

Organic and Biological Chemistry

Electron Delocalization in Molecules Containing Formally Orthogonal π Systems. The Synthesis of 2,4,6,2',4',6'-Hexa-*t*-butyldiphenylacetylene and a Study of Its Radical Anion and Dianion

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Abstract: 2,4,6,2',4',6'-Hexa-*t*-butyldiphenylacetylene (**1**, hexa-*t*-butyltolan) was synthesized in order to investigate the distribution of the odd electron in the radical anion and of the two extra electrons in the corresponding dianion of this molecule having two orthogonal π systems. The anions of dimesitylacetylene (**2**) were also studied. Molecular models indicated that **2** can easily attain a planar conformation and that at most a 10° twist from perpendicularity is possible for **1**. The radical anions of **1** and **2** were stable at both room temperature and at -80° . Both dianions could be prepared at -80° , but only the hexa-*t*-butyltolan dianion was stable at room temperature. Ultraviolet-visible and esr spectra were run on all four species, and the nmr spectrum of the hexa-*t*-butyltolan dianion was obtained. The esr spectra of the radical anions showed the odd electron to be distributed equally in both aromatic rings in both hexa-*t*-butyltolan (**1**) and dimesitylacetylene (**2**). The dianions of **1** and **2** were shown to be singlets. Reduction potential data revealed no additional radical anion stabilization due to the presence of a second ring in hexa-*t*-butyltolan. Consideration of configuration interaction matrix terms between the two configurations of the radical anion (*i.e.*, the odd electron being in either of the two perpendicular π systems) predicted lack of configurational mixing and thus lack of stabilization by any type of configurational wave function mixing in accord with observation. Similar considerations of the various dianion configurations led to a prediction of a ground-state triplet in the absence of molecular distortion. Consideration of twisting of diarylacetylene radical anions and dianions, however, revealed the dramatic prediction that rotation from one planar conformation to another through a 90° conformation is symmetry forbidden. When applied to the case of the hexa-*t*-butyltolan radical anion which is sterically constrained to near perpendicularity, this reasoning leads to the prediction of a unique Jahn-Teller B_1 twisting distortion from exact perpendicularity. B_1 vibrational interaction allows vibronic admixing of the two configurations with electrons localized in the perpendicular molecular planes and thus accounts for the observed equal odd electron distribution in the two rings. An alternative, but related, rationale involves a static B_1 Jahn-Teller twisting which is energy lowering but has a low enough barrier between twisted conformations that a rapid conformational interconversion is possible; this rationale leads to the same equal odd electron distribution. Similar reasoning applied to the dianion predicts a Jahn-Teller effect leading to a singlet.

The present research was concerned with the distribution of electrons introduced into a molecule having truly orthogonal π moieties.¹ Such a molecule appeared to be 2,4,6,2',4',6'-hexa-*t*-butyldiphenylacetylene (**1**, hexa-*t*-butyltolan for brevity), since the *o*-*t*-butyl groups promised to keep the two aromatic rings perpendicular to one another (see Figure 1).

One question posed was whether an odd electron introduced into the π system would be distributed in the two rings or instead be confined to one plane. A second matter involved the multiplicity of the dianion, in which two electrons are introduced. A species having one electron assigned to each of the two planes would be a triplet by Hund's rule and would also be essentially isoelectronic with molecular oxygen. The alternative singlet has two electrons confined to one molecular plane. Additionally, the anions promised to be particularly stable because the *t*-butyl groups would shield the molecule from external attack.

Synthetic Aspects. For this study both 2,4,6,2',4',6'-hexa-*t*-butyldiphenylacetylene (**1**) and dimesitylacety-

lene (**2**) were used; the latter compound promised to be useful for comparison purposes.

The synthesis of hexa-*t*-butyltolan (**1**) began with the reaction of 2,4,6-tri-*t*-butylphenyllithium² with iodine which afforded 2,4,6-tri-*t*-butyliodobenzene (**3**) in 47% yield. This product was found to react in 30% yield with cuprous ethyl propiolate in *N*-methylpyrrolidone to give ethyl 2,4,6-tri-*t*-butylphenylpropiolate (**4**). The corresponding acid (**5**) was found to decarboxylate as the cupric salt to afford 2,4,6-tri-*t*-butylphenylacetylene (**6**, 66%). The cuprous salt of **6** was then treated with 2,4,6-tri-*t*-butyliodobenzene (**3**) in pyridine at 115° to give 2,4,6,2',4',6'-hexa-*t*-butyldiphenylacetylene (**1**), mp $201-203^\circ$, in 21% yield. The synthesis is outlined in Chart I. The required dimesitylacetylene was obtained by a modification of the method of Fuson³ (see Experimental Section for details).

Results

Preparation of the Radical Anions and Dianions. In exploratory runs the radical anions and dianions of

(2) E. E. Betts and L. R. C. Barclay, *Can. J. Chem.*, **33**, 1768 (1955).

(3) R. C. Fuson, P. L. Southwick, and A. P. Rowland, *J. Amer. Chem. Soc.*, **66**, 1109 (1944).

(1) Orthogonal is taken in its one-electron quantum mechanical rather than its geometric sense and is meant to signify a lack of interaction in a one-electron approximation.

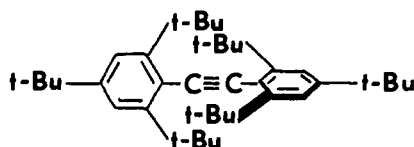
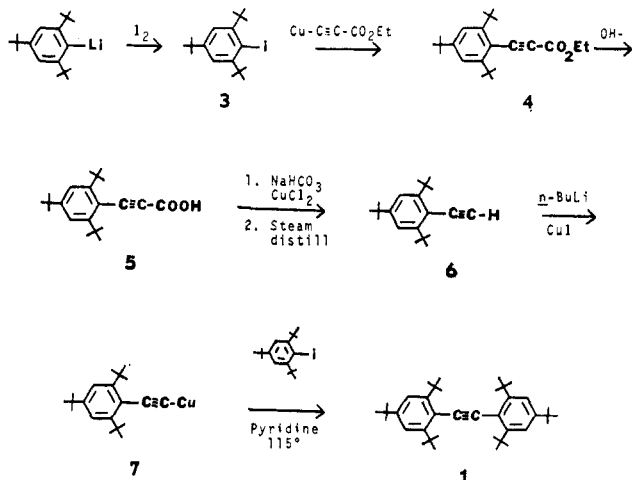


Figure 1. Sterically constrained perpendicular conformation of 2,4,6,2',4',6'-hexa-*t*-butyldiphenylacetylene.

hexa-*t*-butyltolan (**1**) and dimesitylacetylene (**2**) were prepared in quartz tubes (see Experimental Section) in order that the ultraviolet-visible spectra (300–750 nm) could be studied while the esr signal intensity was monitored.

Chart I. Synthesis of 2,4,6,2',4',6'-Hexa-*t*-butyldiphenylacetylene



Reduction of hexa-*t*-butyltolan (**1**) with potassium at -80° in 2:1 tetrahydrofuran–1,2-dimethoxyethane gave a reddish orange solution of the radical anion which showed absorption maxima at 414, 470, and 554 nm. Extended treatment with potassium gave a deep blue solution of hexa-*t*-butyltolan dianion with maxima at 340 and 645 nm. As the ultraviolet-visible absorption spectrum changed from that of the radical anion to that of the dianion, the esr signal intensity diminished correspondingly.

Reduction of dimesitylacetylene (**2**) with potassium at -80° in 2:1 tetrahydrofuran–1,2-dimethoxyethane gave a yellow solution of the radical anion with absorption maxima at 425, 454, and 495 nm. Extended reduction produced a blue solution of dimesitylacetylene dianion with an absorption maximum at 655 nm. The radical anion esr signal continued to diminish in intensity as the dianion ultraviolet-visible band intensified.

Esr Studies. The reddish orange radical anion of hexa-*t*-butyltolan (**1**), formed by reduction with sodium-potassium alloy or potassium at -80° in 1,2-dimethoxyethane, tetrahydrofuran, or 2:1 tetrahydrofuran–1,2-dimethoxyethane, showed a hyperfine pattern of five lines at intervals of 0.98 G from splitting by four equivalent protons (Figure 2). The observed intensity ratio was 0.8:4.2:6.0:4.1:0.8. The line width (between derivative extrema) was 0.46 G. The additional, very weak but observable, absorption is from a small concentration of ion pairs of hexa-*t*-butyltolan radical anion (*vide infra*).

Reduction of hexa-*t*-butyltolan (**1**) in tetrahydrofuran with potassium at 25° was more complex than in

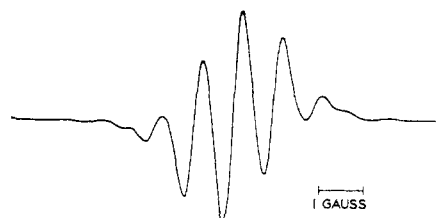


Figure 2. Esr spectrum of the 2,4,6,2',4',6'-hexa-*t*-butyldiphenylacetylene radical anion in 2:1 tetrahydrofuran–dimethoxyethane at -80° .

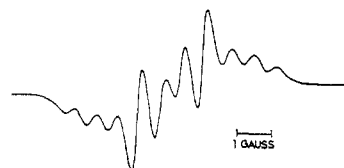


Figure 3. Esr spectrum of the 2,4,6,2',4',6'-hexa-*t*-butyldiphenylacetylene radical anion in tetrahydrofuran at 25° .

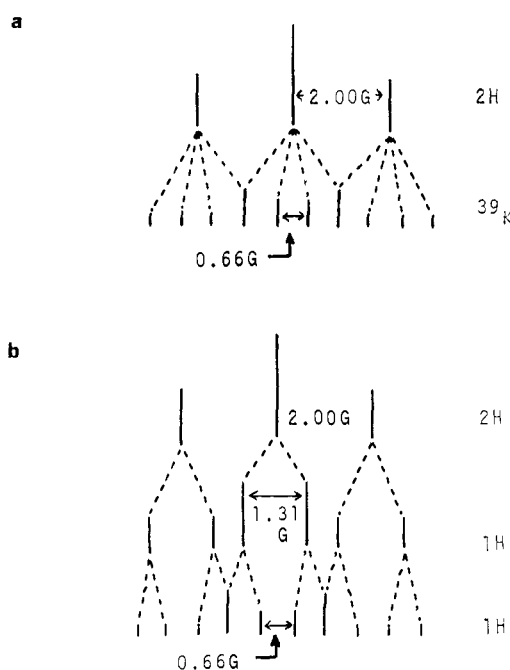


Figure 4. Line diagram illustrating the two interpretations of the esr spectrum of hexa-*t*-butyltolan ion pair: (a) splitting by two equivalent protons and potassium, (b) splitting by two equivalent protons and two nonequivalent protons.

the low-temperature runs and produced a red solution showing a hyperfine esr spectrum of ten lines (Figure 3). This pattern can be interpreted as that of an unsymmetrical ion pair with the extra electron localized in one ring. In this interpretation there would be a hyperfine coupling constant of 2.00 G from just two equivalent protons and a coupling of 0.66 G from one ^{39}K nucleus. The latter nucleus with nuclear spin $I = 3/2$ would then split each triplet component into a 1:1:1:1 quartet; the overlapping of two pairs of lines would reduce the total number of lines to ten (note Figure 4a).

This ten-line pattern might alternatively be interpreted as arising from a set of two equivalent protons

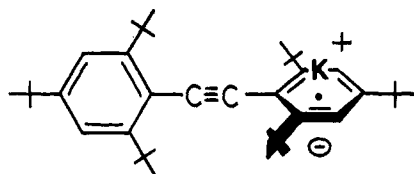


Figure 5. Representation of hexa-*t*-butyltolan ion pair necessary for second interpretation (Figure 4b).

with hyperfine splitting of 2.00 G and two other non-equivalent protons with hyperfine splittings of 1.31 and 0.66 G. Here splitting by potassium would not be resolved (note Figure 4b.) Such a situation would result from the presence of a potassium counterion situated above one ring as shown in Figure 5.

The yellow radical anion of dimesitylacetylene (**2**) formed by reduction at -80° with sodium-potassium alloy or potassium in 1,2-dimethoxyethane or 2:1 tetrahydrofuran-1,2-dimethoxyethane showed a complex hyperfine esr spectrum consisting of 19 overlapping pentuplets (Figure 6). The outer pentuplets were observed only with a high signal amplitude. The pentuplet splitting was 0.66 G resulting from coupling with four equivalent *meta* protons. The 19 pentuplets were spaced at intervals of 2.69 G due to splitting by 18 *p*- and *o*-methyl protons. Further splitting of 0.17 G resulted from the nonequivalence of the *o*- and *p*-methyl protons.

Samples of the dianions of hexa-*t*-butyltolan and dimesitylacetylene in 1,2-dimethoxyethane and 2:1 tetrahydrofuran-1,2-dimethoxyethane glasses did not show any esr absorption over a broad magnetic field range (0-10,000 G) at temperatures ranging from -80 to -196° , with the exception of a weak signal from the small amount of radical anion present. No triplet could be detected under conditions where the triplet of 1,3,5-triphenylbenzene dianion⁴ could be observed. A solid sample of the dianion of hexa-*t*-butyltolan (**1**) also failed to show an esr signal aside from that of the radical anion at temperatures from -80 to 35° . It was concluded from this as well as nmr evidence (*vide infra*) that the dianion is diamagnetic.

Nmr Observation of the Dianion. The reduction of hexa-*t*-butyltolan (**1**) in 1,2-dimethoxyethane at -77° to give the dianion was followed by nmr analysis at -35° . The nmr resonances of hexa-*t*-butyltolan itself disappeared after the first color appeared, as expected⁵ from rapid spin exchange between radical anions and neutral molecules of **1**. The nmr spectrum of the dianion did not appear until the radical anion concentration was virtually zero, and the two-electron reduction to the dianion was complete.

At this stage three singlets appeared in the nmr spectrum at τ 3.88, 8.68, and 8.96 (area 1:9:4.7) which were assigned to the dianion of hexa-*t*-butyltolan (**1**) (see Table I). The resonances were broadened by no more than 1.5 Hz at half-height from the corresponding signals of the hydrocarbon (**1**). After the nmr of the dianion was obtained, the hexa-*t*-butyltolan was recovered, with no detectable decomposition, upon oxidation with iodine.

(4) R. E. Jesse, P. Biloen, R. Prins, J. D. W. van Voorst, and G. J. Hoijtink, *Mol. Phys.*, **6**, 633 (1963).

(5) R. J. Lawler and C. V. Ristagno, *J. Amer. Chem. Soc.*, **91**, 1534 (1969).

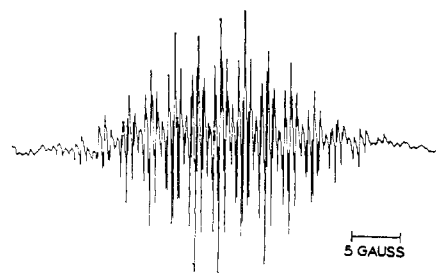


Figure 6. Esr spectrum of the dimesitylacetylene radical anion in 2:1 tetrahydrofuran-dimethoxyethane.

Polarography. Polarographic reduction data for the compounds under investigation in anhydrous 1,2-dimethoxyethane are summarized in Table II, along

Table I. Nmr Data of 2,4,6,2',4',6'-Hexa-*t*-butyldiphenylacetylene and Dianion

	Arom	<i>o</i> - <i>t</i> -Bu	<i>p</i> - <i>t</i> -Bu
τ_H (hydrocarbon)	2.56	8.47	8.67
τ_D (dianion)	3.88	8.68	8.96
$\Delta\tau = \tau_D - \tau_H$	1.32	0.21	0.29
Relative area dianion signals (obsd/theor)	1.0/1.0	9.0/9.0	4.7/4.5
Dianion signal widths (half-height, Hz)	2.5	3.5	3.0

Table II. Polarographic Data for Some Diphenylacetylenes and Reference Compounds in Anhydrous 1,2-Dimethoxyethane^a

Compd	$E_{1/2}$	I_D	n
Dimesitylacetylene	-2.70	2.51	1
2,4,6,2',4',6'-Hexa- <i>t</i> -butyldiphenylacetylene	-2.93	2.23	1
2,4,6-Tri- <i>t</i> -butylphenylacetylene	-2.75	3.43	1 or 2
Diphenylacetylene	-2.48	3.88	
	$\sim -3.08^b$	$\sim 3.81^b$	
Anthracene	-2.00	2.72	1
	-2.69	2.41	1
Tetraphenylethylene	-2.30	4.27	2

^a $E_{1/2}$ = half-wave potential in volts vs. sce (estimated error = ± 0.02 V); I_D = diffusion current constant in $\mu A \downarrow \text{mmol}^{-1} \text{mg}^{-2/3} \text{sec}^{1/2}$ (estimated error = ± 0.2); n = number of electrons associated with the wave. ^b Solvent and/or electrolyte decomposition prevents accurate measurement.

with the data for anthracene and tetraphenylethylene which serve as suitable reference compounds. In anhydrous dimethylformamide, anthracene is reduced in two one-electron waves⁶ and tetraphenylethylene is reduced in a single two-electron wave.⁶ That the same electron changes occur in anhydrous 1,2-dimethoxyethane is suggested by the identical relative diffusion current constants wherein tetraphenylethylene gave twice the value of anthracene. The data for diphenylacetylene, whose polarography has been extensively studied in dimethylformamide,⁷ is included for comparison purposes.

Both dimesitylacetylene (**2**) and hexa-*t*-butyltolan (**1**) show only a single polarographic wave before potentials

(6) S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

(7) R. E. Sioda, D. O. Cowan, and W. S. Koski, *J. Amer. Chem. Soc.*, **89**, 230 (1967).

are reached where extensive decomposition of the solvent and/or electrolyte occurs. The values of the diffusion current constants relative to those of the reference compounds indicate that the single wave of each compound is a one-electron wave. The absolute magnitude of the diffusion current constants for these compounds is also indicative of a one-electron wave, since a one-electron wave of an aromatic hydrocarbon typically has a diffusion current constant of approximately $2 \mu\text{A l. mmol}^{-1} \text{ mg}^{-2/3} \text{ sec}^{1/2}$.⁷

Reversibility of Electron Introduction. A solution of the dianion of hexa-*t*-butyltolan (**1**) under nitrogen at -25° required a total of 2.55 mequiv of iodine/mmol of hydrocarbon to discharge the color. Nmr analysis of the recovered residue showed that hexa-*t*-butyltolan had been largely regenerated. In runs on a vacuum line, nmr analysis of the iodine treated dianion showed quantitative regeneration.

Interpretative Discussion of Results. The most exciting aspect of the present research is the preparation of the relatively stable radical anion and dianion of hexa-*t*-butyltolan. This is paralleled by the great stability of the radical anion of tetramesitylethylene reported by us earlier⁸ where even treatment with proton donors regenerated the parent hydrocarbon. The stability of these systems seems to derive from blocking of centers of high electron density from external attack.

All of the evidence presented (*vide supra*) indicates that the odd electron of the radical anion of hexa-*t*-butyltolan (**1**) is equally distributed between the two essentially perpendicular aromatic rings. The esr spectrum of the radical anion shows both rings to have equal odd electron density except in the situation where solvent conditions lead to ion pairing preferentially with one ring. The question, however, remains whether this equivalency of both rings is true, time-independent delocalization, or, instead, a very rapid electron tautomerization. It can be seen, to begin with, that this electron distribution does not arise from simple quantum mechanical mixing with energy lowering. Thus lack of appreciable stabilization due to any such delocalization is evident from the polarographic results which show hexa-*t*-butyltolan (**1**) to be reduced at a potential not too different from that for 2,4,6-tri-*t*-butylphenylacetylene (**6**) (note Table II).

From the theoretical viewpoint, consideration of the two configurations in which the odd electron is first assigned to one ring and then the other (Φ_1 and Φ_2) reveals that there is no off-diagonal matrix element, F_{12} , between the two; hence, there is no configuration interaction. This turns out to be true, independent of the assumption of zero differential overlap at the acetylenic carbon atoms (see eq 1).

$$F_{12} = \int \Phi_1 \bar{F} \Phi_2 d\tau = 0 \quad (1)$$

where $\Phi_1 = |\text{closed shell orbitals} \cdot \Psi_{5a}(17)|$ and $\Phi_2 = |\text{closed shell orbitals} \cdot \Psi_{5b}(17)|$. Here Ψ_{5b} and Ψ_{5a} are the two lowest degenerate antibonding molecular orbitals with one localized in each of the two perpendicular molecular planes, Φ_1 and Φ_2 are the configurational wave functions, and 17 is the antibonding electron.

(8) H. E. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.*, **86**, 2149 (1964).

Hence, for truly perpendicular geometry, one would anticipate no energetic gain as a result of admixing the two perpendicular configurations. This is a fundamentally different situation than that of spiro conjugation⁹ where admixing between overlapping molecular orbitals of the two perpendicular moieties of the molecule occurs even in the Hückel approximation. The reason is that in spiro conjugating systems molecular orbitals localized in one-half of the molecule may be found with the same symmetry as overlapping orbitals deriving from the other portion. In the present instance, the two sets of localized molecular orbitals are proximate only on the acetylenic carbons and transmission of any potential conjugation would have to be through this linear two carbon system. Different symmetry and orthogonality of the perpendicular p orbitals in this moiety, however, preclude such interaction.

Space-filling molecular models, however, suggest that some slight twisting from perpendicularity is possible as long as this is less than *ca.* 10° . With such twisting, the off-diagonal matrix element, F_{12} , is no longer zero, and the two rings become weakly conjugated.

This interaction resulting from twisting, together with the degeneracy of the antibonding molecular orbital pair accommodating the odd electron, suggests consideration of Jahn-Teller¹⁰ type effects. The requirement for a Jahn-Teller distortion leading to molecular stabilization, *i.e.*, ΔE in eq 2, is that the direct product of the electronic wave function symmetries contain the symmetry of an available molecular vibration; this vibration then corresponds to a molecular distortion leading to electronic stabilization.

Thus in eq 2^{10c} we must inspect the symmetry of the Slater determinantal wave function, Φ . More simply, we can look at the symmetry of the antibonding pair of degenerate molecular orbitals Ψ_{5+} and Ψ_{5-} . This is possible since the closed shell portion is totally symmetric and thus the overall symmetry is controlled by the molecular orbital holding the odd electron. For this treatment symmetrized linear combinations, $\Psi_{5+} = (1/\sqrt{2})(\Psi_{5a} + \Psi_{5b})$ and $\Psi_{5-} = (1/\sqrt{2})(\Psi_{5a} - \Psi_{5b})$, must

(9) (a) H. E. Simmons and T. Fukunaga, *ibid.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967); (c) S. Weissman, *J. Chem. Phys.*, **38**, 2028 (1963).

(10) (a) H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, **161**, 220 (1937); (b) H. A. Jahn, *ibid.*, *Ser. A*, **161**, 117 (1937); (c) G. W. King, "Spectroscopy and Molecular Structure," Holt, Rinehart and Winston, New York, N. Y., 1964, p 411; (d) there is one point of potential confusion in considering the correlation diagram in Figure 7. It should be recognized that in drawing correlation diagrams, it is a necessity that an element of symmetry used in a reactant must be retained throughout the molecular transformation. This is done in Figure 7. This means that the C_2' axis of the reactant ($\theta = 180^\circ$) is oriented perpendicular to the molecular plane while this axis eventually lies in the molecular plane at the end of the molecular twisting (*i.e.*, at $\theta = 0^\circ$). This means that the first antibonding MO is termed B_3 in the 180° species and B_2 in the 0° product. Yet the first antibonding MO will have the same eigenfunction, same electron distribution, and same inherent symmetry both before and after the twisting process. Similarly confusing is the overall symmetry designation for the radical anion which is found to be termed B_3 on the left of the diagram and B_2 on the right.

However, the paradox is only superficial. B_2 or B_3 symmetry designation depends on choice of an axis of symmetry and we note the C_2' axis changes its orientation relative to the plane of the molecule as a result of the twisting process. Thus the symmetry designations used for correlation diagram purposes may be bothersome because of apparent lack of consistency in choice of orientation of elements of symmetry.

Additionally, we note that the use of D_{3d} designation at the 90° conformation derives from this conformation lying along a reaction coordinate and the symmetries given are those for the lower order group obtained by perturbation from the 90° conformation.

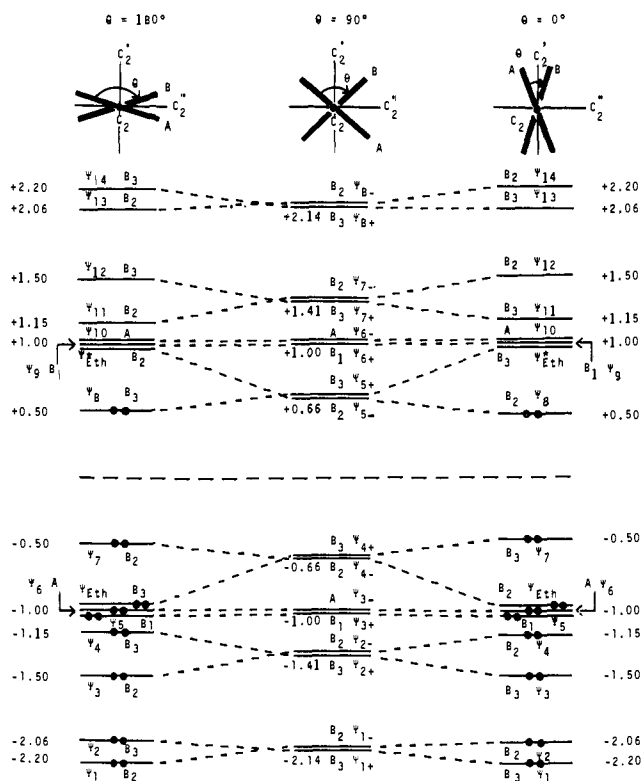


Figure 7. Correlation diagram for twisting of tolan. The electron population shown with black circles represents the radical anion configuration. These black circles plus the open circles represent the dianion population. The molecular orbitals, $\psi_{n+} = (1/\sqrt{2})(\psi_{na} + \psi_{nb})$ and $\psi_{n-} = (1/\sqrt{2})(\psi_{na} - \psi_{nb})$, are linear combinations of the molecular orbitals localized in the separate rings; here n refers to the molecular orbital number and a and b designate the ring. ψ_{Eth} is an ethylenic molecular orbital confined to the two acetylenic carbons.

$$\Delta E = \int \Phi \left(\frac{\partial H_e}{\partial Q} \right)_0 \Delta Q \Phi d\tau_e \quad (2)$$

be used. Here $(\partial H_e/\partial Q)_0$ represents the change in the electronic Hamiltonian with a deformation along normal coordinate Q and is evaluated at the equilibrium configuration. ΔQ is the magnitude of the deformation.

The wave function, Φ , and molecular orbitals, Ψ_{5+} and Ψ_{5-} , have E symmetry in the D_{2d} group. The direct product symmetry for Φ^2 can be shown to be $E \cdot E = A_1 + A_2 + B_1 + B_2$. The requirement that an energy-lowering distortion of one of these symmetries be present is met by the torsional twisting of the two rings about the acetylenic bond which has B_1 symmetry in the D_{2d} group. Any such twisting tends to make the system isoelectronic with that of the stilbene radical anion and an orthogonal ethylene moiety. Indeed, this latter system is lower in energy, even in the Hückel approximation, than the combination of two orthogonal styrene groupings, containing one antibonding electron, as present in the perpendicular hexa-*t*-butyltolan radical anion.

A correlation diagram, as depicted in Figure 7, is highly instructive.^{10d} This utilizes the D_2 symmetry present throughout the twisting process in which the torsional angle, θ , varies from the 90° initially present downward to 0° and also upward to 180° . It is found that the lowest antibonding orbital of the species twisted

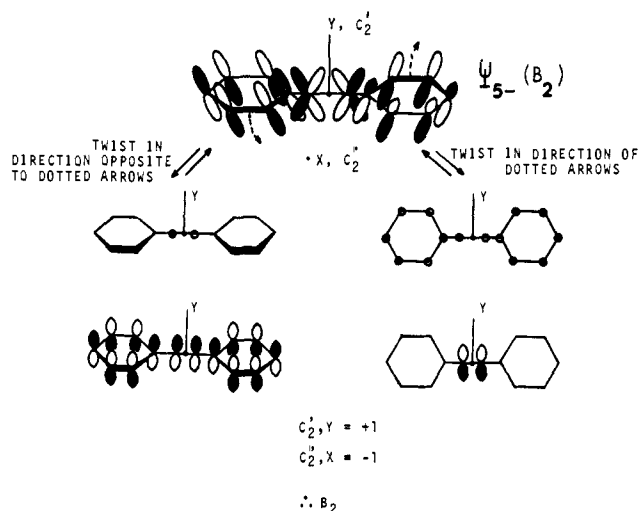


Figure 8. Behavior of one member of the lowest energy degenerate pair of antibonding molecular orbitals on twisting.

in one direction from 90° becomes the second antibonding orbital in the species twisted in the other direction from 90° with an energy crossing corresponding to the degeneracy in the perpendicular species.¹¹ Thus, free rotation of tolan radical anions (and dianions; *vide infra*) is predicted to be symmetry forbidden and the 90° conformer to be Jahn–Teller active.

The energetic effect of twisting on the first antibonding molecular orbitals may be seen qualitatively by reference to Figure 8. Thus twisting of the B_2 member of the first antibonding degenerate pair in the direction shown by the arrows (equivalent to decreasing θ of Figure 7) can be seen to lead to two B_2 components, one corresponding to the lowest antibonding MO of the stilbene-like moiety generated and the other to a bonding ethylenic MO. As a consequence of the noncrossing rule, the ethylenic MO can be dismissed as a resulting MO. Correlation of a B_2 antibonding MO with a B_2 bonding MO would require crossing of two B_2 correlation lines, since 90° reactant and 0° product have an equal number of bonding B_2 MO's. Actually, the ethylenic component generated is "absorbed" by the ethylenic MO of the 0° conformer which itself correlates with a bonding MO.

Twisting in the reverse direction (*i.e.*, increasing θ) leads to a bonding stilbene-like MO and an antibonding ethylenic molecular orbital (note Figure 8). For similar reasons as above, it can be deduced that only the antibonding ethylenic MO results.

Thus, twisting in one direction converts this first antibonding MO of the 90° conformer into a stilbenoid MO and twisting in the other affords an ethylenic one.

This treatment therefore shows both the energy lowering by molecular twisting from the 90° conformation and also the availability of a Jahn–Teller active B_1 twisting vibration. Note Figure 9 in which the resulting double-well potential energy surface is shown.

In drawing these potential energy surfaces, the sharp steric interaction on appreciable twisting is taken into

(11) A related, but contrasting, example is the *cis-trans* isomerization of ethylenes in which a bonding molecular orbital becomes antibonding as has been described by E. Evleth, 3rd Menton Summer Institute on the Chemical Application of Quantum Mechanics, Menton, France, July 1968.

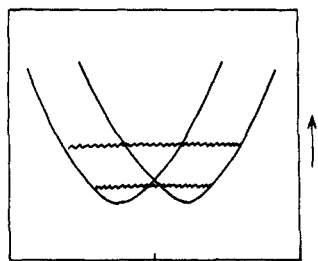


Figure 9. Jahn-Teller potential energy surface with two possible zero vibrational levels.

account and is the source of the energy rise on continued twisting toward 0 and 180°.

If the zero point energy is near the top of the surface connecting the two wells or above this point, one would expect a species vibrationally stabilized by oscillation between the two twisted radical anion conformations and with an electron density distributed in both rings.¹² If the zero point energy is lower, one would then anticipate two separate species in equilibrium, one populating each energy well. We note that all molecular orbitals utilized (note Figure 7) weight the rings equally as demanded by the group D_2 symmetry, therefore the odd electron density in all conformations, including the two minima, is equally distributed in the two rings.^{13a,b} This is then in accord with the evidence above.

In the case of the dianion, the presence of a nonparamagnetic species, a singlet, was evidenced by the lack of a triplet esr signal and by the sharp nmr spectrum of the dianion (*vide supra*). Furthermore, the nmr spectrum indicates that any electron redistribution process between the two planes must be faster than $ca. 10^2 \text{ sec}^{-1}$.^{13c}

The off-diagonal matrix element, F_{34} , between the two configurations Φ_3 and Φ_4 , *i.e.*, those having two excess electrons in one perpendicular plane or the other, is nonzero as long as differential overlap is not neglected; the value of this matrix element is given in eq 3. Here Ψ_{5a} and Ψ_{5b} are the pair of lowest degenerate antibonding molecular orbitals, 17 and 18 represent the two extra electrons present in the dianion, and $r_{17, 18}$ is the distance between electrons 17 and 18.

$$F_{34} = \int \Phi_3 \bar{F} \Phi_4 d\tau = \int \Psi_{5a}(17) \Psi_{5b}(18) \frac{1}{r_{17,18}} \times \Psi_{5b}(17) \Psi_{5a}(18) d\tau \neq 0 \quad (3)$$

The energy of the resulting state, however, lies considerably above that of the triplet configuration (note Calculations) and cannot account for the preference for a singlet dianion. The correlation diagram in Figure 7,

(12) H. M. McConnell and A. D. McLachlan, *J. Chem. Phys.*, **34**, 1 (1961).

(13) (a) The esr hyperfine splitting is not useful in distinguishing between electron delocalization as postulated and a rapid rate limited electron redistribution; the 0.98 G splitting multiplied by $2.8 \times 10^6 \text{ cps G}^{-1}$ affords only a lower limit of electron redistribution of $3 \times 10^6 \text{ sec}^{-1}$ (note ref 13b); (b) in the literature one finds similar situations where limits may be set, *e.g.*, S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 6462 (1958), and J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963); (c) this limit is obtained by the use of the relationship, $\tau(\nu_a - \nu_b) \leq (2)^{1/2}$ [see H. Conroy, *Advan. Org. Chem.*, **2**, 312 (1960)] which is valid for observation of single nmr lines as a result of the exchange of the role of two hydrogens in different environments. Here τ is the maximum lifetime of a separate species with two electrons localized in one ring, ν_a is the frequency expected for a *meta* hydrogen in a ring containing two localized electrons (taken as twice the difference between the value for neutral hexa-*t*-butyltolan and the value found for the dianion), and ν_b is the absorption frequency for a neutral ring *meta* hydrogen (estimated from that for hexa-*t*-butyltolan itself).

however, reveals that splitting of the degeneracy present in the perpendicular species will result from slight twisting and will then afford a singlet dianion. Furthermore, the situation is again one where the Jahn-Teller effect can lead to an oscillating dianion.

Experimental Section¹⁴

1,4-Di-*t*-butylbenzene. This material was prepared according to the procedure of Ipatieff, Corson, and Pines,¹⁵ which in a typical run gave a 21% yield, mp 77.5–79° (lit.¹⁵ mp 78–78.5°) after recrystallization from pentane.

1,3,5-Tri-*t*-butylbenzene. This compound was prepared by the method of Barclay and Betts,¹⁶ which in a typical run gave a 58% yield, mp 72.5–73.5° (lit.¹⁶ mp 74.8–75°) after recrystallization from ethanol.

2,4,6-Tri-*t*-butylbromobenzene. The procedure of Myhre¹⁷ was modified to allow use of silver nitrate in lieu of silver perchlorate. 1,3,5-Tri-*t*-butylbenzene (10.0 g, 40.7 mmol) was dissolved in 330 ml of glacial acetic acid and 90 ml of dioxane. A solution of 10.6 g (62.6 mmol) of silver nitrate, 2.90 ml (45.8 mmol) of concentrated nitric acid, and 45 ml of water was added. Bromine (3.41 ml, 62.6 mmol) was added with stirring; the stirring was continued at 25° for 16 hr. The reaction mixture was diluted with 1.4 l. of water, decolorized with sodium bisulfite, and pentane extracted. The pentane solution was washed with 10% sodium hydroxide and water. Drying over sodium sulfate and concentration *in vacuo* afforded 10.9 g of a yellow waxy solid.

The crude product was chromatographed on a $4.5 \times 137 \text{ cm}$ silica gel column (Grace 950, 60–200 mesh), slurry packed in pentane. Elution in 200-ml fractions gave: fractions 1–12, pentane, nil; 13–19, pentane, 5.38 g of 2,4,6-tri-*t*-butylbromobenzene; 20–24, pentane, 1,3,5-tri-*t*-butylbenzene containing some 2,4,6-tri-*t*-butylbromobenzene.

Fractions 13–19 on recrystallization from ethanol gave 4.47 g (34%) of pure 2,4,6-tri-*t*-butylbromobenzene, mp 173–175.5° (lit.¹⁷ mp 173–174°). The spectral data were ir (CCl₄) 3.32, 3.36, 3.47, 6.78, 7.19, 7.32, 7.90, 8.05, 8.21, 9.88, 11.39, and 15.45 μ ; nmr (CCl₄) τ 2.79 (s, 2 H, arom), 8.44 (s, 18 H, *o-t*-Bu), and 8.72 (s, 9 H, *p-t*-Bu).

Anal. Calcd for C₁₈H₂₉Br: C, 66.45; H, 8.98; Br, 24.56. Found: C, 66.61; H, 8.92; Br, 24.49.

2,4,6-Tri-*t*-butyliodobenzene. To 5.00 g (15.4 mmol) of 2,4,6-tri-*t*-butylbromobenzene in 115 ml of dry ether, 7.95 ml (19.5 mmol) of 2.4 M *n*-butyllithium in hexane was added under nitrogen and refluxed for 1.0 hr.¹⁸ Iodine (4.97 g, 19.5 mmol) in 45 ml of dry ether was added over 20 min at 0°; the resulting solution was stirred at 25° for 0.5 hr. This solution was diluted with ether, treated with aqueous sodium sulfite, and washed with water. Drying over sodium sulfate and concentration *in vacuo* afforded a yellow solid.

The crude material was chromatographed on a $3.5 \times 100 \text{ cm}$ silica gel column (Grace 950, 60–200 mesh), slurry packed in pentane. Elution in 100-ml fractions gave: fractions 1–10, pentane, nil; 11–14, pentane, 2.76 g of 2,4,6-tri-*t*-butyliodobenzene; 15–16, pentane, 806 mg of 2,4,6-tri-*t*-butyliodobenzene containing a small amount of 1,3,5-tri-*t*-butylbenzene; 17–18, pentane, 280 mg of a mixture of 2,4,6-tri-*t*-butyliodobenzene and 1,3,5-tri-*t*-butylbenzene; 19–24, pentane, 411 mg of 1,3,5-tri-*t*-butylbenzene.

Fractions 11–16 on recrystallization from ethanol gave 2.25 g (47%) of pure 2,4,6-tri-*t*-butyliodobenzene, mp 175.5–177°. The spectral data were ir (CCl₄) 3.38, 3.49, 6.75, 7.10, 7.15, 7.22, 7.33, 8.10, 8.23, 10.05, 11.41, and 15.52 μ ; nmr (CCl₄) τ 2.67 (s, 2 H, arom), 8.34 (s, 18 H, *o-t*-Bu), and 8.68 (s, 9 H, *p-t*-Bu).

Anal. Calcd for C₁₈H₂₉I: C, 58.06; H, 7.85; I, 34.08. Found: C, 58.04; H, 7.79; I, 34.10.

Ethyl 2,4,6-Tri-*t*-butylphenylpropionate. Cuprous chloride (9.35 g, 0.095 mol) was dissolved in 75 ml of concentrated ammonium hydroxide and the solution was diluted to 300 ml with water. Concentrated hydrochloric acid (110 ml) was added to bring the solution pH to 7.5. This was then diluted to 500 ml with water and added

(14) All melting points were taken on a hot-stage apparatus checked with known compounds.

(15) V. N. Ipatieff, B. B. Corson, and H. Pines, *J. Amer. Chem. Soc.*, **58**, 919 (1936).

(16) L. R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672 (1955).

(17) P. C. Myhre, *Acta Chem. Scand.*, **14**, 219 (1960).

(18) E. E. Betts and L. R. C. Barclay [*Can. J. Chem.*, **33**, 1768 (1955)] have described the preparation of 2,4,6-tri-*t*-butylphenyllithium.

to a stirred suspension of 9.24 g (94.2 mmol) of ethyl propiolate in 200 ml of water. The yellow precipitate was washed sparingly and successively with 100 ml of 1 *N* ammonium hydroxide, water, and 90 ml of *N*-methyl-2-pyrrolidone.

The wet precipitate in 150 ml of *N*-methyl-2-pyrrolidone was heated to 86° with 5.00 g (13.4 mmol) of 2,4,6-tri-*t*-butyliodobenzene over 45 min and held at 86° for 24 hr. The reaction mixture was cooled, diluted with water, acidified with 3 *N* hydrochloric acid, and benzene extracted. The benzene solution was washed with water, dried over sodium sulfate, and concentrated *in vacuo* giving 6.50 g of a crude brownish black product.

The crude product was chromatographed on a 3.3 × 100 cm silica gel column (Grace 950, 60–200 mesh), slurry packed in hexane. Elution in 200 ml fractions gave: fractions 1–2, hexane, nil; 3, 1% benzene in hexane, 21.8 mg of an unidentified white semisolid; 4, 1% benzene in hexane, nil; 5, 2% benzene in hexane, 16.7 mg of 2,4,6-tri-*t*-butyliodobenzene; 6, 2% benzene in hexane, and 7–9, 4% benzene in hexane, 360 mg of impure 1,3,5-tri-*t*-butylbenzene; 10, 4% benzene in hexane, and 11–12, 8% benzene in hexane, 81.1 mg of an unidentified oil; 13, 8% benzene in hexane, nil; 14, 8% benzene in hexane, and 15–17, 16% benzene in hexane, 126.2 mg of 2,4,6-tri-*t*-butylphenol; 18–19, 16% benzene in hexane, 20–21, 30% benzene in hexane, 22–23, 40% benzene in hexane, and 24, 1% ether in hexane, nil; 25, 1% ether in hexane, 26–29, 2% ether in hexane, 30–33, 3% ether in hexane, 34–39, 4% ether in hexane, 2.83 g of ethyl 2,4,6-tri-*t*-butylphenylpropionate.

Fractions 25–39 were recrystallized from hexane, affording 1.31 g (30%) of pure ethyl 2,4,6-tri-*t*-butylphenylpropionate, mp 109–110.5°. The spectral data were ν (CCl₄) 3.36, 3.46, 4.54, 5.88, 6.26, 6.75, 6.84, 7.18, 7.32, 7.82, 8.03, 8.25, 8.45, 8.79, 8.94, 9.76, 10.78, 11.36, 14.10, and 15.20 μ ; nmr (CCl₄) τ 2.71 (s, 2 H, arom), 5.74 (q, 2 H, *J* = 7.0 Hz, CH₂), 8.44 (s, 18 H, *o*-*t*-Bu and low-field portion of CH₃ triplet), 8.54 (s, 1.5 H, center of CH₃ triplet), and 8.68 (s, 9 H, *p*-*t*-Bu and high-field portion of CH₃ triplet).

Anal. Calcd for C₂₂H₃₄O₂: C, 80.65; H, 10.01. Found: C, 80.40; H, 9.87.

2,4,6-Tri-*t*-butylphenylpropionic Acid. Ethyl 2,4,6-tri-*t*-butylphenylpropionate (1.77 g, 5.17 mmol) was refluxed for 1 hr with 580 mg (10.3 mmol) of potassium hydroxide and 10 ml of ethanol. The solution was cooled, diluted with water, and acidified with 1 *N* hydrochloric acid (congo red), affording a slightly yellow precipitate. Crystallization from ether–hexane yielded 1.42 g (88%) of white needles, mp 200° dec.

The spectral data were ν (CCl₄) 3.33, 3.37, 3.42, 3.47, 3.75 (weak), 3.91 (weak), 4.54, 5.99, 6.27, 6.78, 6.98, 7.14, 7.34, 7.80, 8.04, 8.21, 8.35, 8.79, 10.80, 11.35, 14.50, and 15.20 μ ; nmr (CDCl₃) τ -0.58 (s, 1 H, COOH), 2.64 (s, 2 H, arom), 8.44 (s, 18 H, *o*-*t*-Bu), and 8.68 (s, 9 H, *p*-*t*-Bu).

Anal. Calcd for C₂₁H₃₀O₂: C, 80.21; H, 9.62. Found: C, 80.12; H, 9.64.

2,4,6-Tri-*t*-butylphenylacetylene. 2,4,6-Tri-*t*-butylphenylpropionic acid (1.37 g, 4.38 mmol) was added to 1.15 g (13.7 mmol) of sodium bicarbonate dissolved in 55 ml of water and heated until in solution. A solution of 982 mg (4.77 mmol) of cupric chloride dihydrate in 5.0 ml of water was added, giving a green precipitate. The mixture was heated on the steam bath for 10 min, then steam distilled. The distillate was ether extracted; the extract was dried over sodium sulfate and concentrated *in vacuo* affording 1.06 g of crude product. Sublimation *in vacuo* at 100° and crystallization from hexane yielded 785 mg (66%) of pure 2,4,6-tri-*t*-butylphenylacetylene, mp 124–125°.

The spectral data were $\lambda_{\text{max}}^{\text{C}_6\text{H}_4}$ 217 nm (ϵ 29,300), 254 (15,800), 265 (12,200), 283 (850), and 292 (720); ν (CCl₄) 3.02, 3.37, 3.43, 3.47, 4.76, 6.26, 6.78, 7.05, 7.18, 7.34, 7.90, 7.95, 8.03, 8.22, 8.35, 8.80, 10.79, 10.99, 11.27, 11.37, 15.28, and 15.82 μ ; nmr (CCl₄) τ 2.73 (s, 2 H, arom), 6.44 (s, 1 H, -C≡CH), 8.44 (s, 18 H, *o*-*t*-Bu), and 8.69 (s, 9 H, *p*-*t*-Bu).

Anal. Calcd for C₂₀H₃₀: C, 88.82; H, 11.18. Found: C, 89.04; H, 11.29.

2,4,6,2',4',6'-Hexa-*t*-butyldiphenylacetylene. *n*-Butyllithium in hexane (2.00 ml, 4.38 mmol) was added slowly to a stirred mixture of 600 mg (2.22 mmol) of 2,4,6-tri-*t*-butylphenylacetylene, 646 mg (3.33 mmol) of cuprous iodide, 20 ml of dry ether, and 10 ml of dry benzene under nitrogen at -12°. The mixture was stirred for 10 min at -12°. After an additional 2.00 ml (4.38 mmol) of *n*-butyllithium was added, the mixture was stirred at 25° for 10 min. Water was added dropwise until the excess *n*-butyllithium was destroyed and no further gas evolution was observed. Additional water was added, the mixture was filtered, and the ether and benzene were removed under a stream of nitrogen. The precipitate was washed

with 1 *M* ammonium hydroxide, water, and ethanol, then dried *in vacuo* leaving a light yellow amorphous solid.

This cuprous 2,4,6-tri-*t*-butylphenylacetylide was refluxed under nitrogen with 920 mg (2.47 mmol) of 2,4,6-tri-*t*-butyliodobenzene and 8.0 ml of dry pyridine for 14 hr. The solution was cooled, diluted with water, acidified with 1 *M* hydrochloric acid, and ether extracted. The extract was washed with water, dried over sodium sulfate, and concentrated *in vacuo*, affording 1.22 g of crude product.

The crude material was chromatographed on a 3.3 × 100 cm silica gel column (Grace 950, 60–200 mesh), slurry packed in hexane. Elution in 100-ml fractions gave: fractions 1–10, hexane, nil; 11–14, hexane, 343 mg of 2,4,6-tri-*t*-butyliodobenzene; 15, hexane, 54.2 mg of a mixture of 2,4,6-tri-*t*-butyliodobenzene and 2,4,6,2'-4',6'-hexa-*t*-butyldiphenylacetylene; 16–31, hexane, 495 mg of 2,4,6,2',4',6'-hexa-*t*-butyldiphenylacetylene containing some 2,4,6-tri-*t*-butylphenylacetylene.

Fractions 16–31 were washed with hot ethanol, removing most of the 2,4,6-tri-*t*-butylphenylacetylene. The remaining 439 mg of material was recrystallized from hexane, yielding 244 mg (21%) of pure 2,4,6,2',4',6'-hexa-*t*-butyldiphenylacetylene, mp 201–203°. The spectral data were $\lambda_{\text{max}}^{\text{C}_6\text{H}_4}$ 257 nm (ϵ 39,200); ν (CCl₄) 3.37, 3.43, 3.47, 6.26, 6.51, 6.76, 7.18, 7.34, 8.04, 8.23, 8.91, 11.38, 13.82, and 15.31 μ ; nmr (CCl₄) τ 2.66 (s, 4 H, arom), 8.46 (s, 36 H, *o*-*t*-Bu), and 8.66 (s, 18 H, *p*-*t*-Bu); mass spectrum (70 eV) showed molecular ion at *m/e* 514.5 (calcd 514.45 for C₃₈H₅₈) as the most intense peak.

Anal. Calcd for C₃₈H₅₈: C, 88.65; H, 11.36. Found: C, 88.80; H, 11.52.

1,2-Dichloro-1,2-dimesitylethane. A modification of the procedure of Fuson³ was used to prepare mixtures of 1,2-dichloro-1,2-dimesitylethane diastereomers. A 40% yield of a mixture (mp 181.5–186.5°) of 1,2-dichloro-1,2-dimesitylethane diastereomers was obtained from *meso*-1,2-dihydroxy-1,2-dimesitylethane¹⁹ and a 48% yield of a mixture (mp 183–188°) of 1,2-dichloro-1,2-dimesitylethane diastereomers was obtained from *dl*-1,2-dihydroxy-1,2-dimesitylethane.¹⁹ These mixtures were used in the next reaction without further separation.

Dimesitylacetylene. A modification of the procedure of Fuson³ was used. A mixture, mp 181.5–186.5°, of the 1,2-dichloro-1,2-dimesitylethane diastereomers (1.40 g, 4.17 mmol) was heated to 180° with stirring with 26.7 g (0.477 mol) of potassium hydroxide and 60 ml of *n*-butyl alcohol over 1.5 hr. It was maintained at 180° for 26 hr. The solution was cooled, diluted with water, and chloroform extracted. Drying over sodium sulfate and concentration *in vacuo* afforded 3.13 g of a yellowish white solid.

The crude product was chromatographed on a 2.1 × 75 cm silica gel column (Grace 950, 60–200 mesh), slurry packed in hexane. Elution in 100-ml fractions gave: fraction 1–8, hexane, nil; 9–13, hexane, 87.3 mg of a mixture of dimesitylacetylene and an unidentified substance; 14–32, hexane, 859.8 mg of dimesitylacetylene; 33–36, hexane, 15.4 mg of a mixture of dimesitylacetylene and dimesitylethylene; 37, hexane, 38–42, 3% benzene in hexane, and 43–48, 6% benzene in hexane, 276 mg of dimesitylethylene. Fractions 14–32 on recrystallization from petroleum ether (bp 90–100°) afforded 558 mg (25%) of pure dimesitylacetylene, mp 129–130.5° (lit.³ mp 127.5–128.5°).

Essentially equivalent results were obtained starting with the other mixture of diastereomers (mp 183–188°).

The spectral data were $\lambda_{\text{max}}^{\text{C}_6\text{H}_4}$ 280 nm sh (ϵ 23,100), 285 sh (25,600), 296 (36,100), 302 sh (28,300), and 314 (34,500); ν (CCl₄) 3.32, 3.35, 3.37, 3.42, 3.49, 3.65, 6.20, 6.73, 6.85, 6.96, 7.25, 7.82, 8.95, 9.68, 9.89, 11.75, and 13.78 μ ; nmr (CCl₄) τ 3.22 (s, 4 H, arom), 7.55 (s, 12 H, *o*-CH₃), and 7.75 (s, 6 H, *p*-CH₃).

Anal. Calcd for C₂₀H₂₂: C, 91.55; H, 8.45. Found: C, 91.47; H, 8.43.

Hydrocarbon Radical Anions and Dianions. General Method of Preparation for Spectral Analysis. Solvents used in the preparation of samples were distilled from calcium hydride and stirred 10 hr with lithium aluminum hydride. Approximately 70 ml of the desired solvent was distilled on a vacuum line from the lithium aluminum hydride into a storage flask containing 1.00 g of anthracene and ca. 0.60 ml of sodium–potassium alloy. The flask was degassed and agitated lightly until the deep blue color of the anthracene radical anion developed. The solvents were stored in this manner until used.

Samples for esr, ultraviolet-visible, and nmr spectral measurements were prepared in 4-mm Pyrex, 4-mm quartz, and nmr tubes,

(19) R. C. Fuson, E. C. Horning, M. L. Ward, S. P. Rowland, and J. L. Marsh, *J. Amer. Chem. Soc.*, **64**, 30 (1942).

respectively. Each sample tube was sealed to the bottom of a 7 × 125 mm tube with a 25-mm side arm attached approximately 75 mm above the seal and aiming 35° downward. The 7-mm tubing was attached to the vacuum line with an O-ring fitting.

The desired amount of hydrocarbon weighed on a Cahn electrobalance was placed in the bottom of the sample tube. Approximately 100 μ l of sodium-potassium alloy (4:1 potassium-sodium weight ratio) or several small pieces of sodium or potassium was placed in the side arm. The entire apparatus was attached to the vacuum line and degassed; the desired volume of solvent was vacuum transferred from a storage flask using liquid nitrogen. The sample was degassed with four freeze-thaw cycles *in vacuo*. The reducing metal or alloy was distilled *in vacuo*, using a microflame, from the side arm down the main tubing, forming a mirror at the top of the tube. The sample tube was sealed off above the mirror at 1 μ . The sample was reduced by inverting the tube in a toluene slush or Dry Ice-acetone bath.

Esr Spectra. The concentrations of tolan derivatives used for radical anion generation were *ca.* 10⁻³ M, while samples used for obtaining the dianion varied from 10⁻³ to 10⁻² M. The samples were reduced in a hexane slush (-96°). The esr spectra were recorded on a Varian V-4502-13 spectrometer or a Varian E-3 spectrometer equipped with 100-kc field modulation and a standard Varian variable-temperature accessory. For spectra recorded at 77°K, the sample was placed in a small dewar filled with liquid nitrogen that fitted directly into the esr cavity.

Electronic Spectra. Each sample (1.5-6.0 × 10⁻⁴ M) was reduced in a stepwise manner by successive tube inversion. After each period of reduction the ultraviolet-visible spectrum (300-750 nm) was recorded and the approximate relative concentration of radical anion present at that period was determined from the relative intensity of the esr signal. The ultraviolet-visible spectrum recorded at maximum radical anion concentration was taken as characteristic of the radical anion. The hyperfine esr spectrum of the sample at this point was in each case identical with that obtained in the previous section.

The ultraviolet-visible spectra were recorded at -80° on a Cary 14 spectrophotometer with the sample placed inside a specially constructed quartz dewar designed for use in conjunction with a Varian variable-temperature controller. The dewar²⁰ was 34 cm in total length with a cylindrical neck 26 cm long. The neck was constructed from concentric 7 mm and 10 mm quartz tubing coated entirely with black paint except for a 3 × 40 mm rectangular slit through which the light beam passed. The lower portion was designed to fit inside the housing of a Varian V-4557 variable-temperature accessory. A similarly constructed quartz reference cell was used.

The intensity of the esr signal of the radical anion was monitored on a Varian E-3 spectrometer with the sample in a dewar filled with liquid nitrogen. The signal was recorded under the same conditions after each stage of reduction, except that the amplitude control was reset each time in order that the esr signal would span the recording paper. The approximate relative intensities of the esr signals at various stages of reduction were taken as the inverse of the relative settings of the amplitude control.

Nmr Spectrum. An nmr sample was prepared on a vacuum line using 10.1 mg of hexa-*t*-butyltolan, approximately 0.3 ml of 1,2-dimethoxyethane, and enough potassium metal to ensure an excess after reduction. The sample was reduced in a Dry Ice-acetone bath and its nmr spectrum periodically recorded at -35° on a Varian A-60-A. The resonances of the hydrocarbon were no longer observed when the sample became colored. Resonance signals of the dianion were observed after the two-electron reduction was virtually complete. The resonance lines of the solvent remained well resolved throughout the reduction.

The positions of the nmr absorptions of the dianion were determined relative to the methylene resonance of 1,2-dimethoxyethane. The latter absorption position was determined relative to tetramethylsilane from the nmr spectrum of a sample of 1,2-dimethoxyethane and tetramethylsilane at -35°. The resonance lines of hexa-*t*-butyltolan were measured relative to the methylene resonance of 1,2-dimethoxyethane at -35° in a sample of hexa-*t*-butyltolan and 1,2-dimethoxyethane.

After the nmr spectra of the dianion were recorded, the sample was quickly warmed to room temperature, opened, and quenched

with 0.40 ml of 0.14 N iodine in 1,2-dimethoxyethane. The sample was agitated until only the color of excess iodine remained. The residue was taken up in ether and washed with a dilute solution of sodium bisulfite and water. Drying over sodium sulfate and concentration *in vacuo* afforded a white solid whose nmr and ir were identical with that of pure hexa-*t*-butyltolan.

Polarography. Polarograms were recorded using a 5.00 × 10⁻³ M solution of each compound in dry 1,2-dimethoxyethane containing 0.1 M tetra-*n*-butylammonium perchlorate. The 1,2-dimethoxyethane was freshly distilled from lithium aluminum hydride under nitrogen immediately before use.

The polarograms were run on a Sargent Model XV polarograph equipped with a Sargent ir compensator. A saturated calomel electrode was used as the reference electrode, and it was connected to the sample cell by means of a closed ground-glass stopcock. The rate of flow of mercury, *m*, and the drop time, *t*, for the dropping mercury electrode were determined with the electrode immersed in 1,2-dimethoxyethane containing 0.1 M tetra-*n*-butylammonium perchlorate. The above quantities were measured with an open circuit and a mercury column height of 60 cm. For the above conditions, the drop time was 6.65 sec and the rate of flow of mercury was 0.914 mg/sec. The value of $m^2/3t^{1/6}$ used in obtaining the diffusion current constant, $i_d/Cm^{2/3}t^{1/6}$, was 1.292 mg^{2/3} sec^{-1/2}. Here *C* is the concentration in mmoles per liter and *i_d* is the measured diffusion current in microamperes.

Each polarogram was obtained under the same conditions with a 60-cm mercury column height and a sensitivity setting of 0.30 μ A/mm. The half-wave potential, *E*_{1/2}, and the diffusion current, *i_d*, for each polarographic wave were evaluated from the polarogram. In the case of hexa-*t*-butyltolan, a substantial portion of the reduction wave is located at potentials where the supporting electrolyte and/or solvent is reduced appreciably. The half-wave potential was obtained from a plot of the corrected diffusion current, *i_d* - *i_d*⁰, *vs.* the voltage. Here *i_d* is the diffusion current at a given voltage of a solution of the substrate, supporting electrolyte, and solvent, and *i_d*⁰ is the diffusion current at the same voltage of the supporting electrolyte and solvent.

Titration of Hexa-*t*-butyltolan Dianion. The dianion of hexa-*t*-butyltolan was prepared and titrated in a special glass apparatus containing a round-bottomed flask enclosed in a cooling jacket.

A sintered-glass funnel at the bottom of the flask provided for filtration. Below the funnel, a second flask was attached. The top flask was assembled on a high-speed stirrer, and dry nitrogen was passed through the entire system.

1,2-Dimethoxyethane was dried, purified by distillation from calcium hydride and lithium aluminum hydride, and stored over sodium-potassium alloy. Hexa-*t*-butyltolan (20.8 mg, 0.0403 mmol) and 30 ml of the dry 1,2-dimethoxyethane were stirred in the apparatus under dry nitrogen (passed through benzophenone ketyl) for 1.5 hr. Nitrogen was cooled by passage through a Dry Ice-acetone bath and then passed through the outer jacket at such a rate that the temperature at the exit was -25°.

Sodium-potassium alloy (200 μ l) was added with stirring, initially giving a yellow solution. After 10 min of stirring the color changed to reddish orange (radical anion formation); after 0.5 hr of stirring, to reddish brown; and after 40 min of stirring, to deep blue (dianion formation). This blue solution was stirred an additional 2 hr and then filtered into the bottom flask immersed in a Dry Ice-acetone bath.

A standard solution of iodine in dry 1,2-dimethoxyethane was added dropwise with stirring. The blue solution gradually changed to green, red, and yellow, finally becoming colorless. A total of 0.103 mequiv of iodine or 2.55 mequiv of iodine/mmol of hydrocarbon was required to produce a colorless solution.

The solution was diluted with water and ether extracted. The ether phase was washed with water, dried over sodium sulfate, and concentrated *in vacuo*. The nmr of the residue was that of hexa-*t*-butyltolan, slightly contaminated with impurity having peaks in the region τ 8.4-9.1.

Calculations. Configuration interaction matrix elements were evaluated using a configuration interaction program developed by Zimmerman and Binkley²¹ to calculate MO repulsion and exchange integrals.

The following resonance integrals were used: benzene bonds, -2.39 eV; acetylenic bonds (1.20 Å), -3.30 eV; phenyl to acetylenic overlap (1.40 Å), -2.25 eV.

(20) The apparatus was patterned after that described recently by E. Carberry, R. West, and G. Glass, *J. Amer. Chem. Soc.*, **91**, 5446 (1969). We acknowledge with pleasure Professor West's advice on this technique.

(21) (a) R. Binkley, Ph.D. Thesis, University of Wisconsin, 1967; (b) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

The numbering for the two styryl moieties in the perpendicular species was taken as 1 (β -styryl); 2 (α -styryl); 3 (carbon bearing the ethynyl group); 4,8 (*ortho*); 5,7 (*meta*); 6 (*para*) in the first styryl group and 9 (β); 10 (α); 11; 12, 16 (*ortho*); 13, 15 (*meta*); 14 (*para*). Semiempirical AO repulsion integrals were taken as (in electron volts; AO's given in parentheses) (1,1), 10.53; (1,2), 7.68; (1,3), 5.15; (1,4), 3.95; (1,9), 7.39; (1,10), 9.39; (1,12), 5.51; (1,13), 3.77; (1,14), 3.35; (2,8), 5.43; (3,4), 7.28; (3,5), 5.44; (3,6), 4.88; (3,10), 5.13; (3,11), 3.49; (4,11), 2.91; (4,16), 2.51; (5,10), 2.91; (5,11), 2.29; (5,15), 1.71; (5,16), 2.04; (6,10), 2.63; (6,11), 2.10; (6,14), 1.50; (6,15), 1.60; and (6,16), 1.88.

The values of the multicenter integrals used when differential overlap at the acetylenic carbon atoms is included are (in electron volts) (1,1,1,2), 3.26; (1,2,1,2), 1.33; (1,9,1,9), 0.07; (1,1,10,9), 2.98; (1,9,10,2), 0.07; (1,12,10,9), 1.19; (1,10, 1,10), 0.57; (1,10, 2,9), 0.14; and (1,10,1,9), 0.14.

Φ_1 and Φ_2 are the two lowest configurations of the radical anion with the odd electron in ψ_9 and ψ_{10} , respectively. The off-diagonal matrix element, F_{12} , between these two configurations is given below. This is zero even if differential overlap of the acetylenic carbon atoms is included, since each of the molecular orbital repulsion and exchange integrals is zero.

$$F_{12} = \int \Phi_1 F \Phi_2 d\tau = 2 \sum_I^8 G_{k_9 k_{10}}^{\text{MO}} - \sum_I^8 G_{k_9 k_{10}}^{\text{MO}} = 0 \quad (4)$$

Relative to the energy of the lowest triplet configuration of the dianion Φ_5 , the energy of the two singlet configurations, Φ_3 and Φ_4 (two electrons in ψ_9 and ψ_{10} , respectively), is

$$G_{10,10,10,10}^{\text{MO}} - G_{9,10,9,10}^{\text{MO}} + G_{9,10,10,9}^{\text{MO}} = 2.124 \text{ eV} \quad (5)$$

The off-diagonal matrix element, F_{34} , between the configurations Φ_3 and Φ_4 with differential overlap included is

$$F_{34} = \int \Phi_3 F \Phi_4 d\tau = G_{9,10,10,9}^{\text{MO}} = 0.0089 \text{ eV} \quad (6)$$

The energy of the lower state upon mixing is 2.11 eV above the energy of the lowest triplet configuration.

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Singlet-Triplet Differentiation and Dibenzoyl ethylene Photochemistry. Mechanistic and Exploratory Organic Photochemistry. LIX¹

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Abstract: The photochemistry of dibenzoyl ethylene is frequently quoted as a classic case where direct irradiation gives a rearrangement product and photosensitization with benzophenone in 2-propanol affords dibenzoyl ethane. The conclusion usually drawn is that the product of direct irradiation must therefore be derived from the singlet excited state and the product arising on use of benzophenone can therefore be assumed to come from the triplet. The present paper provides evidence that this textbook example has been oversimplified. Instead, the reduction product, dibenzoyl ethane, has now been shown to result from hydrogen transfer from solvent to dibenzoyl ethylene by triplet benzophenone. Methods are presently provided to differentiate between energy transfer and chemical intervention of the sensitizer. One test relies on the use of nonhydrogen abstracting sensitizers and the other depends on knowledge of the lifetime of the sensitizers employed.

Previously we reported the rearrangement of dibenzoyl ethylene to esters of 4-phenyl-4-phenoxy-3-butenoic acid on photolysis in alcoholic solvents³ (note Chart I). We also noted the generality of the transformation and reported an unusual selectivity in the case of dibenzoyl styrene wherein only one of two possible migrations occurred.³ The dibenzoyl ethylene example was independently uncovered by Griffin.⁴

Also, we found that acetophenone sensitization in *t*-butyl alcohol gave rise to the same rearrangement, however, with lower quantum efficiency ($\Phi = 0.0034$) than in the direct irradiations ($\Phi = 0.037$). It was our con-

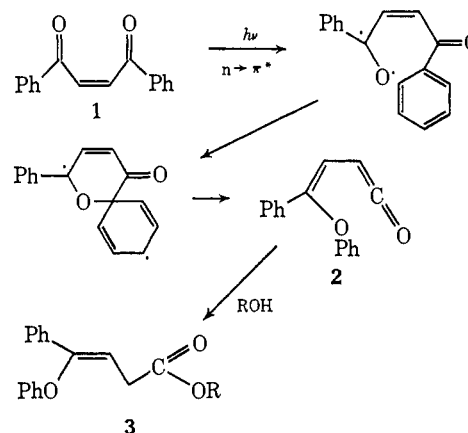
(1) For paper LVIII, see H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **92**, 3474 (1970).

(2) NSF Graduate Fellow, 1965-1969.

(3) H. E. Zimmerman, H. G. Dürr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967); H. E. Zimmerman, H. G. Dürr, R. G. Lewis, and S. Bram, *ibid.*, **84**, 4149 (1962).

(4) G. W. Griffin and E. J. O'Connell, *ibid.*, **82**, 4148 (1962).

Chart I



clusion that the direct irradiation reaction utilized the