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This project focuses upon some specific problems that exist in the synthetic procedures for two key energetic compounds, trinitroazetidine (TNAZ) and trinitrotoluene (TNT). In preparing TNAZ, a low yield is obtained in one of the steps, in which NO_2^- displaces $^-OSO_2CH_3$ on the azetidine ring. In synthesizing TNT, the elimination of undesired isomers creates environmental hazards. As an initial step in investigating the possibility that zeolite catalysts might help to circumvent these problems, we have carried out ab initio computations of the electrostatic potentials on the surfaces of zeolite fragments of variable compositions, having as many as 600 electrons. We have also analyzed in detail the surface potentials of toluene and the three isomeric nitrotoluenes, computing not only the electrostatic potential itself but also its average deviation and its total variance.

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COMPUTER-ASSISTED EVALUATION AND DESIGN OF PHASE TRANSFER CATALYSTS FOR TRINITROAZETIDINE AND TRINITROTOLUENE SYNTHESES

FINAL REPORT

Peter Politzer

February 26, 1993

U. S. Army Research Office

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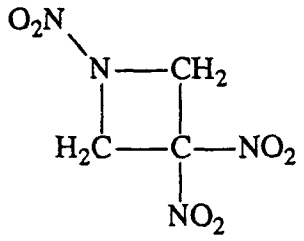
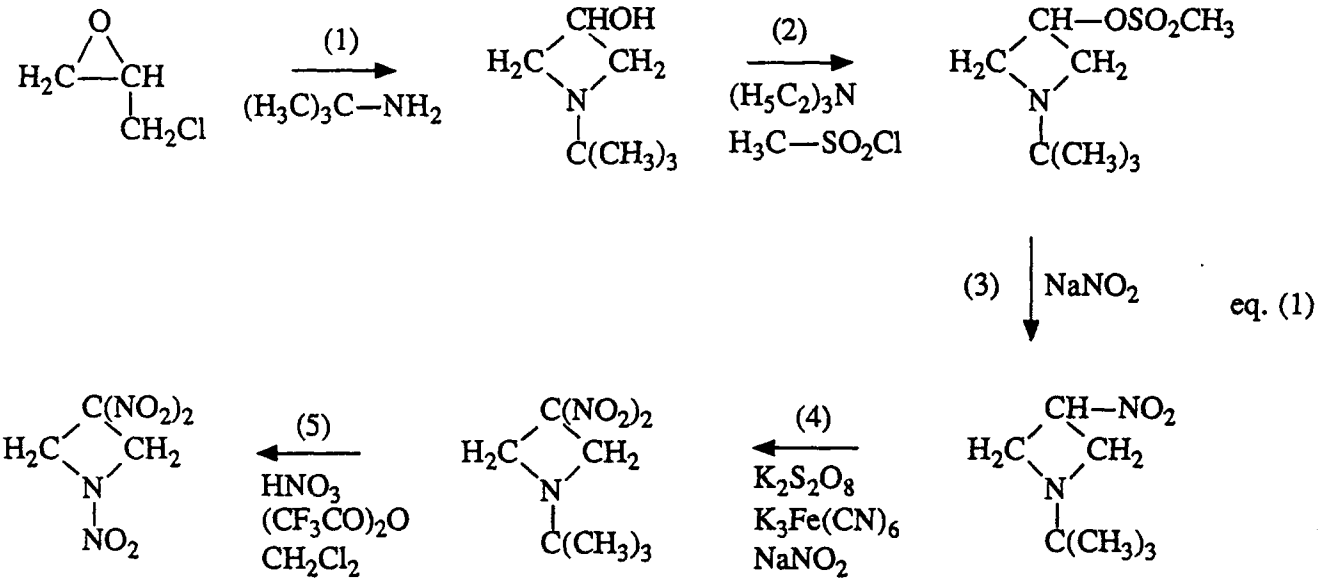
Introduction - Statement of Problems Studied

Trinitroazetidine (TNAZ; **1**) is of considerable interest to the U. S. Army Armament Research, Development and Engineering Center as an energetic material. It has a significant degree of strain [1], which contributes to its energy content, and a specific impulse that is 2% better than that of HMX [2].



1 (TNAZ)

A five-step preparative procedure that has been developed at Fluorochem [2] is outlined in eq. (1):

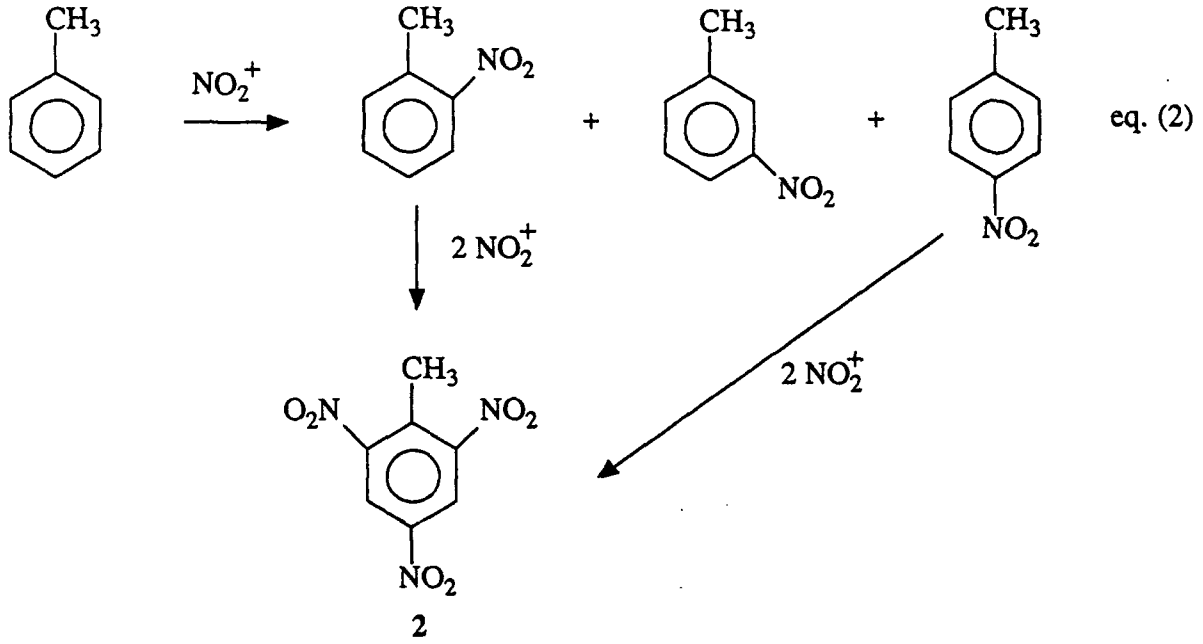


eq. (1)

Step 3 has been described as the "critical step for the scale-up of TNAZ" [2]. This is an S_N2 displacement of the mesylate, $^-OSO_2CH_3$, by the nitrite ion, NO_2^-; it is carried out in a two-phase medium, water and Freon 113. Unfortunately, efforts to scale up the production of TNAZ have considerably lowered the yield obtained in step 3. Thus, an extremely important objective is to increase the rate and yield of this step. A reasonable approach toward this goal is to investigate the introduction of a phase-transfer catalyst which would carry the NO_2^- from the aqueous to the organic phase, thus facilitating its interaction with the mesylate derivative. Such a catalyst could be

a macrocyclic or a network-type system (e.g. a crown ether, cryptand, cyclophane, zeolite or clay) which would interact with the NO_2^- [3-6]. For example, a cyclophane-catalyzed S_N2 reaction has been reported earlier [7], as has the ability of several clays to direct aromatic nitration [8].

In response to suggestions from Drs. Jayasuriya and Reddy (Army Research, Development and Engineering Center, Dover, NJ), we have expanded this project to include another problem in which a network-type catalyst might be able to play a key role. This involves the synthesis of 2,4,6-trinitrotoluene (TNT, 2), shown in eq. (2). The initial nitration step yields primarily the



2

ortho isomer, but also a significant amount of the *para* and some *meta* [9,10]. Since the *meta* directing power of NO_2 is dominant in these products, either the *ortho* or the *para* could lead to **2** by successive nitrations. Unwanted isomers, e.g. the *meta*, are traditionally removed by treatment with Na_2SO_3 forming sulfonates, which are water-soluble and are washed out in what is called "red water". These sulfonates are environmentally undesirable. It would be very important to identify a catalyst, perhaps a zeolite, which would promote selective nitration to form only the *ortho* or *para* isomer in the initial step, thereby providing a TNT synthesis procedure that is environmentally safe.

In this project we have investigated computationally a model for the zeolite ZSM-5, the channels of which can be regarded as built up of units composed of 12 silicon or aluminum atoms and 26 oxygens [11], as well as several related frameworks. Our aim has been to identify one or more systems that show promise of being effective catalysts for the mesylate displacement (step 3) in the synthesis of TNAZ [eq. (1)], and for selective nitration to either *ortho*- or *para*-nitrotoluene.

Computational Approach

Since electrostatic interactions are a major factor in the binding of guests to host macromolecules, we have used the electrostatic potential V(**r**) as an analytical tool in this project. The nuclei and electrons of a molecule create a potential V(**r**) in the surrounding space, given by eq. (3).

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')\, d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (3)$$

Z_A is the charge on nucleus A, located at $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the electronic density function.

V(**r**) is a real physical property which can be determined experimentally by diffraction methods, as well as computationally [12]. It is well established as an effective tool in the study of molecular reactivity, including intermolecular interactions [12,13]. In this work we have computed V(**r**) using an *ab initio* self-consistent-field molecular orbital approach [14] on molecular surfaces defined, following Bader *et al* [15], as the 0.001 electrons/bohr^3 contour of the electronic density. We have shown that this surface approach is well-suited for the study of recognition processes [12,16] and intermolecular interactions in crystalline environments [17-19].

We have recently introduced two statistical properties related to V(**r**) which provide additional detailed information about the electrostatic properties of a molecular surface and also facilitate quantitative comparisons between molecules. These are the average deviation, Π, and the total variance, σ^2_{tot}. They are defined by eqs. (4) and (5):

$$\Pi = \frac{1}{n}\sum_{i=1}^{n} \left| V(\mathbf{r}_i) - \bar{V}_S \right| \qquad (4)$$

$$\sigma^2_{tot} = \sigma^2_+ + \sigma^2_- = \frac{1}{m}\sum_{i=1}^{m}\left[V^+(\mathbf{r}_i) - \bar{V}_S^+\right]^2 + \frac{1}{n}\sum_{j=1}^{n}\left[V^-(\mathbf{r}_j) - \bar{V}_S^-\right]^2 \qquad (5)$$

$V(\mathbf{r}_i)$ is the potential at the i^{th} point on the molecular surface, and$V^+(\mathbf{r}_i)$ and $V^-(\mathbf{r}_j)$ are the positive and negative values of V(**r**) on the surface. $\bar{V}_S$, $\bar{V}_S^+$ and $\bar{V}_S^-$ are the respective averages:

$$\bar{V}_S = \frac{1}{n}\sum_{i=1}^{n} V(\mathbf{r}_i) \qquad \bar{V}_S^+ = \frac{1}{m}\sum_{i=1}^{m} V^+(\mathbf{r}_i) \qquad \bar{V}_S^- = \frac{1}{n}\sum_{j=1}^{n} V^-(\mathbf{r}_j).$$

Π is a measure of the charge separation, or local polarity, that may be present even in molecules having zero dipole moment, while σ^2_{tot} is particularly sensitive to extreme variations in the potential on the surface. We have shown that these properties correlate well with intermolecular interaction tendencies [20-24].

A major effort in this project has involved constructing a realistic wall fragment of the zeolite ZSM-5, and then to examine V(**r**) on this surface. Our results, which will be discussed in the next section, led us to investigate modifications of the traditional zeolite framework. In order to help us understand what features of a zeolite or other host macromolecule might promote selective nitration to *ortho-* or *para*-nitrotoluene, we have computed surface electrostatic potentials, Π and σ^2_{tot} for toluene itself and for *ortho-*, *meta-* and *para-* nitrotoluene. All potentials and related properties that are presented and discussed in this report were computed at the STO-5G* level, which we have found to be reliable for this purpose [13,16-19].

Results

A. *Calculations relating to TNAZ synthesis:*

We used the crystal coordinates of the ZSM-5 secondary building unit [25] to generate a full ZSM-5 unit cell. We then extracted a portion of this unit cell to represent a fragment of the wall of a ZSM-5 channel. After some experimentation, we constructed a wall fragment consisting of a ring of alternating Si and O atoms (Figure 1). To each Si in the ring, two $-OSi(OH)_3$ groups were attached. All silicon and oxygen atoms were placed according to crystal coordinates. Hydrogens were attached to the external oxygens in order to satisfy electroneutrality, and were oriented such that the OH bonds pointed away from the ring.

Figure 2 presents the electrostatic potential plotted on the surface of the ZSM-5 wall fragment shown in Figure 1. This system has 45 oxygens, 15 silicons and 30 hydrogens; the total number of electrons is 600. This is certainly one of the largest *ab initio* electrostatic potential calculations to have ever been carried out! It can be seen that the potential along the central portion of the wall fragment is negative, and therefore would be predicted to be most attractive towards electrophiles, such as cations or hydrogen-bond donors. These results suggest that the zeolite ZSM-5 would not be a practical candidate for trapping NO_2^- in the mesylate displacement shown in step 3 of eq. (1).

We accordingly began investigating the possibility of replacing silicons in our wall fragment with phosphorus atoms. Since phosphorus has a valence of five and thus could accomodate a fifth singly-bonded oxygen, the absence of the latter may introduce a positive site on the wall fragment for each phosphorus that is present. As preliminary studies in this direction, we computed structures at the HF/6-31G* level for $T(OSiH_3)_n H_{4-n}$, where T = Al or P, and n = 1-4.

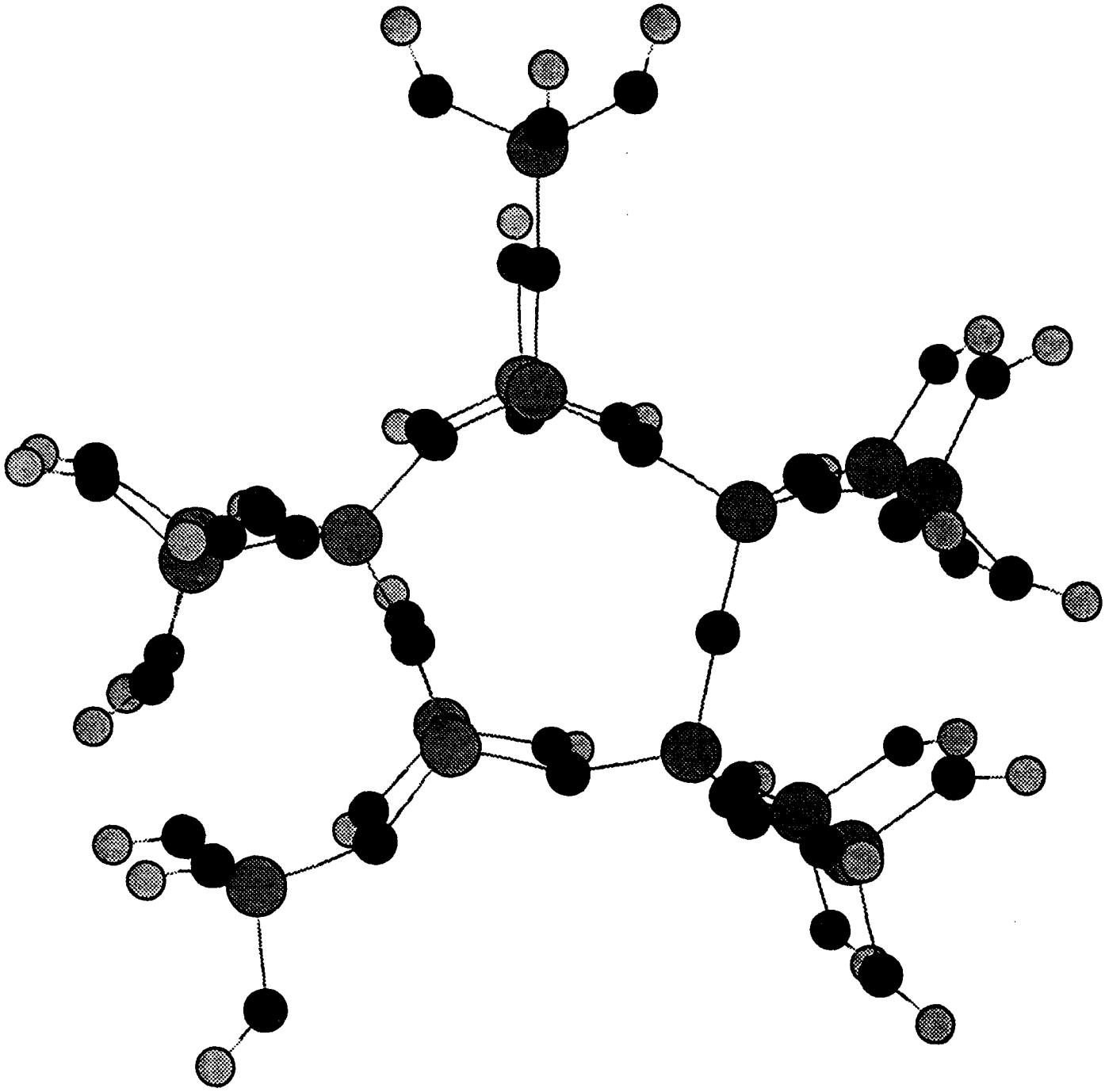


Figure 1. Ball-and-stick representation of our model for the ZSM-5 wall fragment. Large gray balls are silicon atoms, small dark gray balls are oxygens and small light gray balls are hydrogens.

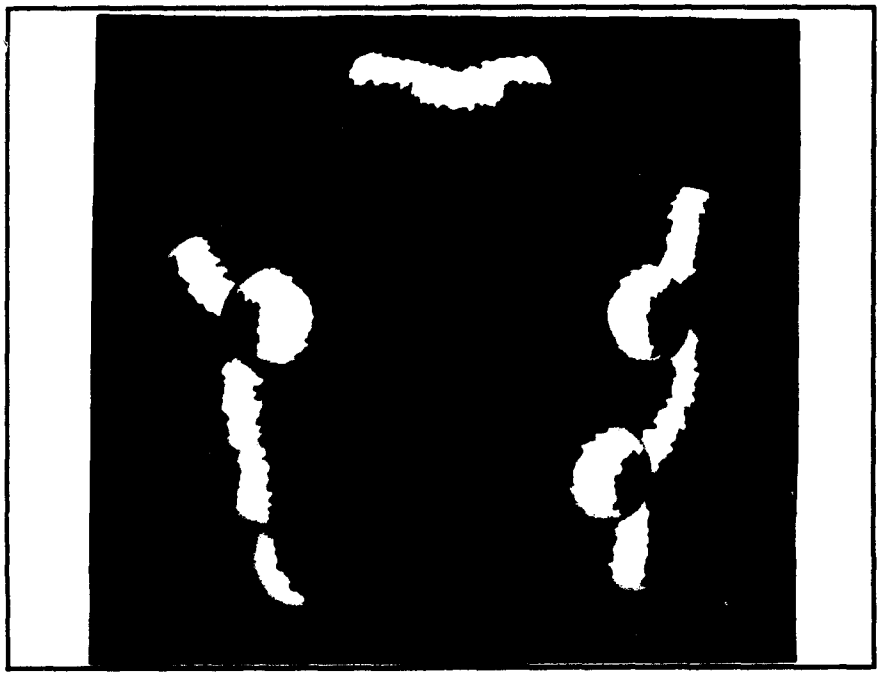


Figure 2. Calculated electrostatic potential on the molecular surface of the ZSM-5 model shown in Figure 1. Color ranges, in kcal/mole, are: red for V(r) > 20; yellow for V(r) from 20 to 0; green for V(r) from 0 to -20; blue for V(r) from -20 to -40; pink for V(r) more negative than -40.

Our purpose was to examine differences between the inclusion of aluminum in the zeolite framework, which leads to negative sites, and phosphorus.

Using structural data obtained in these preliminary calculations, we have constructed a wall fragment containing silicon, aluminum and phosphorus sites. It is shown in Figure 3. We are currently optimizing the internal coordinates of the ring. Our planned next step will be to compute the surface electrostatic potential of this fragment.

B. *Calculations relating to TNT synthesis:*

In a recent calculation of the average local ionization energies on the molecular surface of toluene [26], we found minima above all five unsubstituted carbons, indicating that some electrophilic substitution should occur at the *meta* position as well as the *ortho* and *para*, despite the usual classification of the methyl group as an *ortho*, *para* director. This is borne out by the observed results in the nitration of toluene [9,10].

In much earlier work [27], we have demonstrated the importance of electrostatic interactions in the mononitration of toluene. Accordingly we have now computed and compared the surface electrostatic potentials of toluene and of *ortho*-, *meta*- and *para*-nitrotoluene. As seen in Figure 4, toluene has a large negative region above and below the entire ring, especially over its center, and extending to the methyl carbon. The only positive potentials on the surface are associated with the hydrogens, particularly those of the methyl group. The three nitrotoluene isomers are quite similar, electrostatically. Negative regions are associated with the nitro group oxygens, consistent with previous experience [13], and which can be seen in Figures 5 and 6 for the *meta*- and *para*- derivatives. The regions above the aromatic rings are now positive, due to the strongly electron-withdrawing NO_2 groups. The buildups of positive potential found above the C-NO_2 bond regions in Figures 5 and 6 are characteristic of aromatic C–NO_2 bonds [13], and are indicative of these being possible sites for nucleophilic interactions.

Table 1 lists the calculated values of the average deviation, Π, and the total variance, σ^2_{tot}, of the surface potentials of toluene and the isomeric nitrotoluenes. These show that toluene has much less local polarity and a considerably less variable surface potential than do the nitrotoluenes; its intermolecular interactions can be expected to be much weaker. There is a striking similarity in these properties for the three nitrotoluenes, although the *para* form has slightly more local polarity while the *ortho* has a somewhat more extremely varying surface potential and should interact slightly more strongly with its surroundings.

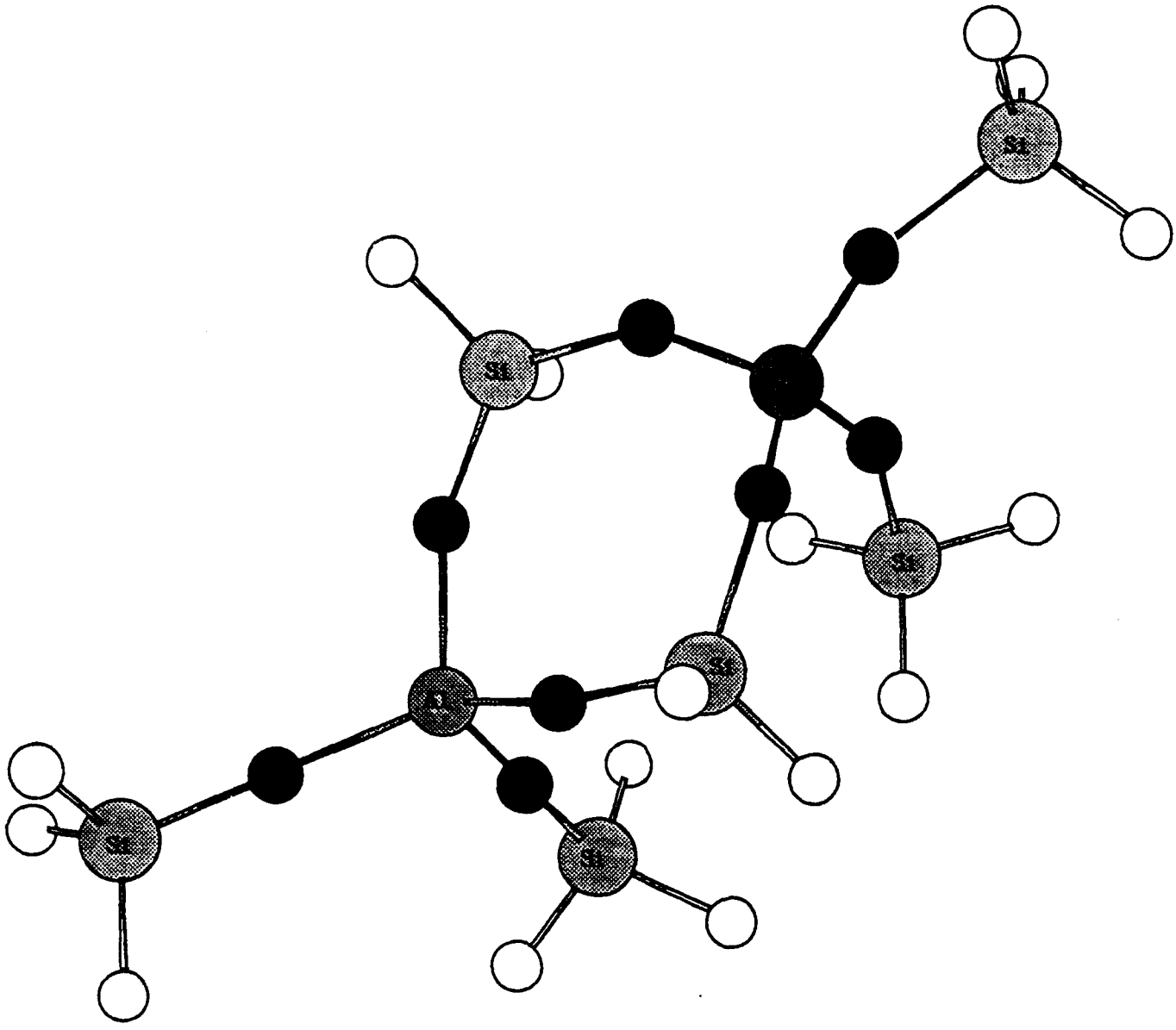


Figure 3. Ball-and-stick representation of our model containing a ring of silicon, aluminum, phosphorus and oxygen atoms. Silicon, aluminum and phosphorus atoms are designated by their atomic symbols. Small gray and white balls are oxygens and hydrogens, respectively.

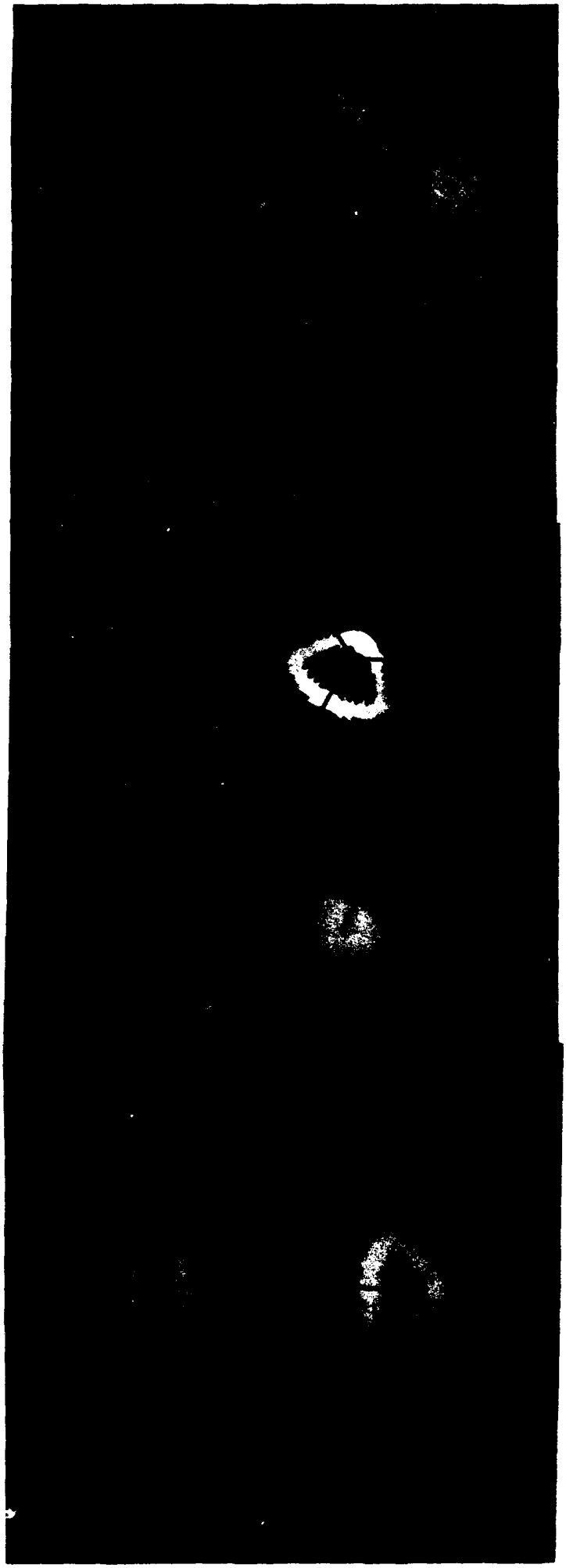


Figure 4. Calculated electrostatic potential on the molecular surface of toluene. Color ranges, in kcal/mole, are:
red for V(r) > 8;
yellow for V(r) from 8 to 0;
green for V(r) from 0 to 8;
blue for V(r) from -8 to -11;
pink for V(r) more negative than -11.

Figure 5. Calculated electrostatic potential on the molecular surface of *meta*-nitrotoluene. Color ranges, in kcal/mole, are:
red for V(r) > 15;
yellow for V(r) from 15 to 10;
green for V(r) from 10 to 0;
blue for V(r) from 0 to -20;
pink for V(r) more negative than -20.

Figure 6. Calculated electrostatic potential on the molecular surface of *para*-nitrotoluene. Color ranges, in kcal/mole, are:
red for V(r) > 15;
yellow for V(r) from 15 to 10;
green for V(r) from 10 to 0;
blue for V(r) from 0 to -20;
pink for V(r) more negative than -20.

Table 1. Calculated Π and σ^2_{tot} values.

Molecule	Π (kcal/mole)	σ^2_{tot} (kcal/mole)^2
toluene	4.57	18.1
ortho-nitrotoluene	10.83	158.6
meta-nitrotoluene	10.98	142.5
para-nitrotoluene	11.19	146.3

There is an interesting contrast in the shapes of toluene and the three nitrotoluenes, which can be seen in Figures 4 - 6. Toluene and *para*-nitrotoluene are clearly more streamlined than the *ortho* and *meta* isomers. This is relevant to the possibility of selectively trapping the former two in zeolite frameworks with appropriate channel diameters. It should also be noted that the surface electrostatic potential of our ZSM-5 wall fragment model (Figure 2), while not suitable for interacting with NO_2^- in preparing TNAZ, would be very suitable for trapping positively charged species, such as NO_2^+ in synthesizing TNT.

Summary

In the phase of this project that has just been completed, we have demonstrated the capability for *ab initio* computations on an extremely large scale (600 electrons). We have begun a systematic study of the electrostatic properties of various zeolite compositions and structures, and we have also carried out detailed analyses of the electrostatic natures of the molecular surfaces of toluene and the isomeric nitrotoluenes. The next phase should be to merge this knowledge and insight that has been obtained and to use it, in conjunction with experimental work, as the basis for developing effective catalytic systems for the synthesis of TNAZ and TNT.

Publications Resulting from this Work

"*Ab Initio* Computed Surface Electrostatic Potentials of Zeolite Fragments"
J. S. Murray, M. E. Grice and P. Politzer, Molecular Engineering, to be submitted.

Scientific Personnel Involved in Project

Dr. M. Edward Grice	Postdoctoral Research Associate
Dr. Jane S. Murray	Postdoctoral Research Associate
Dr. Jorge M. Seminario	Postdoctoral Research Associate
Ms. Anita H. Buckel	Research Associate

Inventions

None.

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