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Stability of a Planar Molecular Conformation in a 4,4′-Difluorobiphenyl Crystal*

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Abstract

Intra- and intermolecular energies of 4,4′-difluorobiphenyl were calculated in two possible crystal structures, $P2_1/a$ and $P2_1/n$, which correspond to a planar and a twisted molecular conformation, respectively. The result shows that the planar conformation is more stable than the twisted, in contrast to the case of the biphenyl crystal. This is due to the greater stability of the π-conjugated system produced by the fluorine substitution.

Introduction

Biphenyl and its derivatives have attracted much attention for some time (for example, Casalone, Mariani, Mugnoli & Simonetta, 1968; Busing, 1983; Brock & Haller, 1984) because the ease of internal rotation about the central C–C bond makes their conformation susceptible to the environment. Thus, the conformation of the biphenyl molecule has been referred to as staggered or twisted in the gaseous and the liquid states (Bastiansen, 1949; Suzuki, 1959; Eaton & Steele, 1973) and as planar in the crystal at room temperature (Trotter, 1961; Robertson, 1961; Hargreaves & Rizvi, 1962; Charboneau & Delugeard, 1977). The dihedral angle, 40°, in the gaseous phase (Bastiansen, 1949) is a result of compromise between two opposing effects, *i.e.* the delocalization of π electrons favors the planar conformation whereas the repulsion between the H atoms at the 2 and 2′ positions tends to make the molecule staggered at a right angle (D_{2d}). The planar conformation in the solid state at room temperature indicates that a third factor, intermolecular forces, affects the compromise in order to re-establish the minimum Gibbs energy. In the absence of evidence for statistical disorder in the room-temperature structure of biphenyl, it seems reasonable to suppose that there is a single broad minimum in the potential energy curve, corresponding to the relatively low frequency of the twisting vibration about the central C–C bond. The conformation of the molecule further changes on cooling, and below 40·4 K (Atake, Saito & Chihara, 1983), it resumes the staggered shape with incommensurate modulation in two directions (Cailleau, Baudour & Zeyen, 1979; Cailleau, Moussa & Mons, 1979; Baudour & Sanquer, 1983; Cailleau, Messager, Moussa, Bugaut, Zeyen & Vettier, 1986). Thus, biphenyl is an unusual case in which thermal energy plays a critical role in determining the molecular conformation.

Substitution at the 4 and 4′ positions may also affect the balance of competitive interactions and cause a change in the molecular conformation.

We measured the heat capacities of 4,4′-difluorobiphenyl to study the effect of fluorine substitution at the ends of the biphenyl molecule on the structural characteristics. If the substitution helps to increase the π delocalization, the phase transition will be found at a lower temperature than in the case of biphenyl. The result (Saito, Atake & Chihara, 1985) was that there were no phase transitions between 3 and 300 K.

In the gaseous state, the 4,4′-difluorobiphenyl molecule is twisted with a dihedral angle of about 44° as demonstrated by an electron diffraction study (Bastiansen & Smedvik, 1954). Some spectroscopic studies (Barrett & Steele, 1972; Michelsen, Klaeboe, Hagen & Stroyer-Hansen, 1972) show the twisted conformation in the liquid state. In the crystalline state, however, the molecular conformation has not been established. It was reported that the crystal structure was the same as that of other 4,4′-dihalogenobiphenyls (Dhar, 1946), *i.e.* molecules are twisted by about 40° (Kronebusch, Gleason & Britton, 1976; Brock & Kuo, 1978). Recently, on the other hand, the planar molecular conformation was claimed from space-group determination using X-rays (Halstead, Spiess & Haeberlen, 1976), which was compatible with the results of high-resolution NMR experiments (Halstead, Tagenfeldt & Haeberlen, 1981). In the following, these two structural data will be referred to as 'experimental'.

In spite of such controversy about the crystal structure, 4,4′-difluorobiphenyl is a good model substance to study the subtle balancing of intra- and

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Table 1. *Parameters for the non-bonded interatomic potentials taken from Gavezzotti & Simonetta* (1975)

$$U(r) = A \exp(-Br) - Cr^{-6}.$$

For crossed interactions except for C–H, the geometric mean was used for A and C, and the arithmetic mean for B.

	A (kJ mol^{-1})	B (Å^{-1})	C (kJ mol^{-1} Å^{6})
C–C	$3{\cdot}499\times10^{5}$	3·60	$2{\cdot}38\times10^{3}$
C–H	$3{\cdot}688\times10^{4}$	3·67	$5{\cdot}23\times10^{2}$
H–H	$1{\cdot}110\times10^{4}$	3·74	$1{\cdot}14\times10^{2}$
F–F	$1{\cdot}548\times10^{5}$	4·26	$5{\cdot}42\times10^{2}$

intermolecular interactions that determines the molecular conformation of biphenyls because the key factors are not obscured by phase transitions as in other biphenyls (Saito, Atake & Chihara, 1985).

Intramolecular potential

We first examine the effect of fluorine substitution at the 4 and 4′ positions on the intramolecular potential because the energy difference between twisted and planar molecular conformations is needed for discussion of the stability of the planar conformation in the next section.

The intramolecular potential relating to a twist about the central C–C bond is a resultant of two opposing contributions, *i.e.* delocalization of π electrons and interaction between non-bonded atoms, which will be treated separately.

For the π-electron delocalization part of the potential, the simple Hückel molecular orbital method was adopted; all the resonance integrals between neighboring C atoms except that between the central C atoms are the same (β) and the dependence of the resonance integral between the central C atoms on the twisting angle (θ) was taken into account in the form $\beta \cos \theta$ (Parr & Crawford, 1948). The effects of fluorine substitution were included using the Coulomb integral $\alpha + 3\beta$ for an F atom and the resonance integral $0{\cdot}7\beta$ between the F atom and its neighboring C atom (Hirota, 1969), where α is the Coulomb integral for a C atom. The energy of π electrons in a 4,4′-difluorobiphenyl molecule is twice the sum of the lowest eight Hückel molecular orbital energies and that in the biphenyl molecule is twice the sum of the lowest six, in units of β. To convert the energy values, the value of β was chosen as -89 kJ mol^{-1}, which reproduces experimental data of a benzene molecule (Barrow, 1979).

For the non-bonded interatomic potential, a potential function of Buckingham (exp-6) type was used with the parameters given in Table 1 (Gavezzotti & Simonetta, 1975). The bond distances adopted for calculation were C–C(ring) = 1·40, C–C(center) = 1·50, C–H = 1·10 and C–F = 1·49 Å and the summation was taken over all atom pairs within a molecule.

The calculated overall intramolecular potentials for the twisting motion are shown in Fig. 1 for biphenyl and 4,4′-difluorobiphenyl. The barrier height of the order of 10 kJ mol^{-1} and a potential minimum around 40° are reasonable and consistent with experimental results (Bastiansen, 1949; Bastiansen & Smedvik, 1954; Grumadas, Poshkus & Kiselev, 1979). Comparison of the two curves (a) shows three features arising from the fluorine substitution: lowering of the barrier at 0° by about 8 kJ mol^{-1}, and shift of the minimum toward a smaller twist angle. These features are a result of greater π conjugation in the 4,4′-difluorobiphenyl molecule in the planar conformation.

Lattice energies and stability of planar conformation

Since the crystal structure of 4,4′-difluorobiphenyl at 3 K is the same as that at room temperature, we will calculate the static lattice energy to compare a crystal of planar molecules with that of twisted molecules.

Two probable crystal structures were examined. The structure of a crystal consisting of planar molecules was chosen to be the same as that of biphenyl at room temperature (Halstead, Spiess & Haeberlen, 1976), *i.e.* $P2_1/a$ and $Z = 2$ with half a molecule in the asymmetric unit (Charboneau &

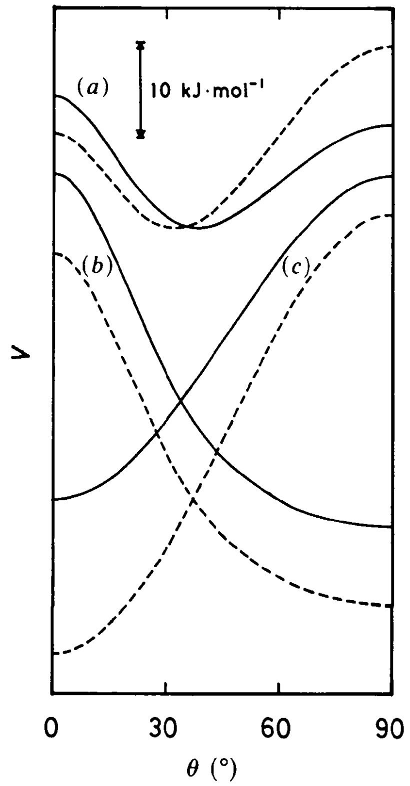

Fig. 1. Portion of the calculated intramolecular potential that depends on the twist angle in the biphenyl molecule (solid curve) and in 4,4′-difluorobiphenyl (dashed curve). (a) Overall potential; (b) sum of non-bonded interatomic potentials; (c) energy of π-conjugated system. Note that only the difference between the solid and dashed curves is significant.

Table 2. *Calculated and 'experimental' unit-cell dimensions and static lattice energies of 4,4′-difluorobiphenyl for the two possible structures*

		a (Å)	b (Å)	c (Å)	β (°)	V/Z (Å^3)	E (kJ mol^{-1})
$P2_1/a$	calc.	7·541	5·535	9·930	88·66	207·2	−113
$Z = 2$	expt*	7·76	5·81	9·96	92·6	224·3	—
planar	Δ†	−2·8	−4·7	−0·3	−4·3	−7·6	—
$P2_1/n$	calc.	15·00	12·70	9·484	94·91	224·9	−96
$Z = 8$	expt‡	14·83	13·30	9·45	96·8	231·3	—
twisted	Δ†	1·1	−4·5	0·4	−2·0	−2·8	—

* Dhar (1946).
† Δ = 100 × (calc. − expt)/expt.
‡ Halstead, Spiess & Haeberlen (1976).

Delugeard, 1977). The other structure consisting of twisted molecules is the same as that of other 4,4′-dihalogenobiphenyls (Dhar, 1946), *i.e.* $P2_1/n$ and $Z = 8$ with two inequivalent molecules in an asymmetric unit (Kronebusch, Gleason & Britton, 1976; Brock & Kuo, 1978).

The bond distances used were the same as in the calculation of intramolecular potential.

Calculation of intermolecular potential was carried out in the same way as described for the nonbonded interatomic potential in the preceding section.

Static lattice energies of two crystal structures were calculated using the accelerated convergence method (Williams, 1971) and they were minimized with respect to 7 and 16 variables for $P2_1/a$ and $P2_1/n$, respectively. In the case of $P2_1/n$ structure, the twist angle was fixed at 40° rather than leaving it adjustable. As will be seen, the difference in lattice energy between the two conformations is only 17 kJ mol^{-1} for a twist angle as large as 40°. This value was chosen because it is what is observed in other crystalline 4,4′-dihalogenobiphenyls (Kronebusch, Gleason & Britton, 1976; Brock & Kuo, 1978). Moreover, it is within the error of the experimental value for a free molecule (Bastiansen & Smedvik, 1954) and, therefore, we could neglect the first derivative of the intramolecular potential curve.

The crystal structure parameters and lattice energies obtained by such calculations are shown in Table 2 with 'experimental' data (Dhar, 1946; Halstead, Spiess & Haeberlen, 1976) for comparison. The discrepancies between the calculated parameters and the 'experimental' values for both structures are rather large being of the same order of magnitude as reported in the case of the biphenyl crystal (Brock, 1979). We will thus concentrate on the relative energies of the two crystal structures.

Static lattice energies of the $P2_1/a$ (planar molecule) and the $P2_1/n$ (twisted molecule) structures are −113 and −95 kJ mol^{-1}, respectively, *i.e.* the $P2_1/a$ structure has an energy lower by 17 kJ mol^{-1}. However, the difference, 17 kJ mol^{-1}, does not include the difference in the intramolecular energy between the planar and twisted conformations which is 10 kJ mol^{-1}. This must be subtracted from 17 kJ mol^{-1} if we take the ideal gas of twisted molecules as the reference state. Therefore, the $P2_1/a$ structure consisting of planar 4,4′-difluorobiphenyl molecules is expected to be the more stable structure at 0 K in contrast to the case of the biphenyl crystal.

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