenone radical. The spin densities calculated with this set are also tabulated in Table I.

If one employs $Q = -75.6$ Mc, several "good" sets are readily obtained with $0.8 \leq h \leq 1.4$, $0.8 \leq k \leq 1.2$, and $0.9 < \gamma \leq 1.0$. The calculated results of one such typical set of parameters are shown in Table I.

Finally, for the sake of completeness, experimental and calculated spin densities obtained by Rieger and Fraenkel[21] for the benzophenone radical in N,N-dimethylformamide are also presented in Table I. The reported "best" values of parameters are $h = 1.5$, $k = 1.6$, and $\gamma = 0.9$, which are somewhat different from values chosen in the present work. Their experimental spin densities based on $Q = -66.4$ Mc are also somewhat different from those of the present work. These differences, however, may be attributed to the different solvents employed in the two works.[36]

In conclusion one notes that the $h$ and $k$ values which best describe the thiocarbonyl group in the present work are smaller than those of the carbonyl group. This is in accord with values dictated by other spectroscopic and chemical findings.[23] It is clear from the present discussion that estimates of $\rho_S$ and $\rho_O$ have helped considerably in narrowing down the limits for the parameters $h$, $k$, and $\gamma$ for the benzophenone and thiobenzophenone radicals. However, in the absence of $C^{13}$ splittings due to the carbonyl and thiocarbonyl carbons, a firm choice of "best" values of $h$ and $k$ cannot be made. Moreover, it must be remembered that the McLachlan procedure, like the Hückel approach, is only approximate. The $h$, $k$, and $\gamma$ values obtained here are therefore suggestive and instructive, but not necessarily binding.

**3. On the Photochemical Reactions of Thiobenzophenone.** In a recent study of the photochemical reactions of thiobenzophenone, Oster, *et al.*,[9] have found the following results for alcoholic solutions of thiobenzophenone: (1) irradiation with 5800-A light of an aerated solution gave only benzophenone; irradiation with 3660-A light gave no over-all reaction; (2) irradiation of oxygen-free solutions with 3660-A light resulted in the predominant formation of benzhydril mercaptan and dibenzhydryl disulfide.

No direct comparison can be made between the present work and the above results since here basic solutions were utilized and no attempt was made to isolate products. However, the marked buildup of esr signals due to the benzophenone anion radical upon prolonged irradiation with 3660-A light indicates that benzophenone is a by-product of irradiation at this wavelength. At 5770 A no esr signals due to benzophenone are observed, but this does not preclude the possible formation of benzophenone at this wavelength. The long persistence of the strong esr signals of the thiobenzophenone radical with irradiation at 5770 A would indicate that, if conversion to benzophenone does occur, its quantum yield is small. This would be in agreement with the results of Oster, *et al.*[9]

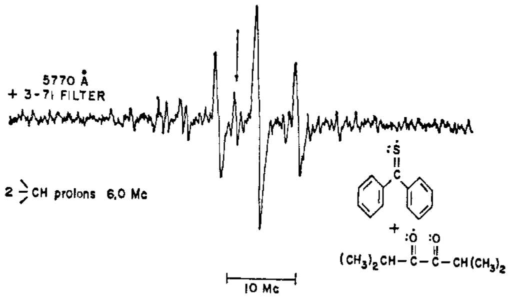

Figure 3. Photosensitized formation of the isobutyril anion radical by thiobenzophenone at 5770 A. The three esr lines with intensity ratio of 1:2:1 are due to the isobutyril anion radical, and the arrow points to the central line of the weak signals of the thiobenzophenone anion radical.

By analogy with benzophenone[1,37] one may assume that the thiobenzophenone anion radical is formed *via* a triplet state of thiobenzophenone. That is, the triplet thiobenzophenone scavenges a hydrogen atom from the solvent alcohol to form $(C_6H_5)_2\dot{C}SH$, or $(C_6H_5)_2C{=}\dot{S}$ in a basic medium.[38]

It has been previously demonstrated[1] that benzophenone can photosensitize the formation of acylil ($\alpha,\beta$-diketone) anion radicals from acyloins. A similar sensitization capability is found for thiobenzophenone. Figure 3 shows the esr spectrum obtained when a mixture of isobutyroin, $(CH_3)_2CHC({=}O)$-$C(OH)HCH(CH_3)_2$, and thiobenzophenone is exposed to 5770-A light in a basic alcohol solution. The three strong lines have intensity ratios of 1:2:1 and are due to the hf couplings of the two $\alpha$ protons in the isobutyril anion radical. Since isobutyroin does not absorb appreciably at wavelengths greater than 3400 A, it is incapable of oxidizing to the radical at 5770 A in the absence of thiobenzophenone.

Two possible mechanisms were suggested for the sensitizing action of benzophenone on acyloins.[1] The first involves a triplet–triplet energy transfer from the excited benzophenone to the unexcited acyloin, followed by the oxidation of the acyloin triplet. The second mechanism involves the direct oxidation of the acyloin *via* the loss of a hydrogen atom (or electron in the basic medium) to the benzophenone triplet. The energies of the triplet states of thiobenzophenone and isobutyroin are as yet unknown. However, the large differences in the energies of the $(n,\pi^*)$ singlets for the two compounds (16,950 cm$^{-1}$ for thiobenzophenone and 34,500 cm$^{-1}$ for isobutyroin) would suggest that the triplet state of thiobenzophenone is considerably

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therefore, $\Delta g_y = \Delta g_y' \simeq {}^2/_3$ of the total increase in $g$ value and, by comparison, suggests $\rho_O \simeq 0.2$ for the benzophenone radical. This, of course, is only a suggested value, since the nitroxide radical differs from the benzophenone radical by virtue of its charge, spin–orbit coupling of N, large $\rho_O$ on the nitroxide's oxygen, etc.

(36) J. Gendell, J. H. Freed, and G. K. Faenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

(37) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959); W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

(38) By analogy with benzophenone, a small portion of the radicals may actually form *via* a homolytic dissociation of such possible products as thiobenzopinacol or dibenzhydril disulfide: G. A. Russell and E. J. Geels, *Tetrahedron Letters*, 1333 (1963).

lower than the triplet state of isobutyroin. Hence, triplet–triplet energy transfer from the former to the latter would be extremely inefficient and may be neglected. The concentration of the isobutyril radical formed in the thiobenzophenone-sensitized reaction is an order of magnitude smaller than in the benzophenone-sensitized reaction. It is not clear yet whether this is due to the absence of the first mechanism in the thiobenzophenone case or to the weaker hydrogen-scavenging capacity of the excited triplet of thiobenzophenone when compared with that of benzophenone.

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# An Electron Spin Resonance Study of the Dihydroxy- and Dimethoxydurene Cation Radicals[1]

**Paul D. Sullivan**

*Contribution from the Chemistry Department, University of Waterloo, Waterloo, Ontario, Canada.* *Received February 27, 1967*

**Abstract:** The duroquinol cation radical has been studied in aluminum chloride–nitromethane in the temperature range $-90$ to $+10°$. At low temperatures the spectrum was analyzed in terms of *cis* and *trans* isomers, in agreement with earlier predictions. A four-jump model gives good agreement with the experimental data throughout the temperature range and the effective potential barrier to rotation is estimated to be $4.2 \pm 0.6$ kcal/mole. The dimethoxydurene cation radical was shown, on the other hand, to exist as only one species throughout the temperature range, and possible conformations of this radical are discussed. The line-width asymmetries of the duroquinol spectrum indicate that the signs of the isotropic splitting constants of the hydroxyl and methyl protons are negative and positive, respectively.

Modulations of the isotropic splitting constants of esr spectra are known to occur in a variety of ways, such as by hindered rotations,[2] fluctuating complexes with "gegenions" or solvent molecules,[3,4] and conformational interconversions.[5,6] The effect of these modulations[7,8] on the shape of esr lines can be related to the lifetime ($\tau$) of the contributing species. In the limit of long $\tau$ values, one observes a spectrum which is the sum of the individual spectra of the contributing species. When $\tau$ is short, a time-averaged spectrum of the individual species is observed. At intermediate values of $\tau$, the phenomenon of line-width alternation often occurs and such spectra can be simulated provided an adequate model for the exchange process is available.

Since the lifetime ($\tau$) of each species depends on the temperature, it should be possible to observe the spectra of the individual forms at low-temperature, line-width alternation on raising the temperature and eventually the time-averaged spectra. In the few instances, where this has been done,[9,10] the postulated model can then be tested, and the potential barrier between the individual forms can be estimated.

The duroquinol cation radical lends itself to this type of treatment and has been studied previously in $H_2SO_4$ by Bolton and Carrington[11] in the range $+10$ to $+50°$. The 13 lines from the four methyl group protons were found to be alternatively sharp and broad at lower temperatures, and the methyl group splittings were assumed to depend on the orientation of the hydroxyl groups with respect to the benzene ring plane. This suggests a model of rapid interconversion between four possible conformations (four-jump model), corresponding to two *cis* and two *trans* forms, and can account for the observed line-width alternation.[2,11] However, as pointed out by Fraenkel,[8] if one form (*cis* or *trans*) is present in excess, the problem reduces to a two-jump model, which can also account for the observed spectral changes. To decide between the two models, one should obtain a low-temperature spectrum, when the interconverting forms can be isolated and identified. This is not possible in $H_2SO_4$, because of the high viscosity of sulfuric acid solution at low temperatures.

However, a recent study of the related hydroquinone cation[10] radical in aluminum chloride–nitromethane[12] suggested that this system would similarly prove advantageous for the duroquinol and dimethoxydurene cation radicals. The latter radical is of interest because of the additional steric interactions.

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(1) Presented, in part, at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

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(3) E. DeBoer and E. L. Mackor, *J. Am. Chem. Soc.*, **86**, 1513 (1964).

(4) T. E. Gough and M. C. R. Symons, *Trans. Faraday Soc.*, **62**, 269 (1966).

(5) E. DeBoer and A. P. Praat, *Mol. Phys.*, **8**, 291 (1964).

(6) M. Iwaizumi and T. Isobe, *Bull. Chem. Soc. Japan.*, **38**, 1547 (1965).

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