$\overset{(0)}{\sum}$ type: $\cos 2\pi(0 + 0 + 0)$
because $\mathbf{h}_1 R_1 + \mathbf{h}_2 R_1 + \mathbf{h}_3 R_1 = \mathbf{0}$
$\cos 2\pi(\frac{1}{2} + \frac{1}{2} + 0)$
because $\mathbf{h}_1 R_2 + \mathbf{h}_2 R_2 + \mathbf{h}_3 R_2 = \mathbf{0}$
$\cos 2\pi(\frac{1}{4} + \frac{1}{4} + \frac{1}{2})$
because $\mathbf{h}_1 R_3 + \mathbf{h}_2 R_3 + \mathbf{h}_3 R_3 = \mathbf{0}$
$\cos 2\pi(\frac{3}{4} + \frac{3}{4} + \frac{1}{2})$
because $\mathbf{h}_1 R_4 + \mathbf{h}_2 R_4 + \mathbf{h}_3 R_4 = \mathbf{0}$
$\cos 2\pi(0 + \frac{3}{4} + 0)$
because $\mathbf{h}_1 R_1 + \mathbf{h}_2 R_4 + \mathbf{h}_3 R_2 = \mathbf{0}$
$\cos 2\pi(\frac{1}{2} + \frac{1}{4} + 0)$
because $\mathbf{h}_1 R_2 + \mathbf{h}_2 R_3 + \mathbf{h}_3 R_1 = \mathbf{0}$
$\cos 2\pi(\frac{1}{4} + 0 + \frac{1}{2})$
because $\mathbf{h}_1 R_3 + \mathbf{h}_2 R_1 + \mathbf{h}_3 R_4 = \mathbf{0}$
$\cos 2\pi(\frac{3}{4} + \frac{1}{2} + \frac{1}{2})$
because $\mathbf{h}_1 R_4 + \mathbf{h}_2 R_2 + \mathbf{h}_3 R_3 = \mathbf{0}$.

Therefore, $\langle A \rangle = \sigma_3 \sigma_2^{-3/2} 4^{-1}(4 + 0) = \sigma_3 \sigma_2^{-3/2}$.

For the calculation of $\langle B \rangle$ the same contributions can be used with the cosines replaced by sines, so

$$\langle B \rangle = \sigma_3 \sigma_2^{-3/2} 4^{-1}(0 - 4) = -\sigma_3 \sigma_2^{-3/2}.$$

From (18) and (20) the most probable phase for this triple product in $P4_1$ appears to be

$$q = \arctan[\langle B \rangle / \langle A \rangle] = -45°.$$

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Modeling the Phase Change in Crystalline Biphenyl by using a Temperature-Dependent Potential*

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Abstract

The structures of two crystalline phases of biphenyl ($C_{12}H_{10}$) were modeled using an exp-6-1 nonbonded potential and $(1 - \cos^2 \varphi)$ terms for the phenyl–phenyl conjugation energy. Preliminary calculations were made by minimizing the energy of a model starting from the 110 K structure, space group $P2_1/a$, with planar molecules. Doubling the b axis and relaxing all symmetry caused the model to transform to a structure with twisted molecules, space group Pa, essentially the same as the approximate structure reported from neutron diffraction studies at 22 K. Increasing the contribution of the conjugation energy reversed the transformation, and calculations show that the potential that produces planar molecules in the crystal predicts twisted molecules in the gas phase, in agreement with experiment. A new temperature-dependent potential is described in which the nonbonded terms are modified according to the thermal motions of the atoms involved. Motion parallel to the interaction vector tends to push atoms apart, whereas motion perpendicular to it permits their mean positions to get closer together. Ways of combining the motions of the two atoms involved are considered. This new potential was applied to biphenyl to calculate successfully the observed unit-cell volumes and thermal expansion. The model reproduces the torsion angles in the 22 K

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structure, and increasing temperature produces the experimental phase change, although the predicted transition temperature is higher than that observed.

Introduction

The molecular geometry of biphenyl, C_6H_5–C_6H_5, has been a source of considerable interest for a long time. Electron diffraction studies (Karle & Brockway, 1944; Bastiansen, 1949; Almenningen & Bastiansen, 1958) indicate that the molecule in the gas phase is twisted with a phenyl–phenyl torsion angle of 42°. On the other hand, early X-ray diffraction studies of the crystalline material at room temperature (Hengstenberg & Mark, 1929; Clark & Pickett, 1931; Dhar, 1932, 1949; Kitaigorodsky, 1946) placed the molecules on centers of inversion in a monoclinic structure (space group $P2_1/a$), implying that the molecules must be planar, at least on the average. Later precise structure determinations (Trotter, 1961; Robertson, 1961; Hargreaves & Rizvi, 1962) confirmed this symmetry and appeared to rule out a disordered arrangement of twisted molecules, indicating that biphenyl really is planar in the crystal. More recently, this structure has been verified by further complete X-ray studies at 110 and 293 K (Charbonneau & Delugeard, 1976, 1977). This work included careful refinement of the thermal-motion parameters at these temperatures and showed that there is a large component of librational motion about the long molecular axis, much of which may be the result of intramolecular torsional vibration. The mean-square amplitude of this libration was found to be approximately proportional to the temperature, and this is a further indication that it is not the result of a static disorder.

There had been indications of a low-temperature phase transition in biphenyl from EPR and ENDOR studies (Brenner, Hutchison & Kemple, 1974) and also from Raman spectroscopy (Friedman, Kopelman & Prasad, 1974; Bree & Edelson, 1977). Then recently a single-crystal neutron-diffraction study of the deuterated material at 22 K (Cailleau, Baudour & Zeyen, 1979) showed superlattice reflections which were interpreted as indicating a doubling of the high-temperature *b* axis. The structure was refined assuming space group *Pa*, four molecules per cell, yielding values of 10·2° for the magnitudes of the phenyl–phenyl torsion angles in two kinds of non-equivalent molecules. Later the low-temperature neutron diffraction experiment was repeated at higher resolution (Cailleau, Moussa & Mons, 1979), showing that this refined structure is only an approximation to the true structure. Instead of a *b* axis that is exactly doubled, the crystal has incommensurate modulations in both the $\mathbf{b}^*$ and $\mathbf{a}^*$ directions below 38 K. The modulation in the $\mathbf{a}^*$ direction disappears below another transition at 21 K. The two transitions have now been observed by Raman spectroscopy (Bree & Edelson, 1978) and by heat capacity measurements (Atake & Chihara, 1980).

The origins of these phenomena can be understood qualitatively in terms of the intramolecular torsion potential plotted as a solid curve in Fig. 1. This consists primarily of two terms: the nonbonded interaction, W_N, and the conjugation energy, W_φ. W_N arises mostly from the repulsion of the *ortho* hydrogen atoms and has a maximum at 0° and a minimum at 90°. W_φ comes from the partial-double-bond character of the phenyl–phenyl link, which tends to make the molecule planar, and has a minimum at 0° and a maximum at 90°. The sum of these terms, W, is a rather flat curve with maxima at both 0 and 90° and a shallow minimum between these extremes. A torsion angle of 42° is then reasonable for the gas-phase molecule. In the crystal, on the other hand, if the molecule can gain only a few kJ mol^{-1} in packing energy by adopting a zero torsion angle, then this will be the favored geometry. Nonbonded packing forces acting on the molecules may be expected to depend on their thermal motion, so the existence of phase changes is not surprising. The purpose of this paper is to pursue this model quantitatively and to show that it predicts the approximate low-temperature *Pa* structure and its transition to the $P2_1/a$ arrangement with increasing temperature. Modeling of the incommensurate structure will not be attempted at this time.

There have been many theoretical publications on biphenyl including several computations of the conjugation energy for the isolated molecule (Polansky, 1963; Fischer-Hjalmars, 1963; Casalone, Mariani, Mugnoli & Simonetta, 1968; Dewar & Harget, 1970; Almlöf, 1974) and some crystal packing calculations (Casalone, Mariani, Mugnoli & Simonetta, 1968; Brock, 1979). More recently some lattice-dynamics

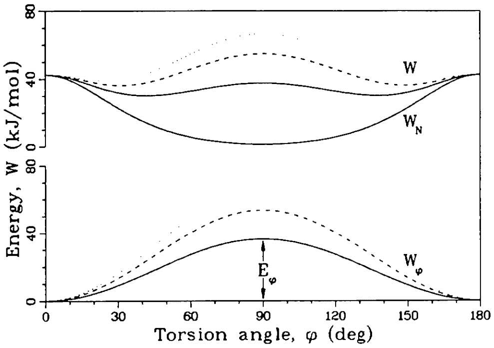


Fig. 1. Intramolecular torsion potential for an isolated molecule of biphenyl. W_N is the contribution from non-bonded interactions, W_φ is the conjugation energy, and W is the sum of these. The three curves (solid, dashed, and dotted) for W_φ and W show the effect of increasing the conjugation energy parameter, E_φ.

calculations have been made for the high-temperature phase, which reveal soft modes related to the phase transition (Natkaniec, Bielushkin & Wasiutynski, 1981; Takeuchi, Suzuki, Dianoux & Allen, 1981), and the mean-square vibrational amplitudes have also been obtained (Bonadeo & Burgos, 1982).

Preliminary calculations

In order to understand these observed changes in the conformation of the biphenyl molecule, potential-energy models have been constructed for the gas and crystalline phases. Some preliminary results will be described first, and then work with an improved model will be presented. All calculations were made with the program *WMIN* (Busing, 1981), and the methods used have been described in detail previously (Busing, 1982).

The energy of any model of given geometry is calculated as a sum of two kinds of potential-energy terms. Each nonbonded atom–atom interaction, both intermolecular and intramolecular, contributes a term

$$V(r) = -A_{ij}r^{-6} + B_{ij}\exp(-C_{ij}r) + q_iq_jr^{-1}. \quad (1)$$

Here r is the interatomic distance, A_{ij}, B_{ij}, and C_{ij} are coefficients for each chemical kind of atom pair, and q_i is the Coulomb charge on each kind of atom. Values of these coefficients were taken from Williams & Starr (1977) and are listed in Table 1. Justification for the selection of this potential has been presented previously (Busing, 1982).

Table 1. *Potential parameters used for modeling biphenyl*

Energies are in kJ mol^{-1}, lengths in Å, and charges in electrons. The Coulomb term in equation (1) is multiplied by 1389·4 to obtain kJ mol^{-1}.

(*a*) Basic nonbonded potential (Williams & Starr, 1977)

	H–H	C–H	C–C
A	136	573	2414
B	11677	65485	367250
C	3·74	3·67	3·60
$q_{\rm H}$	0·153		

(*b*) Parameters of the final temperature-dependent potential. The k's are the correlation coefficients of equation (13), and primed symbols refer to intramolecular contacts.

E_φ	33·5	k_z	0·803
u_0	0·055	k_w	0·803
		k'_z	0·803
		k'_w	−1·000

The intramolecular conjugation energy is computed as

$$V(\varphi) = (E_\varphi/4)(1 - \cos^2\varphi), \quad (2)$$

where E_φ is a parameter of the potential, and the divisor of 4 compensates for the fact that a term is included for each of the four torsion angles φ about a phenyl–phenyl link. E_φ was initially set at 36·3 kJ mol^{-1}, a value determined from the crystal structure of 1,3,5-triphenylbenzene (Busing, 1982).

In a first calculation, the energy of the high-temperature crystal structure was minimized, starting from the experimental structure at 110 K (Charbonneau & Delugeard, 1976) and maintaining the symmetry of space group $P2_1/a$. Individual molecules were held rigid and essentially planar with carbon atoms in the experimental geometry. Hydrogen positions were calculated as described before (Busing, 1982) with C—H distances of 1·02 Å as required by the nonbonded potential (Williams & Starr, 1977). Seven structural parameters were adjusted, including three rotations of the molecules about the inversion centers and the four parameters of the monoclinic lattice. The observed and calculated parameters are listed in Table

Table 2. *Observed (Charbonneau & Delugeard,* 1976, 1977) *and calculated crystal-structure parameters for biphenyl at* 110 *and* 293 K

Lengths are in Å, angles in °; V is the cell volume, and θ is the overall molecular rotation.

		Preliminary model			Temperature-dependent model		
	Obs	Calc	Calc–Obs	%	Calc	Calc–Obs	%
110 K							
a	7·82	8·06	0·24	3·1	8·13	0·31	4·0
b	5·58	5·49	−0·09	−1·6	5·44	−0·14	−2·5
c	9·44	9·30	−0·14	−1·5	9·29	−0·15	−1·6
β	94·6	90·3	−4·3		90·8	−3·8	
$V/2$	205·3	205·8	0·5	0·2	205·4	0·1	0·0
θ	0	4·1	4·1		3·4	3·4	
293 K							
a	8·12				8·31	0·19	2·3
b	5·63				5·55	−0·08	−1·4
c	9·51				9·38	−0·13	−1·4
β	95·1				92·2	−2·9	
$V/2$	216·5				216·1	−0·4	−0·2
θ	0				2·7	2·7	

2, which shows that the agreement is slightly better than that obtained by Brock (1979), who used an earlier version of the nonbonded potential.

In order to determine what structure of lower symmetry would be predicted by this model, a further calculation was made starting with the above $P2_1/a$ arrangement. On the basis of the reported structure at 22 K (Cailleau, Baudour & Zeyen, 1979), the crystal b axis was doubled and all symmetry was relaxed so that the structure was treated as triclinic with four independent molecules in the doubled cell. Each molecule was treated as two rigid phenyl groups with one internal degree of freedom, the rotation about the phenyl–phenyl link. Although the ability of the *ortho* hydrogens to bend away from each other may be important, this additional freedom was not included in the model. The variables then included the internal rotation plus three overall rotations and three translations for each of the four molecules. With the six triclinic lattice parameters these made a total of 34 variables. In attempting to minimize the energy, program *WMIN* reports the eigenvalues of the Hessian matrix of second derivatives of the energy with respect to these variables. Of the 34 eigenvalues, three were zero, as expected, corresponding to three redundant translations. Two other eigenvalues were negative, indicating that the starting structure was unstable, *i.e.* that the variables were at a saddle point in the energy function. Examination of the corresponding eigenvectors showed that these instabilities involved internal twisting of the molecules.

The structure was then deliberately distorted in the direction of one of these eigenvalues and varied until a new stable energy minimum was reached. Although the lattice angles α and γ wandered during the search, they returned to 90° at convergence. Inspection of the resulting arrangement showed that pairs of molecules were equivalent within round-off error, that the symmetry was that of space group Pa, and that, after a simple coordinate transformation, the molecular positions were close to those of the reported 22 K structure. The two non-equivalent internal torsion angles, however, had magnitudes of 21·3 and 20·4° rather than the 10·2° observed for both angles.

At this point, in order to save computing time, the structure was constrained to the symmetry of space group Pa with two molecules in the asymmetric unit. In this polar space group the x and z translations of one molecule are irrelevant, so the parameters adjusted were four molecular translations, six molecular rotations, two internal rotations, and four lattice parameters, for a total of 16. Increasing the conjugation-energy parameter E_φ to 53·5 kJ mol^{-1} reduced the internal torsion angles in the minimum-energy model to 10·3 and 10·2, very close to the observed values. Table 3 compares some parameters of this model with the reported 22 K structure and shows that the agreement is reasonably good.

In a final calculation the conjugation-energy parameter E_φ was increased to 65·3 kJ mol^{-1}, and the energy was again minimized with respect to the 16 variables of the Pa model. The result is a structure with planar molecules in all respects identical with the $P2_1/a$ model of the first calculation described above. Thus, it has been demonstrated that by increasing the importance of the conjugation energy with respect to the nonbonded interactions, the model can be made to undergo a phase change to the high-temperature form.

Fig. 1 shows curves of the intramolecular torsion potential W in the isolated biphenyl molecule calculated from the potential-energy expressions used above. The solid curve was made with the initial value of E_φ, the dashed one is based on the E_φ that produced the torsion angles observed at 22 K, and the dotted curve was computed from the E_φ that caused the model to change to the high-temperature form. Even with this largest value of the conjugation energy, the curve for the isolated molecule has a minimum at a φ of about 25°. Thus these model calculations demonstrate that a molecule which would be twisted in the gas phase may indeed become planar in the crystal because of the effects of intermolecular packing forces.

Table 3. *Observed (Cailleau, Baudour & Zeyen,* 1979) *and calculated crystal-structure parameters for biphenyl at* 22 K

Lengths are in Å, angles in °; x is the overall molecular translation; θ is the overall molecular rotation.

		Preliminary model			Temperature-dependent model		
	Obs	Calc	Calc–Obs	%	Calc	Calc–Obs	%
a	7·77	8·15	0·38	4·9	8·08	0·31	4·0
b	11·14	10·90	−0·24	−2·2	10·78	−0·36	−3·2
c	9·44	9·32	−0·12	−1·3	9·27	−0·17	−1·8
β	93·7	90·8	−2·9		90·7	−3·0	
$V/4$	203·8	207·0	3·2	1·6	201·8	−2·0	−1·0
x_1	0	0·02	0·02		0·02	0·02	
x_2	0	0·09	0·09		0·09	0·09	
θ_1	0	2·7	2·7		2·7	2·7	
θ_2	0	2·6	2·6		2·7	2·7	
φ_1	−10·2	−10·2	0·0		−10·0	0·2	
φ_2	10·2	10·3	0·1		10·1	−0·1	

Introducing temperature effects

In spite of their success, the above model calculations must be regarded as somewhat artificial. A phase change results from a change in temperature, but temperature would not be expected to affect the conjugation-energy term. On the other hand, temperature changes can be interpreted as modifying the average contribution of the nonbonded terms, and this suggests that one way of introducing temperature into the model would be by means of a temperature-dependent nonbonded potential.

Such potentials have been described previously. Amoros & Bork (1967) proposed a potential with parameters that depend on the temperature in a way which they determined empirically from crystal structures measured at several temperatures. A more theoretical approach was taken by Williams (1972), who derived a potential based on the anisotropic thermal motion observed for atoms in the crystal. Nonbonded terms were modified by increasing the repulsion coefficient B_{ij} of (1) in a way which depends on the components of thermal motion parallel to the atom–atom interaction vector.

Experimental rigid-body thermal-motion coefficients are available for biphenyl at 293 and 110 K (Charbonneau & Delugeard, 1977). The translation and libration matrices, **T** and **L**, are nearly diagonal, and for the present work the off-diagonal terms were omitted. To obtain the thermal motion at lower temperatures the methods described by Cruickshank (1956) were used, his equations (1) for **T** and (5) for **L**. In general, the low-temperature matrices obtained from the 293 K data are similar to, but not identical with, those from the 110 K data, and averages of the two results were used. Table 4 lists the thermal-motion matrices for five temperatures, and Fig. 2 shows the thermal-motion ellipsoids at 293 and at 22 K. For the low-temperature models with twisted molecules it was assumed that these rigid-body matrices describe the thermal motion of each individual phenyl segment. The **S** matrix, which describes screw motion, is zero by symmetry in the high-temperature crystal and was assumed to be zero at low temperature also.

Table 4. *Rigid-body thermal motion for crystalline biphenyl*

Translation **T** is in Å^2 ($\times 10^5$); libration **L** is in rad^2 ($\times 10^5$). The origin is in the center of the phenyl–phenyl link, axis 1 is parallel to this link, and axis 2 lies in the phenyl plane.

	Experimental (Charbonneau & Delugeard, 1977)		Calculated (see text)		
	293 K	110 K	80 K	40 K	22 K
T_{11}	5930	2810	1853	971	605
T_{22}	4530	2160	1424	756	485
T_{33}	4030	1330	1054	571	381
L_{11}	3330	1390	977	524	346
L_{22}	260	70	64	40	32
L_{33}	350	110	91	52	38

In further calculations Williams's temperature-dependent potential was used with these rigid-body thermal-motion matrices to model the biphenyl crystal at 22, 110, and 293 K. One goal of this work was to reproduce the unit-cell volumes and thermal expansion of the material, and for this purpose the model was reasonably successful. A second aim was to reproduce the internal torsion angle φ at 22 K and to show that this angle decreases with increasing temperature, thus producing a phase change. For that purpose, all models with this potential were unsuccessful; the torsion angle φ always increased with temperature. In retrospect it is now clear that a potential based only on the components of thermal motion parallel to the interaction vector can never be expected to produce this phase change. This point will be discussed again below.

A new temperature-dependent nonbonded potential

A new nonbonded potential will now be described that depends on the known thermal-motion coefficients of the atoms, but which differs from the potential of Williams in several ways.

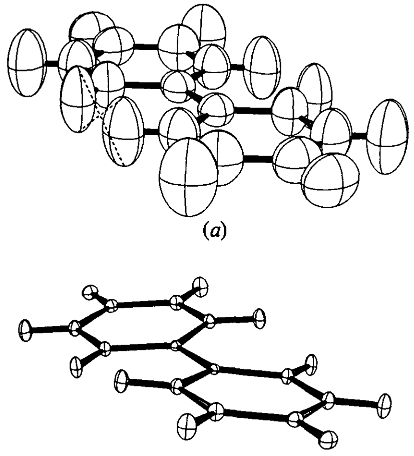
Thermal motion parallel to **r**

Consider a typical exp-6 potential

$$V(r) = -Ar^{-6} + B\exp(-Cr), \tag{3}$$

and assume that r is described by a Gaussian distribution

$$\rho(r) = (2\pi\overline{z^2})^{-1/2}\exp[-(r-r_0)^2/2\overline{z^2}], \tag{4}$$



(*a*)

(*b*)

Fig. 2. Rigid-body thermal motion in crystalline biphenyl represented by 50% probability ellipsoids (*a*) at 293 K and (*b*) at 22 K.

where $\overline{z^2}$ is the mean-square deviation of r from a central value r_0. Integrating to average $V(r)$ over this distribution yields

$$V(r_0, \overline{z^2}) = -Ar_0^{-6}[1 + 21\overline{z^2}\,r_0^{-2} + \dots] + B\exp(C^2\,\overline{z^2}/2 - Cr_0). \tag{5}$$

The integration of the exponential term is exact, but that of the inverse powers is approximate, the first omitted term in the brackets being $378(\overline{z^2}\,r_0^{-2})^2$ or about 4% for $\overline{z^2}\,r_0^{-2} = 0{\cdot}01$.

Fig. 3 shows the original potential for a H–H interaction, a typical Gaussian distribution in r, and the new average potential. It is clear that the principal effect of the distribution is to increase the effective repulsion radius by $C\overline{z^2}/2$.

Thermal motion perpendicular to r

It has been shown by Busing & Levy (1964) that thermal motion perpendicular to the vector between atoms increases their mean instantaneous separation so that

$$\bar{r} = (r_0^2 + \overline{x^2} + \overline{y^2})^{1/2} \simeq r_0 + u, \tag{6}$$

where

$$u = \overline{w^2}/2r_0, \tag{7}$$

and

$$\overline{w^2} = \overline{x^2} + \overline{y^2}. \tag{8}$$

Substituting $\bar{r}$ for r_0 in (5) produces

$$V(r_0 + u, \overline{z^2}) = -A(r_0 + u)^{-6} - 21A\overline{z^2}(r_0 + u)^{-8} + B\exp(C^2\,\overline{z^2}/2 - Cr_0 - Cu). \tag{9}$$

The net effect of thermal motion perpendicular to the interaction vector $\mathbf{r}_0$ is to permit the mean positions of the atoms to get closer to each other. This is in contrast with the effect of motion parallel to $\mathbf{r}_0$, which tends to push atoms apart.

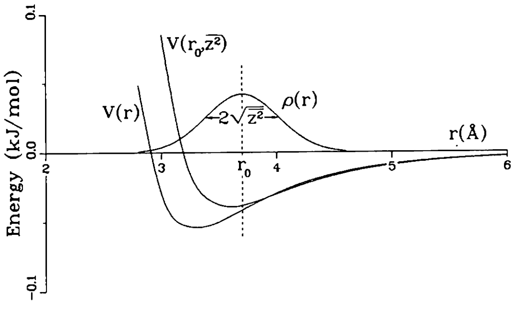


Fig. 3. A temperature-dependent nonbonded potential. $V(r)$ is the exp-6 potential for a H–H interaction; $\rho(r)$ is a typical Gaussian distribution in r; $V(r_0, \overline{z^2})$ is the new average potential.

Since *WMIN* uses accelerated convergence methods (Williams, 1971) to compute the term $-Ar_0^{-6}$, it is desirable to expand the first two terms of (9) to obtain

$$V(r_0 + u, \overline{z^2}) = -Ar_0^{-6} + 6Aur_0^{-7} - 21A(u^2 + \overline{z^2})\,r_0^{-8} + 56A(u^3 + 3u\overline{z^2})\,r_0^{-9} + B\exp(C^2\,\overline{z^2}/2 - Cr_0 - Cu). \tag{10}$$

Combining the motions of two atoms

In order to evaluate $\overline{z^2}$ and $\overline{w^2}$, which describe the distribution of an interatomic vector **r**, it is necessary to consider the thermal motions of the two atoms which define this vector. Ideally what is needed is the joint distribution of the two sets of coordinates, but often only the temperature-factor coefficients of the individual atoms are available. In this case it is necessary to make assumptions as to the extent of the correlation between the motions. It has been shown (Busing & Levy, 1964) that if the motions of the two atoms are completely uncorrelated then the components of mean-square displacements for the two atoms, $\overline{z_1^2}$, $\overline{z_2^2}$, $\overline{w_1^2}$, and $\overline{w_2^2}$, should be added. Thus

$$\overline{z^2} = \overline{z_1^2} + \overline{z_2^2},$$
$$\overline{w^2} = \overline{w_1^2} + \overline{w_2^2}. \tag{11}$$

On the other hand, if the motions are highly correlated they should be subtracted.

$$\overline{z^2} = |\overline{z_1^2} - \overline{z_2^2}|,$$
$$\overline{w_2} = |\overline{w_1^2} - \overline{w_2^2}|. \tag{12}$$

Equation (12) describes the 'riding model' of Busing & Levy (1964).

Correlation coefficients, k_z and k_w, can then be defined so that

$$\overline{z^2} = (1 - k_z)(\overline{z_1^2} + \overline{z_2^2}) + k_z|\overline{z_1^2} - \overline{z_2^2}|,$$
$$\overline{w^2} = (1 - k_w)(\overline{w_1^2} + \overline{w_2^2}) + k_w|\overline{w_1^2} - \overline{w_2^2}|. \tag{13}$$

From arguments presented by Busing & Levy (1964) it can be shown that permissible values of k_z or k_w range from +1 for correlated motion, through 0 for uncorrelated motion, to −1 for negatively correlated motion of the two atoms. Although there is no basis for believing that these coefficients will have the same values for all nonbonded interactions in a given crystal, it will nevertheless be assumed that they are constant for certain classes of these interactions, and these coefficients will be adjusted empirically as parameters of the model.

Because the potential of (1) and Table 1 was derived for no specific temperature, another empirical constant, u_0, has been included in (7) to obtain

$$u = u_0 + \overline{w^2}/2r_0. \tag{14}$$

This correction term, which is the value of u for no thermal motion, will also be used as an energy parameter of the model.

Calculating the components of thermal motion

If $\mathbf{T}$ and $\mathbf{L}$ are the rigid-body thermal-motion matrices for translation and libration, and $\mathbf{v}_i$ defines the position of atom i in the rigid-body Cartesian system, then the thermal motion of this atom is given by (Johnson, 1970)

$$\mathbf{U}_i = \mathbf{T} + \mathbf{A}_i \mathbf{L} \mathbf{A}_i^T, \tag{15}$$

where

$$\mathbf{A}_i = \begin{pmatrix} 0 & v_{i_3} & -v_{i_2} \\ -v_{i_3} & 0 & v_{i_1} \\ v_{i_2} & -v_{i_1} & 0 \end{pmatrix}. \tag{16}$$

If $\mathbf{l}$ is a unit vector parallel to the interaction vector $\mathbf{r}_0$ and referred to the rigid-body coordinate system, then

$$\overline{z_i^2} = \mathbf{l}^T \mathbf{U}_i \mathbf{l}, \tag{17}$$

$$\overline{w_i^2} = \operatorname{tr} \mathbf{U}_i - \overline{z_i^2}. \tag{18}$$

Certain simplifications can be made when $\mathbf{T}$ and $\mathbf{L}$ are diagonal.

For calculations with *WMIN* these quantities are computed in a user's subroutine for general potentials. The values of $\overline{z^2}$ and $\overline{w^2}$ for each atom–atom interaction are computed only once for each cycle of energy minimization and saved for use during that cycle. The energy terms are then calculated according to (10). The Coulomb terms of (1) are obtained by accelerated convergence methods without any modification for thermal motion.

Application to biphenyl

In applying this new temperature-dependent potential to biphenyl the goals were to reproduce thermal expansion by fitting the unit-cell volumes as a function of temperature, to reproduce the low-temperature torsion angles, and to show that these angles decrease with increasing temperature, leading to a phase change.

It was arbitrarily assumed that for intermolecular contacts the correlation coefficients for parallel and perpendicular motion are equal, $k_z = k_w$, and this quantity was adjusted together with the zero correction u_0 to reproduce the unit-cell volumes at 110 and 293 K. The energy of the model was minimized for space group $P2_1/a$ using rigid planar molecules, so that these results are independent of the values chosen for the conjugation parameter E_φ and the correlation coefficients for intramolecular contacts. The parameters of the potential are listed in Table 1, and the resulting structural parameters are given in Table 2.

The value of the correlation coefficient is 0·803, corresponding to high positive correlation, as is to be expected if the thermal motion arises largely from long-wavelength lattice vibrations.

To model the 22 K structure, the parallel correlation coefficient for intramolecular interactions, k'_z, was set to the value determined above for the intermolecular coefficients. The correlation coefficient for intramolecular motion perpendicular to the interaction, on the other hand, was chosen as $k'_w = -1$, a value which appeared to give the model the best chance of reproducing the observed phase change. This negative correlation for the important *ortho*-hydrogen contacts implies that the intramolecular torsion vibration makes a large contribution to the thermal motion. Using these coefficients, the value of E_φ was adjusted to reproduce the torsion angles when the energy of the low-temperature model (space group *Pa*) was minimized at 22 K. Table 1 gives the energy parameters and Table 3 lists some of the parameters of the model structure, which are in reasonable agreement with the experimental quantities.

Energies were then minimized for this model at temperatures of 40, 80, and 110 K, and values of the resulting torsion angles are plotted in Fig. 4. It can be seen that the predicted phase change occurs at about 94 K, somewhat higher than the observed temperature of about 40 K (Bree & Edelson, 1977, 1978; Cullick & Gerkin, 1977; Atake & Chihara, 1980).

Conclusions

It has been shown in preliminary calculations with a potential-energy model that when the b axis is doubled the high-temperature structure with planar biphenyl molecules transforms to the reported low-temperature arrangement (space group *Pa*) with twisted molecules. It was further shown that increasing the intramolecular conjugation potential causes the model to undergo the reverse phase change to the $P2_1/a$ structure with planar molecules, even though the intramolecular potential is such that the isolated molecule would be twisted.

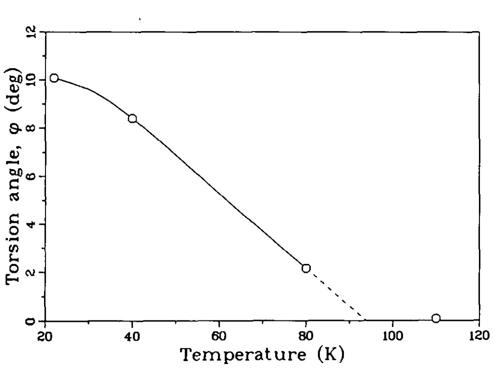


Fig. 4. Calculated torsion angle, φ, for crystalline biphenyl (space group *Pa*) as a function of temperature. The predicted transition temperature is 94 K; the observed temperature is about 40 K.

A new temperature-dependent nonbonded potential has been developed, and model calculations using this potential reproduce cell volumes and thermal expansion. They also produce a phase change with increasing temperature, although the predicted temperature is higher than that observed. This potential takes account of thermal motion parallel to the atom–atom interaction, which tends to push atoms apart. It also depends on thermal motion perpendicular to the interaction vector, which permits mean atomic positions to get closer to each other. This latter effect is of critical importance for the *ortho*-hydrogen contacts in biphenyl. If the thermal motion shown in Fig. 2 includes a large contribution from the intramolecular torsional vibration, then at high temperatures the molecule can be planar, on the average, because the mean instantaneous distance between the hydrogen atoms (shown as dashed lines in the figure) is much larger than the distance between mean atomic positions. At low temperatures, on the other hand, the thermal motion is much smaller, and the molecules must twist to increase the hydrogen–hydrogen distances.

This provides an interpretation of the phase change which is approximately equivalent to the concept of a double-well potential invoked by others (Baudour, Cailleau & Yelon, 1977; Cailleau, Baudour, Meinnel, Dworkin, Moussa & Zeyen, 1980). In that description the molecule is symmetric when the torsional vibration is excited to high-energy levels, but at low temperature the energy is less than the barrier height, and the molecule becomes twisted.

Although the cell volumes have been reproduced satisfactorily, the agreement for the individual lattice constants, as listed in Tables 2 and 3, is not so good as might be expected. The calculated *a* and *b* parameters are too large and too small, respectively, and the computed β angles are generally too small. These discrepancies may arise from the principal problem with the new potential, namely that it is not clear how the distribution of the interaction vector **r** should be obtained from the motions of the two atoms involved. It can be hoped that the overall agreement will be improved when the required joint distribution can be extracted from the results of some of the complete lattice-dynamics calculations which are beginning to appear (Natkaniec, Bielushkin & Wasiutynski, 1981; Takeuchi, Suzuki, Dianoux & Allen, 1981).

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