Theoretical Determination of Hypervalent Bond Energy of 10–S–3 Sulfurane Derivatives

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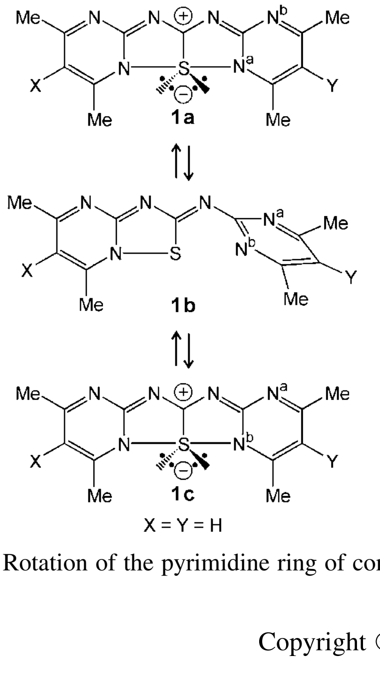
The energy of a 10–S–3 hypervalent, i.e., N–S–N, bond was theoretically determined to be 60.6 kcal/mol using bond energy density analysis with the density functional theory. Upon rotation of the pyrimidine ring of a sulfurane compound, the hypervalent bond is broken. The total energy of the system changes by 15.7 kcal/mol. The broken N–S bond is destabilized by 56.5 kcal/mol, while another is stabilized by 44.2 kcal/mol. The results support previous experimental data.

10–S–3 Sulfurane is a typical three-coordinate hypervalent compound. It has a three center-four electron (3c–4e) bond, which is rectilinear in a direction perpendicular to the sp^2 plane composed of a σ bond and two unshared electron pairs of the central sulfur atom. The chemical behavior of such compounds is interesting from both experimental and theoretical points of view.[1] To evaluate the dissociation energy of the N–S–N hypervalent bond, 10–S–3 sulfurane fused with two pyrimidine rings (**1**; $X = Y = H$) has been prepared and the free energy of rotation of the pyrimidine ring has been experimentally determined to be 16.6 kcal/mol by Akiba et al.[2] The S–N_a bond in **1a** is exchanged for the S–N_b bond in **1c** through rotation. However, the energy for this transition involves not only cleavage of the hypervalent bond but also the recombination of other chemical bonds. It would be interesting to extract only the effect of 3c–4e bond cleavage from among the effects of all kinds of chemical bonds. In the present study, we investigated the process of rotation between **1a** and **1c** by density functional theory (DFT) calculations. An energy partitioning technique was applied to estimate the dissociation energy of the N–S–N hypervalent bond (Scheme 1).



Scheme 1. Rotation of the pyrimidine ring of compound **1**.

First, geometry optimization of the 10–S–3 sulfurane derivative **1a** was carried out using the DFT with Becke's three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP)[3] and Dunning's correlation consistent polarized valence double-ζ (cc-pVDZ)[4] basis set. The optimized geometry was verified by a frequency analysis with the same computational level. Next, partial geometry optimizations were performed to estimate the rotation barrier. A degree of freedom (DoF), i.e., the dihedral angle of the pyrimidine ring shown in Figure 1, was restricted and the other DoFs were optimized. Gaussian03[5] was used for the calculations.

To obtain information for deducing the nature of a local region, various techniques for partitioning the energy of a system obtained by an electronic state calculation have been proposed by many reseachers.[6–9] In this study, we used the bond energy density analysis (Bond-EDA) developed and implemented in the GAMESS package[10] by Nakai and Kikuchi,[6c] which divides the total energy into atoms and interatomic regions:

$$E = \sum_{\mathrm{A}} E_{\mathrm{AA}} + \sum_{\mathrm{A,B}} E_{\mathrm{AB}}, \qquad (1)$$

where A and B indicate atoms. E_{AA} and E_{AB} correspond to the atomic and bond energies, respectively.

The potential energy curve (PEC) of the barrier was evaluated by rotating a pyrimidine ring in **1**. The dihedral angle was varied from 0 to 90 degrees in 5-degree increments. Figure 1 shows the calculated PEC. The total energy gradually rises and the barrier height is estimated to be 15.7 kcal/mol, which agrees well with the experimental value of 16.6 kcal/mol.[2] Frequency-analysis calculations confirm that **1a** is a stable compound, whereas **1b** is a transition state (TS). The normal coordinate for one negative frequency of $-36.8\,\mathrm{cm}^{-1}$ implies that the TS is for the rotation of pyrimidine.

The calculated S1–C5 and S1–N2 (or S1–N8) bond lengths

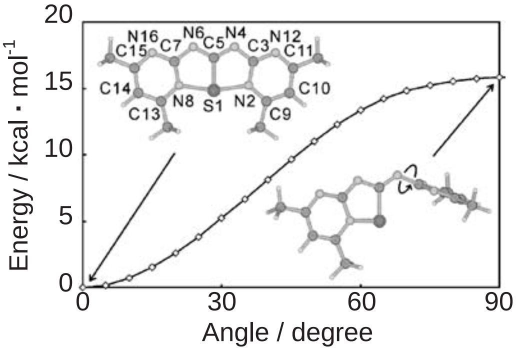


Figure 1. Potential energy curve for the restricted rotation of the pyrimidine ring from **1a** to **1b**.

Table 1. Four largest changes of atomic and bond energies in the reaction from **1a** to **1b**

	E (**1a**)	E (**1b**)	ΔE
S1–N2	−60.6	−4.0	56.5
C3	−23605.9	−23654.0	−48.0
S1–N8	−60.6	−104.8	−44.2
C3–N4	−201.9	−161.0	40.9

in **1a**, of which the labels are shown in Figure 1, are 1.85 and 2.00 Å, respectively. They are a little bit longer but reasonably agree with the experimental values: 1.78 and 1.94 Å, respectively.[2a] In the process from **1a** to **1b**, the S1–C5 bond slightly elongates to 1.92 Å. This elongation is speculated due to a decrease of the electrostatic attraction between S1 and C5. The S1–N8 bond changes from 2.00 (**1a**) to 1.74 (**1b**) Å, which indicates that a weaker hypervalent bond becomes an ordinary single bond. The C3–N4 bond elongates slightly from 1.34 (**1a**) to 1.39 (**1b**) Å. The rotation seems to make the conjugated bond change from quasi-double to quasi-single bonds.

The total energy of the system was partitioned into atoms and interatomic regions by using the Bond-EDA technique (See Supporting Information for the detailed data[11]). Table 1 summarizes the atomic and bond energies that change the most in the reaction from **1a** to **1b**. The energy for the N–S–N hypervalent bond is evaluated to be −60.6 kcal/mol, which corresponds to E_{AB} of S1–N2 and S1–N8 in **1a**. Here, the negative sign of E_{AB} means a stable bond. The rotation of pyrimidine leads to cleavage of S1–N2 bond, of which E_{AB} is −4.0 kcal/mol in **1b**. Namely, the cleavage of the S1–N2 bond brings a large destabilization of 56.5 kcal/mol. In contrast, the S1–N8 bond, which is the counter side of the S1–N2 bond, is greatly stabilized by 44.2 kcal/mol: −60.6 (**1a**) to −104.8 (**1b**) kcal/mol. The atomic energy E_{AA} for S, a central atom of the hypervalent bond, is changed from −398.0852 (**1a**) to −398.0821 (**1b**) hartree, of which the difference is only 1.9 kcal/mol. Note that the absolute values of E_{AA} are remarkably large owing to the core-electron contributions, which are less important for reactions involving valence-bond reformulations.

The second-most important site is the rotation axis in the reaction from **1a** to **1b**. The C3 atom is stabilized by 48.0 kcal/mol, and the C3–N4 bond is destabilized by 40.9 kcal/mol. This means that the π electron on the C3–N4 bond transfers to the C3 atom. Thus, the quasi-double bond becomes a quasi-single bond. These results correspond to the change in the molecular structure.

Table 2 shows the substituent dependence of these energy differences. X and Y are the substituents on C14 and C10, respectively. Experimental free energies of rotation $\Delta G_{298}{}^{\ddagger}$ are estimated in ref 2a. The calculated total energy differences $\Delta E_{\mathrm{Total}}$ correspond to the experimental results. Owing to the asymmetric hypervalent bond of **2**, $\Delta E_{\mathrm{Total}}$ values for H-side and Br-side rotations are 17.4 and 13.7 kcal/mol, respectively. Furthermore, the energy difference for the S–N bond, i.e., $\Delta E_{\mathrm{S1-N2}}$ for the H side is 70.7 kcal/mol and that for the Br side is 42.7 kcal/mol in compound **2**. Thus, the S–N bond attached to an electron-withdrawing group (Br-side) is weaker, and the rotation barrier is lower.

Table 2. Substituent depedence of the energy differences (kcal/mol)

	X	Y		$\Delta G^{\ddagger}_{298}$	$\Delta E_{\mathrm{Total}}$	$\Delta E_{\mathrm{S-N}}$
1:	H	H		16.6	15.7	56.5
2:	Br	H	(H-side)	18.3	17.4	70.7
			(Br-side)	15.5	13.7	42.7

In summary, we have evaluated bond energies of 10–S–3 sulfurane derivatives based on Bond-EDA for DFT results. Bond-EDA can reflect delicate electronic effects and can provide the energy components in $\Delta E_{\mathrm{Total}}$ of **1** and **2**, which agree with the experimental results to within an error of 1–2 kcal/mol. Thus, the Bond-EDA technique is confirmed to be a powerful tool for analyzing the chemical behavior of a complicated molecule. Instead of using the traditional semiexperimental techniques for bond energy, e.g., the Huggins equation,[12] we can now calculate the bond energy directly by using Bond-EDA, even for the TS.

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