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Gauche Conformers Relatively Stabilized by Hypercoordination

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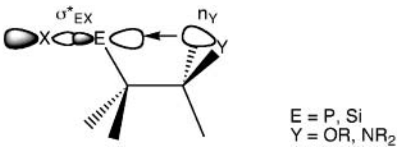
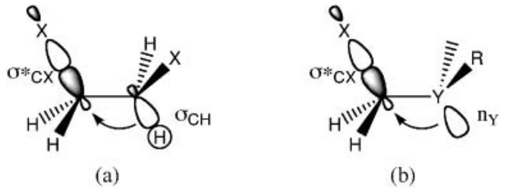
ABSTRACT



We theoretically confirmed that hypercoordination results from the delocalization of lone pair electrons on the first-row atom Y to the σ bond between the second-row atom E and X. We designed gauche conformers of $EX_nCH_2CH_2Y$ (EX_n = PR_2, SiR_3; Y = OR, NR_2) that are stable relative to the anti conformers, due to the hypercoordination.

The anti conformers of saturated organic molecules are usually the more stable conformer. However, some molecules favor gauche conformers. The gauche effect[1] (Figure 1a) and anomeric effect[2] (Figure 1b) can be interpreted in terms of the stabilization of the gauche conformers by the donor−acceptor interaction between the vicinal bonds (including lone pairs as donors) in the antiperiplanar relation. The destabilization of the anti conformer was recently proposed as an alternative interpretation of the gauche effect.[3] Here we theoretically design relatively stable gauche conformers of $EX_nCH_2CH_2Y$ (EX_n = PR_2, SiR_3; Y = OR, NR_2) by a 1,4-nonbonded attraction between the saturated atoms or by 1,4-hypercoordination.[4]



(a) (b)

Figure 1. The antiperiplanar donor−acceptor bond interaction in the (a) gauche and (b) anomeric effects.

We employed $PH_2CH_2CH_2OH$ (**1a**) as a model molecule to investigate the 1,4-hypercoordination. The geometries of all possible conformers were optimized by ab initio molecular orbital calculations at the RHF/6-31G* level with the Gaussian 94 program.[5] We investigated the bond interaction[6]

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(1) For example, see: Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

(2) Lemieux, R. U. *Pure Appl. Chem.* **1971**, *27*, 527. Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer: New York, 1983. Szarek, W. A.; Horton, D. *Anomeric Effect*; American Chemical Society: Washington, 1979. Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Elmsford, NY, 1983; p 4.

(3) Wiberg, K. B.; Murcko, M. A.; Laidig, K. E.; MacDougall, P. J. *J. Phys. Chem.* **1990**, *94*, 6956.

(4) Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reyé, C.; Declercq, J.-P.; Dubourg, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1430. See also: Nakanishi, W.; Hayashi, S.; Sakaue, A.; Ono, G.; Kawada, Y. *J. Am. Chem. Soc.* **1998**, *120*, 3635. Nakanishi, W.; Hayashi, S.; Toyota, S. *J. Org. Chem.* **1998**, *63*, 8790. Iwaoka, M.; Komatsu, H.; Tomoda, S. *Chem. Lett.* **1998**, 969.

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision C. 3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

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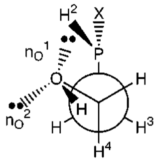
in the most stable gauche conformer. The interbond energy[7] (IBE = −7.31 kcal/mol) (Table 1) showed that the significant attractive interaction occurs between the lone pair of O atom (n_O^1) directed toward P and the PH^1 bond antiperiplanar to the CC bond. The hypercoordination was shown by the separation of the lone pair−bond interaction into the interactions of the n orbital with the bonding and antibonding orbitals of the PH bond to result from the delocalization of the lone pair electrons on the O atom to the PH σ bond. The stabilizing delocalization from n_O^1 to σ^*_{PH1} [$IBE_{(n,\sigma^*)} = -9.04$ kcal/mol] overcomes the repulsion between n_O^1 and σ_{PH1} [$IBE_{(n,\sigma)} = 1.73$ kcal/mol] (Table 2).

Table 1. The IBE[a] and ΔIBE[b] Values (in kcal/mol) of the Gauche Conformers of **1a** and **1b**



	IBE		
	X = H¹	X = Cl	ΔIBE
$(P-X)-(n_O^1)$	−7.31	−14.35	−7.04
$(C-P)-(C-H^4)$	26.93	21.37	−5.56
$(C-H^3)-(C-O)$	5.87	6.06	0.19

[a] Reference 7. [b] $\Delta IBE = IBE_{Cl} - IBE_{H1}$.

Table 2. IBE Values (in kcal/mol) between the Orbitals

	IBE
$n_O^1-\sigma_{PH1}$	1.73
$n_O^1-\sigma^*_{PH1}$	−9.04

The hypercoordination suggests the possibility that a gauche conformer of some derivatives of **1a** should be more stable than the anti conformers. Replacement of the hydrogen atoms on the P atom by electron-withdrawing groups (X) lowers the σ^*_{PX} energy and enhances the hypercoordination to result in the relatively stable gauche conformers. We optimized the geometries of all conformations of the chloro-substituted molecules $ClPHCH_2CH_2OH$ (**1b**) and $Cl_2PCH_2CH_2OH$ (**1c**). The most stable gauche conformers of **1b** and **1c** were found to be more stable than the most stable anti conformers by 1.04 and 1.50 kcal/mol, respectively while there is no preference for the gauche conformer **1a** (Table 3). In the most stable gauche conformers, a lone pair of the O atom is directed toward the backside of the PCl bond antiperiplanar to the CC bond. For example, see Figure 2 for **1c**.

Table 3. Relative Energies Δ*E*[a] (in kcal/mol) of the Gauche Conformers of $EX_nCH_2CH_2Y$

	EX_n	Y	ΔE
1a	PH_2	OH	0.22
1b	PHCl	OH	−1.04
1c	PCl_2	OH	−1.50
2a	PH_2	NH_2	0.24
2b	PHCl	NH_2	−1.63
2c	PCl_2	NH_2	−1.31
3a	SiH_3	OH	−0.53
3b	SiH_2Cl	OH	−1.62
3c	$SiHCl_2$	OH	−1.96
3d	$SiCl_3$	OH	−0.43
4a	SiH_3	NH_2	−0.73
4b	SiH_2Cl	NH_2	−2.42
4c	$SiHCl_2$	NH_2	−2.13
4d	$SiCl_3$	NH_2	−0.69

[a] $\Delta E = E_{gauche} - E_{anti}$. E_{gauche} and E_{anti} denote the most stable gauche and anti conformers, respectively, and include zero point energies.

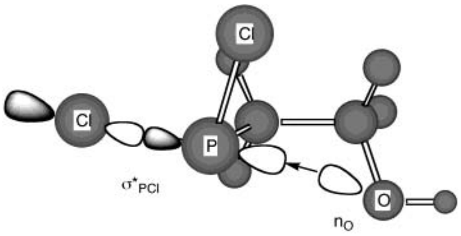


Figure 2. The most stable gauch conformer of **1c**.

The n_O^1-PX bond interaction stabilizes both **1a** and **1b** (Table 1). The stabilization increases (ΔIBE = −7.04 kcal/mol) on going from **1a** to **1b**, showing the significance of the hypercoordination. The vicinal $CP-CH^4$ bond interactions destabilize **1a** and **1b**. The destabilization decreases (ΔIBE = −5.56 kcal/mol) and contributes to the increase in the relative stability of the gauche conformer **1b**. However, the contribution is smaller than that from hypercoordination. The $CO-CH^3$ bond interaction destabilizes **1a** and **1b**. The destabilization is greater in **1b** (ΔIBE = 0.19 kcal/mol). These results suggest that the stabilization of the gauche conformers should be more significantly controlled by the hypercoordination rather than the antiperiplanar donor−acceptor interaction.[8]

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(6) Inagaki, S.; Ikeda, H. *J. Org. Chem.* **1998**, *63*, 7820. See also: Inagaki, S.; Goto, N.; Yoshikawa, K. *J. Am. Chem. Soc.* **1991**, *113*, 7144. Inagaki, S.; Yoshikawa, K.; Hayano, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3706. Inagaki, S.; Ishitani, Y.; Kakefu, T. *J. Am. Chem. Soc.* **1994**, *116*, 5954.

(7) Inagaki, S.; Yamamoto, T.; Ohashi, S. *Chem. Lett.* **1997**, 977. The interbond energy between the bond orbitals *i* and *j* is defined as $IBE_{ij} = P_{ij}(F_{ij} + H_{ij})$, where P_{ij}, F_{ij}, and H_{ij} are the elements of the density, Fock, and core Hamiltonian matrixes, respectively. The IBE values are the sums of the all-bond orbital interactions between a pair of bonds.

The hypercoordination can also be expected for saturated silicon and nitrogen atoms in place of the phosphorus and oxygen atoms, respectively. In fact, the gauche conformers of most of the molecules examined (**2**−**4**) were calculated to be more stable than the anti conformers (Table 3). Full substitution of the silicon atom by chlorine atoms diminishes the relative stabilities of the gauche conformers compared to those of the parent molecules, possibly due to the repulsions of the lone pairs between the first-row atoms and the Cl atom close to each other.

In summary, we theoretically investigated the bond interactions in $EX_nCH_2CH_2Y$ ($EX_n = PR_2$, SiR_3; $Y = OR$, NR_2) to show that the hypercoordination results from the delocalization of the lone pair electrons on the first-row atom Y to the σ bond between the second-row atom E and X. The gauche conformers were predicted to be stable relative to the anti conformers, due to the hypercoordination.[9]

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(8) The stabilities of gauche conformers of $NH_2CH_2CH_2OH$ (**5a**) and $ClNHCH_2CH_2OH$ (**5b**) corresponding to the most stable conformers of **1a** and **1b** were also found to be more stable by −0.87 and −1.90 kcal/mol than the anti conformations, respectively. The greater relative stabilities of the gauche conformer of **5b** are suggested by the analysis of the bond interaction to be more significantly controlled by the antiperiplanar donor−acceptor interaction, in contrast to **1a** and **1b**. There is no appreciable difference ($\Delta IBE = 0.12$ kcal/mol) in the stabilization due to the $n_O{}^1$−NX bond interaction between **5a** and **5b**, showing little significance of the hypercoordination. The stabilization due to the antiperiplanar $CN-CH^4$ bond interactions increases to a great extent ($\Delta IBE = -13.77$ kcal/mol) on going from **5a** to **5b**. The antiperiplanar CO−CH³ bond interaction gives no considerable difference ($\Delta IBE = 1.49$ kcal/mol).

(9) Kawashima, T.; Okazaki, R.; Okazaki, R. Unpublished results. The X-ray structure of bis[2,2-bis(4-chlorophenyl)-2-hydroxyethyl]phenylphosphine showed a gauche conformer, i.e., dihedral angle ϕ PCCO = 51.9° (calculated: 54.1° for **1c**) and atomic distance P···O = 2.97 Å (calculated: 3.03 Å for **1c**). The couplings between OH (OCH_3) and P (δ_H 3.11 (d, $J_{HP} = 3.7$ Hz), δ_C 50.5 (d, $J_{CP} = 3.0$ Hz)) observed in the ^1H and ^{13}C NMR spectra (in $CDCl_3$) of the phosphine and its dimethyl ether, respectively, are consistent with those of the gauche conformers.