Fluorinated Bicyclics. III. Free-Radical Chlorination of 5,5,6,6-Tetrafluoro-2-norbornene

BRUCE E. SMART

Contribution No. 1986 from the Central Research Department, Experimental Station, E. I. Du Pont de Nemours and Company, Wilmington, Delaware 19898

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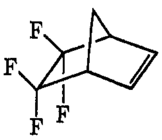
Free-radical chlorination of 5,5,6,6-tetrafluoro-2-norbornene (1) in carbon tetrachloride with a limited amount of molecular chlorine gave a mixture of cis (2a) and trans (3a) adducts in 3.2:1 ratio. Polychlorination occurred with excess chlorine to afford 2,2-dichloro-*exo*-3-chloro-5,5,6,6-tetrafluoronorbornane (4). The importance of endo 5,6-fluorine substitution in directing the stereochemistry of these reactions is discussed.

The free-radical bromination of 5,5,6,6-tetrafluoro-2-norbornene (1) was shown to proceed stereospecifically to the cis-exo dibromide **2b**.[1] Poutsma demonstrated that free-radical chlorination of norbornene itself gave a 17:19 ratio of cis (**2c**) to trans (**3c**) dichloride products.[2] In light of these results, a comparative investigation of the free-radical chlorination of **1** and norbornene was undertaken to evaluate the effect of fluorine substitution.



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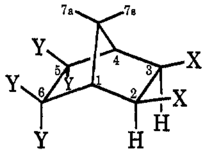
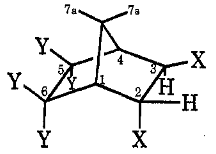


2a, X = Cl; Y = F
b, X = Br; Y = F
c, X = Cl; Y = H
d, X = Br; Y = H

Results

The fluorinated olefin **1** was inert to molecular chlorine in carbon tetrachloride solution at 25° in the dark. Upon irradiation with a 275-W sun lamp, the reaction was instantaneous. Treatment of **1** with 0.88 equiv of chlorine under these conditions afforded two products (>98%) in the ratio of 19:6 by vpc. Nmr analysis identified the cis adduct **2a** as the major product and **3a** as the minor product.

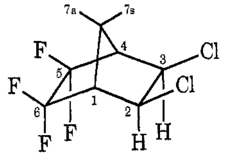


3a, X = Cl; Y = F
b, X = Br; Y = F
c, X = Cl; Y = H
d, X = Br; Y = H

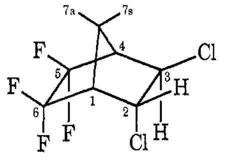
The 100-MHz spectra of **2a** and **3a** are displayed in Figures 1a and 1b. The chemical-shift and coupling-constant data are given in Tables I and II. Appropriate double-resonance experiments allowed for the assignment of long-range couplings.

TABLE I

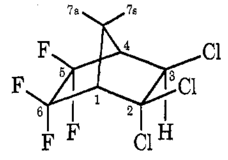
CHEMICAL SHIFTS[a] IN CARBON TETRACHLORIDE



2a



3a



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Nucleus	2a	3a	4
H_1, H_4	2.86	2.84	3.23, 2.81
H_2, H_3	4.51	4.23	. . . , 4.67
H_{7a}	1.98	2.05	2.11
H_{7s}	2.42	2.19	2.57
F_{5x}	118.9	118.7	119.9
F_{5n}	122.4	123.1	120.1
F_{6x}	118.9	110.5	108.5
F_{6n}	122.4	119.3	118.5

[a] All proton chemical shifts are in parts per million (δ) relative to internal tetramethylsilane. All fluorine chemical shifts are in parts per million (ϕ) relative to internal fluorotrichloromethane (F-11) internal standard. All values refer to the high-field side of F-11.

TABLE II

COUPLING CONSTANTS (HERTZ) IN CARBON TETRACHLORIDE

Nuclei	2a	3a	4
$H_{7s}H_{7a}$	12.5	12.5	13
H_3H_{7a}	1.9		2
$H_{7s}F_{5n}$	~5	~4	
$H_{7s}F_{6n}$	~5	3–4	5.8
$F_{5x}F_{5n}$	239	241	
$F_{6x}F_{6n}$	239	244	244

The vicinal H_2, H_3 protons in **2a** gave a sharp doublet (J = 1.9 Hz) at δ 4.51. The methylene bridge proton H_{7a} was the source of this splitting. The ^{19}F nmr spectrum of **2a** displayed a single AB quartet (J = 239 Hz), which suggests a symmetrical structure with the exo fluorines equivalent and the endo fluorines equivalent. Structure **2a** is consistent with these data. *exo-cis*-2,3-Dibromo-5,5,6,6-tetrafluoronorbornane[1] (**2b**) and **2a** gave very similar spectra.

The nmr structure proof for **3a** was less straightforward. Both H_2 and H_3 appeared as a multiplet at δ 4.23. This multiplet was not further resolved at 220 MHz. The ^{19}F nmr spectrum displayed a *pair* of AB quartets for the geminal fluorines, which suggests structure **3a**. The presence of an AB quartet of multiplets for H_{7a}, H_{7s} with long-range $F_{5n}H_{7s}$ and

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(1) B. E. Smart, *J. Org. Chem.*, **38**, 2027 (1973).
(2) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965).

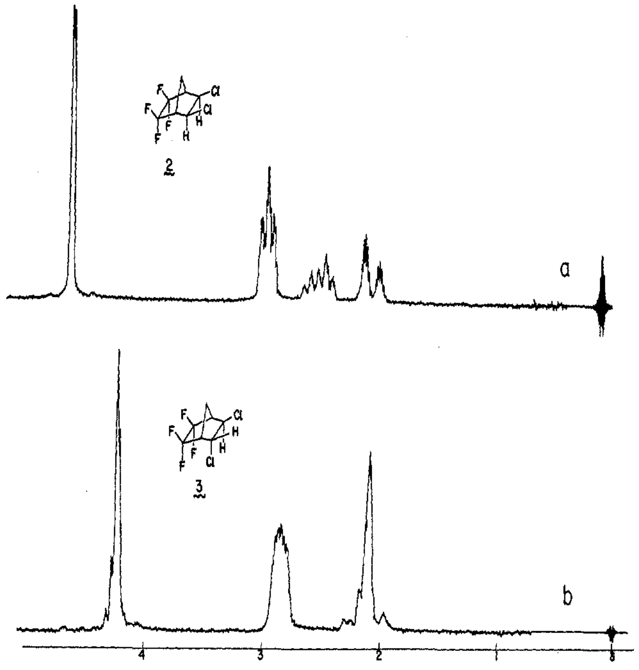


Figure 1.—Nmr (100 MHz) spectrum: a, *exo-cis*-2,3-dichloro-5,5,6,6-tetrafluoronorbornane (**2a**); b, *endo*-2-chloro-*exo*-3-chloro-5,5,6,6-tetrafluoronorbornane (**3a**).

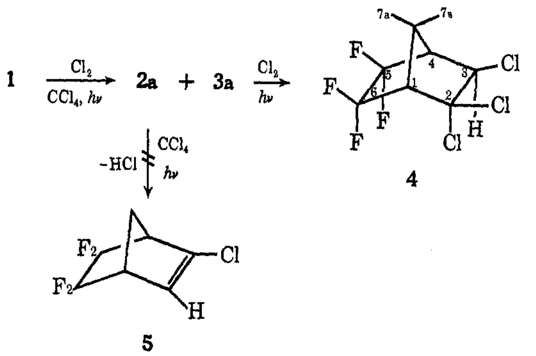
$F_{6n}H_{7s}$ couplings rules out an unprecedented rearranged 2,7-dichloride structure.

The equivalence of H_2 and H_3 in **3a** can be explained as follows. Comparison of the chemical shifts of the protons adjacent to chlorine in the cis (**2c**) and trans (**3c**) adducts with **2a** establishes the following shielding effects. Protons H_{2n} and H_{3n} in **2c** appear at δ 3.94[3] and fluorine substitution (**2a**) deshields H_n by 0.57 ppm (δ 4.51–3.94). With the assumption that 5,6-fluorine substitution does not appreciably affect the chemical shift of H_{2x},[4] H_{2x} in **3a** should appear at *ca.* δ 4.23, which is the value for H_{2x} in **3c**.[5] However, H_{3n} (δ 3.67)[5] in **3c** will be deshielded by the calculated value of 0.57 ppm upon fluorine substitution at C_5. Therefore, H_{3n} in **3a** should appear at *ca.* δ 3.67 + 0.57 = 4.24, which is equivalent to the chemical shift of H_{2x}. Both H_{2x} and H_{2n} are indeed observed at δ 4.23 in **3c**, which is in excellent agreement with these calculations.

The radical chlorination of **1** with 2.5 equiv of chlorine gave a quantitative yield of two products. The major product (97%) was assigned structure **4** and the minor product (3%) was *exo*-2-trichloromethyl-*exo*-3-chloro-5,5,6,6-tetrafluoronorbornane.[4]

The 100-MHz nmr spectrum of **4** displayed a narrow multiplet ($W_{1/2}$ = 4 cps) for a single proton adjacent to chlorine at δ 4.67 (Table I). Decoupling experiments established that this proton was not coupled to H_4 with the expected value of ∼4 Hz for an exo proton. Coupling of *ca.* 2 Hz with the methylene bridge proton H_{7a} was present. The source of additional fine couplings (<0.5 Hz) was not established.

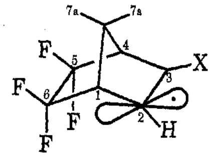
Solutions of pure **2a** and pure **3a** were irradiated under the reaction conditions in the absence of chlorine. No isomerization occurred and elimination of HCl was not observed. Polychlorination therefore proceeds by



direct attack on **2a** and **3a**, without the intermediacy of olefin **5**.

Discussion

The preference for cis-exo-chlorination of 5,5,6,6-tetrafluoro-2-norbornene relative to norbornene is consistent with the previously observed stereochemical control by fluorine substitution.[1,4] Potential severe coulombic repulsion between the propagating chlorine molecule and an endo fluorine in intermediate **6a** results in a preference for exo attack.



6a, X = Cl
b, X = Br

The difference in stereospecificity of bromination and chlorination of **1** is noteworthy. While bromination is exclusively cis-exo,[1] a significant amount of trans product (24%) is formed on chlorination. In comparison of attack of halogen on **6a** and **6b**, it is reasonable to predict a preference for exo attack by chlorine on **6a** relative to exo bromine attack on **6b**, since Br–Br interaction is more severe than Cl–Cl interaction. The relative amount of radical cis chlorination *vs.* bromination of norbornene itself supports this contention.[1,2] However, the opposite is predicted for endo attack, where F–Br nonbonded repulsion is more severe than F–Cl repulsion assuming similar pathways of attack on **6**. The observed preference for cis attack on bromination relative to chlorination suggests that the difference between F–Br and Br–Br nonbonded interactions is greater than between F–Cl and Cl–Cl interactions.

A semiquantitative approach to this problem can be given as follows. As a first approximation, assume that the transition state for halogenation occurs very late along the reaction coordinate with considerable bond making present. The geometry of the transition state will then be very similar to that of the product. The appropriate transition-state geometries can be expressed in cartesian coordinates with the further assumption that no changes in bond angles or bond lengths from norbornane itself exist (Appendix A). The van der Waals interactions of the propagating halogen species and the norbornane substituents in the transition state can then be approximated by the halogen atom substituent interactions in the product.

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[3] Value taken from D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33**, 38 (1968).

[4] B. E. Smart, *J. Org. Chem.*, **38**, 2035 (1973).

[5] Values taken from ref 2.

For example, exo attack of bromine on **6b** will result in the nonbonded interactions Br_{2x}–Br_{3x}, H_{7s}–Br_{2x}, F_{6n}–H_{2n}, and H_{2n}–H_{3n}. The magnitude of these individual interactions can be calculated from the Hill equation[6] and the sum of such interactions will represent the approximate net coulombic interaction in a late transition state. The results are given in Tables III and IV.

TABLE III
VAN DER WAALS INTERACTIONS

Nonbonded interaction	Distance, Å	E_V, kcal/mol
H_7Cl_{2x}	3.018	−0.13
H_7H_{2x}	2.772	−0.03
H_7Br_{2x}	3.007	−0.15
$H_{2x}Cl_{3x}$	2.618	0.08
$H_{2x}Br_{3x}$	2.707	0.20
$H_{6n}Cl_{2n}$	2.291	1.64
$H_{6n}Br_{2n}$	2.329	3.01
$F_{6n}Cl_{2n}$	2.198	8.01
$F_{6n}Br_{2n}$	2.219	14.09
$Br_{2x}Br_{3x}$	2.872	10.11
$Cl_{2x}Cl_{3x}$	2.732	4.91
$H_{2n}H_{3n}$	2.304	−0.05
$H_{2n}H_{6n}$	2.246	−0.04
$H_{2n}F_{6n}$	2.557	−0.08

TABLE IV
SUMMATION OF VAN DER WAALS INTERACTIONS

Product	Nonbonded interactions	ΣE_V, kcal/mol
2a	$H_{2n}F_{6n}$, $H_{2n}H_{3n}$, $H_{7s}Cl_{2x}$, $Cl_{2x}Cl_{3x}$	4.65
2b	$H_{2n}F_{6n}$, $H_{2n}H_{3n}$, $H_{7s}Br_{2x}$, $Br_{2x}Br_{3x}$	9.84
2c	$H_{6n}H_{2n}$, $H_{2n}H_{3n}$, $H_{7s}Cl_{2x}$, $Cl_{2x}Cl_{3x}$	4.70
2d	$H_{6n}H_{2n}$, $H_{2n}H_{3n}$, $H_{7s}Br_{2x}$, $Br_{2x}Br_{3x}$	9.88
3a	$H_{7s}H_{2x}$, $H_{2x}Cl_{3x}$, $H_{3n}Cl_{2n}$, $F_{6n}Cl_{2n}$	8.14
3b	$H_{7s}H_{2x}$, $H_{2x}Br_{3x}$, $H_{3n}Br_{2n}$, $F_{6n}Br_{2n}$	14.46
3c	$H_{7s}H_{2x}$, $H_{2x}Cl_{3x}$, $H_{3n}Cl_{2n}$, $H_{6n}Cl_{2n}$	1.77
3d	$H_{7s}H_{2x}$, $H_{2x}Br_{3x}$, $H_{3n}Br_{2n}$, $H_{6n}Br_{2n}$	3.38

These calculations clearly reflect the preference for trans product formation from norbornene and cis product from **1**. A net coulombic repulsion of 9.88 kcal is observed for the formation of **2d**, while 3.38-kcal repulsion is observed for **3d**. In the fluorinated case, exo attack by bromine results in 9.84-kcal repulsion whereas endo attack nets 14.46-kcal repulsion. The preference for cis-exo product formation in bromination of **1** is correctly predicted. The same trend is evident for chlorination. It should be emphasized that the absolute values obtained from the Hill equation are subject to error owing to uncertainty in the parameters employed, although the differences in net coulombic interactions are meaningful.

A second approximation which includes dipole–dipole interactions also can be made. If the assumption of a late transition state is retained, the net dipole–dipole interaction can be calculated as a sum of the individual C–X (X = Br, Cl, F) dipole interactions. The dipoles were taken as vectors along the C–X bond axis in the case of X = Br, Cl and the same norbornane skeletal geometry described above was employed. The C–F dipole was taken as a vector sum of the C–F_{6n} and C–F_{6x} dipoles with a net charge separation of 0.4 eu.[7] Since the cartesian coordinates of each atom are already assigned, the net dipole–dipole interaction can most easily be calculated as the sum of the coulombic charge–charge interactions assuming 0.19- and 0.22-eu charge separation for the C–Br and C–Cl bonds, respectively.[7,8] Table V summarizes the results.

TABLE V
DIPOLE–DIPOLE INTERACTIONS

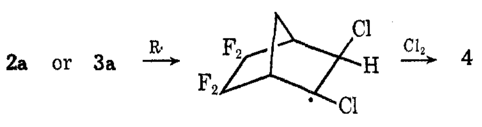
Product	ΣE_D, kcal/mol
2a	4.12
3a	1.21
2b	3.91
3b	1.70
2c	0.48
3c	−1.40
2d	0.55
3d	−0.81

For the chlorination and bromination of **1** the dipole–dipole and van der Waals interaction sum ($E_V + E_D$) gives 8.77 kcal for **2a**, 9.35 kcal for **3a**, 13.75 kcal for **2b**, and 16.16 kcal for **3b**. If entropy effects are neglected, these values predict 94% cis-exo-bromination ($\Delta\Delta G^{\ddagger}$ = 2.41 kcal) and 73% cis-exo-chlorination ($\Delta\Delta G^{\ddagger}$ = 0.58 kcal). These values are in excellent agreement with the experimental results.

An approximation of the coulombic interactions involved in an early transition state model was also attempted (Appendix B). Attack of halogen at C_2 perpendicular to the C_1–C_2–C_3 plane with C–X distances twice that of the normal carbon–halogen bond distance was examined. This model indicates that only interaction with the 6-endo substituent is important, and exclusively cis-exo halogenation is predicted for both **1** and norbornene. The magnitude of the endo-fluorine halogen interaction (65–98 kcal) is also suspect. This model is at variance with the experimental results and was not further examined.

Polychlorination of **1** involves the initial formation of **2a** and **3a** followed by subsequent radical chlorination.

Hydrogen abstraction from **2a** necessarily affords intermediate radical **7**. Preferential exo hydrogen abstraction from **3a** is anticipated since the endo 3-hydrogen is shielded from attack by both endo 5-fluorine and endo 2-chlorine substituents. Hence, both **2a** and **3a** give the same intermediate radical **7** and subsequent chlorine attack (either exo or endo) affords **4**.



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Experimental Section

All melting and boiling points are uncorrected. The gas chromatography work was performed as before[1] with a 6 ft × 0.375 in. 20% QF-1 fluorosilicone on 60/80 Chromosorb P column. The ^1H and ^{19}F nmr spectra and decoupling experiments were run as before.[1]

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(6) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

(7) W. A. Sheppard, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, pp 19–21, and references cited therein.

(8) Calculation of dipole–dipole interactions by the procedure of Lehn and Ourisson gave comparable results; see J.-M. Lehn and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1113 (1963).

***exo-cis*-2,3-Dichloro-5,5,6,6-tetrafluoronorbornane (2a) and *endo*-2-Chloro-*exo*-3-chloro-5,5,6,6-tetrafluoronorbornane (3a).**—A solution of 8.3 g (0.05 mol) of **1** in 75 ml of carbon tetrachloride in a nitrogen atmosphere was treated with 3.1 g (0.044 mol) of chlorine and irradiated with a 275-W sun lamp at *ca.* 6 in. from the reaction vessel. Uptake was rapid, as evidenced by the disappearance of the yellow-green color. Irradiation was discontinued 5 min after complete addition of chlorine and the carbon tetrachloride solvent was removed by flash distillation. Nmr of the crude product indicated a mixture of 26% unreacted **1** and 74% (**2a** + **3a**). Vpc analysis (150°) gave **1** (25%) at 1.65 min, **2a** (57%) at 6.6 min, and **3a** (18%) at 8.8 min. Preparative vpc with collection in a −78° trap gave 1.91 g of **1**, 6.52 g of pure **2a**, mp 52–53°, and 1.54 g of **3a**, mp 25.5–26°.

Anal. Calcd for $C_7H_6Cl_2F_4$: C, 35.47; H, 2.55; Cl, 29.92. Found (**2a**): C, 35.48; H, 2.67; Cl, 29.78. Found (**3a**): C, 35.20; H, 2.73; Cl, 29.72.

Samples of pure **2a** and **3a** in carbon tetrachloride (0.1 g/4 ml) were individually irradiated for 30 min with a 275-W sun lamp. The isomers remained unchanged by vpc and nmr.

2,2-Dichloro-*exo*-3-chloro-5,5,6,6-tetrafluoronorbornene (4).—A solution of 5.8 g (0.035 mol) of **1** in 75 ml of carbon tetrachloride was treated with 4.2 g (0.087 mol) of chlorine as above. Irradiation was continued for 30 min after chlorine addition, and removal of excess chlorine and solvent afforded a mixture of 97% **4** and 3% *exo*-2-trichloromethyl-*exo*-3-chloro-5,5,6,6-tetrafluoronorbornane by vpc (175°). The latter compound was identified by coinjection and identical retention time with an authentic sample.[4] Fractionation afforded 7.1 g of pure **4** as a ceraceous, bad-smelling solid, bp 72–73° (0.7 mm), mp 56–59°. A pot residue (1.2 g) of 83% **4** and 17% carbon tetrachloride adduct along with three unidentified minor products (<10%) remained.

Anal. Calcd for $C_7H_3Cl_3F_4$: C, 30.97; H, 1.86; Cl, 39.18. Found: C, 30.97; H, 1.76; Cl, 39.00.

A similar reaction with 1.0 g (6 mmol) of **1** in 50 ml of methylene dichloride with 6.2 g (87 mmol) of chlorine afforded 100% **4**.

Registry No.—**1**, 2822-56-2; **2a**, 39037-49-5; **2b**, 39037-29-1; **2c**, 14627-75-9; **2d**, 2843-50-7; **3a**, 39037-53-1; **3b**, 39037-54-2; **3c**, 2843-43-8; **3d**, 2843-42-7; **4**, 39037-57-5.

Acknowledgments.—Dr. Derick Ovenall and Mr. Lou Walther are acknowledged for their assistance in obtaining the nmr spectra. Dr. H. E. Simmons is also acknowledged for his many helpful suggestions.

Appendix A. Geometries and van der Waals Interactions

The cartesian coordinates (Table VI) were derived from the published values for norbornane.[9] The following bond distances were employed: C–H, 1.12 Å; C–Cl, 1.78 Å; C–Br, 1.93 Å; C–F, 1.38 Å. The heteroatom coordinates were determined by extending the C–H vector of length 1.12 Å to a new C–X vector with the appropriate C–X bond length. Otherwise the reported C, H coordinates for norbornane were used.

TABLE VI

H_{2x}	(0, −0.902, 1.699)	Cl_{2x}	(1.384, 1.063, −2.577)
H_{2n}	(1.152, −2.184, −0.472)	Cl_{2n}	(1.384, −1.063, −2.577)
H_{6n}	(1.152, −1.123, −1.931)	Cl_{6n}	(1.384, −2.780, −0.216)
H_{7s}	(1.152, 1.123, −1.931)	F_{6x}	(1.248, 2.430, −0.366)
Br_{2x}	(1.436, −2.912, −0.159)	F_{6n}	(1.248, 1.098, −2.197)
Br_{2n}	(1.436, −1.050, −2.720)		

The nonbonded coulombic atom–atom interactions were calculated from the Hill equation (eq 1). The published nonbonded constants were employed.[6,10]

$$E_V/\epsilon = -2.26\alpha^{-6} + 8.28\cdot10^5 e^{-\alpha/0.0736} \qquad (1)$$

Appendix B. Early Transition-State Geometries and van der Waals Interactions

The C, H, and heteroatoms at C_6 and C_{3x} were defined by the above coordinates and the published coordinates for norbornane. Atom C_2 (0.776, −1.220, −0.886) was transposed to (0, 0, 0) and the cross products C_1–C_2 × C_2–C_3 and C_2–C_3 × C_1–C_2 defined the axis of exo and endo attack at C_2 perpendicular to the C_1–C_2–C_3 plane. The C_2–X distance was chosen and the coordinates for the heteroatom X (Table VII) were determined by the ratio of the cross product length and the C_2–X length. Transposition of this new vector C_2–X to C_2 (0.776, −1.220, −0.886) finally assigned the coordinates of X in this model. The appropriate nonbonded interactions (Table VIII) were calculated from the Hill equation.

TABLE VII

		Coordinates	
C–X	Å	Br_{2x}	Br_{2n}
X = Br	3.86	(0.776, −3.444, 2.238)	(0.776, 1.004, −4.010)
X = Br	5.76	(0.776, −4.556, 3.800)	(0.776, −2.116, −5.572)
		Cl_{2x}	Cl_{2n}
X = Cl	3.56	(0.776, −3.272, 1.996)	(0.776, 0.832, −3.768)
X = Cl	5.34	(0.776, −4.298, 3.437)	(0.776, 1.858, −5.209)

TABLE VIII

Interaction	Distance, Å[a]	E_V,[a] kcal/mol
H_7Br_{2x}	2.712, 4.286	0.18, −0.05
$H_{6n}Br_{2n}$	2.116, 3.793	8.83, −0.09
$H_{3n}Br_{2n}$	3.545, 5.241	−0.12, −0.01
H_7Cl_{2x}	2.511, 3.885	0.34, −0.05
$H_{6n}Cl_{2n}$	1.897, 3.380	13.84, −0.10
$H_{3n}Cl_{2n}$	3.304, 4.832	−0.12, −0.02
$F_{6n}Cl_{2n}$	1.662, 3.142	97.75, −0.22
$F_{6n}Br_{2n}$	1.876, 3.557	65.13, −0.23
$Cl_{2x}Cl_{3x}$	3.130, 4.507	0.29, −0.17
$Br_{2x}Br_{3x}$	3.305, 4.824	0.95, −0.25

[a] First entry corresponds to C–X transition state of length twice normal C–X bond distance and the second entry to a length three times the normal bond length.

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[9] J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968).

[10] E. Eliel, *et al.*, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 449–453.