In sum, a positive charge uniformly causes a bending away of ring hydrogens while lithium orbitals cause only a minor perturbation. Only for Cp^- itself without added positive charge do lithium basis functions provide a significant superposition effect.

Conclusion

This study shows that in monomeric CpLi the ring hydrogens are bent away from the lithium to a significant extent and that this bending is essentially a simple Coulombic effect of the cation. The results imply that CpLi can be considered as an ion pair with negligible C–Li covalent interaction. The present results do not preclude the possibility that in some cases ring hydrogens bend away from a metal with diffuse orbitals in order to increase covalent interactions, but they do require some degree of covalency in those cases where the bending is toward the metal. Since the bending in CpIn is away from the metal,[5] the argument for covalency in this compound must rely on other factors. We note that the isoelectronic CpTl has been claimed to be ionic based on NMR studies.[21,22] Finally, this study emphasizes the importance of superposition errors when molecular geometries are calculated and shows that the carbon basis set can be effectively balanced against that of lithium by including a diffuse sp shell on the former.

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Registry No. Cyclopentadienyllithium, 16733-97-4.

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Steric Effects on Rates of Dehalogenation of Anion Radicals Derived from Substituted Nitrobenzyl Halides

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Abstract: One-electron reduction of nitrobenzyl halides produces the anion radicals, which subsequently undergo dehalogenation to form nitrobenzyl radicals. The rate constants for these processes have been studied by pulse radiolysis in aqueous alcoholic solutions. α-Substitution with a methyl group increases the rate of dehalogenation by weakening the C–X bond. On the other hand, substitution with a *tert*-butyl group was found to decrease the rate of dehalogenation considerably. Since the *tert*-butyl is not expected to increase the C–X bond dissociation energy, it is concluded that its effect is a result of steric interaction, which rotates the C–X bond toward the ring plane and thus decreases the overlap between this bond and the ring π system and slows down the transfer of the electron. Other related compounds have also been examined.

Recent results on the $S_{RN}1$ reactions[1] of sterically hindered *p*-nitrobenzylic substrates have revealed that not only is the regiochemistry[2] and stereochemistry[3] of this reaction subject to steric effects (namely, branching at the position α to the benzylic carbon), but also reaction rates are greatly reduced in sterically hindered benzylic substrates.[2] In order to identify the factors that might be causing this rate reduction, the rate of dissociation of anion radicals involved in these and other, as yet unreported, $S_{RN}1$ processes were examined.

One-electron reduction of nitrobenzyl halides[4,5] has been shown to produce initially the anion radicals

$$XCH_2C_6H_4NO_2 \xrightarrow{e^-} XCH_2C_6H_4\dot{N}O_2^- \qquad (1)$$

which subsequently dehalogenate.

$$XCH_2C_6H_4\dot{N}O_2^- \rightarrow X^- + \dot{C}H_2C_6H_4NO_2 \qquad (2)$$

The rate of reaction 2 was found to be controlled to a large extent by the C–X bond dissociation energy. This was deduced from the findings that k_2 increases in the order X = F < Cl < Br < I and also increases with additional substitution on the benzylic position.[4,5] In the present work we examine the effect of substitution with a *tert*-butyl group and the possibility of a steric effect on the rate of reaction 2. We find a substantial decrease in k_2, which is ascribed to a steric effect causing rotation of the C–X bond toward the ring plane.

Method

The pulse radiolysis technique was utilized for monitoring the spectra of the anion radicals produced by reaction 1 and the benzyl radicals formed by the subsequent reaction 2 and for the determination of k_1 and k_2. The experiments were carried out in deoxygenated (or N_2O saturated) aqueous solutions containing 10–20% *i*-PrOH or *t*-BuOH. Further details on the system and on the experimental conditions are as given previously.[4,5]

Results and Discussion

***α-tert*-Butyl-*p*-nitrobenzyl Chloride (1).** Several solutions containing between 3.8×10^{-5} and 2.3×10^{-4} M of this compound at pH 7 were pulse irradiated, and the rate of reduction by the radical from *i*-PrOH was followed at 310 nm. The second-order rate constant (for X = Cl, R = *t*-Bu) was found to be $k_3 = (1.0 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$. The transient spectrum monitored after

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(1) For review, see: Kornblum, N. In "The Chemistry of Functional Groups. Supplement F"; Patai, S., Ed.; Wiley: Chichester, 1982; Part 1, Chapter 10. Norris, R. K. In "The Chemistry of Functional Groups. Supplement D"; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983; Part 1, Chapter 16.

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(5) Bays, J. P.; Blumer, S. T.; Baral-Tosh, S.; Behar, D.; Neta, P. *J. Am. Chem. Soc.* **1983**, *105*, 320.

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completion of this reaction (60–80 μs after the pulse) exhibited λ_{max} 310 nm with ϵ_{max} 1.4×10^4 M^{-1} cm^{-1}. All these values are in agreement with those observed with other nitroaromatic compounds[4,5] and point to the occurrence of reaction 3.

$$XC(R)HC_6H_4NO_2 + (CH_3)_2\dot{C}OH \rightarrow XC(R)HC_6H_4\dot{N}O_2^- + (CH_3)_2CO + H^+ \quad (3)$$

At longer times the 310-nm absorption of the anion radical decays while a 365-nm absorption is concomitantly formed, in agreement with previous observations,[4,5] indicating the occurrence of reaction 4.

$$XC(R)HC_6H_4\dot{N}O_2^- \rightarrow X^- + \dot{C}(R)HC_6H_4NO_2 \quad (4)$$

The resultant α-*tert*-butyl-*p*-nitrobenzyl radical exhibits λ_{max} 365 nm with ϵ_{max} 1.5×10^4 M^{-1} cm^{-1}. The rate of reaction 4 for this compound was determined from the decay at 310 nm and the buildup at 365 nm and found to be the same in all cases, $k_4 = (4.0 \pm 0.4) \times 10^2$ s^{-1}. This value was also independent of the concentration of the parent compound, as expected for an intramolecular process. Similar results were obtained at pH 13, except that the rate constant of the initial reduction was slightly higher because of the ionic dissociation of the reducing radical, $k_5 = (1.7 \pm 0.2) \times 10^9$ M^{-1} s^{-1}. The rate of reaction 4 at the higher pH remained unchanged within experimental error.

$$XC(R)HC_6H_4NO_2 + (CH_3)_2\dot{C}O^- \rightarrow XC(R)HC_6H_4\dot{N}O_2^- + (CH_3)_2CO \quad (5)$$

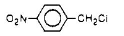
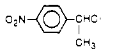
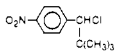
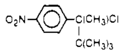
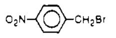
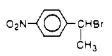
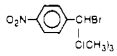
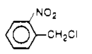
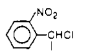
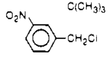
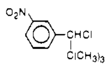
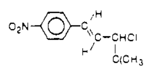
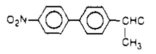
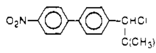
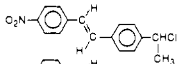
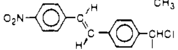
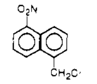
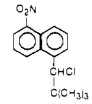
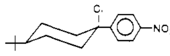
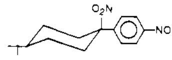
α-*tert*-Butyl-α-methyl-*p*-nitrobenzyl Chloride (2). This compound exhibited spectral and kinetic behavior similar to those of **1** (Table I). The additional α-Me substitution is expected, on one hand, to increase k_4 by lowering the C–Cl bond energy (cf. the first two compounds in the table) and, on the other hand, to decrease k_4 owing to extreme steric hindrance. These two effects apparently cancel out to give the same k_4 for **2** and **1**. An attempt to measure k_4 for the nonhindered α,α-dimethyl-*p*-nitrobenzyl chloride did not succeed because of rapid hydrolysis of this compound in water. The sterically hindered *tert*-butyl derivatives are resistant to hydrolysis.

α-*tert*-Butyl-*p*-nitrobenzyl Bromide (3). The results obtained with this compound were parallel to those obtained with the chloride. One-electron reduction by reaction 3 led to formation of the anion radical that exhibits λ_{max} 325 nm and ϵ_{max} $\sim 1.2 \times 10^4$ M^{-1} cm^{-1}. The dehalogenation reaction 4 yields the same benzyl radical with λ_{max} 365 nm and ϵ_{max} 1.5×10^4 M^{-1} cm^{-1}. However, the rate of reaction 4 was 2 orders of magnitude higher with the bromide than with the chloride; $k_4 = (6.2 \pm 1.0) \times 10^4$ s^{-1} was determined for the bromide.

α-*tert*-Butyl-*o*-nitrobenzyl Chloride (4). This compound was reduced via reaction 3 with $k_3 = (2.5 \pm 0.4) \times 10^8$ M^{-1} s^{-1}, i.e. about 4 times more slowly than the para analogue. This difference is a result of the decrease in the reduction potential of the ortho compound owing to steric interaction, which does not allow complete allignment of the $\dot{N}O_2^-$ plane with the ring plane, as discussed previously with regard to other ortho-substituted nitrobenzenes.[6] The anion radical formed from this compound exhibits a weaker absorption (λ_{max} 295 nm, ϵ_{max} 6.5×10^3 M^{-1} cm^{-1}) for the same reason, as noted before with other compounds.[5] The dehalogenation then occurs with $k_4 = (2.1 \pm 0.3) \times 10^2$ s^{-1}. The resultant α-*tert*-butyl-*o*-nitrobenzyl radical has a broad and weak absorption (λ_{max} ~370 nm, ϵ_{max} $\sim 2.5 \times 10^3$ M^{-1} cm^{-1}), similar to that observed previously for the *o*-nitrobenzyl radical.[4]

Other Compounds. α-*tert*-Butyl-*m*-nitrobenzyl chloride (**5**) was also studied under similar conditions and found to yield the anion radical which decayed very slowly, $k_4 < 10$ s^{-1}. This result is not surprising since the decay of the *m*-nitrobenzyl chloride anion radical is also very slow (Table I). These findings are rationalized[4] by the very low charge density on the carbon meta to the nitro group, as deduced from the ESR hyperfine constants of the anion radicals.

Table I. Rates of Dehalogenation and Absorption Maxima

			λ_{max}, nm	
no.	compound[a]	k_4, s^{-1}	anion radical	benzyl radical
		4×10^3	310	350
		9.7×10^4	315	360
1		4.0×10^2	310	365
2		4.0×10^2	310	370
		1.7×10^5	320	350
		3.5×10^6	320	360
3		6.2×10^4	325	365
		1.0×10^4	295	~400
		2.1×10^2	295	~370
		<5	290	~400
5		<10	~305	
6		1.1×10^3	345	410
7		<50	~350	
8		<30	~350	
9		≤20	~400	
10		≤10	~400	
		~10	390	
11		≤3	~395	
12		4.3×10^4	~300	370
13		<4	310	

[a] The numbered compounds were studied in this work, the rest are from ref 4 and 5.

An allylic derivative, **6**, was also examined and found to have $k_4 = 1.1 \times 10^3$ s^{-1}, higher than that of the benzylic analogue **1**. Clearly, the steric hindrance is less severe in this case while the allylic double bond serves as an efficient bridge for the electron transfer.

Derivatives (**7**–**11**) of biphenyl, stilbene, and naphthalene were also found to give long-lived anion radicals, whose decay under our experimental conditions was by radical–radical reactions rather than by first-order dehalogenation. Table I gives only the upper limits of k_4 for these compounds.

The anion radical of the cyclohexyl derivative **12** undergoes efficient dehalogenation with $k_4 = (4.3 \pm 0.6) \times 10^4$ s^{-1}. This value is slightly lower than that observed for the α-Me derivative (Table I, second compound).

The results obtained for compound **13** (as compared with **12**) indicate that denitration of the anion radical is a much less favorable process than dehalogenation.

Rate Constants of Dehalogenation. It is clear from Table I that, with both *p*-nitrobenzyl chloride and bromide, α-substitution with a methyl group increases the rate constant of dehalogenation by

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(6) Neta, P.; Meisel, D. *J. Phys. Chem.* **1976**, *80*, 519 and references therein.

a factor of ~20, while α-substitution with a *tert*-butyl group *decreases* the rate by a factor of ~3–10. The same decrease was also observed with the ortho analogue. Both Me and *t*-Bu cause a decrease in the C–X bond dissociation energy, which should result in an increase in k_4. However, the *t*-Bu exerts an additional effect, which predominates, i.e., a steric effect on the orientation of the C–X bond. The rate of dehalogenation is determined to a large extent by the probability that an electron, which is initially delocalized over the π system of the nitro group and the aromatic ring, will reach the C–X σ bond. The most favorable configuration for this electron transfer is that in which the C–X bond is in a plane perpendicular to the ring. The bulky *t*-Bu does not allow this configuration and tends to rotate the C–X bond toward the ring plane. As a result, the overlap necessary for electron transfer is decreased and so is the observed rate constant for the dehalogenation. The magnitude of this effect could be derived from a comparison of the results with *t*-Bu vs. Me and is found to be a factor of 240 for the chloride and 56 for the bromide. It is conceivable that the lower effect found with the bromide is a result of the larger size of this halogen, which may resist the rotation of the C–X bond to some extent or may allow greater overlap with the π system.

It should be noted that *o*-nitrobenzyl halide undergo reaction 4 slight more rapidly than the para derivatives. Since the spin density distribution leads to prediction of the opposite effect, it was concluded that the ortho anion radicals react partially direct electron transfer between the two adjacent groups through space.[4] This effect appears to be reversed in the presence of α-*t*-Bu substitution, where α-*tert*-butyl-*o*-nitrobenzyl chloride is found to have k_4 only half that of the para analogue. Apparently, the steric effect of the *t*-Bu decreases both routes of electron transfer.

In view of the present findings it is necessary to modify the interpretation of the previous results obtained with halonitrobenzenes.[7] Despite the fact that the halogen is bound directly to the ring and is thus nearer to the electron source than in the case of the benzyl compounds, the dehalogenation of halonitrobenzene anion radicals was very slow ($k_4 < 1$ s^{-1}, i.e., about 6 orders of magnitude slower than with benzyl). This difference was ascribed to the increase in C–X bond energy or the decrease in radical stabilization of phenyl vs. benzyl. However, it is clear from the present results that the difference in configuration also plays a major role. The fact that in the phenyl halides the C–X bond is in the ring plane must be a major cause for the lowered probability of electron transfer.

Experimental Section

Melting points were determined on a Kofler melting point apparatus and are uncorrected. ^{1}H NMR spectra were determined on a Varian Associates HA 100 or EM 390 or Bruker WM 400 spectrometer with Me_4Si as internal standard on 10% w/v solutions in $CDCl_3$ (unless other wise stated). IR spectra were recorded on a Perkin-Elmer 221 spectrophotometer and UV spectra on a Perkin-Elmer 402 spectrophotometer. Mass spectra were recorded on an AEI MS902 spectrometer at 70 eV. Light petroleum refers to the fraction of bp 60–65 °C. Analyses were carried out at the Australian Microanalytical Service, Melbourne. Preparative thin-layer chromatography (PLC) was performed with Merck silica gel grade $60PF_{254+366}$; column chromatography with Merck grade 60 silica gel and HPLC was performed on a Waters Associates Prep LC/System 500.

p-(1–Chloro-2,2-dimethylpropyl)nitrobenzene (**1**),[2] *p*-(1-chloro-1,2,2-trimethylpropyl)nitrobenzene (**2**),[8] *o*-(1-chloro-2,2-dimethylpropyl)nitrobenzene (**4**),[2] *m*-(1-chloro-2,2-dimethylpropyl)nitrobenzene (**5**),[9] (*E*)-3-chloro-4,4-dimethyl-1-(*p*-nitrophenyl)-1-pentene (**6**),[10] and *c*-4-*tert*-butyl-*r*-1-nitro-1-(*p*-nitrophenyl)cyclohexane (**13**)[11] were prepared by the indicated literature procedures.

***p*-(1-Bromo-2,2-dimethylpropyl)nitrobenzene (3).** 2,2-Dimethyl-1-(*p*-nitrophenyl)-1-propanol[2] (2.0 g) in pyridine (10 mL) and benzene (40 mL) was cooled to 10 °C and $SOBr_2$ (10 mL) was added dropwise over 15 min. The reaction mixture was allowed to warm to 25 °C and was stirred for a further 4 h. The reaction was worked up by extraction with ether, after dilution with excess 3M hydrochloric acid. The ether extracts were dried ($MgSO_4$) and evaporated to give a mixture of sulfur, the desired bromide **3**, and the brominated rearrangement product, *p*-(1,2-dibromo-1,2-dimethylpropyl)nitrobenzene. The sulfur was separated from the bromo compounds by PLC (8% ethyl acetate/light petroleum). The inseparable mixture of mono- and dibromo compounds was then subjected to reflux with NaI (4 g) in acetone (20 mL) for 15 min followed by treatment of the isolated mixture of bromide **3** and α,β,β-trimethyl-*p*-nitrostyrene with $KMnO_4$ (2 g) in acetone (25 mL) at 20 °C for 3 h. Workup (ether/aqueous bisulfite) gave a mixture, readily separable by PLC (7% ethyl acetate/light petroleum), of *p*-nitroacetophenone (150 mg) and the bromide **3** (780 mg): mp 65–67 °C (light petroleum); ^{1}H NMR δ 1.09 (s, 9 H, CMe_3), 4.88 (s, 1 H, ArC*H*), AA′XX′ pattern 7.50 (m, 2 H), 8.13 (m, 2 H), $J_{AX} + J_{AX'} = 8.7$ Hz, aromatic protons; IR ($CHCl_3$) 1520, 1400, 860 cm^{-1}; UV (EtOH) 278 nm (ϵ 9.9×10^3).

Anal. Calcd for $C_{11}H_{14}BrNO_2$: C, 48.55; H, 5.19; N, 5.15. Found: C, 48.53; H, 5.31; N, 4.94.

4-(1-Chloroethyl)-4′-nitrobiphenyl (7). 1-(4′-Nitro-4-biphenylyl)ethanol (696 mg, 2.9 mmol)[12] was added to thionyl chloride (680 mg, 6 mmol) at 0–5 °C. After 10 min the reaction mixture was diluted with water and extracted with ether in the usual fashion. Recrystallization of the crude product from ether/light petroleum gave 85% (637 mg) of chloride **7**: mp 107–108 °C; ^{1}H NMR δ 1.89 (d, 3 H, Me, $J = 6.9$ Hz), 5.15 (q, 1 H, CHCl, $J = 6.9$ Hz), 7.58 (m, 4 H, H2,3,5,6), AA′XX′ pattern 7.71 (m, 2 H, H2′,6′), 8.26 (m, 2 H, H3′,5′), $J_{AX} + J_{AX'} = 8.9$ Hz; IR ($CHCl_3$) 1608, 1520, 1494, 876, 851 cm^{-1}; UV (EtOH) 212 nm (ϵ 1.54×10^4), 231 (1.22×10^4, 314 (1.72×10^4); mass spectrum, *m/z* 263 (M^+ + 2, 4%), 261 (M^+, 18), 227 (22), 226 (100), 225 (63), 178 (33), 36 (20).

Anal. Calcd for $C_{14}H_{12}ClNO_2$: C, 64.25; H, 4.62; N, 5.35. Found: C, 64.31; H, 4.55; N, 5.44.

4-(1″-Chloro-2″,2″-dimethylpropyl)-4′-nitrobiphenyl (8). 1-(4′-Biphenylyl)-2,2-dimethyl-1-propanone (8.5 g)[13] in acetic acid (250 mL, 17 M) was stirred with nitric acid (150 mL, 16 M) at 60 °C for 20 h. The reaction mixture was then diluted with water (1.5 L) and extracted with ether. The ether extracts were washed with water and saturated $NaHCO_3$ solutions and dried ($MgSO_4$), and the ether was removed under reduced pressure. The mixture of mononitroketones was separated by HPLC (20% EtOAc/80% light petroleum) to give **2,2-dimethyl-1-(4″-nitro-4′-biphenylyl)-1-propanone** (A) (3.6 g, 36%): mp 106–109 °C (light petroleum); ^{1}H NMR δ 1.38 (s, 9 H, CMe_3), AA′XX′ pattern 7.65 (m, 2 H, H2′,6′), 7.84 (m, 2 H, H3′,5′), $J_{AX} + J_{AX'} = 8.7$ Hz, AA′XX′ pattern 7.75 (m, 2 H, H2″,6″), 8.32 (m, 2 H, H3″,5″), $J_{AX} + J_{AX'} = 9.0$ Hz; IR ($CHCl_3$) 1671, 1596, 1517, 1362 cm^{-1}; UV (EtOH) 304 nm (ϵ 2.12×10^4); mass spectrum, *m/z* 283 (M^+, 2%), 227 (15), 226 (100), 180 (7), 152 (13), 151 (7), 57 (15).

Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.10; H, 6.01; N, 4.81.

The above ketone (A) (5.0 g) was dissolved in a mixture of ether (30 mL) and ethanol (30 mL) and was treated with $NaBH_4$ (0.7 g) with stirring at room temperature for 30 min. Dilution with water followed by workup by ether extraction gave a product that on further purification by column chromatography (5% Et_2O/light petroleum) gave 91% (4.61 g) of **2,2-dimethyl-1-(4″-nitro-4′-biphenylyl)-1-propanol** (**B**): mp 98–100 °C (light petroleum); ^{1}H NMR δ 0.96 (s, 9 H, CMe_3), 2.04 (s, 1 H, OH), 4.45 (s, 1 H, ArC*H*), AA′*bb*′ pattern 7.41 (m, 2 H, H3′,5′), 7.58 (m, 2 H, H2′,6′), $J_{AB} + J_{AB'} = 7.3$ Hz, AA′XX′ pattern 7.71 (m, 2 H, H2″,6″), 8.27 (m, 2 H, H3″,5″), $J_{AX} + J_{AX'} = 8.9$ Hz; IR ($CHCl_3$) 3610, 1600, 1512, 1364, 842 cm^{-1}; UV (EtOH) 315 nm (ϵ 1.76×10^4); mass spectrum, *m/z* 285 (M^+, 1%), 229 (34), 228 (100), 212 (8), 182 (5), 154 (20), 153 (11), 152 (10), 57 (22).

Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71, N, 4.91. Found: C, 71.61; H, 6.58; N, 4.73.

The above alcohol (B) (1.0 g) was added to excess thionyl chloride (10 mL), and the mixture was stirred for 1 h. Workup in the usual fashion, followed by purification by column chromatograpy (5% Et_2O/light petroleum) gave 94% (1.0 g) of chloride 8: mp 74–5 °C; ^{1}H NMR δ 1.06 (s, 1 H, CMe_3), 4.77 (s, 1 H, ArC*H*Cl), AA′BB′ pattern 7.46 (m, 2 H, H3′,5′), 7.59 (m, 2 H, H2′,6′), $J_{AB} + J_{AB'} = 7.0$ Hz, AA′XX′ pattern 7.71 (m, 2 H, H2″,6″), 8.29 (m, 2 H, H3″,5″), $J_{AX} + J_{AX'} = 9.1$ Hz; IR ($CHCl_3$) 1515, 1361 cm^{-1}; UV (EtOH) 311 nm (ϵ 1.29×10^4); mass spectrum, *m/z* 305 (M^+ + 2, 1%), 303 (M^+, 3), 249 (13), 248 (8), 247 (39), 230 (6), 165 (7), 57 (100).

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Anal. Calcd for $C_{17}H_{18}ClNO_2$: C, 67.21; H, 5.97; Cl, 11.67; N, 4.61. Found: C, 67.21; H, 5.60; Cl, 11.7; N, 4.65.

(*E*)-4-(1″-Chloroethyl)-4′-nitrostilbene (9). (*E*)-4-Acetyl-4′-nitrostilbene (1.4 g, 5.3 mmol)[14] was reduced in refluxing ethanol (380 mL) with $NaBH_4$ (1.2 g). Workup after a 20-min reflux followed by purification of the product by PLC (30% EtOAc/light petroleum) gave 37% (0.53 g) **(*E*)-1-[4′-(4″-nitrostyryl)phenyl]ethanol (C)**: mp 113–114 °C (benzene/light petroleum); ^{1}H NMR δ 1.50 (d, 3 H, Me, $J = 6.7$ Hz), 2.25 (s, 1 H, OH), 4.91 (q, 1 H, ArC*H*, $J = 6.7$ Hz), AB pattern, 7.09 and 7.22 (each d, 1 H, $J = 16.6$ Hz), AA′BB′ patern 7.37 (m, 2 H, H2′,6′) 7.49 (m, 2 H, H3′,5′), $J_{AB} + J_{AB'} = 8.2$ Hz, AA′XX′ pattern 7.58 (m, 2 H, H2″,6″), 8.15 (m, 2 H, H3″,5″), $J_{AX} + J_{AX'} = 8.9$ Hz; IR ($CHCl_3$) 3600, 1600, 1518, 1350 cm^{-1}; mass spectrum, *m/z* 269 (M^+, 74%), 254 (100), 252 (50), 251 (71), 178 (56).

Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.14; H, 5.58; N, 5.07.

The alcohol C (0.28 g) was treated at 0 °C with excess thionyl chloride (4 mL) for 1 h. Workup in the usual fashion gave 90% (0.27 g) of chloride 9: mp 109–110 °C (benzene/light petroleum); ^{1}H NMR δ 1.86 (d 3 H, Me, $J = 6.9$ Hz), 5.10 (q, 1 H, ArC*H*, $J = 6.9$ Hz), AB pattern 7.10 and 7.23 (each d, 1 H, $J = 16.4$ Hz), AA′BB′ pattern 7.42 (m, 2 H, H2,6), 7.53 (m, 2 H, H3,5), $J_{AB} + J_{AB'} = 8.5$ Hz, AA′XX′ pattern 7.61 (m, 2 H, H2′,H6′), 8.20 (m, 2 H, H3′,5′), $J_{AX} + J_{AX'} = 9.0$ Hz; IR ($CHCl_3$) 1600, 1515, 1348, 850 cm^{-1}; mass spectrum, *m/z* 289 (M^+ + 2,10%), 287 (M^+, 30), 243 (28), 242 (100), 241 (47), 235 (10), 202 (17), 189 (16), 178 (18).

Anal. Calcd for $C_{16}H_{14}ClNO_2$: C, 66.78; H, 4.90; N, 4.87. Found: C, 66.81; H, 4.84; N, 4.71.

(*E*)-4-(1″-Chloro-2″,2″-dimethylpropyl)-4′-nitrostilbene (10). Benzoyl peroxide (240 mg) was added to a mixture of *N*-bromosuccinimide (27.0 g) and 4-methylpivalophenone (26.7 g) in CCl_4 (150 mL), and the mixture was refluxed for 24 h. The precipitate of succinimide was filtered off and washed with hot CCl_4, and the combined filtrate and washings were evaporated. The product was recrystallied twice from methanol at -60 °C to give 68% (26.2 g) of **4-(bromomethyl)pivalophenone (D)**: mp 32–34 °C; ^{1}H NMR δ 1.33 (s, 9 H, CMe_3), 4.50 (s, 2 H, CH_2), AA′XX′ pattern 7.40 (m, 2 H, H3,5), 7.67 (m, 2 H, H2,6), $J_{AX} + J_{AX'} = 8.6$ Hz; IR ($CHCl_3$) 1668, 1607 cm^{-1}; UV (MeOH) 251 nm (ϵ 5.6 × 10^3); mass spectrum, *m/z* 256 (M^+ + 2, 5%), 254 (5), 200 (12), 199 (100), 198 (13), 197 (100), 119 (63), 118 (35), 91 (14), 90 (23), 89 (12), 57 (36).

Anal. Calcd for $C_{12}H_{15}BrO$: C, 56.49; H, 5.93; Br, 31.31. Found: C, 56.19; H, 5.93; Br, 30.9.

A solution off triphenylphosphine (12.1 g) in benzene (100 mL) was added dropwise to a solution of the bromide D (11.8 g) in benzeen (100 mL), and the mixture was refluxed overnight. The solution was cooled, and the precipitate was filtered off and was recrystallized from chloroform/benzene to give 84% (20.0 g) of **[4-(2,2-dimethyl-1-oxopropyl)-benzyl]triphenylphosphonium bromide (E)**: white crystals, mp 186–187 °C; ^{1}H NMR δ 1.27 (s, 9 H, CMe_3), 5.60 (d, 2 H, ArC*H*$_2$P, $J_{H,P} = 15.0$ Hz), 7.2–8.0 (m, 19 H, aromatic protons); IR ($CHCl_3$) 1677, 1436, 1122, 962 cm^{-1}.

Anal. Calcd for $C_{30}H_{30}BrOP$: C, 69.63; H, 5.84; Br, 15.44; P, 5.99. Found: C, 69.20; H, 5.53; Br, 15.3; P, 5.9.

A solution of the phosphonium bromide E (40.5 g) in methanol (300 mL) was added to a solution of sodium methoxide in methanol, prepared from sodium (18.0 g) and methanol (100 mL), under nitrogen, and *p*-nitrobenzaldehyde (11.8 g) in methanol (150 mL) was added. The mixture was stirred for 3 days, and the solvent was removed. The crude product was chromatographed on alumina with 50% benzene/50% light petroleum as eluent. The product was dissolved in benzene (100 mL), a few crystals of iodine were added, and the solution was irradiated with a 500-W sunlamp at 60 °C for 1 h. The solution was washed with sodium thiosulfate solution and dried ($MgSO_4$) and the solvent removed. The product was recrystallized from benzene/light petroleum to give 76% (18.6 g) of **(*E*)-2,2-dimethyl-1-[4′-(4″-nitrostyryl)phenyl]-1-propanone (F)**: yellow crystals, mp 137–137 °C; ^{1}H NMR δ 1.36 (s, 9 H, CMe_3), 7.24 (s, 2 H, vinyl H), AA′XX′ pattern 7.56 (m, 2 H, H3′,5′), 7.77 (m, 2 H, H2′,6′), $J_{AX} + J_{AX'} = 8.3$ Hz, AA′XX′ pattern 7.65 (m, 2 H, H2″,6″), 8.22 (m, 2 H, H3″,5″), $J_{AX} + J_{AX'} = 8.6$ Hz; IR ($CHCl_3$) 1670, 1603, 1512, 1272, 1019 cm^{-1}; UV (MeOH) 265 nm (ϵ 1.10 × 10^4), 332 (1.07 × 10^4); mass spectrum *m/z* 309 (M^+, 1%), 279 (28), 278 (51), 277 (100), 252 (14), 201 (15), 149 (72), 78 (25), 77 (27), 57 (57).

Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.74; H, 6.20; N, 4.52.

The ketone F (2.0 g) was reduced in ethanol (20 mL) and ether (20 mL) with $LiBH_4$ (120 mg) for 1 h, and the reaction mixture was worked up in the usual fashion. Recrystallization of the crude reaction product from ethanol gave 94% (1.9 g) of **(*E*)-2,2-dimethyl-1-[4′-(4″-nitrostyryl)phenyl]-1-propanol (G)**: yellow crystals, mp 158–160 °C; ^{1}H NMR δ 0.94 (s, 9 H, CMe_3), 1.96 (s, 1 H, OH); 4.44 (s, 1 H, ArC*H*), AB pattern 7.12 (d, vinyl H, $J = 16.6$ Hz), 7.25 (d, vinyl H, $J = 16.6$ Hz), AA′BB′pattern 7.33 (m, 2 H, H2′,6′), 7.50 (m, 2 H, H3′,5′) $J_{AB} + J_{AB'} = 8.4$ Hz, AA′XX′ pattern 7.61 (m, 2 H, H2″,6″), 8.21 (m, 2 H, H3″,5″), $J_{AX} + J_{AX'} = 9.0$ Hz; IR ($CHCl_3$) 3630–3300, 3570, 1630, 1590 cm^{-1}; UV (MeOH) 252 nm (ϵ 1.27 × 10^4), 345 (1.19 × 10^4); mass spectrum, *m/z* 311 (M^+, 4%), 278 (23), 277 (43), 255 (23), 254 (100), 178 (14), 57 (14).

Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.34; H, 6.65; N, 4.25.

The alcohol G (1.5 g) was stirred with thionyl chloride (20 mL) at room temperature for 1 h. Workup in the usual fashion followed by recrystallization from light petroleum gave 83% (1.3 g) of chloride 10: yellow crystals, mp 86–87 °C; ^{1}H NMR δ 1.04 (s, 9 H, CMe_3), 4.73 (s, 1 H, ArC*H*Cl), AB system 7.14 (d, 1 H), 7.24 (d, 1 H), $J_{AB} = 15.4$ Hz, vinyl H, AA′BB′ pattern 7.37 (m, 2 H, H2,6), 7.50 (m, 2 H, H3,5), $J_{AB} + J_{AB'} = 8.6$ Hz, AA′XX′ pattern 7.62 (m, 2 H, H2′,6′), 8.22 (m, 2 H, H3′,5′), $J_{AX} + J_{AX'} = 8.8$ Hz; IR($CHCl_3$) 1590, 1502, 1382 cm^{-1}; UV (MeOH) 248 mn (ϵ 1.43 × 10^4), 340 (1.25 × 10^4); mass spectrum, *m/z* 331 (M^+ + 2, 3%), 329 (M^+, 9%), 263 (25), 262 (13), 57 (100).

Anal. Calcd for $C_{19}H_{20}ClNO_2$: C, 69.19; H, 6.11; N, 4.25. Found: C, 69.42; H, 6.19; N, 4.17.

1-(1′-Chloro-2′,2′-dimethylpropyl)-5-nitronaphthalene (11). Nitric acid (50 mL, *d* 1.506) was added dropwise to a solution of 1-pivalonaphthone[15] (10.0 g) in acetic acid (100 mL, 17 M) and the resulting mixture was stirred at room temperature for 4 days. The reaction mixture was worked up in the usual fashion and the mixture of mononitro ketones separated by column chromatography (2% Et_2O/light petroleum) followed by HPLC (2% EtOAc/light petroleum) to give 31% (3.7 g) of **5-nitro-1-pivalonaphthone (H)**: yellow crystals mp 81–82 °C (light petroleum); ^{1}H NMR δ 1.32 (s, 9 H, CMe_3), 7.50 (br d, H2), 7.58 (br dd, H7), 7.71 (br dd, H3), 7.90 (br d, H8), 8.20 (br d, H6), 8.53 (br d, H4), $J_{2,3} = 7.1$, $J_{3,4} = 8.9$, $J_{6,7} = 7.8$, $J_{7,8} = 8.4$ Hz (other J_{meta} and cross-ring couplings were not resolved); IR ($CHCl_3$) 1679, 1510, 1368, 975 cm^{-1}; UV (MeOH) 330 nm (ϵ 4.2 × 10^3); mass spectrum, *m/z* 257 (M^+, 7%), 201 (34), 200 (100), 184 (19), 154 (22), 126 (30), 57 (54).

Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.85; H, 5.83; N, 5.24.

Lithium borohydride (500 mg) was added to a solution of the ketone H (5.0 g) in ether (25 mL) and ethanol (25 mL), and the mixture stirred for 4 h. The reaction mixture was worked up in the usual fashion, and the product was recrystallized from light petroleum to give 98% (4.8 g) of **2,2-dimethyl-1-(5′-nitro-1′-naphthyl)-1-propanol (I)**: yellow crystals, mp 125–127 °C; ^{1}H NMR δ 0.95 (s, 9 H, CMe_3), 2.19 (s, 1 H, OH), 5.33 (s, 1 H, ArC*H*), 7.45 (dd, H3′), 7.62 (dd, H7′), 7.77 (dd, H2′), 8.01 (dd, H6′), 8.29 (ddd, H8″), 8.43 (ddd, H4′), $J_{2',3'} = \sim 7.5$, $J_{2'4'} = \sim 1.5$, $J_{3',4'} = \sim 8.5$, $J_{4',8'} = \sim 0.5$, $J_{6',7'} = \sim 7.5$, $J_{6',8'} = \sim 1$, $J_{7',8'} = \sim 8$ Hz; IR ($CHCl_3$) 3600, 1520, 1391 cm^{-1}; UV (EtOH) 245 nm (8.7 × 10^3), 350 (3.7 × 10^3); mass spectrum, *m/z* 259 (M^+, 9%), 204 (10), 203 (92), 186 (100), 156 (37), 128 (31), 127 (32), 57 (100).

Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.75; H, 6.72; N, 5.32.

The alcohol I (4.0 g) was stirred with thionyl chloride (20 mL) overnight, and the reaction mixture was then worked up in the usual fashion. Recrystallization of the product from light petroleum gave 91% (3.9 g) of the chloride **11**: mp 74–75 °C; ^{1}H NMR δ 1.08 (s, 9 H, CMe_3), 5.79 (s, 1 H, ArC*H*Cl), 7.59 (dd, H3 or H7), 7.74 (dd, H7 or H3), 8.00 (dd, H2 or H6), 8.10 (dd, H6 or H2), 8.38 (ddd, H4 or H8), 8.39 (ddd, H8 or H4), $J_{2,3} = J_{6,7} = 7.5$, $J_{2,4} = J_{6,8} = 1.0$, $J_{3,4} = J_{7,8} = 8.6$, $J_{4,8} = \sim 0.5$ Hz; IR ($CHCl_3$) 1601, 1580, 1517, 1463, 1390 cm^{-1}; UV (EtOH) 245 nm (ϵ 8.5 × 10^3), 335 (3.7 × 10^3); mass spectrum, *m/z* 279 (M^+ + 2, 1%), 277 (3), 223 (15), 221 (42), 204 (13), 139 (10), 57 (100).

Anal. Calcd for $C_{15}H_{16}ClNO_2$: C, 64.86; H, 5.81; N, 5.04. Found: C, 64.80; H, 6.01; N, 5.12.

***c*-4-*tert*-Butyl-*r*-1-Chloro-1-(*p*-nitrophenyl)cyclohexane (12).** *c*-4-*tert*-Butyl-*r*-1-chloro-1-phenylcyclohexane[16] (0.5 g) in Ac_2O (0.3 mL) was added dropwise to a solution of fuming nitric acid (0.61 g) in Ac_2O

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[16] Berlin, K. D.; Lyerla, R. O.; Gibbs, D. E. *J. Org. Chem.* **1972**, *37*, 528–530.

(0.39 g) at −5 °C. After it was stirred for 10 min at 0 to −5 °C the reaction mixture was diluted with ice–water and was then worked up by extraction with ether in the usual fashion. The crude product was purified by PLC (5% ethyl acetate/light petroleum) to give on recrystallization from light petroleum 27% (0.135 g) of chloride **12**: mp 135–136 °C; ^{1}H NMR δ 0.93 (s, 9 H, CMe$_3$), 1.1–2.5 (br m, 9 H, cyclohexyl protons), AA′XX′ pattern 7.76 (m, 2 H), 8.21 (m, 2 H), $J_{AX} + J_{AX'} =$ 9.0 Hz; IR (CHCl$_3$) 1600, 1510, 1395, 860 cm^{-1}; UV (EtOH) 203 nm (ϵ 1.05 × 10^4), 273 (9.1 × 10^3); mass spectrum, *m/z* 297 (M$^+$ + 2, 0.7%), 295 (M$^+$, 2), 260 (12), 239 (27), 57 (100), 41 (51).

Anal. Calcd for $C_{16}H_{22}ClNO_2$: C, 64.96; H, 7.50; N, 4.74. Found: C, 65.29; H, 7.45; N, 4.74.

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Registry No. 1, 62558-02-5; $\mathbf{1}^{-\cdot}$, 89727-61-7; **1** (benzyl radical), 89727-79-7; **2**, 40637-42-1; $\mathbf{2}^{-\cdot}$, 89727-62-8; **2** (benzyl radical), 89727-80-0; **3**, 89727-55-9; $\mathbf{3}^{-\cdot}$, 89727-63-9; **3** (alcohol), 61986-33-2; **4**, 62558-03-6; $\mathbf{4}^{-\cdot}$, 89727-65-1; **4** (benzyl radical), 89727-81-1; **5**, 86096-90-4; $\mathbf{5}^{-\cdot}$, 89727-66-2; **6**, 86983-99-5; $\mathbf{6}^{-\cdot}$, 89824-63-5; **6** (benzyl radical), 89727-82-2; **7**, 66360-61-0; $\mathbf{7}^{-\cdot}$, 89727-67-3; **7** (alcohol), 13629-87-3; **8**, 89727-56-0; $\mathbf{8}^{-\cdot}$, 89727-68-4; **9**, 89727-57-1; $\mathbf{9}^{-\cdot}$, 89824-64-6; **10**, 89727-58-2; $\mathbf{10}^{-\cdot}$, 89824-65-7; **11**, 89727-59-3; $\mathbf{11}^{-\cdot}$, 89727-64-0; **12**, 89727-60-6; $\mathbf{12}^{-\cdot}$, 89824-66-8; **12** (benzyl radical), 89727-69-5; **13**, 78928-45-7; $\mathbf{13}^{-\cdot}$, 89824-67-9; A, 89727-71-9; B, 89727-72-0; C, 89727-73-1; C (ketone), 41468-01-3; D, 52449-32-8; E, 89727-74-2; F, 89727-75-3; G, 89727-76-4; H, 89727-77-5; I, 89727-78-6; *p*-(1,2-dibromo-1,2-dimethylpropyl)nitrobenzene, 89727-70-8; α,β,β-trimethyl-*p*-nitrostyrene, 13399-43-4; *p*-nitroacetophenone, 100-19-6; 1-(4-biphenylyl)-2,2-dimethyl-1-propanone, 34546-86-6; 4-methylpivalophenone, 30314-44-4; *p*-nitrobenzaldehyde, 555-16-8; 1-pivalonaphthone, 25540-73-2; *c*-4-*tert*-butyl-*r*-1-chloro-1-phenylcyclohexane, 28140-28-5.

Nonvertical Triplet Excitation Transfer to *cis*- and *trans*-Stilbene[1]

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Abstract: Rate constants, k_{obsd}, for triplet excitation transfer from anthracene (E_T = 42.7 kcal/mol) and from 9,10-dichloroanthracene (E_T = 40.3 kcal/mol) to the stilbenes have been measured as a function of temperature in toluene. These are converted to rate constants, k_{en}, for the excitation transfer step within the donor/acceptor encounter cage by using empirical values for the rate constants of diffusion, k_{dif}, and the rate constants of back energy transfer, k_{-en}, from stilbene triplets to the donors. Activation parameters for k_{en} are as follows: for *trans*-stilbene $\Delta S^\ddagger = -12.3 \pm 0.1$ and -20.5 ± 0.6 eu and $\Delta H^\ddagger = 5.3 \pm 0.1$ and 5.2 ± 0.5 kcal/mol for anthracene and 9,10-dichloroanthracene, respectively; and for *cis*-stilbene $\Delta S^\ddagger = -16.3 \pm 0.1$ and -22.49 ± 0.53 eu and $\Delta H^\ddagger = 3.95 \pm 0.08$ and 4.30 ± 0.22 kcal/mol, in the same order. The striking result is that the difference in triplet energy between the two donors is reflected almost entirely in the activation entropy and not in the activation enthalpy in sharp contrast to predictions from recent classical and quantum mechanical treatments. This result, together with the observation that all $\Delta S^\ddagger$ values are smaller than expected for vertical triplet excitation transfer, strongly suggests that endothermic triplet excitation transfer is nonvertical to both stilbene isomers. It follows that twisted stilbene triplet conformations, ^{3}p*, must be lower in potential energy than either cisoid, ^{3}c*, or transoid, ^{3}t*, conformations. The same conclusions can be reached somewhat more crudely by a consideration of Arrhenius parameters obtained directly from the temperature dependence of k_{obsd}. Modified potential energy curves for twisting about the central bond of stilbene in S_0 and T_1 are proposed.

About 20 years ago it was recognized that rate constants for endothermic triplet-excitation transfer from a series of donors to *cis*-stilbene, k_{obsd}^{c}, far exceeded predicted values when the observed $T_1 \leftarrow S_0$ spectral origin was used to estimate the triplet energy[3] of *cis*-stilbene. Hammond and co-workers reasoned that the $T_1 \leftarrow S_0$ spectrum did not reveal the true energy of the relaxed, twisted *cis*-stilbene triplet state because of the severe Franck–Condon (F–C) restrictions on the transition. For this reason the twisted *cis*-stilbene triplet state was referred to as a phantom state. In general, a spectroscopic transition between states having different nuclear positions (and/or kinetic energies) is referred to as a nonvertical transition. A transition of this type can also be promoted by excitation transfer, and by analogy to the spectroscopic transitions the latter process is also called nonvertical although the mechanisms of the two processes may be considerably different. The concept of nonvertical excitation transfer has been applied generally to cases in which substantially different geometries between ground and excited states of either the acceptor or the donor lead to vanishingly small F–C terms that prevent direct observation of the 0–0 band of the vibronic progression.[4]

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[1] (a) Supported by National Science Foundation Grants CHE 77-23582 and CHE 80-26701. (b) A preliminary report on part of this work has appeared: Saltiel, J.; Charlton, J. L.; Mueller, W. B. *J. Am. Chem. Soc.* **1979**, *101*, 1347.

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[3] (a) Hammond, G. S.; Saltiel, J. *J. Am. Chem. Soc.* **1963**, *85*, 2516. (b) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *Ibid.* **1964**, *86*, 3197. (c) Herkstroeter, W. G.; Hammond, G. S. *Ibid.* **1966**, *88*, 4769.

[4] Analogy for the concept of nonvertical transitions can be found in the spectroscopic literature. For example, in discussing the spectrum of acetylene which involves "F–C forbidden transitions" from a linear ground state to a trans-bent excited state,[5] Ingold and King state that "the change in shape is so drastic that the transitions are far from being 'vertical' transitions in the Franck sense", ref 5a, p 2741.