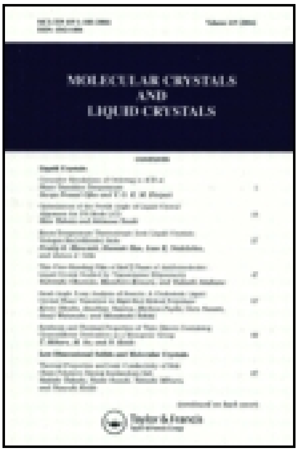

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Erwin Buncel [a], Andrew J. McKerrow [a] & Peter M. Kazmaier [b]

[a] Department of Chemistry, Queen's University, Kingston, Ontario, Canada, K7L 3N6

[b] Xerox Research Centre of Canada, Mississauga, Ontario, Canada, L5K 2L1

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MOLECULAR MODELLING OF PHOTOACTIVE PIGMENTS. INVESTIGATIONS OF POLYMORPHISM USING THE DREIDING FORCE FIELD.

ERWIN BUNCEL[a], ANDREW J. MCKERROW[a] and
PETER M. KAZMAIER[b]
(a) Department of Chemistry, Queen's University, Kingston, Ontario, Canada, K7L 3N6.
(b) Xerox Research Centre of Canada, Mississauga, Ontario, Canada, L5K 2L1.

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Abstract The role of polymorphism in controlling the properties of organic photoconductors is central to the design of such materials. Insights into this problem may be gleaned through molecular modelling. This paper describes studies aimed at modelling crystal structures for a series of perylene photoactive pigments with the DREIDING force field. Extensions of this method to understanding polymorphism of these photogenerators are also discussed.

Keywords: molecular modelling, polymorphism, organic photoconductors, perylene pigments

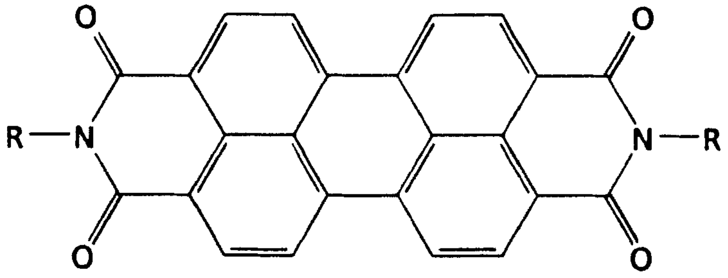
INTRODUCTION

The development of organic photoconductors has generally involved the design and synthesis of materials that would subsequently be tested in order to characterize their xerographic properties. Progress by such a route is complicated by packing effects in the solid state that may impact on the properties of these materials in a fashion that cannot easily be anticipated.

For example, in 1972 Weigl *et al.*[1] noted that different polymorphs of metal - free phthalocyanine were characterized by distinctly different photoconductivities. Further studies of photogenerator pigments in our laboratories have been concerned with the effects of solid state packing on photoconductivity.[2-3] From this work it was clear that researchers involved in the development of novel photoconductors must be concerned with both molecular and solid state properties of such materials.

As part of an overall plan for developing rational methods for the design of photoactive pigments, we have examined the possibility of computationally modelling solid state materials. Specifically, the recently developed DREIDING force field,[4] as utilized by POLYGRAF, allows for molecular mechanics calculations to be carried out on periodic systems. Accordingly, it was our objective to examine the possibility of modelling properties of crystalline solids using the DREIDING force field.

Hädicke and Graser reported single crystal X-ray structures for a series of N,N′-dialkylperylene-3,4:9,10-bis(dicarboximides), I-XIV.[5] Their results served as a starting point for our computational studies as we sought to validate the DREIDING method through a comparison of the modelled perylene lattices with this literature data. Furthermore, Hädicke and Graser's data was recognized as a source of information on potential perylene packing motifs and was therefore utilized in investigations of polymorphism.



R Substituents

I Methyl
II Ethyl
III Propyl
IV Butyl
V Pentyl
VI 2-Xylyl
VII 2-Ethoxyethyl
VIII 3-Methoxypropyl
IX 3-Ethoxypropyl
X 4-Methoxybenzyl
XI Benzyl
XII 2-Phenethyl
XIII 2-Phenylpropyl
XIV 2-Methylbutyl

CALCULATIONS

All calculations were carried out using BioDesign's POLYGRAF program, version 2.10, incorporating the DREIDING force field . Optimizations using the conjugate gradient method and graphics manipulations were carried out on a Silicon Graphics Personal Iris 4D/25TG workstation.

Atomic coordinates were available from Hädicke and Graser's studies for the following series of N,N' -dialkylperylene -3,4:9,10- bis(dicarboximides): methyl, ethyl, propyl, n-butyl and n-pentyl, **I-V**. These were used within POLYGRAF to generate a unit cell that was replicated with periodic boundary conditions so as to create an aggregate. As information on the position of hydrogen atoms in the unit cell was not readily available, these atoms were explicitly added to the perylenes with default bond lengths and angles. Energy minimization calculations were carried out so that both molecular and unit cell parameters could change.

RESULTS AND DISCUSSION

Force Field Calibration

For perylenes **I** - **V** comparison of the calculated lattices with Hädicke and Graser's data revealed that the DREIDING force field could accurately model both molecular and crystalline features of these compounds.

Specifically, for each of the five compounds perylene molecules were extracted from the calculated lattice and compared with the appropriate molecule in the literature unit cell. Errors in minimized bond lengths, angles and torsions were calculated and are reported in Table 1. The agreement between the calculated and experimental molecular geometries is seen to be very good.

The largest deviations in these studies occurred in bonds between carbon and nitrogen as these were 5-6% shorter than their literature values. The carbon skeleton of the perylenes was accurately reproduced by DREIDING.

TABLE 1 RMS errors in geometry for DREIDING calculations

Substituent	Bond Lengths (Angstroms)	Bond Angles (Degrees)	Torsions (Degrees)
Methyl	0.038	2.421	2.013
Ethyl	0.040	2.478	2.813
Propyl	0.039	2.116	1.507
Butyl	0.036	2.093	1.627
Pentyl	0.039	2.058	1.108

The DREIDING force field differs from other force fields in that its force constants and geometry parameters are selected on the basis of the hybridization state of atoms.[4] Using such a generic approach this method can be applied to the study of molecules for which experimental data, i.e. bond lengths, is lacking. The errors in carbon - nitrogen bond lengths in this study are a direct manifestation of this approach as designating the imide nitrogen as a resonant nitrogen introduces too much double bond character to all imide nitrogen - carbon bonds.

Comparison of the modelled lattices with their literature counterparts revealed that errors in unit cell parameters were minor.

Charge Distribution Calculations

It was anticipated that electrostatic charges in the lattice could affect the quality of these minimizations. In order to include such effects an accurate description of the charge distribution within these molecules was required.

Within POLYGRAF there are several possible methods for calculating molecular charges. Gasteiger's[6] partial equalization of orbital electronegativity (PEOE) and the Del Re scheme[7] are both methods that generate charges on the basis of molecular topology (bond connections). Rappé and Goddard's charge equilibration method[8] calculates charge distribution for molecules on the basis of geometry and responds to changes in the molecular environment.

The energy of the N,N'-dimethylperylene-3,4:9,10-bis(dicarboximide) was minimized using these three approaches. Comparison of errors in molecular geometry for the resulting lattices did not reveal considerable differences from the original calculations (Table 2). Deviations in the unit cell parameters were also of the same magnitude as those obtained in the original calculations.

TABLE 2 RMS errors in geometry for DREIDING calculations of N,N'-dimethylperylene -3,4:9,10-bis(dicarboximide) with various charging schemes

Charge Option	Bond Lengths (Angstroms)	Bond Angles (Degrees)	Torsions (Degrees)
None	0.038	2.421	2.013
Del Re	0.040	2.451	2.730
PEOE	0.040	2.474	1.814
Charge Equil.	0.040	2.647	1.871

Based on these results it was concluded the the DREIDING force field could accurately model both molecular and crystalline features of the perylenes **I** - **V**.

Investigations of Polymorphism

As previously mentioned, the existence of polymorphic forms of the same compound complicates the development of novel photoconductors. With the validated DREIDING force field, efforts have been directed towards establishing protocols for investigating this polymorphism problem.

One approach that has been investigated involved truncating alkyl residues of the dipentylperylene in order to generate N,N' -dimethylperylene -3,4:9,10-bis(dicarboximide) in a triclinic lattice. Minimization of aggregates of this modified unit cell yielded a high energy polymorph with considerable void volume.

Three different approaches were examined as methods for annealing this aggregate into a polymorph with both reasonable energy and density. One avenue that was investigated involved carrying out molecular dynamics simulations on the aggregate. A second approach involved editing the unit cell so as to manually remove the void volume. A third method for annealing the aggregate involved applying external stresses to the unit cell during the minimization.

Of these three approaches, the application of external stresses to the triclinic unit cell was most successful in generating reasonable polymorphs. Specifically, the high energy aggregate obtained after editing the dipentylperylene unit cell was minimized with a full array of expansive and compressive stresses. The resulting aggregate was further minimized without any stresses in order to obtain a minimum energy aggregate.

TABLE 3 Stress / strain annealing of the dimethyl perylene triclinic polymorph

Direction of Stress	Stress (GPa)	Final Energy (Kcal mol-1)	Final Density
XX	1	91.99	0.7687
YY	1	82.84	1.0928
ZZ	1	83.25	1.0762
YZ	1	78.58	1.3296
XZ	1	79.68	1.4037
XY	1	85.91	1.1174
XX	-1	74.52	1.4763
YY	-1	84.26	1.1703
ZZ	-1	76.14	1.4741
YZ	-1	76.68	1.3863
XZ	-1	79.45	1.4041
XY	-1	82.44	1.2994

Initial Energy = 84.38 kcal / mol
Initial Density = 1.0707 g / cm^3

Compare to
E = 72.84 kcal / mol
and Dm = 1.5331
for monoclinic polymorph

As shown in Table 3, this approach was able to locate a polymorph of N,N′-dimethylperylene -3,4:9,10-bis(dicarboximide) whose energy and density compared favorably with the monoclinic polymorph of this compound.

CONCLUSIONS

Based on the results of this study it is apparent that the DREIDING force field can model both molecular and crystalline features of the N,N-dialkylperylene-3,4:9,10-bis(dicarboximides), I - V. In situations where there was difficultly reproducing experimental geometry, such as the nitrogen - carbon bonds, the source of these errors was linked to the assumptions used to define the DREIDING force field.

The problem of polymorphism is central to the field of photoconductor design. In this study it has been possible to locate a feasible polymorph for N,N′- dimethylperylene -3,4:9,10- bis(dicarboximide), I, by placing the molecule in a related polymorph and applying stresses to anneal the lattice. Further work is planned in which X-ray powder diffraction data will be calculated for these theoretical polymorphs and compared with experimental spectra.

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