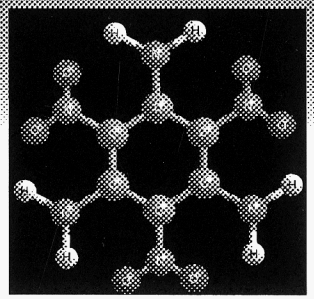
LA-UR- 01-4491

Computational Studies of TATB – Kel-F 800 Adhesion in PBX 9502

Neil J. Henson, T-12
Thomas D. Sewell, Edward M. Kober, T-14

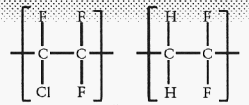
Los Alamos

PBX 9502 : TATB/Kel-F



1,3,5-triamino-2,4,6-trinitrobenzene (TATB)

Kel F-800 polymer



TFCE DFE
3 : 1

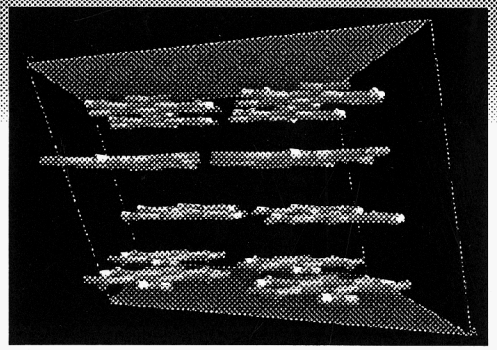
TFCE – 1,2,2-trifluoro-1-chloroethene
DFE – 1,1-difluoroethene

- PBX 9502 : 95% TATB, 5% polymer

Theoretical Division

Los Alamos NATIONAL LABORATORY

TATB crystal structure (010)

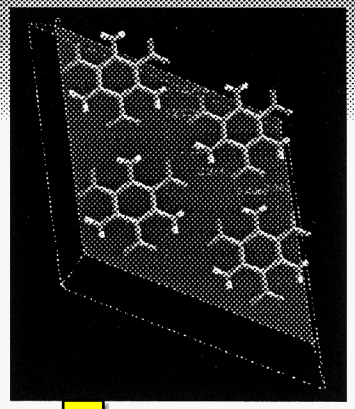


- interlayer separation = 3.0Å (NO_2–NH_2 at 3.17Å)

Theoretical Division

Los Alamos NATIONAL LABORATORY

TATB crystal structure (001)



Theoretical Division

Los Alamos NATIONAL LABORATORY

LOS ALAMOS NATIONAL LABORATORY
3 9338 01038 9491

Aims of project

- Simulate the structure and properties of the TATB/polymer interface at the atomic level
- Is there a preference for either of the co-monomer components for the TATB surface?

General Approach

- Find an accurate method to simulate the TATB bulk structure and apply it to surfaces
- Calculate the energetics of the interaction between single co-monomers and the TATB surface and use this data to simulate the interface.

Simulations of bulk TATB (1)

- Generalised forcefield fitted by Fillipini and Gavezzotti already validated for bulk TATB
- Standard harmonic functions for bonded terms (harmonic springs for bonds and angles) and Buckingham potential for intermolecular terms

$$E_{ij} = A_{ij} \exp - \left(\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

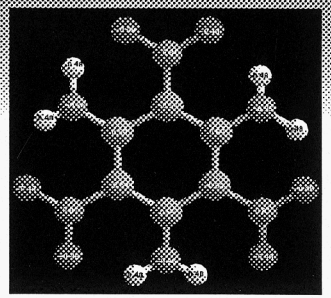
Simulations of bulk TATB (2)

- Performance of potential :-

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	9.01	9.03	5.81	108.6	91.8	120		40.2
[illegible]	8.87	8.88	6.63	110.7	91.4	113.9		44.3

- cell parameters to within 3%, sublimation energy to within 10%
- but no electrostatics! Is this a problem?

DFT calculation on single TATB molecule

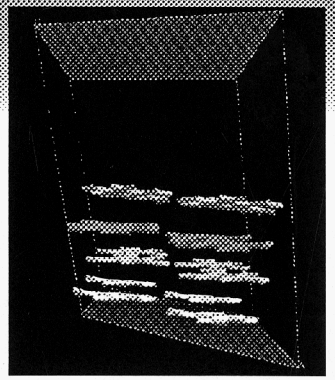


- calculation with Gaussian98, B3LYP, 6-31G*, CHelpG

Generation of TATB surfaces

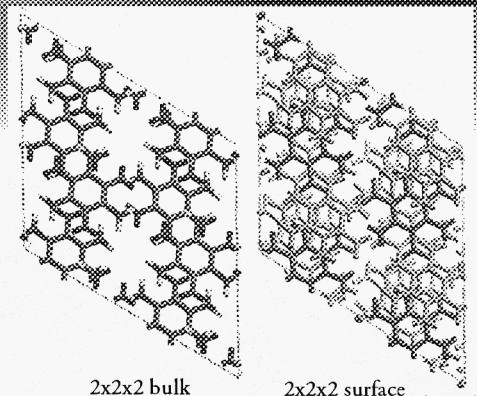
- which surface is the dominant one in a crystallite?
- the obvious one from symmetry is (001)
- first, for comparison take a 2x2x2 bulk cell and minimise the structure
- then build the same structure with a "vacuum gap" above the surface and minimise this.

Picture of "vacuum gap" model



- 10Å gap

Minimisation of surface models



2x2x2 bulk

2x2x2 surface
white, yellow, magenta, brown

Limitations of the Fillipini *et al* potential

- The potential is fitted to a wide range of organic crystal structures and has parameters for C, N, O, S, and Cl.
- But no parameters for F, so we can't do TCFE and DFE
- Need to fit new potentials for F
- Good source of "ozone destroying" data

Available fluorocarbon crystal structures

[illegible]	-23.6	Cockcroft and Fitch (1990)
[illegible]	-128	Fitch and Cockcroft (1993)
[illegible]	-29.8	Cockcroft and Fitch (1991)
[illegible]		Torrie, Bisbrek and Powell (1996)
[illegible]		Pridmore, Torrie, Bisbrek and Powell (1996)

- perform a simultaneous least-squares fit to each of these crystal structures using the existing forcefield parameters to obtain new F–X parameters

Results with new F–X parameters

		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	experiment	4.76	6.63	8.52	122.0	227.80
	theory	4.44	6.06	7.78	119.9	181.52
[illegible]	experiment	15.51	5.87	9.53		868.65
	theory	15.50	5.70	9.44		834.43
[illegible]	experiment	10.17	14.96	5.10		776.0
	theory	10.01	14.84	5.27		782.59
[illegible]	experiment	10.66	8.58	7.86		717.83
	theory	10.68	8.50	7.31		694.18

- fit is adequate across the range of CFC structures
- now to use the parameters for something useful

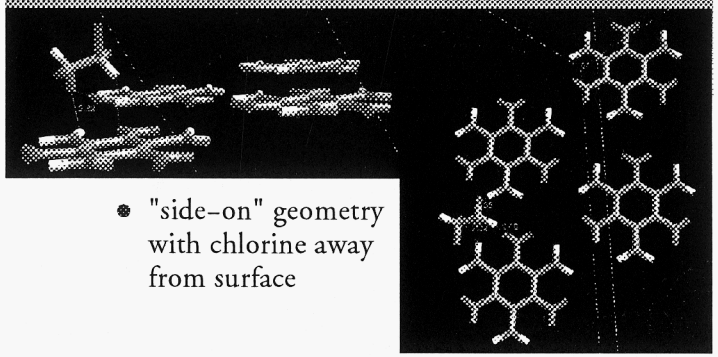
Monte Carlo docking calculations

- efficient method to probe possible binding sites for molecule
- high temperature dynamics on organic to generate a conformational database
- random insertion of organic with TATB surface fixed
- minimise position of organic and TATB surface together
- generates a number of binding sites

Docking of TCFE on TATB

- binding energies of docked sites range from 37.2–55.9 kJmol
- most favourable geometries have H, and F oriented towards TATB surface rather than Cl.
- perhaps the binding energies are a little too high

Most favourable binding site for TCFE/TATB surface

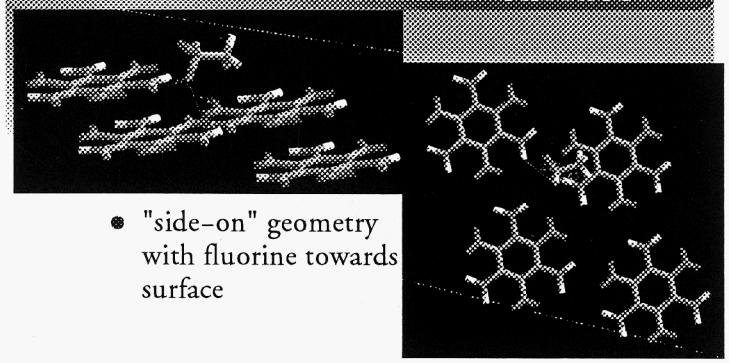


- "side-on" geometry with chlorine away from surface

Docking of DFE on TATB surface

- binding energies of docked sites range from 28.0–49.1 kJmol^{-1}
- slightly lower range than for TCFE
- would be expected for dispersive type interaction, but perhaps not for an electrostatic interaction?
- preference for side-on geometry more marked than for TCFE
- most favourable sites have F towards surface

Most favourable binding site for DFE/TATB surface

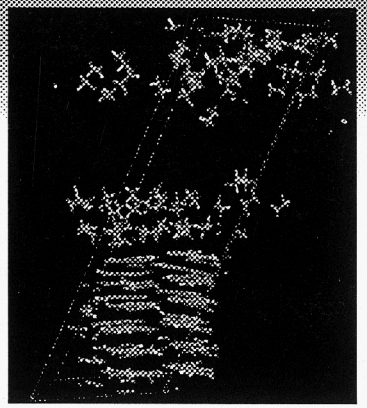


- "side-on" geometry with fluorine towards surface

Molecular Dynamics on TATB/monomer models

- now for a more realistic model
- construct a monomer "soup" with 3:1 ratio of TCFE:DFE at a realistic density
- perform MD on this model to equilibrate then place the "soup" above the TATB surface in the "vacuum" gap.
- perform MD simulation at 298K to observe any preferences for two monomers

Snapshot from MD simulation



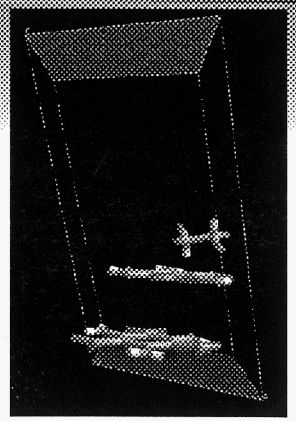
Improving the interaction potential

- important problem for the simulation of adsorption phenomena with empirical forcefields.
- use *ab initio* methods for guidance
- lack of description of dispersive interactions in Hartree-Fock or DFT methods
- need correlated method (e.g. HF/MP2) to reproduce energies
- are dispersive interactions important?

First step : Gaussian98 calculations on clusters

- disadvantages : clusters only, limited system size
- advantage : examine HF and DFT, and also MP2
- construct model consisting of a single TATB molecule with associated TCFE from most favourable docked binding site

VASP calculations on TATB/TCFE

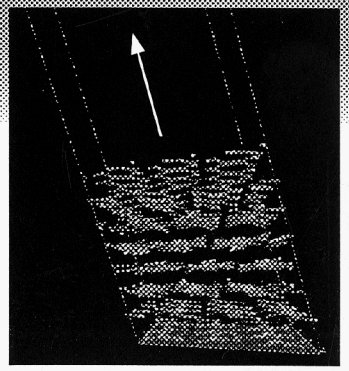


- but the binding energy is calculated to be +2.1 $kJmol^{-1}$

Future Directions

- MP2 optimisations on models to alleviate non-planar geometries
- Gaussian98 and VASP calculations on larger TATB slabs
- use of a commercial forcefield to perform calculations (MSI's COMPASS)
- calculations of surface energies to predict TATB crystal morphology

Surface energies with COMPASS

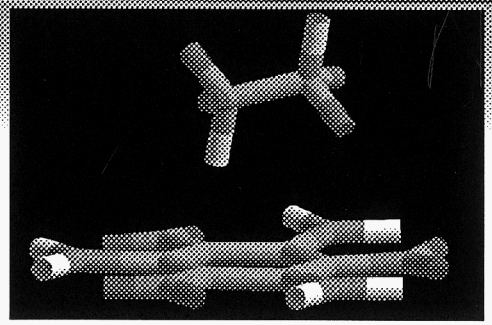


- preliminary calculations show (001) to be the most stable surface

Binding energies with COMPASS

- take most stable sites from docking calculations and calculate binding energy with COMPASS (with TATB surface fixed)
- TCFE binding energy is 26.1 $kJmol^{-1}$ vs. 55.9 $kJmol^{-1}$
- DFE binding energy is 15.4 $kJmol^{-1}$ vs. 49.1 $kJmol^{-1}$

Starting model for Gaussian98 calculations



- 31 atoms. 3-21G basis (236 basis functions), 6-31G* (380 basis functions)

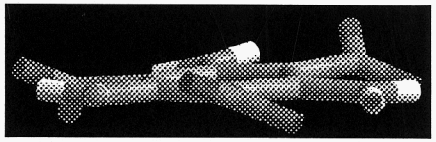
Results of Gaussian98 binding calculations

[illegible]	[illegible]
3-21G HF	-7.8
3-21G MP2	-15.7
3-21G MP2 FSSE	4.5
6-31G* HF	-11.7
6-31G* HF FSSE	4.1
3-21G DFT	-16.0
3-21G DFT FSSE	2.1
6-31G* DFT	-7.1
6-31G* DFT FSSE	7.2

- the best calculation we can do predicts the monomer to be unbound!
- And.....

Optimised geometries

- 3-21G, 6-31G* DFT 3-21G HF predict that the most stable conformation of the TATB molecule is planar
- 6-31G* HF gives :-



- nitro groups rotate out of plane by 28° so we can't use this for an MP2 calculation

Periodic DFT calculations

- advantages : periodic – no problem with finite size clusters
- disadvantages : DFT, so no dispersive interactions included
- first step, perform optimisation on bulk structure

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	9.01	9.03	6.81	108.6	91.8	120
[illegible]	9.08	9.11	6.82	109.6	92.1	120

- remarkably good agreement

Acknowledgements

- Tommy Sewell
- Ed Kober
- ASCI program