

Molecular modelling of poly(aryl ether ketones). I. Aryl-aryl interactions in crystal structures

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SUMMARY

Non-bonded potentials for the aryl-aryl interaction have been derived using crystal structure data of a number of small aromatic molecules. The potentials, based on atom-centred interactions, give an accurate reproduction of the benzene crystal geometry and sublimation energy when used in conjunction with coulombic energies evaluated using point atomic charges. An examination of the charge distribution on benzene suggested values of 0.13e (H) and $-0.13e$ (C) to be suitable. The transferability of the potentials has been shown by prediction of crystal geometries and sublimation energies of other hydrocarbon molecules and, with additional interactions for the oxygen atom included, preliminary polymer crystal structure calculations have been carried out. These demonstrate the validity of the derived parameters by successfully predicting crystallographic unit cell dimensions and ring conformations in the poly(phenylene oxide) and poly(aryl ether ketone) crystals.

INTRODUCTION

Poly(phenylene oxide), PE [1], poly(aryl ether ketone), PEK [2–4] and poly(aryl ether ether ketone), PEEK [5–8] (Fig. 1) have broadly similar crystal structures but exhibit some differences in the unit cell parameters, ring conformations and structural variation with temperature. An explanation of this behaviour may be possible using a molecular mechanics model. Here we describe the method and results of the parameterisation of such a model and show the applicability of the derived potential functions to the polymer crystals by the successful prediction of the global minima in the PE and PEK crystals.

Any computational model of the aryl ether ketone materials clearly demands, as an integral

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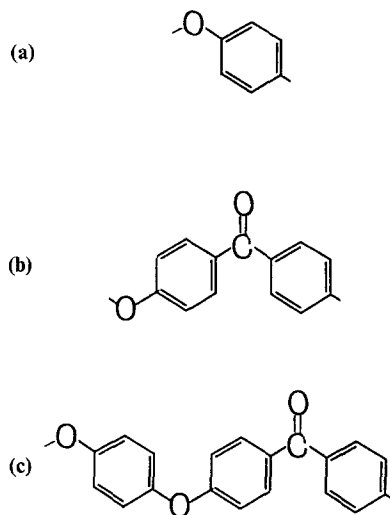


Fig. 1. The chemical repeat units of (a) PE, (b) PEK and (c) PEEK.

part, a reliable aryl-aryl interaction potential. In addition to its importance in this particular case the interaction is of some intrinsic interest, e.g. considerable effort has been expended in attempts to obtain the gas phase dimer structure of benzene and quantify the intermolecular forces involved. Experimental observations of the dimer have given somewhat limited information; molecular beam studies [9,10] have shown it to have a dipole moment, thus indicating a non-symmetrical structure and precluding the parallel dimer. A perpendicular dimer (orthogonal ring planes) was suggested to be the likely structure [10], this being the same relative orientation of neighbouring rings to that found in liquid benzene [11] and in the solid state [12,13], a favoured orientation since the positively charged hydrogen atoms point into the π electron clouds of the ring. Law et al. [14], in contrast, suggest a parallel displaced dimer from detection of optical absorption spectra by TOF mass spectroscopy with a predicted displacement of about 2 Å [15]. The difficulty of obtaining clear experimental evidence of the dimer structure has stimulated the development of computational approaches to the problem and the two studies commonly quoted are those of Evans and Watts [16,17] and Karlstrom et al. [18], the latter being an *ab initio* study and the former concerned with deriving a semi-empirical potential function based on known physical properties of benzene. Unfortunately there is poor quantitative agreement in the dimer structures and energies calculated by the two potentials.

The uncertainties in the available experimental studies present a major problem when trying to obtain a reliable empirical model. The use of crystal structure data as an additional (and more dependable) data source was pioneered for aromatic molecules by Williams [19–23] and the potentials and charges derived (to fit the benzene crystal lattice constants at 135K) by Williams and Starr (WS) [23] are still extensively used. Charges of 0.153e (H) and $-0.153e$ (C) were reported to be the optimum values [23]. A rigorous comparison of the WS and Karlstrom potentials, and the development of more computationally efficient potentials based upon them, has recently been undertaken [24]. The sensitivity of the aryl-aryl interaction to the size of the partial charges em-

played was clearly shown by calculating the Euler angles in the benzene crystal, using various atomic charges and a 12-6-1 potential derived from the WS parameters. Whilst this work [24] also indicates 0.15e (H) and $-0.15e$ (C) to be the optimum charges, it must be remembered that the plots (error in Euler angle vs. atomic charge) obtained are a function of the non-bonded potentials employed. The interdependence of charge and non-bonded potentials is further emphasised by the model derived by Powell et al. [25], which was shown to give a satisfactory reproduction of the crystal structure without placing charges on the atoms and compensating for this omission in the potential functions.

The question thus arises – what are the ‘correct’ atomic point charges in the benzene molecule? An optimum charge of $\pm 0.15e$ was obtained when fitting ab initio benzene dimer structures and using the MMP2 functions [26], which agrees with the WS charges. In their attempts to reproduce the dimer structure using the WS potentials Schauer and Bernstein commented that the atomic charge was too high to obtain the postulated experimental structure [15]. In contrasting the functions constructed from non-bonded and electrostatic interactions using the WS and MMP2 non-bonded parameters with the ab initio derived potential of Karlstrom et al. and the potentials of Powell et al. (parameterised without charges) it seems the major requirement is for the repulsive nature of the C··C and H··H curves to be offset by an equally attractive C··H curve. This explains the success of the Powell model in entirely eliminating the electrostatic term and still reproducing the experimental crystal structure. Since this is the most important requirement, there is nothing wrong with this approach, however, as noted by Shi and Bartell [24], models including electrostatic interactions are favoured since they can be made to reproduce the experimental quadrupole moment.

$$\begin{aligned} Q &= 3Q_{zz} - (Q_{xx} + Q_{yy} + Q_{zz}) \\ Q_{xx} &= 4.803 \cdot 0.5 \cdot (q_i \cdot (x_i - c_x)^2) \\ Q_{yy} &= 4.803 \cdot 0.5 \cdot (q_i \cdot (y_i - c_y)^2) \\ Q_{zz} &= 4.803 \cdot 0.5 \cdot (q_i \cdot (z_i - c_z)^2) \end{aligned} \quad (1)$$

where q_i is the charge on atom i , x_i , y_i and z_i are the coordinates of atom i , c_x , c_y and c_z are the coordinates of the centre of charge and the units of Q are eA^2 .

An approximation to the molecular quadrupole moment (Q) may be obtained from the point charges using equation (1) [27]. The model we wish to use does not include a specific representation of the π system and hence makes the approximation of $Q_{zz}=0$. In practice Q_{zz} will make a small and, due to the π electron density, negative contribution to the overall quadrupole and the calculated values given below are, therefore, assumed to be underestimates of the correct value. Experimentally the benzene quadrupole moment has been given [28–30] as $-5.6 \pm 2.8eA^2$ (a value now considered to be an underestimate), $-8.68 \pm 0.5eA^2$ and $-10.0 \pm 0.6eA^2$. Calculations (with $Q_{zz}=0$ and hence $Q = -2Q_{xx}$) using the CHARGE2 programme [31] give charges of 0.091e (H) and $-0.091e$ (C) and a molecular quadrupole of $-5.6eA^2$, whilst $\pm 0.15e$ charges give a value of $-9.1eA^2$. Assuming a correction for Q_{zz} is required we conclude that the WS charges are slightly high (as noted by Schauer and Bernstein [15]) whilst the CHARGE2 value is too low. This is supported by a recent infra-red study [32] which, from a consideration of gas phase band intensities, indicated a charge of 0.135e on each hydrogen. In the following calculations a charge of 0.13e (H) and $-0.13e$ (C) are employed with the $C(sp^2)\cdots H$ bond factor parameter in CHARGE2 (original-

ly 23.76) being reduced to 13.40. This value is used in charge calculations for all molecules in this paper.

Computational approach

$$E_{\text{vdW}} = E_{\text{min}}*(z^2 - 2z) \quad (2)$$

where $z = \exp[b_s*(1 - (r_{ij}/r_{\text{min}}))]$
 $b_s = \ln 2 * r_{\text{min}} / (r_{\text{min}} - r_0)$
 r_0 is the value of r for $E_{\text{vdW}} = 0$
 r_{ij} is the distance between atoms i and j .

$$E_{\text{elec}} = 332 * q_i * q_j / r_{ij} * D \quad (3)$$

where q is the atomic charge
 D is the dielectric constant.

$$E_{\text{sub}} = E_{\text{vdW}} + E_{\text{elec}}$$

Having decided on the value of the partial atomic charges, evaluation of the non-bonded potentials can be achieved directly from the crystal geometries and, where available, sublimation energies (E_{sub}) of the relevant molecules. The lattice energies comprise electrostatic and non-bonded (van der Waals) contributions, in each case calculated for atom-centred interaction using equations (2) and (3) respectively. We use, as previously [33,34], non-bonded potentials expressed in the Morse formulation, however these can be transformed to the equivalent $\exp-r^6$ function very easily. Molecular packing in crystals occurs such that few intermolecular interactions will occur at distances below r_0 and, additionally, these few exceptional cases will almost exclusively be H··H interactions for aromatic hydrocarbon molecules. The repulsive part of the H··H potential has already been considered in detail [33] and the value of the steepness parameter, b_s , (which essentially determines the shape of the function in this region) obtained as 5.643 (the value obtained if the MM3 H··H function [35] is converted to Morse format). Since the repulsive parts of the remaining potentials will be relatively unimportant in the crystal structure calculations this value was also used in these cases, reducing the required parameters to six, i.e. E_{min} and r_{min} for the H··H, C··C and O··O interactions. The mean combining law was used for the C··H, C··O and H··O interactions, hence E_{min} and r_{min} in each of these cases were taken as the respective arithmetic and geometric means of the relevant parent potentials. The electrostatic energy was calculated using atomic point charges from the CHARGE2 programme (with the modification outlined above).

The basic thinking behind the computational approach is summarised as follows. For the ‘correct’ set of potential functions and atomic charges the calculated global energy minimum must occur at the experimental crystal geometry. Thus if the energies of two lattices – one slightly contracted along all three crystallographic axes, the other slightly expanded – are calculated, the differential of the energy with respect to the cell volume ($\partial E/\partial V$) will be zero, assuming an approximate parabolic curve over the small range considered. Expansions and contractions of 0.001 Å along each axis give the best results and, as will be shown, this extremely simple approach produ-

ces parameters which are transferable to larger molecules. When available, data from neutron studies of deuterated molecules was used to give accurate hydrogen coordinates. In the absence of such data hydrogen atoms were added using standard bond lengths (C-H 1.08 Å) and angles in the COSMIC package [36].

The calculated energy is for the interaction of a single molecule placed centrally in a lattice which extends at least three crystallographic axes lengths in each direction, which is sufficient to encompass all significant electrostatic and non-bonded interactions (20–30 Å, see Table 1). Calculations on larger lattices indicated that whilst there may be significant attractive or repulsive coulombic forces exerted from molecules outside this range, these tend to cancel and do not effect the calculated value of the lattice energy. For the non-bonded interactions a 6Å cutoff is used in such a way as to include all lattice molecules which have any atoms within 6Å of any part of the central

TABLE I
EXPERIMENTAL (IN BRACKETS) AND CALCULATED UNIT CELL PARAMETERS AND SUBLIMATION ENERGIES (kcal/mol) FOR MOLECULES USED IN THE MODEL PARAMETERISATION^a

Reference	Molecule	a (Å)	b (Å)	c (Å)	–E _{sub} ^b	% elec ^c
13	Benzene	7.34 (7.360)	9.37 (9.375)	6.73 (6.703)	12.54 (12.51)	36.1
37	Naphthalene	8.11 (8.108)	5.94 (5.940)	8.75 (8.647)	17.82 (17.33)	28.0
38	Anthracene	8.37 (8.37)	6.00 (6.00)	11.22 (11.12)	25.17 (24.43)	32.1
39	Biphenyl	7.80 (7.78)	5.47 (5.565)	9.52 (9.44)	23.18 (18.12)	31.6
40	Fluorene	8.35 (8.365)	18.70 (18.745)	5.63 (5.654)	20.16 (19.79)	22.2
41	<i>o</i> -Benzoquinone	6.26 (6.314)	5.72 (5.799)	6.88 (6.886)	18.96 (-)	46.2
42	<i>p</i> -Benzoquinone	5.71 (5.711)	6.75 (6.735)	6.71 (6.763)	19.16 (15.01)	54.0
43	1,4-Anthraquinone	8.44 (8.430)	19.66 (19.846)	5.88 (5.927)	25.76 (26.30)	25.0
44	<i>p</i> -Dimethoxybenzene	7.15 (7.173)	6.28 (6.277)	16.58 (16.552)	20.26 (-)	36.0

^ar_{min} (H··H) 3.110, (C··C) 3.820, (O··O) 2.910, (C··H) 3.447, (O··H) 3.008, (O··C) 3.334.

E_{min} (H··H) 0.011, (C··C) 0.041, (O··O) 0.105, (C··H) 0.026, (O··H) 0.058, (O··C) 0.073.

^bFrom Ref. 45, except for benzene (see text).

^cThe percentage electrostatic contribution to the total lattice energy.

molecule, thus avoiding anomalous results which may be obtained if only those interactions between the central molecule and fragments of outer molecules (i.e. those parts within 6 Å) are calculated.

RESULTS AND DISCUSSION

(a) Small molecule calculations

Given the accuracy of the data for the benzene crystal structure, relative to that available for other hydrocarbons, the chosen approach was to obtain a potential set which accurately reproduces the benzene geometry and sublimation energy and then assess the transferability of these parameters to other hydrocarbon structures. The recent neutron diffraction study of deuterated benzene at 15K [13] was considered to be the most reliable data to use as a starting point in the parameterisation, since accurate hydrogen coordinates are available and the low temperature reduces the problem of molecular vibration considerably. The sublimation energy of the benzene crystal at 0K has been estimated to be 12.51 kcal/mol, a value considered accurate enough to be worthy of exact reproduction [24]. In the initial stages of the parameterisation an attempt was made to separate the crystal geometries and energies, making the latter dependent on E_{\min} and the former on r_{\min} . However, it became clear that, in the benzene crystal, both geometry and energy show significant dependence on both terms in each of the functions (H··H, C··C and C··H) with the unit cell dimensions being particularly sensitive to the C··H r_{\min} value. The insignificance to the geometry of the C··C r_{\min} below 3.80 Å clearly indicates the majority of the C··C distances to be above the optimum r_{\min} and also illustrates the difficulties encountered in parameterising inter-

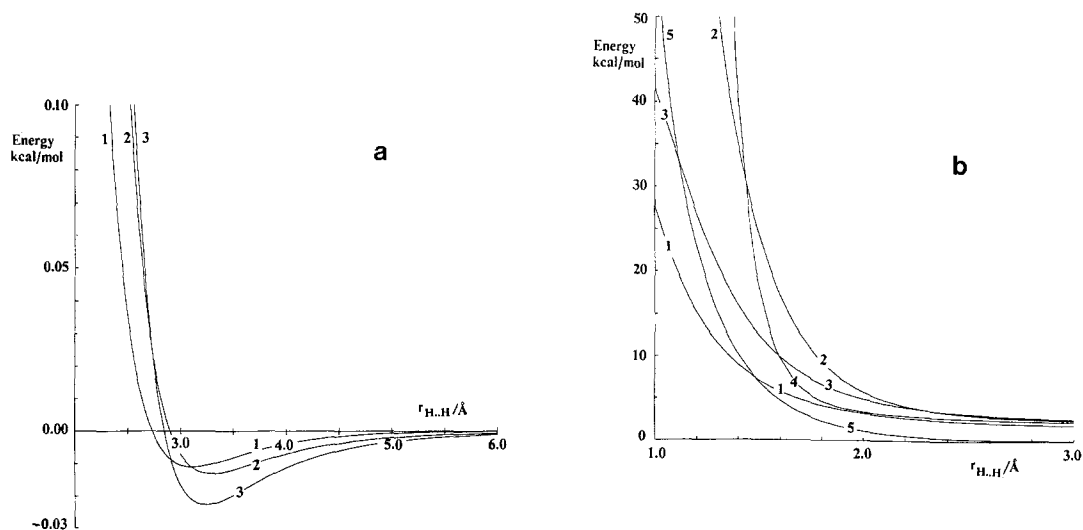


Fig. 2. Comparison of literature potential functions with those derived in this paper. (a) H··H non-bonded interaction potentials from (1) this work, (2) MM3 and (3) WS. (b) H··H interaction potential including non-bonded and coulombic energies from (1) this work, (2) MMP2 and 0.15e charges, (3) WS and 0.153e charges, (4) Karlstrom ab initio potential and (5) Powell (no charges).

action potentials between atoms that are effectively 'buried' under other atoms in the molecular structure.

Figure 2 contrasts the derived H··H potential functions with those obtained in previous studies. A direct comparison with the MM3 and WS H··H potentials (Fig. 2a) indicates the WS function to be somewhat 'hard' at short internuclear distances. This is, however, of limited importance in the context of crystal structure calculations and may also be somewhat compensated for by the larger well depth. For more general applications the softer MM3-type curve is probably a better representation of the repulsive part of the function. The offset nature of our H··H potential (to lower r_{\min} and smaller well depth, relative to MM3) reflects the different treatment of the interaction in the two cases, i.e. based on either atom-centred interactions or, as in MM3, between the effective centres of electron density. To obtain a comparison with the ab initio derived potentials of Karlstrom it is necessary to include coulombic interactions in the empirical curves. Figure 2b clearly indicates the Karlstrom H··H potential to be excessively steep at short internuclear distances.

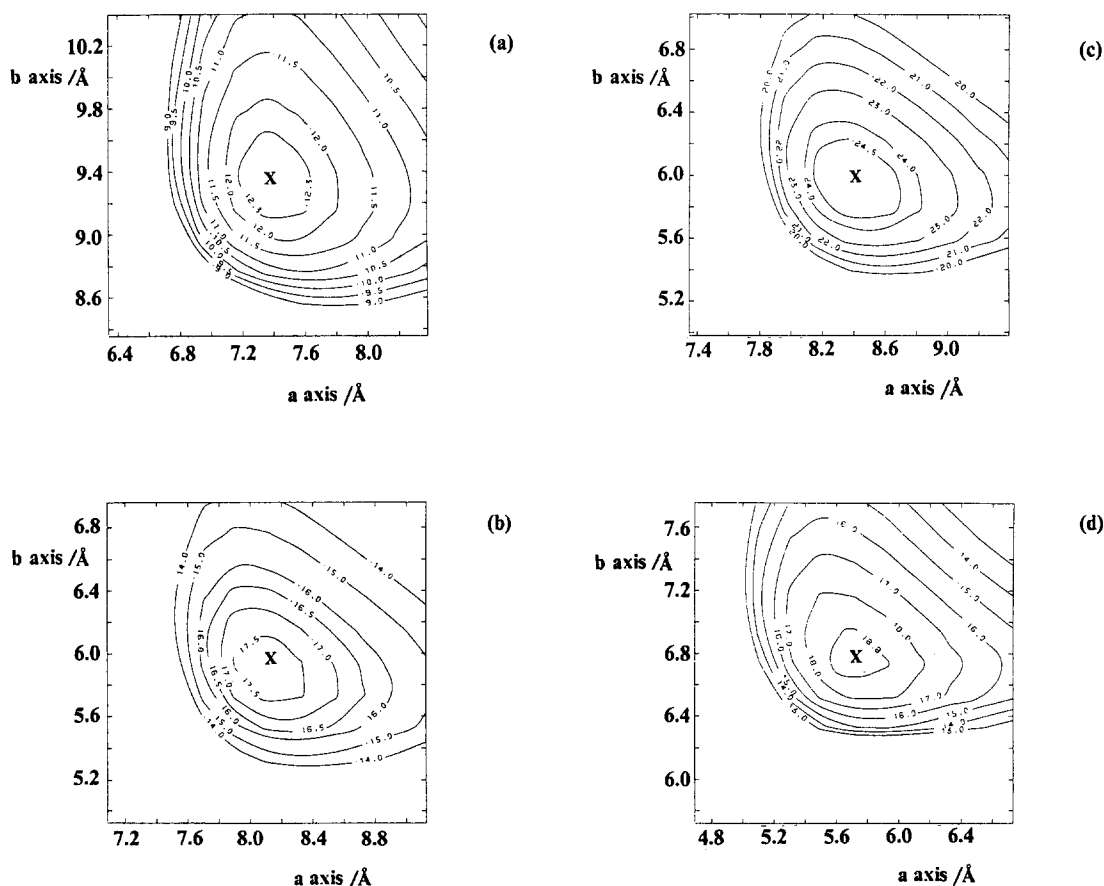


Fig. 3. Energy contour plots (kcal/mol) showing the calculated global minima in crystals of (a) benzene, (b) naphthalene, (c) anthracene and (d) *p*-benzoquinone as a function of a- and b-axes' lengths (at the calculated c-axis). The experimental values are denoted by X.

ces, however, for larger separations (1.8–2.6 Å) it is almost identical to the functions derived in this work. This is taken as a further indication of the correctness of the model and is particularly relevant to the charge distribution (since the coulombic interaction is dominant in this part of the curve). The MM2 and WS curves (0.15e charges) are both more repulsive than the Karlstrom potential, again suggesting the charges to be too high. The compensating nature of functions within a potential set is clearly shown by comparing the H··H curves with the C··H curves (not shown), as mentioned earlier the major requirement seems to be an offset of the H··H (and C··C) repulsion with an equally attractive C··H interaction.

The transferability of the final parameters obtained for the carbon and hydrogen functions was then assessed for a number of other structures. Figure 3 shows surfaces for the variation of energy with a- and b-axes' lengths for benzene, naphthalene, anthracene and *p*-benzoquinone unit cells having a fixed (the calculated) c-axis. It is clear that good agreement between calculated and experimental unit cell parameters is obtained in these cases and the remaining calculated geometries (Table 1) were considered to be satisfactory. The deviations from experimental sublimation energies can also be adequately explained. Thus to a first assumption the extrapolated value (to 0K) of the benzene sublimation energy does not include effects of thermal molecular vibrations, but this is not true for experimental values obtained at or above room temperature. Clearly the calculated values do not account for this and consequently will be larger (i.e. more negative). For rigid molecules such as naphthalene and anthracene there will essentially be no internal torsional motion, but for biphenyl this is likely to be considerable and is probably the reason for the much larger difference in experimental and calculated sublimation energies. A further problem is the inherent uncertainty in the experimental values, particularly for larger aromatic systems and oxygen containing aromatics. Additionally the parameterisation of the oxygen interaction potentials is limited by the smaller number of atoms involved and the dominance of the electrostatic term.

(b) Energy minima in the PE and PEK crystals

Interactions between aryl rings are of primary importance to the chain packing in both the PE and PEK crystals. The PE crystal (viewed along the c-axis) is illustrated in Fig. 4 and clearly shows the aryl rings in the same ab-plane to be oriented in a similar manner to that found in crystalline benzene with the protons of one ring pointing into the π electron cloud of the neighbouring ring. The inter-ring linkages are positioned in the bc-plane and, as might be expected from the benzophenone [46,47] and diphenyl ether [47–49] structures, neighbouring rings in the same chain adopt a helical conformation. Whilst the polymer crystals show many similarities the crystallographic axes differ consistently, specifically the a-axis length decreases and the b- and c-axes' lengths increase with increasing ketone content, i.e. from PE to PEK [8]. It will be shown that the derived empirical parameters can reproduce this effect in the extreme cases (PE and PEK) whilst also correctly estimating the degree of ring twist from the bc-plane.

$$E_{\text{tors}} = V_2(1 - \cos 2\theta)/2 \quad (4)$$

A rigid rotor approach was used for the polymer calculations with a torsional energy contribution evaluated for rotation of the ring around the ether and carbonyl linkages. V_2 values (Eq. 4) of 4.8 kcal/mol (C-C(=O) bond) and 2.6 kcal/mol (C-O_{ether} bond) were used (these had been previously evaluated from ab initio calculations [46,50]). The electrostatic energies are based on point

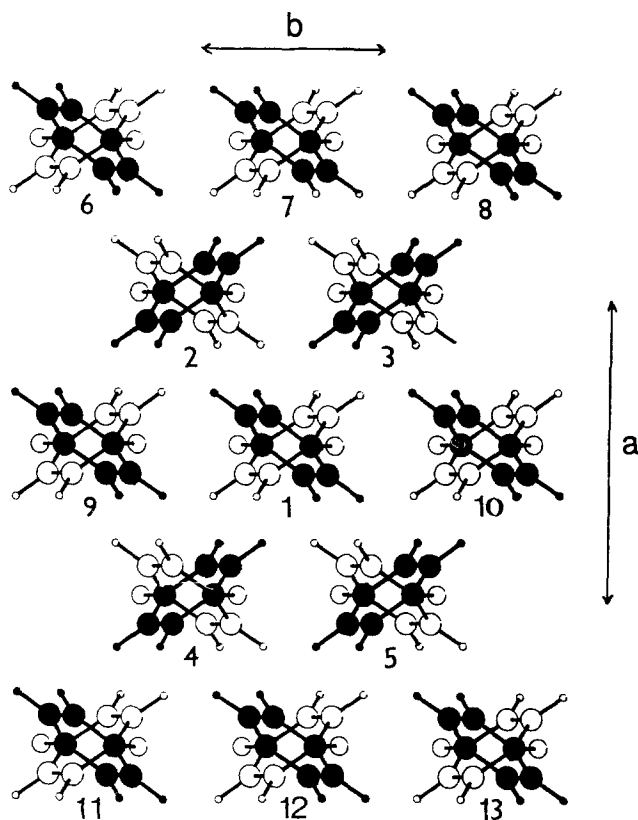


Fig. 4. Schematic representation of the PE crystal viewed along the c -axis – shaded rings are in the same ab -plane and clearly show the t -shape orientation.

charges calculated by the CHARGE2 programme (with the small modification detailed above) and a dielectric constant of unity. A full discussion of the geometry employed (derived from semi-empirical and *ab initio* calculations) and the implications this has for current thinking on the structure of the poly(aryl ether ketones) will be given elsewhere [51]. The quoted total energies are those obtained for the interaction of a fibre repeat unit (f.r.u.) of PE or PEK (Fig. 5) with the surrounding matrix and thus include intra- and intermolecular interactions. In the PE case the f.r.u.

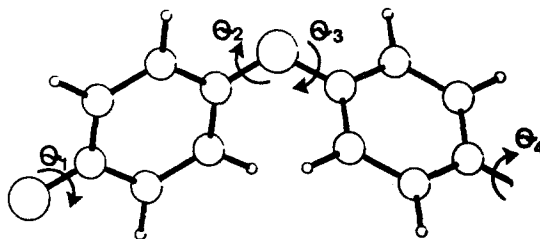


Fig. 5. Definition of the variable dihedrals in the polymer fibre repeat unit.

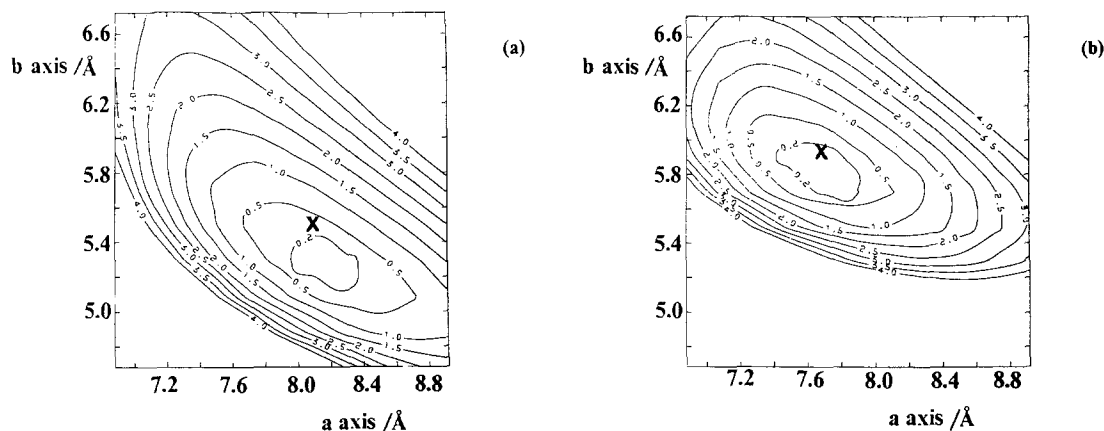


Fig. 6. Energy contour plots (kcal/mol) showing the calculated global minima in crystals of (a) PE and (b) PEK as a function of the a- and b-axes' lengths. The experimental values are denoted by X.

comprises two chemical repeat units (c.r.u.) whilst in PEK the f.r.u. and c.r.u. are identical. The conformation of the f.r.u. is defined by four rotation angles, θ_1 – θ_4 (Fig. 5). The interacting f.r.u. is positioned centrally in a chain of 5 f.r.u.'s in length (chain 1), which itself is centrally placed in a matrix of 12 further chains (2–13), all of which are also 5 f.r.u.'s long and are positioned as in Fig. 4. In the first series of calculations the a- and b-axes' lengths were varied with simultaneous rotation of the aryl rings, allowing derivation of the favoured ring conformation for a particular pair of a- and b-axes. The conformations of chains 6–13 were varied identically to chain 1 whilst the rings in chains 2–5 had the opposite ring twist but the same absolute value of θ . In this way conformation-dependent energy minima were obtained for a series of PE and PEK unit cells having different dimensions and these are illustrated in the surfaces shown in Fig. 6. The results of this initial study were extremely encouraging. The global energy minimum for both PE and PEK occurs at axes' lengths close to the experimentally observed values for the a- and b-axes and the shortening of the a-axis and lengthening of the b-axis in moving from PE to PEK is satisfactorily reproduced by the model. Furthermore the ring conformation at the global minimum was, in each case, close to that obtained in X-ray studies. Thus for PEK the calculated value of $\sim 32^\circ$ compares with an observed twist angle of 34° [4] whilst in PE the approximate experimental value of about 40° [1] is in reasonable agreement with the calculated twist angle of 36 – 38° . The energy differences between the calculated and experimental minima are, in each case, very small.

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