



# Proton affinities and gas phase basicities of epoxides and episulfides: Exceptional superbasicity of compounds with oxygen and sulfur sites

Younes Valadbeigi

Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran

## ARTICLE INFO

### Article history:

Received 15 May 2018

Received in revised form 23 June 2018

Accepted 27 June 2018

Available online 28 June 2018

### Keywords:

Epoxides  
Episulfides  
Superbase  
Ring opening  
Protonation

## ABSTRACT

Proton affinities (PA) and gas phase basicities (GB) of epoxide and episulfide derivatives with 2–6 carbon atoms were computed at the B3LYP/6-311++G(d,p) level of theory. These simple derivatives did not undergo ring opening upon protonation and their PAs were lower than 880 kJ mol<sup>-1</sup>. The PAs of the episulfides were higher than those of the corresponding epoxides. By substitution of strong electron donating groups such as phosphazene and guanidine, we stimulated ring opening upon protonation. This strategy led in designing of compounds with exceptional superbasicity of oxygen and sulfur sites. The calculated PAs were in the range of 1000–1200 kJ mol<sup>-1</sup>.

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## 1. Introduction

Compounds with high acidity and basicity have vast applications in all branches of chemistry and chemical industry [1–3]. Hence, several laboratories and companies are synthesizing and producing these compounds and many theoretical chemists are attempting to design more effective superbases and superacids [4–9]. A Brønsted superbase is a compound with high ability to accommodate and delocalize the positive charge of the entering proton; therefore, substitution of electron donating groups (EDG) is a tactic to increase basicity [10,11]. Formation of strong intramolecular hydrogen bonds after protonation in another strategy for designing of superbases such as “proton sponges” [12–14]. Recently, some superbases have been suggested and theoretically assessed in which the positive charge is delocalized in an aromatic ring [15–18]. Cyclic compounds suffer from ring strain [19]; hence, ring opening upon protonation has been used to obtain stable conjugate acids and consequently strong organic bases [20–24]. Because of higher intrinsic basicity of nitrogen atom, usually this atom is used as proton acceptor site in the design of organic Brønsted superbase. However, there are few studies that suggest some superbases with other heteroatoms such as oxygen, germanium, and silicon as proton acceptor sites [25–29].

Epoxides (Oxiranes) and episulfides (thiiranes) are three-membered heterocyclic compounds with O and S atoms as heteroatoms, respectively. Epoxides and episulfides are gener-

ally synthesized by addition of oxygen and sulfur to alkenes, respectively. These compounds participate in many organic reactions [30,31]. Electronic structure, geometrical and energetic properties of epoxides and episulfides, especially ethylene oxide and ethylene sulfide, have been studied employing *ab initio* and atom-in-molecules (AIM) methods [32–34]. These studies show that the epoxides suffer from internal strain [33]. On the other hand, protonation of epoxides in gas phase and possibility of ring opening upon protonation has been studied both experimentally and theoretically [30,31,35–37]. Although acid-catalyzed ring opening relieves the strain, this process requires an activation energy [38]. However, the activation energy depends on the structure of the epoxides; for example, the activation energy of the ring opening for ethylene oxide is about 12–17 kcal mol<sup>-1</sup> higher than that of propene oxide [38].

In this work, we design epoxide and episulfide derivatives with special structures so that they undergo ring opening upon protonation. Since ring opening upon protonation relieves the internal strain of the epoxides and episulfides, the protonated species are more stable than the corresponding neutral ones. This strategy leads in compounds with exceptional superbasicity of their O and S sites.

## 2. Computational details

Structures of all epoxide and episulfide isomers and their protonated forms were fully optimized employing B3LYP functional and 6-311++G(d,p) basis set. The frequency calculations were carried out at the same level of theory in gas phase and at 298 K to obtain

E-mail address: [y.valadbeigi@ch.iut.ac.ir](mailto:y.valadbeigi@ch.iut.ac.ir)

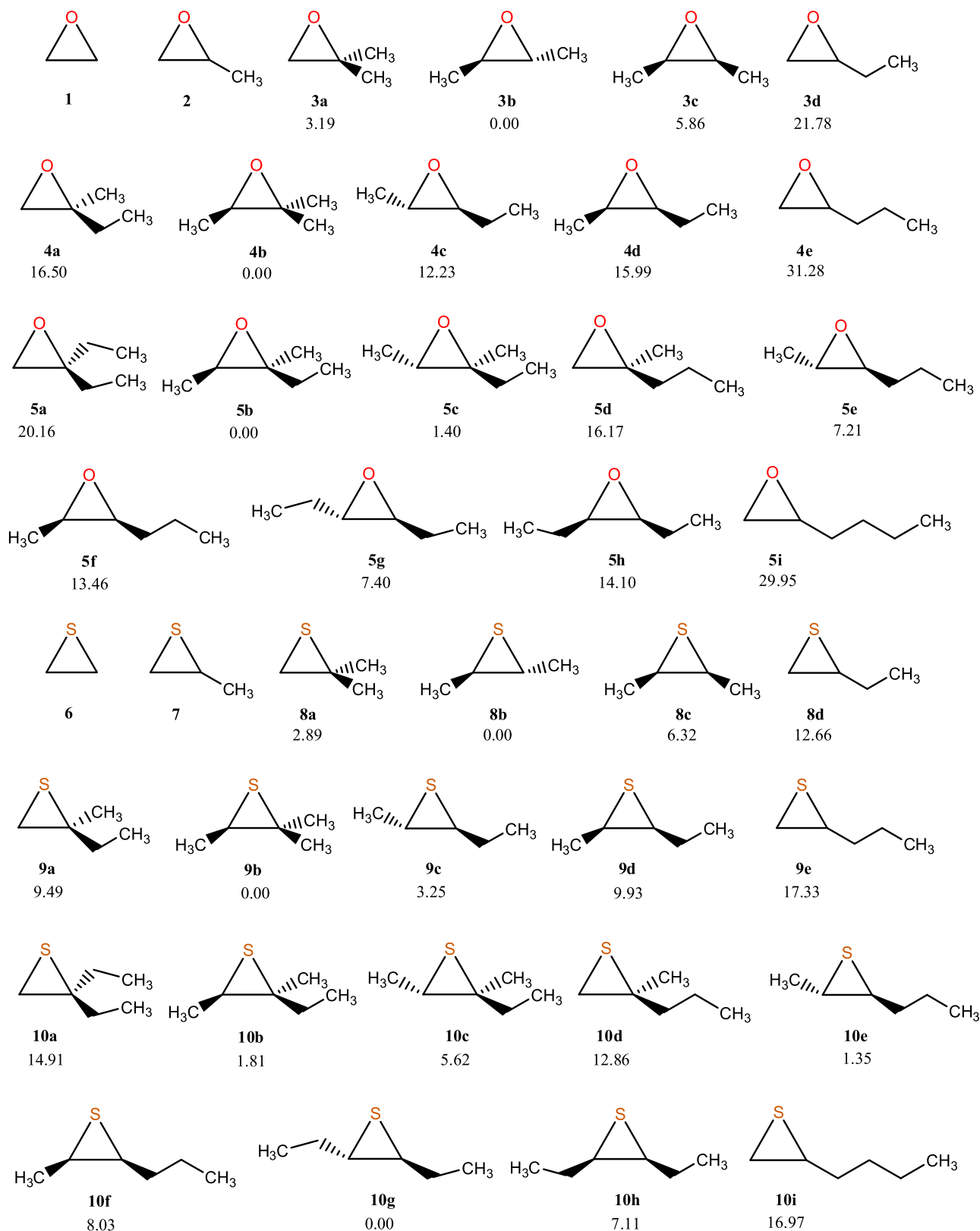
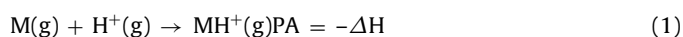


Fig. 1. The simple epoxides and episulfides with 2–6 carbon atoms. The numbers are the relative energies of the isomers in kJ mol<sup>-1</sup>.

the thermodynamic quantities. All calculations were performed by Gaussian 09 software [39].

Proton affinity (PA) and gas phase basicity (GB) are the main indices for evaluation of basicity of compounds in gas phase. PA

of a molecule, M, is defined as  $-\Delta H$  of its protonation in gas phase



And GB of M is defined as  $-\Delta G$  for reaction (1).

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