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# Energetics of Bond Shift in Monohalogen-Substituted Cyclooctatetraenes

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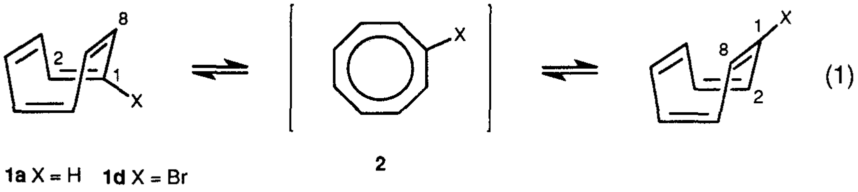
***Abstract.*** The free energies of activation for bond shift in fluoro-, chloro-, bromo- and iodocyclooctatetraene in THF-$d_8$ were determined by $^{13}$C NMR spectroscopy to be 12.7, 15.0, 15.4 and 16.1 kcal/mol, respectively, at 298 K. Analysis of HF/6-31G*-optimized geometries and natural atomic charges for the ground state and ring inversion transition state for cyclooctatetraene (COT) and its monofluoro and monochloro derivatives indicates that the bond shift transition state for COT-F is stabilized (relative to COT) by electrostatic interactions between the fluorine and the flanking hydrogens, whereas those of the larger halogens are destabilized by steric interactions with the vicinal CH groups. © 1997 Elsevier Science Ltd.

The bond shift process in cyclooctatetraene (COT) (eq. 1) is of considerable theoretical interest owing to the strained geometry and 4n π-electron ("antiaromatic") cyclic array of its transition state.[1] Other than alkyl and aryl groups,[1-4] only a limited number of substituents have been investigated in nonannulated cyclooctatetraenes.[5-10]



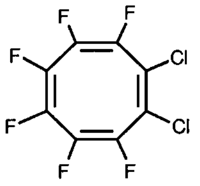
(1)

1a X = H 1d X = Br
1b X = F 1e X = I
1c X = Cl

2

Unsubstituted cyclooctatetraene (**1a**) has been shown to have a free energy of activation for bond shift ($\Delta G^{\neq}_{b.s.}$) of 12.7 kcal/mol at 248 K.[11] All substituents studied to date except fluoro cause $\Delta G^{\neq}_{b.s.}$ to increase by at least several kcal/mol. Two estimates are available for the latter substituent, one of *ca.* 12 kcal/mol at 240

K from $^{19}F$ NMR spectroscopy[6] and one of *ca.* 13 kcal/mol at 248 K from $^{1}H$ and $^{19}F$ NMR spectroscopy.[7] In addition, compounds **3** and **4** have been shown to have $\Delta G^{\neq}_{b.s.}$ values of 32.7 and 33.4 kcal/mol, respectively, at 438 K, whereas heptafluorocyclooctatetraene has a value of 24.6 kcal/mol at 389 K.[10]



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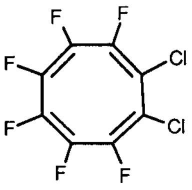


**4**

The present study was motivated by a desire to clarify the factors behind the apparent rate-enhancing effect of the monofluoro substituent as well as to determine the effect of the larger halogens. Both attractive and repulsive steric effects are shown to play a significant role in the bond shift reaction in this series of compounds.

## EXPERIMENTAL SECTION

### *Materials.*

Monohalocyclooctatetraenes **1b**,[7] **1c**,[12] **1d**,[12] and **1e**[12] were synthesized by literature procedures. $^{13}C$ NMR spectra (75 MHz) are as follows; **1b** (THF-$d_8$, -81 °C, $J_{^{13}C^{19}F}$ in parentheses): δ 156.8 (245.4 Hz), *137.8* (11.0 Hz), 134.1 (3.3 Hz), *132.4* (1.6 Hz), *132.0* (1.6 Hz), *128.6* (9.2 Hz), *125.8* (35.2 Hz), *109.9* (28.3 Hz); **1c** (THF-$d_8$, -80 °C): δ *134.2*, 133.4, *132.9*, *131.8*, 131.6, *131.6*, *130.6*, *130.2*; **1d** (THF-$d_8$, 25 °C): δ *134.1*, *133.8*, 133.5, *133.3*, *132.8*, *131.6*, *131.5*, 122.1; **1e** (THF-$d_8$, 25 °C): δ *142.4*, *138.1*, 133.6, *132.8*, *132.7*, *131.4*, *131.3*, 98.1. The italicized values are those for $C_2$ and $C_8$, $C_3$ and $C_7$, and $C_4$ and $C_6$, which undergo pairwise exchange during bond shift. The signal for $C_5$ appears between 133.4 and 134.1 in every case whereas the remaining signal is that of $C_1$.

### *NMR Measurements.*

NMR samples were prepared by dissolving *ca.* 0.2 mmol of monohalocyclooctatetraene and 10 μL of cyclohexane in 0.75 mL of THF-$d_8$. The sample was degassed with six freeze-pump-thaw cycles and sealed under vacuum. Temperatures above and below 313 K were calibrated with an ethylene glycol[13] and a methanol[14] chemical shift thermometer, respectively, and are reliable to ± 1 °C.

The rate constants for bond shift ($k_{b.s.}$) in **1b-e** were determined by measurement of the line widths of the $^{13}C$ signals that undergo pairwise exchange ($C_2$ and $C_8$, $C_3$ and $C_7$, $C_4$ and $C_6$). Measurements were made over ranges of 20-40 °C after the onset of line broadening at temperatures just above the low temperature regime.[15] Rate constants, averaged for at least two samples and extrapolated to 298 K by plotting ln ($k/T$) vs. $1/T$, are reported in Table I along with the corresponding values of $\Delta G^{\neq}_{b.s.}$ calculated from the Eyring equation.

Table I. Kinetic Data for Bond Shift in Monohalocyclooctatetraenes

| Cmpd | Substituent | Temp. Range (K)[a] | $k_{b.s.}$ (298 K)[b] | $\Delta G^{\neq}_{b.s.}$ (298 K)[c] |
|---|---|---|---|---|
| **1a** | H | 248-443 | | 13.3[d] |
| **1b** | F | 222.5-241.5 | 2860 | 12.7 |
| **1c** | Cl | 281-251 | 62.8 | 15.0 |
| **1d** | Br | 258-300 | 30.3 | 15.4 |
| **1e** | I | 281-311 | 10.2 | 16.1 |

[a] ± 1 °C.

[b] ± 20%.

[c] ± 0.1 kcal/mol.

[d] Calcd from data in Ref. 9. The rate constant was corrected to the unidirectional value, as discussed in Ref. 10.

### *Computational Methods.*

Ab initio optimized geometries were calculated with the GAUSSIAN 92 series of programs[16] at the Hartree Fock (HF) level of theory with 3-21G[17] and 6-31G*[18] basis sets. Optimized ground states and ring inversion transition states were shown to have zero and one imaginary frequency, respectively, by analytical frequency analysis. Atomic charges were calculated by a natural population analysis (NPA).[19]

## RESULTS AND DISCUSSION

We have determined $\Delta G^{\neq}_{b.s.}$ for **1b** at 241.5 K to be 12.8 kcal/mol, a value that lies between the two previous estimates of 12 kcal/mol (240 K)[6] and 13 kcal/mol (248 K).[7] Thus studies based on $^1$H, $^{19}$F and $^{13}$C lineshapes all agree for this compound and confirm that fluorine is the only nonannulated substituent so far known not to increase the barrier to bond shift in COT.

As seen in Table I, $\Delta G^{\neq}_{b.s.}$(298 K) increases monotonically on going down the halogen group of the periodic table. Interestingly, the $\Delta G^{\neq}_{b.s.}$ (298 K) values for **1b-e** correlate with Pauling ($\chi_P$) or Mulliken ($\chi_M$)

electronegativity values ($r^2 = 0.991$ and 0.987, respectively) (Figure 1). $\chi_P$ values are based on an analysis of

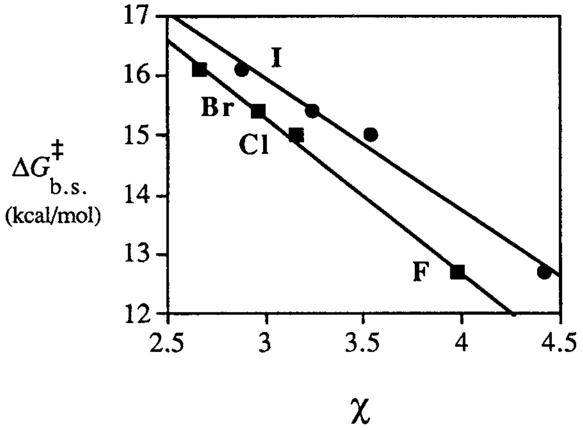


Figure 1. Plots of the free energy of activation for bond shift at 298 K vs. the Pauling (□) and Mulliken (●) electronegativities.

bond energies whereas $\chi_M$ is based on the average value of the ionization energy and the electron affinity of the atom.[20] Interestingly, the $^{13}C$ chemical shift of the halogen-substituted carbon ($C_1$) also gives a good correlation ($r^2 = 0.91$) when plotted against $\Delta G^{\neq}_{b.s.}$.

In order to determine the factor or factors responsible for the correlation in Figure 1, we have performed geometry optimizations on the ground states of **1a-e** and **1a-c** at the HF/3-21G and HF/6-31G*, respectively, levels of theory. Because of the large contribution of configuration interaction requiring a multiconfiguration wave function, we did not calculate the bond shift transition states (**2a-e**). However, since the CASSCF/6-31G//HF/6-31G* correlation energy for the planar transition state for ring inversion in COT is only 3% greater than that for the $D_{2d}$ ground state, compared with a 131% increase calculated for the $D_{8h}$ bond shift transition state,[21] we concluded that the corresponding ring inversion transition states (**5a-e**), can be reliably compared with ground states **1a-e** at the HF level of theory. It is also expected that **5a-e** will serve as good steric models for the structurally similar bond shift transition states, with the caveat that, as previously discussed for methyl-substituted cyclooctatetraenes,[22] steric effects might be slightly larger in the former species. Accordingly, HF/3-21G and HF/6-31G* optimizations of **5a-e** and **5a-c**, respectively, were also performed. Total and relative ground and transition state energies for **1a-e** are listed in Table II and key structural parameters are listed in Table III.

The halogen substituents might influence the ground and bond shift transition states in at least three ways: 1) by steric effects (both attractive and repulsive), 2) through changes in the hybridization of the bonding orbitals

Table II. Total and Relative Energies for Optimized Ground States and Ring Inversion Transition States of Cyclooctatetraene and its Monohalogen Derivatives

| | | Ground State | Transition State | |
|---|---|---|---|---|
| Cmpd | Calculation | Total Energy[a] | Total Energy[a] | Relative Energy[b] |
| **1a** | HF/3-21G + ZPE | | | 16.66 |
| | HF/6-31G* | -307.52422 | -307.50308 | 13.27 |
| | HF/6-31G*+ ZPE | | | 13.88 |
| **1b** | HF/3-21G + ZPE | | | 14.75 |
| | HF/6-31G* | -406.37758 | -406.35749 | 12.61 |
| | HF/6-31G*+ ZPE | | | 13.05 |
| **1c** | HF/3-21G + ZPE | | | 18.01 |
| | HF/6-31G* | -766.42584 | -766.40096 | 15.62 |
| | HF/6-31G*+ ZPE | | | 16.16 |
| **1d** | HF/3-21G + ZPE | | | 18.85 |
| **1e** | HF/3-21G + ZPE | | | 20.56 |

[a] In hartrees.

[b] Energy relative to the ground state in kcal/mol.

of the substituted carbon ($C_1$), and 3) by π–delocalization. While the above calculations cannot give a quantitative answer to the contributions of these factors, they can give some qualitative guidance.

### *Steric Effects.*

These effects can be assessed through structural changes in the vicinity of the substituent, especially through changes in the bond angles involving the hydrogens flanking the substituent ($\angle C_1C_2H_2$ and $\angle C_1C_8H_8$). As seen in Table III, these angles are calculated to decrease by *ca.* 0.6° on going from the ground state of **1a** to that of **1b** and by a slightly greater amount in the sterically more congested transition state. In contrast, all of these angles except $\angle C_1C_8H_8$ in the sterically uncrowded ground state *increase* by at least 0.4° on going from **1a** to **1c**. The latter behavior can be attributed to steric repulsion by the chlorine atom. Similar increases (slightly smaller for bromo, slightly larger for iodo) are calculated for **1d** and **1e** when **1a**-**e** are optimized at the HF/3-21G level.

Interestingly, the *decrease* of these angles in **1b** is greater in the more crowded transition state than in the ground state. This is consistent with coulombic *attraction* between F and the flanking hydrogens or, alternatively, between the C→F dipole and the vicinal C←H dipoles. An increased interaction in the transition state relative to the ground state is consistent with increased C-F and C-H bond dipoles in the transition state as calculated from a natural population analysis[19] of atomic charges (Figure 2), as well as with a decrease in the

$FC_1C_8H_8$ dihedral angle from 45.4° in the ground state to 0° in the transition state. Related interactions have been suggested by Houk and coworkers for the inward rotation of fluorine in the disrotatory electrocyclization of 1-fluoro-1,3,5-hexatriene.[23]

Table III. Selected Structural Parameters for HF/6-31G*-Optimized Ground States (**1a-c**) and Ring Inversion Transition States (**5a-c**) of Cyclooctatetraene and its Monofluoro and Monochloro Derivatives[a]

| substituent (X)[b] | state | $\angle C_1C_2H_2$ | $\angle C_1C_8H_8$ | $\angle C_2C_1C_8$ | $r(C_1C_2)$ | $r(C_1C_8)$ | $r(CX)$[b] |
|---|---|---|---|---|---|---|---|
| H | **1a** | 117.7 | 114.8 | 127.3 | 1.3237 | 1.4780 | 1.0790 |
| | **5a** | 114.0 | 111.1 | 135.0 | 1.3261 | 1.4792 | 1.0772 |
| F | **1b** | 116.9 | 114.3 | 130.5 | 1.3167 | 1.4713 | 1.3402 |
| | **5b** | 112.9 | 110.3 | 137.2 | 1.3190 | 1.4745 | 1.3443 |
| Cl | **1c** | 118.4 | 114.9 | 128.4 | 1.3195 | 1.4763 | 1.7599 |
| | **5c** | 114.4 | 111.5 | 135.1 | 1.3233 | 1.4840 | 1.7687 |

[a] Angles in degrees; distances in angstroms.

[b] X is H, F and Cl in **1a-c**, respectively.

### *Hybridization Changes at $C_1$.*

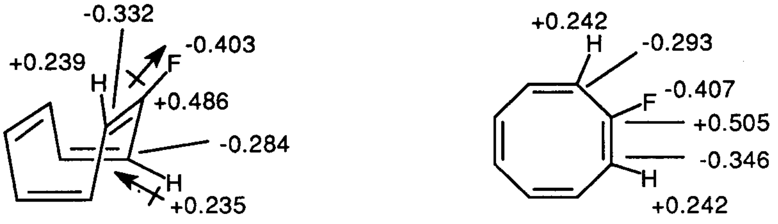
Extensive structural studies of substituted benzenes have shown that $\angle CCC$ at the position of substitution increases as the electronegativity of the substituent increases.[24] It has been found by electron diffraction measurements, for example, that $\angle C_2C_1C_6$ in para-disubstituted benzenes varies from 115.7 ± 0.6° for *p*-trimethylsilyl substituents to 123.5 ± 0.1° for *p*-difluorobenzene. The corresponding angles were found to be 121.6 ± 0.2° and 121.8 ± 0.2° for *p*-dichloro and *p*-dibromobenzene, respectively.[24]

These and related x-ray diffraction results and optimized ab initio geometries have been explained on the basis of hybridization effects.[25] In order to maximize the total bond strength, the p character of the substituted carbon is expected to concentrate in the hybrid orbital directed towards the most electronegative substituent.[26] According to this model, a highly electronegative substituent would cause an increase in the s character of the $C_1$ hybrid orbitals in the $C_1C_2$ and $C_1C_6$ bonds, resulting in a shortening of these bonds while increasing $\angle C_2C_1C_6$.

Alternatively, geometric changes caused by substituents may be analyzed[27] in terms of a valence-shell electron-pair repulsion (VSEPR) model.[28] In this model, withdrawal of electron density in the C-F bond by the electronegative fluorine atom in **1b** reduces the repulsion between the C-F bond and the $C_1$-$C_2$ and $C_1$-$C_8$

bonds. This causes the latter two bonds to shorten and $\angle C_2C_1C_8$ to increase. The opposite changes occur for an electropositive substituent such as $SiMe_3$ owing to polarization of the C-Si bond *towards* $C_1$.[24,29]

Our geometry optimizations for **1a-e** are generally consistent with previous results for substituted benzenes.[24] In order to gain an idea of the energy changes caused by ring substitution, we investigated the changes that occur in the bond lengths of **1a-c** on going from the ground state to the ring inversion transition state (Table IV). First, note that the relative lengthening of the C-F bond ($\Delta\Delta r$(C-X)) on flattening **1b** is twice the sum of the corresponding decreases for the eight CC and seven CH bonds. These changes are exactly those expected on the basis of the above hybridization and VSEPR models (see Table III), but the large increase of $\Delta r$(C-F) also suggests an *increase* in $\Delta G^{\neq}_{b.s.}$ relative to COT rather than the essentially no change that is observed.



**1a** **5a**

Figure 2. HF/6-31G* natural charges for selected atoms in the ground state (left) and ring inversion transition state (right) of fluorocyclooctatetraene.

Table IV. Changes in HF/6-31G*-Optimized Bond Lengths on Flattening the Ground State to the Ring Inversion Transition State (Relative to Cyclooctatetraene)[a]

| Cmpd | $\Delta\Delta r$(C-X)[b] | $\Delta\Delta r(C{=}C)^{c}_{tot}$ | $\Delta\Delta r(C{-}C)^{c}_{tot}$ | $\Delta\Delta r(C{-}H)^{c}_{tot}$ |
|---|---|---|---|---|
| **1b** | +0.59 | 0 | -0.16 | -0.14 |
| **1c** | +1.06 | +0.04 | +0.28 | -0.35 |

[a] $\Delta r$(COT-X) - $\Delta r$(COT); in pm.

[b] X is F or Cl.

[c] Total change for all bonds of this type.

Similarly, the calculated changes for **1c** in Table IV are dominated by an increase in $\Delta\Delta r$(C-Cl). This increase is twice as large as that calculated for $\Delta\Delta r$(C-F) even though chlorine is less electronegative than fluorine. In addition, we note that a) an increase of 1.1° in $\angle C_2C_1C_8$ calculated for the ground state of **1c** relative to **1a** completely disappears in the transition state, and b) $r(C_1C_8)$ is 0.17 pm shorter in the ground state of **1c** compared to that of **1a**, but is 0.48 pm *longer* when comparing the corresponding transition states.

Each of these changes is inconsistent with expectations based on the hybridization and VSEPR models but can readily be explained by an increased steric repulsion between chlorine and $C_2H_2$ and $C_8H_8$ on going from the ground state to the more crowded transition state. The effect shows up primarily in the $C_1C_8$ single bond rather than the $C_1C_2$ double bond, presumably because of the smaller force constant for stretching the latter. Similar steric effects are evident for **1d** and **1e** based on HF/3-21G optimizations of **1a-e**.

### *π-Donation.*

As previously noted, we were unable to calculate the bond shift transition states and therefore cannot fully assess the role of π-delocalization in the COT bond shift reaction. However, we have attempted to address this issue in an indirect manner.

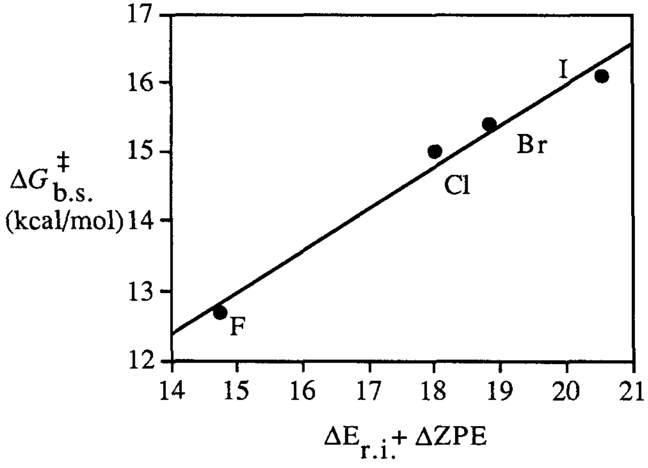


Figure 3. Plot of the free energy of activation for bond shift at 298 K vs. the difference in the HF/3-21G total plus zero point energies between the ground and ring inversion transition states of the monohalocyclooctatetraenes (**1b-e**).

As shown in Figure 3, $\Delta G^{\neq}_{b.s.}$ gives a good linear correlation ($r^2$=0.979) with $\Delta E_{r.i.}$ + $\Delta$ZPE calculated at the HF/3-21G level. Since the NPA π charges on the halogen atoms are nearly unchanged between the ground states and ring inversion transition states, we conclude that the overall trend in $\Delta E_{r.i.} + \Delta ZPE$, and therefore in $\Delta G^{\neq}_{b.s.}$, is largely independent of $\pi$-donation by the halogen.

The fact that the correlation in Figure 3 is not perfect could be due to differential steric effects in **2** vs. **5**, to inadequacies of the relatively small basis set employed, or to the lack of incorporation of electron correlation in our calculations. In any case, we cannot fully exclude the possibility that $\pi$-donation contributes to a reduction in the barrier to bond shift in fluorocyclooctatetraene.

## *Conclusions.*

The energetic effect of halogen substituents on the bond shift process in cyclooctatetraenes is highly linearly correlated with the Pauling and Mulliken electronegativities of the halogens. Analysis of structural and electronic data from HF/6-31G*-geometry optimizations of the ground states and ring inversion transition states suggests that bond shift in **1b** is promoted (relative to **1a**) by stabilizing interactions between the fluorine and the flanking hydrogens, and particularly between the vicinal C-F and C-H bond dipoles, in the transition state. For the larger chloro, bromo and iodo substituents, steric repulsions destabilize the more sterically congested transition state relative to the ground state. Donation of $\pi$ electrons into the ring is probably small in most of the transition states, but the possibility still exists that this effect measurably enhances the rate of bond shift in **1b**.

## *Acknowledgment.*

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## REFERENCES

(1) Review: Paquette, L.A. *Acc. Chem. Res.* **1993**, *26*, 57.

(2) Ganis, P.; Musco, A.; Temussi, P.A. *J. Phys. Chem.* **1969**, *73*, 3201.

(3) Paquette, L.A. Pure Appl. Chem. **1982**, *54*, 987.

(4) Anderson, J.E.; Kirsch, P.A. *J. Chem. Soc. Perkin Trans. 2* **1990**, 885; **1992**, 1951.

(5) Anet, F.A.L.; Bourne, A.J.R.; Lin, Y.S. *J. Am. Chem. Soc.* **1964**, *86*, 3576.

(6) Gwynn, D.W.; Whitesides, G.M.; Roberts, J.D. *J. Am. Chem. Soc.* **1965**, *87*, 2862.

(7) Schröder, G.; Kirsch, G.; Oth, J.F.M.; Huisgen, R.; Konz, W.E.; Schnegg, U. *Chem. Ber.* **1971**, *104*, 2405.

(8) (a) Oth, J.F.M.; Merényi, R.; Martini, T.; Schröder, G. *Tetrahedron Lett.* **1966**, 3087; (b) Oth, J.F.M. *Pure Appl. Chem.* **1971**, *25*, 573.

(9) Gurskii, M.E.; Gridnev, I.D.; Buevich, A.V.; Potapova, T.V.; Mstislavsky, V.I.; Krasavin, A.O.; Bubnov, Y.N. *Mendeleev Commun.* **1994**, 221.

(10) Goldman, G.D.; Roberts, B.E.; Cohen, T.D.; Lemal, D.M. *J. Org. Chem.* **1994**, *59*, 7421.

(11) Naor, R.; Luz, Z. *J. Chem. Phys.* **1982**, *76*, 5662.

(12) Gasteiger, J.; Gream, G.E.; Huisgen, R.; Konz, W.E.; Schnegg, U. *Chem. Ber.* **1971**, *104*, 2412.

(13) Van Geet, A.L. *Anal. Chem.* **1968**, *40*, 2227.

(14) Van Geet, A.L. *Anal. Chem.* **1970**, *42*, 679.

(15) Sandström, J. *Dynamic NMR Spectroscopy,* Academic Press, New York, 1982, pp. 14-18.

(16) Frisch, M.J.; Trucks, G.W.; Head-Gordon, M.; Gill, P.M.W.; Wong, M.W.; Foresman, J.B.; Johnson, B.G.; Schlegel, H.B.; Robb, M.A.; Replogle, E.S.,; Comperts, R.; Andreas, J.L.; Raghavachari, K.; Binkley, J.S.; Gonzalez, C.; Martin, R.L.; Fox, D.J.; DeFrees, D.J.; Baker, J.; Stewart, J.J.P.; Pople, J.A. *GAUSSIAN 92, Revision A*; Gaussian, Inc.; Pittsburgh, PA, **1992**.

(17) a) Binkley, J.S.; Pople, J.A.; Hehre, W.F. *J. Am. Chem. Soc.* **1980**, *102*, 939; b) Gordon, M.S.; Binkley, J.S.; Pople, J.A.; Pietro, W.J.; Hehre, W.J. *J. Am. Chem. Soc.* **1982**, *104*, 2797; c) Dobbs, K.D.; Hehre, W.J. *J. Comput. Chem.* **1986**, *7*, 359.

(18) Hariharan, P.C.; Pople, J.A. *Chem. Phys. Lett.* **1972**, *16*, 217; *Theor. Chim. Acta* **1973**, *28*, 213.

(19) (a) Reed, A.E.; Weinstock, R.B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735; (b) Reed, A.E.; Weinhold, F. *J. Chem. Phys.*, **1985**, *83*, 1736; (c) Reed, A.E.; Curtiss, L.A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(20) Shriver, D.F.; Atkins, P.W.; Langford, C.H. *Inorganic Chemistry*, Freeman, New York, 1990, pp. 31-33, 640-1.

(21) Karadakov, P.B.; Gerratt, J.; Cooper, D.L.; Raimondi, M. *J. Phys. Chem.* **1995**, *99*, 10186.

(22) Gardlik, J.M.; Paquette, L.A.; Gleiter, R. *J. Am. Chem. Soc.* **1979**, *101*, 1618.

(23) Evanseck, J.D.; Thomas, B.E., IV; Spellmeyer, D.C.; Houk, K.N. *J. Org. Chem.* **1995**, *60*, 7134.

(24) Review: Domenicano, A. *Methods Stereochem. Anal.* **1988**, *10* (Stereochem. Appl. Gas-Phase Electron Diffr., Pt. B), 281.

(25) (a) Carter, O.L.; McPhail, A.T.; Sim, G.A. *J. Chem. Soc.* A **1966**, 822; (b) Nygaard, L.; Bojesen, I.; Pedersen, T.; Rastrup-Andersen, J. *J. Mol. Struct.* **1968**, *2*, 209.

(26) (a) Walsh, A.D. *Discuss. Faraday Soc.* **1947**, *2*, 18; (b) Bent, H.A. *Chem. Rev.* **1961**, *61*, 275.

(27) Domenicano, A.; Vaciago, A.; Coulson, C.A. *Acta Cryst.* **1975**, *B31*, 221.

(28) Gillespie, R.J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 819; *J. Chem. Ed.* **1970**, *47*, 18.

(29) Staley, S.W.; Grimm, R.A.; Sablosky, R.A., accepted by *J. Am. Chem. Soc.*

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