tations, the crystal field blue shifts the $n\pi^*$ transitions. The longest wavelength $n\pi^*$ transition is blue-shifted by ca. 30 nm in the scaled calculations and by 40 nm in the unscaled. (Note that in the unscaled calculations on molecule A the lowest energy $n\pi^*$ transition has been obscured by mixing with the $\pi\pi^*$ manifold and has been classified as a $\pi\pi^*$ transition by our criterion.) In the gas-phase calculations, the lowest excited state is $n\pi^*$ but, in the crystal, the first $n\pi^*$ excited state falls between the two lowest energy $\pi\pi^*$ excited states.

With respect to intensity, in the scaled crystal field calculations, only the $n\pi^*$ band predicted for ca. 215 nm has a significant intensity in absorption, with an oscillator strength of ca. 0.03. The unscaled calculations also indicate a relatively strong $n\pi^*$ band at slightly shorter wavelength (ca. 210 nm).

The crystal field extensively mixes $n\pi^*$ and $\pi\pi^*$ transitions, as reflected in the deviations of the angle ϕ between the transition moment and the molecular plane from the 90° characteristic of pure $n\pi^*$ transitions. The extent of this mixing has important implications for the circular dichroism (CD) spectrum of nucleic acids. The CD intensity of a transition depends on the scalar product of the electric and magnetic dipole transition moments.[32] Mixing of $n\pi^*$ and $\pi\pi^*$ transitions can lead to substantial CD intensity because $n\pi^*$ transitions generally have strong in-plane magnetic dipole transition moments, while $\pi\pi^*$ transitions have strong in-plane electric dipole transition moments. Such $n\pi^*$–$\pi\pi^*$ mixing due to local electrostatic fields (the one-electron contribution[33]) has long been recognized as essential for accounting for peptide CD spectra[34,35] but, with a few exceptions,[36–38] has been neglected in theoretical calculations on nucleic acids. The present results indicate that these contributions may be substantial and need to be considered.

Experimentally, there is a dearth of information on $n\pi^*$ transitions in the nucleic acid bases, with data on guanine being especially sparse. Clark[2] suggested that a weak feature observed near 300 nm in the reflection spectrum of 9-ethylguanine crystals, polarized normal to the molecular planes, may be an $n\pi^*$ transition. However, he noted that this feature could also be due to a shifted $0 \rightarrow 0$ component of the first $\pi\pi^*$ transition. If this feature is an $n\pi^*$ transition, our theoretical prediction that the first $n\pi^*$ transition in 9-ethylguanine crystals falls between the first and second $\pi\pi^*$ transitions is incorrect.

In summary, we have shown that local electrostatic fields in 9-ethylguanine crystals have a significant effect upon the electronic spectral parameters. In particular, these local fields alter the transition moment directions of the $\pi\pi^*$ transitions and mix $n\pi^*$ with $\pi\pi^*$ transitions. It is necessary to consider these interactions in interpreting the absorption and circular dichroism spectra of crystals of the bases and of oligo- and polynucleotides.

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Registry No. 9-Ethylguanine, 879-08-3.

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Influence of Molecular Dipole Interactions on Solid-State Organization

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Abstract: A statistical analysis of molecular dipole moments within three space groups ($P1$, $P\bar{1}$, and $P2_1$) was carried out. The magnitude of the molecular dipole moment does not vary significantly between centrosymmetric ($P\bar{1}$) and noncentrosymmetric ($P1$ and $P2_1$) space groups and does not correlate with relative molecular orientations within the $P2_1$ space group. Thus, the high preference for organic molecules to crystallize in one of the centrosymmetric arrangements cannot be attributed to dipole–dipole interactions.

The detailed study of regular and semiregular molecular arrays such as single crystals and liquid crystals has moved into prominence in recent years as the potential for practical applications of such systems has fluorished. Because of our interest in developing new methods for manipulating multimolecular arrays for practical applications, we became aware of the common idea that large molecular dipole moments are an important factor leading to centrosymmetry in organic crystals.[1] This notion appears to be held by many researchers in the area of nonlinear optics, as evidenced by statements such as the following: "It is clear that as the molecular ground-state dipoles become larger, the electrostatic interraction between adjacent molecules increases and the net molecular dipole alignment required to achieve the maximum crystal anisotropy becomes more energetically unfavorable";[2] and "...it is hypothesized that a correlation between the dipolar and conjugation characteristics of nonlinearly enhanced molecules and the common occurrence of antiparallel alignments exists."[3] Because the design of new methods for molecular

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[1] Centrosymmetric arrangements are statistically favored in organic crystals. Of the entries in the Cambridge Structural Database (January 1990 release), 67% are in one of the centrosymmetric space groups. However, crystal structures based on single enantiomers (a substantial fraction of the collection) *cannot* be centrosymmetric. Thus, the value of 67% represents a *lower limit* for the bias toward centrosymmetry; the figure is surely far higher for molecules that could adopt either centrosymmetric or noncentrosymmetric arrangements.

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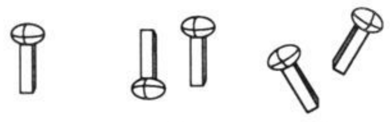

Space Group	P1	$P\bar{1}$	$P2_1$
Dipole - dipole angle			
restrictions due to symmetry	0°	180°	no restriction
Net dipole moment	yes	no	possible

Figure 1. Consequence of molecular dipole moments on crystal bulk dipoles in space groups $P1$, $P\bar{1}$, and $P2_1$.

alignment can proceed in a logical fashion only when the relative significance of the major controlling factors is known, it is important to establish whether or not the magnitudes of molecular dipoles correlate with crystal symmetry.

The significance of dipole–dipole interactions in crystals has been addressed quantitatively by several groups since the pioneering studies of Kitaigorodsky.[4] Unfortunately, such computational methods are just now reaching the point where dipole interactions can be reasonably approximated for *a given* crystal structure and are not yet at the point where all possible alternative arrangements can be evaluated. In a recent study of some small molecule structures containing either a carbonyl or a nitrile group, Gavezzotti concluded on the basis of electrostatic packing energy calculations that dipole–dipole interactions contribute negligibly to total crystal stabilization.[5]

We developed our approach from the pioneering statistical studies of Dunitz[6] that have provided valuable information on chemical dynamics. In our case, the question to be addressed centered on the correlation, or lack thereof, of the magnitude of molecular dipole moment with the relative spatial orientation of these dipoles within the crystal structure. Clearly, if dipole moments were a significant factor in directing crystallization into one of the centrosymmetric space groups, then the average molecular dipole moment in such space groups should exceed that in other packing arrangements.

We selected for study crystal structures in the three space groups $P1$ (restricted to Z (number of molecules/unit cell) = 1), $P\bar{1}$ (Z = 2), and $P2_1$ (Z = 2). For such cases, the symmetry-imposed restrictions on orientation are illustrated in cartoon fashion in Figure 1. As a result of the lack of other than translational symmetry, all dipole moments for $P1$ must point in the same direction and thus any molecular dipole must result in a net crystal dipole. By contrast, in $P\bar{1}$, for each molecule there is a centrosymmetric partner, so net cancellation of dipoles occurs and no bulk dipole moment results. The $P2_1$ space group contains a 2-fold screw axis about which pairs of molecules are related by a combination of rotation and translation. Thus, the magnitude of the net crystal dipole that results for $P2_1$ depends upon the orientation of the molecular dipole relative to the screw axis: when the molecular dipoles are oriented parallel to the screw axis, their effects are additive (as for $P1$), whereas when they are oriented perpendicular to the 2_1 axis, and hence antiparallel to one another, there is net cancellation (as in $P\bar{1}$).

Whereas data for a large number of organic crystal structures are available in the Cambridge Structural Database (CSD)[7], for only a very limited number of these would dipole moment data be available from the literature. Thus, we chose to use semiempirical calculation methods to arrive at dipole moments for molecules using coordinate data as obtained from the CSD. Dewar's AMPAC program using the AM1 parameter set has been demonstrated to provide consistently reasonable dipole moment data for a range of functionalities.[8] However, the AM1 package does not currently handle d-orbitals, thus restricting analysis to molecules containing only first-row elements, as well as divalent sulfur, trivalent phosphorus, and monovalent halogens. Further restrictions were applied in order to simplify analysis leading to the following criteria for inclusion of entries for study: (1) no systems with possible d-orbital interactions, e.g., pentavalent S or P; (2) no organometallic, ionic, or polymeric structures; (3) no solvent or other extraneous molecules present; (4) atomic coordinates supplied; (5) $P1$ limited to one and $P\bar{1}$ and $P2$ limited to two molecules per unit cell; and (6) no strong hydrogen bonding possible (i.e., omit structures containing O–H or N–H). These restrictions serve to limit seriously the number of examples from the $P1$ space group as only 28 structures remain after the exclusions listed above. Surviving structures from space groups $P\bar{1}$ and $P2_1$ two of the most frequently occurring space groups for organic crystals, numbered 1229 and 722, respectively. We

Table I. Mean and Median Dipole Moments (D) for Selected Structures in Space Groups $P1$, $P\bar{1}$, and $P2_1$

	$P1$	$P\bar{1}$	$P2_1$
no. of structures	28	161	179
mean dipole moment	3.41	3.33	3.14
std error of mean	0.37	0.15	0.15
median dipole moment	3.36	3.22	3.04

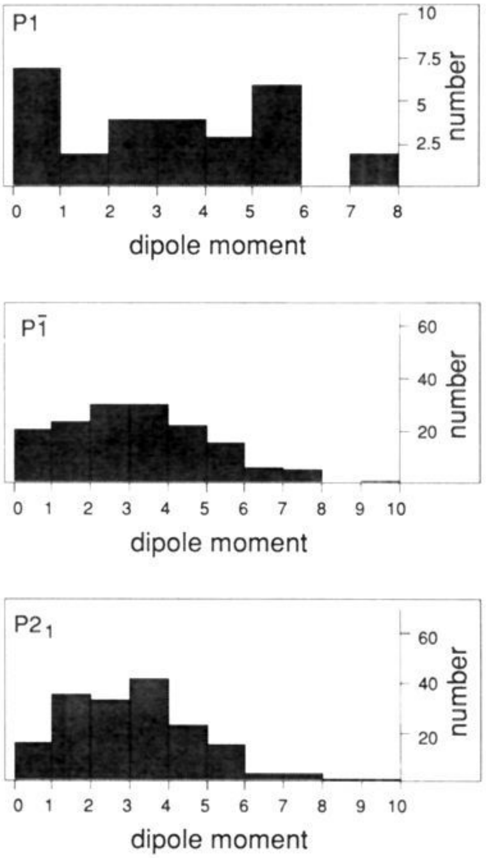

Figure 2. Histogram representations of dipole moment distributions in space groups $P1$, $P\bar{1}$, and $P2_1$.

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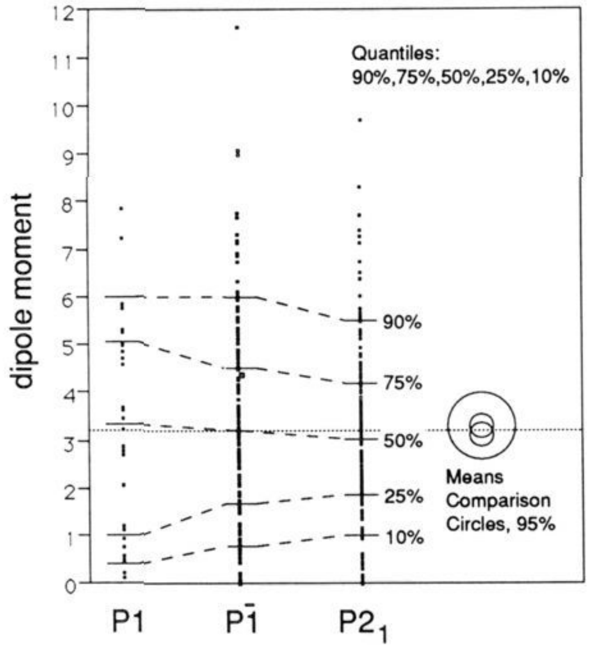

Statistical Summary

$R^2 = 0.00233$

F Ratio = 0.427

Prob > F = 0.653

Analysis of Variance

Source	Sum of Squares
Model	3.2
Error	1384.1
C Total	1387.3

Figure 3. Distribution of dipole moment magnitudes.

randomly selected 161 and 179 structures, respectively, from these two space groups for inclusion in the study.

Because of the low accuracy of hydrogen positions from X-ray structure studies, hydrogens were placed at idealized positions (0.95 Å, ideal angles depending on coordination about bonded atom). Calculations of molecular dipole moments as well as the coordinates for the centers of positive and negative charges were carried out on a VAX workstation II with AMPAC. Each result was then evaluated for reasonableness both in the magnitude and the orientation vector for the dipole. Statistical analyses were performed with the aid of the Macintosh program JMP.[9]

Table I gives mean and median dipole moments (in D) for each of the three space groups. The data are presented in histogram form in Figure 2 and graphically along with means comparisons circles at the 95% level in Figure 3. From the large degree of overlap of these circles, as well as from other statistical measures, it can be inferred that the distributions of dipoles in the three space group samples are not significantly different at the 95% confidence level, notwithstanding the considerable difference in sample sizes.

The same question of the effect of dipole moment on molecular orientations within crystals can be addressed from a different perspective: if dipole–dipole interactions were significant in molecular orientations within crystal structures, then there should be a correlation between the magnitude of dipole moment and the angle, θ, of the dipole relative to the crystallographic axis in the $P2_1$ space group. For large angles, near cancellation of the dipoles of the molecules would result in a quite small crystal dipole while alignment of the dipoles in the direction of the crystallographic axis would lead to a substantial crystal dipole from summation of the individual molecular contributions. Figure 4 presents a histogram of the angle, 2θ, between symmetry-related dipoles. It is important to note that although there is a clear preference for large angles, this *is not* the direct result of dipole–dipole interactions but is a result of uniform spherical distribution.[10]

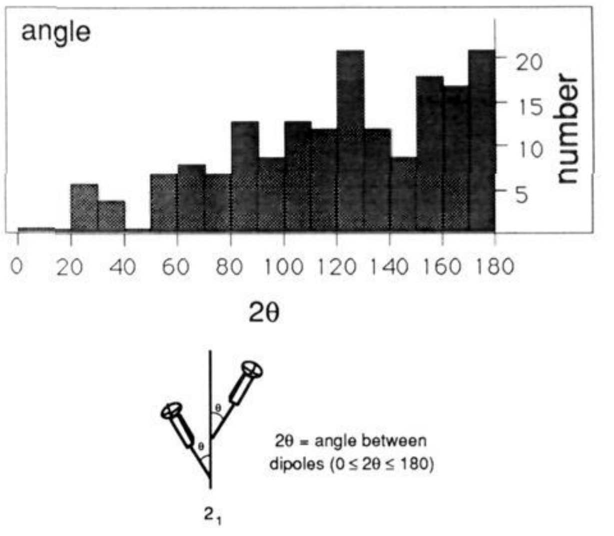

Figure 4. Histogram presentation of distribution of angles between symmetry-related molecules in the space group $P2_1$.

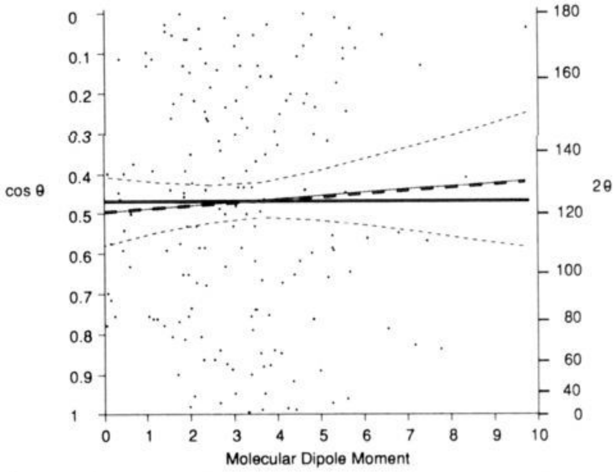

Figure 5. Scatter plot of molecular dipole moment versus angle between symmetry-related molecules in space group $P2_1$.

In Figure 5 is provided a scatter plot of dipole moment versus the angle 2θ between the symmetry-related molecular dipole vectors. The horizontal solid line represents the mean value of cos θ, 0.469 (dipole–dipole angle 124°). This is to be compared with the average cos θ value expected for a random angle distribution, 0.5 (dipole–dipole angle 120°). The heavy dashed line represents the straight-line fit of cos θ vs dipole moment, with the light dashed lines showing the 95% confidence levels; the observation that the confidence area contains the entire response mean line indicates that the slope is not significantly different from zero at the 0.05 confidence level. It is clear from all interpretations that there is no correlation between the magnitude of molecular

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(9) *JMP, Software for Statistical Visualization*, Version 1.0 (1989), SAS Institute Inc., Cary, NC.

(10) The apparent bias toward large angles is an artifact. For a random distribution of points on the surface of a sphere, the number of points in a small shell at azimuthal angle θ (in this case, the angle between the dipole and the 2_1 crystal axis, i.e., half the dipole–dipole angle) is proportional to the area of the shell, and hence to sin θ. Thus it can be shown by integration that it is the cosine of this azimuthal angle, and not the angle itself, that is expected to have a uniform distribution.

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dipole and the relative orientation of the screw axis related molecules.

In conclusion, we have demonstrated through statistical analysis that the magnitude of the molecular dipole moment does not vary significantly between centrosymmetric ($P\bar{1}$) and noncentrosymmetric ($P1$ and $P2_1$) space groups and does not correlate with relative molecular orientations within the $P2_1$ space group. This is not to say that *local* electrostatic interactions between molecules are unimportant; such local effects as hydrogen bonding, interactions of polar groups, etc. obviously do play a significant role, along with molecular shapes, in determining packing in molecular crystals. However, the high preference for organic molecules to crystallize in one of the centrosymmetric arrangements cannot be attributed to molecular dipole–dipole interactions, and attempts to design molecular arrays based primarily on considerations of overall molecular dipole moments have, statistically speaking, a small chance of success.

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Supplementary Material Available: Tables of entries used for each of the three space groups with dipole moments and, for $P2_1$, angles (11 pages). Ordering information is given on any current masthead page.

Hydrogen Abstraction from a Diamond Surface. Ab Initio Quantum Chemical Study with Constrained Isobutane as a Model

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Abstract: Abstraction of terminal hydrogens on a diamond {111} surface by atomic hydrogen has been offered as the possible rate-determining elementary step in the mechanism of low-pressure diamond growth by chemical vapor deposition. We use ab initio multiconfiguration self-consistent-field methods to estimate the activation energy for this abstraction reaction. We do this by first computing features of the potential energy surface for hydrogen abstraction from gas-phase isobutane and then computing features of the potential energy surface for this same system imposing constraints that mimic those found in a diamond lattice. Our results indicate that, although 5.4 kcal/mol of the CH bond energy in isobutane is attributable to structural relaxation of the radical, most of this radical relaxation energy (4.5 kcal/mol of it) is realized even with geometric constraints similar to those in a diamond lattice. We therefore predict bonds to a diamond surface to be only about 1 kcal/mol stronger than corresponding bonds to a gas-phase tertiary-carbon atom. The effect of the geometrical constraints on the activation energy for the hydrogen abstraction reaction is even smaller: all but 0.2 kcal/mol of the gas-phase radical relaxation energy at the transition state is realized even with the imposition of lattice-type constraints. Our results therefore support the use in kinetic modeling or molecular dynamics simulations of activation energies taken from analogous gas-phase hydrocarbon reactions with little or no adjustment.

I. Introduction

Despite the substantial technological advances made over the last decade in low-pressure diamond film growth by chemical vapor deposition (CVD),[1-4] much of the underlying chemical and physical mechanism remains uncertain. The one feature that appears central to the CVD process is the presence of gas-phase atomic hydrogen. One of the roles thought to be played by the hydrogen is the creation of reactive radical sites on the growing diamond surface via hydrogen abstraction. Indeed, detailed reaction mechanisms proposed for the CVD of diamond incorporate this reaction as an important, if not rate limiting, step.[5,6] The activation energy for hydrogen abstraction is therefore an essential parameter for modeling the CVD of diamond films. Yet without the ability to isolate and measure kinetic parameters for this and other related elementary reactions, we are forced either to determine these parameters theoretically or to estimate them by analogy with related experimentally known gas-phase reactions.

Semiempirical self-consistent-field calculations of the abstraction of a surface hydrogen atom from model cluster compounds have yielded disparate results. Huang, Frenklach, and Maroncelli,[7] using the MNDO method and a model ($C_{10}H_{16}$) compound, report an activation energy of 17.4 kcal/mol for hydrogen abstraction along with a caveat that, in addition to the uncertainties inherent in the model, the barrier is likely overestimated due to incomplete optimization of the transition-state structure. More recently, Valone, Trkula, and Laia,[8] using the AM1 semiempirical method, report that no activation at all is required to abstract a hydrogen from their $C_{20}H_{35}$ model compound. While these theoretical studies may be useful for comparing contrasting mechanisms within one model compound and one electronic structure model, the direct theoretical determination of activation energies for elementary chemical reaction steps involving diamond is, for the most part, too inaccurate to be useful for modeling. This is less

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