

Structure of 4-Biphenylcarboxylic Acid, $C_{13}H_{10}O_2$: Comparison of the TLS Tensors Derived from Independent-Atom and Rigid-Group Refinements

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Abstract

$M_r = 198.2$, monoclinic, space group $P2_1/c$, $a = 7.438$ (1), $b = 26.907$ (2), $c = 15.766$ (2) Å, $\beta = 102.93$ (1)°, $V = 3075.3$ (9) Å³, $Z = 12$, $D_m = 1.276$ (5), $D_x = 1.284$ g cm⁻³, $\lambda(\text{Mo } K\alpha)$, graphite monochromator) = 0.71069 Å, $\mu = 0.798$ cm⁻¹, $F(000) = 1248$, $T = 295$ K. The inter-ring dihedral angles for the three independent molecules are 28.7 (2), 35.7 (2), and 32.2 (2)°. The structure was refined both in the usual way [R , $wR = 0.038$, 0.040 for 406 variables and 2848 reflections having $I > 3\sigma(I)$], and using a rigid-group, TLS model with one internal degree of freedom to describe the $C_{12}H_9$ biphenyl moieties (R , $wR = 0.061$, 0.073 for 166 variables and 2848 observed reflections). Descriptions of the rigid-body thermal motion derived from the two types of refinement are essentially the same, although the agreement of the positional parameters is limited by the rather serious assumptions of the rigid-group model. Although rigid-group refinements incorporating anisotropic thermal parameters have been used previously, this appears to be the first direct comparison of the thermal-motion descriptions obtained from the two procedures. The rigid-group refinement procedure has also been tested for several other previously published structures of related molecules with similar results.

Introduction

The structure of 4-biphenylcarboxylic acid was determined as part of our continuing program to study the relationship of crystal packing and molecular conformation (specifically, the inter-ring dihedral angle ψ) in simply substituted biphenyls. The structure was also useful for a second purpose. We had had difficulties refining several related structures because of low observed-data-to-parameter ratios (a result of the crystals being non-centrosymmetric, having large overall temperature factors, and growing as thin needles or plates), and wanted to use a rigid-group refinement procedure (Shmueli & Goldberg, 1974)

incorporating the TLS model (Schomaker & Trueblood, 1968) for rigid-body motion. This approach is similar to that outlined by Prince & Finger (1973), except that their method imposes no constraints on the atomic coordinates. In order to evaluate the results, particularly the reliability of the thermal-motion tensors, we decided to compare full and constrained refinements for a well-behaved, related structure. No such direct comparison seems to have been published previously, although there is an indication that the agreement might be quite good (Chaplot, Lehner & Pawley, 1982). Specifically, we needed to determine the effect on the thermal-motion description derived from the rigid-group approach of the errors in the positional parameters that result from the geometric constraints. The structure of 4-biphenylcarboxylic acid seemed well suited for such a study. The magnitude of the libration about the long molecular axis of a simple biphenyl is interesting since it is related to the combined intra- and intermolecular potential function for torsion and libration about the central C–C bond.

Experimental section

Crystals grown from ethanol, prominent faces {010} and {011}, flat needles cut to 0.50 × 0.45 × 0.15 mm, density measured by flotation in aqueous $ZnCl_2$, 24 reflections ($11 < \theta < 13^\circ$) used for measuring lattice parameters; Enraf–Nonius CAD4/F diffractometer, θ – 2θ scans; $h, k \geq 0$, $2\theta \leq 50^\circ$, 3 standard reflections, $\pm 7.5\%$ variation in I . Of the 5397 unique observed reflections 2848 having $F_o^2 > 3\sigma(F_o^2)$ were included in the refinement; transmission factors 0.962–0.989. The structure was solved without difficulty using MULTAN77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). For the independent-atom refinement all calculations were performed as described previously (Brock & Webster, 1976). Scattering factors were those of Cromer & Waber (1974). Contributions were added for phenyl H atoms fixed at a late stage in the refinement at idealized positions ($r_{C-H} = 1.00$ Å; B values 1.0 Å² greater than that of attached C atom). The carboxyl H atoms were located in difference maps as peaks approximately midway

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Table 1. Positional and thermal parameters for the atoms of 4-biphenylcarboxylic acid

Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The equivalent *B*'s are calculated from the anisotropic thermal parameters β and the direct metric *G* as $\frac{4}{3} \text{tr}(\beta \cdot G)$.

	x	y	z	<i>B</i> (Å ²)		x	y	z	<i>B</i> (Å ²)
O(11)	0.48712 (26)	0.05820 (7)	-0.04571 (12)	6.1	C(204)	-0.2906 (3)	-0.02101 (8)	0.34183 (14)	3.8
O(12)	0.70961 (25)	0.00156 (7)	-0.03020 (12)	6.2	C(205)	-0.0976 (3)	-0.02137 (9)	0.36387 (15)	4.4
O(21)	-0.05870 (23)	0.08446 (7)	0.12622 (11)	5.9	C(206)	0.0030 (3)	0.00382 (9)	0.31418 (15)	4.3
O(22)	0.19796 (24)	0.05928 (7)	0.21650 (11)	6.1	C(207)	-0.3984 (3)	-0.04720 (8)	0.39667 (15)	3.9
O(31)	0.39683 (25)	0.11350 (7)	0.13512 (12)	6.8	C(208)	-0.5649 (4)	-0.07029 (9)	0.36011 (15)	4.8
O(32)	0.14154 (25)	0.14587 (7)	0.05426 (11)	5.9	C(209)	-0.6652 (4)	-0.09432 (10)	0.41167 (19)	5.6
C(100)	0.6426 (4)	0.04401 (10)	-0.05523 (15)	4.6	C(210)	-0.6041 (4)	-0.09512 (10)	0.50066 (19)	5.6
C(101)	0.7524 (3)	0.07720 (9)	-0.09906 (14)	4.1	C(211)	-0.4399 (4)	-0.07237 (10)	0.53822 (16)	5.5
C(102)	0.6785 (3)	0.12226 (9)	-0.13438 (15)	4.5	C(212)	-0.3371 (3)	-0.04890 (10)	0.48681 (16)	4.8
C(103)	0.7805 (4)	0.15253 (9)	-0.17626 (15)	4.5	C(300)	0.3145 (4)	0.14363 (9)	0.07759 (16)	4.4
C(104)	0.9577 (3)	0.13961 (9)	-0.18413 (14)	4.0	C(301)	0.4273 (3)	0.17858 (9)	0.03951 (14)	3.8
C(105)	1.0292 (3)	0.09451 (9)	-0.14776 (16)	4.7	C(302)	0.6181 (4)	0.17642 (9)	0.06300 (15)	4.7
C(106)	0.9277 (4)	0.06388 (9)	-0.10612 (15)	4.6	C(303)	0.7237 (3)	0.21036 (9)	0.03005 (16)	4.7
C(107)	1.0670 (3)	0.17255 (9)	-0.22894 (14)	4.1	C(304)	0.6417 (3)	0.24760 (8)	-0.02734 (14)	3.9
C(108)	1.0438 (4)	0.22386 (9)	-0.23030 (16)	4.8	C(305)	0.4499 (4)	0.24910 (9)	-0.05065 (15)	4.7
C(109)	1.1501 (4)	0.25443 (10)	-0.27002 (17)	5.7	C(306)	0.3439 (3)	0.21504 (10)	-0.01841 (15)	4.6
C(110)	1.2818 (4)	0.23447 (12)	-0.30876 (17)	5.7	C(307)	0.7556 (3)	0.28431 (8)	-0.06181 (15)	4.1
C(111)	1.3064 (4)	0.18390 (12)	-0.30882 (16)	5.6	C(308)	0.9244 (4)	0.29998 (10)	-0.01230 (16)	5.1
C(112)	1.2001 (4)	0.15330 (9)	-0.26954 (16)	4.9	C(309)	1.0310 (4)	0.33448 (10)	-0.04334 (19)	5.8
C(200)	0.0241 (4)	0.05949 (9)	0.19154 (16)	4.3	C(310)	0.9710 (4)	0.35427 (10)	-0.12525 (20)	6.0
C(201)	-0.0848 (3)	0.03046 (8)	0.24112 (14)	3.8	C(311)	0.8048 (4)	0.33928 (10)	-0.17556 (17)	5.7
C(202)	-0.2760 (4)	0.03025 (9)	0.21798 (15)	4.5	C(312)	0.6978 (4)	0.30466 (9)	-0.14493 (15)	4.8
C(203)	-0.3765 (3)	0.00488 (9)	0.26739 (15)	4.5					

Table 2. Comparison of the independent-atom (IA) and rigid-group (RG) refinements

	IA	RG
Number of variables	406	166
<i>R</i> _w <i>wR</i> [*]	0.038, 0.040	0.061, 0.073
Error in an observation of unit weight (e ⁻)	1.96	3.38
Features in final difference Fourier map (e ⁻ Å ⁻³)	+0.1, -0.3	+0.4, -0.3

* $R = \sum |F_o| - |F_c| / \sum |F_o|$, $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$, where $w = 4F_o^2 / \sigma^2(F_o^2)$.

between the H-bonded O atoms of the dimers and treated analogously. Final positional parameters and equivalent *B* values are given in Table 1; measures of the agreement of the model and data are found in Table 2. The structure and atomic thermal ellipsoids are illustrated in Figs. 1 and 2, and Fig. 3 shows the

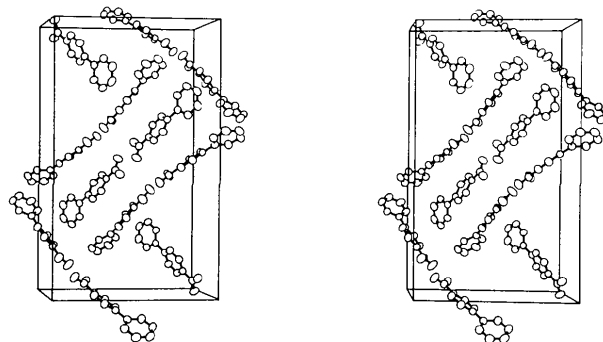


Fig. 1. Stereoscopic view of the unit cell of 4-biphenylcarboxylic acid. The *c* axis is horizontal, the *b* axis is vertical, and the *a* axis points into the plane of the paper. In this and the following drawing the ellipsoids correspond to 50% contours of atomic displacement, and H atoms have been omitted for the sake of clarity.

atom-numbering scheme and gives some average bond lengths and angles. The anisotropic thermal parameters for the 12 C atoms of each biphenyl ring system were analyzed in terms of the Schomaker & Trueblood (1968) rigid-body model using Trueblood's (1978) program *THMI*. The fit was good if extra variables Ω^2 (Dunitz & White, 1973) were

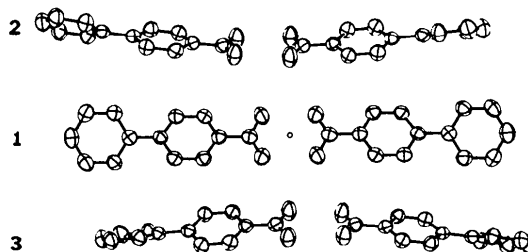


Fig. 2. Perspective drawing of the packing motif of 4-biphenylcarboxylic acid, which is composed of three hydrogen-bonded dimers arranged around an inversion center. The three independent molecules that form the asymmetric unit are identified, and the principal axes of the thermal ellipsoids are shown.

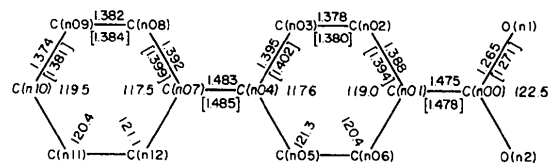


Fig. 3. Diagram showing atom-numbering scheme for 4-biphenylcarboxylic acid and giving bond lengths and angles averaged over assumed molecular *C*₂ symmetry and the three independent molecules. The bond lengths in square brackets have been corrected for rigid-body thermal motion. Estimated standard deviations for individual bond lengths and angles average 3×10^{-3} Å and 0.2° . E.s.d.'s of the means (calculated from the variation in the values of chemically equivalent bond lengths and angles) are 1.2×10^{-3} Å and $0.1-0.2^\circ$ except for the C(n01)-C(n00) bond, for which the e.s.d. is 4×10^{-3} Å.

Table 3. *Some measures of agreement*

	Molecule 1	Molecule 2	Molecule 3
$\langle (U_o^i - U_c^i)^2 \rangle^{1/2}$	0.0025 Å ²	0.0022 Å ²	0.0022 Å ²
$\langle \sigma^2(U_o^i)_{IA} \rangle^{1/2}$	0.0016	0.0015	0.0016
$\langle [(U_o^i)_{IA} - (U_c^i)_{RG}]^2 \rangle^{1/2}$			
Ring atoms	0.0027	0.0025	0.0026
Carboxyl atoms	0.0012	0.0019	0.0017
$\langle x_{IA} - x_{RG} \rangle$			
Ring atoms	0.029 Å	0.029 Å	0.025 Å
Carboxyl atoms	0.004	0.004	0.005
$\langle \Delta_{A,B}^2 \rangle^{1/2}$ *			
Ring C(n01) - C(n06)	0.0019 Å ²	0.0022 Å ²	0.0026 Å ²
Ring C(n07) - C(n12)	0.0026	0.0022	0.0023

* $\langle \Delta_{A,B}^2 \rangle^{1/2} = \langle (z_{A,B}^2 - z_{B,A}^2)^2 \rangle^{1/2}$, where $z_{A,B}^2$ is the mean-square amplitude of atom A in the direction of atom B calculated from the U_{IA} tensors (see Rosenfield, Trueblood & Dunitz, 1978). The averages are taken over the 15 independent C-C vectors in each phenyl ring.

included to allow for internal rotation of the unsubstituted rings about the central C-C bonds (see Table 3). The T, L, and S tensors are given in Table 4 after transformation to a coordinate system compatible with that used for the rigid-group refinement (see below).

For the rigid-group refinement we incorporated Shmueli's & Goldberg's (1974) subroutines into our crystallographic least-squares program (Brock & Webster, 1976). The three C₁₂H₉ biphenyl moieties were treated as rigid groups having bond lengths $r_{C-C} = 1.40$ Å within the rings, $r_{C-C} = 1.50$ Å between the rings, $r_{C-H} = 1.00$ Å, and all bond angles = 120°. The positions of the groups were specified by three translations, three rotations, and an internal rotation ψ about the central C-C bond. The thermal motion of each group was described by the 20 independent components of the T, L, and S tensors, and by an additional parameter Ω^2 that allows for the effects of internal rotation about the central C-C bond. The non-H atoms of the carboxyl groups were refined anisotropically, and the carboxyl H atoms were included as described above. Measures of agreement for this model are also given in Table 2, and thermal-motion parameters are listed in Table 4. Full results of this refinement are available.*

Molecular geometry and crystal packing

We had expected to find H-bonded carboxylic acid dimers in this structure, but the discovery that the packing unit is composed of six molecules - three

dimers arranged around an inversion center (see Figs. 1 and 2) - was a surprise. Since the three independent molecules are approximately parallel, the resulting group is more or less brick-shaped. The crystal structure as a whole is then a herringbone arrangement of these centrosymmetric building blocks.

The identification of a multi-molecule packing unit suggests the presence of interactions within the unit at least somewhat stronger than the interactions between adjacent units. The concavity of the long edges of the aggregate (see Fig. 2) suggests constriction at the center; that is, that the attractions between the six COOH groups are greater than those between the biphenyl moieties. There are five distances between O atoms of adjoining dimers in the range 3.4 to 3.6 Å. While these distances are much longer than those within the dimers [O(11)···O(12), 2.635 (2); O(21)···O(32), 2.644 (2); O(31)···O(22), 2.610 (2) Å], they are among the shortest contacts in the structure.

Actually, the observation of multiple molecules in the asymmetric unit is not uncommon for simple biphenyls, especially if the molecules are arranged so that their long axes are approximately parallel. Other examples are the low-temperature phases of biphenyl (Cailleau, Baudour & Zeyen, 1979), *p*-terphenyl (Baudour, Délugeard & Cailleau, 1976), and *p*-quaterphenyl (Baudour, Délugeard & Rivet, 1978); 4-bromobiphenyl (Brock, 1980), one polymorph of 4-hydroxybiphenyl (Brock & Haller, 1984), and 4-biphenylferrocene (Allen, Trotter & Williston, 1970); and a group of isostructural 4,4'-biphenyl derivatives (see Brock, Kuo & Levy, 1978). In none of these, however, is the existence of an identifiable packing unit composed of several molecules so obvious. Two other 4-biphenylcarboxylic acid structures are known, and both contain only one independent molecule. The 3'-iodo derivative (Sutherland & Mottram, 1972) contains 'chains of dimers', while the 3'-fluoro derivative (Sutherland & Rawas, 1983) is built of stacks of dimers [lattice repeat 3.91 (1) Å] in a herringbone arrangement.

The occurrence of three molecules in the asymmetric unit, each with approximate C₂ symmetry, has a salutary effect on the determination of bond lengths and angles; it makes extensive averaging possible. We wonder, then, whether the deviations from idealized geometry (see Fig. 3), which are in several cases magnified by the thermal motion correction, might actually be real. While we hesitate to interpret these differences chemically without better data, we do note that the imposition of an idealized geometry (as in a rigid-group refinement, see below) is a serious approximation.

Another consideration pertinent to the constrained refinement is the planarity of the phenyl rings and the linearity of the molecular backbone. All deviations of the phenyl C atoms from their six-atom

* Supplementary Publication No. SUP 39264 (51 pp.), available from The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England, includes: atomic anisotropic thermal parameters, H-atom parameters, and selected bond lengths and angles (all for the independent-atom refinement); rigid-group translations and rotations, derived positional and thermal parameters for the group atoms, positional and thermal parameters for the non-group atoms, and H-atom parameters (all for the rigid-group refinement); and observed and calculated structure factor amplitudes (for both refinements). Refined T, L, and S tensors for two similar structures, 2,3,4,5,6-pentafluorobiphenyl and 4-bromobiphenyl, are also given.

Table 4. Comparison of the T, L, and S tensor components for 4-biphenylcarboxylic acid determined by direct refinement in the crystallographic least-squares procedure and by fitting atomic U tensors to a rigid-body model

Numbers in parentheses are estimated standard deviations derived from the rigid-group refinement. The numbers in square brackets are the components of T, L, and S tensors fit to the atomic U tensors and then transformed to a coordinate system analogous to that used for the rigid-group refinement (see text).

	Molecule 1			Molecule 2			Molecule 3		
T (Å ² × 10 ⁴)*	487 (11) [497]	37 (6) [36] 569 (8) [566]	5 (10) [3] -27 (7) [-19] 446 (14) [445]	465 (11) [471]	7 (6) [9] 540 (7) [534]	35 (10) [28] 2 (6) [2] 437 (14) [444]	457 (11) [461]	-62 (6) [-64] 561 (8) [558]	-30 (9) [-22] 30 (7) [27] 467 (14) [478]
L (rad ² × 10 ⁴)	10 (2) [9]	0 (2) [1] 128 (12) [120]	-7 (1) [-7] 7 (3) [6] 18 (2) [17]	13 (2) [14]	-4 (2) [-5] 140 (13) [122]	-5 (1) [-4] 5 (3) [6] 14 (2) [13]	14 (2) [15]	12 (2) [13] 118 (14) [84]	3 (1) [1] 7 (3) [6] 16 (2) [16]
S (Å rad × 10 ⁴)	-17 (3) [-17] 10 (6) [5] 19 (2) [19]	12 (3) [7] 7 (5) [10] 7 (2) [8]	-20 (2) [-17] 9 (4) [9] 9 [7]	-11 (3) [-6] -8 (6) [2] 20 (2) [20]	-15 (3) [-10] 5 (5) [1] -1 (2) [0]	-24 (2) [-24] -4 (4) [2] 7 [5]	8 (3) [5] 47 (6) [44] 21 (2) [23]	6 (3) [8] -2 (5) [-4] -10 (2) [-11]	-30 (2) [-31] -45 (4) [-42] -7 [-1]
Ω ² (rad ² × 10 ⁴)†		35 (17) [34]		41 (18) [55]		94 (18) [127]			

* The y axis is parallel to the long molecular axis, the z axis is perpendicular to the plane of the carboxylated phenyl ring, the x axis completes the orthonormal system, and the origin is at the midpoint of the central C-C bond.

† The value Ω² describes the excess libration of the carboxylated ring about the C(n01)-C(n04) axis; i.e. for this ring $L^{22} = L^{22} + \Omega^2$.

planes are less than 0.01 Å, with most below 0.005 Å. There is some bending at C(n04) and C(n07), but all intramolecular angles involving C(n01), C(n04), C(n07), and C(n10) are less than 2.2°. Consequently, the dihedral and conformation angles describing the twists about the central C-C bonds are essentially the same. The values [28.7 (5), 35.5 (3) and 32.3 (2)°] are close to that expected for the isolated molecule. The (COO)₂ groups of the two independent dimers form considerably poorer planes. Nevertheless, either their dihedral angles with the attached ring (5.0, 8.6, and 9.1°) or their average conformation angles around the C(n00)-C(n01) bonds [4.7 (4), 0.7 (12), and 3.3 (11)°] lead to the same conclusion: the phenyl ring and its acid substituent are approximately coplanar.

Rigid-body thermal motion: comparison of the two descriptions

Comparison of the two sets of T, L, and S tensors and the extra librational parameters Ω² derived from (1) the rigid-group (RG) refinement and from (2) the fit to the atomic U tensors obtained in the independent-atom (IA) refinement is complicated by differences in the coordinate systems used by the two computer programs. The tensors from the RG refinement are expressed relative to the group internal Cartesian coordinate system: the y axis is parallel to the long axis of the molecule, the z axis is perpendicular to

the plane of the carboxylated ring, and the origin is at the midpoint of the phenyl-phenyl bond. Normally the fit to the atomic U tensors using Trueblood's (1978) program *THMI* would be done in a Cartesian system based on the crystal axes; however, in order to facilitate the comparison, we forced the program to do the fit in a coordinate system based on the molecular axes. Because of the distortions of the molecules from idealized geometry, this system is very close to, but not exactly in register with, the rigid-group system described above. Because of uncertainties associated with transforming the e.s.d.'s of the U tensor components, the least-squares fit was unweighted, and for similar reasons e.s.d.'s for the resulting rigid-body tensors are not available. Results of the fit in the Cartesian crystal system, however, indicate these latter e.s.d.'s are very similar in magnitude to those obtained for the RG refinement.

Table 4 gives the two sets of tensors for each of the three independent molecules. We find the agreement, especially considering the geometrical constraints in the RG refinement, astounding. Except for L²² and Ω² of molecule 3, all the components agree to within one e.s.d. The values of $\langle(\Delta_{IA-RG}/\sigma_{RG})^2\rangle^{1/2}$ are 0.59 and 0.93 respectively for the 18 T and 18 L components, and 0.50 for the 24 S components; the value overall is 0.71. This is better agreement than expected, especially considering no allowance has been made for the e.s.d.'s of the IA values. Even the L²² and Ω² values for molecule 3 differ by only 2.4 and 1.8 σ_{RG}. The three ψ values are also essentially identical for

the two refinements. The great benefit of the RG refinement over the IA procedure is that the same information about rigid-body motion is obtained with a large (here, 2-4-fold) reduction in the number of adjustable parameters. On the other hand, information about molecular distortions is lost. The necessary geometrical idealization raises the agreement factors somewhat (although perhaps not unacceptably), and results in a less-flat final difference Fourier map (see Table 2). We also encountered a minor convergence problem.

The most obvious problem with the RG refinement is the imposition of idealized geometry. Table 3 shows that corresponding biphenyl C atoms in the two refinements are about 0.03 Å apart. The atoms of the carboxyl groups are also indirectly affected, but only by about one e.s.d. The requirement that the long axis of the molecule be strictly linear is perhaps the most serious error. An important distortion of this type would probably lead to low, perhaps even negative, values for L^{11} and/or L^{33} . In principle we could allow deformations of the groups, but to account for the bond-length variations would require fundamental alterations of our crystallographic least-squares program and would raise the number of adjustable parameters substantially.

Two other approximations, omission of a libration correction, and neglect of third cumulants, are less important. The libration correction shifts atomic positions by $d\omega^2/2$, where d is the distance of the atom from the axis and ω is the corresponding librational amplitude. In a biphenyl molecule, correcting for an L^{22} value of 50 deg² would move each of the eight off-axis C atoms 0.01 Å perpendicular to the group y axis. The correction of the *para* C atom positions for L^{11} or L^{33} values of 5 deg² is only 0.003 Å. These shifts are minor relative to the other approximations. As for third cumulants, Trueblood (1978) has argued that their inclusion does not alter results significantly, even for r.m.s. amplitudes as high as 0.4 rad. Prince (1983), however, disagrees, and has found third cumulants useful even when the amplitudes are moderate (Choi & Prince, 1976).

In the RG refinement, only displacements that can be formulated in terms of rigid-body motions contribute to the thermal-motion description. This restriction does not, however, preclude contributions from internal modes. Indeed, the low-frequency, out-of-plane deformations may affect the derived rigid-body motion tensors in an important way (see Brock & Dunitz, 1982). But this problem is not unique to the RG refinement; it is also part of the IA procedure. In this study we find (see Table 2) that the r.m.s. differences between observed and calculated U^{ij} components from the *THMI* fit are about the same as those between the observed U_{IA}^{ij} components and the U_{RC}^{ij} components calculated from the refined tensors; both r.m.s. differences are *ca* 1.5 times $\langle\sigma(U_{IA}^{ij})^2\rangle^{1/2}$.

As a further test, we carried out RG refinements for the structures of 2,3,4,5,6-pentafluorobiphenyl (Brock, Naae, Goodhand & Hamor, 1978) and 4-bromobiphenyl (Brock, 1980). For the $C_{12}H_5$ part of the fluorinated biphenyl (the F atoms being refined independently) the results are very similar to, but not quite as good as, those quoted above. The overall $\langle(\Delta_{IA-RG}/\sigma_{RC})^2\rangle^{1/2}$ is 1.14, with the worst agreement ($\Delta/\sigma = 2.25$) between the extra librational parameters Ω^2 . For the original structure R and wR were 0.032 and 0.046 for 90 variables and 538 reflections; in the RG refinement they are 0.048 and 0.078 for 40 variables.* The $C_{12}H_9$ fragments of the 4-bromobiphenyl structure did not refine so satisfactorily, although the agreement factors are acceptable ($R, wR = 0.052, 0.050$ for 114 variables, 620 reflections in the IA refinement; $R, wR = 0.053, 0.054$ for 74 variables in the RG refinement). In this last structure the T tensors for the two independent molecules differ although the crystal environments are similar; they are also much more anisotropic than anticipated. One of the molecules has a negative L^{22} component. The original structure was also poorly defined, and the pattern of the isotropic temperature factors was odd. Thus we are convinced that the RG refinement does not bring apparent order to a thermal-motion description if a normal IA procedure would fail. Further results for the refinements of these two structures are given with the supplementary material.

The overall picture of the rigid-body motion in 4-biphenylcarboxylic acid is about the same as for 4,4'-dichlorobiphenyl (Brock, Kuo & Levy, 1978) which has a different packing arrangement but a similar molecular conformation ($\psi = 39, 42^\circ$). In each of the structures the T tensors for the independent molecules vary only slightly as would be expected for molecules in similar but not identical environments. While the T tensors are all roughly isotropic, the L tensors are markedly anisotropic, the largest eigenvalue in each case being associated with an axis nearly parallel to the long direction of the molecule. The magnitudes of the tensor components in the two structures are comparable. In the carboxylic acid crystal, differences were found between the phenyl rings; in all three independent molecules the librational amplitude around the long molecular axis was larger for the carboxylated ring. No such difference was found for the $C_{12}H_8Cl_2$ structure.

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* Prince (1983) has refined this data set using a TLS model and variable bond lengths and angles within planar phenyl rings. There are no important differences between the TLS tensors determined in his refinement (R and wR of 0.036 and 0.053 for 55 variables) and ours.

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On the Correct Usage of the Cremer–Pople Puckering Parameters as Quantitative Descriptors of Ring Shapes – a Reply to Recent Criticism by Petit, Dillen and Geise

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Abstract

The Cremer–Pople puckering parameters define the conformation of a puckered ring in a quantitative, mathematically well defined manner. Recent results by Petit, Dillen & Geise [*Acta Cryst.* (1983), **B39**, 648–651] on six-membered-ring conformations are due to an erroneous definition of standard boat and twist-boat forms. This is shown by deriving the correct relationships between puckering parameters and internal ring angles for these forms.

The analysis of the puckered forms of an N -membered ring is uniquely carried out by calculating the mean plane (MP) and the puckering parameters of the ring (Cremer & Pople, 1975a; Cremer, 1980). This approach is a generalization of the description of a puckered pentagon first given by Kilpatrick, Pitzer & Spitzer (1947). It can be used (a) to analyze a puckered ring in terms of its basis conformations

(Cremer, 1980), (b) to make a quantitative comparison of puckered rings of different size and symmetry, (c) to generate all conformers along a pseudorotation cycle once the parameters of one conformer are known (Cremer, 1979, 1984), (d) to develop the conformational potential of a ring as a function of $N-3$ parameters q_m and φ_m (Cremer & Pople, 1975b; Cremer, 1979), (e) to define a ring substituent position in a unique manner (Cremer, 1980) and (f) to link the conformational analysis of ring compounds to that of alicyclic rotor molecules (Cremer, 1978).

The Cremer–Pople (CP) parameters have been designed in order to associate the shape of a puckered ring, its conformation and its interconversional motions with a mathematically well defined subset of internal coordinates. This is done by projecting from the $(3N-6)$ -dimensional configuration space of an N -membered ring onto an $(N-3)$ -dimensional conformation subspace (Cremer, 1980). Every point in this subspace corresponds to a nonplanar ring