Surprising Hydrogen Sulphide Scavenger Synergies presented by Inter- and Intra-Molecular Mixed hexahydrotriazines

Grahame N. Taylor

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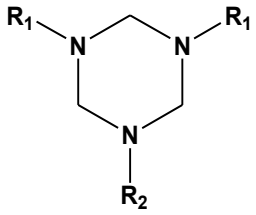
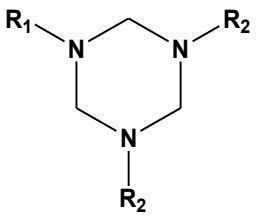
Introduction



(I)



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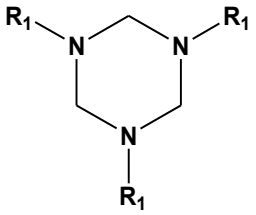

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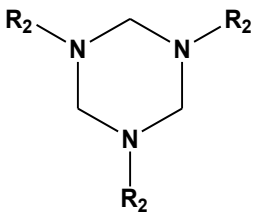
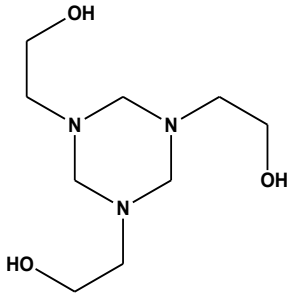


(IV)

Triazines, or more correctly hexahydrotriazines (I) to (IV), are the most ubiquitous H_2S scavengers. The Tris-(2-hydroxyethyl) derivative (V) is the most common.



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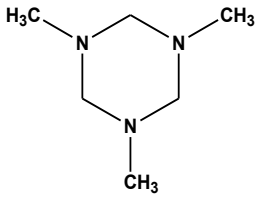

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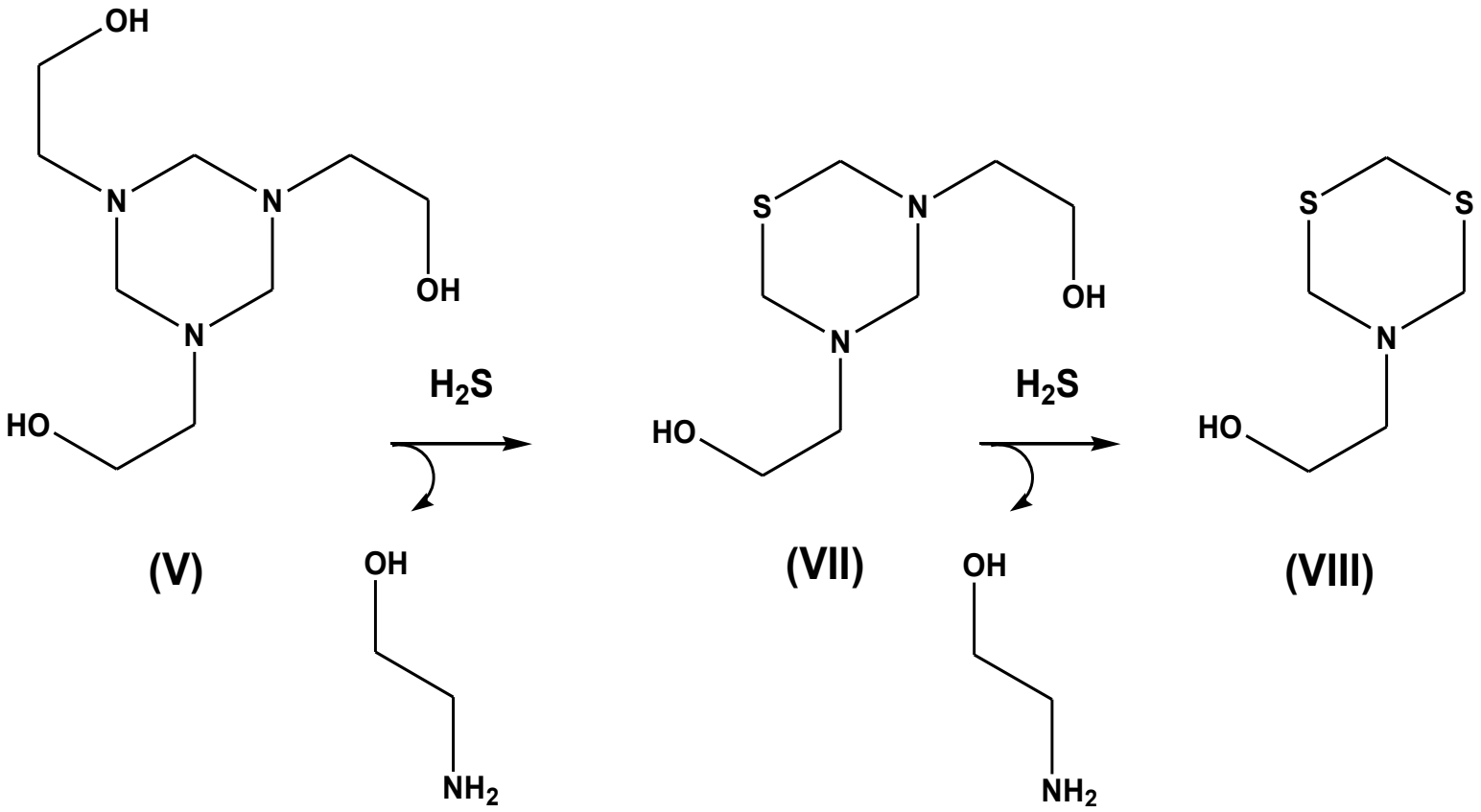
Hexahydrotriazine Reaction with Hydrogen Sulphide



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Mixed hexahydrotriazines

- Two types of mixed hexahydrotriazines
- ***Intra*** molecular mixture or ***Inter*** molecular mixture
- ***Intra*** molecular –
  - synthesis using a mixture of two premixed primary amines added to formalin
  - synthesis using a sequential addition of half equivalent of amine A followed by half equivalent of amine B
- ***Inter*** molecular – mixed two hexahydrotriazines synthesised independently from two primary amines
- Previously report study using methyl and hydroxyethyl mixed hexahydrotriazines using sequential method of addition[1]
- Regardless of how they are made all mixed hexahydrotriazines end up in the same place due to the formaldimine:hexahydrotriazine equilibrium

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1. Fast, High Capacity Hydrogen Sulfide Scavengers. Tauseef Salma; Alexander Lambert, III and Gordon Rivers. U.S. 7,438,877 21st, October 2008.

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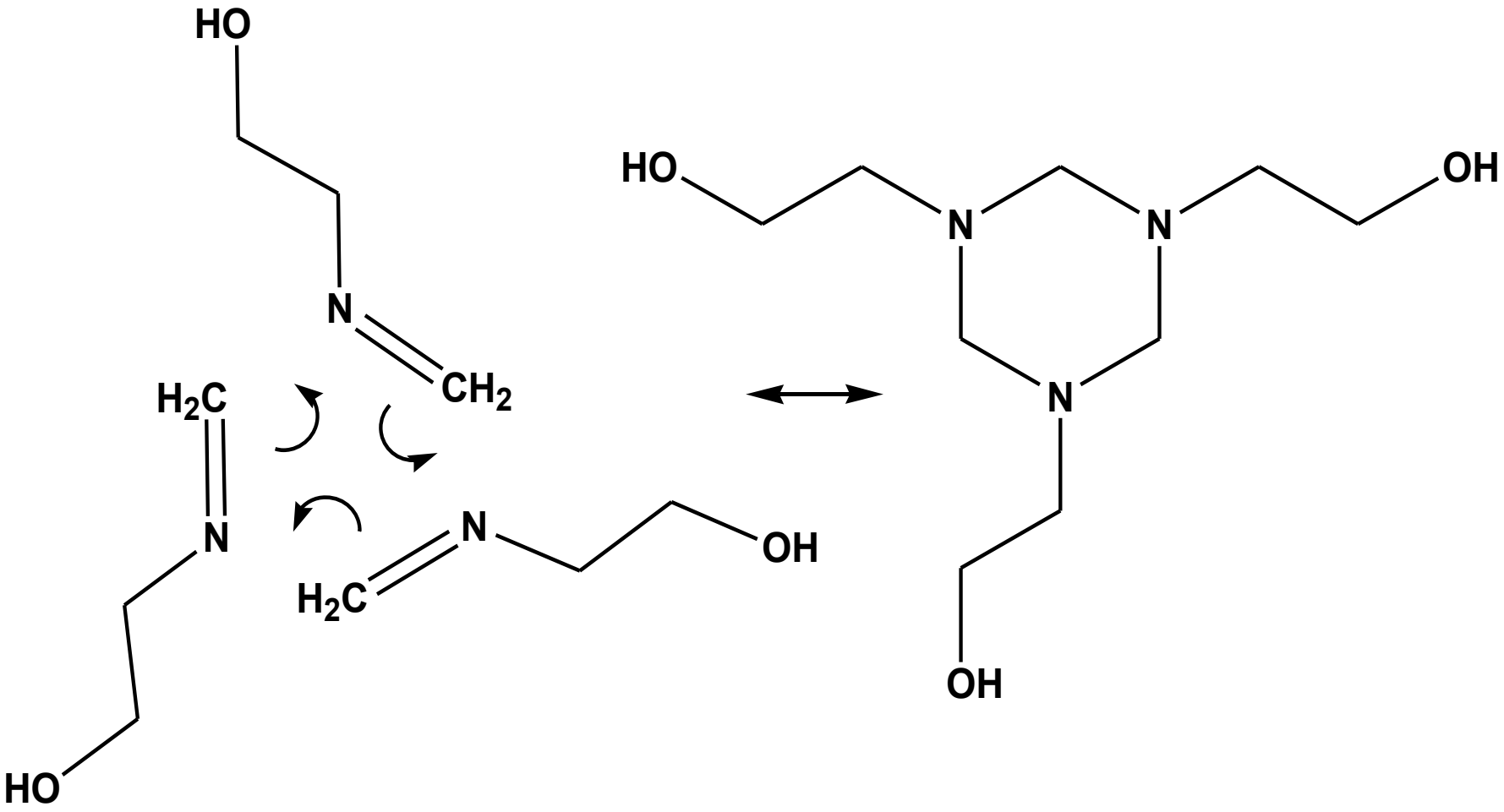
Formaldimine : Hexahydrotriazine Equilibrium



Synthesis - Primary amine and formaldehyde yield the formaldimine via an exothermic reaction. Cyclic trimerisation follows to hexahydrotriazines

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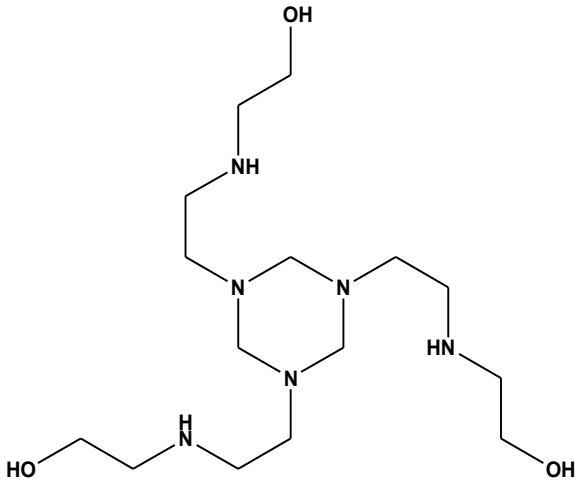
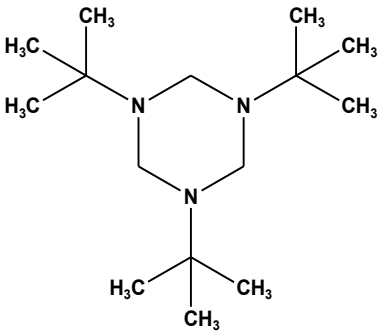
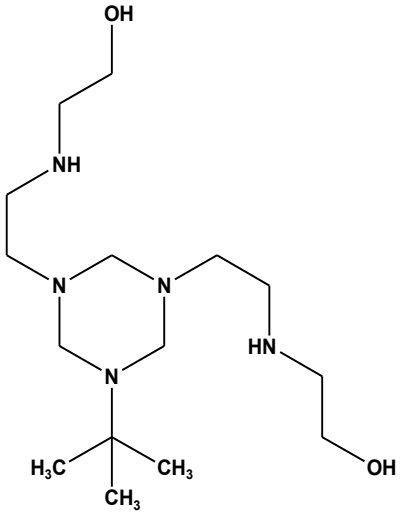
Mixed Hydrophilic and Hydrophobic hexahydrotriazines

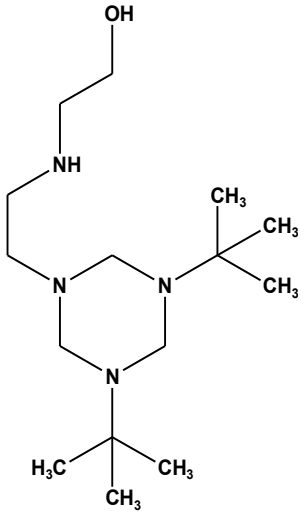


(IX)



(X)





- 2-Aminoethylethanolamine (AEE) and *tert*.Butyl amine were the chosen primary amines.
- 2-Aminoethylethanolamine hexahydrotriazine (IX) is fully water soluble.
- *Tert.* Butylamine hexahydrotriazine[2] (X) is immiscible in water.
- Mixed (50/50 mole %) hexahydrotriazine is also fully water soluble.

2. Method of treating Sour Gas and Liquid Hydrocarbon. Daniel S. Sullivan, III; Allan R. Thomas, Mark A. Edwards, Grahame N. Taylor, Paul Yon-Hin, Juan M. Garcia, III. U.S. Patent 5,674,377, October 7th 1997.

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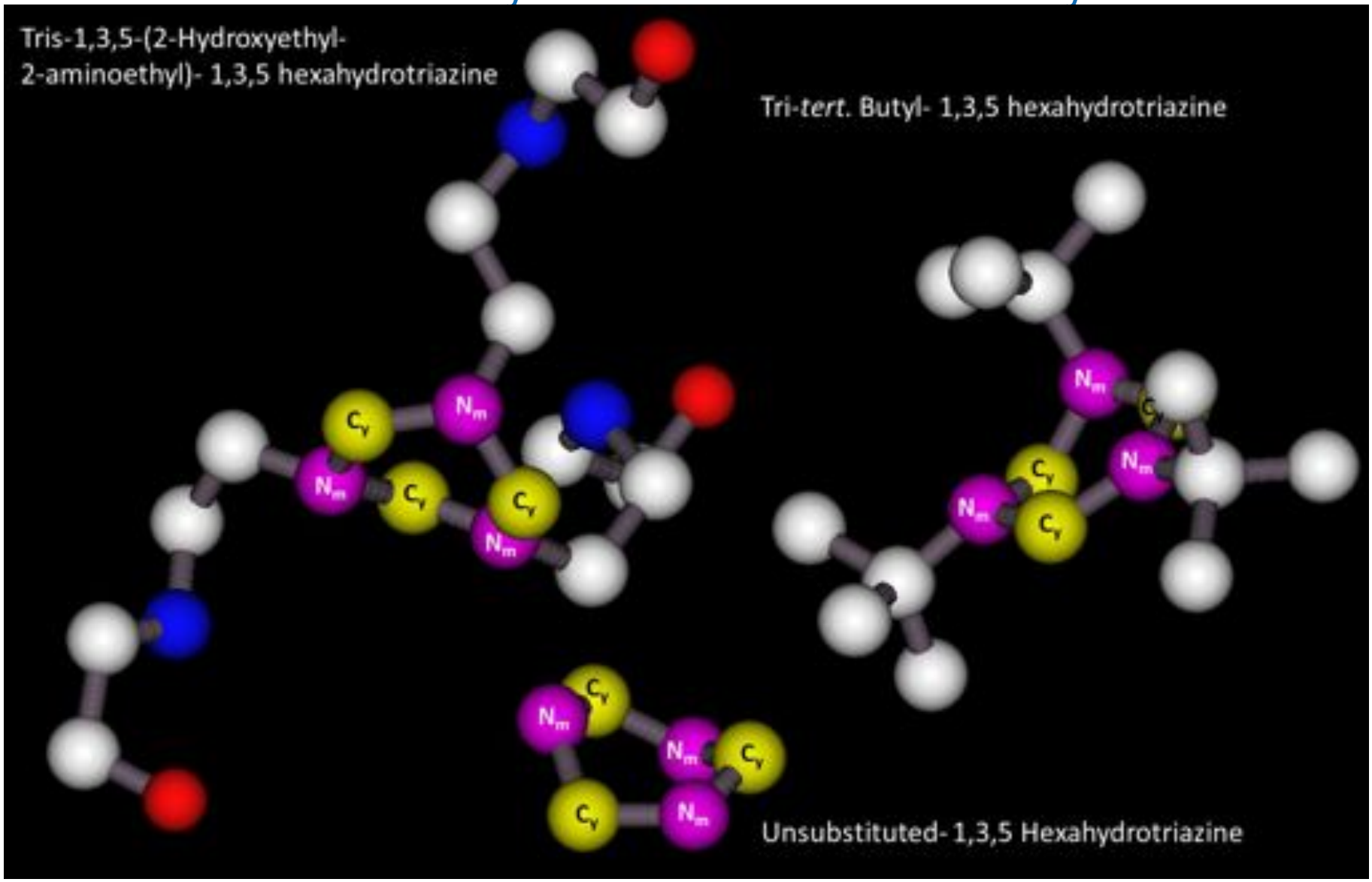
Tris hexahydrotriazine Stereochemistry



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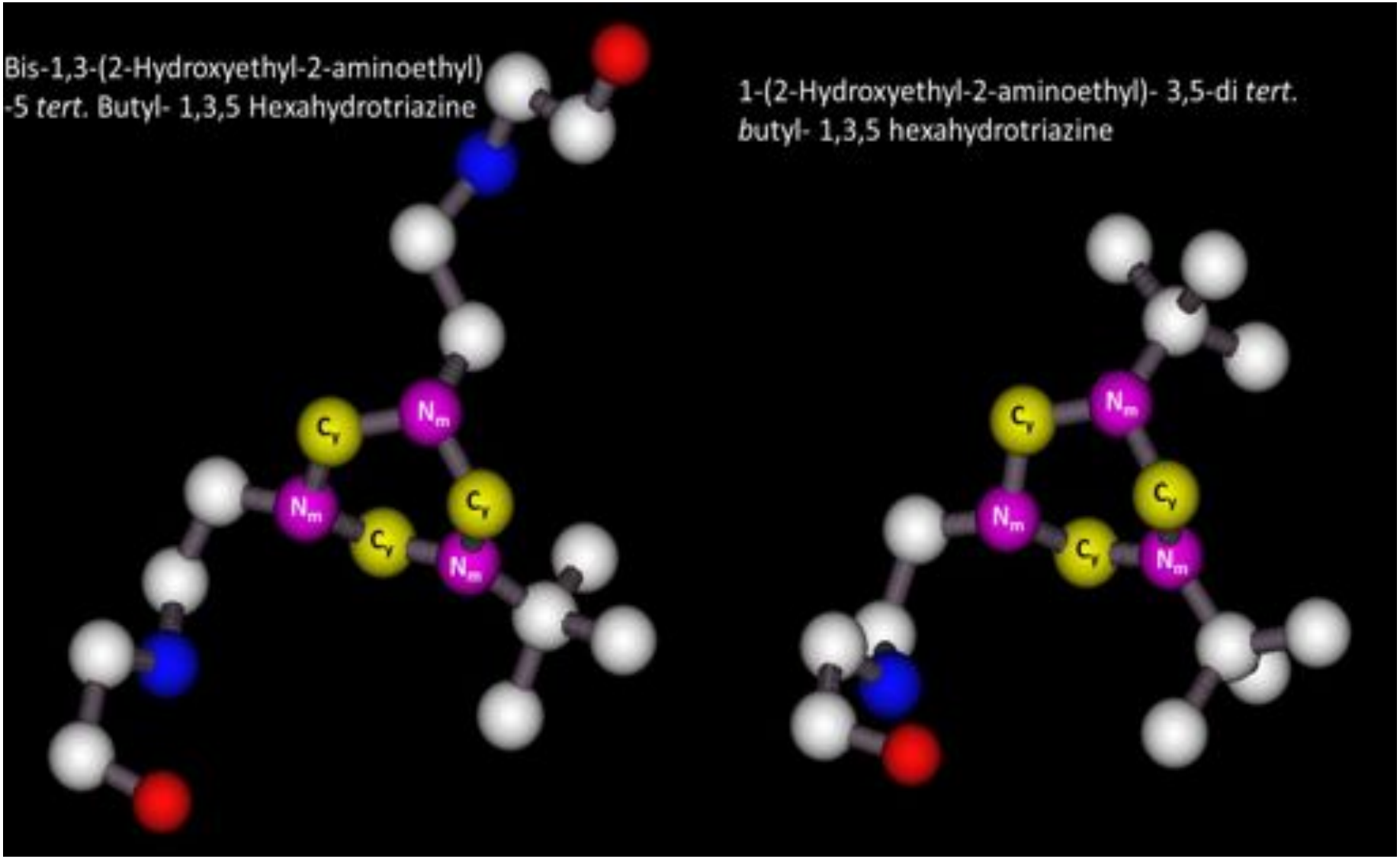
Mixed hexahydrotriazine Stereochemistry



Which amine substituent is retained in the dithiazine?

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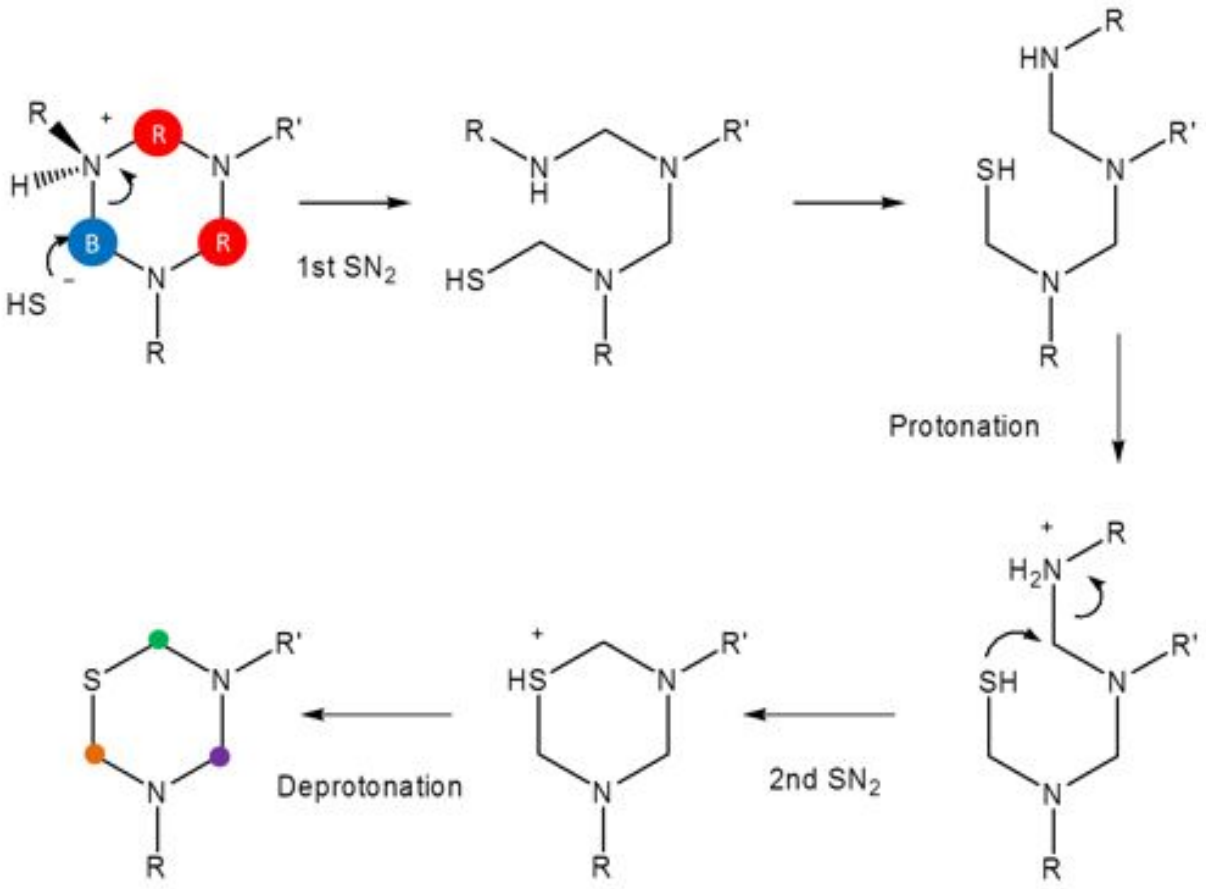
First double SN_2 reaction for hexahydrotriazine



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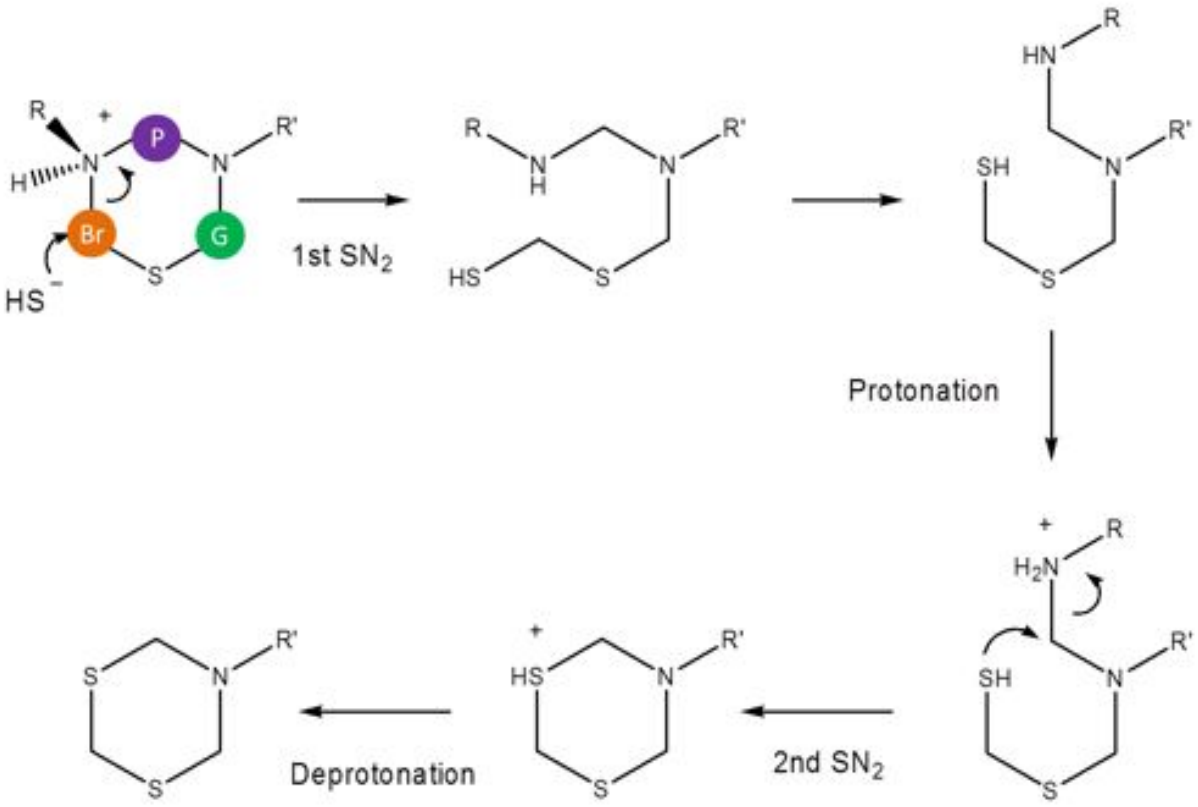
Second double SN_2 reaction for hexahydrotriazine



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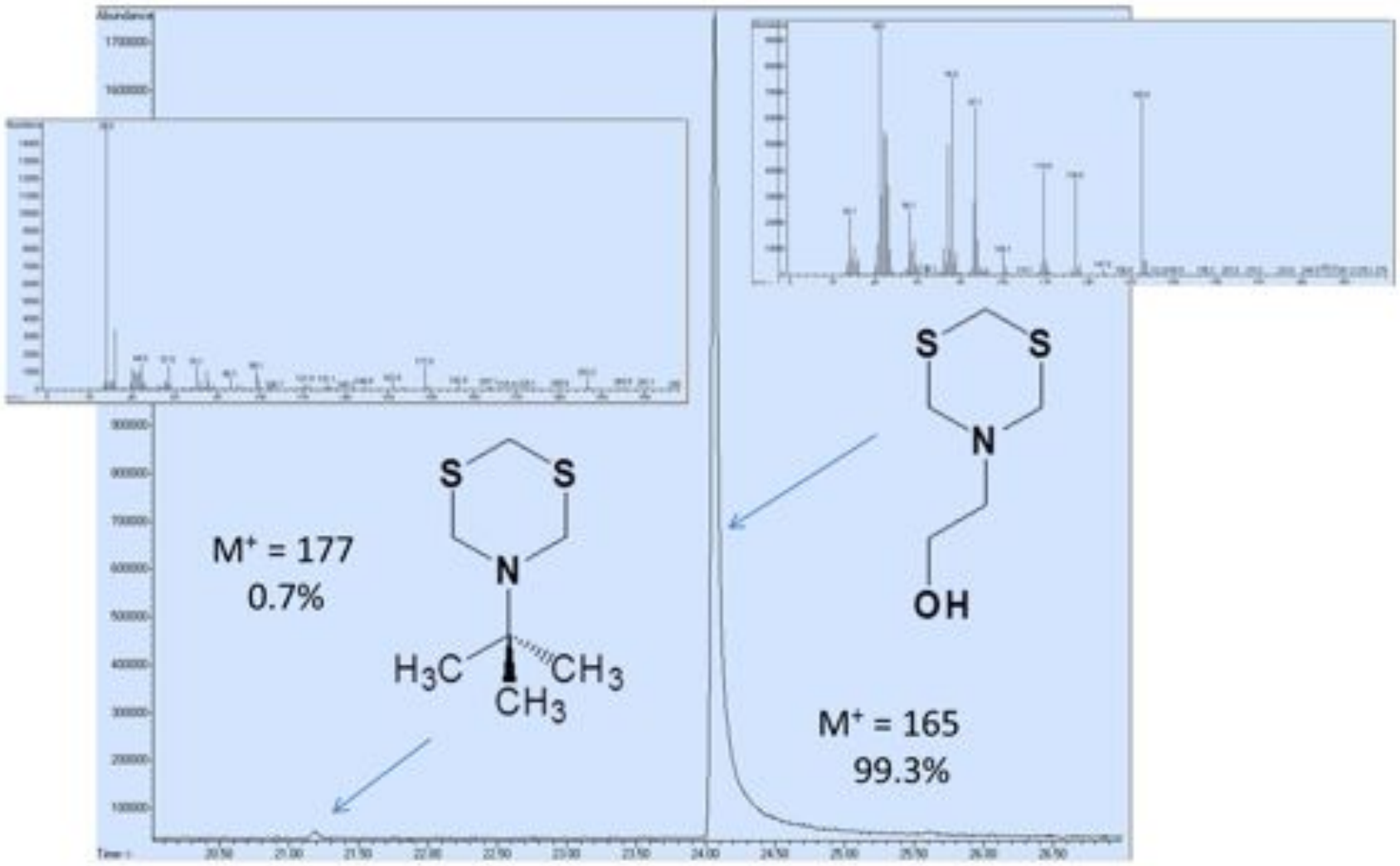
Dithiazine analysis for mixed ethanolamine plus tertiary butylamine hexahydrotriazine



pKa – *tert.* Butylamine = 10.68, Ethanolamine = 9.50

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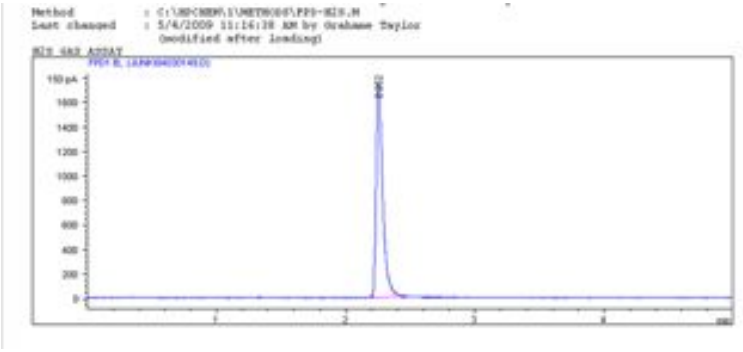
Gas Breakthrough Performance Determination

Gas sample GC using sulphur specific flame ionisation photometric multiplier detector.



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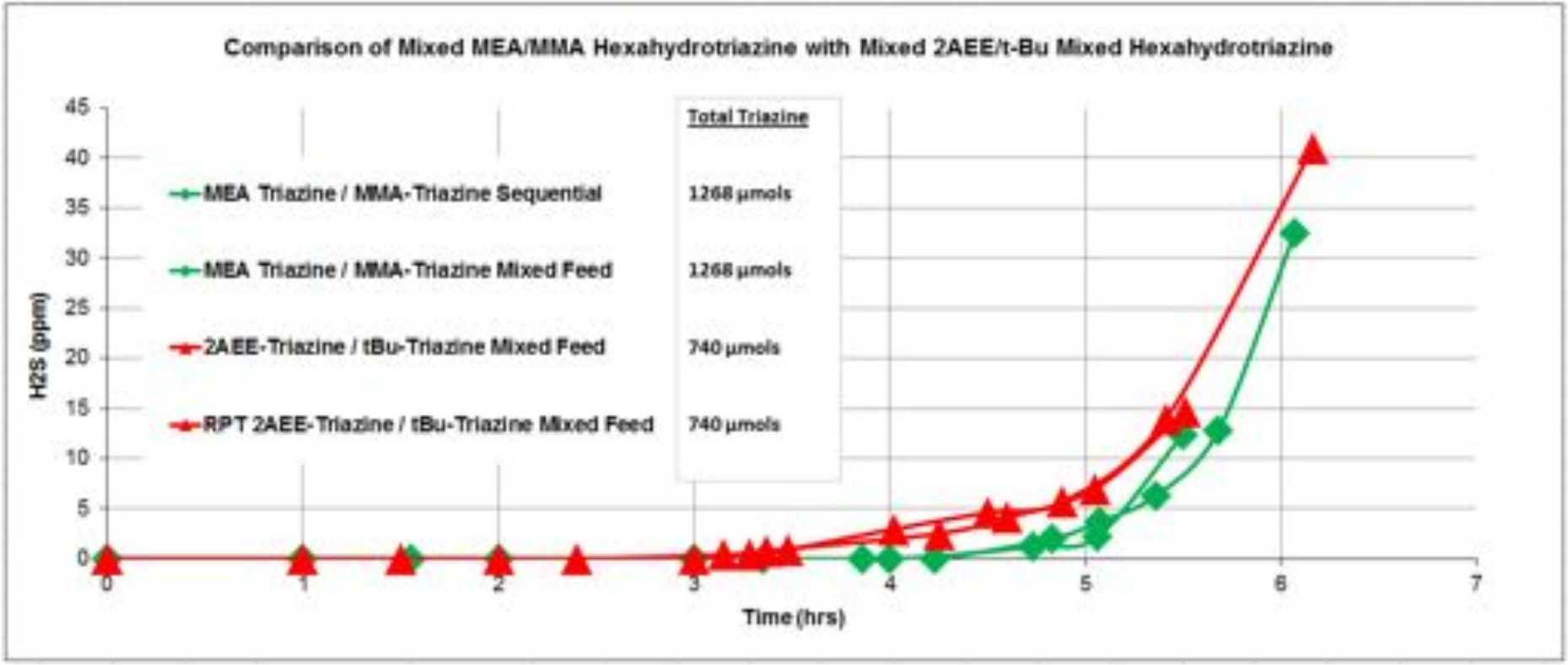
Gas Breakthrough Data



Ethanolamine plus methylamine combination product (green) shown at 1268 micromoles has the same performance as the 2-aminoethylethanolamine (AEE) plus tertiary butylamine hexahydrotriazine (red) at only 740 micromoles. The latter clearly has an advantage as a combination product from both hydrophilic and hydrophobic species.

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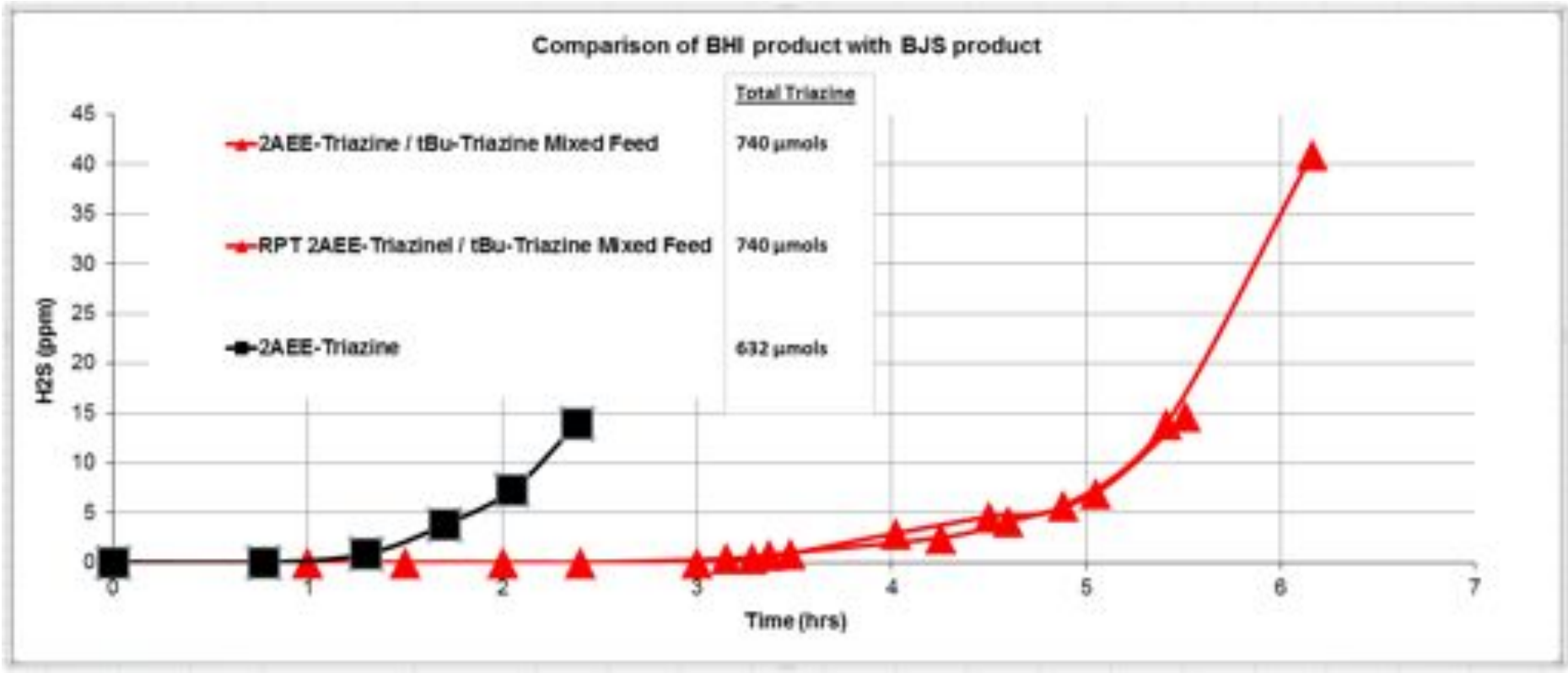
Gas Breakthrough Data



A comparison of 2-aminoethylethanolamine (AEE) plus tertiary butylamine hexahydrotriazine (red) at 740 micromoles has an enormously superior performance to 632 micromoles of 2-aminoethylethanolamine hexahydrotriazine alone (black), far more than could be attributed to the 17% increase in concentration.

This clearly indicates a synergistic interaction for the two dissimilar functional groups on the mixed hexahydrotriazines.

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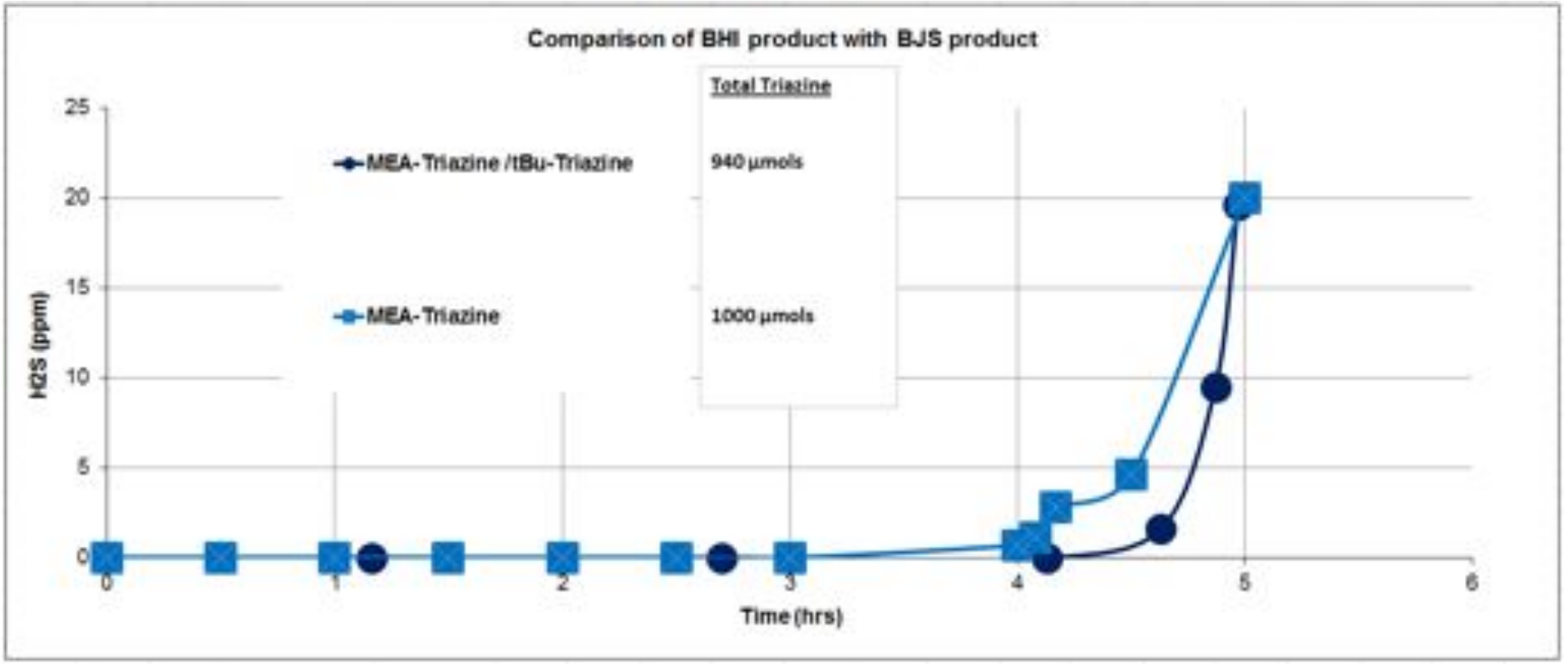
Gas Breakthrough Data



Ethanolamine plus tertiary butyl amine hexahydrotriazine at 940 micromoles (dark blue), was about the same performance as Tris-(2-hydroxyethyl) hexahydrotriazine (V) at 1000 micromoles (light blue).

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Conclusions

- The combination of two contrasting functional groups within a single hexahydrotriazine molecule is of considerable theoretical interest but it has also been demonstrated to have some clear performance benefits over the single hexahydrotriazine itself.

- There are also circumstances where, for example, an amine may have undesirable side effects, for example, ethanolamine. This is very problematic and causes huge corrosion issues in refineries.

- Any product which can give the same performance but reduce the ethanolamine burden on the incoming oil stream would certainly be of benefit.

- These products under consideration for commercialisation.

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Acknowledgements

- Baker Hughes for allowing the presentation of this material which is the subject of a recent US patent 8,734,637 B2.

- Royal Society of Chemistry and EOSCA for their kind invitation to present at this venue.

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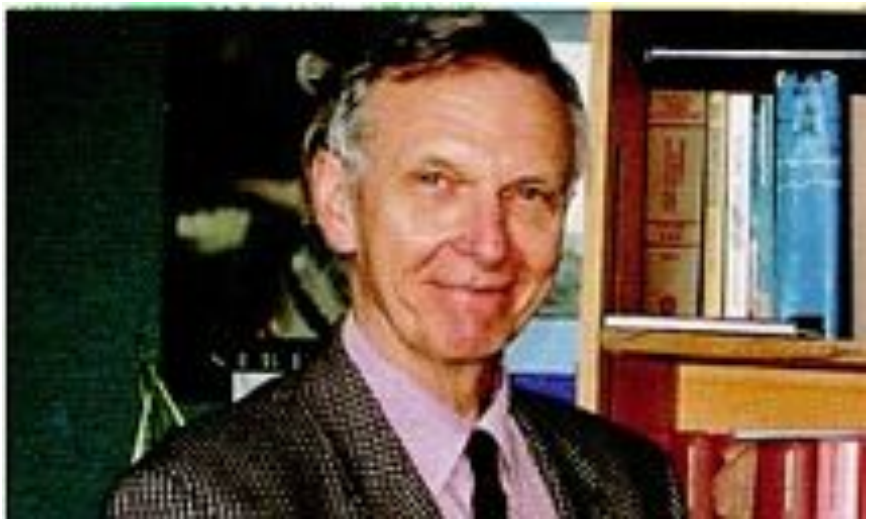
Acknowledgements



- Professor Andrew Gilbert - 1939-2014
- Emeritus Professor of Chemistry, University of Reading, UK

University of Reading

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