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Redetermination of the Structure of the 3:1 Complex of 4,4′-Dinitrobiphenyl with 4-Hydroxybiphenyl,* $3C_{12}H_8N_2O_4.C_{12}H_{10}O$: Crystal Packing, Molecular Geometry and Thermal Motion

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Abstract. $M_r = 902{\cdot}83$, triclinic, $P1$, $a = 11{\cdot}034$ (2), $b = 11{\cdot}166$ (2), $c = 9{\cdot}431$ (3) Å, $\alpha = 90{\cdot}15$ (2), $\beta = 115{\cdot}10$ (2), $\gamma = 81{\cdot}30$ (2)°, $V = 1037{\cdot}7$ (4) Å^3, $Z = 1$, $D_x = 1{\cdot}445$ g cm^{-3}, Mo $K\alpha$, graphite monochromator, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}002$ cm^{-1}, $F(000) = 468$, $T = 295$ K. The structure was refined using a rigid-group refinement procedure incorporating the **TLS** description of rigid-body motion to a final R of 0·062 for 281 variables and 1728 reflections. The structure is similar to that reported originally, except that the 4,4′-dinitrobiphenyl molecules, instead of conforming to mirror symmetry, are twisted by an average of 37·2 (1)° about the central C—C bond. The 4-hydroxybiphenyl molecule is nearly planar. Its mean-square librational amplitude about the long molecular axis is 70 (5) deg^2, a value small enough that it is unlikely that it conceals a static disorder of two more twisted molecules.

Introduction. Biphenyl and its simple derivatives that lie on apparent inversion centers in the solid state have played a central role in the study of the influence of crystallization on molecular conformation (Cailleau, Baudour, Meinnel, Dworkin, Moussa & Zeyen, 1980). Planarity required by crystallographic symmetry has also been reported (Saunder, 1946/47) for the molecules of the 3:1 complex of 4,4′-dinitrobiphenyl with 4-hydroxybiphenyl, but in this case the planarity is a result of mirror, rather than inversion, symmetry (see Fig. 1). We wondered if this rather imprecise structure, which was studied in projection, was really correct. If it were, we wanted to examine the apparent rigid-body libration around the long molecular axes for evidence of hidden disorder or large-amplitude thermal motion such as has been observed for some other planar biphenyls (Cailleau *et al.*, 1980).

Experimental. Crystals grown by slow evaporation of an acetone solution, flat plates with prominent faces {100}, {010}, {001}, and {10$\bar{1}$}; crystal 0·38 × 0·39 × 0·05 mm, Enraf–Nonius CAD-4F diffractometer, θ–2θ scans, $k \geq 0$, $2\theta \leq 55°$, 4755 unique reflections, 1728 with $F^2 > 3\sigma(F^2)$ treated as observed, 3 standard reflections, no absorption correction, correction for decomposition of 1·8% overall, 25 reflections for measuring lattice parameters ($10 < \theta < 13°$); h 0–±14, k 0–14, l 0–±12.

Saunder (1946/47) gave the space group as Cm, although he actually treated the structure as if it belonged to $C2/m$. We measured cell parameters corresponding to his choice of axes as $a = 19{\cdot}984$ (4), $b = 9{\cdot}431$ (3), $c = 11{\cdot}166$ (2) Å, $\alpha = 90{\cdot}15$ (2), $\beta = 99{\cdot}54$ (2) and $\gamma = 90{\cdot}20$ (2)°, in good agreement (better than 0·4%) with his values; the transformation between these values and the cell given in the *Abstract* is

$$\mathbf{a}_{C1} = \begin{pmatrix} \bar{2} & 0 & \bar{1} \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \mathbf{a}_{P1}.$$

Weissenberg photographs (Mn-filtered Fe $K\alpha$ radiation) of the hkl, $k = 0$ to 4, nets (referred to the centered cell) show apparent $2/m$ Laue symmetry. Comparisons of diffractometer-measured intensities for a full sphere of data with $2\theta \leq 15°$ show clearly, however, that $F^2(hkl) = F^2(\bar{h}\bar{k}\bar{l}) \neq F^2(h\bar{k}l) = F^2(\bar{h}k\bar{l})$.

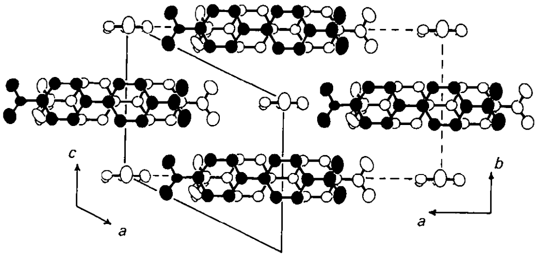

Fig. 1. Projection on the *ac* plane of the structure of the 3:1 complex of 4,4′-dinitrobiphenyl with 4-hydroxybiphenyl. The projection is one unit cell deep. The *a* and *c* axes of the primitive cell used in this study are shown as solid lines; the *a* and *b* axes of the centered unit cell used by Saunder (1946/47) are shown as dotted lines. The mirror planes he reported were located perpendicular to *b* at $y = 0, \frac{1}{2}$. The third axes of the two cells are collinear. In this and Fig. 2 the ellipsoids correspond to 50% contours of atomic displacement, and H atoms have been omitted for the sake of clarity.

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* IUPAC name: 4-biphenylol.

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An isotropic refinement in *C*2/*m* starting from Saunder's (1946/47) parameters and using a monoclinic data set [85 variables, 925 data having $F^2 > 3\sigma(F^2)$] converged with conventional $R = 0{\cdot}35$ overall, with $R = 0{\cdot}19$ and 0·33 for the *hk*0 and *h*0*l* data [the projections used by Saunder (1946/47)] and $R = 0{\cdot}48$ and 0·25 for the 0*kl* data with *l* even and odd, respectively (indices referred to centered cell; see Fig. 1).

The *MULTAN*77 solutions (Main, Lessinger, Woolfson, Germain & Declercq, 1977) in *P*1 showed large parts of the 4,4′-dinitrobiphenyl molecules and indicated they are twisted by *ca* 35° around the central C—C bonds. Packing considerations then preclude space groups *C*2/*m*, *Cm* and $P\bar{1}$, leaving only *C*2 and *P*1 as possibilities, with *C*2 requiring that the OH group of the 4-hydroxybiphenyl molecule be disordered. Considering the unit-cell parameters, the poor agreement of *hkl* and $\bar{h}k\bar{l}$ reflections, the absence of disorder, and the success of the final refinement (see below), we are convinced that the correct space group is *P*1. This choice is also consistent with Saunder's (1946/47) pyroelectricity measurements.

In the space group *P*1 there are 67 non-hydrogen atoms in the asymmetric unit. To refine the structure with individual atoms and anisotropic temperature factors would require 601 variables, and the ratio of observed data to adjusted parameters would be 2·9. Owing to the shortage of data, we chose instead to use a group-refinement procedure suggested by Shmueli & Goldberg (1974) that incorporates the Schomaker–Trueblood (1968) **TLS** model for rigid-body motion. Our experience with this procedure has been detailed elsewhere (Brock, Blackburn & Haller, 1984). The position of each $C_{12}H_8$ or $C_{12}H_9$ group is specified by three translations (except as necessary to fix the unit-cell origin), three rotations, and an internal rotation ψ about the central C—C bond. The thermal motion of each group is described by the 20 independent components of the **T**, **L** and **S** tensors, and by an extra parameter Ω^2 that allows the two phenyl rings to have different librational motion because of torsion about the central C—C bond. N and O atoms refined anisotropically; hydroxyl H atom located in difference map at a late stage in the refinement and included as fixed contribution after shortening O(4)—H(4) to 1·04 Å; scattering factors from tabulation of Cromer & Waber (1974); all computer programs have been described previously (Brock & Webster, 1976); final values of agreement indices [refinement on *F*; $w = 4F_o^2/\sigma^2(F_o^2)$] are $R = 0{\cdot}062$, $wR = 0{\cdot}069$ for 281 variables; error in an observation of unit weight is 3·25; max. Δ/σ in final cycle 0·08 and largest correlation coefficient −0·86; most important features in final difference-Fourier map have heights +0·39 and −0·32 e Å^{-3}.

Table 1. *Positional and thermal parameters for the non-group atoms of the* 3:1 *complex of* 4,4′-*dinitrobiphenyl with* 4-*hydroxybiphenyl*

The nitro groups composed of atoms N(*n*1), O(*n*1) and O(*n*2) and of N(*n*2), O(*n*3) and O(*n*4) are bonded to C(*n*04) and C(*n*10) respectively. The hydroxyl O atom O(4) is bonded to C(404).

	*x**	*y*	*z*	*B*(Å^2)†
N(11)	−0·5038 (14)	0·0788 (11)	0·2394 (21)	5·9
N(12)	0·5049 (12)	−0·0864 (11)	0·7446 (15)	5·0
N(21)	−0·5651 (12)	0·4150 (11)	0·2090 (16)	5·0
N(22)	0·4463 (15)	0·2517 (13)	0·7199 (22)	6·6
N(31)	−0·4386 (12)	0·7400 (12)	0·2793 (17)	5·4
N(32)	0·5681 (13)	0·5784 (11)	0·7777 (17)	5·0
O(11)	−0·5620 (10)	0·1355 (10)	0·3112 (14)	7·0
O(12)	−0·5613 (11)	0·0403 (11)	0·1147 (15)	8·2
O(13)	0·5643 (10)	−0·1403 (10)	0·8778 (13)	6·8
O(14)	0·5655 (10)	−0·0504 (11)	0·6759 (13)	7·6
O(21)	−0·6246 (10)	0·4667 (9)	0·2875 (12)	6·7
O(22)	−0·6239 (10)	0·3852 (10)	0·0791 (12)	7·3
O(23)	0·5032 (11)	0·1992 (12)	0·8453 (15)	8·6
O(24)	0·5026 (13)	0·2853 (12)	0·6391 (17)	10·0
O(31)	−0·4985 (10)	0·7925 (11)	0·3503 (13)	7·5
O(32)	−0·4983 (10)	0·7070 (11)	0·1438 (13)	8·4
O(33)	0·6275 (10)	0·5297 (10)	0·9136 (13)	7·3
O(34)	0·6311 (11)	0·6048 (10)	0·7090 (13)	7·6
O(4)	0·0904 (9)	−0·4437 (8)	0·0600 (12)	8·8

* E.s.d.'s 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 (4/3)trace(β.**G**).

Positional parameters refined for the non-group atoms are given in Table 1; the refined group origins and orientation angles, and the derived C-atom coordinates in Table 2; and the angles ψ and partial descriptions of the **T**, **L** and **S** tensors in Table 3.* All bond lengths and angles determined fall within expected ranges.

Discussion. Infinite, parallel stacks of 4,4′-dinitrobiphenyl molecules dominate the crystal packing of its complex with 4-hydroxybiphenyl (see Figs. 1 and 2); this motif is also found in the structure of the pure compound $C_{12}H_8N_2O_4$ (Boonstra, 1963). In the latter material the lattice repeat in the stacking direction is 3·753 (3) Å, while the corresponding distance in the complex is $b/3 = 3{\cdot}722$ Å. The twists ψ about the central C—C bonds, 33° in the pure compound and 37° in the present complex (see Table 3), are similar, as are the rotations of the nitro groups about the C—N bonds [0, 11° in the pure compound; range 4 (2) to 9 (1)°, average 6·6 (6)° in the complex]. The arrangement of the stacks in the complex is of course altered by the presence of the second component.

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* The full **T**, **L**, and **S** tensors for the rigid groups, **U** tensors for all non-hydrogen atoms, H-atom coordinates and equivalent *B*'s, and observed and calculated structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39322 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Derived parameters for the carbon atoms of the* 3:1 *complex of* 4,4′-*dinitrobiphenyl with* 4-*hydroxybiphenyl*

The atoms of each biphenyl group are numbered C(*n*01) through C(*n*12) consecutively. The central bond connects C(*n*01) and C(*n*07), and C(*n*04) and C(*n*10) are in the *para* positions.

	x	y	z	B(Å^2)		x	y	z	B(Å^2)
C(101)	−0·0742 (6)	0·0081 (6)	0·4587 (8)	3·0	C(301)	−0·0122 (5)	0·6671 (5)	0·4930 (7)	3·6
C(102)	−0·1452 (7)	0·0552 (7)	0·5446 (8)	3·7	C(302)	−0·0836 (6)	0·7098 (6)	0·5803 (8)	4·0
C(103)	−0·2873 (7)	0·0780 (7)	0·4736 (9)	4·0	C(303)	−0·2256 (6)	0·7326 (7)	0·5089 (9)	4·4
C(104)	−0·3583 (6)	0·0536 (7)	0·3165 (9)	3·5	C(304)	−0·2963 (5)	0·7126 (7)	0·3501 (9)	4·5
C(105)	−0·2874 (7)	0·0065 (7)	0·2305 (8)	3·7	C(305)	−0·2250 (6)	0·6698 (8)	0·2628 (8)	4·4
C(106)	−0·1453 (7)	−0·0163 (7)	0·3016 (8)	3·5	C(306)	−0·0829 (6)	0·6470 (7)	0·3343 (7)	3·9
C(107)	0·0780 (6)	−0·0163 (6)	0·5348 (8)	3·1	C(307)	0·1400 (5)	0·6427 (5)	0·5696 (7)	3·5
C(108)	0·1480 (7)	−0·0613 (7)	0·6919 (8)	3·7	C(308)	0·2097 (6)	0·5941 (6)	0·7252 (8)	4·1
C(109)	0·2901 (7)	−0·0841 (7)	0·7630 (9)	4·1	C(309)	0·3517 (6)	0·5713 (7)	0·7966 (9)	4·4
C(110)	0·3621 (6)	−0·0619 (7)	0·6770 (9)	4·0	C(310)	0·4241 (5)	0·5972 (7)	0·7125 (9)	4·0
C(111)	0·2921 (7)	−0·0169 (7)	0·5200 (8)	4·2	C(311)	0·3544 (6)	0·6458 (8)	0·5570 (8)	4·0
C(112)	0·1501 (7)	0·0059 (7)	0·4489 (8)	3·7	C(312)	0·2124 (6)	0·6685 (7)	0·4855 (7)	3·8
C(201)	−0·1371 (6)	0·3483 (5)	0·4266 (7)	4·1	C(401)	0·01441 (8)	−0·068082 (5)	0·00826 (9)	3·6
C(202)	−0·2074 (6)	0·3984 (7)	0·5120 (8)	4·8	C(402)	−0·09295 (19)	−0·13426 (12)	−0·0437 (7)	4·5
C(203)	−0·3494 (6)	0·4213 (7)	0·4417 (10)	4·9	C(403)	−0·0660 (3)	−0·26135 (12)	−0·0283 (7)	4·9
C(204)	−0·4212 (6)	0·3940 (7)	0·2860 (10)	4·4	C(404)	0·0682 (4)	−0·322254 (10)	0·0391 (4)	4·5
C(205)	−0·3509 (6)	0·3439 (7)	0·2006 (8)	4·9	C(405)	0·1756 (3)	−0·25607 (13)	0·0911 (8)	5·2
C(206)	−0·2088 (6)	0·3211 (7)	0·2709 (7)	4·7	C(406)	0·14869 (13)	−0·12899 (13)	0·0757 (7)	4·6
C(207)	0·0152 (6)	0·3238 (5)	0·5020 (7)	4·1	C(407)	−0·01441 (8)	0·068082 (5)	−0·00826 (9)	3·8
C(208)	0·0858 (6)	0·2819 (7)	0·6602 (8)	4·6	C(408)	−0·14868 (19)	0·12897 (12)	−0·0766 (8)	5·0
C(209)	0·2279 (6)	0·2590 (7)	0·7305 (10)	4·9	C(409)	−0·1756 (3)	0·25606 (12)	−0·0920 (8)	6·0
C(210)	0·2993 (6)	0·2781 (7)	0·6426 (10)	4·6	C(410)	−0·0682 (4)	0·322254 (10)	−0·0391 (5)	5·5
C(211)	0·2286 (6)	0·3200 (7)	0·4844 (8)	4·7	C(411)	0·0660 (3)	0·26136 (13)	0·0293 (8)	5·5
C(212)	0·0866 (6)	0·3428 (7)	0·4141 (7)	4·6	C(412)	0·09295 (13)	0·13428 (13)	0·0447 (8)	4·7

Rigid-group parameters

Group	x_C	y_C	z_C	δ	ε	η
BIPH(1)	0·0019 (6)	−0·0041 (6)	0·4967 (8)	−1·5844 (12)	−3·1373 (13)	1·904 (4)
BIPH(2)	−0·0610 (6)	0·3360 (5)	0·4643 (7)	−1·5851 (13)	3·1407 (16)	1·933 (4)
BIPH(3)	0·0639 (5)	0·6549 (5)	0·5313 (7)	−1·5842 (12)	−3·1348 (15)	1·861 (4)
BIPH(4)	0	0	0	0·1905 (11)	3·1277 (10)	3·140 (5)

x_C, y_C and z_C are the fractional coordinates of the origin of the rigid group. The rigid-group orientation angles δ, ε and η (rad) have been defined previously: La Placa & Ibers (1965).

Table 3. *Partial description of the thermal motion tensors refined for the* 3:1 *complex of* 4,4′-*dinitrobiphenyl with* 4-*hydroxybiphenyl*

Group	BIPH(1)	BIPH(2)	BIPH(3)	BIPH(4)
T^{11} (Å^2 × 10^3)*	37 (3)	56 (5)	36 (4)	38 (2)
T^{22}	41 (1)	59 (3)	54 (2)	80 (2)
T^{33}	39 (3)	40 (4)	42 (4)	19 (3)
Eigenvalues of **T**	37,38,42	39,51,65	34,44,55	19,38,80
L^{11} (deg^2)	1 (1)	1 (1)	3 (1)	8 (1)
L^{22}	39 (10)	47 (11)	18 (11)	75 (14)
L^{33}	5 (2)	3 (2)	4 (2)	5 (1)
Eigenvalues of **L**	1,5,39	0,4,47	1,7,18	5,9,75
Ω^2†	−4 (15)	−15 (15)	13 (16)	−10 (21)
ψ (°)	37·4 (3)	37·2 (3)	37·0 (3)	0·5 (5)

* The y axis of the group system is parallel to the long molecular axis, the z axis is perpendicular to the phenyl ring composed of atoms C(*n*01) through C(*n*06), and the x axis completes the orthonormal system. The origin is at the center of the central C–C bond.

† The values of Ω^2 are such that $L^{22} + \Omega^2$ is the librational component $L^{22'}$ about the group y axis of the phenyl ring composed of atoms C(*n*07) through C(*n*12).

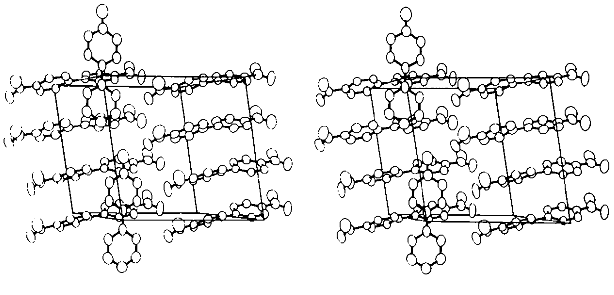

Fig. 2. Stereoscopic view of the unit cell of the 3:1 complex of 4,4′-dinitrobiphenyl with 4-hydroxybiphenyl. The *a* axis points from left to right, the *b* axis points downwards, and the *c* axis points into the plane of the paper.

We were surprised to discover that the 4-hydroxybiphenyl molecules are ordered within the channels between the 4,4′-dinitrobiphenyl stacks, and that all the columns of 4-hydroxybiphenyl molecules have the same orientation. As a result, the macroscopic crystal must be strongly polar. A hydrogen bond between the hydroxyl group and a neighboring nitro group accounts for the ordering. The distances [O(4)···O(21) 2·971 (12), O(4)···O(22) 3·364 (25) Å] show that the hydroxyl group does not interact symmetrically with the two O atoms of the nitro group.

The thermal-motion descriptions for the two components of the complex are markedly different (see Table 3). The **T** tensors for the three 4,4′-dinitrobiphenyl molecules are all roughly isotropic, and their eigenvalues are similar (average 0·045 Å^2). The environments of these three molecules are nearly the same. In comparison, the anisotropy of the **T** tensor for the 4-hydroxybiphenyl molecule, which has a very different environment, is pronounced. Not surprisingly, its largest component, 0·080 (2) Å^2, corresponds to a translation of the molecule along the channel, while its smallest component, 0·019 (3) Å^2, describes motion perpendicular to the molecular plane.

The L^{22} components for the two types of molecules also differ. The mean-square librational amplitude $\langle L^{22}\rangle$ of the six 4-nitrophenyl moieties about their long molecular axes is 34 (4) deg^2; the three corresponding twist angles ψ about the central C—C bonds are all 37°. These values are similar to those found for 4,4′-dichlorobiphenyl [$\langle L^{22}\rangle = 38$ (2) deg^2, $\psi = 39, 42°$; Brock, Kuo & Levy, 1978] and 4-biphenylcarboxylic acid [$\langle L^{22}\rangle = 50$ (5) deg^2, $\psi = 29, 36, 32°$; Brock, Blackburn & Haller, 1984]. On the other hand, $\langle L^{22}\rangle$ for the two rings of the 4-hydroxybiphenyl molecule, which is almost planar with $\psi = 0{\cdot}5\,(5)°$, is much larger at 70 (5) deg^2.

Unfortunately, in biphenyl and its simple derivatives it is not possible to separate the contributions to the observed L^{22} values of molecular libration about the long molecular axis (here y) and of intramolecular torsion about the central C—C bond. The two motions differ only in the relative phases of the two phenyl rings, information that is inaccessible in an ordinary diffraction experiment. Static disorder may, of course, also add to the measured **TLS** tensors, but its contribution can be deduced from measurements at several temperatures. With all that in mind, we make the following inferences about the 4-hydroxybiphenyl molecule as it is observed in this structure.

While the value of $\langle L^{22}\rangle$ in the nearly-planar 4-hydroxybiphenyl is almost twice as large as is observed for several other twisted biphenyl derivatives (see above), it is much smaller than the values of 178 deg^2 and upwards found for the central rings of *p*-terphenyl and *p*-quaterphenyl at temperatures above their order–disorder phase transitions (Cailleau *et al.*, 1980). We therefore conclude that the 4-hydroxybiphenyl molecule in this structure is not affected by any important static disorder. It then follows that the contribution of the inter-ring torsion to L^{22} for this molecule must be much larger than in molecules crystallizing with ψ of 30 to 40°. That result is not unexpected considering that there is a maximum in the intramolecular energy surface at $\psi = 0°$, and a minimum somewhere between 30 and 45°. Presumably the intermolecular energy for this structure has a minimum at $\psi = 0°$, and the effect of the intramolecular component is either to flatten the bottom of this well or to introduce a central barrier that is small relative to kT (see Cailleau *et al.*, 1980). An approximately equivalent interpretation of the molecular motion for biphenyl itself, which has $L^{22} = 109$ (3) deg^2 at 298 K and $\psi = 0$ by symmetry (Charbonneau & Delugeard, 1977), has been given by Busing (1983).

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