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Abstract:

A reanalysis of polyhedral oligomeric silsesquioxane ions and salts

Brent D. Viers, PRSM, Air Force Research Laboratory, 10 Saturn Blvd., Edwards AFB, CA 93524, Timothy S. Haddad, ERC and Air Force Research Laboratory, Edwards AFB, CA 93524, and Michael T. Bowers, Chemistry, U.C. Santa Barbara, Santa Barbara, CA 93106.

Polyhedral Oligomeric Silsesquioxanes (POSS) are of interest because the hydrolysis and condensation of the silane precursors can be controlled to form incompletely condensed "scaffolds" which can then be functionalized (via condensation) with differing moieties. However, conventional wisdom held that isolation of ionized scaffolds was impossible due to the increased reactivity of the ionic siloxy fragments. However, recent results have shown that certain POSS based salts are indeed stable. This talk will review the progress in formation of ionic species, and the potential of these intermediates for "rational synthesis" of other nanostructures.

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MEMORANDUM FOR PRS (In-House/Contractor Publication)

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05 Mar 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-VG-2003-⁰⁵³~~049~~
Brent D. Viers (AFRL/PRSM); Timothy Haddad (ERC); Capt. Rene I. Gonzalez (AFRL/PRSM),
~~"Structure and Modeling of POSS Monomers"~~ "A Reanalysis of POSS Ions & Salts"

American Chemical Society Conference
(New Orleans, LA, 23-27 Mar 2003) (Deadline: 27 Feb 2003 - PAST DUE)

(Statement A)

Viers
5416

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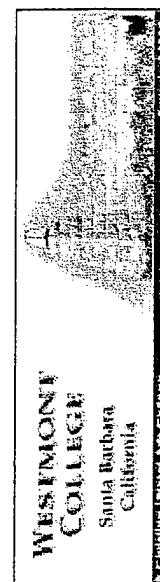
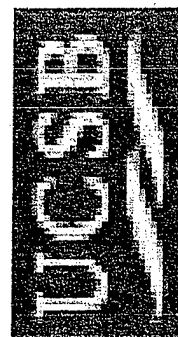
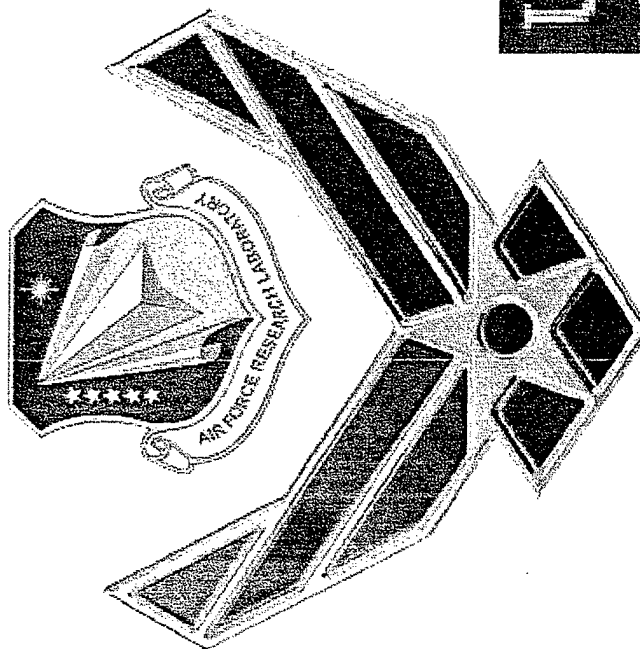
A reanalysis of polyhedral oligomeric silsesquioxane ions and salts

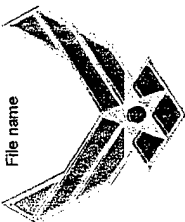
Brent D. Viers; Tim Haddad; Rusty Blanski;
Rene Gonzalez

Air Force Research Laboratory, Propulsion
Materials AFRL/PRSM

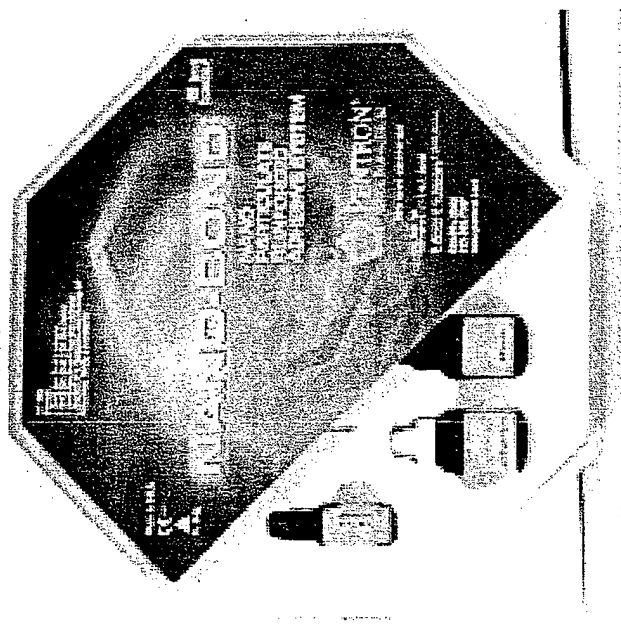
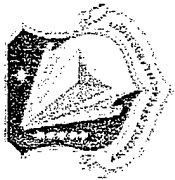
Erin Baker, Jennifer Gidden, Michael
Bowers, †Stan Anderson
Department of Chemistry

University of California Santa Barbara and
†Westmont College

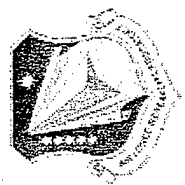
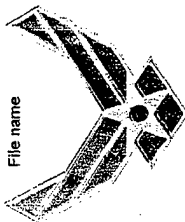




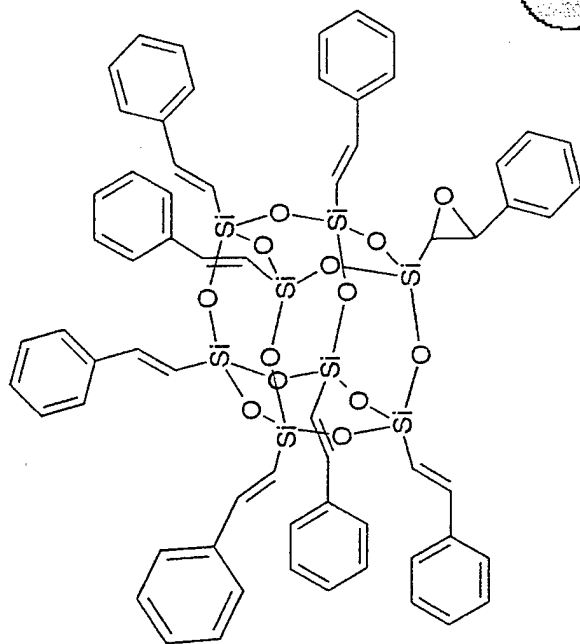
Commercial Success



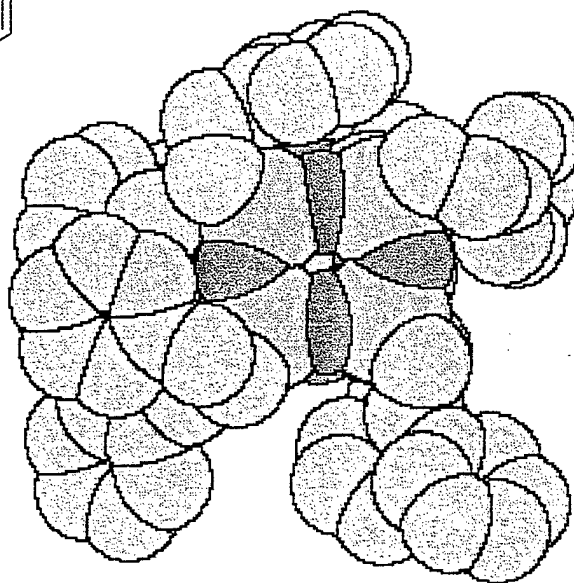
*POSS incorporation leads
to reduced shrinkage upon
cure?*



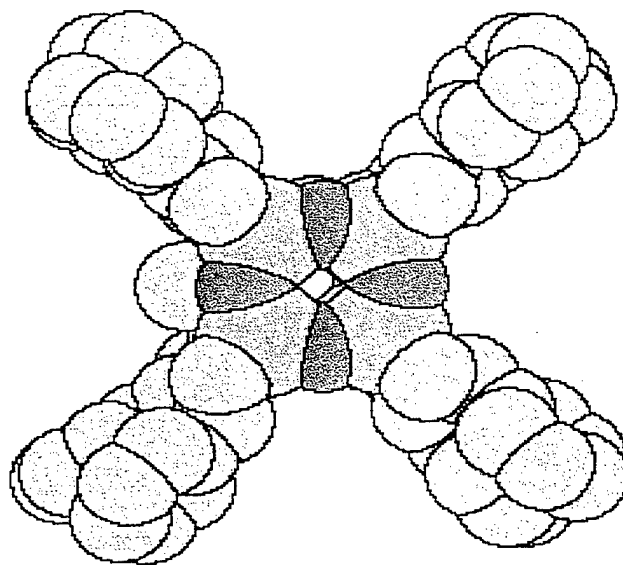
POSSible Structures



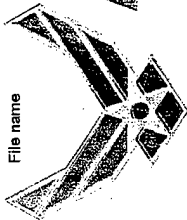
*Epoxy POSS
Intermediate in
Size?*



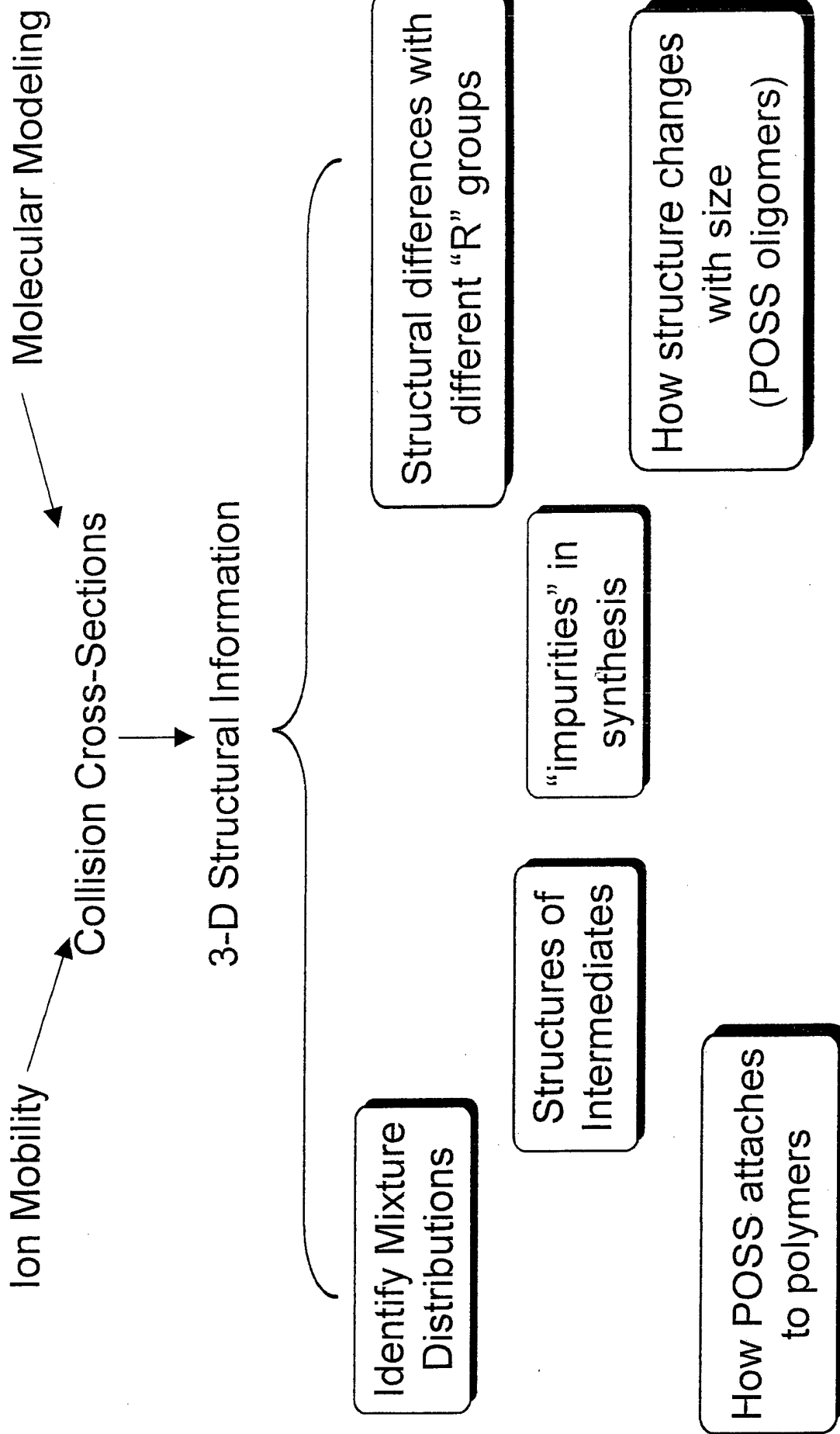
$\text{Na}^+\text{PhenEt}_8\text{T}_8$

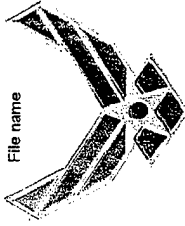


$\text{Na}^+\text{Sty}_8\text{T}_8$

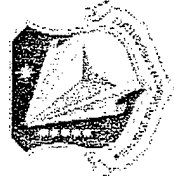


Application Of Ion Mobility Measurements





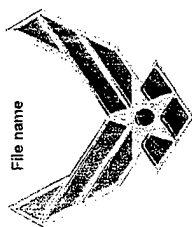
Modifications needed for POSS Modeling



- New parameters for all Si bonds, angles, dihedrals, and torsions (adapted from Si and Si-X parameters obtained from polysiloxane work).

Ref: H.Sun and D. Rigby, *Spectrochimica Acta A*, 1997, 53, 1301.

- Atom charges obtained from Gaussian calculations on model systems and x-ray structures; adjusted using AMBER RESP protocol.
- Starting structures built in Hyperchem and imported into AMBER.



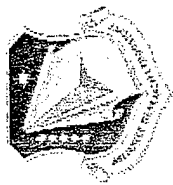
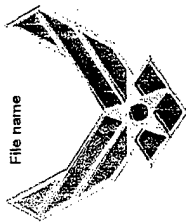
Comparison of Sizes: PhenEt₈T₈ to Sty₈T₈



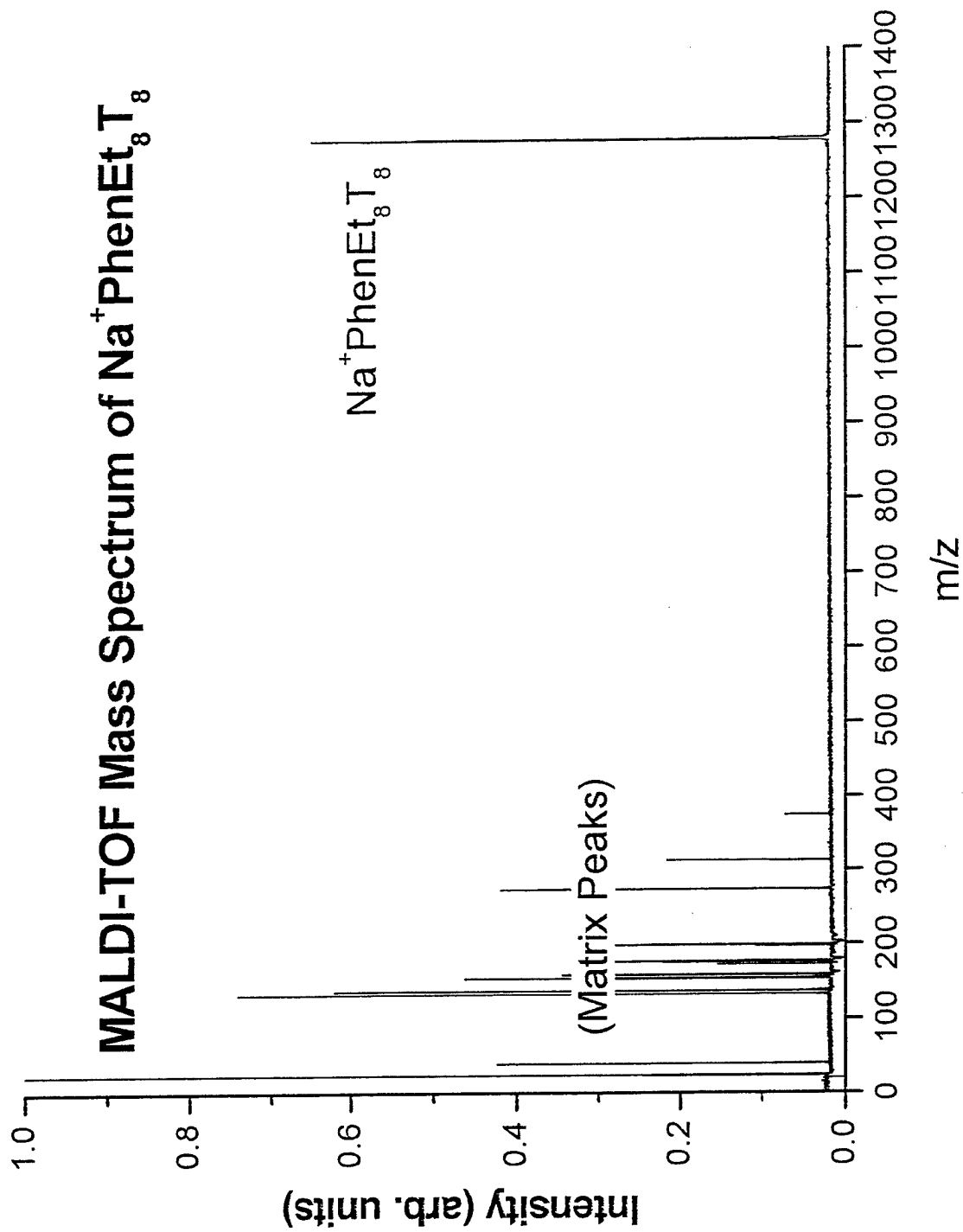
	x-ray	ESI	MALDI	Theory
Na ⁺ Sty ₈ T ₈	341	339	346 ^{a)}	338
Na ⁺ PhenEt ₈ T ₈			267	265 ^{b)}

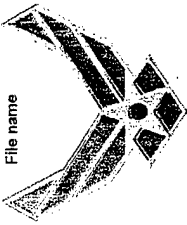
a) most abundant peak

b) from scatter plot – average value of lowest 7 kcal/mol structures

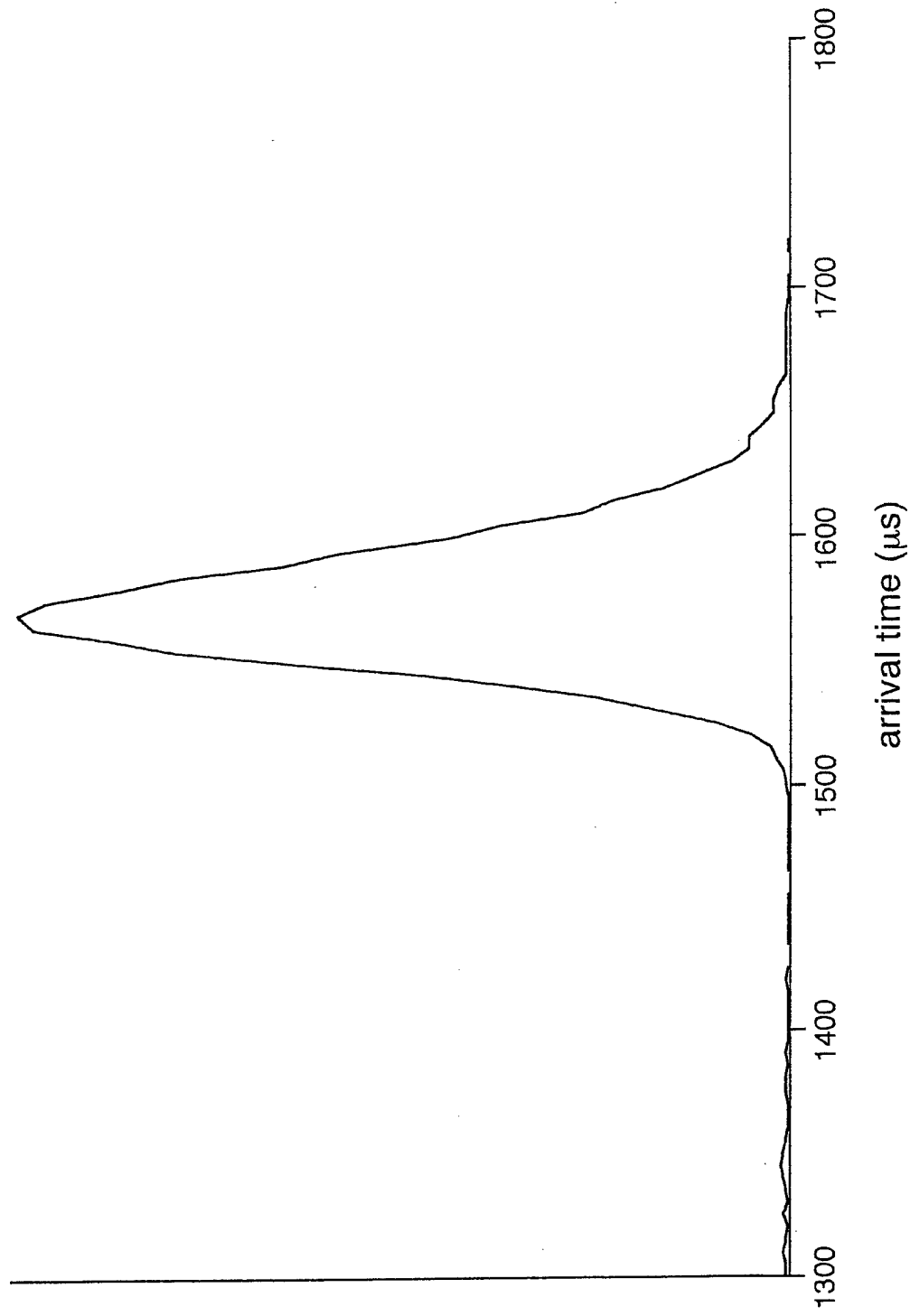
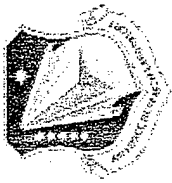


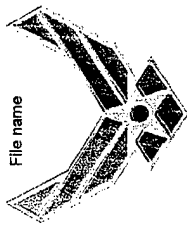
MALDI TOF of $\text{Na}^+\text{PhenEt}_8\text{T}_8$



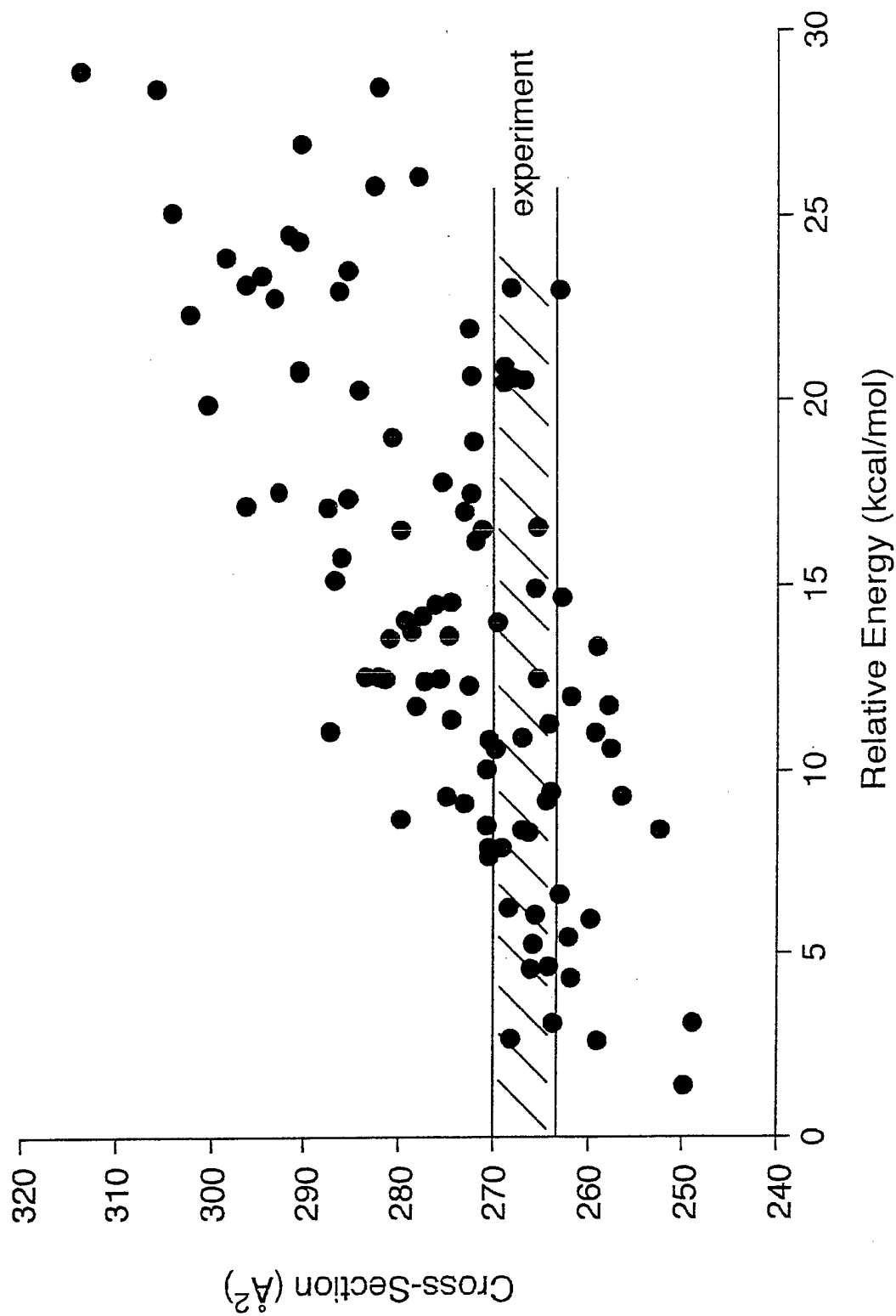


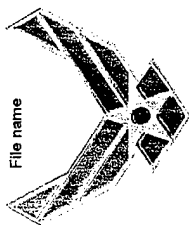
Na⁺PhenEt₈T₈ ATD





Energetic Calculations

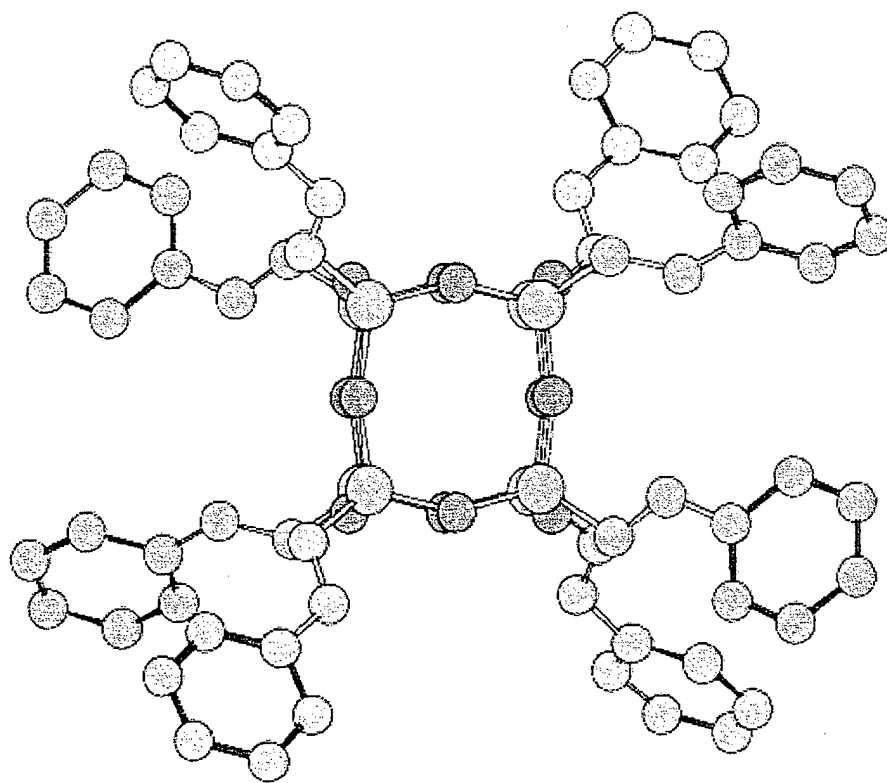




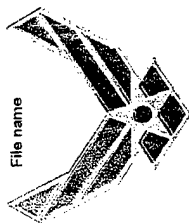
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X-ray Structure of Sty₈T₈

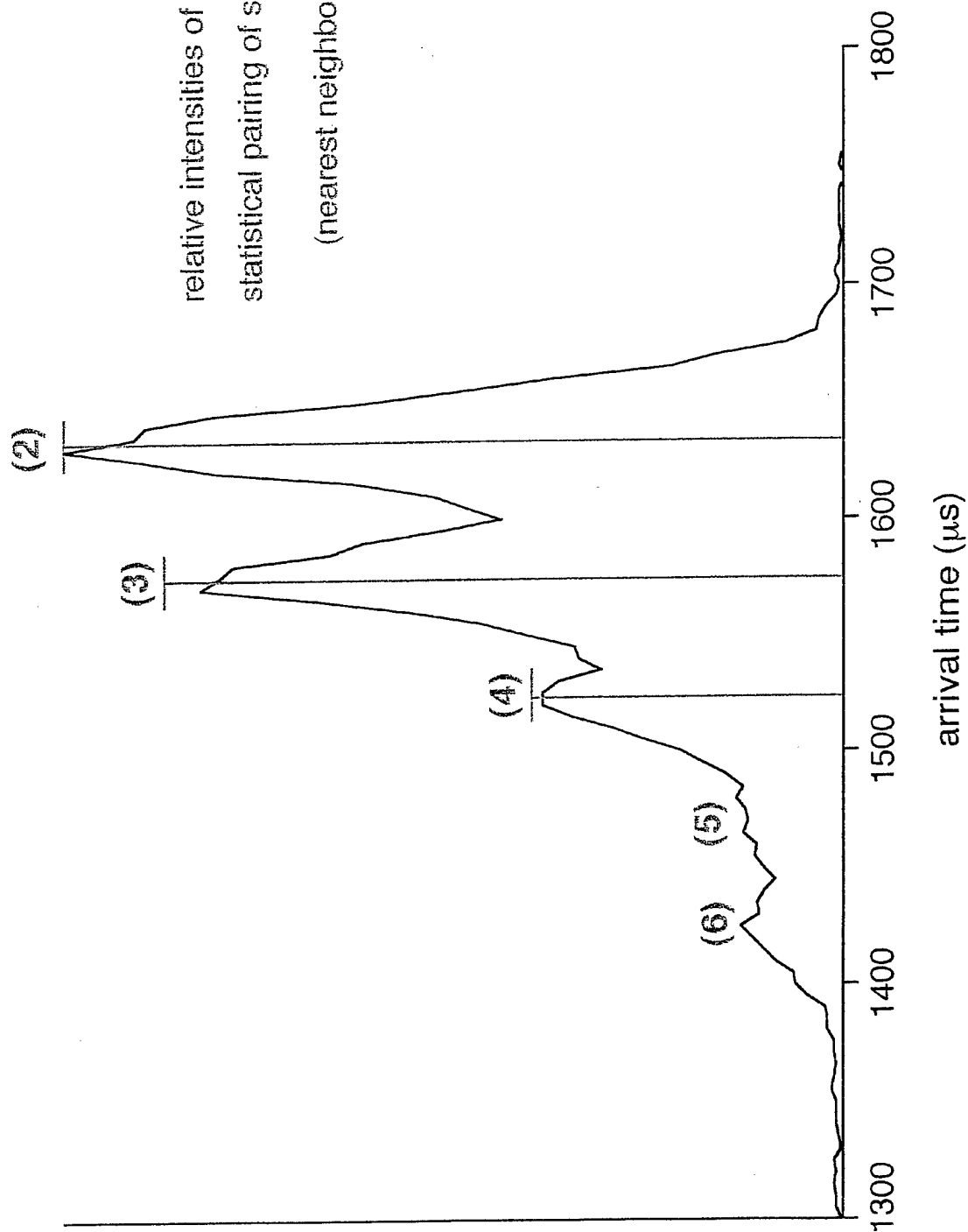


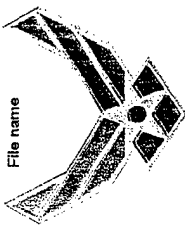
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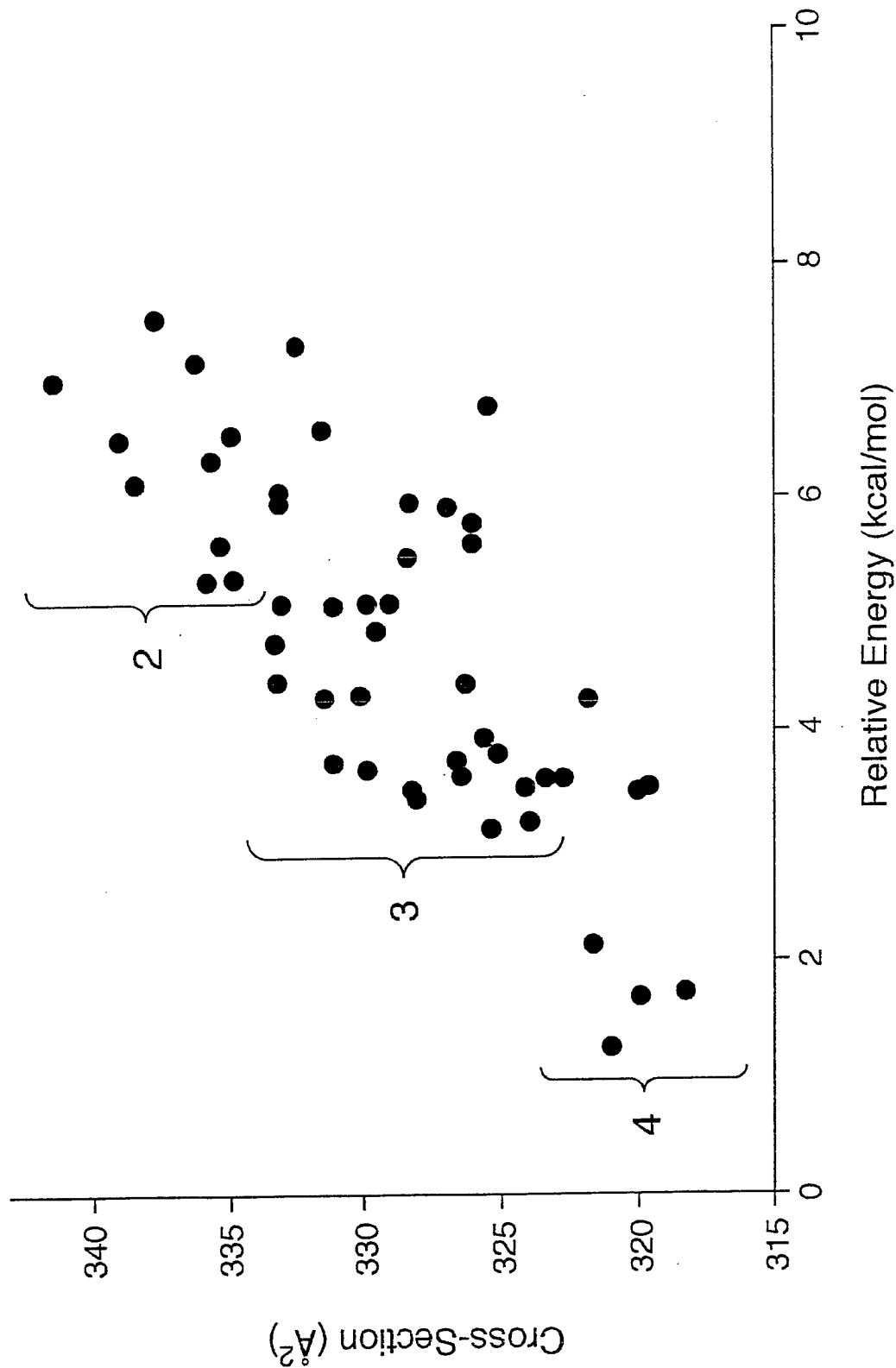
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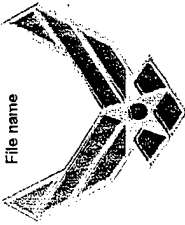
MALDI TOF of $\text{Na}^+\text{Sty}_8\text{T}_8$



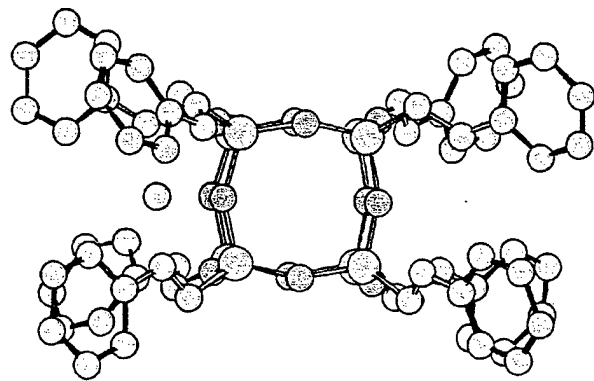


Energetic Calculations





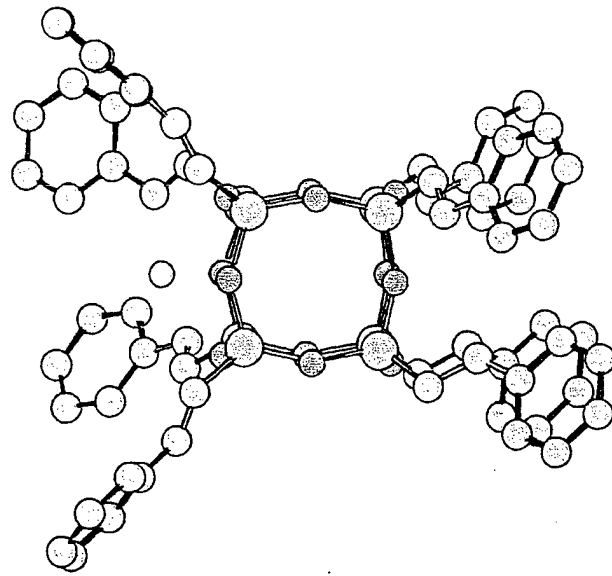
Calculated $\text{Na}^+\text{Sty}_8\text{T}_8$ Structures



(4)

320 Å²

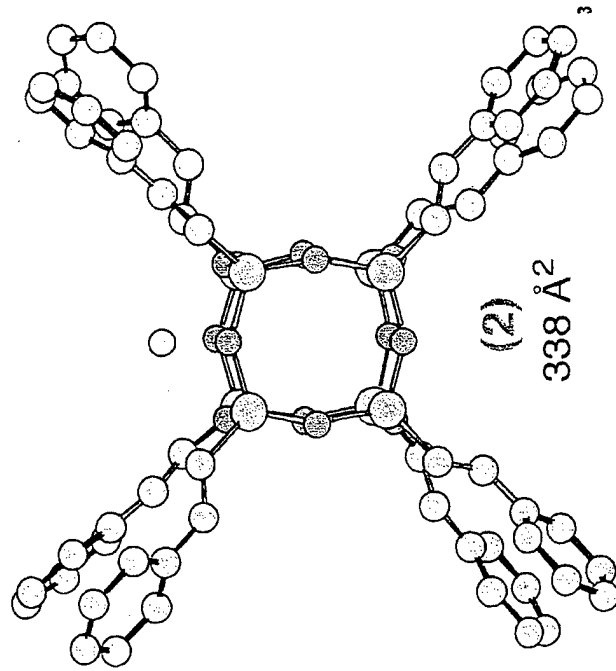
4 pair



(3)

328 Å²

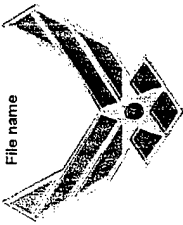
3 pair



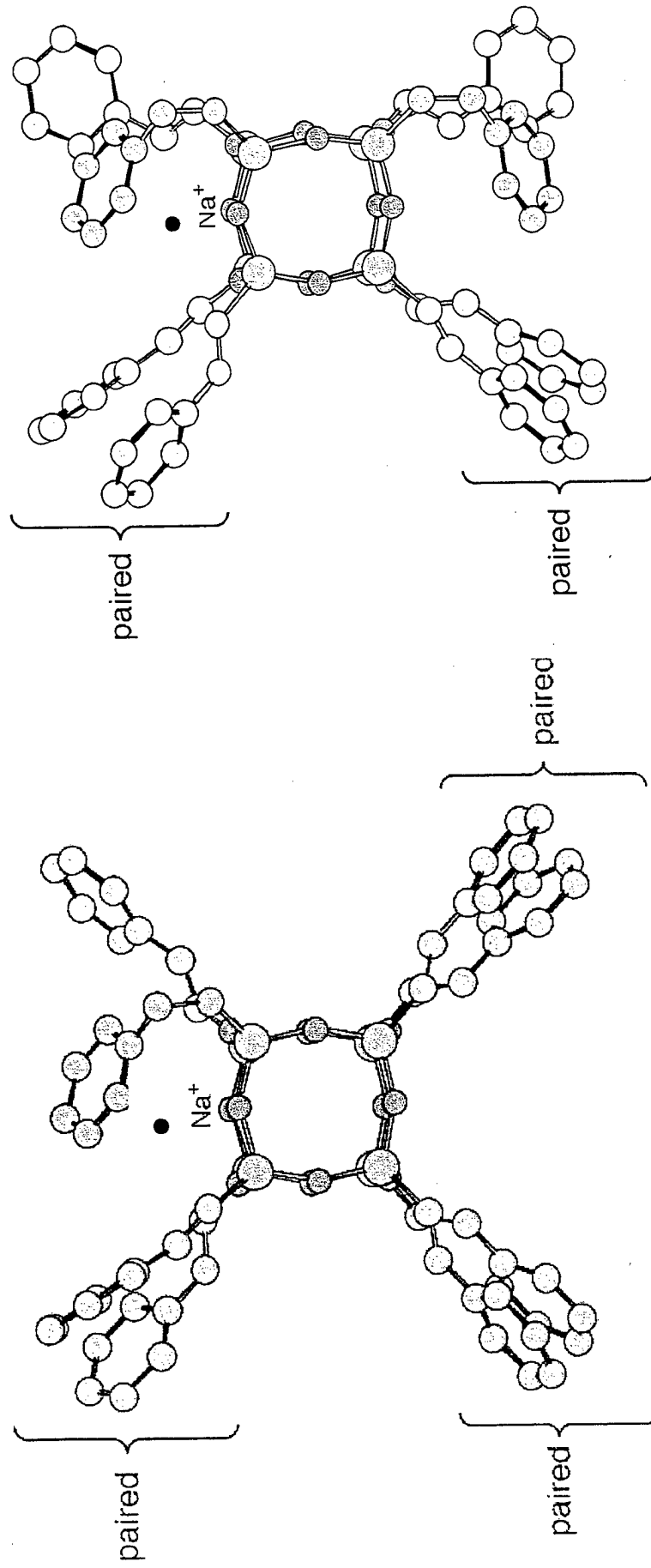
(2)

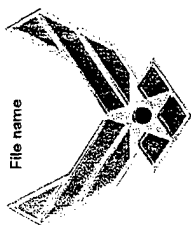
338 Å²

2 pair

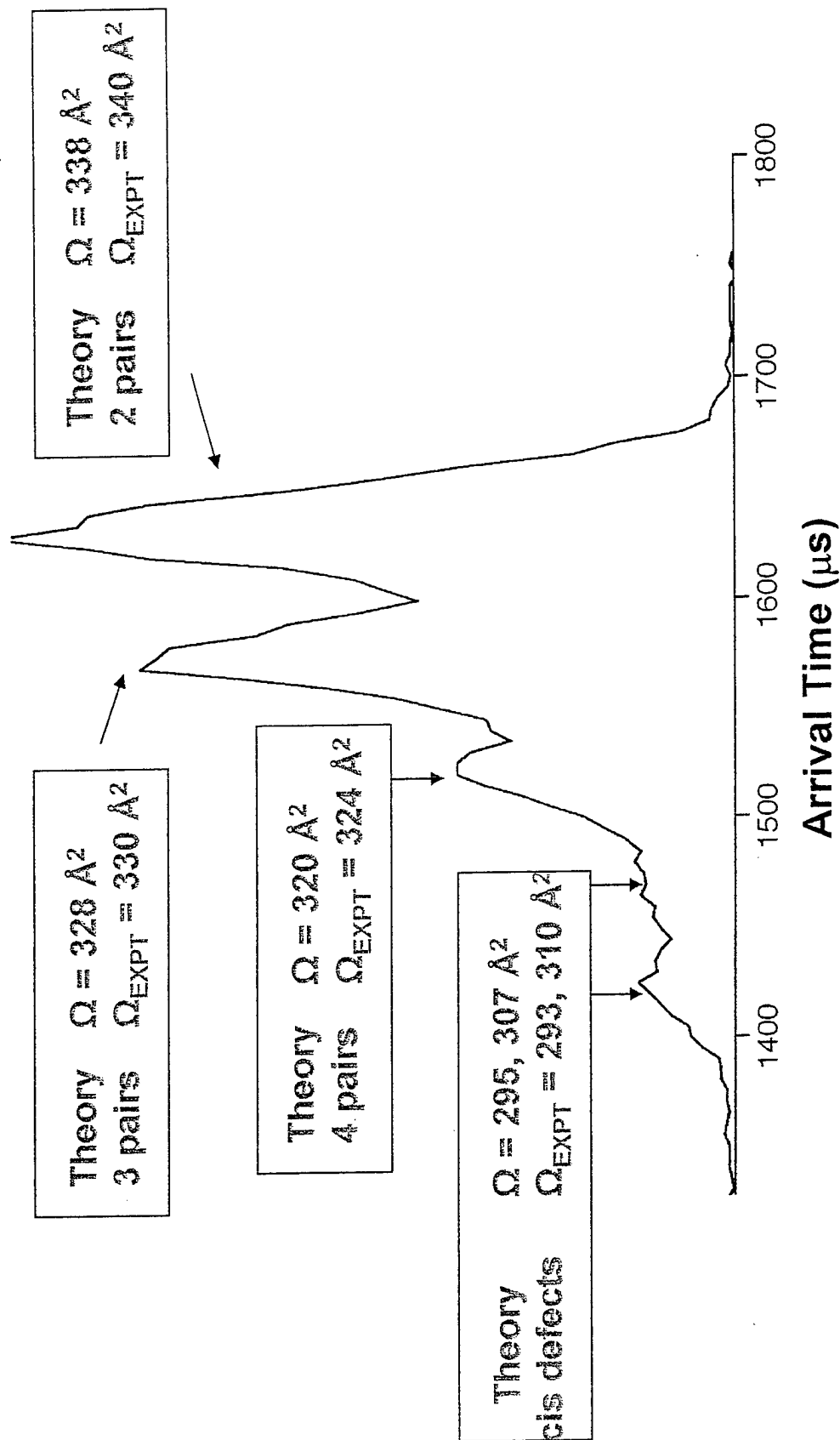
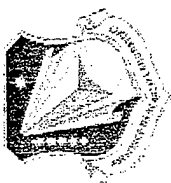


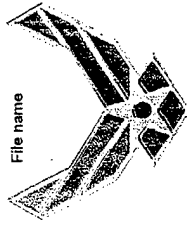
Sty₈T₈ Cis Defect Structures



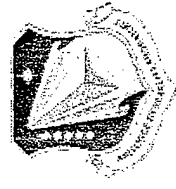


Comparison of Theoretical and Experimental Cross-sections

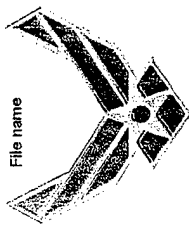




Summary for Sty₈T₈



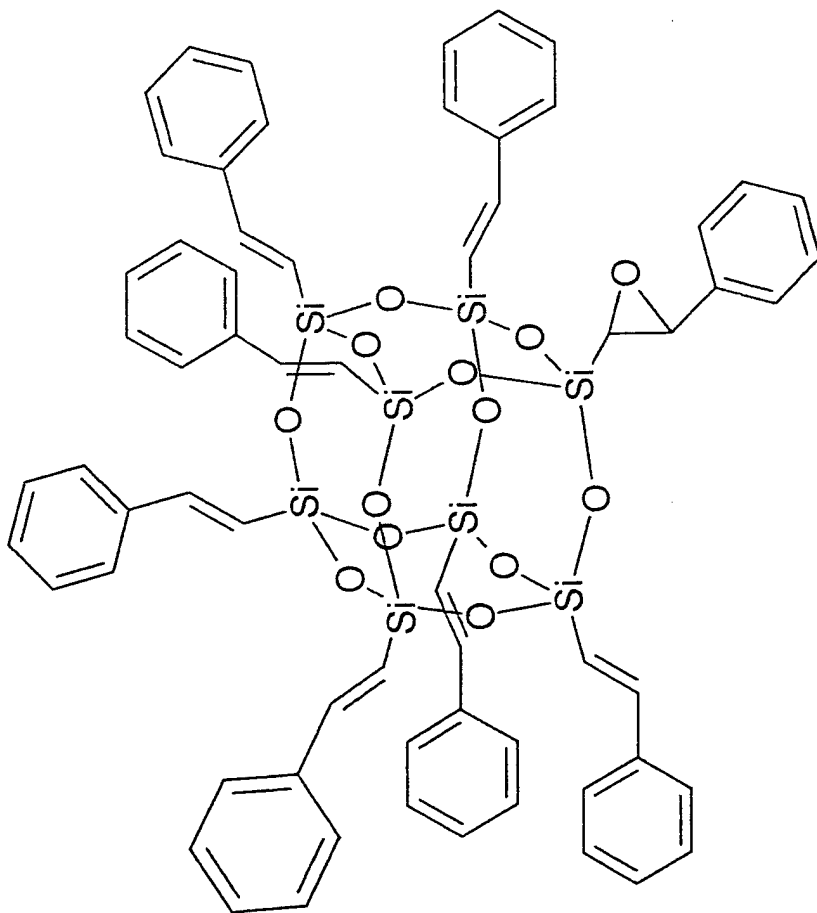
- Most compact structure (lowest σ) is the most stable
- Least compact structures are most abundant
- Quantitative agreement of experimental and theoretical σ 's
- MALDI intensities in semi-quantitative agreement with statistical pairing of phenyl groups
- X-ray structure quantitatively agrees with least compact structure

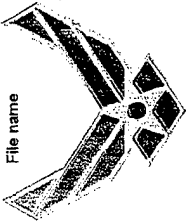


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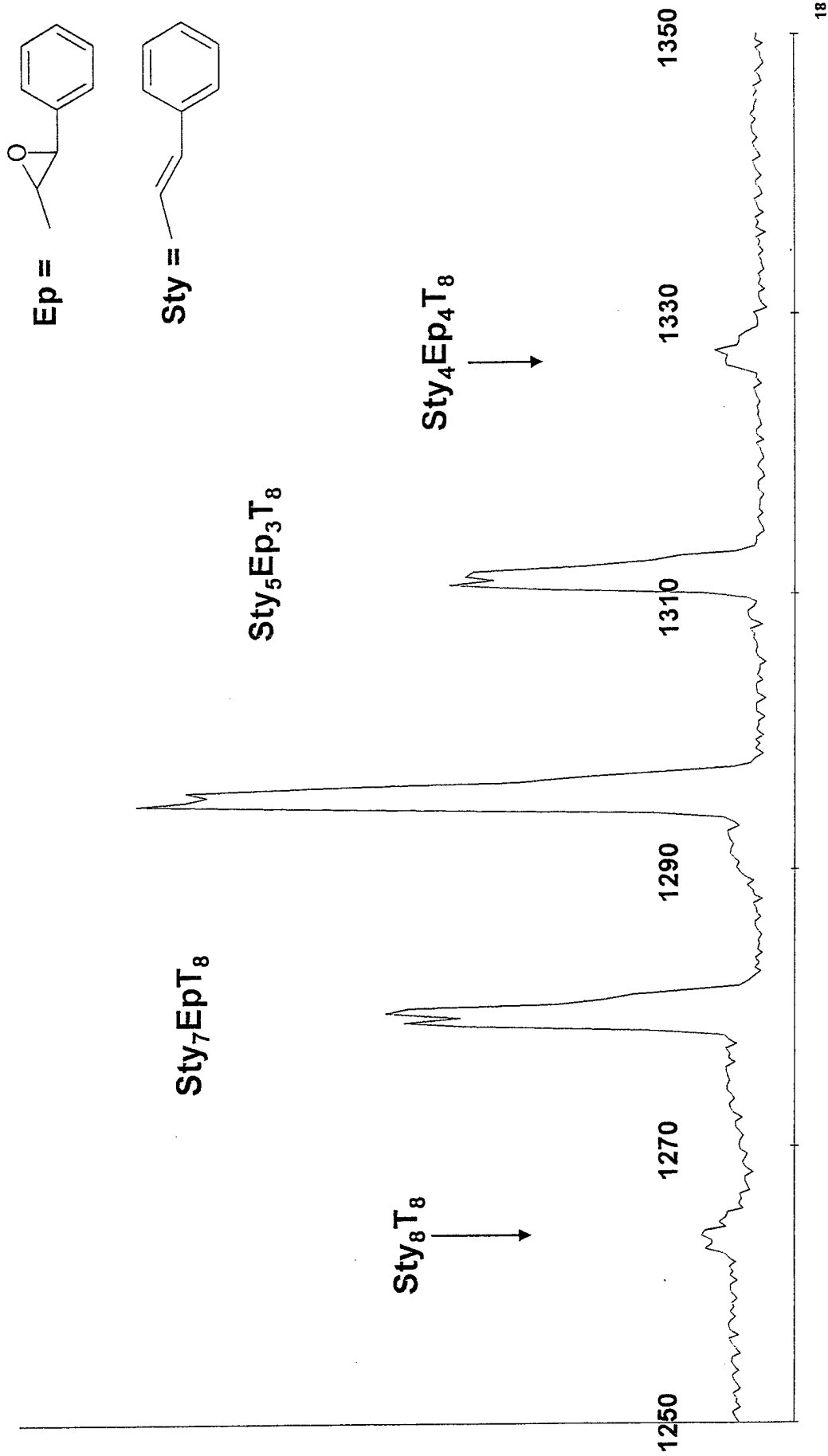
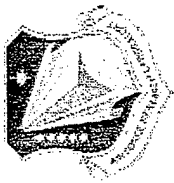


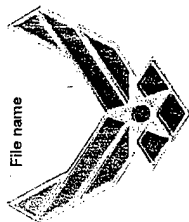
Sty₇-Ept₈





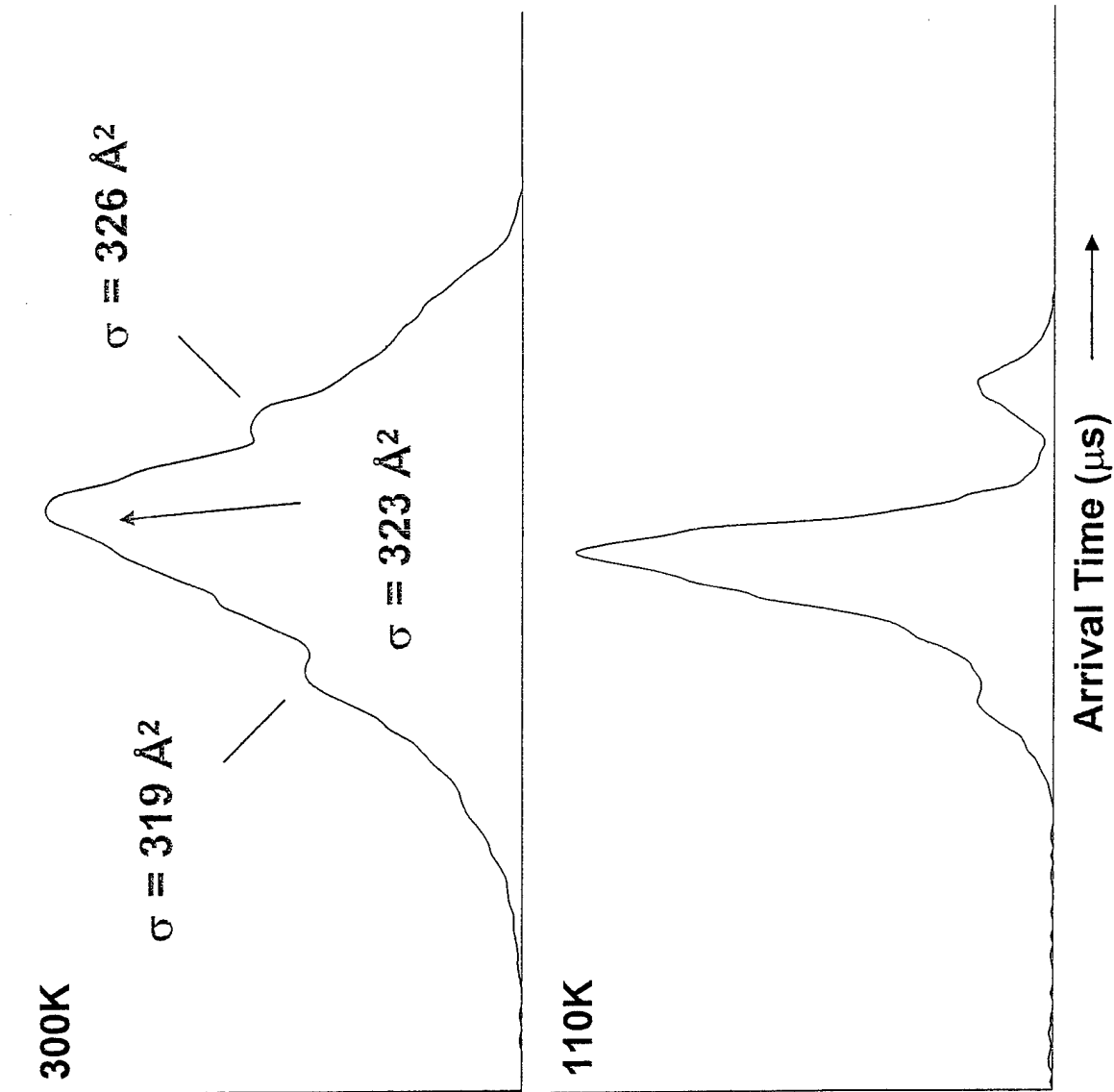
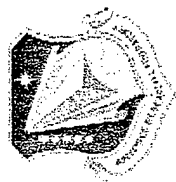
Styrene Epoxy T₈ POSS System Mass Spectrum

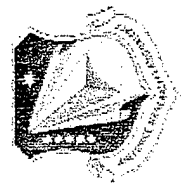
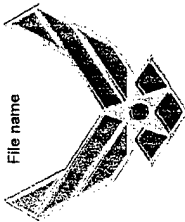




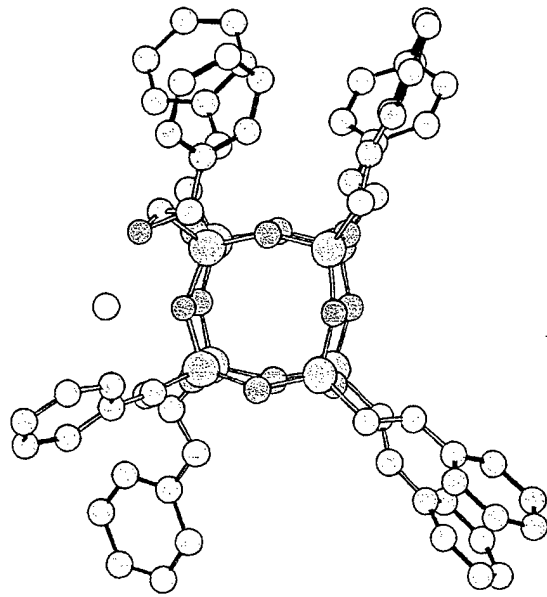
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$\text{Na}^+\text{Sty}_7\text{EpT}_8$ ATDs





Na⁺Sty₇Ept₈ Theoretical Structures

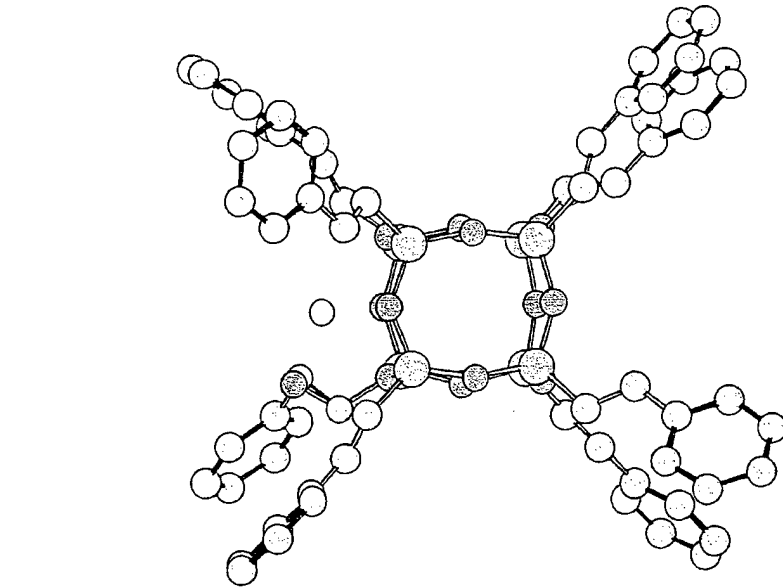


2 Pairs

$$\sigma_{\text{Theory}} = 320 \text{ \AA}^2$$

$$\sigma_{\text{EXPT}} = 319 \text{ \AA}^2$$

~13%

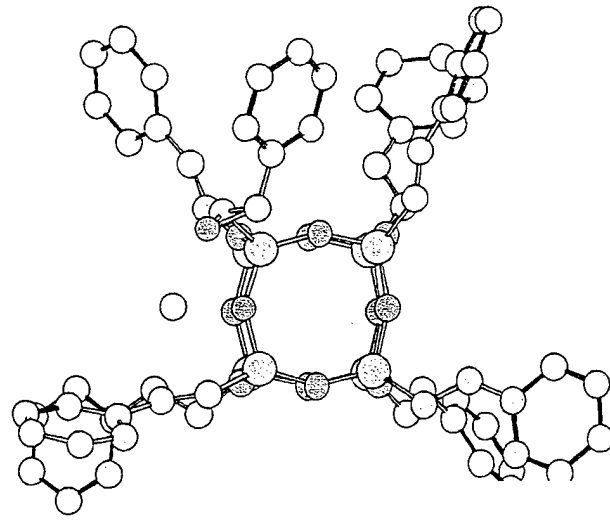


No Pairs

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~13%

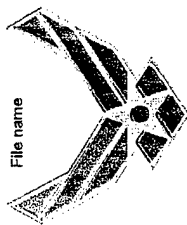


1 Pair

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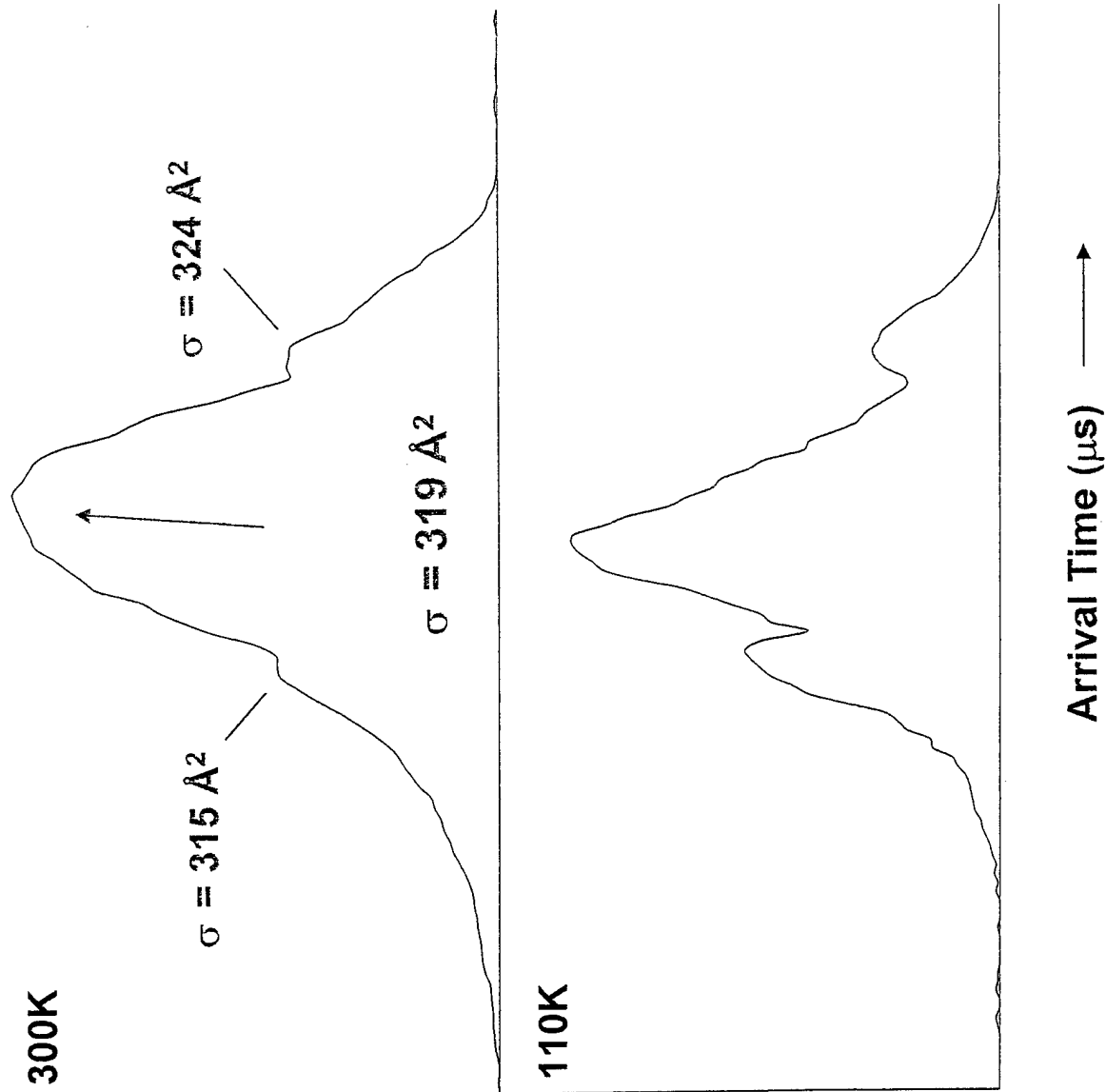
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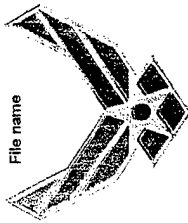
~74%



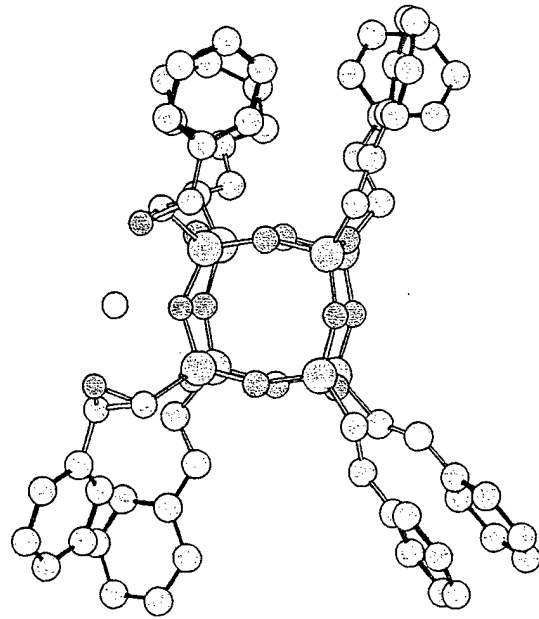
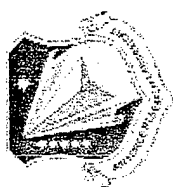
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$\text{Na}^+\text{Sty}_6\text{Ep}_2\text{T}_8$ ATDs





$\text{Na}^+\text{Sty}_6\text{Ep}_2\text{T}_8$ Theoretical Structures

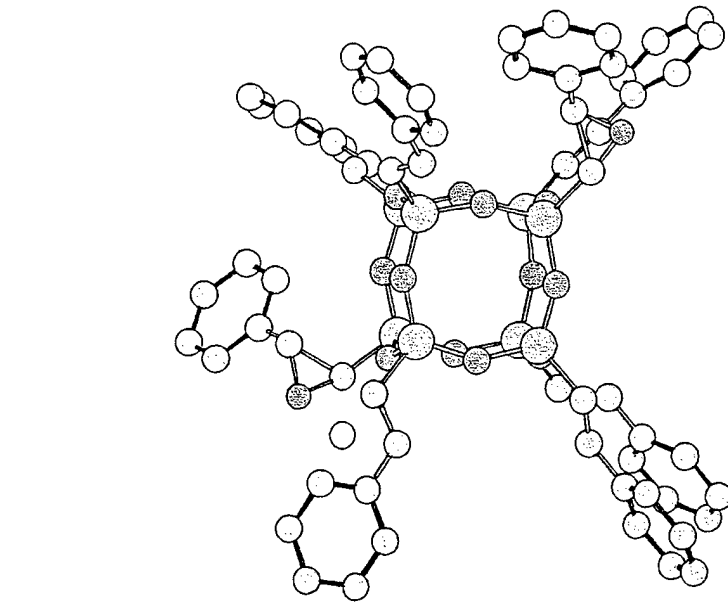


edge

$$\sigma_{\text{Theory}} = 314 \text{ \AA}^2$$

$$\sigma_{\text{EXPT}} = 315 \text{ \AA}^2$$

~22%

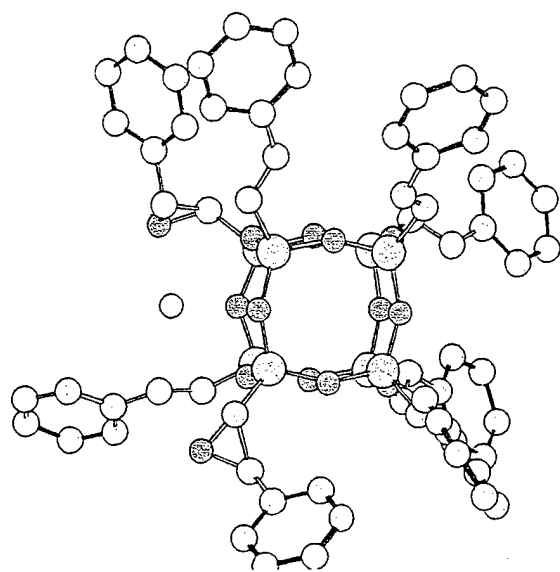


cube diagonal

$$\sigma_{\text{Theory}} = 322 \text{ \AA}^2$$

$$\sigma_{\text{EXPT}} = 324 \text{ \AA}^2$$

~12%

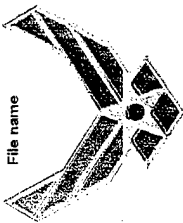


face diagonal

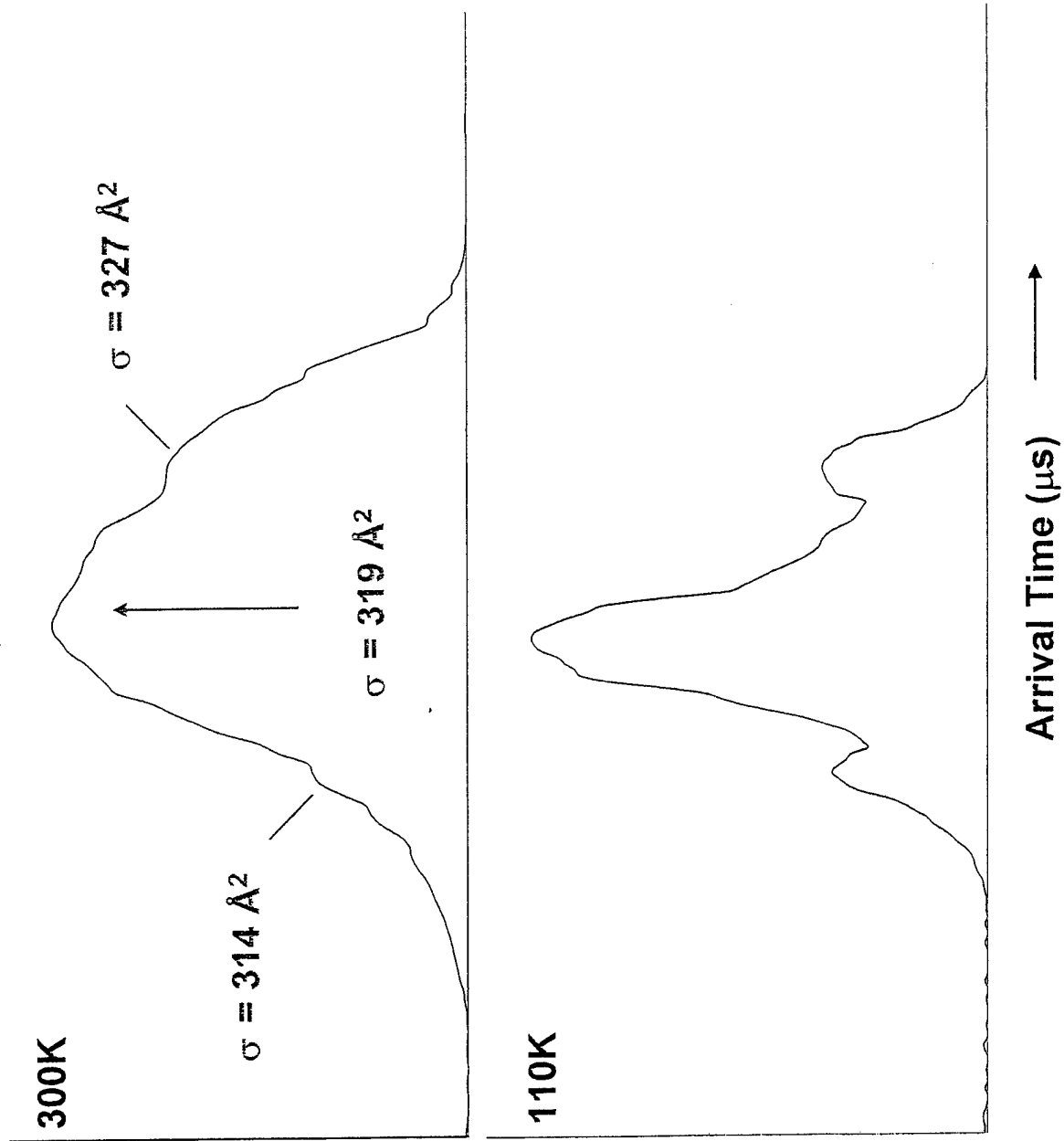
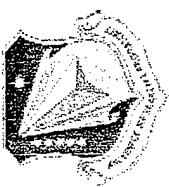
$$\sigma_{\text{Theory}} = 319 \text{ \AA}^2$$

$$\sigma_{\text{EXPT}} = 319 \text{ \AA}^2$$

~66%



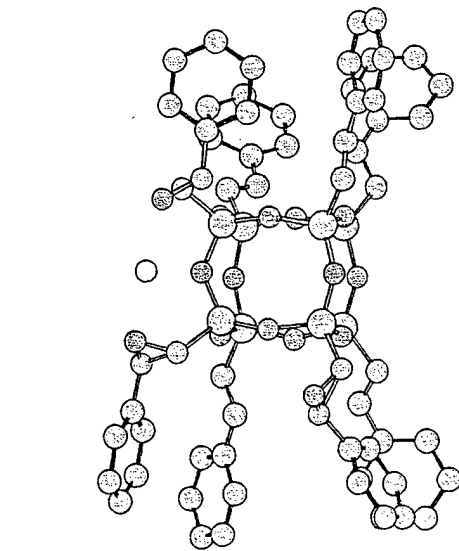
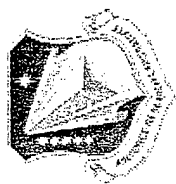
$\text{Na}^+\text{Sty}_5\text{Ep}_3\text{T}_8$ ATDs





File name

$\text{Na}^+\text{Sty}_5\text{Ep}_3\text{T}_8$ Theoretical Structures



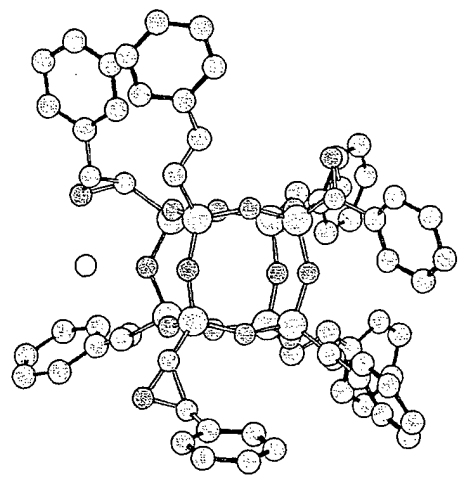
3 epoxides adjacent

on face

$$\sigma_{\text{Theory}} = 314 \text{ \AA}^2$$

$$\sigma_{\text{EXPT}} = 314 \text{ \AA}^2$$

~17%

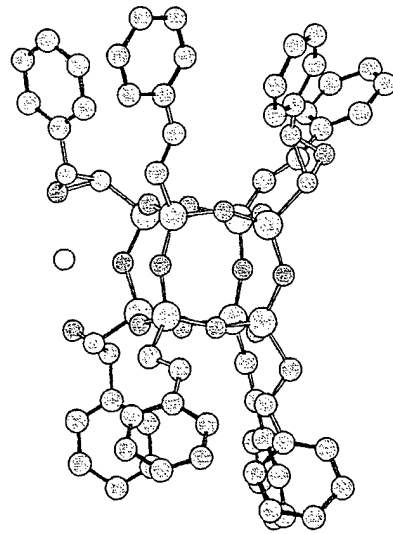


3 on face
diagonals

$$\sigma_{\text{Theory}} = 326 \text{ \AA}^2$$

$$\sigma_{\text{EXPT}} = 327 \text{ \AA}^2$$

~17%

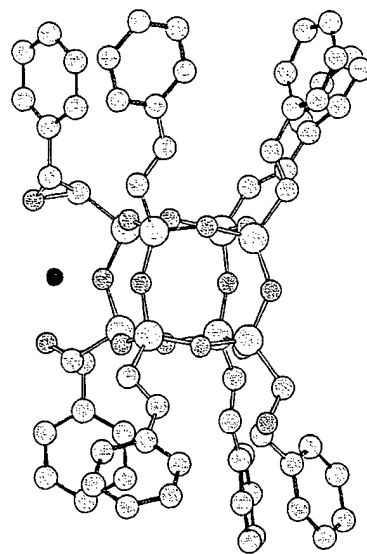


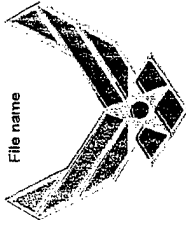
2 adjacent and 1 on the opposite edge:

$$\sigma_{\text{Theory}} = 319 \text{ \AA}^2$$

$$\sigma_{\text{EXPT}} = 319 \text{ \AA}^2$$

~66%

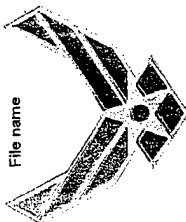




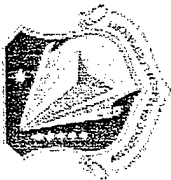
Summary for Styrene Epoxy T_8 POSS System



- For a given x, y the distribution of the geometric isomers can be obtained from ion mobility studies
- Can determine x, y distributions of $Sty_x Ep_y T_8$ from mass spectrum
- Size of Epoxy intermediate between $Sty_8 T_8$ and $PhenEt_8 T_8$
- *Future Work:* Model Hardening reactions with Monofunctional Amine Reagents



Acknowledgments



Erin Baker

Jennifer Gidden

Paul Kemper

Michael T. Bowers

AFOSR-Michael Berman and Charles Lee

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