Study of Radical Anions Derived from *m*-Dibenzoylbenzene and Its *tert*-Butyl Derivative

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Abstract: The esr spectra of the radical anion of *m*-dibenzoylbenzene (DBB) in HMPA have been analyzed. Comparison of the experimental hyperfine coupling constants with those calculated by the McLachlan method reveals that the outer phenyl rings are twisted out of the plane involving the central ring and both carbonyl groups. Two conformations of the anion of DBB exhibit the symmetry required by the esr spectrum. Optical studies of DBB^- in HMPA and THF show that in both solvents the anion exists in equilibrium with its diamagnetic dimer, the dimeric form predominating in THF. In HMPA the dimer arises from the aggregation of free ions, π–π bonding being responsible for its stability.

Ketyls, *i.e.*, radical anions derived from ketones, exhibit complex behavior. They exist not only in the form of free ions and ion pairs but may aggregate into para- or diamagnetic dimers.[1] Furthermore, the tendency of the keto group to be coplanar with aromatic moieties permits the existence of geometric isomers. For example, Maki[2] demonstrated that radical anions of terephthalic aldehyde are a mixture of cis and trans forms, and Fraenkel and his coworkers[3] showed that radical anions of benzaldehyde and acetophenone and of their derivatives are locked into a planar conformation which deprives them of their twofold axis of symmetry expected for a freely rotating substituent. In this respect, the ketyl of benzophenone is an exception; its esr spectrum shows that at not too low temperatures the 2, 2′, 6, and 6′ protons as well as the 3, 3′, 5, and 5′ are equivalent,[4] indicating a relatively easy rotation around each CO–Ph bond. This is not surprising; inspection of the model proves that the simultaneous coplanarity of the keto group with both phenyls is sterically unfavorable and consequently both groups oscillate about their coplanar positions.

Our investigation of radical anions derived from *m*-dibenzoylbenzene was undertaken in order to answer the following questions. To what extent are the outside phenyl groups equivalent, *i.e.*, what is the preferential conformation of these radical ions, do they dimerize, and, if so, what is the structure of the dimer?

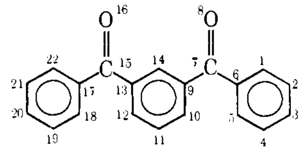
Experimental Section

Commercially available *m*-dibenzoylbenzene (DBB) was used after being recrystallized from cyclohexane and then vacuum sublimed. The *p*-di-*tert*-butyl derivative of *m*-DBB (di-*tert*-BuDBB) was prepared by a Friedel-Crafts reaction between isophthaloyl chloride and *tert*-butylbenzene. The product was purified in the same way as DBB. *Anal.* Calcd: C, 84.40; H, 7.54; O, 8.04. Found: C, 83.38; H, 7.41; O, 9.23. Vpc and nmr confirmed that the product was the pure para derivative.

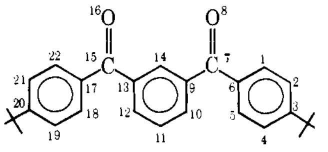
The preparation of sodium biphenyl solutions and the purification of hexamethylphosphortriamide, HMPA, and tetrahydrofuran, THF, have been described elsewhere.[5]

The optical and esr experiments were carried out using the Cary 14 spectrophotometer and the Varian 4500 spectrometer, respectively. The Varian E700 endor spectrometer was used for the endor spectra of *tert*-BuDBB.

The Esr Spectra of Radical Anions of DBB and Di-*tert*-BuDBB



DBB



di-*tert*-BuDBB

The radical anions were prepared in HMPA by mixing a 10^{-3} *M* solution of sodium biphenylide with a slight excess of the respective solid ketone. The conversions were nearly quantitative and the total concentration of the radicals, determined by the double integration of their overmodulated spectrum, was insignificantly affected by the addition of the ketone. The esr spectra of the resulting green solutions, after their dilution, are shown in Figures 1 and 2. Their main feature is a 1:2:1 triplet which shows further, well resolved structure.

The esr spectrum of $DBB\cdot^-$ is more complex than that of di-*tert*-$BuDBB\cdot^-$ because the protons on carbon atoms 3 and 20, which substantially contribute to the splitting of the $DBB\cdot^-$ signal, are eliminated in the di-*tert*-butyl derivative, while the interaction of the odd electron with the *tert*-Bu protons is too weak to be discerned in the spectrum of the latter radical. Even so, the esr spectrum of di-*tert*-$BuDBB\cdot^-$ is too complex for a straightforward analysis, and the study of its endor spectrum was necessary. From the latter, in which the rf field was swept over the interval 12.5–17.0 MHz, the following coupling constants were obtained: 0.239, 0.647, and 1.357 (all the values given in gauss). With this information available, all the proton coupling constants of di-*tert*-$BuDBB\cdot^-$ were deduced and confirmed by the computer simulation. The pertinent results are given in Table I. Substitution of *tert*-Bu groups for protons in positions 3 and 20 should insignificantly affect the distribution of π electrons. Consequently, the respective coupling constants of $DBB\cdot^-$ are expected to only slightly differ from those of

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[1] N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2538 (1964).

[2] A. H. Maki, *J. Chem. Phys.*, **35**, 721 (1961).

[3] (a) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2811 (1962); (b) N. Steinberger and G. K. Fraenkel, *ibid.*, **40**, 723 (1964).

[4] T. Takeshita and N. Hirota, *ibid.*, **51**, 2146 (1969).

[5] T. L. Staples and M. Szwarc, *J. Amer. Chem. Soc.*, **92**, 5022 (1970).

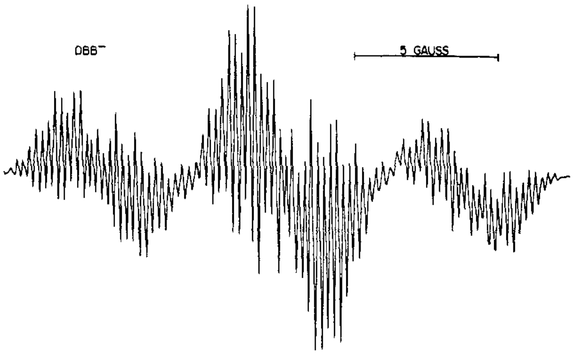

Figure 1. Esr spectrum of $\mathrm{DBB}\cdot^-$ in HMPA at 25°.

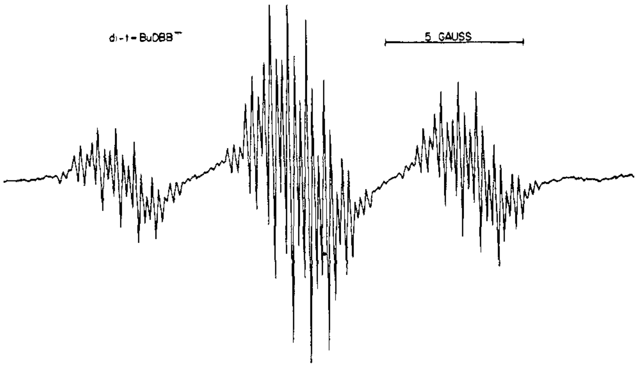

Figure 2. Esr spectrum of di-*tert*-$\mathrm{BuDBB}\cdot^-$ in HMPA at 55°.

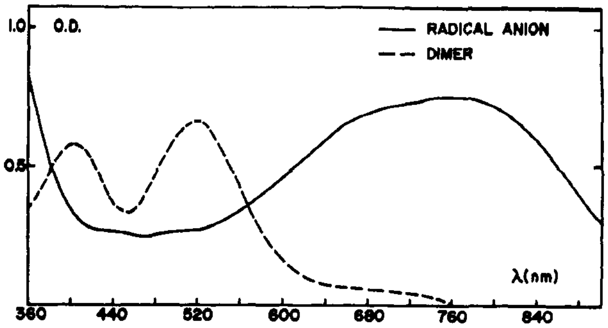

Figure 3. Visible spectrum of $\mathrm{DBB}\cdot^-$ (3.5×10^{-3} *M*, optical path 3.9×10^{-2} cm) in HMPA and of $(\mathrm{DBB}\cdot^-)_2$ (2.8×10^{-3} *M*, optical path 1.8×10^{-2} cm) in THF.

di-*tert*-$\mathrm{BuDBB}\cdot^-$. On this basis, the coupling constants of $\mathrm{DBB}\cdot^-$, also listed in Table I, were obtained, and the results again were confirmed by the computer simulation.

Table I. The Hyperfine Coupling Constants of $\mathrm{DBB}\cdot^-$ and Di-*tert*-$\mathrm{BuDBB}\cdot^-$ in HMPA

Protons[a]	*a*, G, in $\mathrm{DBB}\cdot^-$	*a*, G, in di-*tert*-$\mathrm{BuDBB}\cdot^-$
1, 5, 18, 22 (ortho, outside rings)	0.68	0.647[b]
2, 4, 19, 21 (meta, outside rings)	0.24	0.239[b]
3, 20 (para, outside rings)	0.96	
10, 12 (inner ring)	6.26	6.35
11 (meta to CO, inner ring)	1.36	1.36[b]
14 (between the CO's)	0.68	0.647[b]

[a] The assignment based on MO calculations; see the last part of the paper. Note that protons 1, 5, 8, and 22 are magnetically identical with proton 14. [b] Determined by endor.

The Electronic Spectra of $\mathrm{DBB}\cdot^-$ and of Its Dimer

The addition of an equivalent amount of DBB to a 10^{-3} *M* solution of sodium biphenylide or metallic sodium in HMPA results in a green solution, the spectrum of which is shown in Figure 3. The maximum of absorption in the visible region is at 760 nm, but some slight hypsochromic shift is noted on concentration or cooling of that solution. Simultaneously with that shift, new absorption bands appear at 520 and 400 nm; their intensities increase with concentration or with decreasing temperature. Hence, a 0.1 *M* solution is reddish and the frozen mass is deep red and diamagnetic.

Sodium biphenylide solution in THF turns red on the addition of DBB; its spectrum at $\sim 10^{-2}$ *M* concentration, also shown in Figure 3, reveals two absorption peaks at 520 and 400 nm and none at 760 nm. A 760-nm peak becomes apparent on dilution; however, even at the lowest concentration attainable in this study, its intensity is still weak.

Apparently, two species coexist in these solutions, presumably the monomeric radical ion which absorbs at 760 nm (the correlation of the esr with the optical spectrum confirms this conclusion) and a diamagnetic aggregate absorbing at 520 and 400 nm (the diamagnetism of the frozen solution seems to exclude the formation of triplets).

The concentration dependence of the optical spectrum was studied only in HMPA; the changes occurring in THF were too small to justify quantitative investigation. The required extinction coefficients were derived from the spectrum of the most dilute HMPA solution ($\sim 5 \times 10^{-4}$ *M*), where virtually only the monomeric "green" radical is present, and from the spectrum of the 10^{-2} *M* THF solution which contains only the "red" aggregates—the monomeric radicals being virtually absent. Thus, $\epsilon_{760,\mathrm{G}}$ and $\epsilon_{520,\mathrm{R}}$ were determined to be 5.5×10^3 and 1.34×10^4, respectively. Unfortunately, even the most concentrated HMPA solution still contains an appreciable fraction of the green species, and, therefore, could not be used for determining $\epsilon_{520,\mathrm{R}}$.

The red species does not absorb at 760 nm, but the contribution of the green one to the absorbance at 520 nm is not negligible. Hence, $\epsilon_{520,\mathrm{G}}$ had to be determined, and this was achieved by plotting OD(520)/*C* against OD(760)/*C*, where *C* denotes the total concentration of $\mathrm{DBB}\cdot^-$, in whatever form, in the investigated solution (based on the alkali titration). Such a plot was found to be linear and its slope gives, therefore, $(\epsilon_{520,\mathrm{G}} - \epsilon_{520,\mathrm{R}})/\epsilon_{760,\mathrm{G}}$, while the intercept provides the value of $\epsilon_{520,\mathrm{R}}$, which agreed with that determined from the spectra of the THF solution. Thus, $\epsilon_{520,\mathrm{G}}$ was found to be 0.09×10^4.

On the basis of these data, the concentrations of both species were determined at various dilutions and the plot of log [red] *vs.* log [green], shown in Figure 4, was constructed. It is linear; its slope is 2, indicating that the equilibrium between the monomeric $\mathrm{DBB}\cdot^-$ and its aggregate is represented by 2green $\rightleftarrows$ red. The respective equilibrium constant of association was calculated to be 15 *M* at room temperature.

The behavior of di-*tert*-$\mathrm{BuDBB}\cdot^-$ was not investigated quantitatively; however, qualitative observations show that this radical anion behaves like $\mathrm{DBB}\cdot^-$.

Table II. Molecular Orbital Calculations for DBB$\cdot^-$

		Calculated values for ρ				
Protons	a, G	Hückel,[a] planar	McLachlan,[b] planar	Q,[c] planar	McLachlan,[d] skewed	Q,[e] skewed
1, 5, 18, 22	0.68	0.035	0.048	16.6	0.030	22.5
2, 4, 19, 21	0.24	0.002	−0.015	16.0	−0.010	24.0
3, 20	0.96	0.0435	0.061	15.8	0.041	23.5
10, 12	6.26	0.1565	0.202	31	0.231	27.0
11	1.36	0.000	−0.059	23	−0.069	20.0
14	0.68	0.000	−0.015	45	−0.019	36.0

[a] Hückel-type calculations were performed only for qualitative inspection. They were not included in the discussion; therefore, we used the same α' and β' values as recommended for McLachlan calculations. [b] In these calculations $\alpha_{C'} = \alpha$ and $\beta_{CC'} = \beta$. The α parameters of carbon atoms adjacent to carbonyl were not changed. The parameter $\lambda = 1.2$. [c] Based on the ρ values given in the preceding column. [d] To account for the nonplanarity of DBB$\cdot^-$, we assumed that both carbonyl groups are coplanar with the center benzene ring, but the outside rings are twisted out of plane making the respective $\beta_{CC'} = 0.75\beta$. [e] Based on the ρ values given in the preceding column.

Comparison of the behavior of HMPA and THF solutions is instructive. The dimerization is enormously greater in the latter solvent, indicating that the ion pairs DBB$\cdot^-$, Na$^+$ readily dimerize (the concentration of free DBB$\cdot^-$ ions is probably vanishingly small in that solvent). The degree of aggregation of the free DBB$\cdot^-$ ions, present in large proportion in HMPA, is much smaller. However, the aggregation observed in HMPA is undoubtedly due to free ions and not ion pairs; otherwise, the slope of the line shown in Figure 4 would exceed 2. Such dimerization probably results from interactions arising from the polarizibility of these large molecules which leads to a π–π bonding. Similar observations have been reported previously for the system phenanthrene–quinone radical ions in HMPA, THF, and THP.[5] The existence in HMPA of doubly negatively charged aggregates not associated with cations is plausible. Indeed, it was shown elsewhere[6] that the dianions of tetraphenylethylene are completely dissociated in HMPA.

Molecular Orbital Calculations for DBB$\cdot^-$

The assignment of the coupling constants given in Table I is based on the spin densities determined by the Hückel and McLachlen molecular orbital calculations. In performing these calculations we assigned a value $\alpha + 1.4\beta$ to the Coulomb integral of oxygen and a value of 1.65β to the resonance integral of the C=O bond. These parameters were recommended by Fraenkel[7] and led to an excellent agreement beteen the calculated spin densities and coupling constant for a series of aromatic aldehydes and ketones.[3]

The results of the Hückel calculation are only of qualitative value (see Table II) and do not help in the assignment of the coupling constants. The McLachlen calculations were first performed for a planar species assuming that $\beta_{CC'} = \beta$ for all four C–C bonds linking the carbonyl groups with the aromatic moieties and taking all the aromatic Coulomb integrals to be equal. The results are given in the fourth column of Table II and apparently permit us to assign coupling constants 0.68, 0.24, and 0.96 G to the appropriate protons of the outside rings (note the constancy of the respective Q's). Moreover, the ratios of these coupling constants to the corresponding coupling constants reported for the benzophenone ketyl[3] are 0.27, 0.29, and 0.27, indicating that the relative spin distributions in the outside rings of DBB$\cdot^-$ and in the aromatic moieties of the benzophenone ketyl are virtually identical. However, the total spin density in each outside ring of DBB$\cdot^-$ is about 3.5 times smaller than in each ring of the benzophenone ketyl.

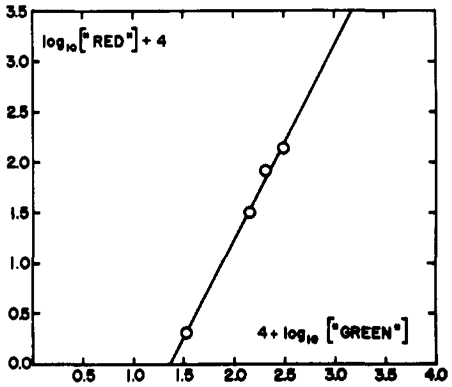

Figure 4. Log–log plot for equilibrium between "green" and "red" species in HMPA.

The assignment of the coupling constant 6.26 G to protons 10 and 12 is ascertained by our results obtained with di-*tert*-BuDBB$\cdot^-$ (see Table I), and it is qualitatively confirmed by the MO calculations (see Table II). The assignment involving protons 11 and 14 is the least certain; on the basis of our calculations we ascribe the coupling constant 1.36 G to proton 11 and attribute the coupling constant 0.68 to proton 14, although the calculated spin densities of protons 1, 5, 18, 22, and 14 are different, while the experimental data suggest that magnetically they are identical.

The Q values calculated from the spin densities are too small for the protons of the outside rings and too large for those on the central ring. This indicates to us that while the carbonyl groups probably are coplanar with the central ring, the outside rings are twisted out of plane. The McLachlan calculations were repeated, therefore, with $\beta_{CC'} = 0.75\beta$ for the C–C bonds linking the outside rings with the carbonyl groups. The results are given in the last two columns of Table II. It should be stressed that insignificantly different values for Q were obtained when $\beta_{CC'}$ was assumed to be 0.78β. On the other hand, Q values are much too low for the outside rings when $\beta_{CC'} = 0.8\beta$, and too high for $\beta_{CC'} = 0.7\beta$. The noncoplanarity of the outside rings accounts for the equivalence of protons 1 and 5, 2

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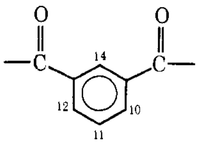
(6) A. Cserhegyi, E. Franta, J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, 89, 7129 (1967).

(7) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, 34, 1333 (1961).

and 4, etc., which would be nonequivalent had the phenyl groups been locked in a particular planar conformation persisting sufficiently long on the esr time scale.

The Q calculated from the ρ value of proton 14 is much too high. We cannot comment on this result, but we could not improve it by introducing different α's for carbon atoms adjacent to the CO groups.

Finally, the stereochemistry of the central ring need be considered. We assumed the carbonyl groups to be coplanar with the inner ring. In this case, three possible conformers could be formed, *viz.*, I–III. We rule out the conformer II because the esr spectrum clearly demonstrates the equivalence of protons 10 and 12. Consideration of steric hindrance makes conformer I more plausible than I, while the dipole–dipole repulsion between the CO groups might favor conformer III.



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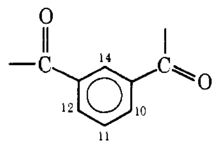

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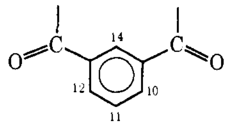

III

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Spectroscopic Studies of Ionic Solvation. X. A Study of the Solvation of Sodium Ions in Nonaqueous Solvents by ^{23}Na Nuclear Magnetic Resonance[1]

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Abstract: Chemical shifts of the ^{23}Na nucleus were measured for sodium tetraphenylborate, perchlorate, iodide, and thiocyanate with reference to aqueous sodium chloride solution at different concentrations in a number of nonaqueous solvents. In the case of the first two salts, the chemical shifts were found to be independent of concentration, while for the iodide and, to a lesser extent, for the thiocyanate, they do depend on the concentration of the salt. It is assumed that in the latter case the chemical shifts are influenced by the formation of contact ion pairs. The magnitude of the chemical shift for the ^{23}Na nucleus in different solvents appears to be directly related to the electron donor abilities of these solvents provided that the shifts are not complicated by the formation of contact ion pairs.

Studies of ionic solvation by proton magnetic resonance have been carried out by numerous investigators during the past few years. While such studies have proven to be quite useful in the elucidation of the structures of electrolyte solutions, the information obtained is limited, since the measurements are usually carried out on the magnetic resonance of either the solvent protons or on protons of solvating species dissolved in an "inert" solvent. In most cases the observed protons are several atoms removed from the interaction site[2] and consequently the chemical shifts are only weakly affected by the solvation. It is obvious that much better information can be obtained if one directly observes the resonance of the solvated ions.

The sodium-23 nucleus seems to be particularly well suited for such studies. The relative sensitivity of 0.1 with respect to the proton indicates that the measurements can be carried out in fairly dilute solutions. Narrow line width of ^{23}Na resonance allows the use of high-resolution nmr equipment. Finally, the large quadrupole moment of 0.1 e/10^{24} cm^2 renders the sodium nucleus a sensitive probe of the neighboring electronic environment.

Most of the studies carried out thus far on ^{23}Na resonance were done in aqueous solutions.[3-9] Jardetzky and Wertz[3] measured the position, width, and area of the resonance signal of a number of sodium compounds in water with reference to a 3 M NaCl solution as the external standard. While the authors did not observe any chemical shifts with changing concentrations or with different sodium salts, they did observe a considerable amount of line broadening in cases where anion–cation interactions were suspected. The authors consequently attributed the line broadening

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(1) Abstracted in part from the Ph.D. Thesis of R. H. E., Michigan State University, 1971.

(2) For example, in dimethyl sulfoxide: B. W. Maxey and A. I. Popov, *J. Amer. Chem. Soc.*, 90, 4470 (1968).

(3) O. Jardetzky and J. E. Wertz, *ibid.*, **82**, 318 (1960).

(4) C. Deverell and R. E. Richards, *Mol. Phys.*, 10, 551 (1966).

(5) M. Eisenstein and M. L. Friedman, *J. Chem. Phys.*, **44**, 1407 (1966).

(6) P. A. Speight and R. L. Armstrong, *Can. J. Phys.*, **45**, 2493 (1967).

(7) O. Lutz, *Z. Naturforsch.*, **23**, 1209 (1968).

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(9) C. Hall, R. E. Richards, G. N. Schulz, and R. R. Sharp, *Mol. Phys.*, **16**, 529 (1969).