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Application of a Computational Systematic Search Strategy to Study Polymorphism in Phenazine and Perylene

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The materials phenazine and perylene have been previously reported to exhibit polymorphic behavior. Experimental evidence suggests that both molecules can exist in at least two polymorphic forms. In the case of phenazine, only one polymorph has a fully described crystal structure. In the case of perylene, two polymorphs have a reported structure, from single-crystal studies; however, one structure solution is of poor quality. This paper reports the results of a molecular modeling study and postulates crystal structures for the two polymorphs which lack a reliable experimental determination. Systematic searches of potential packing arrangements were conducted in the reported cells for both the solved and unsolved polymorphs of phenazine and perylene. A recently validated search method (Hammond, R. B.; Roberts, K. J.; Docherty, R.; Edmondson, M. *J. Phys. Chem. B* **1997**, *101*, 6532) was employed to rank packing arrangements by considering nonbonded atom−atom distances in combination with calculated lattice energies. The molecular packing arrangements were compared and contrasted using the packing energy breakdown routines within the program HABIT95 (Clydesdale, G.; Roberts, K. J.; Docherty, R. Quantum Chemistry Program Exchange **1996**, *16*, 1).

1. Introduction

The purpose of the work reported here is three-fold. First, to provide a further test of the ability of a recently developed, systematic search methodology to fully and accurately elucidate possible packing arrangements for molecular materials in a specified unit cell.[1,2] Second, to demonstrate the usefulness of the approach when applied to polymorphic systems by predicting, as yet, undetermined polymorph structures, and, thereby, third, to gain a fuller understanding of the factors which determine the solid-state chemistry of phenazine, perylene, and related molecules.

A knowledge of the packing arrangements of molecules within a crystal lattice provides valuable insight into the origin of a material's solid-state properties thus providing, in principle, a route to a molecular design strategy for controlling the crystal chemistry in order to enhance performance characteristics of interest. When one considers the importance of crystal engineering concepts and polymorph control in the development and production of speciality chemicals such as pharmaceuticals, agrochemicals, pigments, and dyes, the present limits on our understanding of the solid-state structure of these materials are surprising. One reason for this deficiency is the difficulty in preparing crystals of sufficient size and quality in the particular polymorph of interest to solve its 3-D crystal structure by conventional single-crystal X-ray diffraction techniques.

When single-crystal methods cannot be applied, structural information has to be generated by other means. Two of the main approaches are ab initio structure prediction and structure solution using X-ray powder diffraction data. Approaches to structure prediction from first principals have been developed by Gavezzotti,[3] Holden,[4] Perlstein,[5] and Karfunkel,[6] and a summary of their elegant work has been documented by Docherty and Jones.[7] However, these methods still have limitations due to the difficulties in locating global energy minima as well as problems related to interatomic force field accuracy. Unfortunately, difficulties also arise when solving structures from X-ray powder diffraction data. For instance, there is considerable loss of information compared to single-crystal data due to peak overlap in the diffraction pattern. Good trial structures are necessary for successful determinations, and several methods for generating these initial models have been developed. Harris et al.[8] have reported structures found by the Metropolis Monte Carlo method, which involves random movements of molecules within the unit cell to obtain the best overall fit to the X-ray data. The same author has also recently developed a genetic algorithm[9] as an alternative to the Monte Carlo method, giving some promising results, and a comprehensive discussion of the genetic algorithm method has been presented.[10] Another successful genetic method has been described by David and Shankland.[11]

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TABLE 1: Reported Cell Data, MOPAC/AM1 Geometrically Optimized Molecular Volume, *Z*, and Density for Each Polymorph

structure	CSD ref-code	*a* [Å]	*b* [Å]	*c* [Å]	β [deg]	space group	unit cell volume [Å^3]	MOPAC molecular volume [Å^3]	molecules per unit cell (*Z*)	density [g/cm^3]
α-phenazine	PHENAZ04	7.083	5.072	12.794	102.34	$P2_1/n$	449.0	166.5	2	1.333
β-phenazine	PHENAZ03	11.64	11.58	6.88	99.32	$P2_1/n$	915.1	166.5	4	1.308
α-perylene	PERLEN03	11.264	10.826	10.266	100.55	$P2_1/a$	1230.7	230.3	4	1.362
β-perylene	PERLEN02	9.78	5.90	10.59	96.75	$P2_1/c$	606.8	230.3	2	1.381

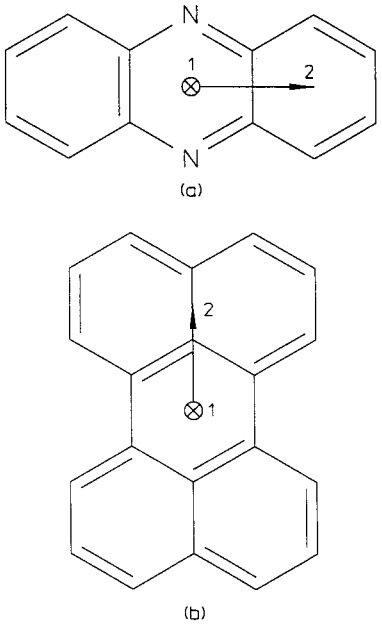

Figure 1. Molecular structures of (a) phenazine and (b) perylene. The vector conventions are defined in text.

Phenazine and perylene (Figure 1) are two simple molecules for which our knowledge of the possible solid-state structures remains incomplete.[12−15] Two polymorphs of each appear in the Cambridge Cystallographic Database (CSD).[16] Both α-phenazine (ref-code PHENAZ04) and α-perylene (PERLEN03) have previously solved crystal structures with weighted residuals fit, R_{wp}, factors less than 0.06. For β-phenazine, only the unit cell parameters and space group have been elucidated (PHENAZ03). The reported structure for the β-perylene polymorph by Tanaka,[17] with $R_{wp} = 0.17$, was not considered reliable for the purposes of this study, hence the structure was treated as only having reported cell parameters and space group from a separate study (PERLEN02). For completeness, however, a comparison of Tanaka's structure mentioned with our prediction of β-perylene is given later. Table 1 contains the cell parameters, space groups, cell volumes, molecular volumes (obtained by molecular optimization described later), number of molecules per cell, and densities for all the polymorphs. The molecular and unit cell volumes are consistent with $Z = 2$ for α-phenazine and β-perylene and $Z = 4$ for β-phenazine and α-perylene, which is reasonable given that the molecules are centrosymmetric. It is interesting that the two solved α-phase structures clearly have different packing motifs. From the density values, one can deduce that the $Z = 2$ polymorphs are more densely packed. If the packing motif types are the same for the structure having the same *Z* values, then it would be reasonable to assume that the structure of β-phenazine would resemble that of α-perylene and similarly β-perylene would resemble α-phenazine. Possible types of packing motifs are reviewed in the following paragraph. Here, we report findings from the systematic trial and error crystal packing procedure. The search method described in the following section was validated against the known α-polymorphs and then utilized to predict the packing arrangements of the unknown β-polymorphic forms.

With reference to the particular systems selected for this study, Gavezzotti and Desiraju[18] have defined four types of packing arrangements for a number of polyaromatic hydrocarbons: herringbone, sandwich herringbone, γ, and β.[19] One plane of the four packing arrangements is qualitatively presented in Figure 2. In this postulated scheme, the length of the shortest unit cell axis is identified as diagnostic of the packing type present. Herringbone structures contain nonparallel nearest neighbor molecules, and the length of the short cell axis is in the range 5.4 to 8.0 Å. Sandwich herringbone motifs consist of diads packed in a herringbone frame with a short axis of more than 8.0 Å. γ-structures have parallel nearest neighbors related by translation along the short axis which is between 4.6 and 5.4 Å in length. β-structures contain molecules in an arrangement reminiscent of graphite, and the short axis is less than 4.2 Å in length. Of the 27 monoclinic polynuclear aromatic hydrocarbons considered by Gavezzotti and Desiraju[18] leading to this classification scheme, all had the shortest cell axis coincident with the unique lattice direction, which in most cases was parallel to a two-fold screw axis.

2. The Systematic Search Method

The systematic search approach uses a grid-based search of rotations and translations to assess *all* the possible packing arrangements. In the past, systematic search methods were often regarded to be too time consuming for practical application in this area. In our strategy,[1,2] however, the use of in-built chemical sense and calculated lattice energies to decide upon the suitability and ranking of potential arrangements provides a fast, efficient, and reliable filter for the selection of trial structures. In general, when solving crystal structures from X-ray powder diffraction data, our philosophy is to use a twin track approach, ranking trial structures both on lattice energy and goodness of fit to the observed X-ray diffraction data. In this paper, however, the predicted structures were ranked on lattice energy alone.

The lattice energy, E_{latt} (often referred to as the crystal binding or cohesive energy), can be calculated for molecular materials by summing all the interactions between a central molecule and all the surrounding molecules. As a result of pioneering work by Williams[20] and Kitaigorodskii,[21] each intermolecular interaction can be considered to consist of the sum of the constituent atom−atom interactions. If there are *n* atoms in the central molecule and *n*′ atoms in each of the *N* surrounding molecules, then a lattice energy (E_{latt}) can be calculated by

$$E_{latt} = {}^1/_2 \sum_{k=1}^{N} \sum_{i=1}^{n} \sum_{j=1}^{n'} V_{kij} \qquad (1)$$

where the factor $^1/_2$ reflects the pairwise nature of intermolecular forces. In most cases, *n* and *n*′ will be equal, but in the case of molecular complexes, they may differ. V_{kij} is the interaction potential between atom *i* in the central molecule and atom *j* in the *k* surrounding molecule. In our search procedure, a truncated

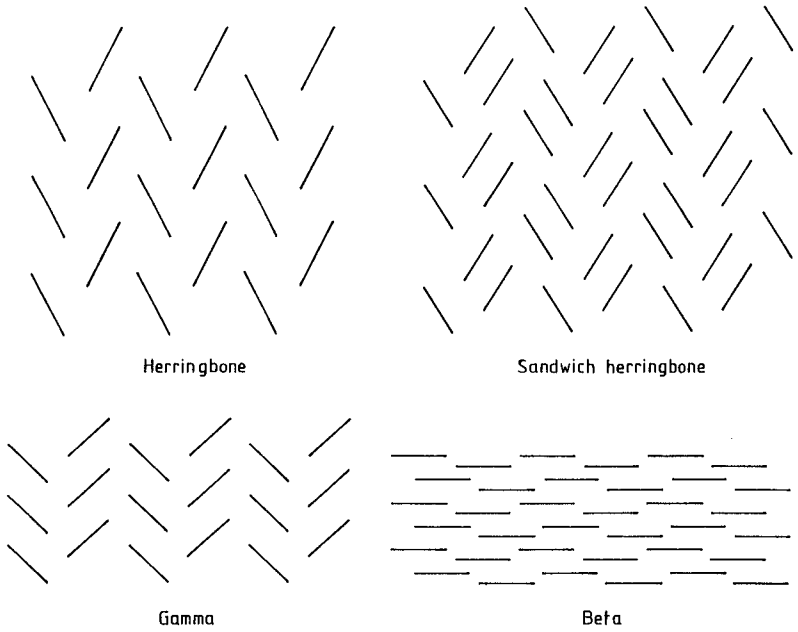

Figure 2. The four types of polyaromatic hydrocarbon packing arrangements.[18]

lattice is constructed during the search based upon reduced radial cutoff distances. This is a reasonable approach since, for electronically neutral molecular materials, the near coordination spheres contribute to the majority of the lattice energy.

Given the large number of possible configurations that have to be checked for a system with three translational and three rotational degrees of freedom, a truncated lattice energy calculation will still be so time consuming as to make the calculations impracticable. An initial screen thus has to be used to cut down the number of possibilities that are to be assessed via a lattice energy calculation. In the packing algorithm, a distance-based cutoff criteria is used as the preliminary screen of possible structures. The use of distance-based search algorithms is well-known in the generation of 3-D molecular structures from 2-D databases.[22] By considering the approach distances of nonbonded atoms, it is easy to reject improbable arrangements found in trial packing configurations within the chosen unit cell, with only "sensible" structures being allowed to pass through this screen. This considerably reduces the number of structural configurations that have to be checked by lattice energy calculations, and therefore it is this screen which enables systematic searches on quite fine grids to be undertaken within reasonable computational time scales.

3. Methodology

3.1. Refinement of Molecular Structures. Crystal structures of the fully elucidated, α-forms of phenazine and perylene were obtained from the CSD (ref-codes PHENAZ04 and PERLEN03, respectively). The hydrogen positions were calculated using standard bond lengths and angles and optimized using the semiempirical molecular orbital method MOPAC[23] at the AM1[24] level. This was needed due to the absence of hydrogens in the reported α-perylene structure as well as to the well-known problem of accurately locating hydrogen atom positions by X-ray diffraction with the resultant tendency to underestimate C−H bond lengths. Upon optimization, the average C−H bond length in α-phenazine was found to increase from 0.96 to 1.10 Å. These molecular structures were used to calculate the lattice energies based upon these reported crystal structures. The full molecular geometries were also optimized, in vacuuo, with the MOPAC/AM1 method and used as starting structures for all the searches carried out in this work. Calculated molecular volumes following this optimization are included in Table 1.

3.2. Force Field Validation. Lattice energies based upon the published crystal structures of α-phenazine and α-perylene, albeit using the corrected hydrogen positions, were calculated using the program HABIT95[25] and compared with experimental enthalpies of sublimation. Separate calculations were made employing (i) Dreiding[26] and (ii) Scheraga[27] force field parameters, both of which use a Lennard-Jones form to describe the van der Waals contribution complemented by a Coulombic potential term to describe the electrostatic interactions. In both cases, the partial atomic charges used in the lattice energy calculations were those determined in the MOPAC optimizations.

Further, the reported crystal structures were minimized with respect to "rigid body" translations and rotations in a fixed cell using the Crystal Packer[28] module of Cerius[2] together with the Dreiding force field parameters. The deviation between the minimized and experimentally observed crystal structures was quantified by calculation of an rms fit over the fractional coordinates of a complete molecule.

3.3. Validation of Search Method. Separate systematic searches were carried out on α-phenazine and α-perylene using the published cell parameters and space group and employing (i) Dreiding and (ii) Scheraga force fields for lattice energy calculations. The fully geometrically optimized molecular structures were initially positioned at the origin of the reported cell in a random orientation. The search criteria used are given in Table 2. Where $Z = 2$, the center of symmetry of a molecule was coincident with an inversion center in the cell; therefore no translations were necessary for the α-phenazine searches. However, this was not the case for α-perylene where $Z = 4$. The minimum approach distance of two nonbonded atoms used throughout was 2.1 Å. The cutoff lattice energy limit for trial configurations is a pragmatic restriction on the number accepted by the search, and this was set to half the calculated minimum lattice energy of each polymorph, in each search. These were all minimized in a manner similar to the reported crystal structures in order to ascertain the number of distinct structures

TABLE 2: Systematic Search Criteria for All Polymorphs

	rotation [deg]		translation		configurations
structure	step size	range	step size	range	tried in total
α-phenazine	5	0−175			46 656
β-phenazine	5	0−175	0.05 of cell lengths	0−1/2*a*, 0−1/2*b*, 0−1/2*c*	46 656 000
α-perylene	5	0−175	0.05 of cell lengths	0−1/2*a*, 0−1/2*b*, 0−1/2*c*	46 656 000
β-perylene	5	0−175			46 656

TABLE 3. Comparison of Experimental Sublimation Energies with Calculated Lattice Energies (kcal/mol) of Hydrogen Optimized Reported Structures Using Scheraga and Dreiding Force Fields

		lattice energy reported structure		lattice energy of minimized reported structure	
structure	ΔH_{sub}	Scheraga	Dreiding	Scheraga	Dreiding
α-phenazine	−23.8	−24.86	−23.68	−24.94	−23.70
α-perylene	−34.6	−34.55	−33.14	−35.38	−34.00

found by each search. A useful working definition of "distinct" molecular packing configurations is, within the present context of a systematic search, those configurations which remain distinct after rigid body energy minimization with respect to position and orientation. To define the molecular orientation in the structures, two orthogonal directions were taken, one, the normal to the molecular plane from the center of symmetry, and two, a vector from the center of symmetry to the centers of a phenyl and naphthalene moiety for phenazine and perylene, respectively (see Figure 1). The angles these vectors made with the crystallographic axes (calculated by the vector dot product) were employed to describe the molecular orientation.

3.4. Application to Undetermined Polymorphs. Systematic searches were carried out in the reported cells of the undetermined β-polymorphs. The search criteria employed are described in Table 2. No molecular translations were required for β-perylene for the reason detailed above.

3.5. Examination of Crystal Structures. The best structures found in a systematic search, ranked in terms of a calculated lattice energy, were examined using the computer program HABIT95. Here, the atom−atom approximation was used in the calculation of intermolecular potential energies. The interactions within a crystal were broken down on a molecule−molecule basis with all energies being referred to a fixed central molecule with the specific pairs of molecules being identified in terms of crystallographic coordinates and grouped by symmetry equivalence.

4. Results and Discussion

4.1. Validation of the Intermolecular Force Fields Against the Known Crystal Structures for the α-Forms of Phenazine and Perylene. Calculated lattice energies for the published α-polymorphs of phenazine and perylene, using the optimized hydrogen positions, are given in Table 3, together with experimentally observed heats of sublimation.[29] The results showed good agreement with the experimental lattice energies V_{exp}[30] derived from experimentally determined sublimation enthalpies ΔH_{sub}.

Lattice energies calculated after minimization, using the Dreiding force field, of the crystal structures with respect to molecular orientation, and in the case of α-perylene molecular position, are also given in Table 3. For α-phenazine, the lattice energy calculated with Dreiding changed from −23.68 to −23.70 kcal/mol on minimization. Re-evaluating the lattice energy of the minimized structure using the Scheraga parameters showed a change in calculated energy from −24.86 to −24.94 kcal/mol. Similarly for α-perylene, the calculated lattice energies before and after minimization were for Dreiding −33.14 and −34.00 kcal/mol and for Scheraga −34.55 and −35.38 kcal/mol.

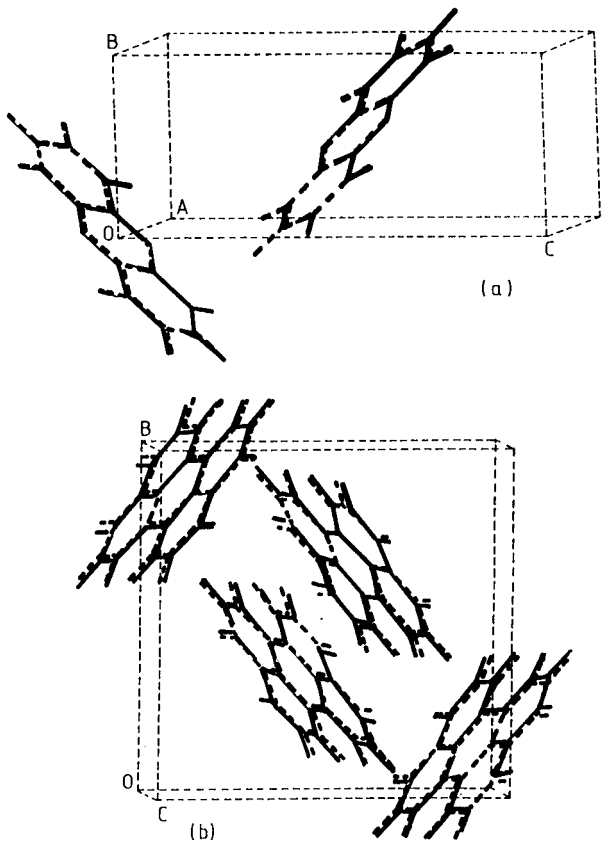

Figure 3. The predicted packing motifs (solid) overlaid with reported structures (dashed) of (a) α-phenazine and (b) α-perylene.

In comparing the experimentally observed and minimized structures the rms fits over the fractional coordinates were found to be 0.1% for phenazine and 0.29% for perylene, respectively. The small change in both the calculated lattice energies and molecular positions, reflected in the rms values upon minimization of the α-polymorphs of phenazine and perylene, was additional evidence that the Dreiding and Scheraga force fields provided a satisfactory model for these systems. Further, the more generic Dreiding force field performed satisfactorily in comparison with the Scheraga force field, parametrized specifically to treat nonbonded intermolecular interactions in molecular crystals of similar materials. It was therefore considered reasonable to attempt to elucidate packing arrangements in the reported cells of the β-polymorphs, using only the Dreiding force field parameters to calculate lattice energies. This strategy, however, was subject to an initial validation of the search method itself through its rigorous application to the modeling of the α-polymorphs.

4.2 Validation of Systematic Search Method Against the Known Crystal Structures for the α-Forms of Phenazine and Perylene. The systematic search for α-phenazine using the Dreiding force field resulted in 56 trial structures with calculated energies below the cutoff limit of −11.4 kcal/mol. An overlay of the lowest energy trial structure, unminimized (−22.7 kcal/mol), with the experimental crystal structure is given in Figure 3a. As can be observed, excellent agreement is achieved, prior to minimization. The 26 lowest energy trial structures minimized

TABLE 4: Calculated Lattice Energies and Geometric Measurements for α-Phenazine

characteristic		reported structure	best predicted structures	
			Scheraga search	Dreiding search
lattice energy [kcal/mol]	Scheraga	−24.9	−25.0	−25.0
	Dreiding	−23.7	−23.5	−23.5
$\pi-\pi$ stack distance [Å]		3.48	3.42	3.43
centroid−centroid distance [Å]		5.07	5.07	5.07
$\pi-\pi$ stack angle [deg]		46.6	47.5	47.5
herringbone angle [deg]		81.4	79.4	79.4
angles between vectors and cell axes [deg]	**1·a, 1·b, 1·c, 2·a**, **2·b**, **2·c**	100.6, 46.7, 43.4, 115.1, 134.5, 49.4	100.7, 47.5, 42.5, 115.4, 135.2, 50.4	100.5, 47.0, 43.0, 117.9, 133.9, 50.6

TABLE 5: The Distinct Structures Resulting from the Dreiding Searches of Each Polymorph

material	rank number of trial where distinct motif first appears	minimized lattice energy	motif type description (see Figure 2)
α-phenazine	1	−23.45	gamma
	27	−17.35	gamma
β-phenazine	1	−24.30	sandwich herringbone
	145	−22.23	gamma
	9	−21.84	beta
	165	−21.46	beta
	163	−20.78	beta
	135	−19.80	beta
	129	−19.75	beta
	179	−19.07	pseudo beta
α-perylene	1	−33.64	sandwich herringbone
	21	−31.55	sandwich herringbone
	23	−31.32	sandwich herringbone
	19	−27.71	sandwich herringbone
β-perylene	1	−36.71	gamma
	9	−31.28	gamma

to the same distinct structure, which tended toward that of the published crystal structure. A number of structural parameters were used to compare this with the reported experimental structure, including the $\pi-\pi$ stack distance and angle, the herringbone angle, and the orientation angles defined in the methodology. Molecular planes and centroids were defined using the heavy atom positions. The comparative values of these parameters are summarized in Table 4, including those for the minimized structure which resulted from the search using the Scheraga force field. The lattice energies based upon the packing motifs predicted from both searches are compared in Table 4 using both the Dreiding the Scheraga force fields. This shows that the same distinct structure was obtained in each case, even though there are minor discrepancies in the $\pi-\pi$ stack distance and the molecular orientation. Minimization of all the trial structures below the cutoff lattice energy revealed that there were in fact two distinct structures. These are summarized in Table 5 using energies which were calculated using the Dreiding force field. Both structures adopted γ packing configurations with different geometric properties within the same, fixed unit cell. The second local minimum had a significantly higher lattice energy (−17.4 kcal/mol) than that based on the structure found at the global minimum (−23.5 kcal/mol) and was originally ranked 27th. The majority of the remaining trial structures also minimized to the global minimum, which was true of all the searches carried out in this study.

The search for α-perylene resulted in 49 trial structures with an upper cutoff lattice energy of −16.2 kcal/mol. In this instance, translational degrees of freedom were included in the search path. A comparison of the unminimized best trial structure (−32.4 kcal/mol) with the reported structure for α-perylene, in Figure 3b, again shows that the agreement was excellent. Upon minimization, this was improved and a comparison of the further structural parameters is given in Table 6. For this polymorph, exactly the same trial structure possessed the lowest energy for the calculation performed for both force fields and minimization obviously resulted in the same distinct structure. After minimization, the first 18 trial structures of α-perylene ranked highest in terms of the calculated lattice energy were found to have the same distinct structure. Interestingly, the systematic search found a number of distinct packing motifs with lattice energy values within a range of ∼10 kcal/mol greater than the most stable structure. These are summarized in Table 5. All alternative structures adopted the sandwich herringbone type of packing motif with different geometric properties having minimized energies, using the Dreiding force field, of −31.6, −31.3, and −27.7 kcal/mol, respectively. Hence, in addition to the global minimum, other local minima were found on the potential energy surface for this cell and space group.

Full atomic coordinates and calculated partial atomic charges based upon the predicted global minima for the α-polymorphs of phenazine and perylene are provided here as Supporting Information.

4.3. Application of the Systematic Search Method to the Determination of the Structure of the Undetermined *β*-Forms of Phenazine and Perylene. As the study of the α-polymorphs revealed the Dreiding force field to be sufficient for modeling these systems, analysis of the β forms involving the Scheraga force field was not carried out.

4.3.1. β-Phenazine. The systematic search for β-phenazine resulted in 3163 trial structures consistent with the lattice energy cutoff at −11.0 kcal/mol. The trial structure ranked highest is illustrated in Figure 4a. The first eight lowest energy structures minimized to the same distinct structure which exhibited a sandwich herringbone configuration, comprised of molecular diads stacked within a herringbone motif. The structural parameters defining the lowest energy structure of β-phenazine, prior to and following minimization, are detailed in Table 7. During this process, the lattice energy reduced from −21.9 to −24.3 kcal/mol. The partial atomic charges and final atomic coordinates are given in Table 8. A number of alternative motifs were identified on the potential energy surface lying within ∼10 kcal/mol range above the lowest minimum. These are summarized in Table 5 and were unusual since their motif types differed from that of the structure at its global minimum. The second distinct motif, which was over 2 kcal/mol less stable than the first one, exhibited the γ-type of packing which was stacked along the *c* axis. It is interesting to note the trial structure only appeared after 145 other unminimized trials, thus emphasising the importance of accepting trial structures within a sufficiently wide lattice energy range. The other distinct motifs found were graphitic, analogous to the β type of packing for hydrocarbons. Their calculated lattice energies are given in Table 5.

4.3.2. β-Perylene. The systematic search for the structure of β-perylene gave 36 trial structures with a calculated lattice energy below the cutoff limit of −17.9 kcal/mol. The calculated lattice energy of the top trial β-perylene structure before

TABLE 6: Calculated Lattice Energies and Geometric Measurements of α-Perylene Results

characteristic		reported structure	best predicted structures: Scheraga search	best predicted structures: Dreiding search
lattice energy [kcal/mol]	Scheraga	−34.6	−35.2	−35.2
	Dreiding	−33.1	−33.6	−33.6
$\pi-\pi$ dimer distance [Å]		3.45	3.41	3.41
centroid−centroid distance [Å]		3.88	3.91	3.91
$\pi-\pi$ dimer angle [deg]		27.1	29.3	29.3
herringbone angle [deg]		76.0	73.9	73.9
distance between dimer centroids		6.10	6.04	6.04
and nearest neighbor centroid [Å]		6.47	6.53	6.53
angles between vectors	**1·a**, **1·b**, **1·c**,	35.1, 124.4, 104.7	33.9, 123.3, 104.2	33.9, 123.3, 104.2
and cell axes [deg]	**2·a**, **2·b**, **2·c**	82.4, 89.6, 18.2	82.4, 88.4, 18.2	82.4, 88.4, 18.2

TABLE 7: Calculated Lattice Energies and Geometric Measurements of *β*-Phenazine Results

characteristic		best predicted by Dreiding: unminimized	best predicted by Dreiding: minimized
lattice energy [kcal/mol]		−21.9	−24.3
$\pi-\pi$ stack distance [Å]		3.45	3.53
centroid−centroid distance [Å]		3.70	3.81
$\pi-\pi$ stack angle [deg]		21.2	21.8
herringbone angle [deg]		71.9	72.9
distance between dimer centroids		7.23	7.11
and nearest neighbor centroid [Å]		8.02	8.10
angles between vectors	**1·a**, **1·b**, **1·c**,	56.2, 34.3, 100.3,	57.4, 34.4, 104.6,
and cell axes [deg]	**2·a**, **2·b**, **2·c**	38.0, 123.9, 112.6	40.0, 124.3, 115.5

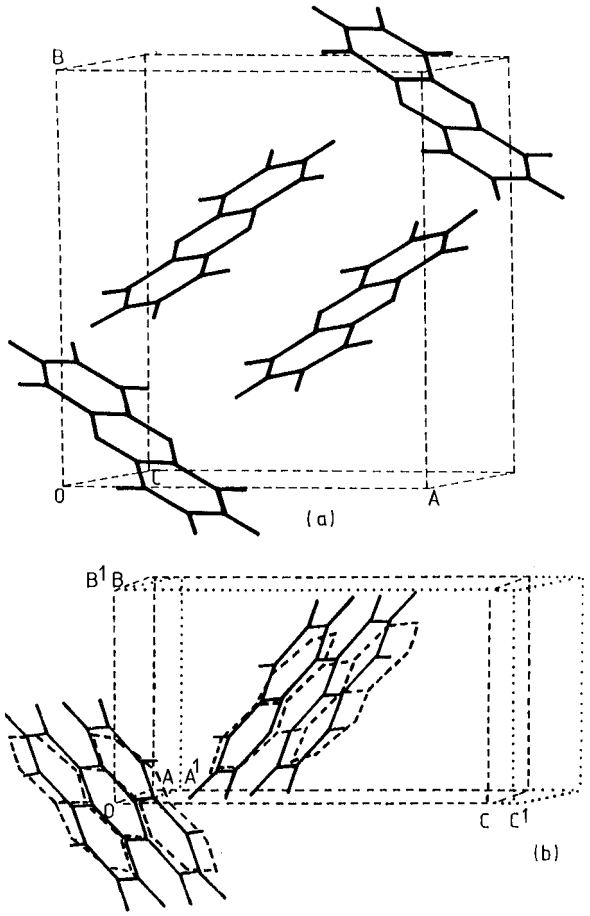

Figure 4. The predicted packing motifs of (a) *β*-phenazine and (b) *β*-perylene (solid) overlaid with lattice translated reported structure with poor R_{wp} factor[17] (dashed molecules and dotted unit cell).

minimization was −35.8 kcal/mol. The molecular packing of the top trial structure for this polymorph is illustrated in Figure 4b, overlaid with the structure proposed by Tanaka[17] whose atomic coordinates have been transformed to match the structure deduced here. Comparison of these two structures reveals that although their packing motifs are both of the *γ* type, they are clearly different. It can be seen that there are some unusual molecular bond lengths and angles. This, in addition to the high R_{wp} value of 0.17, supported a redetermination of this structure as part of this study, choosing unit cell data from ref 14. Comparison of the structural parameters defining the unminimized and minimized best trial structure of *β*-perylene is detailed in Table 9, revealing only slight structural changes following

TABLE 8: Full Atomic Coordinates and MOPAC/AM1 Partial Atomic Charges of the Prediction of *β*-Phenazine Resulting from the Search Strategy and after Minimization within Published Unit Cell Parameters[12]

atom numbers	fractional coordinates: *a*	*b*	*c*	charges
C1	0.01774	0.15051	0.37496	−0.0247
C2	0.08081	0.14549	0.57546	−0.0247
C3	0.03280	0.20478	0.72861	−0.0994
C4	−0.06925	0.26387	0.68513	−0.1207
C5	−0.13107	0.26879	0.48855	−0.1207
C6	−0.09002	0.21456	0.33817	−0.0994
C7	0.16003	0.03785	0.26871	−0.0247
C8	0.20803	−0.02144	0.11556	−0.0994
C9	0.31007	−0.08053	0.15904	−0.1207
C10	0.37190	−0.08545	0.35561	−0.1207
C11	0.33085	−0.03122	0.50600	−0.0994
C12	0.22308	0.03283	0.46920	−0.0247
N13	0.05844	0.09660	0.22507	−0.0950
N14	0.18238	0.08674	0.61909	−0.0950
H15	0.16004	−0.01746	−0.03608	0.1532
H16	0.34693	−0.12584	0.04263	0.1391
H17	0.45405	−0.13437	0.38316	0.1391
H18	0.37837	−0.03484	0.65799	0.1532
H19	0.08078	0.20080	0.88026	0.1532
H20	−0.10610	0.30918	0.80154	0.1391
H21	−0.21321	0.31770	0.46101	0.1391
H22	−0.13754	0.21818	0.18618	0.1532

TABLE 9: Calculated Lattice Energies and Geometric Measurements of *β*-Perylene Results

characteristic	best predicted by Dreiding: unminimized	best predicted by Dreiding: minimized
lattice energy [kcal/mol]	−35.8	−36.7
$\pi-\pi$ stack distance [Å]	3.34	3.33
centroid−centroid distance [Å]	5.90	5.90
$\pi-\pi$ stack angle [deg]	55.6	55.6
herringbone angle [deg]	75.3	76.6
angles between vectors and cell axes [deg]	**1·a**, **1·b**, **1·c**, 76.2, 124.4, 144.3, **2·a**, **2·b**, **2·c** 17.1, 90.4, 79.7	74.8, 124.4, 143.9, 18.8, 90.4, 78.0

TABLE 10: Breakdown of the Important Molecule−Molecule Interactions Using HABIT95 and the Dreiding Force Field for Each Polymorph[34]

material	total energy	UVWZ	distance [Å]	interaction energy [kcal/mol]	number of interactions per molecule	description of molecule−molecule interaction[a]	% contribution to lattice energy
α-phenazine	−23.45	0101	5.07	−3.65	2	a ($\pi-\pi$ dist = 3.54 Å)	31.14
		1001	7.08	−1.26	2	b	10.74
		0002	7.09	−1.00	4	c	17.04
		1−101	8.71	−0.96	2	d	8.18
β-phenazine	−24.30	−1−103	3.81	−3.50	1	f ($\pi-\pi$ dist = 3.45 Å)	14.40
		0002	7.11	−1.78	2	g	14.66
		−1004	8.10	−1.69	2	g	13.90
		0011	6.88	−1.51	2	h	12.42
		−1−1−13	6.39	−1.39	1	h	5.72
		0−103	8.98	−1.37	1	i	5.64
		0004	7.26	−1.22	1	j	5.02
α-perylene	−33.64	1−103	3.91	−6.95	1	f ($\pi-\pi$ dist = 3.41 Å)	20.66
		0002	6.53	−3.99	2	g	23.72
		1003	7.92	−2.78	1	k	8.26
		0004	6.04	−2.47	2	g	14.68
		0011	10.27	−1.60	2	i	9.52
β-perylene	−36.71	0101	5.90	−5.30	2	a ($\pi-\pi$ dist = 3.34 Å)	28.88
		0002	6.06	−3.56	4	e	38.80
		1001	9.78	−2.02	2	b	11.00
		1002	10.96	−0.71	4	c	7.72

[a] (a) $\pi-\pi$ stacks; (b) parallel molecules, side-by-side in adjacent γ planes; (c) nonparallel molecules, in adjacent γ planes; (d) shifted parallel molecules in adjacent γ planes; (e) nonparallel molecules, in same γ plane; (f) $\pi-\pi$ dimer; (g) molecules in nonparallel dimer in same SHB plane; (h) molecules in side-by-side parallel dimer in adjacent SHB plane; (i) molecules in shifted parallel dimer in adjacent SHB plane; (j) molecules in nonparallel dimer in adjacent SHB plane; (k) molecules in shifted parallel dimer in same SHB plane.

minimization. This same structure, having a lattice energy of −36.7 kcal/mol, was found to be the global minimum after minimization of all top structures. Another γ structure consistent with a distinct packing motif, originally ranked ninth, was found within 10 kcal/mol of this value (−31.3 kcal/mol), which is included in Table 5. Atomic coordinates and calculated partial atomic charges of the global minimum have been submitted as Supporting Information.

4.4. Comparison of the Crystal Chemistry of the Polymorphs. Although not a hydrocarbon, α-phenazine can be seen to adopt what Gavezzotti and Desiraju[18] have defined as a γ-motif for hydrocarbons, since nearest neighbors are parallel and related by translation along the shortest cell axis of 5.1 Å (which is within the specified range of 4.6−5.4 Å). This packing arrangement was successfully predicted by the systematic search. The sandwich herringbone structure of α-perylene was also predicted correctly; pairs of molecules held together by $\pi-\pi$ interactions are stacked, inclined to one another, with a herringbone angle of 74°. A short axis of 10.3 Å, although in this instance not coincident with the unique crystallographic direction, was nevertheless consistent with the hypothesis outlined in the Introduction.

Analogously, the β-phenazine structure was predicted, from this work, to be sandwich herringbone. In this structure, the $\pi-\pi$ dimer distance was found to be 3.5 Å with the herringbone angle being 73° and the shortest cell axis length 6.9 Å. While the short axis length was somewhat smaller than the lower limit of 8 Å given in Gavezzotti and Desiraju's[18] classification scheme for sandwich herringbone structures the presence of nitrogen atoms, strictly, renders phenazine outside the range of the applicability of their models. For the β-perylene structure, the length of the shortest cell axis was 5.9 Å, which the classification scheme suggests is a herringbone structure. However, the shortest intermolecular distance was between pairs of molecules lying parallel to each other and related in terms of a lattice translation along the shortest cell edge, which is in contradiction with the definition of a herringbone structure and is actually a property of the γ type of packing. It was therefore concluded that the β-perylene structure was of type γ with a $\pi-\pi$ stack distance of 3.3 Å and a herringbone angle of 77°.

Comparison was made between molecule−molecule interactions, as calculated using HABIT95, for both polymorphic strucutures of both compounds in order to rationalize the predicted structures. The most important interaction energies are summarized in Table 10. The HABIT95 molecular interaction calculations indicated that the $\pi-\pi$ interactions within each stack of the γ motifs of α-phenazine and β-perylene respectively, were strongest. Similarly, the strongest interactions in β-phenazine and α-perylene were between the $\pi-\pi$ dimer pairs within the sandwich dimer structures. These intermolecular interactions were strongest for the perylene polymorphs since this molecule has a higher number of consitituent atoms thus strengthening the intermolecular interaction, relatively against the smaller phenazine molecule, when the molecules are packed parallel to each other. Even though the other intermolecular interactions were weaker in comparison, their contribution to the total lattice energy was only reflecting a large number of comparatively weak intermolecular interactions. This suggests that both the $\pi-\pi$ stacks and the $\pi-\pi$ dimers are the dominant interaction in the solid state and the subtle differences of packing energies explain why both types are observed for both materials.

The total lattice energy calculations, compared in Table 10, seem to suggest that the β-polymorphs are more stable than the α-polymorphs, although it should be noted that the energy differences between these two polymorphic structures are rather small. The isolated $\pi-\pi$ interaction energy in α-phenazine is higher than that in β-phenazine, and the same is true of α-perylene compared with β-perylene. From this, it might be tentatively suggested that $\pi-\pi$ interactions within molecule clusters in a crystal growth environment are stack promoting in the case of phenazine and dimer promoting in the case of perylene, giving rise to the preponderantly observed α-polymorphs. However, caution should be adopted in rationalizing these differences too rigorously, particularly given the sparse preparative detail provided in the source publications for the α-forms,[12,14] since growth environment is well-known to influ-

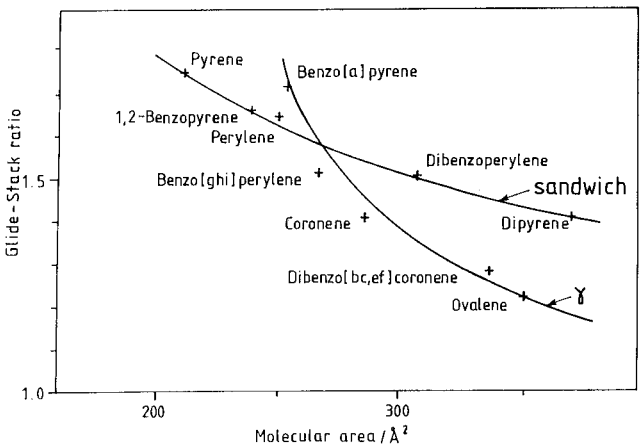

Figure 5. Glide-stack promoting ratios of the surface area of polynuclear aromatic hydrocarbons plotted against total available molecular surface areas (after ref 18).

ence the resultant polymorphic form (see for example cases of solvent-induced polymorphism in the literature such as sulfathiazole[31]).

Gavezzotti and Desiraju[32,33] have proposed a scheme for polynuclear aromatic hydrocarbons to correlate the structural type of the polymorphs formed by a given molecule with the ratio of glide to stack promoting molecular area as a function of the total accessible surface area of the molecule. Interactions between the carbon atoms on adjacent molecules are regarded as stack promoting, while interactions between hydrogen and carbon atoms on adjacent molecules are regarded as glide promoting. Under this scheme, perylene is predicted to have a sandwich herringbone motif. However, examination of the interrelationship between glide to stack promoting ratio and molecular area in Figure 5 (taken from ref 18) reveals it to be in close proximity to the curve derived from γ-structures. Since the present study has elucidated a γ-form for β-perylene, this seems to concur with the proximity of perylene to the intersection of the curves for sandwich dimer and γ-structures in Figure 5.

In the same work, it was concluded that anthracene, the hydrocarbon analogue of phenazine, possesses a herringbone structure with nearest neighbors nonparallel to one another. The effect of substituting the central C−H fragments of anthracene with nitrogens to yield phenazine is to alter the carbon to hydrogen stoichiometric ratio thus affecting the relative balance between C···H and C···C intermolecular bonding, therefore the structure adopted. Crudely, based on the respective numbers of carbon and hydrogen atoms, a 20% reduction in the glide to stack promoting ratio is expected for phenazine with respect to anthracene. Such a reduction would indeed drop the point for anthracene off the curve of herringbone structures and onto the sandwich herringbone curve close to the point of intersection with the curve for the γ structural type. Indeed, the sandwich herringbone and γ-types correspond to the observed and predicted structures for, respectively, α- and β-phenazine and so the possible extension of this correlation to include nitrogen-containing polyaromatics may reward further investigation. Also, if the polymorphs of perylene both fit this model, then perhaps other substances close to curve intersections (cf. Figure 5) might also reveal polymorphic structures with both types of packing.

5. Conclusions

The known α-forms of both phenazine and perylene were successfully elucidated using the systematic search algorithm as the top-ranked trial structures, within the accuracy of the force fields employed. Given this successful validation, the method was then applied to the unknown β-polymorphs. The resulting structure predictions for the β-polymorphs were found to be sensible in terms of calculated lattice energies by comparison with the solved structures of the related polymorphs. Comparing all four polymorphic structures to the type definitions postulated by Desiraju and Gavezzotti for polyaromatic hydrocarbons,[18] the two α-polymorphs were in agreement, the two β-polymorphs were found to agree in terms of the most significant intermolecular interactions present but not in terms of the definition of structural type based on the length of the shortest cell edge. The presence of two polymorphs of perylene, one of sandwich herringbone type and one of γ type, was found to be in agreement with the predictive correlation of glide to stack promoting ratio with accessible molecular surface area. Further, by considering the change in glide to stack promoting ratio for phenazine compared to anthracene, it was estimated that, principally, a sandwich dimer but also potentially a γ-structure would be the predicted forms of the polymorphs of phenazine in concurrence with the forms both observed and predicted, in the present study, for this molecule.

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Supporting Information Available: Full atomic coordinates and MOPAC/AM1 partial atomic charges of α-phenazine, α-perylene, and β-perylene structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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