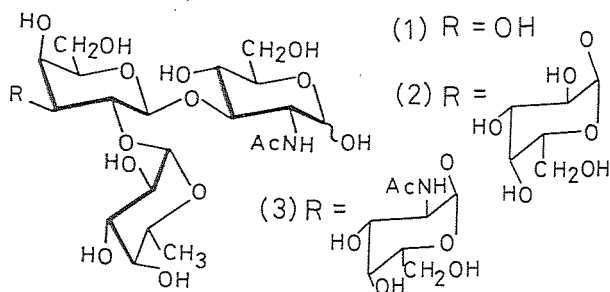


## 17.6-3 CONFORMATIONS OF SOME BLOOD GROUP DETERMINANT OLIGOSACCHARIDES

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The blood group determining factors A (3), B (2) and H (1) were synthesized and characterized by H. Paulsen and C. Kolar (Chem. Ber. 112, P.3190). Here we report on conformational calculations on these substances.

Empirical calculations were carried out with the computer program CPEM (Conformational Potential Energy Calculations for Macromolecules) of G. Barnickel (Doctoral dissertation F.U. Berlin, 1983) that applies the potential functions and energy parameters of Momany, McGuire, Burgess and Scheraga (J.Phys.Chem.79, p.2361). Further results were obtained with the semiempirical PCILO (Perturbation Configuration Interaction using Localized Orbitals) method (QCPE 272). The results are presented and the different methods compared.



## 17.6-4 MOLECULAR ORBITAL MODELING OF SILICON NITRIDES. Maureen M. Julian and G. V. Gibbs, Dept. of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0796.

The bulk characteristics of solids can be modeled and reproduced from short range structural properties. *Ab initio* calculations have been made on silicon nitrides, silicon sulfides, and silicates showing the total energy difference curves.

A potential energy surface has been generated for the  $H_6Si_2N_7$  molecule and compared to the  $H_6Si_2O_7$  molecule. The surface for the silicon nitride has a much deeper well in it than the surface for the sulfate. The surface graphs for both materials show that their potential energy varies relatively slowly with angle in the vicinity of the minimum but relatively rapidly with change in bond lengths. The relative shapes of the surfaces indicate the greater ease of formation of silicate glasses over the corresponding silicon nitride material. Experimentally measured bond lengths and angles are superimposed upon the theoretical calculations.

17.6-5 DETERMINATION OF PAIR INTERACTION ENERGIES FROM KNOWN SHORT RANGE ORDER PARAMETERS  $\alpha_j$ . By J. Kern and V. Gerold, Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Stuttgart, FRG.

A computer method is described which allows the determination of pair interaction energies  $V_i$  in a model crystal having short range order parameters  $\alpha_j$  as determined from a solid solution in thermal equilibrium. In this crystal a large number ( $j_{max} = 10\ 000$ ) of random A-B pair exchanges are simulated (but not performed in order to maintain the short range order) and the local changes  $\Delta N_{i,j}$  of the number of A-A pairs in coordination shells  $i$  for jump number  $j$  is registered. The unknown  $V_i$ 's are calculated from the set of simultaneous equations

$$\sum_j \Delta N_{i,j} w_j = 0 \quad i = 1, 2, \dots, i_{max}$$

Here  $w_j$  is the probability for the occurrence of jump number  $j$  and can be written as

$w_j = \exp(-U_j/kT)/(1+\exp(-U_j/kT))$  with  $U_j = 2 \sum_i \Delta N_{i,j} V_i$ .  $U_j$  is the change in energy for the proposed jump  $j$ . The first set of equations assumes that the total change in the number of A-A pairs in all coordination shells  $l = 1$  to  $i_{max}$  is zero.

This method has been tested first by simulating a crystal with two known energy terms  $V_1/kT$  and  $V_2/kT$  by using a Monte Carlo method. Surprisingly good results were found for  $i_{max} = 2$  to 8. In all cases  $V_1/kT$  and  $V_2/kT$  were reproduced within 5% and the higher order terms were found to be very close to zero.

The method was then applied to experimental short range order data published in the literature. For  $Cu_{85}Al_{15}$  at two annealing temperatures reproducible values were found for the  $V_i$ 's when  $i_{max}$  was larger than 4. The same was true for  $CuPt$ . From these results it is concluded that the first four energies  $V_i$  are significant. In the case of the clustering system  $Cu_{50}Ni_{41}$  only the first two  $V_i$ 's are significant. No good results were found for the alloy  $Cu_3Au$  where all  $V_i$ 's depended more or less strongly on the chosen  $i_{max}$ .

## 17.6-6 THE USE OF X-RAY DIFFRACTION ANALYSES AND MOLECULAR-MECHANICS TO PREDICT STRUCTURES OF HYPOTHETICAL ORGANIC MOLECULES. By Richard Gilardi and Clifford George, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375, U.S.A.

According to empirical density prediction schemes, replacement of most of the hydrogen atoms on polycyclic organic cage compounds with nitro or nitramino groups should, in principle, lead to a new class of very dense ( $d > 2.0\ mg\ mm^{-3}$ ) stable organic molecules. However, accomplishing this through chemical syntheses has thus far proved to be extremely difficult, and the most highly substituted cage compounds known to us are 1,3,5,7- and 2,2,6,6-tetranitroadamantane, which have densities of only 1.605 and 1.617  $mg\ mm^{-3}$ , respectively. It would be of interest if a method could be found to determine whether failure of nitro-substitution methods, for a particular case, is kinetic (caused by high-energy transition states) or energetic (caused by large strain in the equilibrium structure of the desired product).

Several small polynitro and polynitroamino compounds have been determined by X-ray diffraction analyses in our laboratory during the last three years. The results of these analyses, and others from the literature, have been used to develop a set of potential parameters for these moieties in various molecular environments, which were added to the molecular mechanics program MM2 (developed by N. Allinger, Univ. of Georgia, USA). This computational scheme has been used to build reasonable models and evaluate the residual strain in hypothetical molecules such as octanitrocubane, 2,4,6,8,9,10-hexanitro-hexa-azaadamantane, and various polynitroadamantanes. In addition to these results, the structures of two new compounds, 1,3,3-trinitroazetidene ( $C_3H_4N_4O_6$ ) and 2,6-dinitro-3,5-diamino-1,4-pyrazine ( $C_4H_4N_6O_4$ ), will be reported.