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Semi-Empirical Lattice Energy Calculations of Crystalline Biphenyl

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Semi-empirical lattice energy calculations based on the atom-atom potential method have been used to test several models for crystalline biphenyl. Structures considered include planar molecules in space group $P2_1/a$, nonplanar molecules disordered about an inversion center in the same group, and an ordered structure in Pa. The failure of these models to produce satisfactory (2–3%) agreement between observed and calculated cell constants suggests either the presence of a complicated disorder or of a delicate balance between intra- and intermolecular energy terms which is not adequately represented in the calculations.

INTRODUCTION

A series of semi-empirical energy calculations have been made for crystalline biphenyl, $C_{12}H_{10}$, in an attempt to find a model which is in accord with the various experimental and theoretical studies of this compound. Electron diffraction work has shown that the average dihedral angle ψ between the phenyl rings in this molecule is 42° in the gas phase.[1] However, in the solid state X-ray diffraction data at both 293 K[2] and 110 K[3] indicate that the space group is $P2_1/a$ with two molecules in the unit cell. These conditions require that the molecules lie on centers of symmetry and be at least statistically planar.

We were interested in studying the energetics of this apparent change in molecular conformation with physical state, for if crystallographic techniques are to be used routinely to determine molecular geometries it is important to know the extent to which conformation can be influenced by the directed intermolecular forces present in crystals. The biphenyl problem also appears to be an important test of the atom-atom potential method. Since biphenyl is a rather rigid molecule, its conformation can be described adequately for these calculations by a single intramolecular degree of freedom,

the twist angle about the central C—C bond. Therefore it should be possible to study the interplay between intra- and intermolecular forces in determining the solid-state conformation of this molecule.

THE METHOD

Calculations were made using W. R. Busing's program WMIN[4] in which the crystal energy is computed as a pairwise sum over intermolecular atom-atom contacts. The energy of each such nonbonded interaction was calculated according to a form of the Buckingham potential which incorporates the geometric-mean combining law:

$$E_{ij} = (B_i + B_j)\exp\left[\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right] - \frac{C_i C_j}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}}$$

where the parameters A_i, B_i, C_i, and q_i were those given by D. E. Williams.[5] Truncation errors in these sums are virtually eliminated by use of the Ewald–Bertaut–Williams technique for accelerated convergence;[6] limits were set to assure convergence to 0.02 kcal/mol.

It was assumed that the lattice sums are insensitive to small distortions in the molecular geometry. Therefore the dimensions of the biphenyl molecule were idealized ($r_{C-C} = 1.40$ Å and $r_{C-H} = 1.04$ Å within the rings; $r_{C-C} = 1.50$ Å for the central bond), and the only internal degree of freedom allowed was rotation about the central C—C bond. The potential for torsion about this bond depends in a complicated fashion on nonbonded interactions, energies of deformations of bond lengths and angles, and conjugation energy. It can, however, be represented as a smooth function, and when this angle was varied a semi-empirical function (see below) was used to represent the associated energy $E(\psi)$.

Energy minimizations were performed with respect to the unit cell parameters, the molecular position and orientation, and the internal rotation in a manner similar to that described previously.[7] Analyses of second derivatives allowed confirmation of convergence to true minima.

DESCRIPTION OF THE CALCULATIONS

In the gas state, the conjugation energy between the two rings of biphenyl is not sufficient to overcome the repulsive interactions between the *ortho*-hydrogens; the potential for rotation about the central C—C bond has a maximum at $\psi = 0°$ and the molecule is significantly twisted. The apparent

TABLE I

Comparison of observed and calculated cell constants for planar biphenyl in $P2_1/a$

Cell constant	Observed (293 K)[a]	Δ (calc-obs)	Observed (110 K)[b]	Δ (calc-obs)
a (Å)	8.12(2)	0.12 (1.5%)	7.82(2)	0.42 (5.4%)
b	5.63(1)	−0.16 (−2.8%)	5.58(1)	−0.11 (−2.0%)
c	9.51(2)	−0.27 (−2.8%)	9.44(2)	−0.20 (−2.1%)
β (°)	95.1(3)	−5.90 (−6.2%)	94.6(1)	−5.40 (−5.7%)
V/Z (Å^3)	216.5	−8.3 (−3.8%)	205.3	3.1 (1.5%)

[a] G.-P. Charbonneau and Y. Delugeard, *Acta Cryst.*, **B32**, 1420–1423 (1976).
[b] G.-P. Charbonneau and Y. Delugeard, *Acta Cryst.*, **B33**, 1586–1588 (1977).

molecular planarity in the solid state is then most simply explained by invoking "crystal packing forces." This hypothesis was tested by performing an energy minimization in which the molecules were kept strictly planar. This calculation leads to rather large discrepancies between the observed and calculated cell constants, especially in the monoclinic angle β, as can be seen in Table I. A good model for a hydrocarbon crystal should reproduce the observed values to within 2–3%. The comparisons in Table I are made with respect to the cell dimensions observed at both room and low temperatures. Although vibrational effects are not included explicitly in calculations of this type, they are implicit in the potential functions. In determining his recent set of parameters, Williams[5] fit crystallographic data for 18 hydrocarbon structures, 7 of which had been determined at low temperatures. The average temperature for the 18 structures is ca. 240 K, so it might be expected that a good model for crystalline biphenyl would calculate cell dimensions intermediate between those measured at 293 K and 110 K.

The inadequacy of a strictly planar model for crystalline biphenyl is not unexpected in light of recent analyses[2d,3] showing that the rms amplitudes of libration about the long molecular axis are anomalously large at both 293 K and 110 K (10.3° and 6.76° respectively) when a planar molecule is assumed. These findings strongly suggest that the molecules move in a double-well potential or are disordered. We have had some success in refining the diffraction data assuming a nonplanar molecule randomly disordered about the center of inversion, but the proximity of the half-atoms results in high correlation coefficients and poor thermal parameters. This type of refinement gives an interplanar angle ψ in the range 14° to 18°.

A second series of energy minimizations was performed in which nonplanar biphenyl molecules were assumed to be randomly disordered about the centers of inversion in $P2_1/a$. Lattice energy was found to become less favorable with increasing torsion angle ψ, while intramolecular strain energy decreased. When the following potential, which is consistent with the barrier

heights and positions calculated for biphenyl using the full molecular mechanics method,[8] was used the value of ψ at convergence was 11.8°. At this point

$$E(\psi) = A \exp[-1/2(\psi/\psi_0)^2] \quad \text{where } A = 3.0 \text{ kcal/mol} \quad \text{and} \quad \psi_0 = 12°$$

of compromise between the intra- and intermolecular forces the lattice energy is increased by ca. 1 kcal/mol from its value when $\psi = 0°$. More recently, however, Allinger has lowered his estimate of the barrier at the planar conformation of biphenyl to ca. 1.0 kcal/mol. When a barrier of this size is used in the crystal calculation the angle ψ converges to 0°, a value corresponding to molecular planarity.

Since the potential function for internal rotation is not well known, energy minimizations were made for a series of fixed interplanar angles ψ over the range 8° to 20° in order to examine the agreement between the observed and calculated cell constants as a function of ψ. The results of these calculations, which are shown in Figure 1, suggest that the randomly disordered model for biphenyl will not reproduce the known cell dimensions to within a few percent for any value of ψ.

If the accurate reproduction of known cell dimensions is to be used as a criterion for the success of semi-empirical lattice energy calculations, another

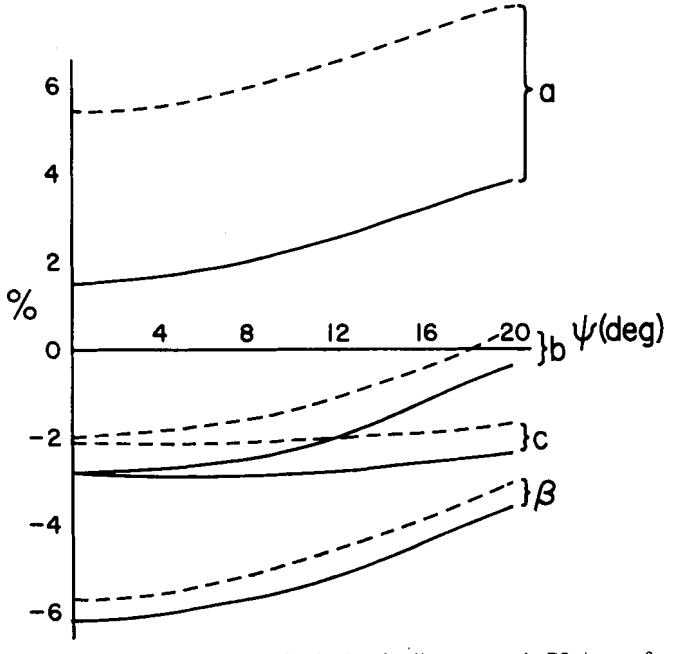

FIGURE 1 Agreement of observed and calculated cell constants in $P2_1/a$ as a function of ψ. Here and in the following Figure % = 100 × (a_i(calc) − a_i(obs))/a_i(obs), and the solid and dotted lines refer to comparisons with cell constants measured at 293 K and 110 K respectively.

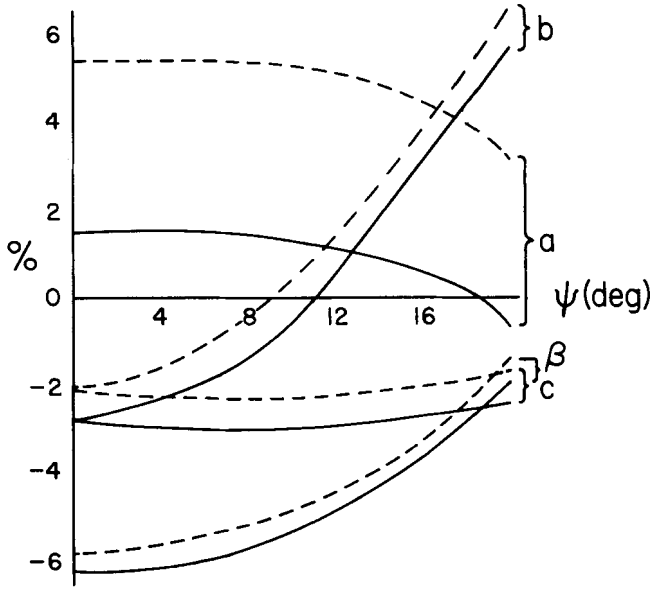

FIGURE 2 Agreement of observed and calculated cell constants in Pa as a function of ψ.

model must be sought for crystalline biphenyl. Other possibilities include structures in lower symmetry space groups (e.g., Pa, $P2_1$, or $P\bar{1}$) in which the observed extinctions 0k0, k odd, and h0l, h odd are accidental rather than crystallographically required. Twinning or short range order might also be involved. An examination of the packing in biphenyl reveals that the molecules are perpendicular to b to within 1°. Coupled with the symmetry of the C_6H_5 rings and the position of the molecule at $y = 1/4$, this relationship may account for the 0k0 extinctions even in the absence of a 2_1 axis. The h0l extinctions, however, seem to require the presence of an a glide plane. Consequently, the energy minimizations for a series of fixed angles ψ were repeated in space group Pa. The removal of the inversion centers allows the biphenyl molecules to be both twisted and ordered.

The calculations in Pa give lattice energies very similar to those for the disordered $P2_1/a$ structure, and the conditions for the accidental 0k0 extinctions are satisfied. However, the agreement between the observed and calculated cell constants, which is shown in Figure 2, is still not satisfactory.

DISCUSSION

Recently, the structure of the low-temperature, ordered phase of *p*-quaterphenyl has been reported.[10] At room temperature this molecule shows

packing very similar to that of biphenyl. Below the order-disorder phase transition it is triclinic with only approximate 2_1 axes and *a* glide planes, and the molecules have interplanar angles ranging from 14° to 24°. Biphenyl also has a low-temperature phase transition. Perhaps the high-temperature $P2_1/a$ form of biphenyl has very short-range order similar to the long-range order seen for low-temperature *p*-quaterphenyl; the effects of such short-range order on the diffraction pattern might not be easily observed. A hypothesis of this type is in accord with low-temperature vibrational,[11] optical,[12] and magnetic resonance[13] spectra of biphenyl which suggest the presence of an order-disorder phase transition near 40 K in which the $\bar{1}$ molecular symmetry is lost and the number of molecules in the asymmetric unit increases from 1/2 to perhaps 2. It may also be noteworthy that the major structural changes occurring during the *p*-quaterphenyl phase transition take place in the *ab* plane. We have found in biphenyl that the calculated cell constants *a* and *b* are much more sensitive to the model chosen than is *c*.

We are continuing to investigate models for crystalline biphenyl in the hope of finding one which is in accord with the experimental evidence and which also reproduces the known cell constants to within several per cent. It may be, however, that the disorder in this system is sufficiently complicated, and the energy effects sufficiently subtle, that successful modeling with the relatively simple semi-empirical atom-atom potential method is precluded.

References

1. A. Almenningen and O. Bastiansen, *Kgl. Norske Videnskab Selskab. Skrifter*, **4**, 1–16 (1958).
2. (a) J. Trotter, *Acta Cryst.*, **14**, 1135–1140 (1961); (b) A. Hargreaves and S. H. Rizvi, *Acta Cryst.*, **15**, 365–373 (1962); (c) G. B. Robertson, *Nature*, 593–594 (1961); (d) G.-P. Charbonneau and Y. Delugeard, *Acta Cryst.*, **B33**, 1586–1588 (1977).
3. G.-P. Charbonneau and Y. Delugeard, *Acta Cryst.*, **B32**, 1420–1423 (1976).
4. W. R. Busing, *Acta Cryst.*, **A28**, S252–S253 (1972).
5. D. E. Williams, *Acta Cryst.*, **A30**, 71–77 (1974).
6. D. E. Williams, *Acta Cryst.*, **A27**, 452–455 (1971).
7. C. P. Brock, *Acta Cryst.*, **A33**, 193–197 (1977); *Acta Cryst.*, **A33**, 898–902 (1977).
8. J. Kao and N. L. Allinger, *J. Amer. Chem. Soc.*, **99**, 975–986 (1977).
9. N. L. Allinger, personal communication.
10. J.-L. Baudour, Y. Delugeard, and P. Rivet, *Acta Cryst.*, **B34**, 625–628 (1978).
11. P. S. Friedman, R. Kopelman, and P. N. Prasad, *Chem. Phys. Lett.*, **24**, 15–17 (1974); A. Bree and M. Edelson, *Chem. Phys. Lett.*, **46**, 500–504 (1977).
12. R. M. Hochstrasser, G. W. Scott, and A. H. Zewail, *Chem. Phys.*, **11**, 273–279 (1975).
13. H. C. Brenner, C. A. Hutchison, Jr., and M. D. Kemple, *J. Chem. Phys.*, **60**, 2180–2181 (1974); A. S. Cullick and R. E. Gerkin, *Chem. Phys.*, **23**, 217–230 (1977).