HOMO and LUMO+1 of thiirenium ion are the π and π* orbitals of the endocyclic C-C double bond.

The HOMO of disulfide may interact with the b_2 LUMO of thiiranium or thiirenium ions (under energy-gap control) when the nucleophile approaches along the y direction, or with the vacant a_1 orbital (orbital-overlap control) when the nucleophile approaches along the *x* direction. The approach along the *z* direction does offer only a limited possibility of overlap. The experimental evidence points to the approach along the *y* direction, that is to the energy-gap control.

The case of bicentric nucleophiles represented by the π system of double and triple C–C bonds is different. The approach along the *x* direction is now favored by the possibility of a double interaction, between the HOMO of the nucleophile and the vacant a_1 orbital, but also between the LUMO of the nucleophile and the occupied b_2 orbital. This latter interaction is minimized, or even cancelled, in the disulfide monocentric nucleophile, because in the LUMO the atomic p orbital is almost totally engaged in the interaction with the orbitals at the adjacent atoms.

The interaction between the LUMO of the π system and the occupied b_2 orbital is possible also along the *z* direction. This is, however, the only interaction along this direction, and this may explain the energy difference found by Radom for A and B pathways.

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[2] G. Capozzi, G. Modena, L. Pasquato in *The Chemistry of Sulfenic Acids and Their Derivatives* (Ed. S. Patai), Wiley, London, **1990**, p. 403.

[3] For example: a) G. H. Smidt, P. H. Fitzgerald, *J. Am. Chem. Soc.* **1971**, *93*, 2547; b) G. Capozzi, V. Lucchini, G. Modena, *Rev. Chem. Intermed.* **1979**, *4*, 347.

[4] V. Lucchini, G. Modena, M. Pasi, L. Pasquato, *J. Org. Chem.* **1997**, *62*, 7018.

[5] M. Fachini, V. Lucchini, G. Modena, M. Pasi, L. Pasquato, *J. Am. Chem. Soc.* **1999**, *121*, 3944.

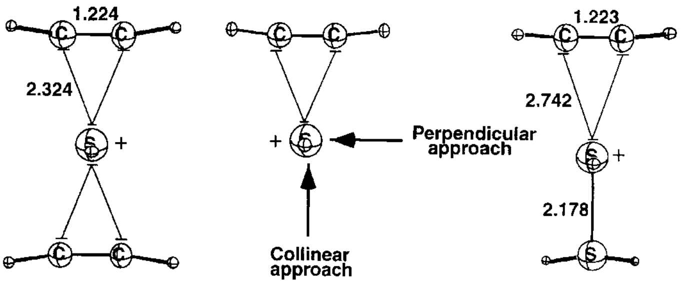
[6] T. L. Solling, S. B. Wild, L. Radom, *Chem. Eur. J.* **1999**, *5*, 509.

Are the Approach Directions of σ and π Nucleophiles to the Sulfur Atom of Thiiranium and Thiirenium Ions Different?

Theis I. Sølling, S. Bruce Wild, and Leo Radom*[a]

We have recently carried out a theoretical examination of nucleophilic substitution at the sulfur atom of thiiranium and thiirenium ions by the unsaturated hydrocarbons ethylene and acetylene using high-level ab initio molecular orbital calculations.[1] These reactions were found to result in π-ligand exchange and to proceed via transition structures that resemble the triple-ion configuration of the traditional S_N2 reaction at carbon ($X^- \cdots CH_3^+ \cdots X^-$), that is the transition structures are arranged so that the donor orbitals of the two π ligands and the vacant orbital at SH^+ are close to collinear (e. g. **1**). This transition structure description is consistent with that obtained from calculations for the analogous reactions of ethylene and acetylene with phosphiranium, phosphirenium, chloriranium and chlorirenium ions.[2, 3]

In an independent experimental study, Modena and co-workers examined the nucleophilic attack of dialkyl disulfides on the sulfur atom of substituted thiiranium and thiirenium ions.[4] They found that the reaction is sensitive to the substitution pattern both at sulfur and at the ring carbon atoms, from which they postulated that the nucleophile approaches in a perpendicular (rather than a near-collinear) direction (as illustrated in **2**).



In an attempt to reconcile the apparently conflicting conclusions from the theoretical and experimental studies, Modena and co-workers have noted in the accompanying comment[5] that the theoretical study was concerned with bicentric nucleophiles whereas the experimental study was concerned with a monocentric nucleophile. From a consideration of orbital interactions in the two cases, they made the interesting observation that there is an additional interaction in the bicentric case that favors a collinear approach. Thus they concluded that the apparently different directions of nucleophilic attack could be associated with a difference in behavior between monocentric and bicentric nucleophiles.

We have, in fact, very recently carried out explicit high-level ab initio calculations on the exchange reactions of prototypical monocentric nucleophiles (specifically NH_3, H_2O, HF,

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[a] Prof. Dr. L. Radom, T. I. Sølling, Dr. S. B. Wild
Research School of Chemistry, Australian National University
ACT 0200, Canberra (Australia)
Fax: (+61) 2-6249 0750
E-mail: radom@rsc.anu.edu.au

0947-6539/00/0604-0590 $ 17.50+.50/0

PH_3, H_2S, and H_2O) with phosphiranium and phosphirenium ions,[6] chloriranium and chlorirenium ions,[7] and thiiranium and thiirenium ions.[8] We find that the reactions in some cases involve an intermediate transition structure whereas in other cases they proceed from reactants to products without the intervention of an intermediate transition structure. The relevant observation, however, is that the transition structures in the former situations resemble triple-ion configurations with near linearity of the appropriate orbitals (e. g. **3**, the transition structure for the exchange reaction of H_2S with thiirenium ion). Thus we find no evidence for a qualitative difference in the direction of the attack on these three-membered heterocyclic ions between the monocentric and bicentric nucleophiles.

The apparent discrepancy between the theoretical and experimental conclusions therefore remains. There are a number of possible alternative explanations: a) Perhaps the sensitivity of the reactivity to substitution may be attributable to some factor other than the approach of the nucleophile in the perpendicular direction. b) The calculations refer to the gas phase whereas the experiments were carried out in solution. Perhaps differential solvation is playing an important role. c) The calculations and experiments refer to different specific systems. Perhaps the experimental conclusions apply to specific systems but do not hold generally. It would seem that this problem deserves further attention and that additional theoretical and/or experimental work is needed before definitive conclusions can be drawn.

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