# Effects of Steric Congestion on Stilbene Radical Anions and Dianions: DFT Calculations in the Interpretation of Stilbene Radical Anion ESR Spectra

James E. Gano,* E. Jean Jacob, P. Sekher, and Girija Subramaniam[†]

*Department of Chemistry, Bowman-Oddy Laboratories, University of Toledo, Toledo, Ohio 43606*

Leif A. Eriksson

*Department of Physics, University of Stockholm, Box 6730, S-113 85 Stockholm, Sweden*

Dieter Lenoir

*GSF-Forschungszentrum fuer Umwelt und Gesundheit, Institut fuer Oekologische Chemie, D-85758 Oberschleissheim, Germany*

Stilbenes are an important class of compounds with a broad range of applications in basic and applied research.[1−3] Sterically congested stilbenes such as 2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene, **3** and **4**, have recently received growing attention.[4−10] The unusual geometries of **3** and **4** are expected to impart unique properties to these materials. The preparation and characteristic properties of the radical anions and dianion of **3** and **4** are investigated and compared to stilbenes **1** and **2**. The application of DFT techniques to the analysis of ESR spectra of these materials is explored.
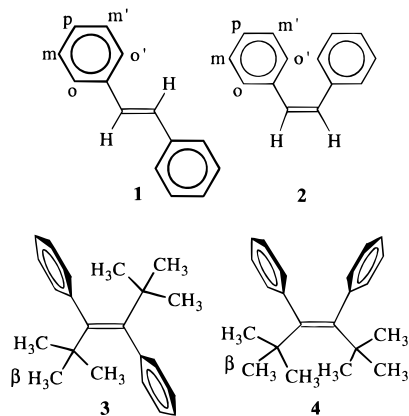


## Results

**Chemical Reduction.** Compounds **3** and **4**, whose preparation has been described,[4,11] reacted with potas-

sium in dry THF under argon to give maroon solutions. Compound **4** reacted more quickly. Methanol quenching of the dianion solutions from **3** or **4** gave similar mixtures of **3**, dihydrogenated **3** (at the double bond and on the ring), and two other minor products that disappeared with time.



| Reactant | | Product Ratio | |
|---|---|---|---|
| | **3** | **5** | **6** |
| **3** | 25 | 10 | 45 |
| **4** | 32 | 5 | 17 |
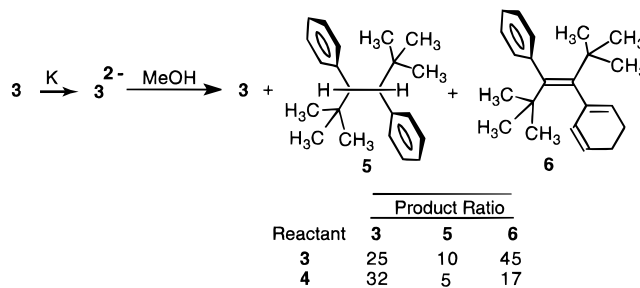
**ESR Parameters.**[12] The dianion of **3** (or **4**) is reported to form when **3** (or **4**) is treated with potassium in dimethoxyethane at 193−213 K. These solutions show no ESR signal, but both gave the same ESR spectrum when the dianion solution was irradiated with light.[12] The species suggested for this signal is **3**[1−]. The reported $a_H$ values for **3**[1−] are given in Table 1 along with experimental data on a series of related compounds, **7**−**9**.
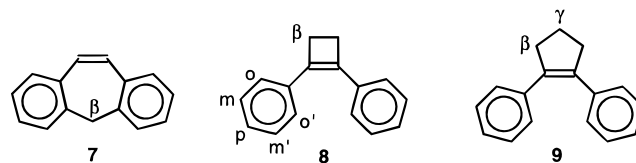


**MOPAC Calculations.** Calculations using MOPAC 94 (AM1, RHF, converged at 0.0001 kcal/mol)[13−15] were performed to gain insight into the structures and energies of radical anions **1**−**4** and **7**−**9** and dianions **1**−**4**. UHF calculations were found to give almost identical geometries. Structures of select neutrals, radical anions and dianions, viewed from a common vantage point directly down the central double bond, are presented in Figure 1. Selected results from these calculations are presented in Table 2.

This energy surface was explored for both the radical anion and dianions of **3** and **4**. These results are presented in Figure 2. Extensive efforts to initiate the calculation at a variety of geometries led only to the energy minima depicted. Energies of the neutral **3** and **4**, which have been studied elsewhere both computationally and experimentally,[4] are also presented in Figure 2.

**DFT Calculations of ESR Spectra.** Efforts to calculate ESR coupling constants, $a_H$, are fraught with

(1) **(1)** Mallory, F. B.; Mallory, C. W. *Photocyclization of Stilbenes and Related Molecules*; Wiley: New York, 1984; Vol. 30, pp 1−456.

(2) (a) Meier, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399−1420. (b) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415−436.

(3) Goerner, H.; Kuhn, H. J. In *Adv. Photochem.*; Neckers; D. C., Volman, D. H., Von Buenau, G. V., Ed.; Wiley: New York, 1995; Vol. 19, pp 1−118.

(4) Lenoir, D.; Gano, J. E.; McTague, J. A. *Tetrahedron Lett.* **1986**, *27*, 5339−5342.

(5) Gano, J. E.; Subramaniam, G.; Birnbaum, R. *J. Org. Chem.* **1990**, *55*, 4760−4763.

(6) Gano, J. E.; Park, B.-S.; Pinkerton, A. A.; Lenoir, D. *J. Org. Chem.* **1990**, *55*, 2688−2693.

(7) Gano, J. E.; Park, B.-S.; Subramaniam, G.; Lenoir, D.; Gleiter, R. *J. Org. Chem.* **1991**, *56*, 4806−4808.

(8) Gano, J. E.; Park, B. S.; Pinkerton, A. A.; Lenoir, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 162−164.

(9) Laali, K. K.; Gano, J. E.; Lenoir, D.; Gundlach, C. W. I. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2169−2173.

(10) Gano, J. E.; Skrzypczak-Jankun, E.; Kirschbaum, K.; Lenoir, D.; Frank, R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, 1985−1988.

(11) Lenoir, D.; Burghard, H. *J. Chem. Res., Synop.* **1980**, 396−397; *J. Chem. Res., Miniprint* **1980**, 4715−4725.

(12) Gerson, F.; Lamprecht, A.; Scholz, M.; Troxler, H.; Lenoir, D *Helv. Chem. Acta* **1996**, *79*, 307−318.

(13) *CAChe Reference Manual*; CAChe Scientific: Beaverton, OR, 1993.

(14) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

(15) (a) Stewart, J. J. P. QCPE no. 581. (b) Gano, J. E.; Jacob, E. J.; Roesner, R. *J. Comput. Chem.* **1991**, *12*, 127−134.

(16) Gerson, F.; Ohya-Nishiguchi, H.; Szwarc, M.; Levin, G. *Chem. Phys. Lett.* **1977**, *52*, 587−589.
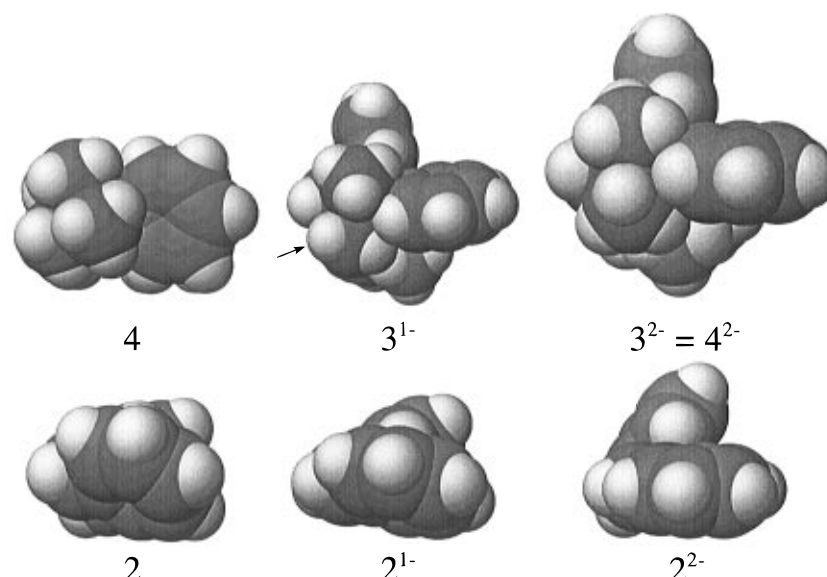
**Figure 1.** Views of a neutral, radical anion and dianion of 2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene and stilbene as calculated by MOPAC. Structure $3^{1-}$ is the UHF structure. In each case, the observer is viewing directly down the C=C double bond, and the plane of the carbon atom nearest the viewer in the double bond is parallel to the abscissa. The arrow by $3^{1-}$ points to the proton on the front of the ion with the exceptionally large $a_H$.

**Table 1. MOPAC(Structure)/DFT($a_H$) Calculated (C) and Experimental (E)[12,16] $a_H$ in mT for Select Radical Anions (Signs of Experimental Values Were Matched (See Text) with Those of the Calculated Values)**

| system | o,o | m,m | p,p | m',m' | o',o' | CH=CH | $\beta$ | $\gamma$ |
|---|---|---|---|---|---|---|---|---|
| $2^{1-}$ (C) | −0.16 | 0.00 | −0.36 | 0.07 | −0.27 | −0.08 | | |
| $2^{1-}$ (E) | −0.19 | 0.03 | −0.39 | 0.09 | −0.29 | −0.27 | | |
| $3^{1-}$ (C)[a] | −0.18 | 0.07 | −0.27 | 0.05 | −0.21 | | | $0.035^b$ |
| $3^{1-}$ (E) | −0.23 | 0.09 | −0.34 | 0.03 | −0.26 | | | 0.086 |
| $7^{1-}$ (C) | −0.18 | 0.01 | −0.37 | 0.06 | | −0.30 | 0.00, 0.02 | |
| $7^{1-}$ (E) | −0.23 | 0.05 | −0.42 | 0.10 | | −0.42 | 0.10, 0.01 | |
| $8^{1-}$ (C) | −0.19 | 0.02 | −0.38 | 0.04 | −0.23 | | $0.43^c$ | |
| $8^{1-}$ (E) | −0.23 | 0.05 | −0.42 | 0.07 | −0.28 | | 0.43 | |
| $9^{1-}$ (C) | −0.18 | 0.02 | −0.36 | 0.06 | −0.22 | | 0.70, 0.28 | −0.02 |
| $9^{1-}$ (E) | −0.21 | 0.04 | −0.38 | 0.08 | −0.26 | | 0.66, 0.29 | $−0.04^d$ |

[a] These values were calculated for the UHF optimized geometry. [b] Values of $a_H$ for individual methyl groups in mT: I(0.08/0.03/0.00), II(−0.03/−0.02/0.29), III(−0.02/−0.03/−0.01), IV(−0.02/−0.00/−0.00), V(0.01/0.05/0.03), VI(−0.03/−0.02/3.03). [c] Individual values of $a_H$ in mT: 0.52, 0.31, 0.49, 0.29. [d] This result suggests the sign of this small $a_H$, which has not been determined experimentally, is negative.

**Table 2. Heats of Formation and Energy-Minimized Geometries Calculated by MOPAC(AM1/RHF unless Noted) for Select Stilbenes and Their Anions and Dianions**

| compd | 2 | $2^{1-}$ ($2^{1-}$, UHF) | $2^{2-}$ | 4 | $4^{1-}$, 69° | $3^{1-}$, 116° (UHF) | $3^{2-}$ or $4^{2-}$ |
|---|---|---|---|---|---|---|---|
| $\Delta H_f$, kcal/mol | 63.98 | 44.72 (36.80) | 108.89 | 48.60 | 38.04 | 34.67 (25.37) | 79.84 |
| $\angle C_i$—C=C—$C_i$,[a] deg | −2.90 | −22.36 (−25.47) | −59.58 | 1.40 | −68.56 | −115.74 (−104.87) | −94.08 |
| $\angle C_o$—$C_i$—C—($t$-Bu),[b] deg | −37.44 | −19.03 (−17.33) | 2.03 | −86.53 | $−10.21^c$ | 12.9 (14.46) | 3.69 |
| | −41.40 | −17.31 (−17.32) | 2.04 | −88.38 | $−0.29^c$ | 9.88 (14.46) | 3.77 |
| $D$, C=C, Å | 1.340 | 1.382 (1.382) | 1.439 | 1.357 | 1.439 | 1.432 (1.451) | 1.472 |

[a] This is the $C_{ipso}$—C=C—$C_{ipso}$ dihedral angle, which describes the twist about the double bond. [b] This is the $C_{ortho}$—$C_{ipso}$—C-($tert$-butyl) angle, which is a measure of the conjugation between the central carbon and the phenyl group to which it is attached. In all cases, there is little pyramidalization about the C=C atoms. [c] A number of conformations with similar energies but differing angles at this point were observed in the RHF but not the UHF calculations of the anions.

difficulties primarily because spin multiplicity is not a quantized property. That leads to spin contamination of the results in the spin unrestricted formalism. Although some methods, such as quartet annihilation, have been utilized successfully in simple systems both with semiempirical[17] and ab initio methods,[18,19] the MOPAC methods have been limited to simple radicals and the Gaussian methods are untenable in large molecules like **3** and **4**. Recently, DFT methods, which can handle larger systems due to a more favorable scaling with

molecular size, hold promise for solving these problems.[20] The DFT approach was utilized to calculate the coupling constants of the radical anions of **3** and **4**. Since the method has not been extensively tested for such large systems, additional calculations were performed on the series of radical anions from **2** and **7**−**9** whose ESR spectra have been well studied. The calculated results are given in Table 1.

## Discussion

**DFT/MOPAC Methods in ESR.** The information in Table 1 for radical anions of **2** and **5**−**7** demonstrates the utility of calculating coupling constants through the use

(17) Nelsen, S. F. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1005−1008.
(18) Glaser, R.; Choy, G. S.-C. *J. Phys. Chem.* **1993**, *97*, 3188−3198.
(19) Glaser, R.; Choy, G. S.-C. *J. Phys. Chem.* **1994**, *98*, 11379−11393.
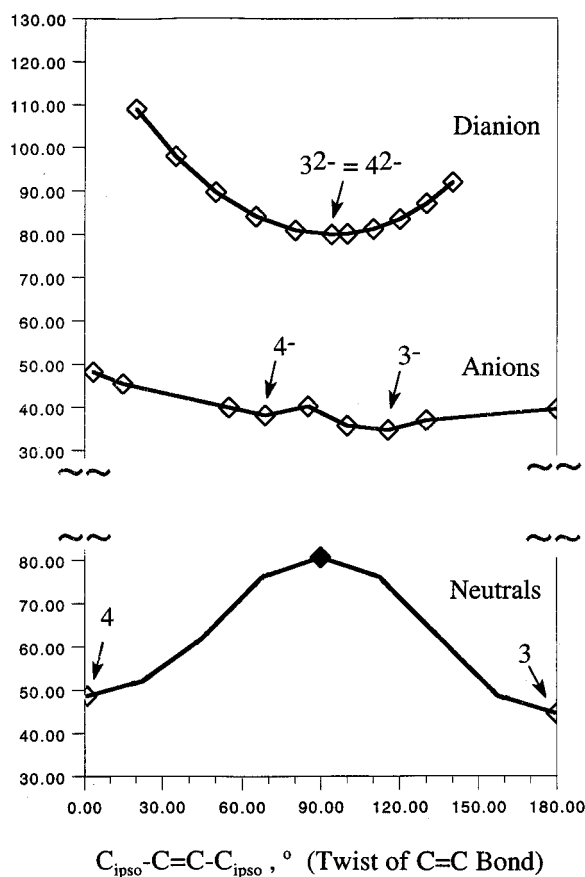
Energy, kcal/mol



**Figure 2.** Calculated (MOPAC/RHF) energy surfaces for the neutral, radical anion and dianion of 2,2,4,4-tetramethyl-3,4-diphenyl-3-hexene. Calculated values, ◇; experimental value ◆.

$C_{ipso}$–C=C–$C_{ipso}$ , ° (Twist of C=C Bond)

of MOPAC(AM1) to calculate a structure and a subsequent single point DFT calculation to calculate the $a_H$ values. For example, the original assignments of $a_H$ in the meta and meta′ and ortho and ortho′ positions of stilbene[16] have been revised by Higuchi through labeling and alkyl substitution studies.[21] At this level of accuracy, the computational results clearly support Higuchi's assignments. The trends in the experimental $a_H$ values are all reflected in the calculated values. The calculated values, at this level, are typically somewhat smaller in magnitude (only three out of 27 are slightly larger) than the experimental values with an average difference = 0.038 mT. Somewhat larger differences are observed for the hydrogens attached to the central double bond in stilbene, $2^{1-}$, and in one case for $7^{1-}$. The main source for the large deviations in the $a_H$ values for the non-ring protons is most likely a strong sensitivity of $a_H$ to the torsion angles. This suggests there may be out-of-plane twisting at this site in $2^{1-}$, which is not reflected in the relatively planar structure calculated by MOPAC. The signs of the $a_H$ values agreed with experiment in all instances in which experimental evidence was available.

Comparison of the structures and properties of the neutral, radical anion and dianion forms of **3** and **4** and the corresponding stilbenes is instructive.

(20) Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salahub, D. R. In *Theoretical and Computational Chemistry*; Seminario, J. M., Politzer, P., Ed.; Elsevier: Amsterdam, 1995; Vol. 2.

(21) Higuchi, J.; Ishizu, K.; Nemoto, F.; Tajima, K.; Suzuki, H.; Ogawa, K. *J. Am. Chem. Soc.* **1984**, *106*, 5403–5407.

**Neutral Stilbenes.** Stilbenes **1** and **2** are structurally very different from their sterically congested counterparts, **3** and **4**. (*E*)-Stilbene, **1**, has been found to be planar in the crystalline state and its lowest lying vibrational state in supersonic jet expansions. In contrast, experimental and computational methods agree that generally in the gas phase, and presumably in solution, the phenyl groups are rotated as much as 32° along a very broad shallow potential to reduce nonbonded repulsions between hydrogen atoms.[2] The C=C bond remains planar. (*Z*)-Stilbene, **2**, is twisted in that manner and also about the C=C bond in both the crystalline and gas phase as seen from the calculated geometry depicted in Figure 1. This modest twisting still allows sufficient π-overlap for a continuous, conjugated π-system between the phenyl groups and the central double bond.[7,8] The resonance energy per C=C bond in **1** is less than that found in benzene.[2] X-ray analyses shows that the introduction of two *tert*-butyl groups onto the central double bond in stilbenes **1** or **2** to form **3** or **4** causes the phenyl groups in both to rotate out of the molecular plane so that their planes become perpendicular and their π-systems become orthogonal to the central C=C bond (Figure 1).[8,22] In both **3** and **4** the three π-systems are not conjugated and the C=C bond is planar and of normal length.[8,22] In spite of the apparent lack of conjugation in **3** and **4**, photoelectron spectroscopy confirms there is still orbital interaction between the π-systems of the phenyl groups.[7]

**Stilbene Radical Anions.** The correspondence between calculated and measured ESR $a_H$ values in $3^{1-}$ provide validation of the calculated geometry for $3^{1-}$. The average differences between calculated and experimental values, 0.035 mT, is almost the same as for the test data, 0.038 mT. However, it is worthy of note that the results in Table 1 and other reports suggest the coupling constants are relatively insensitive to the degree of twisting. It is interesting to note that $3^{1-}$ would seem to represent the first exception to the generalization that the more sterically hindered ortho′ and meta′ hydrogens typically have larger $|a_H|$ values than their ortho and meta counterparts.[12] Although this generalization applies for the ortho hydrogens in $3^{1-}$, the order is shown to be reversed, Table 1, for the meta hydrogens.

The structural patterns, Figure 1, of anions $3^{1-}$ and $4^{1-}$ are significantly different than that of $1^{1-}$ and $2^{1-}$. Whereas $1^{1-}$ and $2^{1-}$ are only moderately twisted so as to retain much of the conjugation throughout the π-system, $3^{1-}$ and $4^{1-}$ are both twisted about the C=C bond. In both $3^{1-}$ and $4^{1-}$ the phenyl group is coplanar, $\angle C_o$–$C_i$–C–(*t*-Bu) in Table 2, with the adjacent C atom creating resonance-stabilized benzyl groups. Evidently when an electron is transferred to $3^{1-}$ and $4^{1-}$, conjugation is lost by twisting about the C=C bond as conjugation is gained by twisting about the Ph–C bond.

Two conformers were found for the radical anions of **3** and **4**. They are characterized by twist angles, $\angle C_i$–C=C–$C_i$, of −115.74° and −68.56°, Table 2, for the (*E*)-isomer $3^{1-}$ and (*Z*)-isomer $4^{1-}$, respectively. Both $1^{1-}$ and $2^{1-}$ show separate ESR signals. Although separate signals are not observed for $3^{1-}$ and $4^{1-}$, the small energy maximum for the 90° twisted conformation, Figure 2, reflects a similarity to $1^{1-}$ and $2^{1-}$. Even after extensive searching, only very broad maxima, Figure 2, were

(22) Gano, J. E.; Subramaniam, G.; Skrypczak-Jankun, E.; Kirschbaum, K.; Kluwe, C.; Sekher, P. Manuscript in preparation.

evident when $\angle C_i$–C=C–$C_i$ was near 0° or 180° for these radical anions.

Since some metal ions form stable complexes, **10**, with the $\pi$-electron-rich cleft of **4**,[5] the likelihood existed that potassium would similarly coordinate with **4**$^{1-}$ to form **11**. The presence of five rather than three coupling constants for ring hydrogens demonstrates this attractive, symmetric sandwich structure is not present. Direct evidence for interaction between and $^{39}$K and **3**$^{1-}$ by observing coupling was not evident, but this would not necessarily be observed since in these systems such $a_K$ values are usually small, 0.01–0.03 mT.[23,24]
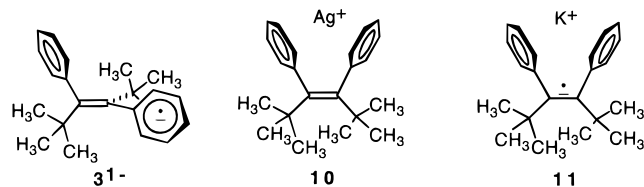


The MOPAC calculations suggest that (*E*)-isomer **3**$^{1-}$ is sufficiently more stable than (*Z*)-isomer, **4**$^{1-}$, $\Delta E = 3.34$ kcal/mol, so that **4**$^{1-}$ should not contribute to the ESR spectrum. Under the measurement conditions, the conformations are expected to be frozen on the ESR time scale.[12] Only one set of signals was reported. It is worth noting, however, that the calculated $a_H$ values for **4**$^{1-}$ and **3**$^{1-}$ are not sufficiently different to make this distinction experimentally.

The unusually large $a_H$ value observed for the hydrogens on the *tert*-butyl group in **3**$^{1-}$ is explained by the DFT calculations. A *single hydrogen*, on each *tert*-butyl group, identified with an arrow in Figure 1, with an $a_H$ of 0.33(0.29) mT raises the averaged value, which without those contributions would be 0.003 mT, to 0.040 mT. Although this hydrogen holds a unique structural position, it is not entirely obvious why this feature should lead to such a large $a_H$. The methyl upon which it is mounted is attached by a C–C bond that is almost perpendicular to the plane of the C=C bond, $\angle CH_3$–C–C=C = $-77.1°$ ($-71.7°$), so it is best positioned to receive unpaired electron density associated with the $\pi$-orbitals in the "planar" benzyl system. However, only one of the three hydrogens on this methyl has an unusually large $a_H$ value, and there is another methyl, above the first in Figure 1, which occupies a similar position with no large coupling constant. The fact that the C–H bond attaching the special hydrogen is almost anti-periplanar to the bond attaching the *tert*-butyl group, $\angle H$–C–C–C = 170.0° (168.2°), would seem to be important, but since this bond is orthogonal to the benzyl $\pi$-system, it is not obvious why this should be so.

**Stilbene Dianions.** Reduction of **3** or **4** leads to a dianion rather than a radical anion. This is supported by the absence[12] of an ESR signal when **3** and **4** are reduced with potassium. An explanation for this difference is suggested by comparing the calculated (MOPAC) heats of reaction for the disproportionation of the stilbene and 2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene radical ions from the heats of formation values given in Table 2.

As shown above, this gas phase calculation shows both processes to be endothermic, but the disproportionation

$$2^{1-} + 2^{1-} + 83.41 \text{ kcal/mol} \rightarrow 2 + 2^{2-}$$

$$4^{1-} + 4^{1-} + 51.78 \text{ kcal/mol} \rightarrow 4 + 4^{2-}$$
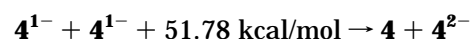
of stilbene is over 30 kcal/mol more endothermic. This difference is due almost entirely to the much greater relative stability of the sterically congested dianion **4**$^{2-}$ over **2**$^{2-}$, *vide infra*.

The structure of dianion **4**$^{2-}$ explains its exceptional *relative* stability. Its most stable conformation is that which minimizes the steric repulsion and the electrostatic repulsion of the 2$^-$ charge. The 90° twisted conformation, **3**$^{2-}$ or **4**$^{2-}$ in Figure 1, accomplishes both these objectives without sacrificing stabilization due to conjugation because neither **4** or **4**$^{1-}$ are conjugated. In contrast, formation of the stilbene dianion must sacrifice resonance stabilization with increasing twist angle as **2** goes to **2**$^{1-}$ and then **2**$^{2-}$, Figure 1.

**Overview of Geometry Changes upon Reduction of 3 and 4.** The geometries of the neutral, radical anion and dianion forms of **3** and **4** are dependent upon the residual strength of the double bond and steric hindrance. This is clearly evident in Figure 2 where the energy of each species is plotted as a function of the twist angle about the C=C bond. In the neutral form, bottom trace, the $\pi$-bond is strong, causing energy minima at the two planar (*Z*)- and (*E*)-isomers and a maximum when the $\pi$-bond twist approaches 90°. When one electron is added, middle trace, the steric effect (steric repulsion of the *tert*-butyl groups) and electronic effects just about balance as rotation occurs about the central double bond, giving an almost flat energy surface. When a second electron is added to form the dianion, no residual electronic stabilization exists and the most stable conformation is dictated by the steric effect to be the 90° twisted form, top trace. This also maximizes the separation of the two negative charges.

## Experimental Section

**ESR Calculations.** In the theoretical studies of the anions of **2**–**4** and **7**–**9**, a combination of semiempirical and density function techniques was used. Due to the sizes of the systems, as well as their rigidity, the systems were first geometry optimized using the AM1 Hamiltonian,[14] as provided by the MOPAC program package.[15] AM1 was chosen over MNDO and PM3 because the former seriously overestimates nonbonded repulsion energies in sterically congested systems and the latter shows no advantages in these systems.[15b] Both UHF and ROHF calculations were performed, but the resulting geometries were found to be highly similar. Once the optimized geometries were obtained, single point density function theory (DFT) calculations were performed to evaluate the hyperfine parameters. All DFT calculations used the deMon program,[25–28] with the gradient correction to the exchange part by Perdew and Wang,[29] and the correlation part by Perdew.[30,31] This was combined with a previously developed routine for ESR calculations by Malkin et al.[32,33] The auxiliary bases applied are (5,2;5,2) for carbon and

(23) Sharp, J. H.; Symons, M. C. R. *Ions and Ion-Pairs in Organic Reactions*; 1972; Vol. 1, Chapter 5.

(24) Gerson, F. *High-Resolution ESR*; Wiley-Verlag Chemie: 1970; Chapter A.2.2.

(25) St-Amant, A.; Salahub, D. R. *Chem. Phys. Lett.* **1990**, *169*, 387.

(26) St-Amant, A. Ph.D. Thesis, Universite de Montreal, 1991.

(27) Salahub, D. R.; Fournier, R.; Mlynarski, P.; Papai, I.; St-Amant, A.; Ushio, J. In *Density Function Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer Verlag: New York, 1991.

(28) Daul, C.; Gourset, A.; Salahub, D. R. In *Numerical Grid Methods and Their Applications to Schrodinger's Equation*; Cerjan, C., Ed.; Kluwer: Dordrecht, 1993.

(29) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1986**, *33*, 8800.

(30) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(31) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(32) Eriksson, L. A.; Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *J. Chem. Phys.* **1993**, *99*, 9756.

(5,1;5,1) for hydrogen.[34] Since we are interested in comparing proton couplings only, the IGLO-III basis set was used for H,[35] whereas for C a basis of DZVP quality was used.[36] Initial tests showed that the C(valence)−H interaction was fully described through the DZVP basis, giving confidence in the computed proton hyperfine coupling constants. A detailed review on the calculation of ESR parameters using the DFT approach has appeared.[20]

**Reaction of 3 and 4 with Potassium.** Freshly cut potassium, 115 mg (2.95 mmol), was flattened with a spatula and added to 5 mL of THF (dried with sodium benzophenone ketyl and outgassed with a rapid stream of argon for 4 h) and 74.8 mg (0.256 mmol) of **3** under argon in a small flask. The flask was sonicated to produce a maroon solution. This color formed slightly slower for **3** than, *vide infra*, **4**. Sonication was continued for 6 days. The colored solution was removed by syringe from the residual potassium. The potassium was washed by sonication with additional THF. The combined THF extracts were quenched with 5 mL of methanol, which was then removed under vacuum. Water was added, and the mixture was extracted with ether. The combined ether extracts were dried with sodium sulfate, and the ether was removed under vacuum to give 39.4 mg of crude product. TLC (pentane) indicated at least four components. Separation by elution with pentane on a 1 × 18 cm flash chromatography (silica gel) column while collecting 5 mL fractions produced five products, two of which had similar ^{1}H NMR spectra, showing two *tert*-butyl signals, but were otherwise not identified because they slowly disappeared

with time. The 39.4 mg sample contained **3** (24%), **5** (10%),[37,38] and a new compound **6** (45%), 3-(cyclohexa-1,5-dienyl)-2,2,4,4-tetramethyl-4-phenylhex-3-ene: mass spectrum *m/z* (relative intensities) 294 (M[+], 2.0), 237 (100), 195 (18), 181 (44); ^{1}H NMR $\delta$ 0.77 (s, 9H), 0.98 (s, 9H), 2.08−2.27 (m, 4H), 5.46 (t, 1H, $J = 4.1$ Hz), 5.79 (d of t, 1H, $J = 9.4$, 4.1 Hz), 5.89 (d, 1H, $J = 9.4$ Hz), 7.06 (m, 2H), 7.17−7.30 (m, 3H); ^{13}C NMR $\delta$ 22.21, 22.92, 32.90, 33.26, 38.11, 38.16, 122.55, 124.06, 126.12, 126.74, 130.50, 131.35, 132.41, 132.58, 139.17, 144.40, 145.65, 145.95 (a signal at 127.06, was assigned to an inseparable impurity). Both **3** and **5** were identified by comparison with authentic samples.

Reaction of **4** was performed in a parallel manner. The recovered material weighed 50.7 mg and contained the same products: **3** (32%), **5** (17%), and **6** (5%).

JO960065D

(33) Eriksson, L. A.; Malkina, O. L.; Malkin, V. G.; Salahub, D. R. *J. Chem. Phys.* **1994**, *100*, 5066.

(34) Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T. K.; Kim, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 7399−7400.

(35) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR-Basic Principles and Progress*; Springer Verlag: Heidelberg, 1990; Vol. 23.

(36) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560−571.

(37) Beckhaus, H. D.; McCullough, K. J.; Fritz, H.; Ruechardt, C.; Kitschke, B.; Lindner, H. J.; Dougherty, D. A.; Mislow, K. *Chem. Ber.* **1980**, *113*, 1867−83.

(38) Pine, S. H.; Munemo, E. M.; Phillips, T. R.; Bartolini, G.; Cotton, W. D.; Andrews, G. C. *J. Org. Chem.* **1971**, *36*, 984−91.