J. Org. Chem. 1988, 53, 4386–4390

needles of **11** (2.9 g, 70%), mp 245 °C.

C. Iodination with Iodocyanogen. C.1. A solution of ICN (1.53 g, 10 mmol) in absolute ether (25 mL) was added to the stirred solution of **8** (3.28 g) in absolute chloroform at room temperature. Stirring of the red solution was continued for 5 days, and the red powder was then filtered off, washed with ether, and dried to afford 2,2′,4,4′,6,6′-hexapiperidin-1-yl-1,1′-bicyclohexadienylium bis(diiodocyanide) (**12b**) (2.52 g, 42%), mp 154–155 °C. Anal. Calcd for $C_{42}H_{66}N_6\cdot(I_2CN)_2$: C, 43.50; H, 5.48; I, 41.77; N, 9.22. Found: C, 43.60; H, 5.37; I, 41.71; N, 9.19.

The filtrate was evaporated to dryness, leaving a dark brown residue (2.5 g), mp 135 °C, which was purified by recrystallization twice from *n*-heptane/activated carbon to afford the educt **8**, mp and mixed mp 182–184 °C (lit.[19] mp 183–184 °C).

C.2. A solution of ICN (3.06 g, 20 mmol) in absolute ether (50 mL) was dropped into a stirred suspension of **8** (3.28 g) in absolute ether (50 mL) at room temperature. The separated red powder of **12b** was filtered off at several times (after 8 h, 515 mg; after 32 h, 770 mg; after 56 h, 290 mg; and after 4 weeks, 1.85 g). Total yield of **12b**: 3.43 g (56%), mp 152–155 °C.

C.3. A solution of ICN (6.12 g, 40 mmol) in absolute ether (100 mL) was dropped into a stirred solution of **9** (6.66 g, 20 mmol) in absolute chloroform (250 mL) at room temperature. After an additional 3 days of stirring of the dark brown solution, the resulting brown powder of the dimeric σ-complex **13** (60 mg), mp 120–125 °C, was filtered off. Further fractions of red-brown-colored product were filtered off within 2 weeks in periods of several days; total yield, 240 mg. The melting points of these fractions increased continuously to 140–145 °C (fourth and fifth fractions)—obviously the anion of the σ-complex **13** changed, e.g., to CN^-, I_2CN^-, and I_3^-, respectively. Anal. Calcd for 2,2′,4,4′,6,6′-hexamorpholin-1-yl-1,1′-bicyclohexadienylium bis(triiodide) (**13d**) $C_{36}H_{54}N_6O_6\cdot(I_3)_2$ (fifth fraction): C, 30.28; H, 3.81; N, 5.87. Found: C, 30.43; H, 3.87; N, 5.75. The filtrate was evaporated to dryness, leaving a brown-colored powder (9.2 g), mp 170 °C. Recrystallization of 4.2 g from dimethylformamide/acetonitrile (1:1) afforded **9** as light yellow colored product, which was filtered off, washed with methanol and ether, and dried, yielding 1.2 g, mp 310–315 °C (lit.[19] mp 308–312 °C).

Reactions of the Dimeric σ-Complexes 12 and 13. 2,2′,4,4′,6,6′-Hexapiperidin-1-yl-1,1′-bicyclohexadienylium Diperchlorate (12c). A solution of 10% aqueous sodium perchlorate (40 mL) was added to a shaken solution of **12a** (1.0 g) in water (100 mL). The precipitated yellow-colored product (0.81 g), mp 210–212 °C, was filtered off after 1 h, washed with water, dissolved in dimethylformamide (17 mL), treated with activated carbon, and filtered. Ether (50 mL) was then slowly added to the filtrate, yielding the diperchlorate **12c** as fiery-red-colored product (0.77 g), which was separated by filtration and recrystallized again from dimethylformamide/ether to afford **12c**, mp 215–216 °C. Anal. Calcd for $C_{42}H_{66}N_6\cdot(ClO_4)_2$: C, 59.07; H, 7.79; Cl, 8.31; N, 9.84. Found: C, 58.97; H, 7.75; Cl, 8.48; N, 9.93.

2,2′,4,4′,6,6′-Hexapiperidin-1-yl-1,1′-biphenyl (14). A. A solution of sodium hydroxide (1.5 g) in water (15 mL) was added to a shaken solution of **12a** (163 mg) in water (20 mL). The resulting precipitate of colorless **14** was separated by filtration after 30 min, washed with water, and dried, to give 130 mg, mp 270–310 °C. The product was purified by recrystallization twice from dimethylformamide, yielding a mp of 319–321 °C. Anal. Calcd for $C_{42}H_{64}N_6$: C, 77.25; H, 9.88; N, 12.87. Found: C, 77.27; H, 9.83; N, 12.86.

B. A solution of 5% aqueous NaOH (2 mL) was dropped into a shaken solution of diperchlorate **12c** (342 mg) in dimethylformamide (10 mL). Water (100 mL) was added after 30 min, and the resulting precipitate of **14** was filtered off, washed with water, and dried, yielding 205 mg (78%), mp 310–315 °C, which was recrystallized from dimethylformamide to afford a mp and mixed mp of 319–320 °C.

C. A solution of 5% aqueous NaOH (20 mL) was added to a filtered and shaken solution of bis(diiodocyanide) **12b** (2.1 g) in dimethylformamide (80 mL). The resulting precipitate, separated by filtration after 1 h (0.99 g, mp 285–320 °C) and recrystallized from dimethylformamide, was identified as **14**, mp and mixed mp 320–322 °C.

2,2′,4,4′,6,6′-Hexamorpholin-1-yl-1,1′-biphenyl (15). A solution of 5% aqueous NaOH (15 mL) was added to a shaken solution of the bis(triiodide) **13d** (200 mg) in dimethylformamide (10 mL). The resulting colorless precipitate of **15** (84 mg) was recrystallized from dimethylformamide (2 mL), yielding colorless crystals of **15**, mp 344–346 °C. Anal. Calcd for $C_{36}H_{52}N_6O_6$: C, 65.02; H, 7.88; N, 12.65. Found: C, 64.89; H, 7.80; N, 12.62.

Acknowledgment. We gratefully acknowledge support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supplementary Material Available: Fractional atomic coordinates, anisotropic temperature factors for non-hydrogen atoms, fractional atomic coordinates, and isotropic temperature factors for H atoms for **2a** and **2c** and a summary of bonding parameters for **2c** (16 pages). Ordering information is given on any current masthead page.

Twisting in the Tetraphenylethylene Dianion

Marye Anne Fox* and David Shultz

Department of Chemistry, University of Texas, Austin, Texas 78712

Received February 9, 1988

The dipotassium salt of the tetraphenylethylene dianion (1^{2-}) has been studied by ^1H and ^{13}C NMR spectroscopy and π-MO calculational techniques. Analysis of one-bond and three-bond carbon–carbon coupling constants permits a description of the geometry of the contact ion pair of 1^{2-}. We find a linear relationship between π bond order and carbon–carbon coupling constants, which provides information concerning the torsional angles about those bonds. The preferred geometry of 1^{2-} is one in which the C_α–$C_{\alpha'}$ torsional angle is closer to the C_α–$C_{\alpha'}$ torsional angle of neutral **1** than to 90°, with the estimated range of this torsional angle being 8.4–28°.

Control of redox reactivity requires a secure chemical basis for discriminating between single and multiple electron transfer. Although the problem can be approached thermally by employing differentially electronically populated transition metal complexes, we sought to find redox catalysts that could be activated photochemically to induce selective two-electron transfer.

In that vein, we were attracted to tetraarylethylenes, a family that included several members known to be reduced electrochemically via two-electron transitions. The conventional explanation involves an overpotential for attachment of the first electron caused by a required geometry change. That is, the radical anion formed by adding a single electron was thought to have twisted slightly from

0022-3263/88/1953-4386$01.50/0

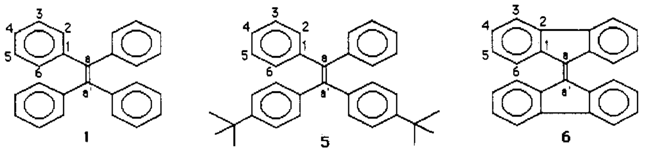

Figure 1.

Table I. ^1H NMR Chemical Shift Data for 1 and 1^{2-}

H	1^a	1^{2-} (24 °C)^a	1^{2-} (−80 °C)^a	$\Delta\sigma^b$
2,6	7.05	6.98	7.61, 6.34	+0.56, −0.71
3,5	7.00	6.45	6.48, 6.43	−0.52, −0.57
4	7.05	5.56	5.56	−1.49

[a] Proton chemical shifts relative to residual THF-d_8 protons at δ 3.58. [b] Chemical shift difference in ppm.

the planar ethylenic geometry of the neutral parent. The addition of a second electron to the radical anion requires a large geometric deformation so that it occurs at a potential less negative than that initially required.

Since electron attachment and detachment can be initiated photochemically, we considered photochemically initiated electron transfer driven geometric isomerization to be a viable route for forming multiple electron transfer catalysts. It became important then to establish the magnitude of the geometric change encountered in the dianion, and to this end we have investigated spectroscopically the tetraphenylethylene dianion.

Tetraphenylethylene dianion (1^{2-}) has been examined previously by IR,[1] ^1H NMR,[1,2] and electrochemical/conductance[3-12] measurements. There is substantial disagreement concerning the C_α–$C_{\alpha'}$ ("ethylenic") torsional angle (Figure 1). In fact, values ranging from 0° (planar) to 90° (orthogonal) have been reported.[1-10] The abnormally large disproportionation constant, K_{dis}, for the reaction

$$2TPE^{\bullet-} \overset{K_{dis}}{\rightleftharpoons} TPE^{2-} + TPE$$

was viewed as evidence for a nearly 90° C_α–$C_{\alpha'}$ torsional angle in 1^{2-}.[3-10] Large steric interactions and coulombic repulsions are thought to be alleviated by twisting about the C_α–$C_{\alpha'}$ bond. In none of these studies was the C_1–C_α torsional angle discussed or probed (Figure 1).

We describe herein the geometry of 1^{2-} established by ^1H and ^{13}C NMR spectroscopy and carbon–carbon coupling constants (J_{CC}) of bis-$^{13}C_\alpha$,$^{13}C_{\alpha'}$-labeled 1^{2-} and a model system, $^{13}C_\alpha$-labeled α,α-diphenyl-α',α'-bis(4'-*tert*-butylphenyl)ethylene (5^{2-}) (Figure 1). π-MO calculation methods were used to correlate π bond order and carbon–carbon coupling constants. A relationship between π bond order and J_{CC} is also discussed.

Table II. ^{13}C NMR Chemical Shift Data for 1 and 1^{2-}

C	1^a	1^{2-} (24 °C)^a	1^{2-} (−80 °C)^a	$\Delta\sigma^b$
α	141.96	96.48	95.92	−45.48
1	144.74	148.44	147.71	+3.70
2,6	132.13	117.45	115.88, 118.11	−14.68
3,5	128.40	128.62	127.83, 129.01	+0.22
4	127.17	106.88	106.36	−20.29

[a] Carbon chemical shifts relative to THF-d_8 carbon at δ 67.4. [b] Chemical shift difference in ppm.

Results and Discussion

TPE Dianion NMR Spectra. We chose potassium as the reducing agent/counterion for three reasons: (1) the decreased polarizing ability of large cations has been shown to give better shift–charge correlations;[13] (2) the perturbation of MO energy levels decreases with an increase in cation radius;[14] and (3) the dipotassium salts of arene dianions exist as contact ion pairs in ether solvents and changes in the structure of the ion pair as a function of temperature are negligible.[14]

Upon reduction with potassium, the ^1H NMR spectrum of 1 changes from a multiplet centered at 7.03 ppm to one exhibiting three sets of signals[15] (Table I): a triplet at 5.56 ppm (H_4), a multiplet at 6.45 ppm ($H_{3,5}$), and a broad doublet at 6.98 ppm ($H_{2,6}$). We ascribe these new signals to the diamagnetic dianion, 1^{2-}. Dramatic changes are also seen in the ^{13}C NMR spectra (Table II) of 1^{2-} relative to 1. Both carbon and proton resonances were assigned by COSY[16] and CH correlation spectra.[17] As the dianion solution is cooled, the ^1H resonance at 6.98 ppm ($H_{2,6}$) broadens, coalesces at ca. −40 °C, and appears as two doublets centered at 7.61 and 6.34 ppm at −80 °C. Also, the multiplet at 6.45 ppm ($H_{3,5}$) broadens and appears as two separate absorptions centered at 6.48 and 6.43 ppm at −80 °C. The triplet at 5.56 ppm remains unchanged throughout this temperature range (Table I). Similar changes upon cooling are seen in the ^{13}C NMR spectra. At −80 °C the ortho and meta carbons appear as four separate absorptions, as would be expected if the dynamic process involves phenyl ring rotation. At low temperature the C_1–C_α rotation is frozen out on the NMR timescale. The two ortho and two meta protons as well as the carbons of the phenyl rings become magnetically nonequivalent (Table II). This higher C_1–C_α rotational barrier in the dianion is in agreement with π-MO calculations discussed below which predict an enhancement of the C_1–C_α bond order upon occupation of the LUMO of 1 by reduction.

Line shape analysis (GENXCH program)[18] of the temperature-dependent ^1H NMR spectra of 1^{2-} allows estimation of the C_1–C_α rotational barrier. A lower limit for the barrier height is estimated as $\Delta H^\ddagger = 12.4$ kcal/mol with $\Delta S^\ddagger = 8.8$ eu. The relatively small $\Delta S^\ddagger$ is an indication that large changes in the solvation are not occurring over the temperature range studied. Furthermore, the intrinsic ^1H and ^{13}C chemical shifts were constant over the temperature range used, showing that the number of species and the structure of the contact ion pair remains constant. Similar thermodynamic values have been reported for the rotational phenomena of *o*-terphenyl dian-

---

(1) Eargle, D. H., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 3859.

(2) Geraldes, C. F. G. C.; Gil, V. M. S.; Eargle, D. H. *J. Chem. Phys.* **1973**, *59*, 1166.

(3) Lundgren, B.; Levin, G.; Claessom, S.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 262.

(4) Levin, G.; Claessom, S.; Szwarc, M. *J. Am. Chem. Soc.* **1972**, *94*, 8672.

(5) Roberts, R. C.; Szwarc, M. *J. Am. Chem. Soc.* **1965**, *87*, 5542.

(6) Cserhegyi, A.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1969**, *91*, 1892.

(7) Garst, J. F.; Zabolotny, E. R.; Cole, R. S. *J. Am. Chem. Soc.* **1964**, *86*, 2257.

(8) Garst, J. F.; Pacifici, J. G.; Zabolotny, E. R. *J. Am. Chem. Soc.* **1966**, *88*, 3872.

(9) Garst, J. F.; Cole, R. S. *J. Am. Chem. Soc.* **1962**, *84*, 4352.

(10) Garst, J. F. *J. Am. Chem. Soc.* **1971**, *93*, 6312.

(11) Grzeszczuk, M.; Smith, D. M. J. *Electroanal. Chem.* **1984**, *162*, 189.

(12) Farnia, G.; Maran, F.; Sandona, G. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1885.

(13) Eliasson, B.; Edlund, U. *J. Chem. Soc., Perkin Trans. 2* **1983**, *79*, 1837.

(14) Reference 13 and references cited therein.

(15) Neither the appearance nor the assignments for the ^1H NMR spectra in ref 1 and 2 are consistent with our ^1H NMR, COSY, and CH correlation spectra.

(16) Bax, A.; Freeman, R.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 164.

(17) Bax, A.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 501.

(18) GENXCH is a line-shape analysis program, which was included with the Nicolet graphics data station.

ion, $\Delta H^{\ddagger} = 13$ kcal/mol,[19] and the diphenylmethyl anion, $\Delta G^{\ddagger} = 11.7$ kcal/mol.[20] The ortho protons are dramatically deshielded relative to the expected upfield shift induced by dianion formation. This may be attributed to severe van der Waals repulsion by the protons on the neighboring rings (Figure 1). The ortho proton on the geminal phenyl ring (distance between geminal ortho protons = $d_g \approx 2.270$ Å by MM2 calculations) produces a greater effect ($\partial(H_6) = 6.34$ ppm, distance between vicinal ortho protons, $d_v \approx 2.541$–3.327 Å by MM2 calculations at various distortions (8.4–88.4°) of the C_α–$C_{\alpha'}$ torsional angle, see below). An additional way to observe the effects of steric hindrance is to measure the longitudinal relaxation time: sterically crowded protons are expected to show the shortest T_1. Indeed, inversion-recovery experiments show that the ortho protons of 1^{2-} have the shortest relaxation time, T_1. Further evidence that the dynamic process is caused by C_1–C_α rotation is obtained from the ^1H NMR spectrum of bifluorenylidene dianion,[21] 6^{2-} (Figure 1), which showed no temperature dependence within the same temperature range.

The relationship of calculated charge density as a function of torsional angles for 1^{2-} is ambiguous as the correlation coefficients of these plots remain constant for various C_α–$C_{\alpha'}$ torsional angles. Therefore, we chose to analyze the structure of the contact ion pair of 1^{2-} via stereochemical analysis of carbon–carbon coupling constants.

Stereochemical Analysis via Carbon–Carbon Coupling Constants. The observation of long-range carbon–carbon coupling constants provides some informative insight into the bonding situation in 1^{2-}. It has been observed[22a–c] that $^3J_{C_2,C_{\alpha'}}$ decreases in the order: *trans*-stilbene ($^3J_{C_2,C_{\alpha'}} = 5.0$ Hz) > *cis*-stilbene ($^3J_{C_2,C_{\alpha'}} = 3.6$ Hz) > 1 ($^3J_{C_2,C_{\alpha'}} = 1.4$ Hz) > 9,10-diphenylphenanthrene ($^3J_{C_2,C_{\alpha'}} = 1.1$ Hz), while $^2J_{C_2,C_{\alpha'}}$ remains constant: 2.2, 2.1, 2.6, 2.1 Hz, respectively, for the same series. The *decrease* in $^3J_{C_2,C_{\alpha'}}$ for this series parallels the *increase* in the phenyl ring torsional angle ($\phi_{C_2-C_{\alpha'}}$): ~0°, ~28°, ~48°, ~60°.[22a] Thus, $^3J_{C_2,C_{\alpha'}}$ follows a Karplus-like relationship similar to that observed for $^3J_{H,H}$ couplings with torsional angle. This correlation holds for a variety of carbon frameworks.[22c] However, the relationship does not hold for olefins unless they are fully *conjugated* systems, suggesting that the coupling is transmitted through the π-framework.[22a–c] Berg and co-workers have proposed an empirical relationship, eq 1.[22a]

$$^3J_{C_2,C_{\alpha'}} = 6.06(\cos \phi_{C_2-C_{\alpha'}})^2 - 1.05 \text{ (Hz)} \qquad (1)$$

The $^{13}C_2$ signal of bis-$^{13}C_\alpha$,$^{13}C_{\alpha'}$-labeled 1^{2-} (at room temperature) appears as a doublet of doublets with coupling constants of 2.64 (±0.1) and 2.53 (±0.1) Hz. The coupling constants $^3J_{C_2,C_{\alpha'}}$ and $^2J_{C_2,C_\alpha}$ in 1^{2-} then have values of 2.64 and 2.53 Hz, respectively, or vice versa. Since neither value is significantly different from $^2J_{C_2,C_\alpha}$ in 1 (2.64 Hz), $^2J_{C_2,C_\alpha}$ is not sensitive to torsional angle or bond order, in agreement with the series discussed above. However, regardless of the assignment, $^3J_{C_2,C_{\alpha'}}$ in 1^{2-} must be ~1.0 Hz larger than $^3J_{C_2,C_{\alpha'}}$ in 1 (1.4 Hz)[22a] and must have a value between *cis*-stilbene and 1. Assuming eq 1 holds for ions, it follows that the phenyl ring torsional angles of 1^{2-} lie between those of *cis*-stilbene and 1 (i.e., ~28 to ~48°). Unlike the series above, however, the torsional angle in 1^{2-} is a composite of twisting about both the C_1–C_α and C_α–$C_{\alpha'}$ bonds. If the magnitude of the $^3J_{C_2,C_{\alpha'}}$ coupling constant is indeed related to the planarity of the π-system, and hence to a composite of torsional angles, eq 1 should now be expressed as

$$^3J_{C_2,C_{\alpha'}} = 6.06 \, [\cos (\phi_{C_\alpha-C_{\alpha'}}) \cos (\phi_{C_2-C_{\alpha'}})]^2 - 1.05 \text{ (Hz)} \qquad (2)$$

Substitution of eq 2 with $^3J_{C_2,C_{\alpha'}} = 2.64$ or 2.53 Hz and $\phi_{C_2-C_{\alpha'}} = \phi_{C_1-C_\alpha} = 30°$ (the origin of this value is discussed below), yields a C_α–$C_{\alpha'}$ torsional angle, $\phi_{C_\alpha-C_{\alpha'}}$, of 25.7° or 27.4°, respectively, for 1^{2-}.

Table III. C–C Coupling Constants for 5, 5^{2-}, and 5-H_2

compd	C–C	$^1J_{CC}$[a]	model system	p[b]
5	α–α'	76.6	1	0.942
	α–1	54.6		0.171
5^{2-}	α–α'	60.6	1^{2-}	0.307
	α–1	64.5		0.551
5-H_2	α–α'	33.9		
	α–1	42.2		

[a] One bond carbon–carbon coupling constants (±2 Hz). [b] Calculated π bond order, see text for relevant geometries.

The dependence of eq 2 on olefinic torsional angle is convincingly shown by examining the pertinent vicinal C–C coupling constants of bis-$^{13}C_\alpha$,$^{13}C_{\alpha'}$-labeled **6** and 6^{2-}. X-ray crystallography has shown that $\phi_{C_\alpha-C_{\alpha'}}$ of **6** has a value of 42°[23a] and that of 6^{2-}, 2(Li^+–TMEDA), is 48°.[23a] Compound **6** shows $^3J_{C_2,C_{\alpha'}} = {}^3J_{C_6,C_{\alpha'}} = 1.90 \pm 0.2$ Hz ($^3J_{CC}$(calcd) = 2.19 Hz). In 6^{2-}, $2K^+$ $^3J_{C_2,C_{\alpha'}} = 1.65 \pm 0.12$ Hz and $^3J_{C_6,C_{\alpha'}}$ = 1.8 Hz (width at half height) with $^3J_{CC}$(calcd) = 1.66 Hz. Thus, $^3J_{CC}$ is a sensitive tool for the estimation of various torsional angles in these systems.

Molecular Orbital Calculations and Correlation of $^1J_{CC}$ with π Bond Order. The π-MO calculations used here have been described previously.[24] This program requires a reasonable input geometry in order to calculate molecular properties. In 1 the C_α–$C_{\alpha'}$ "ethylenic" torsional angle was assumed to be 8.4° (planar), while a C_α–C_1 torsional angle of 48° was used. These two values were taken from X-ray crystallographic data for 1.[25] Calculations on 1^{2-} were performed assuming no perturbation of the MO's by the potassium counterion. A 30° C_α–C_1 torsional angle was used for 1^{2-} because molecular mechanics (MM2) calculations show that at a 30° C_α–C_1 torsional angle the "inner" ortho protons (H_2) of *gem*-phenyl rings are separated by 2.270 Å, slightly less than the sum of the van der Waals radii for two hydrogens (2.4 Å).[26] This value agrees with the C_α–C_1 torsional angle calculated for the radical anion of 1 from its variable temperature absorption spectra.[27]

No C_α–$C_{\alpha'}$ carbon–carbon coupling could be observed for bis-$^{13}C_\alpha$,$^{13}C_{\alpha'}$-labeled 1 or bis-$^{13}C_\alpha$,$^{13}C_{\alpha'}$-labeled 1^{2-}. Therefore, we chose a model system that is asymmetric about the ethylenic double bond, $^{13}C_\alpha$-labeled **5**, to probe the geometry about the C_α–$C_{\alpha'}$ bond. The C_α–$C_{\alpha'}$ and C_1–C_α carbon–carbon coupling constants may then be

---

(19) Huber, W.; May, A.; Mullen, K. *Chem. Ber.* **1981**, *114*, 1318.

(20) Bank, S.; Dorr, R. *J. Org. Chem.* **1987**, *52*, 501 and references cited therein.

(21) Cox, R. H. *J. Magn. Reson.* **1970**, *3*, 223 and references cited therein.

(22) (a) Hanson, P. E.; Poulsen, O. K.; Berg, A. *Org. Magn. Reson.* **1979**, *12*, 43 and references cited therein. (b) Hanson, P. E. *Annu. Rep. NMR Spectrosc.* **1981**, *11A*, 65. (c) Marshall, J. L. *Carbon–Carbon and Carbon–Proton NMR Couplings: Applications to Organic Stereochemistry and Conformational Analysis*; Verlag Chemie: Deerfield Beach, FL, 1983; Chapter 4 and references cited therein.

(23) Walczak, M.; Stucky, G. D. *J. Organomet. Chem.* **1975**, *97*, 313. Walczak, M.; Stucky, G. D. *J. Organomet. Chem.* **1976**, *98*, 5531.

(24) Dewar, M. J. S.; Ruiz, J., private communication. Dewarpi is available from QCPE, Bloomington, IN.

(25) Hoekstra, A.; Vos, A. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *31*, 1722.

(26) Pauling, L. *The Nature of the Chemical Bond*; Cornell University: Ithaca, 1960; p 260.

(27) Suzuki, H.; Koyano, K.; Shida, T.; Akira, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2794.

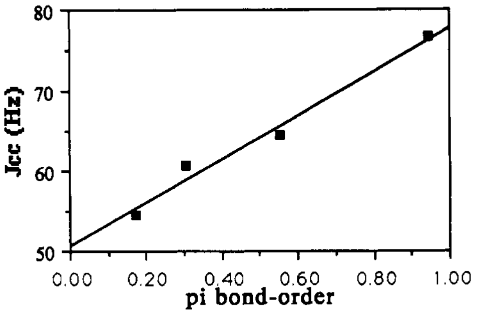

Figure 2. Plot of J_{CC} vs π bond order for 1/1 dianion. A straight line was obtained: $J_{CC} = 27.3p + 50.6$, $r = 0.9925$.

determined directly from the ^{13}C NMR spectra. The carbon–carbon coupling constants thereby obtained are shown in Table III. The C_1–C_α coupling constants of bis-$^{13}C_\alpha$,$^{13}C_{\alpha'}$-labeled 1 and its dianion appeared as multiplets (virtual coupling) and are a sum of one- and two-bond coupling constants, ${}^1J_{C_1,C_\alpha} + {}^2J_{C_1,C_{\alpha'}}$. These sums (56.6 Hz for bis-$^{13}C_\alpha$,$^{13}C_{\alpha'}$-labeled 1 and 66.7 Hz for bis-$^{13}C_\alpha$,$^{13}C_{\alpha'}$-labeled 1^{2-}) are within experimental error of the analogous coupling constants of 5 (57.2 Hz) and 5^{2-} (66.1 Hz). Thus, the *tert*-butyl groups in 5 and its dianion do not alter the carbon–carbon coupling constants observed in 1 and 1^{2-}. Inspection of Table III shows that C_α–$C_{\alpha'}$ "ethylenic" bonding, as measured by ${}^1J_{C_\alpha,C_{\alpha'}}$, in 5^{2-} is intermediate between the C_1–C_α bond in 5 and the C_1–C_α bond in 5^{2-} and is within the typical C(aromatic)–C(aromatic) coupling constant range.[22a] There is a linear relationship (Figure 2) between the magnitude of each observed coupling constant in 5 and 5^{2-} and the bond order calculated by the Dewar π semiempirical method[24] for 1 and 1^{2-}. The linearity of the plot is unaffected by a change in the C_α–$C_{\alpha'}$ torsional angle of 1^{2-} from 8.4° to 25.4°, which may imply that twisting from near planarity occurs in a wide potential well. Having corrected for the intercept of the plot in Figure 2 (50.6 Hz), we suggest that the magnitude of the C_α–$C_{\alpha'}$ coupling constant in 5^{2-} is consistent with 38% [(60.4 − 50.6)/(76.6 − 50.6)] of the double-bond character of the neutral hydrocarbon remaining intact upon dianion formation. This is in good agreement with the calculated bond-order changes that indicate that 33% (0.307/0.942) of the double-bond character is retained upon reduction. Thus, the π interaction (overlap) between the two halves bisected at the center of the "ethylenic" C_α–$C_{\alpha'}$ bond is considerable, and $\phi_{C_\alpha-C_{\alpha'}}$ is between 8.4° and 25.4°.

Rehybridization Effects. Quenching 5^{2-} with water gives the tetraarylethane, 5-H_2, a compound in which both C_α and $C_{\alpha'}$ have been rehybridized to sp^3. In 5-H_2, the C_α–$C_{\alpha'}$ coupling constant is reduced to 33.9 Hz (typical of sp^3–sp^3 coupling: $J_{CC}[CH_3\text{–}CH_3] = 34.6$ Hz),[28] while the C_1–C_α coupling constant is reduced to 42.2 Hz ($J_{CC}[Ph\text{–}CH_3] = 44.2$ Hz).[29] If rehybridization toward sp^3 upon reduction of 1 were the dominant factor influencing the C_1–C_α and C_α–$C_{\alpha'}$ coupling constants in the dianion, then *both* the C_1–C_α and C_α–$C_{\alpha'}$ coupling constants would be *lower* in 1^{2-} than in 1 by analogy with ethane and toluene. Rehybridization of the "ethylenic" carbons in the dianion is therefore not consistent with the observed coupling constants.

Table IV. C–H Coupling Constants[a] for 1 and 1^{2-}

C–H	1	1^{2-}
2,6	159.0	153.7
3,5	158.8	149.5
4	160.7	158.0

[a] ±0.5 Hz.

Table V. C(Aromatic)–C(Aromatic) Coupling Constants[a] for 1 and 1^{2-}

C–C	1	1^{2-}
1–2	58.3	55.7
2–3	56.2	57.7
3–4	55.6	54.6

[a] ±0.7 Hz.

Relatively small changes are seen in the carbon–hydrogen, ${}^1J_{CH}$, and carbon–carbon, ${}^1J_{C(arom)C(arom)}$, coupling constants (double-quantum coherence method[30]) in the phenyl rings (Tables IV and V, respectively) upon reducing 1 to 1^{2-}. ${}^1J_{CH}$ changed by an average of 3.6%, while ${}^1J_{C_\alpha,C_{\alpha'}}$ and ${}^1J_{C_1,C_\alpha}$ changed an average of 21.1%. This may be an indication that the change in coupling constants observed here are caused by enhanced orbital (OB) and spin dipolar (SD) contributions to the coupling constant relative to the contact term, since J_{CH} is primarily determined by the contact term (FC).[22b]

Coulombic, Resonance, and Steric Interactions. Electrostatic repulsion develops between the ethylenic carbons as 1 is reduced to 1^{2-}. Historically[3-10] and intuitively this interaction seems to be a driving force for the twisting about this bond in the dianion. A simple estimation of the energy difference between planar and orthogonal 1^{2-} can be obtained by calculating the repulsion integrals for each species. Utilizing STO-3G p orbitals as the model basis set (neglecting effects of the counter ions), and bond lengths and electron densities from the π-MO calculations, the coulombic repulsion energy, E_{rep}, for orthogonal 1^{2-} ($\phi_{C_\alpha-C_{\alpha'}} = 90°$, $\phi_{C_1-C_\alpha} = 30°$, $q = 1.327$, $r_{C_\alpha-C_{\alpha'}} = 1.512$ Å) is 14.87 eV and for planar 1^{2-} ($\phi_{C_\alpha-C_{\alpha'}} = 0°$, $\phi_{C_1-C_\alpha} = 30°$, $q = 1.286$, $r_{C_\alpha-C_{\alpha'}} = 1.459$ Å) $E_{rep} = 14.58$ eV: $\Delta E_{rep} = 0.29$ eV ≈ 6.7 kcal/mol. Thus near-planar 1^{2-} contains 6.7 kcal/mol *less* coulombic repulsion energy between C_α and $C_{\alpha'}$ than orthogonal 1^{2-}, primarily because less charge is localized at the C_α and $C_{\alpha'}$ positions in the near planar geometry. The electrostatic repulsion energy will also decrease as the C_1–C_α torsional angle decreases since the electron density at the ethylenic carbons diminishes with increasing interaction with the phenyl rings. The difference in resonance stabilization (as estimated by the difference in calculated heats of formation as calculated by Dewarpi) between near-planar and orthogonal 1^{2-} is ∼−8.2 kcal/mol. Therefore, based on coulombic repulsion and resonance stabilization, near-planar 1^{2-} is about 15 kcal/mol more stable than orthogonal ($\phi_{C_\alpha-C_{\alpha'}} = 90°$, $\phi_{C_1-C_\alpha} = 30°$) 1^{2-}.

One source of stabilization of orthogonal 1^{2-} is the relief of steric interactions between the vicinal phenyl rings upon rotation about the "ethylenic" bond. If this steric interaction may be approximated as twice the steric interaction in *cis*-stilbene (∼2.3 kcal/mol),[31] it would have a value of ∼5 kcal/mol. This leaves a residual 10 kcal/mol stabilization energy for near-planar 1^{2-}.

Conclusions

We suggest that there is a linear relationship between π bond order and carbon–carbon coupling constants in a series of structurally related conjugated arenes and dianions (existing as contact ion pairs), which affords the

---

(28) Graham, D. M.; Holloway, C. E. *Can. J. Chem.* **1963**, *41*, 2114.

(29) Frei, K.; Bernstein, H. J. *Chem. Phys.* **1963**, *38*, 1216.

(30) Bax, A.; Freeman, R.; Morris, G. *J. Am. Chem. Soc.* **1980**, *102*, 4849.

(31) Fischer, G.; Muszkat, K. A.; Fischer, E. J. *Chem. Soc. B* **1968**, 156.

torsional angles about respective bonds. Also, the preferred geometry of 1^{2-} is one in which the C_α–$C_{\alpha'}$ torsional angle is closer to the C_α–$C_{\alpha'}$ torsional angle of 1 than to 90°, with the estimated range of this torsional angle being 8.4–28°. These results are in agreement with several X-ray structures[23a,b] of bis(Li^+–TMEDA) arene dianions, which show that in each case the "olefinic" torsional angle is less than 10° more twisted than in the corresponding neutral species. The surprisingly low "olefinic" torsional angles are readily explained by a simple electrostatic model.[32]

Simple π-MO calculations of π bond order and electron density are correlated both with proton[21] and carbon[18,33] chemical shifts and with vicinal H–H coupling.[34] The generality of this relationship remains to be tested, and further studies in this area are ongoing in this laboratory.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on General Electric GN 500 and QE 300 spectrometers or on Varian EM390 and FT80 instruments. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

General Methods. Tetraphenylethylene (1) was purchased from Aldrich, recrystallized from chloroform/ethanol, and sublimed prior to use. **α,α-Diphenyl-α',α'-bis(4-*tert*-butylphenyl)ethylene (5)** and $^{13}C_\alpha$-labeled-**5** were prepared by $TiCl_4$/Zn dust coupling reaction of 4,4′-di-*tert*-butylbenzophenone (4) and benzophenone/carbonyl-^{13}C labeled benzophenone (Aldrich) according to a procedure by Mukiayama.[35] A large excess of 4,4′-di-*tert*-butylbenzophenone was used to insure maximum yield of the unsymmetric product. The product was purified by fractional crystallization and fractional gradient sublimation, mp 209–210 °C: ^{1}H NMR (THF-d_8) 6.92 (d, J = 8.27 Hz, 4 H), 6.95–7.05 (m, 10 H), 7.11 (d, J = 8.27 Hz, 4 H), 1.08 (s, 18 H); ^{13}C NMR ($CDCl_3$, TMS) 149.15, 144.20 (d, J = 54.64 Hz), 140.97 (d, J = 76.60 Hz), 140.72, 140.01, 131.38, 130.94, 127.47, 126.06, 124.33; mass spectra 444/445 (M^+); high-resolution mass spectrometry elemental analysis: m/z calcd 444.28170, m/z meas 444.27912, error (mamu/ppm) −2.58/5.80.

4,4′-Di-*tert*-butylbenzophenone (4) was prepared by the reaction of (4-*tert*-butylphenyl)magnesium bromide and 4-cyano-*tert*-butylbenzene (3) followed by acid hydrolysis. Recrystallization from ethanol gave white needles, mp 136–137 °C (lit.[36] mp 134.1–135.5 °C).

4-Cyano-*tert*-butylbenzene (3) was prepared by the action of CuCN on 4-bromo-*tert*-butylbenzene (2) in DMF according to the procedure of Friedman and Schecter:[37] bp 100–105 °C (0.5 Torr) [lit.[38] bp 132–133 °C (21 mm)]; IR (neat) 3010, 2920, 2880, 2240, 1640, 1520, 1480, 1420, 1385, 1290, 1125, 865 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS) δ 7.53 (s, 4 H), 1.33 (s, 9 H).

4-Bromo-*tert*-butylbenzene (2) was prepared by adding bromine to a stirred mixture of *tert*-butylbenzene and iron filings: bp 60 °C (0.5 Torr) [lit.[39] bp 228–229 °C (740 mm)]; ^{1}H NMR ($CDCl_3$, TMS) δ 7.38 (d, 2 H), 7.10 (d, 2 H), 1.23 (s, 9 H); ^{13}C NMR ($CDCl_3$, TMS) δ 149.76, 131.01, 127.01, 119.18, 34.26, 31.14.

Bifluorenylidene (6) was prepared from fluorenone in a manner identical with the procedure for the preparation of the TPE derivative discussed above and was purified by recrystallization from ethanol, mp 193–194 °C (lit.[40] mp 182–183 °C).

[*Carboxy*-^{13}*C*]biphenyl-2-carboxylic acid was prepared by cannulating the Grignard reagent of 2-bromobiphenyl onto solid $^{13}CO_2$, followed by aqueous acid workup. Crystalline product was obtained by addition of pentane to the crude oil and was used without further purification.

[*Carbonyl*-^{13}*C*]fluorenone was prepared by heating 1.0 g of [*carboxy*-^{13}*C*]biphenyl-2-carboxylic acid in 25 mL of polyphosphoric acid at 130 °C for 10 min with stirring. Cooling and aqueous workup afforded the labeled fluorenone in 78% yield, mp 83–85 °C (lit.[41] mp, 84 °C). The ^{13}C NMR spectrum was identical with that reported in the literature.[41]

[$^{13}C_\alpha$,$^{13}C_{\alpha'}$]Bifluorenylidene was prepared from [*carbonyl*-^{13}*C*]fluorenone in a manner identical with the procedure for the preparation of the TPE derivative discussed above and was purified by recrystallization from ethanol: ^{13}C NMR ($CDCl_3$, TMS) δ 141.01 (C_α), 138.28 (J = 58.7 Hz (C_1)), 141.31 (J = 2.87, 1.90 Hz (C_2)), 119.85 (J = 1.90 Hz (C_3)), 126.81 (J = 2.52 Hz (C_5)), 129.12 (C_4), 126.74 (J = 1.90 Hz (C_6)).

THF-d_8 was purchased from Aldrich and used as received.

Dianion Generation. All sample preparations were carried out under inert atmosphere and vacuum conditions. A preweighed sample was added to the apparatus consisting of a 5-mm NMR tube at the top of which was sublimed a 10-fold excess of potassium mirror attached to a vacuum stopcock. Following addition of solvent, no fewer than five freeze–pump–thaw cycles were performed, and the NMR tube was sealed off just above the metal mirror. The progress of the reaction was followed by ^{1}H NMR spectroscopy. The original peaks soon collapsed, and new, broad absorptions appeared. Within 1 week, well-resolved absorptions were recorded which were attributed to the diamagnetic dianions. All chemical shifts are relative to residual hydrogens in the THF-d_8 solvent.

Acknowledgment. This research was supported by the U.S. Department of Energy, Fundamental Interactions Branch. We are grateful to Steven Sorey and Dr. Ben Shoulders for assistance in obtaining the temperature-dependent spectra and for helpful discussions.

---

[32] Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502.

[33] Olah, G. A.; Mateescu, G. P. *J. Am. Chem. Soc.* **1970**, *92*, 1430.

[34] Jonathon, N.; Gordon, S.; Daily, B. P. *J. Chem. Phys.* **1962**, *36*, 2443.

[35] Mukiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041.

[36] Cristol, S. J.; Hayes, R. A.; Haller, H. L. *J. Am. Chem. Soc.* **1946**, *68*, 913.

[37] Friedman, L.; Shechter, H. *J. Org. Chem.* **1961**, *26*, 2522.

[38] Harvey, L.; Gleicher, G. J.; Totherow, W. P. *Tetrahedron* **1969**, *25*, 5019.

[39] Stock, L. M.; Brown, H. C. *J. Am. Chem. Soc.* **1959**, *81*, 5615.

[40] Fukunaga, K. *Synthesis* **1975**, 442.

[41] Marshall, J. L.; Faehl, L. G.; Kattner, R. *Org. Magn. Reson.* **1979**, *12*, 163.