Photochemical Activation of Distal Functional Groups in Polyfunctional Molecules. Photochemistry and Photophysics of the *syn*-7- and *anti*-7-Chlorobenzonorbornenes[1]

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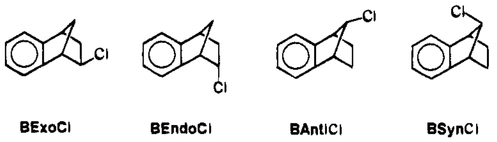
Abstract: The spectroscopic (electronic absorption, fluorescence, and electron transmission (ET)) and photochemical properties of *anti*-7-chlorobenzonorbornene (BAntiCl) and *syn*-7-chlorobenzonorbornene (BSynCl) are reported. These are complemented by ab initio MO calculations. The BSynCl isomer, the LUMO of which contains relatively little C−Cl σ^* character, is relatively unreactive upon photolysis (254 nm) in methanol (Φ_{dis}(BSynCl) = 0.0014). The LUMO of BAntiCl is calculated to contain a significant amount of C−Cl σ^* character, consistent with the much greater reactivity (Φ_{dis}(BAntiCl) = 0.23) of this isomer. The ET spectra reveal that the π^* levels of these compounds and of their *exo*-2- and *endo*-2-chlorobenzonorbornene isomers (BExoCl and BEndoCl, respectively) are appreciably stabilized relative to that of benzonorbornene (BNB). A natural bond orbital (NBO) analysis shows that much of this stabilization derives from inductive effects, with sizable through-space (TS) (0.07 and 0.10 eV) and through-bond (TB) (0.03 and 0.06 eV) coupling between the π^* and C−Cl σ^* orbitals for BAntiCl and BExoCl, respectively.

Introduction

The activation of a carbon−chlorine bond toward photochemical cleavage, when the bond is distal to a chromophoric functionality, has been the subject of interest in our program for some time. Two classes of compounds have been studied, chloronorbornenes and analogues thereof[2] and chlorobenzobicyclics.[3] Both classes of molecules show very large stereoelectronic effects on their singlet-state derived photolytic cleavage of the C−Cl bond. An example is the *ca.* 30-fold increased reactivity of *exo*-2-chlorobenzonorbornene (BExoCl) relative to its *endo* isomer (BEndoCl)[3d] (Chart 1). We have extensively studied the chloronorbornenyl series, with theory, spectroscopy, and photochemistry, and shown that the activation of the C−Cl bond in, e.g., *exo*-6-chloro-2-(trimethylsiloxy)-norbornene (ExoCl) can be understood in terms of large calculated through-space (TS) and through-bond (TB) couplings[4] between the localized π^* and C−Cl σ^* orbitals.[2,5] This large orbital mixing, in turn, leads to large mixing between the π, π^* and n, σ^* excited singlet states. Two different explanations for the activation of the homobenzylic C−Cl bond in the benzonorbornyl series have been published. One involves the transformation of an initially generated π, π^* state into a σ, σ^* state,[3d] and the other invokes intramolecular electron transfer to form a radical−ion pair,[6] more recently described in terms of formation of a π, σ^* excited state.[7] The former mechanism is identical to that which we believe is responsible for the enhanced photochemical activity of ExoCl, except that we consider the n, σ^* excited state, localized on the C−Cl bond, more likely to be involved than the corresponding σ, σ^* excited state.

Chart 1



An interesting feature of the π^*/σ^* orbital mixing phenomenon is that the pseudosymmetry of the 7-chloronorbornenes virtually eliminates interaction between the two functionalities and results in very low reactivity for both the *syn* and *anti* isomers.[2] However, in the corresponding 7-chlorobenzonorbornenes the degenerate LUMO of the benzene moiety is split into a′ and a″ components. Mixing between this a′ orbital and the C−Cl σ^* orbital is symmetry allowed. We have therefore prepared the title compounds and studied their photophysics and photochemistry. Computational studies and electron transmission (ET)[8,9] spectroscopy have also been employed to help rationalize our data.

Results

Syntheses. BAntiCl and BSynCl were synthesized via modifications of published procedures[10] (cf. Scheme 1).

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[1] Organic Photochemistry. 107. Part 106: Agyin, J. K.; Morrison, H.; Siemiarczuk, A. *J. Am. Chem. Soc.*, in press.

[2] Nash, J. J.; Carlson, D. V.; Kasper, A. M.; Love, D. E.; Jordan, K. D.; Morrison, H. *J. Am. Chem. Soc.* **1993**, *115*, 8969 and references therein.

[3] (a) Morrison, H. *Rev. Chem. Intermed.* **1987**, *8*, 125. (b) Morrison, H.; Muthuramu, K.; Severance, D. *J. Org. Chem.* **1986**, *51*, 4681. (c) Morrison, H.; Muthuramu, K.; Pandey, G.; Severance, D.; Bigot, B. *J. Org. Chem.* **1986**, *51*, 3358. (d) Morrison, H.; Miller, A.; Bigot, B. *J. Am. Chem. Soc.* **1983**, *105*, 2398. (e) Morrison, H.; Miller, A. *J. Am.Chem. Soc.* **1980**, *102*, 372.

[4] (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. (d) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245.

[5] For reviews, see: Saeva, F. D. *Top. Curr. Chem.* **1990**, *156*, 59; Maslak, P. *Ibid.* **1993**, *168*, 1.

[6] Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327 and references therein.

[7] Cristol, S. J.; Aeling, E. O.; Strickler, S. J.; Ito, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 7101.

[8] Sanche, L.; Schulz, G. J. *Phys. Rev.* **1972**, *A5*, 1672.

[9] Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

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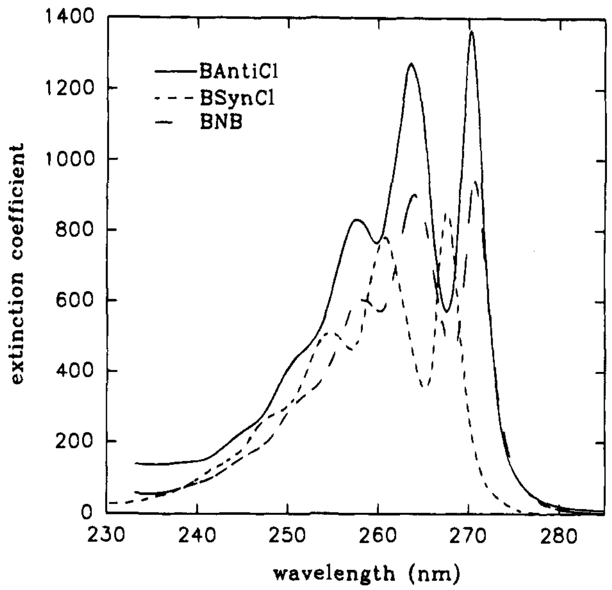
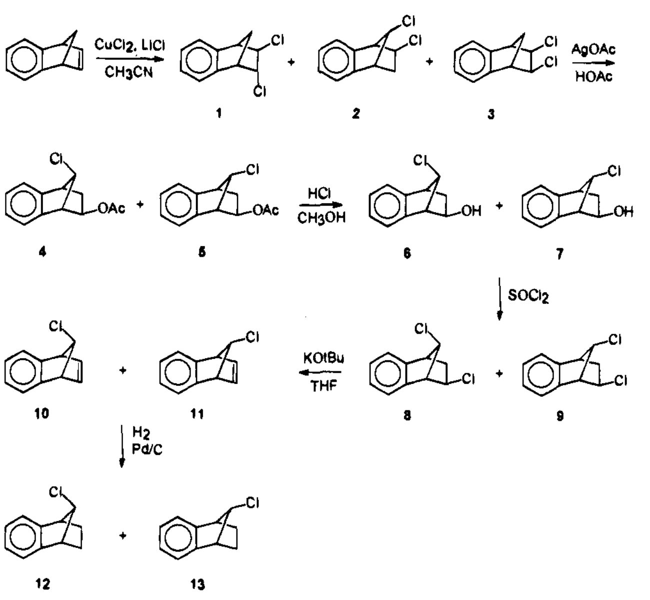


Figure 1. UV absorption spectra for BAntiCl, BSynCl, and BNB.

Scheme 1



Spectroscopy. The UV absorption spectra of both BAntiCl and BSynCl in methanol, shown in Figure 1, show slight blue shifts compared to the parent benzonorbornene (BNB). Moreover, BAntiCl (but not BSynCl) shows hyperchromicity compared to the parent BNB.

The quantum efficiencies of fluorescence (ϕ_f), fluorescence lifetimes (${}^1\tau$), and rate constants for fluorescence (k_f) for BExoCl, BEndoCl, BAntiCl, BSynCl, and BNB in methanol are presented in Table 1. The electron transmission (ET) spectra of BExoCl, BEndoCl, BAntiCl, and BSynCl are shown in Figure 2, and the vertical electron attachment energies determined from the ET spectra of these species and of BNB, *exo*-2-chloronorbornane, and 7-chloronorbornane are presented in Table 2. For each of the chlorobenzonorbornenes, there is a low-energy feature with a series of sharp peaks, starting between 0.67 and 0.90 eV and broader, higher energy features located near 2.5 eV and near 4.5 eV.

Table 1. Fluorescence Efficiencies, Rate Constants, and Singlet Lifetimes for BExoCl, BEndoCl, BAntiCl, BSynCl, and BNB in Methanol[a]

compound	ϕ_f	${}^1\tau$ (ns)	k_f (s^{-1})
BNB[b,c]	0.24	12.6	1.9×10^7
BExoCl[b]	0.007	0.5	1.4×10^7
BEndoCl[b]	0.11	10.9	1.0×10^7
BAntiCl	0.064	3.2	2.0×10^7
BSynCl	0.24	8.1	1.5×10^7

[a] Measured at room temperature with 254 nm excitation for ϕ_f and τ_f. Toluene in hexane served as the fluorescence standard ($\phi_f = 0.14$).[11] [b] Reference 3d. [c] In hexane.

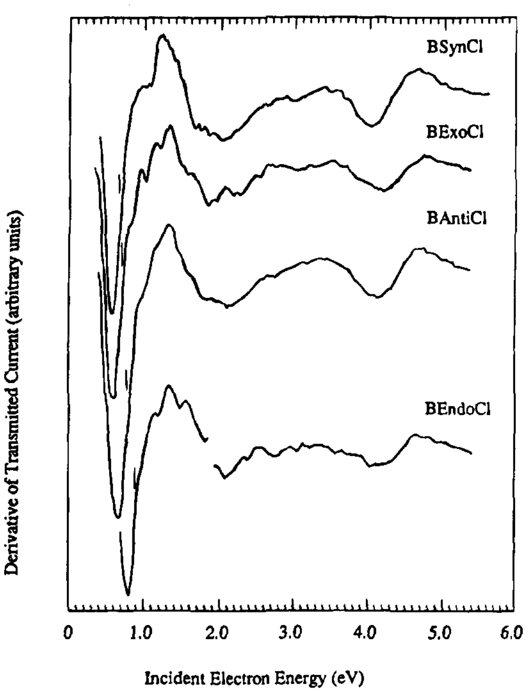


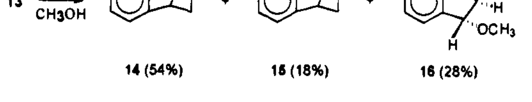
Figure 2. Electron transmission spectra for BSynCl, BExoCl, BAntiCl, and BEndoCl.

Table 2. Vertical Electron Attachment Energies (eV) for BExoCl, BEndoCl, BAntiCl, and BSynCl As Determined by Electron Transmission Spectroscopy

compound	attachment energies
BExoCl	0.71, 0.86, 1.05, 1.25, 2.3, 4.5
BEndoCl	0.90, 1.23, 1.50, 2.4, 4.4
BAntiCl	0.78, 1.02, 1.20, 2.7, 4.4
BSynCl	0.67, 1.1, 2.5, 4.3
BNB[a]	1.12, 1.4, 4.7
7-chloronorbornane[b]	2.20
exo-2-chloronorbornane[c]	2.30

[a] Reference 12. [b] Reference 2. [c] Reference 13.

Photochemistry. Irradiation at 254 nm for 5.0 min of 1.8 $\times 10^{-2}$ M argon-degassed solutions of BAntiCl (**13**) in methanol produced three principal photoproducts (**14**–**16**) in addition to HCl (cf. eq 1). The photoproducts were isolated and identified

 (1)

via comparison of their NMR and mass spectral (MS) data with those of authentic samples or model compounds (see Experimental Section). A quantum efficiency of disappearance for BAntiCl was determined using BExoCl as a secondary acti-

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(10) (a) Cristol, S. J.; Nachtigall, G. W. *J. Org. Chem.* **1967**, *32*, 3727. (b) Cristol, S. J.; Nachtigall, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 7132. (c) Cristol, S. J.; Nachtigall, G. W. *J. Org. Chem.* **1967**, *32*, 3738.

(11) Birks, J. B. *Photophysics of Aromatic Molecules*; John Wiley & Sons Ltd.: New York, 1970; p 126.

(12) Balaji, V.; Ng, L.; Jordan, K. D.; Paddon-Row, M. N.; Patney, H. K. *J. Am. Chem. Soc.* **1987**, *109*, 6957.

(13) Maxwell, B. D.; Nash, J. J.; Morrison, H. A.; Falcetta, M. L.; Jordan, K. D. *J. Am. Chem. Soc.* **1989**, *111*, 7914.

Table 3. Quantum Efficiencies and Rate Constants for C−Cl Cleavage in BExoCl, BEndoCl, BAntiCl, and BSynCl in Methanol[a]

compound	ϕ_{dis}	k_r (s^{-1})	compound	ϕ_{dis}	k_r (s^{-1})
BExoCl[b]	0.55	1.1×10^9	BAntiCl	0.23	7.2×10^7
BEndoCl[b]	0.019	1.7×10^6	BSynCl	0.0014	1.7×10^5

[a] Rate constants calculated from $\phi_{dis} = k_r{}^1\tau$. [b] Reference 3d.

nometer ($\phi_{dis} = 0.55$).[3d] The value determined was 0.23 ± 0.04. An analogous photolysis of BSynCl (**12**) produced two of the three products formed by the *anti* isomer: benzonorbornene (**14**) and *anti*-7-methoxybenzonorbornene (**15**). The quantum efficiency of disappearance for BSynCl was determined to be 0.0014 ± 0.0005. The quantum efficiencies (ϕ_{dis}) and rate constants (k_r) for the disappearance of BExoCl, BEndoCl, BAntiCl, and BSynCl are shown in Table 3; the rates assume reaction from the excited singlet state (see the Introduction and references cited therein).

Molecular Orbital Calculations. Geometry optimizations for BExoCl, BEndoCl, BAntiCl, BSynCl, and BNB were carried out using the Hartree−Fock (HF) procedure and employing the 3-21G* basis set.[14] Single-point HF calculations were then carried out (at the 3-21G* optimized geometries) using the STO-3G basis set.[15] It has previously been shown[16] that the STO-3G basis set is qualitatively adequate for describing TS and TB coupling through norbornyl rings.

The TS and TB components in BAntiCl and BSynCl were "dissected" using a natural bond orbital[17a] (NBO) analysis that we have previously employed in a series of chloronorbornenes.[2] Briefly, in the NBO calculations, the canonical HF MOs are transformed to generate localized bond and lone-pair orbitals.[17b−e] The interactions can then be dissected into their respective electric field (i.e., inductive), hyperconjugative, TS, and TB components. The details of this analysis are described in ref 2.

For BAntiCl and BSynCl, C_s symmetry is retained which allows a direct comparison of the shifts in the orbital energies for these compounds with those of the parent compound BNB. However, symmetry is absent in BExoCl and BEndoCl. Therefore, in order to estimate the contributions of TS and TB interactions in BExoCl and BEndoCl, NBO calculations were also carried out for the *exo*-2,*exo*-3- and *endo*-2,*endo*-3-dichlorobenzonorbornenes (C_s symmetry).[18] The calculated shifts (after dissection, see above) in these compounds were then divided by 2 to derive estimates for the corresponding shifts in the monochlorides.

Table 4. NBO Analysis of the Contributions (eV) of Various Interactions to the π^* and π Orbital Energies of BAntiCl and BSynCl[a,b]

		field effect		TS interaction[c]		TB interaction		net shift from HF calculations[d]	
molecule	orbital symmetry	π^*	π	π^*	π	π^*	π	π^*	π
BAntiCl	a′	0.40	0.42	0.07	0.03	0.03	0.02	0.50	0.46
	a″	0.45	0.42	0.00	0.00	0.00	0.00	0.46	0.40
BSynCl	a′	0.23	0.27	0.00	0.00	0.00	0.02	0.25	0.31
	a″	0.25	0.24	0.00	0.00	0.00	−0.01	0.31	0.23
BExoCl[e]	a′	0.34	0.39	0.10	0.02	0.06	0.00	0.42	0.37
	a″	0.41	0.37	−0.01	0.01	−0.01	0.00	0.42	0.34
BEndoCl[e]	a′	0.21	0.23	0.00	0.00	0.00	0.00	0.20	0.25
	a″	0.19	0.19	0.00	0.00	0.01	0.01	0.24	0.18

[a] Determined from HF/STO-3G//HF/3-21G* NBOs. [b] Positive shifts reflect stabilization of the π^* (or π) orbital whereas negative shifts reflect destabilization of these orbitals. [c] The TS interaction is defined to be the direct interaction between the π^* and C−Cl σ^* (or the π and C−Cl σ) NBOs. [d] Relative to the parent benzonorbornene. [e] Shifts estimated from the corresponding dichlorides (see text).

The individual contributions to the shifts in the π^* and π orbital energies of BExoCl, BEndoCl, BAntiCl, and BSynCl due to electric field effects, TS coupling, and TB coupling, estimated by means of the NBO analysis, are presented in Table 4. As we have pointed out previously,[2] the sum of the interactions (i.e., electric field effect, TS coupling, and TB coupling) does not exactly reproduce the net HF shift in all cases due to the fact that the various interactions are not perfectly additive. Moreover, by referencing the shifts in the HF calculations (last column) to the orbital energies of the parent BNB, hyperconjugative interactions are effectively "removed".

Correlation diagrams of the π^* and π energy levels for BExoCl, BEndoCl, BAntiCl, and BSynCl, where the effects of the shifts due to the various interactions are illustrated, are shown in Figures 3 and 4. As seen from these figures, there are significant TS and TB interactions in both BExoCl and BAntiCl but not in either BEndoCl or BSynCl.

Discussion

The photolytic reactivity of BAntiCl is dramatically enhanced relative to its *syn* isomer (in rate, 420-fold; see Table 3), quite reminiscent of the 650-fold rate enhancement for the *exo*/*endo* pair in the 2-chlorobenzonorbornene series. Also analogous to the 2-chloro series are the reduced quantum efficiency of fluorescence, shortened singlet lifetime (cf. Table 1), and higher quantum efficiency of disappearance (cf. Table 3) for BAntiCl compared to the *syn* isomer. Again, as with BExoCl, reduced (**14**) and extensively rearranged (**16**) products are formed which are uncharacteristic of the corresponding ground-state solvolysis chemistry.[19] In particular, the unusual formation of **16** from the *anti*-7 reactant can be rationalized as occurring via the initial generation of a "hot" carbocation at the 7 position, with subsequent migration of the *syn* 1,2 σ bond. The unique photolytic generation of such a hot species has been invoked to explain the 1,3 insertion and rearrangement chemistry seen among the benzobicyclic halide substrates.[3a,c,d] The absence of such *syn* rearrangement in the relatively unreactive BSynCl may, in part, reflect the lack of benzylic resonance in the cation resulting from 1,6 migration; such incipient stabilization undoubtedly facilitates 1,2 migration. Interestingly, *anti* rearrangement in the ground-state solvolysis of the bromo analogue, BSynBr does lead to a product analogous to **16**.[19] Finally, the substantial level of reduction in the BAntiCl photolysis is also observed for BExoCl and is a consequence of competitive homolytic cleavage of the C−Cl bond.[20]

The results of the NBO calculations (cf. Table 4) show large shifts in both the π and π^* orbital energies for BAntiCl, BSynCl, BExoCl, and BEndoCl due to the electric field caused by the

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(14) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(15) Pople, J. A.; Hehre, W. J.; Stewart, R. F. *J. Chem. Phys.* **1969**, *51*, 2657.

(16) Jordan, K. D.; Paddon-Row, M. N. *J. Phys. Chem.* **1992**, *96*, 1188.

(17) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Falcetta, M. F.; Jordan, K. D.; McMurry, J. E.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1990**, *112*, 579. (c) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710. (d) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 417. (e) Paddon-Row, M. N.: Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 425.

(18) The calculations for the dichlorides employed the same methodology as that used for the monochlorides (i.e., HF/STO-3G//HF/3-21G*).

(19) Wilt, J. W.; Chenier. P. J. *J. Org. Chem.* **1970**, *35*, 1571 and references therein.

(20) The issue of competitive homolytic and heterolytic cleavage of the C−Cl bond, versus a sequential process inolving homolysis followed by electron transfer, has been discussed in earlier papers.[3] Our view is that the former is operative because of the apparent involvement of a hot cation species which we believe is formed directly from the activated C−Cl species.[3d] For a recent example of a photolytic dissociation reaction involving a sequential mechanism, see: DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2180−2190.

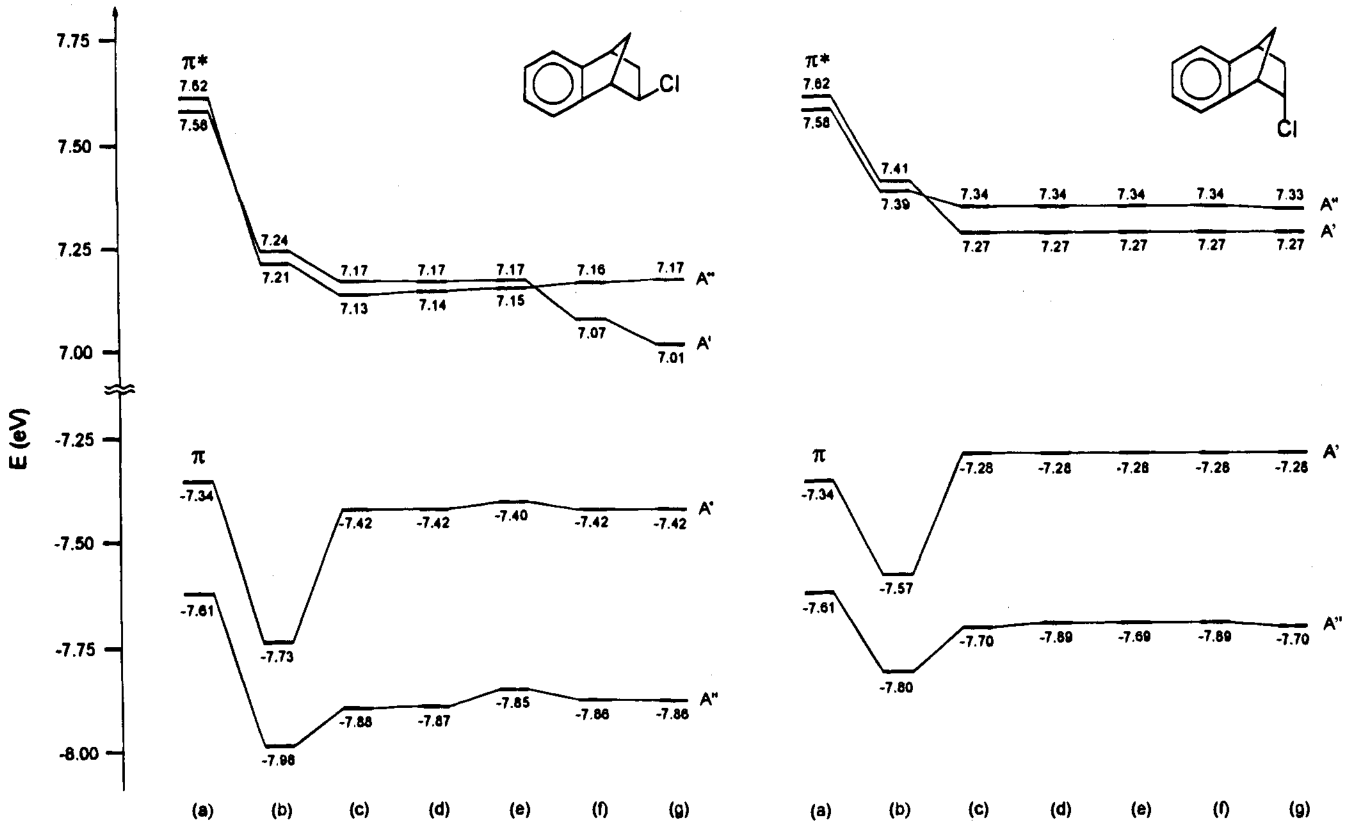

Figure 3. HF/STO-3G NBO interaction diagrams for the aryl π^* and π orbitals of BExoCl and BEndoCl. The steps in the figure are as follows: (a) the noninteracting, localized π^* and π basis NBOs, (b) inclusion of the electric field effect caused by the C−Cl group, (c) inclusion of all hyperconjugative interactions with the norbornyl bridge, (d) inclusion of TS interactions with the C−Cl σ orbital, (e) inclusion of TB interactions with the C−Cl σ orbital, (f) inclusion of TS interactions with the C−Cl σ^* orbital, (g) inclusion of TB interactions with the C−Cl σ^* orbital. The a′ and a″ symmetry labels are based on the calculations on the 2,3-dichlorobenzonorbornenes.

C−Cl group in these molecules. The calculations also show that there are essentially no TS or TB interactions in either BSynCl or BEndoCl, but that there are *substantial shifts, primarily in the a′ π^* orbitals, of BAntiCl and BExoCl due to direct TS (0.07−0.10 eV) and TB interactions (0.03−0.06 eV).* This is in contrast to the results of prior semiempirical calculations, mentioned in the Introduction, which gave no significant C−Cl σ^* component to the LUMOs of these benzobicyclic. The admixture of C−Cl σ^* character into the nominally aryl π^* orbital will lead to enhanced mixing between the $\pi \rightarrow \pi^*$ and C−Cl n $\rightarrow \sigma^*$ (or $\sigma \rightarrow \sigma^*$) singlet excited states. We believe that it is this mixing which is responsible for the bond cleavage upon photoexcitation. In this view, nucleofuge activation in the benzobicyclic substrates would be analogous to that observed for the norbornenyl substrates.

The absence of either TS or TB coupling in the a″ π^* orbitals of BAntiCl and BSynCl can be explained by considering the nodal characteristics of these orbitals (cf. Figure 5). Because the C−Cl group lies in a nodal plane of the aryl a″ π^* orbital, mixing between this orbital and the C−Cl σ^* orbital is symmetry forbidden. However, mixing of the aryl a′ π^* and C−Cl σ^* orbitals is symmetry allowed. The lack of reactivity of BSynCl and BEndoCl is due to the lack of the "*all-trans*" arrangement of σ bonds (present in the *exo* and *anti* isomers) that has been shown to be the preferred conformation for enhanced photoactivity.[21]

Prior ET spectroscopy measurements have shown that the lowest vertical attachment energy occurs at 1.12 eV for BNB and at 2.2 and 2.3 eV for 7-chloronorbornane and *exo*-2-chloronorbornane, respectively.[2,12,13] In addition to the 1.12 eV feature, the ET spectrum of BNB also displays a very weak feature near 1.4 eV. On the basis of the MO calculations, we conclude that both π^* orbitals derived from the degenerate e_{2u} π^* orbital of benzene are responsible for the 1.12 eV feature, and that the 1.4 eV feature derives from vibronic coupling. The 2.2−2.3 eV feature in the ET spectra of the chloronorbornanes is due to electron capture into the C−Cl σ^* orbital. Thus, the low-energy structure between 0.7 and 1.5 eV in the ET spectra of BExoCl, BEndoCl, BAntiCl, and BSynCl is attributed to electron capture into the two low-lying π^* orbitals and the structure near 2.5 eV to electron capture into the C−Cl σ^* orbital. The ET spectra of all four chlorobenzonorbornenes display weak features 0.15−0.4 eV above the lowest energy feature in the spectrum. As for BNB, we believe that this is vibronic in origin, and that the two lowest π^* anion states are, in fact, split by less than 0.1 eV in all of these molecules. The pronounced peak near 4.5 eV in all of the benzonorbornyl compounds is due to electron capture into the totally antibonding π^* orbital.

In all four compounds, a significant portion of the shift of the lowest π^* anion state relative to that for BNB is due to the electric field associated with the C−Cl group. However, as noted above, the NBO calculations indicate sizable TS and TB coupling in the *anti* and *exo* isomers, but no (or negligible) TS or TB coupling in the *syn* and *endo* isomers.

Conclusions

In summary, we have observed facile photochemical dissociation of the C−Cl bond in BAntiCl analogous to that observed earlier with *exo*-2 nucleofuges. A major product results from *syn* rearrangement of a hot carbocation, also in analogy with earlier observations. The theoretical analysis

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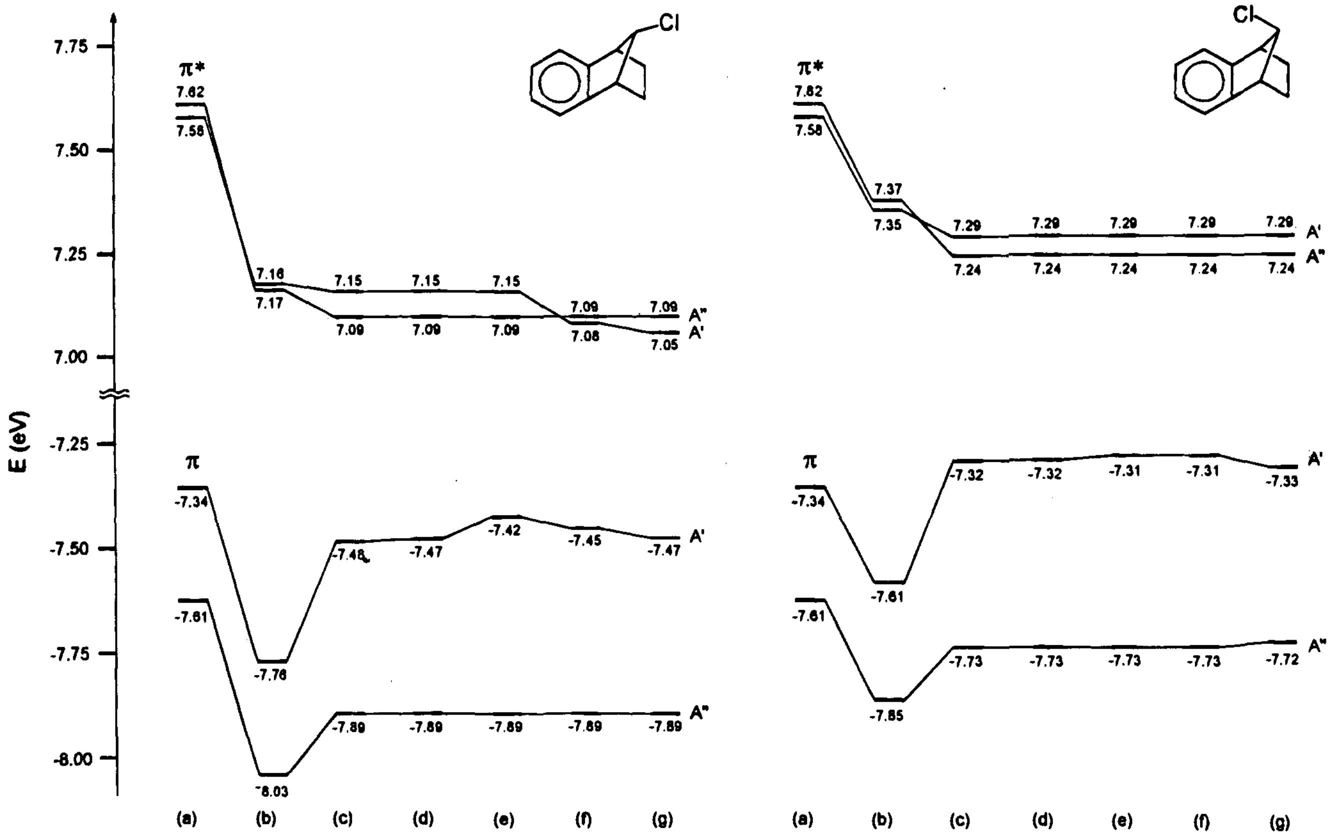
[21] For example, see Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366.



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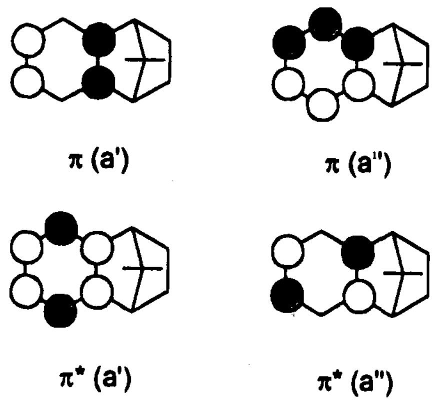

Figure 5.

shows significant TB and TS mixing between the π* and C−Cl σ* orbitals in the *anti* and *exo* compounds. This result is also consistent with a recent report[22] of the requirement for rigidity in related polycyclics containing aryl and halo functionalities in order for aryl activation to be observed.

The presence of significant π*/C−Cl σ* mixing in the LUMO of the *anti* and *exo* compounds should lead to sizable coupling between the π, π* and n, σ* excited states, which, in turn, would explain the enhanced photodestruction of these molecules. However, we do not see any chemistry which can be attributed to the intermediate existence of an aryl radical cation and therefore see no evidence to support a mechanism involving full electron transfer in these substrates.[23]

Experimental Section

Chemicals. THF (Mallinckrodt) was distilled from sodium benzophenone ketyl. Bibenzyl (Matheson) was recrystallized from hexane. The following chemicals were used as received: anhydrous copper(II) chloride, anhydrous lithium chloride, and 5% Pd on carbon from Aldrich, thionyl chloride from Baker, potassium *tert*-butoxide from Calloway Chemical, pyridine from Fisher, and acetonitrile from Mallinckrodt. Spectrograde methanol (Burdick and Jackson, distilled in glass) was used without additional purification and was stored under argon.

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Gemini 200 (200 MHz), a Varian VXR-500 (500 MHz), or a Varian VXR-600 (600 MHz) spectrometer. Chemical shifts are reported in parts per million relative to residual $CHCl_3$ (δ 7.24 and 77.0 for ^{1}H and ^{13}C, respectively). Ultraviolet spectra were recorded using a Perkin-Elmer Model Lambda 3B spectrophotometer. Low-resolution mass spectra were obtained using a Finnigan automated gas chromatograph EI/CI mass spectrometer. EI mass spectra were recorded at 70 eV. CI spectra were recorded at 70 eV with isobutane gas at a pressure of 0.30 Torr. Fluorescence spectra were recorded on a SLM SPF-500C fluorimeter. Fluorescence quantum efficiencies were measured by reference to toluene.[11] Fluorescence lifetimes were determined with a PTI Model LS-100 fluorescence lifetime spectrometer using a H_2 lamp. Fluorescence studies were conducted at room temperature with the solutions purged with argon for at least 20 min prior to use. Gas chromatography utilized a Varian Model 3300 chromatograph for preparative work and a Varian Model 3700 chromatograph coupled to a Hewlett-Packard 3390A digital integrator for quantitative studies. Columns used were (A) 10 ft × 0.25 in., 20% XF-1150 on 40/60 AW-DMCS Chromosorb W and (B) 30 m × 0.25

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[22] Seapy, D. G.; Gonzales, J.; Cameron, K. O. *J. Photochem. Photobiol., A* **1992**, *64*, 35. We note that a polycyclic product ("**8**") is reported in this paper for which the authors can provide no mechanism. In fact, the product appears to be the result of a C−H insertion reaction, analogous to that which has been observed in the photolysis of *exo*-benzobicyclo[2.2.2]octen-2-yl chloride.[4c] This chemistry has been ascribed to the hot carbocation intermediate also deemed responsible for *syn* migration.[4c]

[23] An analogous analysis of C−X cleavage in acylphenyl halides may be found in Wagner, P. J.; Sedon, J.; Waite, C; Gudmundsdottir, A. *J. Am. Chem. Soc.* **1994**, *116*, 10284−10285.

mm, DB-1 capillary (J & W), 0.25 μm film thickness. Photochemical studies employed a Rayonet Model RPR-100 reactor and quartz photolysis tubes. Deoxygenation was accomplished by bubbling argon through the solutions for at least 20 min. Bibenzyl was used as an internal standard for all quantitative work to measure the disappearance of BAntiCl and BSynCl (response factor (RF), weight(std)/weight(x) = m[area(std)/area(x)] + b; BAntiCl, $m = 0.982$, $b = 0.05$; BSynCl, $m = 1.054$, $b = -0.006$; BExoCl, $m = 0.840$, $b = 0.119$). The technique of electron transmission spectroscopy, used to determine the vertical electron attachment energies, has been described in refs 8 and 9. The attachment energies reported here are expected to be accurate to ±0.05 eV.

Molecular Orbital Calculations. The ab initio molecular orbital calculations were carried out with the Gaussian 90[24] and Gaussian 92[25] programs.

Syntheses. Benzonorbornadiene[26] and compounds **4**–**7**[10] were prepared according to literature procedures.

Preparation of 1–3.[27] A 2.0 g (14 mmol) sample of benzonorbornadiene, 4.0 g (30 mmol) of anhydrous $CuCl_2$, 1.3 g (31 mmol) of anhydrous LiCl, and 50 mL of dry CH_3CN were combined under nitrogen. The mixture was then heated to reflux overnight. The mixture was cooled, diluted with 100 mL of ether, and washed with water (3 x 50 mL). The ether extract was dried over $MgSO_4$ and concentrated to give 2.11 g of a yellow oil (9.9 mmol, 71%). GC analysis on column B at 150 °C showed three products in a 1.2:1.4:1.0 ratio. MS analysis showed that the three products were dichlorides. The mixture of dichlorides was used without additional purification.

Preparation of 8 and 9. A 0.99 g (5.1 mmol) sample of the mixture of chloro alcohols **6** and **7**, 50 mL of $SOCl_2$, and 10 drops of pyridine were combined under nitrogen. The mixture was then heated to reflux for 2 h. The $SOCl_2$ was removed via distillation at reduced pressure and the remaining mixture dissolved in hexane. The hexane extract was washed with water and dried over $MgSO_4$. The solvent was removed under vacuum to give 0.811 g (3.83 mmol) of a yellow oil. The oil was purified by flash chromatography on silica gel. GC analysis on column B at 150 °C showed two products in a 2:1 ratio. The mixture of dichlorides was used without further purification.

Preparation of 10 and 11. A 0.81 g (3.8 mmol) sample of the mixture of dichlorides **8** and **9**, 460 mg (4.1 mmol) of potassium *tert*-butoxide, and 100 mL of dry THF were combined. The mixture was then heated to reflux overnight. The mixture was cooled, poured into 200 mL of 5% HCl, and extracted with CH_2Cl_2 (2 x 100 mL). The CH_2Cl_2 extracts were combined, washed with water (2 x 50 mL), and dried over $MgSO_4$. The solvent was then removed under vacuum to give 550 mg of a yellow oil (3.13 mmol, 81%).

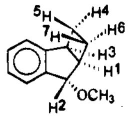
Preparation of BSynCl (12) and BAntiCl (13). A 550 mg (3.13 mmol) sample of the mixture of chloro olefins **10** and **11**, 50 mL of absolute ethanol, and 20 mg of 5% Pd on carbon were combined. The mixture was stirred vigorously under H_2 (balloon), at room temperature, overnight.

The mixture was filtered and the solvent removed under vacuum to give 497 mg of a colorless oil. GC analysis on column B at 150 °C showed two products (BAntiCl, 4.73 min; BSynCl, 4.90 min). The two products were separated by preparative GC on column A at 195 °C to give BAntiCl as a colorless oil and BSynCl as a white solid (after recrystallization from ethanol–water). BAntiCl: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15 (m, 4H), 3.80 (m, 1H), 3.30 (m, 2H), 2.20 (m, 2H), 1.23 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.3, 127.1, 121.7, 68.1, 49.5, 24.0; IR (film) 2978, 1948, 1907, 1804, 1498, 1278, 1114, 928, 854, 825, 782, 743 cm^{-1}; EI MS *m/e* (%) 178 (19), 143 (31), 142 (19), 141 (15), 129 (99), 128 (37), 115 (100), 89 (11), 63 (13); high-resolution EI MS (*m/e*) calcd 178.0549, found 178.0550. BSynCl: mp 94.5–95 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24 (m, 4H), 4.18 (m, 1H), 3.43 (m, 2H), 2.04 (m, 2H), 1.28 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 126.5, 122.3, 73.7, 50.6, 25.1; EI MS *m/e* (%) 178 (19), 143 (33), 142 (13), 129 (100), 128 (34), 115 (85); high-resolution EI MS (*m/e*) calcd 178.0549, found 178.0536.

Photolyses of BAntiCl and BSynCl in Methanol. Typically, a methanol solution of the chloride (2 mL, 0.018 M) was degassed with argon for 20 min and irradiated in a quartz tube in a Rayonet reactor with either four (BAntiCl) or sixteen (BSynCl) 254 nm lamps, which were warmed for at least 30 min. Photolysis times were on the order of 5 min for BAntiCl and 4.5 h for BSynCl. Analysis by GC on column B (150 °C) showed the following percentages for the photoproducts (determined by peak areas) for BAntiCl and BSynCl, respectively: **14**, 3.01 min (54% and 16%); **15**, 4.39 min (18% and 84%); **16**, 5.02 min (28% and 0%). BAntiCl also gave a minor, unidentified peak at 4.49 min.

Preparative photolyses were done analogously, except that higher concentrations of the chlorides were used. The photoproducts were purified by preparative GC on column A (150 °C) and identified on the basis of ^{1}H NMR, mass spectra, exact mass, and comparison to authentic samples. Compound **14** had a retention time, ^{1}H NMR spectrum, and mass spectrum identical with those for an authentic sample. Compound **15** also had a mass spectrum, ^{1}H NMR, and retention time identical with those for an authentic sample: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (m, 4H), 3.37 (s, 1H), 3.35 (s, 3H), 3.28 (m, 2H), 2.03 (m, 2H), 1.12 (m, 2H); EI MS *m/e* (%) 142 (39), 131 (12), 129 (100), 128 (32), 115 (15).

Compound **16** was identified by its ^{13}C NMR spectrum and by a comparison of its ^{1}H NMR spectrum with that of **17**.[19,28] Specifically, the resonance for H^2 in **17** appears as a broad singlet at δ 4.55 whereas the resonance for this hydrogen in the alternate *syn* isomer is a doublet at δ 4.98 with $J = 7$ Hz. The resonance for this hydrogen in **16** appears as a singlet at δ 4.54: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (m, 4H), 4.54 (s, 1H, H-2), 3.82 (dd, 1H, $J = 6.40$ and 7.34 Hz, H-3), 3.29 (s, 1H), 3.15 (quint, 1H, $J = 6.80$, 4.10, and 3.16 Hz, H-1), 2.55 (m, 1H, H-4), 2.25 (m, 1H, H-6), 1.60 (m, 2H, H-5 and H-7); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 142.2, 129.4, 126.8, 126.6, 125.2, 89.8, 55.2, 44.1, 42.2, 26.1, 22.3; EI MS *m/e* (%) 174 (9), 147 (10), 146 (100), 143 (28), 142 (64), 141 (28), 131 (77), 129 (24), 128 (34), 116 (16), 115 (57), 103 (42), 91 (12), 77 (14); high-resolution EI MS (*m/e*) calcd 174.1045, found 174.1050.



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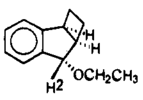

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For the determination of ϕ_{dis}, the Rayonet reactor was equipped with four 254 nm lamps for BAntiCl, sixteen 254 nm lamps for BSynCl, and a turntable. A solution of BExoCl (*ca.* 0.018 M) in methanol was used for actinometry, and duplicate matched phototubes were photolyzed for 5 min with BAntiCl and for 50 s with BSynCl. This was done several times over the course of the photolysis and the average photon flux (4.58×10^{16} and 4.69×10^{16} photons/s, respectively) was determined. Simultaneously, solutions of BSynCl (*ca.* 0.017 M) and BAntiCl (*ca.* 0.018 M) in methanol were irradiated in duplicate for 4.5 h and 5 min, respectively. All photolysis solutions were analyzed by GC using column B. Losses of starting material varied from 13% to 25%.

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[24] Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*; Gaussian, Inc.: Pittsburgh, PA, 1990.

[25] Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Gill, P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Replogle, E. S.; Gomberts, R.; Andres, J. L.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Baker, J.; Martin, R. L.; Pople, J. A. *Gaussian 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

[26] Wilt, J. W.; Gutman, G.; Ranus, W. J., Jr.; Zigman, A. R. *J. Org. Chem.* **1967**, *32*, 893.

[27] Uemura, S.; Onoe, A.; Okano, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3702.

[28] See also, Tori, K.; Aono, K; Hata, Y.; Muneyuki, R.; Tsuji, T.; Tanida, H. *Tetrahedron Lett.* **1966**, 9.