# Studies of the Equilibria between Tetraarylallyl-type Radicals and Their Dimers

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Tetraarylallyl-type radicals are stable radicals. In these series, TPA is obtained as radical crystals. However, BDA, BDAA and DDA are obtained as diamagnetic dimerized substances. These are partially dissociated in solution. These can be detected in solution by ESR and optical spectra measurements of these radicals about the equilibrium between the radical monomer and its dimer. The equilibrium constants and the energy of the formation of the dimer are thus determined. The order of the magnitudes of the dimer's formation energies can be explained in terms of the frontier electron densities of the bond-forming positions of radicals.

In a previous paper,[1] hereafter referred as I, we reported that abnormal hyperfine splittings in the ESR spectra of tetraarylallyl-type radicals had been observed, and that the splitting can be explained on the basis of the "twisted allyl" model. Another feature of the tetraarylallyl-type radicals is the existence of an equilibrium between the radical monomer and its diamagnetic dimer in solution.[2—4] $\alpha,\alpha,\gamma,\gamma$-Tetraphenylallyl(TPA) is a stable radical in solution and is also obtained as pure radical crystals.

However, $\alpha,\alpha,\gamma,\gamma$-bisdiphenyleneallyl(BDA), $\alpha,\alpha,\gamma,\gamma$-bisdiphenylene-$\beta$-azoallyl(BDAA), and $\alpha,\alpha$-diphenyl-$\gamma,\gamma$-diphenyleneallyl(DDA)(Fig. 1) are partially dimerized in solution, as is triphenylmethyl. These substances can be detected in solution by ESR and optical spectra measurements of these radicals about the equilibrium between the radical monomer and its dimer, carried out at various temperatures. The equilibrium constants and the enthalpy of the formation of the dimer are determined. In the following section, some factors for stabilizing the radical will be considered.

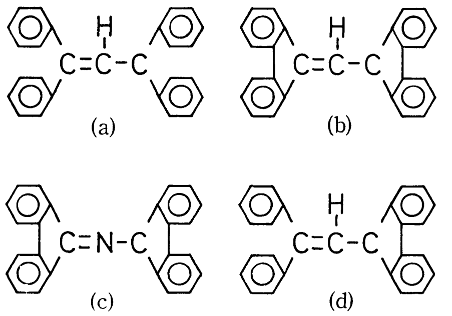

Fig. 1. Tetraarylallyl-type radicals.
(a) TPA (b) BDA (c) BDAA (d) DDA

As is shown in Fig. 1, these radicals resemble one another closely in structure. However, BDA has no degree of free rotation of the four phenyl rings attached to the $\alpha$ and the $\gamma$ carbons after the partially-hindered DDA, by comparison with the TPA radical which has the degree of free rotation of the four phenyl rings. A comparison of the structures of BDA and DDA shows that DDA has more steric hindrance of phenyl groups than that of BDA. On the other hand, BDAA is an azoallyl which is replaced by a nitrogen at the $\beta$-position of the allyl group of BDA. By a comparison of BDA and BDAA, which have the same structures, one can ascertain the influence of the distribution of electron densities. These differences reflect the relative factor of the radical stabilities, which will be discussed in the following section.

## Experimental

The samples were prepared following the processes described in Refs. 2, 3, 4 and 5. Their physical constants and the results of the elemental analyses are shown in Table 1.

TABLE 1. PHYSICAL CONSTANTS AND ELEMENTAL ANALYSES

| | Mp[a)] (°C) | Obsd<br>Calcd | C | H | N |
|---|---|---|---|---|---|
| TPA | | | 92.98<br>93.86 | 5.58<br>6.14 | |
| BDA | 244.5—245.5<br>245—246[2)] | | 94.85<br>95.00 | 5.01<br>5.00 | |
| BDAA | 270.0—271.5<br>270—272[3)] | | 90.91<br>91.62 | 4.97<br>4.71 | 3.80<br>3.78 |
| DDA | 236.0—237.5<br>235—237[4)] | | 94.59<br>94.42 | 5.38<br>5.58 | |

a) Melting points are not corrected.

For the observation of the ESR spectra in solution, the solvents were well purified, dehydrated, and degassed by the usual methods.[6)] The ESR signal intensity ($I$) was measured at various temperatures in the usual way (amplitude of magnetic field modulation: 8 G). The logarithm of the intensity ($I$) *vs.* the reciprocal of the temperature($T$) plot gives directly the association energy of the two radical monomers to the dimer (Fig. 2). $Mn^{2+}$ in MgO was used as the standard for the ESR signal intensity. All the ESR measurements were carried out with an X-band ESR spectrometer, JES-ME3, equipped with a 100 KHz field modulation, while the integration of the signal intensity was carried out by the use of a spectrum computer, EC-5, of the JEOL. Co.

The optical spectra were also measured at various temperatures and at several concentrations with an evacuated quartz cell with a path length of 1 cm, using a MPS-50-type spectrophotometer of the Shimadzu Co. The solvents used were treated in the afore-mentioned way.

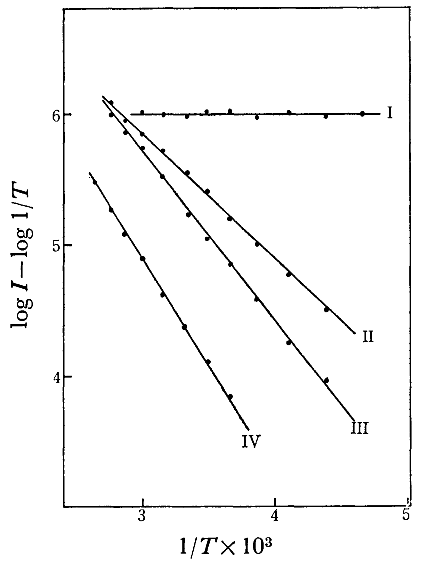

Fig. 2. Temperature dependence of integrated ESR signal intensity (I) TPA (II) BDAA (III) BDA (IV) DDA.

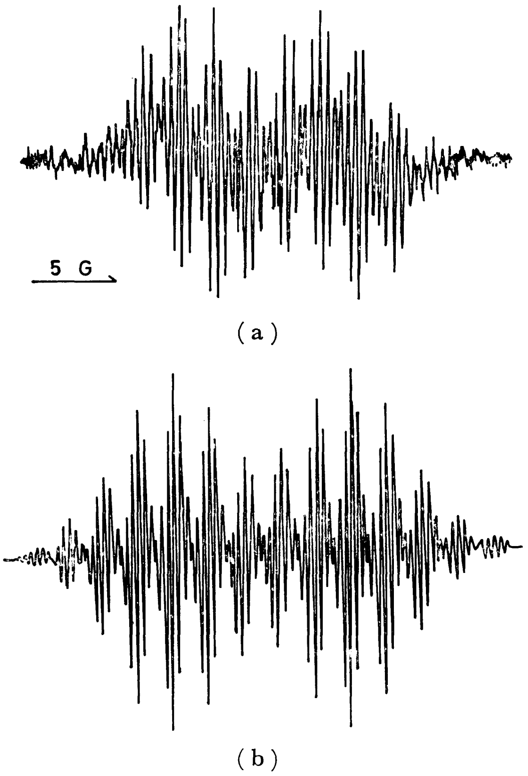

Fig. 3. ESR spectrum of DDA.
(a) Observed spectrum (b) Calculated spectrum

## Results and Discussion

The ESR hyperfine structures of TPA, BDA, and BDAA have been reported elsewhere.[1] The ESR hyperfine spectrum of DDA observed in a diluted benzene solution at 60 °C is shown in Fig. 3 with the spectrum reconstructed by the ESR-spectrum computer using the hyperfine coupling constants given in Table 2. Those of the other radicals are also tabulated in Table 2. The values of $A^{\rm H}_\beta$ reflect the degree of twisting of the allyl skeleton, because the value of $A^{\rm H}_\beta$ is represented by the function of a twisted angle around the bond-axis and the spin densities on the carbons of the allyl skeleton.[1] Furthermore, the fact that the values of the twisted angles around the bond-axis of each allyl skeleton tabulated in Table 2 are in order of BDA→DDA→TPA can be well understood by a comparison with the molecular structure of each.

Now, in order to compare the relative stability among these radicals, each association energy from the two radical monomer to a dimer was determined by measuring the ESR and optical spectra at various temperatures. The equilibrium between a radical monomer (S·) and a dimer (S-S) can be quantitatively explained by the following equations:[9]

$$2\mathrm{S}\cdot \rightleftharpoons \mathrm{S{-}S}$$

$$K = [\mathrm{S{-}S}]/[\mathrm{S}\cdot]^2, \tag{1}$$

where $K$ is the equilibrium constant expressed by;

$$K = A\exp(-\Delta H/RT), \tag{2}$$

$A$ : proportionality constant
$\Delta H$: association energy
$R$ : gas constant
$T$: temperature

Hence,

$$\ln K = (-\Delta H/R)(1/T) + \ln A. \tag{3}$$

On the other hand, the intensity of the ESR signal ($I$) is simply expressed as a function of the radical concentration divided by the temperature, provided that $I$ follows the Curie law in a dilute solution; thus,

$$I = B(1/T)[\mathrm{S}\cdot], \tag{4}$$

where $B$ is a proportionality constant. From Eqs. (1)

TABLE 2. HYPERFINE COUPLING CONSTANTS OF TETRAARYLALLYL-TYPE RADICALS (in G) AND TWISTED ANGLE OF ALLYL GROUP

| | $A_\beta$ | $A^{\rm H}_1$ | $A^{\rm H}_2$ | $A^{\rm H}_3$ | $A^{\rm H}_4$ | $A^{\rm H}_5$ | $A^{\rm H}_6$ | $A^{\rm H}_7$ | Twisted angle of allyl group |
|---|---|---|---|---|---|---|---|---|---|
| TPA | 8.90[a] | 1.95 | 1.30 | 0.65 | | | | | ≃26° |
| BDA | 13.4[a] | 1.99 | 1.99 | 0.46 | 0.1> | | | | ≃37° |
| (Ref. 7) | 13.2[a] | 1.92 | 1.86 | 0.48 | 0.36 | | | | |
| (Ref. 8) | 13.2[a] | 1.89 | 1.89 | 0.42 | 0.06 | | | | |
| BDAA | 3.38[b] | 1.69 | 1.69 | 0.30 | 0.14 | | | | |
| DDA | 9.57[a] | 2.45 | 2.45 | 2.45 | 2.45 | 0.46 | 0.1> | 0.1> | ≃32° |

a) $A^{\rm H}_\beta$. b) $A^{\rm N}_\beta$.

and (2),

$$I = B(1/T)([\text{S-S}]/K)^{1/2}$$
$$= B(1/T)\{[\text{S-S}]/(A\exp(-\Delta H/RT))\}^{1/2}, \qquad (5)$$

Hence,

$$\ln I = 1/2(\Delta H/R)(1/T) + \ln(1/T) + \ln B$$
$$+ 1/2\ln[\text{S-S}] - 1/2\ln A. \qquad (6)$$

In the limiting case of a low concentration of the radical monomer, the equilibrium lies so much to the side of the dimer that we finally have:

$$\ln I - \ln(1/T) = 1/2(\Delta H/R)(1/T) + C, \qquad (7)$$

where $C$ is a constant which involves $\ln B$, $\ln A$, and $\ln[\text{S-S}]$. The slopes of $\log K$ *vs.* $1/T$(Fig. 4) and $\log I$ *vs.* $1/T$(Fig. 2) enable us to calculate the values of the association energy.

The optical spectra of BDA and BDAA are shown in Figs. 5 and 6, the maximum absorptions being $\lambda_1=750$, $\lambda_2=488(\varepsilon_{\text{max}}=2119)$, $\lambda_3=422$ and $\lambda_1=775$, $\lambda_2=466(\varepsilon_{\text{max}}=2560)$, $\lambda_3=435$, $\lambda_4=404$, respectively. It may be seen in Figs. 5a(488 nm and 335 nm) and 6a(466 nm and 325 nm) that these dimers dissociate completely into monomers in the concentration of $10^{-6}$ M. at 20 °C. In this concentration, then, the spectra do not show the temperature dependence explicitly. From the radical concentration obtained from the $\varepsilon_{\text{max}}$, the equilibrium constants, $K$, can be enumerated at each temperature. $\log I$ *vs.* $1/T$ and $\log K$ *vs.* $1/T$ are shown in Figs. 2 and 4 respectively, while the association energies thus obtained are tabulated in Table 3. Table 3 shows that TPA is very stable as a radical molecule and that the two values determined by different measuring methods coincide fairly well. Thus, the approximate equations, (3) and (7), have been shown to be correct.

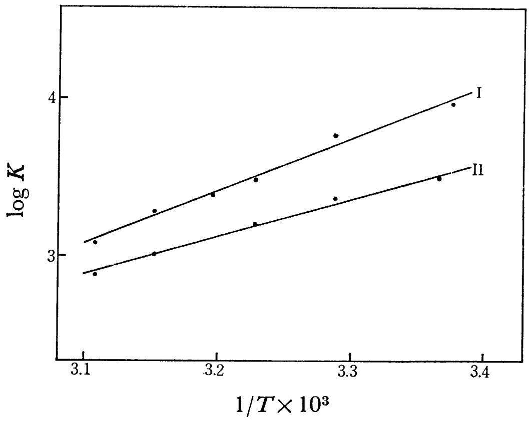

Fig. 4. Temperature dependence of equilibrium constant (I) BDA (II) BDAA.

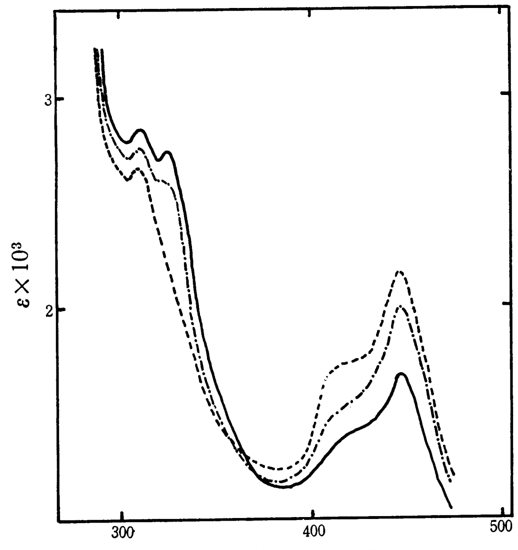

Fig. 5a. Optical spectra of BDA in benzene at 20 °C.
—— $10^{-4}$ M. —·—·— $10^{-5}$ M. ---- $10^{-6}$ M.

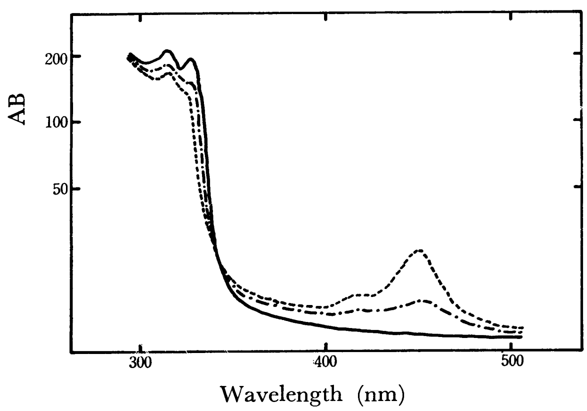

Fig. 5b. Optical spectra of BDA in ether.
---- +20 °C, —·—·— −30 °C, —— −60 °C

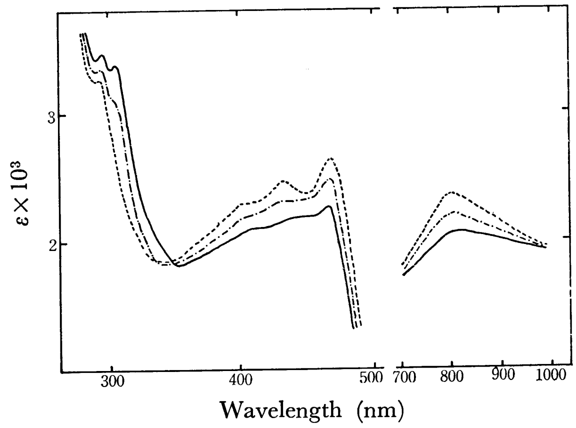

Fig. 6a. Optical spectra of BDAA in benzene at 20 °C.
—— $10^{-4}$ M. —·—·— $10^{-5}$ M. ---- $10^{-6}$ M.

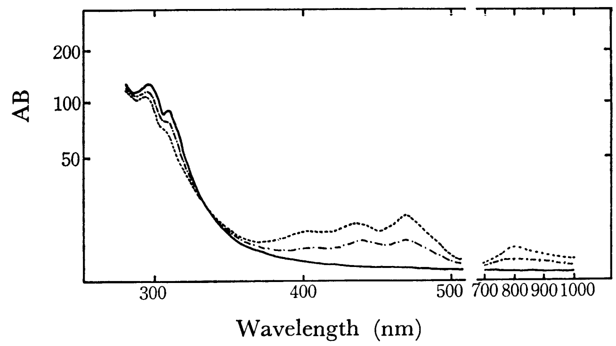

Fig. 6b. Optical spectra of BDAA in ether.
---- +20 °C, —·—·— −30 °C, —— −60 °C

Table 3. Association energy from radicals to dimer (kcal/mol)

| | From ESR | From optical spectra |
|---|---|---|
| TPA | ≃0 | |
| BDA | 11.9 | 12.6 |
| (Ref. 2) | | (≃13) |
| BDAA | 8.7 | 9.2 |
| DDA | 14.7 | |

On the other hand, the reactivity from the radicals to the dimer may be explained by the "frontier electron" theory,[10] where the frontier electron density plays an important role. The frontier electron density of a neutral radical is approximately equal to its odd-electron density. Thus, the odd-electron density in each radical will reflect directly the reactivities of the radicals.

On the other dimerizable radicals, such as triphenylmethyl and phenoxyl, their bond formations do not all occur at the same position. For example, two triphenylmethyls form a bond between the center carbon of one radical and the *para*-position of one phenyl group of the other radical.[11] Of these tetraarylallyl-type radicals, TPA itself is not dimerized, but BDA, BDAA, and DDA are dimerized. According to the IR spectra of these dimerized substances, the bond formation of these dimerized radicals must occur at the $\alpha$ or the $\gamma$ position of the allyl group.[12]

Table 4 shows the values of the frontier electron densities on the allyl group of each radical, as calculated by the McLachlan method on the basis of the "twisted allyl" model.[1] As has been mentioned above, TPA has never been dimerized in spite of possessing the largest frontier electron density on the possible position of the bond formation in this radical. This fact can be considered as showing that two TPA radicals are difficult of access to each other because of the steric hindrance of the four phenyl rings on the $\alpha$ or the $\gamma$ position of the allyl group.

On the other hand, since two phenyl groups at one or both ends of the allyl group in DDA, BDA, and BDAA are fixed to each other, these radicals can approach each other and be dimerized in such a manner as to form a bond at the positions with the largest frontier electron densities in the radical molecules. From the values of these densities of the bond-forming position, which are the $\alpha$ or the $\gamma$ carbon atoms of the allyl groups, one can expect that DDA associates more easily to form a dimer than do BDA and BDAA. This expectation shows a good parallelism to the results of Figs. 2 and 4.

Table 4. Frontier electron densities on allyl group

| | $\alpha$ | $\beta$ | $\gamma$ | $(\alpha+\gamma)/2$ |
|---|---|---|---|---|
| TPA[a] | +0.318 | −0.097 | +0.318 | +0.318 |
| BDA[b] | +0.260 | −0.086 | +0.260 | +0.260 |
| BDAA[b] | +0.253 | −0.051 | +0.253 | +0.253 |
| DDA[c] | +0.285 | −0.067 | +0.270 | +0.277 |

a) Each phenyl group is rotated by 30° as that of triphenylmethyl and allyl group is also twisted by 26°. b) Allyl group is twisted by 37°. c) Diphenyl fitt to $\alpha$ position, Phenyl groups are rotated as TPA and allyl group is twisted by 32°.

In general, the stabilization of the radical is mainly affected by the following two factors: the magnitude of the delocalization of an odd-electron, and the magnitude of the steric repulsion around the bond-forming position in the radical molecular frame. For the case of TPA, the latter is the predominant factor, and it is well known to be the predominant factor in the association of the triphenylmethyl derivatives.[13] In the other tetraarylallyl-type radicals, however, the former must be the dominant factor, because the magnitude of the steric repulsion of DDA may be larger than those of BDA and BDAA, judging from the molecular structure of each radical.

On the other hand, the molecular structures of BDA and BDAA are similar except that either a carbon atom or a nitrogen atom occupies the $\beta$-position of the allyl group. Then, one may assume that this difference in the occupied atom will not affect the magnitude of steric repulsion, but the magnitude of the delocalization of the odd-electron. In fact, the difference in the magnitudes of the association energy of BDA and of BDAA may be found in Table 3.

It can be concluded that the TPA radical is the most stable radical in these series, since no indication of dimerization has so far been experimentally observed for this radical.

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