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Steric effects on the C6–C1–C2 valence angle in *exo*-6-chloronorbornenes: implications for orbital coupling

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Abstract

Ab initio calculations on norbornenyl derivatives indicate that steric interactions between bridgehead and *exo*-6-chlorine substituents result in a diminished C6–C1–C2 valence angle. Computational and spectral data are presented which indicate that this diminution leads to enhanced through-space orbital coupling. © 1999 Elsevier Science Ltd. All rights reserved.

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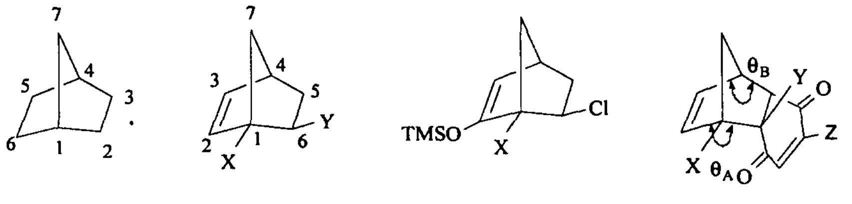
Norbornane (**1**) and norbornene (**2**) derivatives have been used extensively to investigate stereoelectronic effects on through-space (TS) and through-bond (TB) electronic interactions between substituents. We have found that the photochemical and photophysical properties of chloronorbornenyl[1] and chlorobenzonorbornenyl[2] systems are influenced by the stereoelectronic orientation of the C–Cl and π groups; C–Cl photoactivation (254 nm) and UV perturbation are maximal when the C–Cl group is in an *exo* orientation as in compound **3a**.[1a] In the chlorobenzonorbornenyl systems, these results have been attributed to enhanced coupling between the π,π^* and $n,\sigma^*_{C\text{–}Cl}$ states when the chlorine is in the *exo* orientation (Scheme 1).[2a]



1 **2** **3a** X=H **b** X=TMS **4**

Scheme 1.

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Table 1
Selected X-ray crystal data for derivatives of **4**

	Substitutent			Valence Angle	
Compound	X	Y	Z	θ_A	θ_B
4a[a]	H	H	S(O)Ar	105.77	107.03
4b[b]	Me	H	OCH_3	105.72	107.72
4c[c]	H	Br	Br	102.83	106.53
4d[b]	Me	Br	Br	100.67	104.79

[a]Ref. 6. [b]Ref 7. [c]Ref 8.

Table 2
MP2/6-31G* optimized valence angles for derivatives of compound **2**[a]

	X	Y	θ_A[b]	θ_B[c]		X	Y	θ_A	θ_B
2a	H	H	106.06	106.05	**2f**	H	Cl	104.59	106.04
2b	Me	H	105.18	105.93	**2g**	THS	Cl	102.96	105.79
2c	THS	H	104.91	105.84	**2h**	Me	Cl	102.94	105.69
2d	TMS	H	104.44	105.86	**2i**	TMS	Cl	102.13	105.50
2e	tBu	H	103.98	105.92	**2j**	tBu	Cl	100.53	105.01

[a]Geometries were optimized using Gaussian 94.[10] [b]∠C6-C1-C2. [c]∠C5-C4-C3.

The n,π* excited states of ketones are nearly pure HOMO→LUMO transitions[3] and bathochromic shifts in the UV spectra of α-halo[4] and β-chloro[1c] ketones (relative to the parent ketones) result from coupling of C-X σ* character into the LUMO. The first singlet excited state of **3a** is principally a π,π* excited state[1a,b] and we have correlated hyperchromic and bathochromic shifts in the absorption spectrum of **3a** (relative to its *endo*-chloro isomer and 2-trimethylsiloxynorbornene) with electron transmission spectroscopy (ETS) data.[1a] The ETS data show that the π* orbital of **3a** is lower in energy than the π* orbital of its *endo*-chloro isomer. The lower energy of the π* orbital in **3a** is associated with greater σ^*_{C-Cl} orbital involvement in the LUMO (π*).[1a] Since TS and TB orbital interactions are known to depend upon orbital overlap, which itself is controlled by geometric relationships, it should be possible to enhance TS and TB σ^*_{C-Cl}/π^* orbital interactions via simple geometric manipulations.

The norbornane skeleton (**1**) is susceptible to geometric deformations. A statistical survey of a set of norbornane derivative X-ray data showed that the C6–C1–C2 valence angle is "much more deformable than the other valence angles" and ranges from 95.6 to 119.4°.[5] Norbornenes are also susceptible to geometric deformations. The X-ray data in Table 1 illustrate that the valence angles (θ_A and θ_B) of **4** are influenced by substitution at the bridgehead and *exo* positions. Bridgehead substitution (**4b**) results in a relatively small decrease in θ_A relative to **4a**, while *exo* substitution (**4c**) results in a larger decrease in θ_A. The combination of bridgehead and *exo* substituents results in the greatest degree of change in both θ_A and θ_B (cf. **4d** versus **4a**).

These observations suggested that attaching a functional group at the bridgehead position of **3a** might compress the valence angle (θ_A) and bring the C–Cl and π groups within closer spatial proximity, thus potentially increasing the TS (and/or TB) interactions between the two groups. The valence angles θ_A (C6–C1–C2) and θ_B (C5–C4–C3) of compound **2** were therefore computationally investigated with varying X and Y groups; the results are shown in Table 2. Either an *exo*-chloro substituent (**2a** versus **2f**) or a bridgehead substituent (**2a** versus **2b–e**) produces decreases in the valence angles θ_A and θ_B. A combination of bridgehead and *exo* substituents produces the smallest valence angles, particularly θ_A; cf. **2g–2j**.

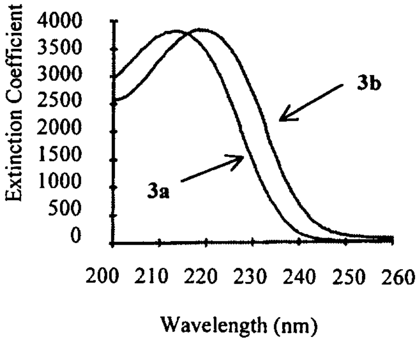

Figure 1. UV absorption spectra of **3a** and **3b** in hexane

The results in Table 2 suggest that large bridgehead and *exo* substituents cause the valence angles to compress, a trend that is consistent with the X-ray data presented in Table 1. Extrapolating the results shown in Table 2, the maximal valence angle compression for **3** should occur with a *t*Bu group at the bridgehead position. We anticipated that this might be observable by a bathochromic shift in the UV spectrum of **3**. However, it was synthetically easier to place a TMS group at the bridgehead-position (**3b**). We find that the UV absorption spectrum of **3b** indeed shows a ca. 5 nm bathochromic shift relative to **3a** ($\lambda_{max} \approx 220$ and ≈ 215 nm, respectively, cf. Fig. 1).[9]

NBO calculations[1a,11] allow one to 'dissect' orbital interactions into TS and TB components. Such calculations for **3a** and a derivative of **3b** (using THS as a substitute for TMS[12]) indicate that **3b** contains both enhanced TS σ^*_{C-Cl}/π^* (0.06 eV) and marginally enhanced TB σ^*_{C-Cl}/π^* orbital interactions relative to those of **3a**. Thus, the bathochromic shift of **3b** can be explained as resulting from primarily TS σ^*_{C-Cl}/π^* orbital coupling. Further photochemical and spectroscopic experiments designed to investigate valence angle compression–enhanced orbital coupling phenomena are in progress.[13]

Although we have focused on the potential consequences of valence angle compression–enhanced orbital coupling for the excited state, its ramifications for ground state chemistry should be equally important. The rapid solvolysis of some *exo*-5-norbornenyl compounds relative to their *endo*-5 isomers is attributed to anchimeric assistance.[14] Such anchimeric assistance should be increased by compression of the valence angle between the π and C–X groups.

Acknowledgements

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