Towards a Complete Description of a Polymorphic Crystal: The Example of Perylene
Redetermination of the Structures of the ($Z = 2$ and 4) Polymorphs

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Dedicated to Professor *Jack D. Dunitz*, FRS, on the occasion of his 80th birthday – A Guide to the Perplexed

Crystal structures of the two polymorphs of perylene have been determined at low temperatures (150 and 200 K), and the molecular geometry was compared with earlier crystallographic and NMR measurements. Cell dimensions have been measured for both polymorphs over the ranges 150–320 K for (EI-β) and 150–420 K for (EII-α). Combination of thermodynamic and crystallographic measurements has permitted inference of pressure–temperature phase diagrams for perylene and pyrene that are compatible with available measurements up to *ca.* 50 kbar. Perylene and pyrene are both enantiotropic systems, while phenazine appears to be monotropic.

1. Introduction. – In the present context, a crystalline system is considered to be 'completely described' when the structural and thermodynamic relations among its cluster[1]) of polymorphs are known. Examples of almost complete descriptions are those available for tin, carbon (graphite and diamond), and adamantane; this information has been summarized by *Herbstein* [2]. We assume that all crystals are polymorphic in an appropriate region of pressure and temperature. However, it is operationally convenient to divide crystals into two groups: those where polymorphism occurs at atmospheric pressure in the temperature range 'from low to melting' (*e.g.*, pyrene and perylene), and those where it is encountered only at higher pressures (*e.g.*, benzene, naphthalene, and anthracene). The one-component pressure–temperature (P–T) phase diagram provides a convenient way to summarize the available information [3]. Not many P–T phase diagrams have been determined for molecular crystals, but a combination of crystallographic and thermodynamic information permits a schematic approximation to the (low-pressure) P–T diagram to be derived for those substances showing polymorphism at atmospheric pressure. We illustrate this approach first by considering the polymorphism and crystallography of perylene, and then extending the discussion to include the polymorphs of pyrene and phenazine.

Perylene, $C_{20}H_{12}$, has two polymorphs. The structure of α-perylene ($P2_1/c$, $Z = 4$, room temperature; perylene [EII; > 413 K]-(α) ([EII-α] for short using the polymorph nomenclature[2]) of *Herbstein* [4]) was first reported by *Donaldson et al.* [5a] (not in CSD); later analyses were performed by *Camerman* and *Trotter* [5b] (CSD refcode

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[1])   The term used for the collection of polymorphs found for a particular chemical entity [1].
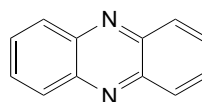
[2])   See *Appendix* for discussion of nomenclature of polymorphs.
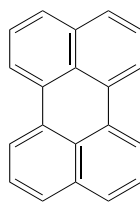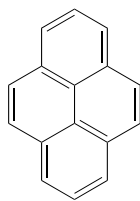
Perylene   Pyrene   Phenazine

PERLEN02), *Krygowski et al.* [5c] (PERLEN03), and *Näther et al.* [5d] (PER-LEN04). The structure of β-perylene ($P2_1/c$, $Z = 2$; perylene [EI; < 413 K]-(β)) was first reported by *Tanaka* [5e] (PERLEN); a revision (*Kerr* [5f]) (PERLEN01) gave little additional detail.

The polymorphism of perylene has been considered by a number of authors. *Tanaka* [5e]) reported that '*The β form is transformed into α at about 140°C. At and below room temperature, both forms are stable, and no transformation was found at lower temperatures*'. The specific heat of [EII-α] has been measured from very low temperatures to above the melting point [6a]. DSC Measurements [6b] do not show a transition; presumably the [EII-α] polymorph was used. A room-temperature high-pressure infrared study provided no evidence for a phase transition below 45 kbar [7]. A systematic computational search strategy has been used to study polymorphism in perylene [8] (and, also, in phenazine, where the XRD structures of both polymorphs (*cf.* [9a, b]) are in good agreement with the predictions, as they are for perylene).

The thin-plate habit of both perylene polymorphs and the ability of both to be cooled to low temperatures without intervening phase transformations made it possible to carry out an extensive spectroscopic study of both polymorphs down to 4.2 K [5e], and this has been supplemented by later work (*e.g.*, [10]).

We report here cell dimensions for both polymorphs measured over the range 150 – 320 K for [EI-β] and 150 – 420 K for [EII-α]. We also report new refinements of the structures of both polymorphs ([EII-α] at 150 K and [EI-β] at 200 K). The three independent determinations of the [EII-α] structure allow detailed assessment of the precision of the averaged molecular geometry; the single [EI-β] measurements were of lower precision and do not allow such an assessment.

Combining these results makes it possible to propose a comprehensive (but still, in some respect incomplete) view of the crystal chemistry of perylene. The major deficiency in current knowledge is the absence of C_p measurements on the [EI-β] polymorph; direct measurement of the [EI-β] to [EII-α] (thermodynamic) trans-formation temperature and ΔH([EI-β]) $\Rightarrow$ [EII-α]) would also be desirable, as would determination of the P−T phase diagram.

2. Results. – Cell dimensions, molecular dimensions, and deviations from planarity are compared for both polymorphs, and with NMR results for the [EII-α] polymorph. Atomic numbering is shown in *Fig. 1*.
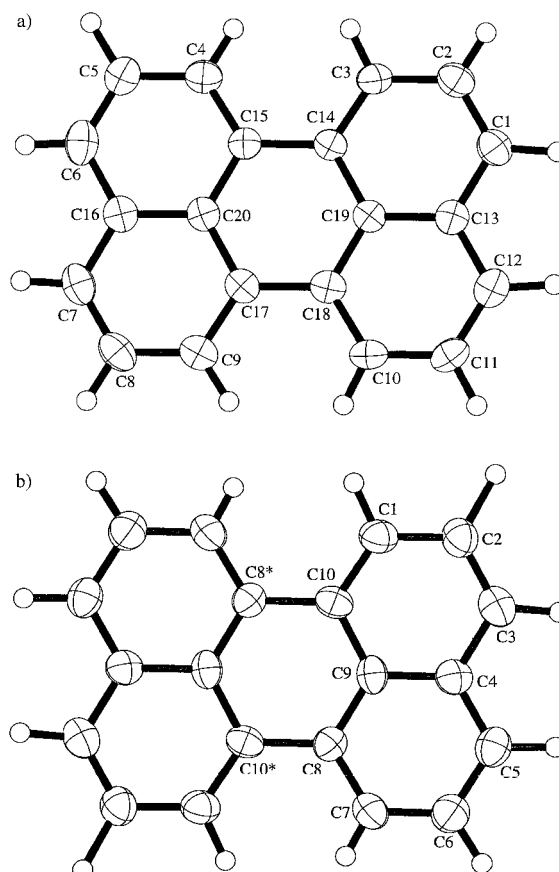
Fig. 1. *Numbering of atoms in the* a) *[EII-α] and* b) *[EI-β] polymorphs* (in the latter, starred and unstarred atoms are related by a centre of inversion). Note that different atomic (and ring) numbering schemes were used by *Krygowski et al.*, [5c], *Camerman* and *Trotter* [5b], *Näther et al.* [5d], and *Iuliucci et al.* [11a]; we follow *Krygowski*. The 50% probability ellipsoids are for [EII-α] at 150 K and [EI-β] at 200 K.

2.1. *The [EII-α] Polymorph.* 2.1.1. *Cell Dimensions.* Measurements for [EII-α] were made over the temperature range of 295 – 423 K, with some additional measurements at lower temperatures (Table A in *Supplementary Material*). The diffraction pattern disappeared at *ca.* 420 K. A single crystal grown from the melt in a capillary was the [EII-α] polymorph (*cf. Footnote 9*). Behavior of the diffraction patterns, represented as 'volume per molecule', is shown in *Fig. 2*.

The results reported by various authors are compared in *Table 1*. Our 300-K values appear low, and we give preferred values at 300 K by averaging the other three sets: $a = 10.266(4)$, $b = 10.830(8)$, $c = 11.273(8)$ Å, $\beta = 100.54(2)°$, $V_{mol} = 308.05$ Å^3. The sample s.u.'s (bracketed)[3]) are some 2 – 4 times as large as the s.u.'s quoted by the original investigators, supporting (again) the conclusions of *Taylor* and *Kennard* [12] that s.u.'s

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[3]) The sample variance is given by $\{(1/(N-1))\Sigma(x_i - \langle x \rangle)^2\}$ and the population variance by $\{(1/N)\Sigma(x_i - \langle x \rangle)^2\}$.
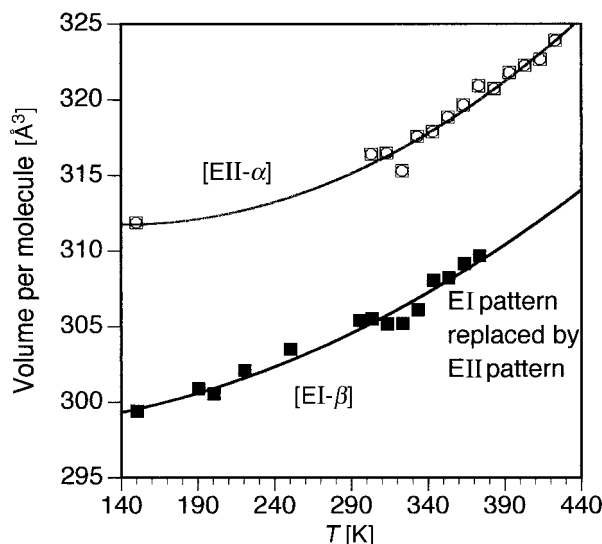
Fig. 2. *Volume per molecule* [Å³] *plotted against temperature for the two perylene polymorphs.* The [EII-α] points have been shifted upwards by 10 Å³ for clarity; the curves are guides to the eye.

Table 1. *Comparison of Measured Cell Dimensions for [EII-α] Perylene.* The 300-K 'present results' were measured on a *Philips PW1100* sequential diffractometer (25 reflections, $MoK_α$) and those at 150 K on an area detector diffractometer. S.u.'s are not given for 'present results at 300 K' because of a suspected systematic error (see *Sect. 2.1.1*).

Reference	a [Å]	b [Å]	c [Å]	$β$ [deg]	V_{mol} [Å³]
At 300 K					
Camerman and *Trotter* [5b]	10.263(2)	10.826(2)	11.277(2)	100.55(3)	307.9(1)
Krygowski et al. [5c]	10.266(2)	10.826(2)	11.264(2)	100.55(3)	307.7(1)
Näther et al. [5d]	10.270(1)	10.839(1)	11.278(1)	100.51(1)	308.60(4)
Present results	10.242	10.812	11.247	100.45	306.2
At 150 K					
Present results	10.239(1)	10.786(1)	11.132(1)	100.92(1)	301.78(4)

from least-squares refinements of parameters are 2.5 to 5 times smaller than those obtained by comparing independent sets of measurements.

2.1.2. *Molecular Dimensions.* Fractional coordinates at different temperatures cannot be compared directly because of changes in molecular orientation, but molecular dimensions derived from measurements at different temperatures can be compared directly on the usual assumption that such dimensions do not change with temperature. Average bond lengths and deviations from the best plane through the 20 C-atoms from the three most-recent structure determinations (*Krygowski et al.* [5c] and *Näther et al.*[4]) [5d] at 300 K; present results at 150 K) are given in Tables B and C in *Supplementary Material*. The s.u.'s of averaged bond lengths and deviations are 2–4

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[4]) The following remark of *Näther et al.* [5d] obviously has a typographical error: ']*[α-perylene]* *exhibits a planar molecular skeleton, with the largest deviations of the individual centers amounting to* ± 0.39 Å'.

times larger than the LS values. Bond lengths averaged in accordance with D_{2h} molecular symmetry are given in *Table 3* below. H-Atom parameters were refined in the hope that it would be possible to observe distortions in the 'bay' regions of the molecule, but this was not achieved because of inadequate precision (for example, $d(C(2)-H(2)) = 1.30$ Å).

2.2. *The [EI-β] Polymorph.* 2.2.1. *Cell Dimensions.* Measurements for [EI-β] were made over the temperature range 150–373 K (Table A in *Supplementary Material*). The [EI-β] diffraction pattern disappeared at *ca.* 373 K, and was replaced by a single-crystal diffraction pattern (somewhat distorted) of [EII-α] that persisted up to *ca.* 430 K (*Fig. 2*). The results reported by various authors are compared in *Table 2*.

Table 2. *Cell Dimensions of Perylene [EI-β] at Room Temperature*

	a [Å]	b [Å]	c [Å]	β [deg]	V_{mol} [Å^3]
Earlier results at 300 K					
Tanaka [5e]	9.65(3)	5.88(2)	11.27(3)	92.1(3)	319.5
Kerr [5f]	9.78	5.90	10.59	96.75	303.4
Present results at 295 K	9.813	5.887	10.649	96.93	305.3

2.2.2. *Molecular Dimensions.* Bond lengths averaged in accordance with D_{2h} molecular symmetry are given in *Table 3*. Although the agreement appears to be excellent, there are differences of up to 0.019 Å between symmetry-related bonds for [EI-β] (details in Part 2 of Table B, *Supplementary Material*). The s.u.'s of averaged bond lengths and deviations are 2–4 times larger than the LS values. Deviations from the best plane through the 20 C-atoms of the centrosymmetric molecule are deposited in Table D (*Supplementary Material*). The precision of the present results for [EI-β] is not sufficient to establish any significant deviations from planarity, in contrast to the situation in [EII-α]; H-atom parameters were not precise enough to allow discussion.

Table 3. *Comparison of Measured Bond Lengths* (averaged assuming D_{2h} symmetry) *for the Perylene [EII-α] and [EI-β] Polymorphs with Various Calculated Values.* Numbering according to [EII-α][a]).

Bond	Average measured bond lengths [Å]		Calculated bond lengths			
	[EII-α]	[EI-β]	Naphthalene KH96	LJ95	VVO92	GL92
C(13)−C(1)	1.414	1.421	1.420	1.423	1.420	1.421
C(1)−C(2)	1.359	1.368	1.357	1.386	1.369	1.372
C(2)−C(3)	1.396	1.401	1.416	1.405	1.409	1.411
C(3)−C(14)	1.382	1.380	1.357	1.400	1.380	1.385
C(14)−C(19)	1.428	1.425	1.420	1.428	1.427	1.432
C(13)−C(19)	1.426	1.421	1.408	1.427	1.411	1.419
C(14)−C(15)	1.474	1.467		1.457	1.462	1.459

[a]) References and computational details: GL92: *Grimme* and *Löhmannsröben* (AM1; [13a]); KH96: *Kjaergaard* and *Henry* (HF/6-311G**; [13b]); LJ95: *Li* and *Jiang* (VB; [13c]); VVO92: *Viruela-Martin et al.* (PM3; [13d]).

2.3. *Crystal Structures of the Polymorphs.* The arrangement of the molecules in the $Z = 4$ polymorph is often described as 'dimeric' (or 'sandwich herringbone') and that in the $Z = 2$ polymorph as 'monomeric' ('γ arrangement'; *Desiraju* and *Gavezzotti* [14]).

In fact, the two arrangements (*Figs. 3* and *4*) are more similar than is usually remarked. The overall arrangement is of the 'herringbone' type in both polymorphs, as, indeed, it must be because both have the same space group and molecular arrangement with respect to the unique [010] axis. The difference is that the packing unit in the $Z = 4$ polymorph is a pair of molecules arranged *about* a center of symmetry, whereas that in the $Z = 2$ polymorph is a single molecule centered *at* a center of symmetry. Other examples of the dimeric structure are the two polymorphs of pyrene [15a], [15b], β-phenazine [9b], 1,2,3,4-tetrafluorobenzene (ZELDOJ at 153 K [16]), benzperylene (BNPERY), dinaphthoanthracene (DNAPAN), and quaterrylene (QUATER10) (these three listed in [14], with references). These structures are all variations of $P2_1/c$, $Z = 4$; the 'dimer' interplanar spacing in β-phenazine is 3.498(3) Å, and 3.36 Å in ZELDOJ.
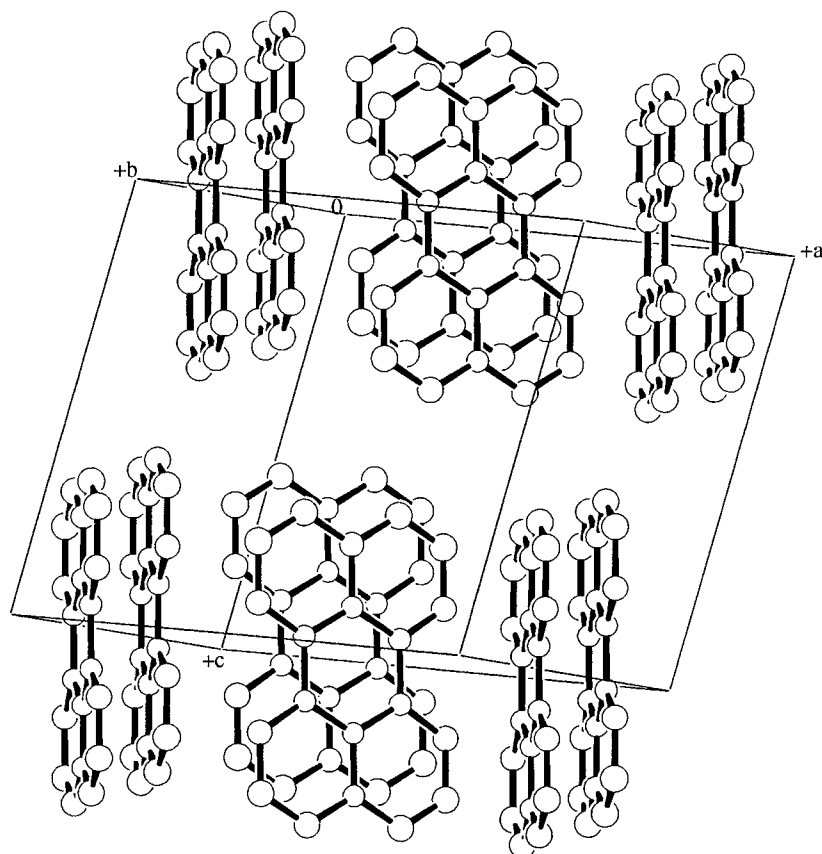

Fig. 3. *View of the molecular packing in the [EII-α] polymorph, showing the arrangement of 'dimeric' pairs of molecules.* The interplanar spacing in the dimeric pair is 3.415 Å.

The volume difference on change of phase is $\Delta V = V_{II} - V_I = 2.8$ Å^3 per molecule at 300 K and 2.5 Å^3 at 150 K (*Table 6* below). Expansion on passing from the polymorph
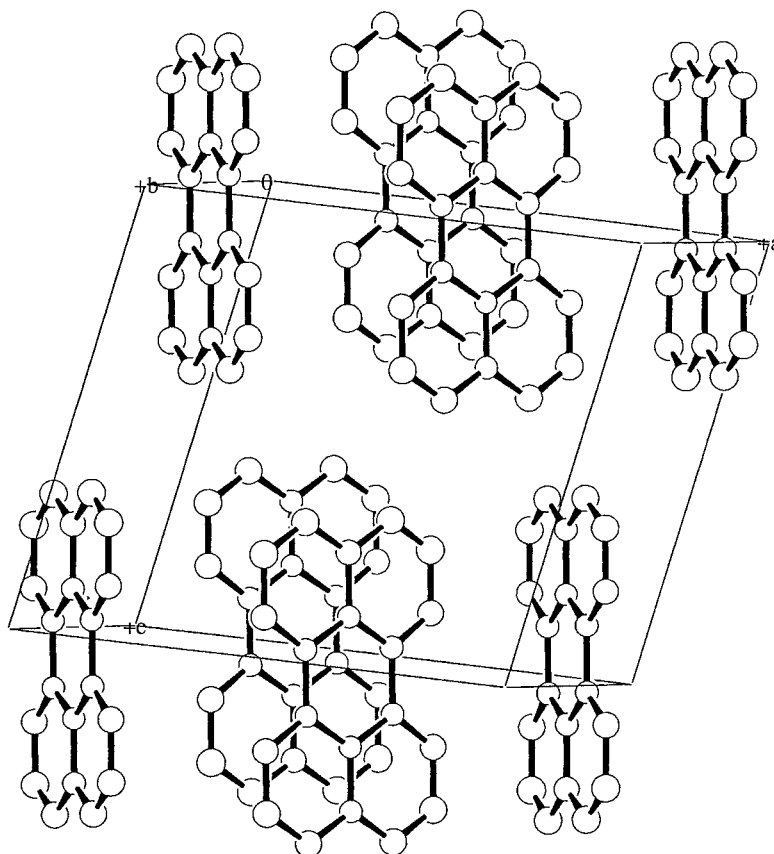
Fig. 4. *View of the molecular packing in the [EI-β] polymorph, showing the arrangement in the stacks.* The inclination of the projection direction to the molecular plane is the same as that in *Fig. 3*. The spacing between planes of adjacent molecules is 3.46 Å, but this has little physical meaning, as there is no significant overlap between such molecules.

stable at the lower temperature to that stable at the higher temperature is the usual situation (to the extent of 93% according to *Gavezzotti* and *Filippini* [1]).

2.4. *Thermal Expansion.* The overall volume expansion in the two polymorphs is essentially equal at 0.015 and 0.014%/K for [EI-β] and [EII-α], but the individual changes of cell dimensions with temperature are anisotropic in different ways (*Table 4*).

Table 4. *Comparison of Relative Thermal Expansions for the Two Perylene Polymorphs, Expressed as Δx/x %/K.* These are average values calculated over the temperature ranges of the measurements.

Polymorph	$\Delta a/a$	$\Delta b/b$	$\Delta c/c$	$\Delta\beta/\beta$
[EI-β]	0.0046	0.0080	0.0030	0.0009
[EII-α]	0.0015	0.0026	0.0097	− 0.0031

2.5. *Thermal-Motion Analysis.* The standard *Schomaker – Trueblood* analysis (based on the rigid-body assumption) was applied to the U^{ij} values. The results for both polymorphs are given in *Table 5* for a temperature of 150 K[5]). The translational motion is rather isotropic, as is usually found, and not very different in the two polymorphs. On the other hand, the librational motions about the three molecular axes are markedly anisotropic. The librational motion is somewhat larger for the [EII-α] than for the [EI-β] polymorph. It is reasonable to assume that the major contribution to the entropies of the two phases comes from the thermal motion, and, thus, the values from the thermal motion analysis are in accord with the (presumably) endothermic nature of the phase transition[6]).

Table 5. *The Molecular Thermal-Motion Parameters* **L** *and* **T** *for the Two Polymorphs at 150 K*

Parameter	Perylene [EI-β]	Perylene [EII-α]
$L1$ [deg^2]	7.71	7.11
$L2$	2.78	4.67
$L3$	0.52	2.11
$T1$ [Å^2]	0.031	0.036
$T2$	0.029	0.032
$T3$	0.020	0.019

2.6. *Tentative P – T Phase Diagrams for Pyrene and Perylene.* The *Clausius – Clapeyron* equation is $(dP/dT) = \Delta H/(T_c \times \Delta V)$, where T_c is the equilibrium phase-transformation temperature at the pressure of measurement, $\Delta H = H_{II} - H_I$, $\Delta V = V_{II} - V_I$. We neglect the variation of ΔH and ΔV with T and P, and use values obtained at 1 bar. We first derive a tentative P – T phase diagram for pyrene, where the parameter values (summarized by *Herbstein* [4]) are much better established than for perylene: $\Delta H = +285$ J/mol, $T_c = 120.9$ K[7]) (*Wong* and *Westrum* [17]), and $\Delta V = +3.7$ Å^3/molecule. (dP/dT) has a positive slope, here 10.6 bar/K. A linear extrapolation into the high-pressure region from 121 K at 1 bar gives a transformation pressure of 1.9 kbar at 300 K (*Fig. 5*). This is in reasonable agreement with the values at 300 K of 2.6 kbar given by *Vaidya* and *Kennedy* (volumetric measurements [18a]) and 4.0 kbar by *Zallen et al.* (*Raman* scattering [18b]). *Hamann* [7] did not find the *ca.* 3 kbar transition but reported a transition in the 30 – 45 kbar range, to which the present calculation does not apply.

In the absence of a measured value for ΔH for perylene, we use the value of 12.8 kJ/mol calculated by *Hammond et al.* [8], and for ΔV our measured value of 2.8 Å^3/molecule (*Hammond et al.* [8] give 4.3 Å^3/molecule in their *Table 1*). Our high-temperature X-ray-diffraction study shows that [EI-β] converts to [EII-α] at *ca.* 420 K *in the solid state*, in agreement with *Tanaka* [4e]. This is an upper bound on T_c, and not necessarily the thermodynamic equilibrium temperature. The β/α equilibrium line in the *tentative* P – T phase diagram (*Fig. 5*) has a positive slope, with a minimum value of

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5)　As the intensity measurements for the [EI-β] polymorph were performed at 200 K, the thermal parameters were corrected by a factor of 0.75 (150/200).

6)　That the phase transition is endothermic has not yet been demonstrated experimentally, but seems unlikely to be wrong. The calculations of *Hammond et al.* [8] give an endothermic transition.

7)　The crystallographic studies and *Zallen et al.* [18b] both give $T_c = 110$ K.
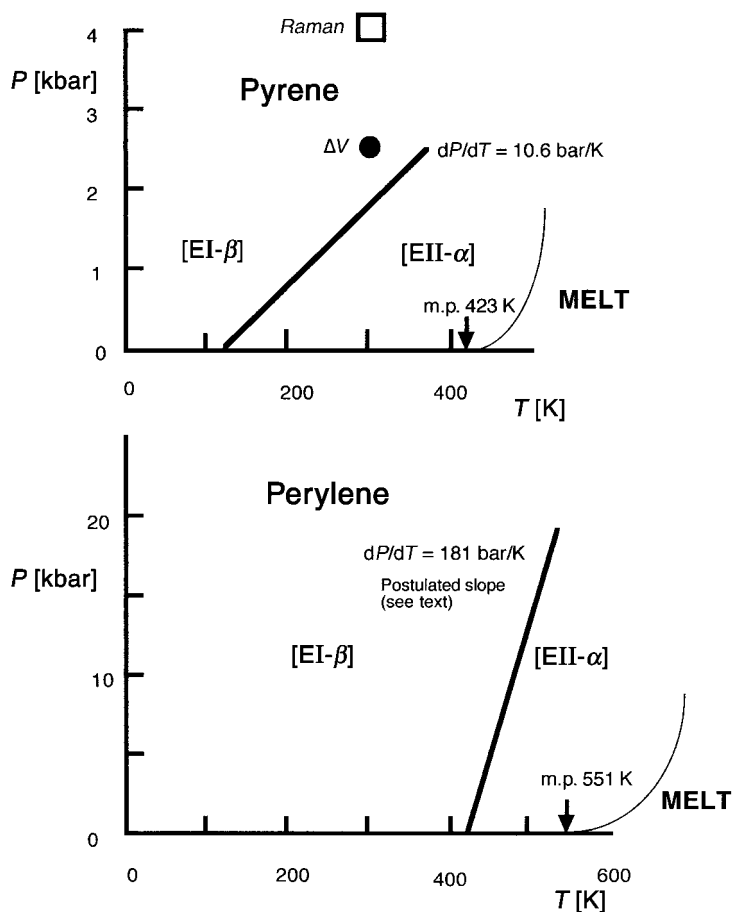
Fig. 5. *Tentative P−T phase diagrams for pyrene and perylene.* The lighter lines are indicative only of the dependence of melting point on pressure.

181 bar/K; this is shown as a 'postulated slope' in *Fig. 5* and is subject to revision. Temperatures above T_c are required for application of pressure to bring about an [EII-α] to [EI-β] phase transformation; for example, assuming $T_c = 420$ K, the transformation pressure at 500 K would be 14.5 kbar. Neither *Hamann* [7] nor earlier workers found evidence for a pressure-induced phase change in perylene (at 300 K) below 45 kbar.

3. Discussion. – 3.1. *Molecular Structure.* A comparison of bond lengths in [EII-α] perylene with those found in its many π-π* charge transfer compounds with various electron acceptors did not show any significant differences (*Krygowski et al.* [5c]). Bond lengths have been calculated at a number of levels of approximation (*Table 3*) assuming D_{2h} symmetry. The agreement among the calculated values is about as good as their agreement with the averaged measured values. Indeed, a description of perylene as

consisting of two naphthalene moieties joined by sp^2-sp^2 bonds ($d(C-C)=1.471(6)$ Å) as, for example, in binaphthyl (*Kerr* [5f]) gives dimensional agreement not much inferior to that obtained from elaborate calculations.

The conclusion, from the quadrupolar splittings in the deuterium NMR spectrum of perylene at 320 K (*Shilstone et al.* [19]), that the average twist angle between naphthalene portions was 11.6° is not reconcilable with the various crystal-structure results, which show that the molecule is planar to within a few hundredths of an Å. However, there is a significant difference between the two polymorphs, the deviations from planarity in the [EI-β] polymorph being appreciably less than those in the [EII-α] polymorph. *Camerman* and *Trotter* [5b] suggested that the molecule in [EII-α] was slightly folded about its long axis, and the more-precise later results are compatible with this model. The two 'biphenyls' (separately planar with RMS deviations of 0.006 and 0.013 Å, resp.) are 'hinged' along C(13), C(19), C(20), C(16) with an angle of 1.6° between the two planes. The physically more appealing model of two 'naphthalene' portions is marginally worse (separately planar with RMS deviations of 0.010 and 0.017 Å, resp.). Presumably, the small deviations from planarity are due to intermolecular interactions as suggested by *Cruickshank* [20] for anthracene.

This description is satisfactorily compatible with the results of *Iuliucci et al.* [11a][8]) who measured the ^{13}C chemical-shift tensors for single-crystal [EII-α) perylene[9]) by NMR spectroscopy (methodology summarized by *Grant et al.* [11b]) and ascribe the deviations of the measured spectra from hypothetical D_{2h} symmetry to intermolecular crystal effects; there is impressive detail in the values of the ^{13}C chemical-shift tensors for individual atoms and groups of atoms. In particular, the deviations of the individual δ_{33} principal tensor elements from the mean δ_{33} direction were approximately correlated with the minor structural deformations due to folding along the C(13)$\cdots$C(16) axis; a full treatment requires the inclusion of the effects of direct intermolecular interactions and of differential vibrational effects.

3.2. *Relations between the Perylene Polymporphs.* 3.2.1. *Phenomenology. Desiraju* and *Gavezzotti* [14] have identified four characteristic packing arrangements in a sample of 32 polycyclic aromatic hydrocarbons (27 monoclinic, 5 orthorhombic). In terms of this classification, the [EII-α] structure is of the 'sandwich herringbone' type and the [EI-β] structure of the 'gamma' type. Assuming cell dimensions and space group, *Hammond et al.* [8] have calculated the minimum lattice-energy structures for the perylene polymorphs (Table 10 in [8]), obtaining good agreement with the [EII-α] crystal structure. We have compared their results for [EI-β] with our crystal structure (their comparison had to be made with the much less-precise *Tanaka* [5e] structure) and find good agreement. The global minimum lattice energy calculated for [EII-α] perylene (-140.7 kJ/mol (*Dreiding* force field)) is in good agreement with the measured ΔH_{sub} of 145 kJ/mol. The analogous calculated value for [EI-β] perylene is -153.6 kJ/mol. Thus, $\Delta H_{trans}(calc) = H_{II} - H_I = -140.75 - (-153.59) = 12.84$ kJ/mol

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[8]) '…*the π electrons remain essentially localized in the naphthalene fragments…the peri bonds behave as biaryl linkages and not as typical bridgeheads. This conclusion is consistent with the simple Kekule description of perylene*…'

[9]) A '*bright orange-yellow*' crystal of 5-mm diameter and 4-cm long grown from the melt by the *Bridgman* method and shown to be in the α-polymorphic form.

(endothermic). The entropy of transformation is $12840/T_c$ J/mol K, where T_c is the temperature at which the two phases are in equilibrium; *if* $T_c = 420$ K, then $\Delta S_{trans} = 12840/420 = 30.6$ J/mol K. The phase transformation [EI-β] to [EII-α] is entropy-driven, and it seems likely that this is due to increased thermal motion in the [EII-α] polymorph.

Some statements in the literature about the relations between the polymorphs have not been phrased with the desired precision. *Tanaka* [5e] writes (footnote on p. 1246) '*The phase transformation from β to α occurs at ca. 140°C. The β form is the metastable form at room temperature, and it is inconceivable that the $\alpha \rightarrow \beta$ transformation occurs at lower temperature. In fact, we can recover the α crystal after its immersion in liquid helium without any of the damage to the original shape which would be expected if a phase transformation had occurred*'. *Iuliucci et al.* [11a] write '*The α form of perylene is stable at all temperatures up to its melting point while the β form is only stable below 140°C*'. 'Metastable' and 'stable' are not used in a strictly thermodynamic sense in either of these quotations.

In summary, our interpretation of all the available experimental results is that the [EI-β] polymorph ($Z = 2$) is stable from the lowest temperatures up to *ca.* 420 K, where it transforms in the solid state (in approximately single crystal to single crystal fashion) to the [EII-α] polymorph ($Z = 4$); we have already noted that the equilibrium transformation temperature may be less than 420 K. This polymorph is stable up to the melting point at 551 K. The [EII-α] polymorph crystallizes first from solution, this process being kinetically rather than thermodynamically controlled. Behavior of this kind, where the low-temperature polymorph transforms on heating to a high-temperature form that can then be cooled below the transformation temperature without reverting to the low-temperature phase (*i.e.*, there is hysteresis), has been encountered often in the past. It is also found that the 'metastable' polymorph crystallizes first and then, in contact with solvent, transforms to the stable polymorph. Thallium picrate is a classic example where the 'metastable' yellow polymorph in contact with solvent transforms to the stable red polymorph [21a]; earlier references dating back to 1866 are given. Among other examples are pyridinium picrate [21b], *N*-anilinophthalimide, and *N*-(*N*′-methylanilino)phthalimide [21c]; diethyl 3,6-dibromo-2,5-dihydroxyterephthalate behaves similarly [21d].

3.2.2. *Specific Interactions in the Perylene Polymorphs.* Hammond et al. ([8]; their Table 10) have identified the principal interactions in both polymorphs with the HABIT95 program ([22]). This allows them to partition the major portion of the lattice energy among various interactions. For example, in [EII-α] perylene, 21% is from π-π dimer interaction and 24% from molecules in nonparallel dimers in the same sandwich herringbone, and the rest from other interactions. In [EI-β] perylene, the in-stack interaction contributes 29% and nonparallel molecules in the same plane 39%. Although π-π interactions are important (and easily recognized), they do not appear to be the largest of the specific interactions; the overall lattice energy comes from a subtle interplay of many interactions. The relative stability of the different polymorphs is, of course, determined by their lattice *free* energies; here the decisive contribution at higher temperatures (above, say, 50–75% of the absolute melting point) comes from the entropy, which is understood less well than the enthalpy.

3.3. *Comparison of the Pyrene, Perylene, and Phenazine Systems.* The relevant data are given in *Table 6*. When comparing pyrene and perylene, one should remember that the polymorph clusters differ. Both pyrene phases are 'dimeric' ($P2_1/a$, $Z = 4$); the enthalpy of transformation is small (0.29 kJ/mol), and one could be tempted to predict that the transformation is displacive. However, caution is warranted, as the crystals shatter on cooling below 110 K [23]. The perylene transformation is from a low
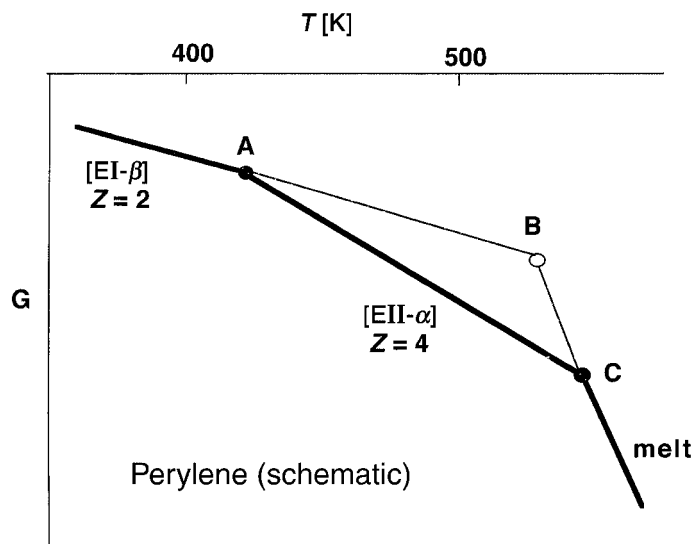

Fig. 6. *Perylene: schematic free energy* – T *diagram.* Heavy lines show $G-T$ curves for stable phases; lighter lines show extrapolations in metastable regions. Analogous $G-T$ diagrams have been given by *McCrone* ([25]: *Figs.* 3 and 5), *Herbstein* and *Kaftory* [26a], and *Richardson et al.* [26b]. *A:* Transition from [EI-β] ($Z = 2$) to [EI – α] ($Z = 4$); shown as *ca.* 420 K but uncertainty is noted in the text. *B:* Virtual melting point of [EI-β] ($Z = 2$); not realized in practice. *C:* Melting point of [EII-α] ($Z = 4$). *AB* and *CB* are metastable regions not realized in practice.

Table 6. *Data for Comparison of Polymorphism in Pyrene, Perylene, and Phenazine.* In each cluster, the phase stable at lower temperatures is on the left and that at higher temperatures on the right (subscripts L, R). As noted in the text, the stability ranges of the two phenazine polymorphs are not known.

	Pyrene [EI-β] ($Z = 4$)	Pyrene [EII-α] ($Z = 4$)	Perylene [EI-β] ($Z = 2$)	Perylene [EII-α] ($Z = 4$)	Phenazine ($Z = 2$)	Phenazine ($Z = 4$)
V_{mol} [Å³]	251.98	255.7	305.3	308.1	224.5	228.6
$\Delta V (= V_R - V_L)$ [Å³]		+3.7		+2.8		+4.1
M. P. [K]		423.81[a])		550.9[b])	449[c])	431[c])
Calc. lattice energy [kJ/mol][d])			– 153.59	– 140.75	– 98.11	– 101.67
$\Delta E (= E_R - E_L)$ [kJ/mol]		+0.29[a])		+12.84		– 3.56

[a]) Measured value from *Wong* and *Westrum* [17]. [b]) Measured value from *Wong* and *Westrum* [6a]. [c]) Phenazine (measured values) melting points from *Janowski* and *Gdaniec* [9b]; triple point ($Z = 2$) 447.89 ± 0.01 K; sublimation enthalpy ($Z = 2$) 96.97 ± 0.36 kJ/mol (*Sabbah* and *El Watik* [24]). [d]) Calculated lattice energies from *Hammond et al.* [8] with HABIT95 and *Dreiding* force field.

temperature ($Z = 2$) to a higher temperature ($Z = 4$) phase, and ΔH_{trans} is 44 times as large as in pyrene; we have noted evidence (somewhat to our surprise) for a 'single crystal' to 'single crystal' transformation mechanism. The two systems are both well-behaved enantiotropic (defined in the *Appendix*), as shown schematically for perylene in *Fig. 6*.

Comparing perylene and phenazine (where the relation between the phases has not yet been established experimentally), one notes that, in both systems, the ($Z = 2$)[10]) phases are more closely packed than the ($Z = 4$) phases. They differ in that the ($Z = 2$) phase of perylene has a lower lattice energy than the ($Z = 4$) phase, while the reverse applies to phenazine[11]). The denser ($Z = 2$) phase of phenazine has a higher melting point than the ($Z = 4$) phase, which does not fit the requirements of an enantiotropic system. The phenazine ($Z = 4$) phase appears to be monotropic, and this is supported by the absence of a transition in a DTA study of ($Z = 2$) phenazine [24]. Specific heat measurements on the two phenazine polymorphs would be of great interest for further understanding of this system.

Experimental Part

Preparation of Crystals of the Polymorphs. Tanaka [5e] wrote '*Crystals of both…forms have been obtained together from petroleum ether or benzene solutions, but they are easily distinguished from each other by their general appearance. The α (Z = 4) form is usually obtained as a rectangular tabular yellow crystal (monoclinic) while the β (Z = 2) form is obtained as hexagonal, greenish-yellow prisms (monoclinic)*'.

Our source of perylene was *Fluka* (*purum*; red-brown powder; > 99% HPLC; analysis number 291185/1 34296; m.p. 549–552 K (*Wong* and *Westrum* [6a] give 550.9 K)). Our sample was further purified here by column chromatography and recrystallized by r.t. evaporation of a benzene soln. Our results are compatible with those of *Tanaka* [5e]. The [EII-α] form crystallizes much more readily than [EI-β]; we were able to obtain sufficient [EI-β] for diffraction measurements but not enough for DSC measurements.

Vacuum-sublimation techniques for growing [EII-α] and [EI-β] have been described in some detail in [27]; a sublimation temp. of 423 K gave a mixture of [EII-α] and [EI-β] crystals, while [EII-α] alone grew at 533 K. The [EII-α] crystals of *Näther et al.* [5d] were grown by sublimation. Sublimation methods were not available to us.

Structure Determination. Structures were determined by standard techniques (*Table 7* and deposited CIFs, which include atomic parameters and molecular dimensions). Atomic numbering is shown in *Fig. 1.* The crystals of [EII-α] were of good diffraction quality, but those of [EI-β] were very thin plates and the diffraction quality was reduced.

Cell Dimensions over a Range of Temperatures. Cell dimensions of single crystals of the two perylene polymorphs were determined on a *Philips PW1100* four-circle diffractometer by heating (*Tuinstra* and *Fraase Storm*, 1978) [28] and cooling (*Oxford Cryostream*) devices (MoK$_\alpha$, 25 reflections, $3.8 \leq 2\theta \leq 21.8°$).

Geometric and Thermal-Motion Calculations. Geometric and thermal-motion calculations were carried out with PLATON (*Spek* [29]) and SHELXL (*Sheldrick* [30]).

Deposit Arrangements. Crystallographic data (excluding structure factors) have been deposited with *Cambridge Crystallographic Data Centre* as deposition No. CCDC 198723 ([EII-α] polymorph) and CCDC 198724 ([EI-β] polymorph). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44(1223)336 033; e-mail: deposit@ccdc.cam.ac.uk).

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[10]) We use Z values to identify the phases because the literature designations (α, β) of the polymorphs are opposite in the perylene and phenazine systems.

[11]) *Richardson et al.* [26b] note '…*evidently, the denser the crystal, the lower its internal energy. (This can be considered a general rule, but there are many exceptions)*'.

Table 7. *Details of Experimental and Refinement Procedures for the [EII-α] (Z=4) and [EI-β] (Z=2) Perylene Polymorphs*

	Perylene [EII-α] (Z=4) polymorph	Perylene [EI-β] (Z=2) polymorph
Formula	$C_{20}H_{12}$	$C_{20}H_{12}$
Solvent	See text	See text
Space group	$P2_1/c$	$P2_1/c$
Crystal system	monoclinic	monoclinic
Formula weight	252.32	252.32
Radiation	MoK_α; $\lambda = 0.71073$ Å	MoK_α; $\lambda = 0.71073$ Å
a [Å]	10.2390(7)	9.7630(15)
b [Å]	10.7860(8)	5.8430(9)
c [Å]	11.1320(11)	10.608(2)
β [°]	100.924(3)	96.770(6)
V [Å³]	1207.12(17)	600.92(17)
Z	4	2
D_{calc} [g cm⁻³]	1.388	1.394
$F(000)$	528	264
T [K]	150.0(2)	200.0(2)
$2\theta_{(max)}$ [°]	50.10	50.06
Data collection	*Kappa CCD* diffractometer; ϕ scan	*Kappa CCD* diffractometer; ϕ scan
Absorption correction	none ($\mu = 0.079$ mm⁻¹)	none ($\mu = 0.079$ mm⁻¹)
Total refl. measured; R_{int}	3755; 0.0360	1881; 0.0792
Symmetry-independent refl.	2141	1056
Obs. refl. ($F^2 > 2\sigma(F^2)$)	795	400
Refinement on	F^2	F^2
H-Atoms	all parameters refined	all parameters refined
R ($F^2 > 2\sigma(F^2)$)	0.0361	0.0500
wR	0.0677	0.1039
Goodness-of-fit	0.782	0.761
Final Δ_{max}/σ	0.001	0.000
$\Delta\rho$ (max; min) e·Å⁻³	0.148; −0.122	0.173; −0.155

Appendix. Nomenclature of Polymorphs. – The 'Report of an IUCr Working Group on Phase Transition Nomenclature' (*Tolédano et al.* [31]) provides background information and a proposal for a 'Six-field phase-transition nomenclature'. This proposal has the virtue of completeness but the deficiencies of not distinguishing enantiotropic and monotropic systems[12]), and of using only inorganic substances as illustrative examples. A more compact nomenclature for convenient designation within a text has been proposed (*Herbstein* [4]). This revises an earlier proposal of *McCrone* ([25], pp. 736 – 737) and incorporates part of the information included in the Working Group proposal. A shortened version is given here.

Polymorphs of a compound are designated as follows:

Enantiotropic system: Name (of Compound) [EI (< T1 K) (other information); EII (T1 – T2 K) (other information); ....]

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[12])   '*When each of two polymorphs is thermodynamically stable in a definite range of temperature and pressure, the pair is said to be* enantiotropic.....*When one of two polymorphs is thermodynamically unstable at all temperatures below the melting point, the two are said to be* monotropic' (see *Westrum* and *McCullough* [32], p. 73). This definition tacitly assumes working at fixed (generally atmospheric) pressure.

The polymorphs are listed as I, II, . . . in order of increasing temperature stability ranges, which is the inverse of *McCrone*'s suggestion. $< T1$, $T1 - T2$. . . give the regions of temp. stability. The 'other information' can include former designations, number of molecules in unit cell, space group *etc*. Newly discovered polymorphs would have to be inserted between known examples, perhaps with revision of the previous I, II. . . order.

We illustrate for perylene: [EI $(< 420$ K(?))-(β; $Z = 2$); EII $(420(?) - 551$ K)-(α; $Z = 4$)]. These designations have been abbreviated in the text.

Monotropic System: Name [MI (other information); MII (other information)].

A combination of the two types of nomenclature will be needed when the compound has both enantiotropic and monotropic systems. Only temp. has been used in the above examples, atmospheric pressure being assumed, but pressure as a variable can be accommodated.

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