



Unclassified SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) READ INSTRUCTIONS BEFORE COMPLETING FORM **REPORT DOCUMENTATION PAGE** 3. RECIPIENT'S CATALOG NUMBER 1. REPORT NUMBER 2. GOVT ACCESSION NO. 01 ONR-NR093064-TR1 PERIOD COVERED TITLE (and Subtitle) TYPE OF RED Summary rept Quantum Chemical Investigations of the Sep Octob Mechanism of Cationic Polymerization . AUTHOR(+) CONTRACTO NUMBER(+) ¥ 1, 1 NÓØOT 4~8Ø Joyce J./Kaufman C. 5 PERFORMING ORGANIZATION NAME AND ADDRESS PROJECT, TASK PROGRAM The Johns Hopkins University NR 093-064 Charles and 34th Streets Baltimore, MD 21218 11. CONTROLLING OFFICE NAME AND ADDRESS REPORT DATE Octo Office of Naval Research Code 473 3. NUMBER C' 26 Arlington, Virginia 22217 MONITORING AGENCY NAME & ADDRESS(II dilloroni from Controlling Office) Mr. Richard Main 15. SECURITY CLASS. (of this report) Unclassified ONRRR, George Washington University 2110 G St. 154. DECLASSIFICATION/DOWNGRADING SCHEDULE Washington, D.C. 20037 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; Distribution Unlimited. 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, If different from Report) 18. SUPPLEMENTARY NOTES 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) molecular orbital oxiranes cationic polymerization quantum chemical nitro polymers fluoro ab-initio cyclic ethers electrostatic molecular azido oxetanes potential contour maps azidomethy1 20. ABSTRACT (Continue on reverse elde if necessary and identify by block number) Please see reverse DD 1 JAN 73 1473 EDITION OF I NOV 65 IS OBSOLETE **Unclassified** 5/N 0102-LF-014-6601 SECURITY CLASSIFICATION OF THIS PAGE (When Date Ente

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

20.

У

- I. Ab-initio quantum chemical investigations of the mechanism of cationic polymerization. (commenced October 1, 1979)
- II. Development of theoretical procedures for prediction of crystal structures and densities. (commenced April 1, 1980)

I. In the research on part I of this project we are carrying out ab-initio quantum chemical calculations and generating electrostatic molecular potential maps for cationic polymerization: on energetic monomers, on their interaction with catalysts and on the attack of the monomer-catalyst complexes on the substrates. This research is in support of an ongoing overall project of the Power Program Branch of ONR designed to develop energetic binders for use with energetic propellants. The propensity of polymerization of more conventional cyclic ethers had been shown experimentally to be proportional to their basicity and ring strain. We derived a theoretical index which should be proportional to the basicity of the monomers: namely, from the ab-initio quantum chemical calculations on the monomers generating the electrostatic molecular potential maps in space around the monomer. The more negative the map contours the farther out in space, the more basic should be the monomer.

The ab-initio calculations were calculated with our own programs which also incorporate several desirable options for calculations on large molecules and the maps were generated from these ab-initio wave functions.

The electrostatic molecular potential contour maps generated around the exotically substituted cyclic ether monomers proved to indicate correctly their different propensities for polymerization when the monomers were subsequently synthesized and polymerized experimentally by the other researchers on this overall ONR project. These electrostatic molecular potential contour maps can also shed insight on the question raised as to good copolymer candidates.

We have also carried out some necessary program development activities in connection with this research in improving convergence stability of our current ab-initio programs since this is sometimes a problem for nitro, fluoro and azido substituents and implementing new approaches to forming and solving SCF equations for reasonably large and closely related molecules or molecular systems.

II. We are pursuing several approaches to the prediction of crystal structures and densities. The first is to calculate (from calculations on the supermolecules) the SCF intermolecular interaction, separate it into its various components and use these to construct the crystal structure.

The second approach is to carry over the concept recently used successfully in calculations for biological systems where the same ab-initio calculations between two or several of such molecules for a large variety of intermolecular configurations is used to derive atom class-atom class pair-pair and three-body potentials which are then used to calculate the intermolecular structure of an arrangement of molecules.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Date Entered)

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF

CATIONIC POLYMERIZATION

Joyce J. Kaufman, Principal Investigator

TABLE OF CONTENTS

| Con | ncise Summary | S1 |
|------|--|----|
| Sun | mary | 1 |
| Ι. | Ab-Initio Quantum Calculations and Electrostatic Molecular Potential Maps For the Mechanism of Cationic Polymerization | 4 |
| II. | Prediction of Crystal Structure | 13 |
| III. | Joyce J. Kaufman - Invited Lectures Presented on this ONR research | 15 |
| IV. | Project Personnel | 16 |
| Dis | tribution List | 17 |

| Accession For | | | | | | |
|---------------------|--------|-------|--|--|--|--|
| NTIS GRA&I | | | | | | |
| DDC TAB | | | | | | |
| Unannounced | | | | | | |
| Justification | | | | | | |
| By Distribution/ | | | | | | |
| Availability Codes | | | | | | |
| | Availa | nd/or | | | | |
| Dist. | spec1 | al | | | | |
| | 1 1 | | | | | |
| | | | | | | |
| | | | | | | |

1

Ś

ን

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF

CATIONIC POLYMERIZATION

Joyce J. Kaufman, Principal Investigator

CONCISE SUMMARY

I. Ab-initio quantum chemical investigations of the mechanism of cationic polymerization. (commenced October 1, 1979)

II. Development of theoretical procedures for prediction of crystal structures and densities. (commenced April 1, 1980)

I. In the research on part I of this project we are carrying out ab-initio quantum chemical calculations and generating electrostatic molecular potential maps for cationic polymerization: on energetic monomers, on their interaction with catalysts and on the attack of the monomer-catalyst complexes on the substrates. This research is in support of an ongoing overall project of the Power Program Branch of ONR designed to develop energetic binders for use with energetic propellants. The propensity of polymerization of more conventional cyclic ethers had been shown experimentally to be proportional to their basicity and ring strain. We derived a theoretical index which should be proportional to the basicity of the monomers: namely, from the ab-initio quantum chemical calculations on the monomers generating the electrostatic molecular potential maps in space around the monomer. The more negative the map contours the farther out in space, the more basic should be the monomer.

The ab-initio calculations were calculated with our own programs which also incorporate several desirable options for calculations on large molecules and the maps were generated from these ab-initio wave functions.

The electrostatic molecular potential contour maps generated around the exotically substituted cyclic ether monomers proved to indicate correctly their different propensities for polymerization when the monomers were subsequently synthesized and polymerized experimentally by the other researchers on this overall ONR project. These electrostatic molecular potential contour maps can also shed insight on the question raised as to good copolymer candidates.

We have also carried out some necessary program development activities in connection with this research in improving convergence stability of our current ab-initio programs since this is sometimes a problem for nitro, fluoro and azido substituents and implementing new approaches to forming and solving SCF equations for reasonably large and closely related molecules or molecular systems. S2

II. We are pursuing several approaches to the prediction of crystal structures and densities. The first is to calculate (from calculations on the supermolecules) the SCF intermolecular interaction, separate it into its various components and use these to construct the crystal structure.

The second approach is to carry over the concept recently used successfully in calculations for biological systems where the same ab-initio calculations between two or several of such molecules for a large variety of intermolecular configurations is used to derive atom class-atom class pair-pair and three-body potentials which are then used to calculate the intermolecular structure of an arrangement of molecules.

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISMS OF

CATIONIC POLYMERIZATION

Joyce J. Kaufman, Principal Investigator

SUMMARY

- I. Ab-initio quantum chemical investigations of the mechanism of cationic polymerization. (commenced October 1, 1979).
- II. Development of theoretical procedures for prediction of crystal structures and densities. (commenced April 1, 1980).

In the research on Part I of this project we are carrying out ab-initio Ι. quantum chemical calculations and generating electrostatic molecular potential maps for cationic polymerization: on energetic monomers, on their interaction with catalysts and on the attack of the monomer-catalyst complexes on the substrates. This research is in support of an ongoing overall project of the Power Program Branch of ONR designed to develop energetic binders for use with energetic propellants. A binder which itself was energetic would contribute significantly to the propellant effectivity/weight ratio. The compounds of choice were cyclic ethers (preferably 3- and 4- membered rings) substituted with exotic energetic substituents such as fluoro-, nitro-, azido-, azidomethyl-, etc., either singly or multiply substituted. The primary initial question asked was could one predict the relative propensities of cationic polymerization for these exotic monomers -- even before the monomers were synthesized. The only previous old experimental Japanese paper reported that for cyclic ethers substituted with more conventional substituents (alkyl-, alkoxy-, ary1-) the rate of polymerization was proportional to the basicities of the monomers and the ring strain. We derived a theoretical index which should be proportional to the basicity of the monomers: namely, from the ab-initio quantum chemical calculations on the monomers generating the electrostatic molecular potential maps in space around the monomer. The more negative the map contours the farther out in space, the more basic should be the monomer.

The ab-initio calculations were calculated with our own programs which also incorporate several desirable options for calculations on large molecules: ab-initio effective core model potentials (MODPOT) which enable calculations of the valence electrons only explicitly, yet accurately; an integral prescreening evaluation (which we named VRDDO -variable retention of diatomic differential overlap) especially effective for spatially extended systems; and a MERGE technique which allows efficient reuse of integrals from common skeletal fragments. These electrostatic molecular potential contour maps were generated around the exotically substituted monomers and some of the more conventionally substituted monomers which had earlier been studied experimentally.

The electrostatic molecular potential contour maps generated around the exotically substituted cyclic ether monomers proved to indicate correctly their different propensities for polymerization when the monomers were subsequently synthesized and polymerized experimentally by the other researchers on this overall ONR project. These electrostatic molecular potential contour maps can also shed insight on the question raised as to good copolymer candidates. Since the rates of polymerization are governed by basicity which in turn are predictable from these maps, the more closely these maps match for two different monomers, the more well suited these two monomers are for copolymer partners.

We have also carried out some necessary program development activities in connection with this research. These have encompassed two areas: improving the convergence stability of our current ab-initio MODPOT/VRDDO/MERGE program systems, since convergence stability can sometimes be a problem particularly for non-equilibrium orientations of molecules containing fluoro, nitro, or azido groups, and implementing new approaches to forming and solving SCF equations for reasonably large and closely related molecules or molecular systems.

See next page for summary of Part II.

3

II. The arrangement of molecules in crystals is important in understanding intermolecular interactions which occur in crystals during detonation phenomena. Crystals densities are one of the important factors influencing detonation pressure and detonation velocity. Crystal structures and crystal densities can be calculated by ab-initio MODPOT/VRDDO/MERGE SCF supermolecule calculations, supplemented by an estimate of the dispersion energies (which are known to be much smaller than the other terms for nitro compounds). However, it would be most desirable to be able to calculate crystal structures and crystals densities by a intermolecular perturbation technique.

We are pursuing several approaches. The first approach is to calculate the SCF intermolecular interaction between two or several such molecules, then to separate this interaction into its electrostatic, polarization, exchange and charge-transfer components and then to use these components (with an estimate of the dispersion energy) to construct the crystal structure. We have done the analysis for this approach and are implementing it.

The second approach which we have just initiated is to carry over the concept recently used successfully in calculations for biological systems where the same ab-initio calculations between two or several of such molecules for a large variety of intermolecular configurations is used to derive atom class-atom class pair-pair and three-body potentials which are then used to calculate the intermolecular structure of an arrangement of molecules.

I. Ab-Initio Quantum Calculations and Electrostatic Molecular Potential Maps For the Mechanism of Cationic Polymerization

By making energetic binders for propellants, the efficiency/weight ratio of propellants could be increased significantly.

ONR Power Program Branch is sponsoring an overall effort in this area which combines other groups in experimental synthesis and polymerization with our theoretical group. The objective of the ONR project is to prepare energetic monomers of cyclic ethers (of ring sizes three-to-five-membered) substituted with energetic groups (such as nitro-, fluoro-, azido-, azidomethyl-) both single substituents and mixed substituents. We were asked by ONR what insight quantum chemical calculations could shed on

- the question of the propensity of the cyclic ethers with energetic substituents to undergo cationic polymerization prior even to synthesis of the energetic monomers themselves;
- what happens as a catalyst (a Lewis acid) approaches the cyclic ether monomer and what might be preferable catalysts;
- what happens as a complex of cyclic ether + catalyst approaches another molecule of cyclic ether monomer;
- 4) what would be good partners for co-polymerization in the event the polymer from a single monomer was too refractory -- too brittle.

It had been observed by Japanese investigators (Aoki, et al.), who earlier studied experimentally three-to-six membered cyclic ethers with more conventional substituents (alkyl, alkoxy, aryl) that the rate of polymerization of cyclic ethers was proportional to

- a) the base strength of the cyclic ether
- b) the ring strain of the cyclic ether.

Thus, to determine propensity for polymerization, we had to come up with theoretical quantum chemical indices that would be predictive of basicity and of ring strain. Our previous ab-initio quantum chemical calculations on morphine (an N-methyl narcotic agonist) and on nalorphine (an N-allyl narcotic agonist-antagonist) had shown that charge alone on an atom does not seem to be sufficiently sensitive to distinguish different degrees of basicity especially for closely related molecules. However, the use of electrostatic molecular potential contour maps did hold promise of being a sensitive criterion for basicity. Comparisons of negative regions of the maps around the O atom in the cyclic ether ring (both spatial extent and magnitude) should be indicative of the relative basicities of these exotic monomers. For the cyclic ether monomers, we reasoned that the larger in space the negative contours of the map around the oxygen atom in three dimensions, the more basic the monomer would be and the more prone to cationic polymerization. For each monomer we are carrying out the ab-initio calculations to optimize the geometry of the monomer. As the geometry is optimized we then generate electrostatic molecular potential contour maps in three dimensions around the monomer from the

calculated electronic wave functions of the monomer. These maps indicate vividly the basicity of the oxygen, from which direction a cation will prefer to attack the monomer and are especially valuable in comparing three dimensional relative basicities of various monomers. These maps have been generated around a number of the monomers and around some monomer-catalyst complexes.

We are carrying out ab-initio MODPOT/VRDDO and ab-initio MODPOT/VRDDO/MERGE calculations for 3-, 4-, 5- and 6-member cyclic ethers with various substituents. The 3- and 4-member rings are the ones of choice for the experimental program. In particular, the four member rings 3,3-fluoronitrooxetane and 3,3-dinitrooxetane were of the first interest experimentally. We carried out ab-initio MODPOT/VRDDO/MERGE calculations on oxetane and on the 3,3-fluoronitrooxetane and 3,3-dinitrooxetane and generated electro-static molecular potential maps around the molecules in three directions i) parallel to the mean molecular plane (xz); ii) parallel to the (xy) plane and iii) parallel to the (yz) plane. The results for

- (a) Oxetane (Figures la and lb)
- (b) 3,3-Fluoronitrooxetane (Figures 2a and 2b)
- (c) 3,3-Dinitrooxetane (Figures 3a and 3b)

indicate quite clearly that oxetane is the most basic, 3,3-fluoronitrooxetane is next and 3,3-dinitrooxetane is the least basic. The ring strains are not expected to differ nearly as drastically in these molecules as do the basicities. The maps suggested that the 3,3-dinitrooxetane should be so weakly basic that it would have trouble undergoing cationic polymerization. Very recent experimental data which indicates it appears to be very difficult to polymerize dinitrooxetane validates our hypothesis. Thus, it now seems possible that by carrying out the ab-initio quantum chemical calculations on these cyclic ether monomers with combinations of exotic energetic substituents even prior to the synthesis of the monomers themselves, we will be able to get considerable insight into the propensity of these monomers to undergo cationic polymerization. We are currently developing theoretical procedures for calculating relative ring strains in these cyclic ethers. Thus, in response to question 1), it would be expected that oxetane would polymerize more easily than fluoronitrooxetane and that more easily than dinitrooxetane.

These electrostatic molecular potential contour maps can also be used to help answer question 4) as to good candidate partners for copolymerization. We hypothesized that since the rate of polymerization is very dependent on the basicity of the cyclic ethers, for good copolymerization the copolymer molecules should have reasonably similar basicities (as well as ring strains), because if one compound was much more basic than the other, it would self-polymerize so fast that it would not have much tendency to copolymerize. 3,3-bis(azidomethyl)oxetane forms a polymer which is too refractory (too brittle). The question was asked as to possible good copolymer candidates for 3,3-bis(azidomethyl)oxetane. The maps showed that 3,3-bis(azidomethyl)oxetane was less basic than oxetane, more basic than 3,3-fluoronitrooxetane and apparently fairly similar in basicity to 3-azidooxetane. Thus, 3-azidooxetane might be a good choice for a copolymer candidate.

5

and the second second



To shed insight on questions 2) and 3) we are also carrying out ab-initio MODPOT/VRDDO and ab-initio MODPOT/VRDDO/MERGE calculations on BF3 approaching various series of substituted cyclic ethers and generating the electrostatic molecular potential contour maps. These results indicate the charge redistribution and changes in the maps as the reactants approach. Similar calculations are carried out for attack of H^{+} on the substituted cyclic ethers since there has been speculation by experimental polymer chemists that perhaps it is the attack of H⁺ (formed from a Lewis acid-H₂O complex) that triggers the polymerization. However, experimentally it has been observed that different Lewis acid catalysts have different effects on polymerization of the same monomer. For example, it is possible to polymerize certain of these energetic monomers with PF5 but not with BF3. This would seem to indicate that a catalyst-monomer complex might still be important. We suggested several experiments that could help clarify the picture. First, to measure the differing amounts of H^+ formed by various Lewis-acid catalysts in the polymerization solvent mixture (without any monomer as well as with monomers) to see if the amount of H⁺ formed could explain the difference in propensity of a monomer to polymerize with. different Lewis-acid catalysts. Second, to add various amounts of H' to solutions of monomer plus ineffective Lewis-acid catalyst to see if the $_+$ extra H⁺ could trigger the reaction. Third, to add various amounts of H⁺ to solutions of monomer plus effective Lewis-acid catalysts to see if the rate or character of the polymerizations are affected.

Molecular Calculation Summary

The parent molecules studied so far have come from three sources:

- ONR molecules of interest
- Molecules from the Aoki, Harita et al. reaction rate study [J. Polymer Sci. Al 6, 2585 (1968)]
- A systematic study of single alpha substituents to round out and extend the Aoki et al. results.

These parent molecules are also being investigated in attack by a proton and by boron trifluoride.

The following abbreviations are used in the table:

1.1

| for origin: | N | = | ONR molecule of interest. |
|-------------|-------|---|---|
| | J | = | Aoki et al. study. |
| | S | = | Systematic single α substituent study. |
| for status: | 0 | = | Geometry optimization completed. |
| | Α | = | Geometry optimization approaching completion. |
| | G | = | Geometry optimization being done. |
| | C | Ŧ | Convergence difficulties encountered, but stability problems are in the process of being overcome. |
| | I(x) | | In plane proton attack (where the reacting species approaches in the plane of the parent that contains the hetero-oxygen and its ring neighbors). Geometry optimization completed. x is the equilibrium H^+ - 0 distance. |
| | IA(x) | Ξ | Similar to I(x) but geometry optimization approaching completion. |
| | PA(x) | = | Out of plane proton attack geometry optimization x is the angle of optimal attack. |

| PARENT RING SYSTEM | MOLECULE | ORIGIN | C PARENT MOLECULE | ALCULATIONAL ST | ATUS | ^{BF} 3 ATTACK |
|---------------------------|--|-------------------------|-------------------------|--------------------------|----------|---------------------------|
| Jan - 10 | Oxirane 2-Methyloxirane 2-Ethyloxirane 2-Hydroxyoxirane 2,3-Bis(azidomethyl)oxirane 2-Azidomethyl)oxirane 2-(2,2-Dinitro-2-fluoroethoxy)oxfran | a د د د د د د د د | 0<00500 | I (1.031Å) | PA(±46°) | U |
| w ن س | Oxetane 2-Methyloxetane 2-Ethvloxetane | ی د م د | 0.00 | I (1.028Å) | PA(±10°) | IJ |
| 2Ca | 2-Hydroxyoxetane 3-Azidooxetane 3,3-Bis(azidomethyl)oxetane 3,3-Dinitrooxetane 3-Fluoro-3-nitrooxetane | nnzzzz | 000°00 | I (1.029Å) IA(1.035Å) | PA(-15°) | ප |
| | Oxolane(THF) 2-Methyloxolane 2-Ethyloxolane 2-Hydroxyoxolane | ۍ د ۲۰۰۰ ۲۰۰۰ | 0 4 ⁰ 4 | () 10° 1) | PA(5°) | J |
| Cs a 3CB | Oxane 2-Methyloxane 2-Ethyloxane 2-Hydroxyoxane | ۲, ۲ ۲ ۲ | o∢aa | IA(1.022Å) | | G |
| 5 10 10 10 10 | 4,7-bis(fluorodinitromethyl)-dioxepane | z | 0 | | | |

12 ******

Y

Contraction of the second

C 6 ----5C



Calculational Status

Electrostatic Molecular Potential Contour Maps Calculated

Oxirane with BF_3 distances of 1.0, 1.5, 2.0, 2.5, 5.0 Å

2-Hydroxyoxirane

Oxetane

3,3-Dinitrooxetane

3-Fluoro-3-Nitrooxetane

3-Azidooxetane

3-Azidooxetane with BF_3 B-O distances of 1.0, 2.0, 2.5, 5.0 Å

Server 200

3,3-Bis(azidomethyl)oxetane

Oxolane (THF)

Oxolane with BF_3^{B-0} distance of 1.0 Å

Oxane

Oxane with BF_3 B-O distances of 1.5, 2.0, 5.0 Å

4,7-Bis(fluorodinitromethyl)dioxepane

We have also carried out some necessary program development activities in connection with this research. These have encompassed two areas.

We have improved the convergence stability of our ab-initio MODPOT/ VRDDO/MERGE program systems since SCF convergence stability can sometimes be a problem, particularly for non-equilibrium orientations of molecules containing fluoro, azido or nitro substituents. A simple, but elegant, attempt at stability control is to monitor the quality of the density matrix. Normally the reduced density matrix is computed as a sum over all occupied orbitals. In a destabilized iteration, a normally occupied orbital can become unoccupied. In our new approach, this orbital is not included in the density sum and the density is weighted to correct for its absence. This prevents the contamination of unoccupied orbitals and contributes to iterative stability. In essence, this is a ersatz projection technique and works well for these systems.

The improvement to traditional SCF methodology is based on the chemical knowledge that if one part of the environment of a reasonably large molecule changes, then radical restructuring of the electronic structure will most likely be confined to the locality of the change. This is reflected in changes to the coefficients of atomic basis functions in the vicinity of the site. We have formulated an exact, variational process for freezing in the molecular wave function the coefficients of some of the atomic basis functions (derived as a result of a previous molecular calculation) and iteratively computing the unfrozen "reactions" functions coefficients. In practice, however, one needs the entire set of coefficients unfrozen, so we have devised and implemented a revised SCF scheme whereby some coefficients are frozen, SCF convergence achieved for the unfrozen set, and then converging the entire unfrozen set. The potentialities for computational enhancement are great since the effective basis set size is reduced substantially during freezing. Consider a calculation of BF. attacking THF using a small basis of 4 functions per atom, except for hydrogen, which has one. Freezing all functions except those on oxygen, boron or fluorine leaves 20 unfrozen. The work to construct the Fock matrix to perform a diagonalization is proportional to the cube of the size, so by freezing we expect to perform only 9.4% of the work. If we additionally freeze the F basis functions, the work is now only 0.6% of the original! And we can unfreeze in stages. First keep unfrozen B and O. Then unfreeze F, and finally the whole system. This leads not only to speed enhancement but also to convergence stability. This technique will be particularly valuable as we sequentially bring catalyst up to monomer, then allow the monomer-catalyst to attach the substrate building up polymer chains.

II. Prediction of Crystal Structure

7

We are using two different approaches to tackle the problem of prediction of crystal structure.

In the first approach, while crystal structure predictions could be done by carrying out ab-initio SCF calculations of the entire supermolecule, it is more desirable to try to carry out such calculations in terms of the interactions between molecules and perturbation theory. For this purpose we need to be able to calculate separately the electrostatic, exchange (repulsion), polarization and charge transfer energy contributions to intermolecular interactions (these come from proper partitioning of the SCF solution) and to estimate accurately the dispersion energies, and we are working on these aspects. In particular the polarization term must be modified to take neighbor effects into account. We are carrying out the preliminary analysis and are coding and putting together various program pieces necessary for this approach for ab-initio calculations for prediction of crystal structures.

Concomitantly, through the graciousness of Dr. P. Claverie (who spent time with us at Johns Hopkins twice last year), we are putting up on the computers we use a less rigorous program for analysis of crystal geometries and for intermolecular interaction energy. This was the method that had success in his previous analysis of the crystal structure of nitrobenzene. We shall explore the features of this method while we are writing our ab-initio method.

The second approach which we have just initiated is to carry over the concept used successfully recently in biological systems of carrying out ab-initio SCF calculations between several such molecules (in a variety of orientations), from these deriving ab-initio atom class-atom class pair-pair and three body potentials which can then be used to calculate intermolecular molecular structure accurately. We have examined these available biological ab-initio potentials and they lack the potentials for nitro, fluoro, azido and for aromatics and for aliphatic heterocyclics substituted with these. Thus we shall carry out the ab-initio intermolecular calculations on such exotic species and derive the necessary potentials. A large number of such ab-initio calculations are necessary but we have the advantage of being able to use our ab-initio MODPOT/VRDDO/ MERGE technique, which saves considerable time. For example, for nitrobenzene which was our original test molecule the ab-initio calculation with the entire 6-3 G basis set took (on a CDC 6600 NOS/BE 1.3) 2691 seconds, the VRDDO calculation took 1000 secs., the MODPOT calculation took 717 secs., and the MODPOT/VRDDO calculation took only 321 secs. The savings in time with our method go up as n^{X} as the molecules get larger or as calculations are carried Out on intermolecular systems (where 1 < x < 4 depending on the size and shape of the molecule, since n^4 is the ultimate increase in the number of integrals with the number of atomic basis functions provided no integrals are small). Our previous extensive testing on a number of molecules had shown that the orbital energies and gross atomic populations for all four calculations agreed to almost 0.001-0.002 a.u. or e, and

potential energy curves agreed even better, to 0.001 - 0.0001 a.u. As an extra bonus, we showed last year that the MODPOT basis sets we use are so well balanced that there is very little superposition error when these are used in intermolecular calculations.

The derived atom class-atom pair potentials are then general for a particular substituent or skeleton. Thus, they can then be used to predict crystal structures of any energetic compound containing those structural subunits.

无亡

III. Joyce J. Kaufman - Invited Lectures Presented on this ONR Research

- A. Invited Lectures Presented at the Following National and International Meetings, Including Results on the Energetic Monomers.
- March 1980. International Sanibel Symposium on Atomic, Molecular and Solid State Theory, Palm Coast, Florida.
- March 1980. Symposium on Electrostatic Potentials in Chemistry, National American Chemical Society Meeting, Houston, Texas. In press in the Proceedings of the Meeting.
- June 1, 1980. 7th Canadian Theoretical Chemistry Conference, Banff, Alberta.
- July 1980. NATO Advanced Study Institute on Fast Reactions in Energetic Systems, Preveza Beach, Greece. Also presented tutorial lectures. In press in the Proceedings of the Meeting.
 - B. Invited Lectures Presented at ONR or DOD Meetings.
- August 1979. Quantum Chemical Calculations for Energetic Compounds (Explosives, Propellants, Etc.), Conference on Thermal Decomposition of Propellants and Explosives, Air Force Academy, Boulder, Colorado.
- September 1979. Quantum Chemical Investigations on the Mechanisms of Cationic Polymerization and Cationic Graft Polymerization; Workshop on Energetic Binders, ONR, Washington, D.C.
- April 1980. Ab-Initio Quantum Chemical Calculations and Electrostatic Molecular Potential Contour Maps Around Energetic Cyclic Ethers. ONR Contractors' Meeting, SRI, Palo Alto, California.
- April 1980. Ab-Initio Quantum Chemical Techniques for Large Molecules and Application to Cationic Polymerization. Discussion of Navy research interests, Naval Research Laboratories.
 - C. In addition, at the request of Dr. Richard Miller, our ONR contract monitor, we have made a number of trips to ONR and NRL to discuss various aspects of research.

IV. Project Personnel

Joyce J. Kaufman, Ph.D., Principal Investigator

Frank C. Tobin, Ph.D.

The majority of the quantum chemical calculations and the new SCF program development reported here are due to him.

P. C. Hariharan, Ph.D.

Working part time with this project initially since he was already familiar with our various computer programs necessary for the ab-initio quantum chemical calculations and electrostatic molecular potential contour maps and he has also made various addition to these programs as needed for the present research. Now participating in the development of the program for predicting crystal structure.

6/80

ENERGETIC MATERIALS RESEARCH

17

DISTRIBUTION LIST

No. Copies

12. V.

| Assistant Secretary of the Navy (R, E, and S) Attn: Dr. R.E. Reichenbach | 1 | AFATL Eglin AFB, FL 32542 Attn: Dr. Otto K. Heiney | 1 |
|--|-----|--|---|
| Pentagon Washington, DC 20350 | | AFRPL Code PACC | 1 |
| Office of Naval Research Code 473 | 10 | Edwards AFB, CA 93523 Attn: Mr. W. C. Andrepont | |
| Arlington, VA 22217 Attn: Dr. R. Miller | | AFRPL Code CA | 1 |
| Office of Naval Research | . 1 | Attn: Dr. R. R. Weiss | |
| Arlington, VA 22217 Attn: Dr. J. Enig | _ | Code AFRPL MKPA Edwards AFB, CA 93523 Attn: Mr. R. Geisler | 1 |
| Office of Naval Research Code 260 Arlingon, VA 22217 Attn: Mr. D. Siegel | 1 | Code AFRPL MKPA [•] Edwards AFB, CA 93523 Attn: Dr. F. Roberto | 1 |
| Office of Naval Research Western Office 1030 East Green Street Pasadena, CA 91106 Atta: Dr. T. Hall | 1 | AFSC Andrews AFB, Code DLFP Washington, DC 20334 Attn: Mr. Richard Smith | 1 |
| Office of Naval Research Eastern Central Regional Office 495 Summer Street Boston, MA 02210 | 2 | Air Force Office of Scientific Research Directorate of Chemical & Atmospheric Sciences Bolling Air Force Base Washington, DC 20332 | 1 |
| Office of Naval Research San Francisco Area Office One Hallidie Plaza Suite 601 San Francisco, CA 94102 Attn: Dr. P. A. Miller | 1 | Air Force Office of Scientific Research Directorate of Aero- space Sciences Bolling Air Force Base Washington, DC 20332 Attn: Dr. L. H. Caveny | 1 |
| Defense Technical Information Center DTIC-DDA-2 Cameron Station Alexandria, VA 22314 | 12 | Anal-Syn Lab Inc. P.O. Box 547 Paoli, PA 19301 Attn: Dr. V. J. Keenan | 1 |

.

6/80

No. Copies

18

Army Ballistic Research Labs 1 Code DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Mr. L. A. Watermeier Army Ballistic Research Labs 1 ARRADCOM Code DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Dr. Ingo W. May Army Ballistic Research Labs 1 ARRADCOM Code DRDAR-BLT Aberdeen Proving Ground, MD 21005 Attn: Dr. Philip Howe Army Missile Command 2 Code DRSME-RK Redstone Arsenal, AL 35809 Attn: Dr. R. G. Rhoades Dr. W. W. Wharton Atlantic Research Corp. 1 5390 Cherokee Avenue Alexandria, VA 22314 Attn: Dr. C. B. Henderson Ballistic Missile Defense 1 Advanced Technology Center P.O. Box 1500 Huntsville, AL 35807 Attn: Dr. David C. Sayles 1 Ballistic Research Laboratory **USA ARRADCOM** DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Dr. A. W. Barrows 2 Hercules Inc. Cumberland Aerospace Division Allegary **Ballistics** Lab P.O. Box 210

Cumberland, MD 21502 Attn: Dr. Rocco Musso

No. Copies 1 Hercules Inc. Eglin AFATL/DLDL Eglin AFB, FL 32542 Attn: Dr. Ronald L. Simmons Hercules Inc. Magna 1 Bacchus Works P.O. Box 98 Magna, UT 84044 Attn: Mr. E. H. DeButts 1 Hercules Inc. Magna Bacchus Works P.O. Box 98 Magna, UT 84044 Attn: Dr. James H. Thacher HQ US Army Material Development 1 Readiness Command Code DRCDE-DW 5011 Eisenhower Avenue Room 8N42 Alexandria, VA 22333 Attn: Mr. S. R. Matos Johns Hopkins University APL 1 Chemical Propulsion Information Agency Johns Hopkins Road Laurel, MD 20810 Attn: Mr Theodore M. Gilliland 1 Lawrence Livermore Laboratory University of California Livermore, CA 94550 Attn: Dr. M. Finger 1 Lawrence Livermore Laboratory University of California Livermore, CA 94550 Attn: Dr. R. McGuire Lockheed Missiles and Space Co. 1 P.O. Box 504 Sunnyvale, CA 94088 Attn: Dr. Jack Linsk Org. 83-10 Bldg. 154

i. E

6/80

| | No. Copies | |
|--|------------|---|
| Lockheed Missile & Space Co. 3251 Hanover Street Palo Alto, CA 94304 Attn: Dr. H. P. Marshall | 1 | Naval Research Lab Code 6100 Washington, DC 20375 |
| Dept. 52-35 | | Washington, DC 20362 |
| Los Alamos Scientific Lab P.O. Box 1663 Los Alamos, NM 87545 Attn: Dr. R. Rogers, WX-2 | 1 | Attn: Mr. G. Edwards, Code 62R3 Mr. J. Murrin, Code 62R2 Mr. W. Blaine, Code 62R |
| Los Alamos Scientific Lab P.O. Box 1663 Los Alamos, NM 87545 Attn: Dr. B. Craig, M Division | 1 | Naval Sea Systems Command Washington, DC 20362 Attn: Mr. R. Beauregard SEA 64E |
| Naval Air Systems Command | 1 | Naval Surface Weapons Center |
| Washington, DC 20360 Attn: Mr. R. Heitkotter | | White Oak, Silver Spring, MD 20910 |
| Mr. R. Brown | · | Attn: Dr. H. G. Adolph |
| Naval Air Systems Command Code 310 Washington, DC 20360 | 1 | Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD |
| Attn: Dr. H. Mueller Dr. H. Rosenwasser | | Attn: Dr. R. Bernecker |
| Naval Explosive Ordnance Disposal Facility | 1 | Naval Surface Weapons Center Code R10 White Oak Silver Spring MD |
| Attn: Lionel Dickinson Code D | | Attn: Dr. S. J. Jacobs |
| Naval Ordnance Station | 1 | Naval Surface Weapons Center Code R11 |
| Indian Head, MD 20640 Attn: Mr. S. Mitchell | | White Oak, Silver Spring, MD 20910 |
| Naval Ordnance Station | 1 | Attn: Dr. M. J. Kamlet |
| Code PM4 Indian Head, MD 20640 Attn: Mr. C. L. Adams | | Naval Surface Weapons Center Code RO4 White Oak, Silver Spring, MD 20910 |
| Dean of Research | 1 | Attn: Dr. D. J. Pastine |
| Monterey, CA 93940 Attn: Dr. William Tolles | | Naval Surface Weapons Center Code R13 White Oak Silver Series MD |
| Naval Research Lab Code 6510 | 1. | Attn: Dr. E. Zimet |
| Washington, DC 20375 | | · · |

Attn: Dr. J. Schnur

No. Copies

20

6/80

No. Copies

1 Naval Weapons Center Naval Surface Weapons Center Code 388 Code R101 China Lake, CA 93555 Indian Head, MD 20640 Attn: D. R. Derr Attn: Mr. G. L. MacKenzie I Naval Weapons Center Naval Surface Weapons Center Code 388 Code R17 China Lake, CA 93555 Indian Head, MD 20640 Attn: Dr. R. Reed Jr. Attn: Dr. H. Haiss Naval Weapons Center 1 Naval Surface Weapons Center Code 385 Code R11 China Lake, CA 93555 White Oak, Silver Spring, MD Attn: Dr. A. Nielsen 20910 Attn: Dr. K. F. Mueller Naval Weapons Center Code 3858 1 Naval Surface Weapons Center China Lake, CA 93555 Code R16 Indian Head, MD 20640 Attn: Mr. E. Martin Attn: Dr. T. D. Austin Naval Weapons Center 1 China Lake, CA 93555 Naval Surface Weapons Center Attn: Mr. R. McCarten Code R122 White Oak, Silver Spring, MD Naval Weapons Support Center 20910 Code 5042 Attn: Mr. L. Roslund Crane, Indiana 47522 1 Attn: Dr. B. Douda Naval Surface Weapons Center Code R121 Rohm and Haas Company White Oak, Silver Spring, MD 723-A Arcadia Circle 20910 Hunsville, Alabama 35801 Attn: Mr. M. Stosz Attn: Dr. H. Shuey 1 Naval Weapons Center Strategic Systems Project Office 1 Code 3853 China Lake, CA 93555 Dept. of the Navy Room 901 Attn: Dr. R. Atkins Washington, DC 20376 Attn: Dr. J. F. Kincaid 1 Naval Weapons Center Code 3205 Strategic Systems Project Office 2 China Lake, CA 93555 **Dept.** of the Navy Attn: Dr. L. Smith Room 1048 1 Washington, DC 20376 Naval Weapons Center Attn: Mr. E. L. Throckmorton Code 3205 Mr. R. Kinert China Lake, CA 93555 Attn: Dr. C. Thelen Thiokol Chemical Corp. Brigham 1 Naval Weapons Center City Code 385 Wasatch Division Brigham City, UT 84302 China Lake, CA 93555 Attn: Dr. G. Thompson Attn: Dr. A. Amster

No. Copies

1

1

1

1

1

1

1

6/80

No. Copies

1

1

• 1

1

1

1

1

1

1

21

USA ARRADCOM DRDAR-LCE Dover, NJ 07801 Attn: Dr. R. F. Walker

USA ARRADCOM DRDAR-LCE Dover, NJ 07801 Attn: Dr. N. Slagg

U.S. Army Research Office Chemistry Division P.O. Box 12211 Research Triangle Park, NC 27709

Fluorochem, Inc. 680 South Ayon Ave. Azusa, CA 91702 Attn: Dr. Kurt Baum

Univ. of Illinois at Chicago Circle 1 Dept. of Chemistry Box 4348 Chicago, Illinois 60680 Attn: Professor J.H. Boyer

University of Massachusetts Department of Chemistry Amherst, MA 03003 Attn: Professor J.C. Chien

Rockwell International Rocketdyne Division 6633 Canoga Avenue Canoga Park, CA 91304 Attn: Dr. Karl O. Christe

Rockwell International Rocketdyne Division 663? Canoga Ave. Canoga Park, CA 91304 Attn: Dr. M.B. Frankel

Polysciences, Inc. Paul Valley Industrial Park Warrington, PA 18976 Attn: Dr. B. David Halpern

The Johns Hopkins University Department of Chemistry Baltimore, MD 21218 Attn: Dr. Joyce J. Kaufman

No. Copies 1 Univ. of Massachusetts Department of Chemistry Amherst, MA 03003 Attn: Professor P. Lillya Office of Naval Research 1 800 N. Quincy St. Arlington, VA 22217 Attn: Dr. G. Neece Code 472 1 SRI International 333 Ravenswood Ave.

Menlo Park, CA 94025

Attn: Dr. D.L. Ross