BECALLI, E., MARCHESINI, A. & PILATI, T. (1989). *Tetrahedron,* **45,** 7485–7500.

FRENZ, B. A. (1983). *Enraf–Nonius Structure Determination Package; SDP Users Guide.* Version of 6 January 1983. Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

LARSON, A. C. (1967). *Acta Cryst.* **23,** 664–665.

MAIN, P., FISKE, S. J., HULL, S. E. LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MARCHESINI, A. (1989). Unpublished.

NARDELLI, M. (1983). *Comput. Chem.* **7,** 95–98.

PILATI, T. (1988). *Acta Cryst.* **C44,** 1256–1262.

PILATI, T. (1989). *Acta Cryst.* **C45,** 923–926.

Structures of Double-Hydrogen-Bonded Adducts of 1,8-Biphenylenediol and Related Compounds

BY JACK HINE,† KYUNGHYE AHN, JUDITH C. GALLUCCI* AND SHWN-MEEI LINDEN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA

Abstract. X-ray crystal structures were determined for 1,8-biphenylenediol (1) and its 1:1 adducts with hexamethylphosphoric triamide (4), 2,6-dimethyl-4-pyrone (5) and 1,2,6-trimethyl-4-pyridone (6), for the adduct of 4,5-dinitro-1,8-biphenylenediol (2) with (5), for the adduct of 2,7-dimethyl-1,8-biphenylenediol (3) with (6), and for 1,8-dimethoxybiphenylene (7). 1,8-Biphenylenediol, (1), $C_{12}H_8O_2$, $M_r = 184·20$, orthorhombic, $Pca2_1$, $a = 14·056$ (2), $b = 4·952$ (1), $c = 24·134$ (3) Å, $V = 1680$ Å^3, $Z = 8$, $D_x = 1·46$ g cm^{-3}, λ(Mo $K\bar\alpha$) = 0·71069 Å, $\mu = 0·92$ cm^{-1}, $F(000) = 768$, $T = 150$ K, final $R = 0·048$ for all 1985 unique reflections. 1,8-Biphenylenediol–hexamethylphosphoric triamide, (1.4), $C_{12}H_8O_2$. $C_6H_{18}N_3OP$, $M_r = 363·40$, monoclinic, $P2_1/n$, $a = 8·527$ (1), $b = 15·099$ (4), $c = 15·354$ (3) Å, $\beta = 95·17$ (1)°, $V = 1969$ Å^3, $Z = 4$, $D_x = 1·23$ g cm^{-3}, λ(Mo $K\bar\alpha$) = 0·71069 Å, $\mu = 1·54$ cm^{-1}, $F(000) = 776$, $T = 217$ K, final $R = 0·077$ for the 2351 unique reflections with $F_o{}^2 \geq 2\sigma(F_o{}^2)$. 1,8-Biphenylenediol–2,6-dimethyl-4-pyrone, (1.5), $C_{12}H_8O_2.C_7H_8O_2$, $M_r = 308·34$, triclinic, $P\bar1$, $a = 8·983$ (1), $b = 13·450$ (2), $c = 6·926$ (1) Å, $\alpha = 85·15$ (1), $\beta = 106·19$ (1), $\gamma = 109·72$ (1)°, $V = 756$ Å^3, $Z = 2$, $D_x = 1·35$ g cm^{-3}, λ(Mo $K\bar\alpha$) = 0·71069 Å, $\mu = 0·88$ cm^{-1}, $F(000) = 324$, $T = 148$ K, final $R = 0·048$ for the 2592 unique reflections with $F_o{}^2 \geq 1·5\sigma(F_o{}^2)$. 1,8-Biphenylenediol–1,2,6-trimethyl-4-pyridone, (1.6), $C_{12}H_8O_2.C_8H_{11}NO$, $M_r = 321·38$, monoclinic, $P2_1/n$, $a = 7·639$ (1), $b = 22·130$ (4), $c = 9·411$ (1) Å, $\beta = 90·66$ (1)°, $V =$

1591 Å^3, $Z = 4$, $D_x = 1·34$ g cm^{-3}, λ(Mo $K\bar\alpha$) = 0·71069 Å, $\mu = 0·84$ cm^{-1}, $F(000) = 680$, $T = 150$ K, final $R = 0·048$ for the 2188 unique reflections with $F_o{}^2 \geq 3\sigma(F_o{}^2)$. 4,5-Dinitro-1,8-biphenylenediol–2,6-dimethyl-4-pyrone, (2.5), $C_{12}H_6N_2O_6.C_7H_8O_2$, $M_r = 398·33$, monoclinic, $P2_1/n$, $a = 12·298$ (4), $b = 9·173$ (2), $c = 16·247$ (6) Å, $\beta = 102·59$ (2)°, $V = 1789$ Å^3, $Z = 4$, $D_x = 1·48$ g cm^{-3}, λ(Mo $K\bar\alpha$) = 0·71069 Å, $\mu = 1·10$ cm^{-1}, $F(000) = 824$, $T = 292$ K, final $R = 0·122$ for 1886 unique observed reflections with $F_o{}^2 \geq 0$. 2,7-Dimethyl-1,8-biphenylenediol–1,2,6-trimethyl-4-pyridone, (3.6), $C_{14}H_{12}O_2.C_8H_{11}NO$, $M_r = 349·43$, orthorhombic, *Cmca*, $a = 20·489$ (5), $b = 7·736$ (1), $c = 24·930$ (6) Å, $V = 3951$ Å^3, $Z = 8$, $D_x = 1·17$ g cm^{-3}, λ(Mo $K\bar\alpha$) = 0·71069 Å, $\mu = 0·73$ cm^{-1}, $F(000) = 1488$, $T = 294$ K, final $R = 0·130$ for the 921 unique observed reflections with $F_o{}^2 \geq 0$. 1,8-Dimethoxybiphenylene, (7), $C_{14}H_{12}O_2$, $M_r = 212·25$, monoclinic, $P2_1/c$, $a = 15·378$ (3), $b = 13·360$ (3), $c = 10·896$ (2) Å, $\beta = 109·57$ (1)°, $V = 2109$ Å^3, $Z = 8$, $D_x = 1·34$ g cm^{-3}, λ(Mo $K\bar\alpha$) = 0·71069 Å, $\mu = 0·83$ cm^{-1}, $F(000) = 896$, $T = 159$ K, final $R = 0·041$ for the 3011 unique observed reflections with $F_o{}^2 \geq 3\sigma(F_o{}^2)$. Each molecule of (1) is hydrogen bonded through its two hydroxy groups, either as donor or acceptor, to four other molecules of (1). For each of the five adducts both hydroxylic H atoms of the diol are hydrogen bonded to the same basic O atom of the base. This basic O atom is within 0·45 Å of the least-squares plane of the biphenylene ring in all cases. In the adducts the distances between the two hydroxy O atoms are increased to an average 4·28 (4) from the average

---

† Deceased 6 July 1988.

* Author to whom correspondence should be addressed.

3·88 (6) Å found in (1). The average O—O distances in the hydrogen bonds of the adducts range from 2·546 (3) to 2·607 (9) Å, which show that these hydrogen bonds are rather strong. These distances tend to decrease with increasing basicity of the base and increasing acidity of the diols. In (7) both methoxy groups are essentially coplanar with the biphenylene ring; one is *syn* and the other is *anti*. The six-membered rings in the biphenylene moieties of all the compounds show the characteristic alternation in bond lengths, which tends to keep double-bond character out of the four-membered rings.

Introduction. Molecules that are capable of forming two strong acidic hydrogen bonds simultaneously with the same basic atom are expected to be effective hydrogen-bonding agents. The geometry of 1,8-biphenylenediol (1), in the conformation with the hydroxy groups coplanar with the rings and with the H atoms oriented inward, is almost optimum for this purpose.
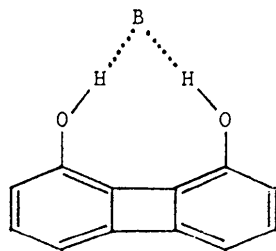

(1)

A preliminary account of the single-crystal X-ray structures of the 1:1 adducts of (1) with hexamethylphosphoric triamide (4), with 2,6-dimethyl-4-pyrone (5), and with 1,2,6-trimethyl-4-pyridone (6) reported that two strong hydrogen bonds are formed between (1) and an O atom in each of these bases (Hine, Ahn, Gallucci & Linden, 1984). Determination of the equilibrium constants for hydrogen bonding by (1) to various bases in cyclohexane (Hine, Hahn & Miles, 1986) and by 4,5-dinitro-1,8-biphenylenediol (2) to various bases in chloroform (Hine & Ahn, 1987*a*), along with measurements of the activity of (1) as a catalyst (Hine, Linden & Kanagasabapathy, 1985*a,b*) indicate that this double hydrogen bonding also occurs in solution.

In addition to the full structural reports for the (1.4), (1.5) and (1.6) adducts, we present here the structures for two new 1:1 adducts involving derivatives of 1,8-biphenylenediol: the adduct of (2), whose acidity (Hine & Ahn, 1987*b*) is more than 200 times that of (1) but whose steric factors around the two hydroxy groups are not expected to be significantly different from (1), with (5), and the adduct of 2,7-dimethyl-1,8-biphenylenediol (3), whose acidity

(Hine, Hahn, Miles & Ahn, 1985) is about the same as that of (1) but whose hydroxy groups are both flanked by *ortho* methyl substituents, with (6).

The structures of 1,8-biphenylenediol (1) and 1,8-dimethoxybiphenylene (7) are also reported here for comparison with the 1:1 adducts.

(1) *X* = *Y* = *Z* = H

(2) *X* = *Y* = H, *Z* = NO₂

(3) *X* = *Z* = H, *Y* = Me

(7) *X* = Me, *Y* = *Z* = H
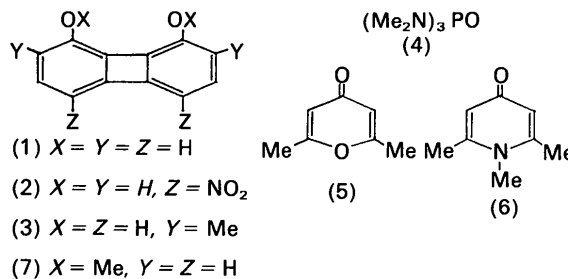
Experimental. For all the structures, intensity data were measured by the ω–2θ scan technique using a Syntex (Nicolet) $P\bar{1}$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation [$\lambda(K\alpha_1) = 0.70926$ Å]; for data collection below room temperature a Syntex LT-1 low-temperature device was used. In each structure determination six standard reflections were measured after every 100 reflections during data collection and indicated a negligible decay rate, except in the cases of (1) and (1.4). Both data sets were corrected for the small amount of decomposition: the intensities at the end of data collection had decreased on average by about 2% for (1) and 4% for (1.4). All data sets were corrected for Lorentz and polarization effects and put onto an approximately absolute scale by means of a Wilson plot with the *CRYM* crystallographic system (Duchamp, 1964).*

Each structure was solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), with the full model developed by standard Fourier methods. With the exception of (1), all full-matrix least-squares refinements were performed with the *SHELX*76 package (Sheldrick, 1976), where the function minimized in least squares is $\sum w^2(k|F_o| - |F_c|)^2$ with $w = 1/[\sigma(F_o)]$. For (1), least-squares refinements were performed with the *CRYM* crystallographic computing package (Duchamp, 1964), where the function minimized is $\sum w^2(k^2|F_o|^2 - |F_c|^2)^2$ with $w = 1/[\sigma(F_o^2)]$. Scattering factors for the non-H atoms of (1) were from *Inter-*

---

* Integrated intensities were calculated as $I = R[C - T(B_1 + B_2)]$ where R is the variable scan rate, C is the scan count, B_1 and B_2 are the background counts, and T is the ratio of the scan time to the total background counting time, which is equal to 2·0 for all the structures reported here. The standard deviations in the observations were calculated as $\sigma^2(I) = R^2[C + T^2(B_1 + B_2)] + (pI)^2$ where the terms are the same as those defined above, with a value of 0·02 for p to account for the standard deviation being proportional to the diffracted intensity.

Table 1. *Crystallographic details for* 1,8-*biphenylenediol and related compounds*

	(1)	(1.4)	(1.5)	(1.6)	(2.5)	(3.6)	(7)
Crystal size (mm)	$0.24 \times 0.28 \times 0.66$	$0.38 \times 0.51 \times .0.51$	$0.13 \times 0.29 \times 0.36$	$0.17 \times 0.29 \times 0.48$	$0.04 \times 0.26 \times 0.53$	$0.05 \times 0.33 \times 0.34$	$0.33 \times 0.44 \times 0.48$
2θ limits (°)	$4 \le 2\theta \le 55$	$4 \le 2\theta \le 48$	$4 \le 2\theta \le 55$	$4 \le 2\theta \le 57$	$4 \le 2\theta \le 45$	$4 \le 2\theta \le 42$	$4 \le 2\theta \le 55$
Data collected, h,k,l	0–18, 0–6, 0–31	−9–9, 0–17, 0–17	−11–10, −16–17, 0–9	−10–10, 0–29, 0–12	−13–12, 0–9, 0–17	0–20, 0–7, 0–24	−19–18, 0–17, 0–14
Scan speed (°min⁻¹ in 2θ)	2.0–24.0	2.0–24.0	2.0–24.0	2.0–24.0	2.0–24.0	1.0–12.0	4.0–24.0
Scan range (°)	$(K\alpha_1 - 0.9)$ to $(K\alpha_2 + 0.9)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.1)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.1)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.0)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.0)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.0)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.1)$
Number and 2θ range (°) of reflections used in unit-cell determination	23; 17 to 28	25; 17 to 29	25; 20 to 30	24; 20 to 29	26; 18 to 23	22; 17 to 24	25; 21 to 30
Unique reflections	1985	3108	3488	4063	2334	1105	4866
Unique reflections used in refinement	1985	2351	2592	2188	1886	921	3011
R_{int}		0.018	0.015	0.019	0.027		0.015
Parameters refined	316	234	240	225	270	128	337
R	0.048	0.077	0.048	0.048	0.122	0.130	0.041
wR	0.083	0.064	0.045	0.047	0.051	0.070	0.040
Error in observation of unit weight	$1.57e^2$	$2.12e$	$1.74e$	$1.74e$	$1.33e$	$1.93e$	$1.61e$
$(\Delta/\sigma)_{max}$ in final refinement cycle	0.12	0.11	0.09	0.16	0.06	0.15	0.04
$(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$ in final difference map (e Å⁻³)	0.26, −0.25	0.28, −0.29	0.27, −0.25	0.21, −0.28	0.43, −0.41	0.48, −0.33	0.20, −0.23

national Tables for X-ray Crystallography (1962) and those for the H atoms were obtained from Stewart, Davidson & Simpson (1965). For the other structures reported here the scattering factors used were from *International Tables for X-ray Crystallography* (1974). Crystallographic details are listed in the *Abstract* and in Table 1.

1,8-*Biphenylenediol* (1). Crystallization of (1) from chloroform gave yellow rectangular rods. The crystal system is orthorhombic and the systematic absences, $0kl$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$, are consistent with space groups *Pbcm* and *Pbc2₁* (nonstandard setting for *Pca2₁*).

In accordance with the intensity statistics, *Pbcm* was assumed to be the correct space group. However, *MULTAN*80 (Main *et al.*, 1980) failed to give a reasonable solution, with only a small portion of one molecule appearing on an electron density map. *MULTAN*80 was then tried in the noncentrosymmetric space group *Pbc2₁*, which requires two independent molecules in the asymmetric unit. Both molecules, labeled A and B, were easily located in the resulting electron density map. The data were converted to the standard setting for this space group, *Pca2₁*, in which all further calculations were done.

All H atoms were subsequently located on a difference electron density map and were added to the model and allowed to refine isotropically. Because of the limitations imposed by the *CRYM* least-squares program, the model was blocked during the final stages of the refinement such that molecules A and B were refined in alternate cycles. In the final refinement cycle, the positional parameters of both molecules were refined in one block and the thermal parameters were refined in a second block; for all the 1985 unique reflections, including $F^2 \ge 0$, the final agreement indices are $R = 0.048$ and $wR = 0.083$. A final structure-factor calculation for $F_o^2 \ge 3\sigma(F_o^2)$ gave $R = 0.038$.

The adduct (1.4). The adduct of (1) and (4), denoted (1.4), crystallized from cyclohexane containing a little chloroform as yellow crystals, m.p. 405–407 K. As the crystal appears to undergo a destructive phase transition at a temperature below approximately 203 K, the data collection was performed at 217 K. After anisotropic refinement, most of the H atoms could be located on a difference electron density map, and these H atoms were included in the model at calculated positions with C—H = 1.00 Å. The methyl-group H atoms were idealized to sp^3 geometry. The H atoms bonded to the O atoms of the diol were also located and were allowed to refine isotropically. The final refinement cycle used the 2351 unique reflections with $F_o^2 \ge 2\sigma(F_o^2)$ and 234 variables to yield $R = 0.077$ and $wR = 0.064$.

The adduct (1.5). The adduct of (1) and (5) crystallized as clear yellow plates by slow evaporation from ethyl acetate, m.p. 455–456 K. Successful solution and refinement of the structure was done in space group $P\bar{1}$. All the H atoms, including the methyl H atoms, clearly appeared on a difference electron density map. The methyl and hydroxyl H atoms were refined isotropically; the remaining H atoms were added to the model as fixed contributions in their calculated positions with C—H = 1.00 Å. The final refinement cycle yielded agreement indices of $R = 0.048$ and $wR = 0.045$ based on the 2592 intensities with $F_o^2 \ge 1.5\sigma(F_o^2)$ and the 240 variables.

The adduct (1.6). The adduct of (1) and (6) formed yellow rod-like crystals upon slow evaporation from acetonitrile. The crystals decompose without melting at 541–544 K. After anisotropic refinement all the H atoms, with the exception of the methyl H atoms on C(20), were easily located on a difference electron density map. Upon close inspection of the map there appeared to be two sets of H atoms on C(20), consistent with a rotation of the methyl group about the N(4)—C(20) bond. H atoms were added to the

model as fixed contributions in their calculated positions with C—H = 1·00 Å. Two sets of methyl H atoms on C(20) were included, each with a population factor of 0·5, since both sets appeared on the difference map with roughly equivalent electron densities. The hydroxyl H atoms were allowed to refine isotropically. The final refinement cycle resulted in agreement indices of $R = 0·048$ and $wR = 0·047$ for the 2188 intensities with $F_o^2 \geq 3\sigma(F_o^2)$ and the 225 variables.

The adduct (2.5). The adduct of (2) and (5) crystallized from a mixture of acetonitrile and benzene as clear orange thin rectangular plates, m.p. 466·5–468 K. Because of the thinness of the crystal used for data collection, the data set was weak; 874 out of the total 2334 unique reflections satisfied the condition $F_o^2 \geq 3\sigma(F_o^2)$. The structure was solved using *MULTAN*80 (Main *et al.*, 1980) with the biphenylenediol molecule input as a random group in order to obtain recognizable features on an electron density map. Once this was done, the whole complex was clearly evident on the map. The data were corrected for absorption by the Gaussian grid method with an $8 \times 8 \times 8$ grid (Coppens, Leiserowitz & Rabinovich, 1965). Transmission factors ranged from 0·973 to 0·995. Methyl H atoms (idealized to sp^3 geometry) and hydroxyl H atoms were included in the model based on their positions as located on an electron density map. The remaining H atoms were also included in the model as fixed contributions in their calculated positions with C—H = 0·98 Å. For the final refinement cycles all the non-H atoms were refined anisotropically, the two hydroxyl H atoms were refined isotropically, and the rest of the H atoms remained as fixed contributions. The final results, $R = 0·122$ and $wR = 0·051$, were based on all 1886 unique intensities with $F^2 \geq 0$ and 270 variables. A structure-factor calculation for those intensities with $F_o^2 \geq 3\sigma(F_o^2)$ gave an R value of 0·048.

The adduct (3.6). The adduct of (3) and (6) crystallized from acetonitrile as very thin yellow plates, m.p. 531–533 K (dec.). The crystal system is orthorhombic and the systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) restrict the space-group possibilities to *Cmca* or *C2cb* (non-standard setting for *Aba*2) with $Z = 8$. Because of the thinness of the data-collection crystal, and the subsequent weakness of the data set, data were only collected out to a 2θ value of 42°. Intensity statistics appear to be centric and the structure was solved in *Cmca*. A crystallographic mirror plane is imposed on the adduct. This plane contains atoms O(3), C(13), N(4) and C(20) of the pyridone ring system and bisects the C(1)—C(7) and C(6)—C(12) bonds of the diol moiety. The data were corrected for absorption by the Gaussian grid method with an $8 \times 8 \times 8$ grid

(Coppens, Leiserowitz & Rabinovich, 1965). Transmission factors ranged from 0·980 to 0·997. After a cycle of anisotropic refinement only the H atoms bonded to C(4), C(5), C(14) and C(18) were included in the model as fixed contributions with C—H = 0·98 Å. The H atom bonded to O(1) was added as a fixed contribution at its position as located on the difference electron density map. No H atoms were added to the methyl C(20) and C(21) atoms because the positions of these H atoms were indeterminate. For the final refinement cycle all non-H atoms were refined anisotropically and all H atoms were fixed, except for the H atom bonded to O(1), which was refined isotropically. The final cycle used all 921 unique intensities with $F_o^2 \geq 0$ and 128 variables, and resulted in agreement indices of $R = 0·130$ and $wR = 0·070$. A final structure-factor calculation on the 479 intensities with $F_o^2 \geq 3\sigma(F_o^2)$ gave an R value of 0·070.

1,8-Dimethoxybiphenylene (7). Compound (7) was synthesized as described previously (Baker, Barton & McOmie, 1958) and crystallized from methanol to give yellow rectangular crystals with well defined faces. The structure was solved with difficulty by *MULTAN*80 (Main *et al.*, 1980). With $Z = 8$, there are two independent molecules to be located in the asymmetric unit. The initial solution from *MULTAN* located one of these molecules; the second molecule was found by standard Fourier techniques. However, this model would not refine below an R value of 0·40. Recycling this model back into *MULTAN* gave a different solution, which refined with no further difficulties.

All the H atoms were ultimately located on a difference electron density map. The H atoms on the biphenylene portion of the molecule were added as fixed contributions in calculated positions with C—H = 1·00 Å, while the H atoms of the methyl groups were isotropically refined. The final refinement cycle on the 3011 intensities with $F_o^2 \geq 3\sigma(F_o^2)$ converged to R and wR values of 0·041 and 0·040, respectively.

Metrical parameters for these seven structures are listed in Tables 2 and 3. The biphenylene, pyrone and pyridone rings are each essentially planar. For this reason only two out of the three angles for an sp^2 hybridized atom are listed in Table 2; the third angle may be calculated to within 0·2°. Final positional parameters for the non-H atoms are listed in Tables 4–10.*

ORTEP drawings (Johnson, 1976) for (1), (1.4), (1.5), (1.6), (2.5), (3.6) and (7) are shown in Fig. 1. A

Table 2. *Bond angles* (°) *in derivatives of* 1,8-*biphenylenediol*

	(1A)*	(1B)*	(1.4)	(1.5)	(1.6)	(2.5)	(3.6)†	(7A)*	(7B)*
O(1)—C(2)—C(1)	120·8 (3)	121·4 (3)	126·2 (4)	128·1 (2)	127·8 (2)	129·1 (6)	128·5 (8)	128·5 (2)	128·1 (2)
O(2)—C(8)—C(7)	125·4 (3)	121·6 (3)	128·3 (4)	127·9 (2)	128·6 (2)	128·7 (6)		119·9 (2)	119·9 (2)
C(1)—C(2)—C(3)	116·5 (3)	116·5 (4)	116·0 (5)	115·7 (2)	115·7 (2)	115·9 (6)	118·2 (7)	116·7 (2)	117·2 (2)
C(7)—C(8)—C(9)	116·8 (3)	116·6 (4)	115·9 (6)	115·8 (2)	115·6 (2)	116·1 (6)		116·0 (2)	116·1 (2)
C(2)—C(3)—C(4)	122·1 (3)	121·8 (3)	122·5 (6)	123·0 (2)	122·7 (2)	123·4 (6)	118·8 (8)	122·3 (2)	122·0 (2)
C(8)—C(9)—C(10)	121·4 (3)	121·2 (3)	122·1 (7)	123·1 (2)	122·9 (2)	122·4 (6)		121·9 (2)	122·1 (2)
C(3)—C(4)—C(5)	121·8 (3)	122·3 (3)	122·7 (7)	121·6 (2)	121·9 (2)	119·9 (7)	123·4 (8)	121·8 (2)	121·7 (2)
C(9)—C(10)—C(11)	122·3 (3)	122·4 (3)	121·9 (8)	121·5 (2)	121·6 (2)	120·8 (5)		122·5 (2)	122·2 (2)
C(4)—C(5)—C(6)	115·4 (3)	115·1 (3)	115·3 (6)	115·1 (2)	114·9 (2)	117·6 (6)	114·1 (7)	115·1 (2)	115·2 (2)
C(10)—C(11)—C(12)	115·1 (3)	115·3 (4)	117·0 (8)	115·1 (2)	115·0 (2)	118·3 (6)		115·0 (2)	115·1 (2)
C(5)—C(6)—C(1)	123·1 (3)	122·9 (3)	123·7 (7)	124·0 (2)	124·2 (2)	121·8 (6)	124·3 (7)	124·2 (2)	124·3 (2)
C(11)—C(12)—C(7)	123·3 (3)	123·3 (3)	121·6 (7)	124·2 (2)	124·6 (2)	121·1 (6)		123·5 (2)	123·7 (2)
C(6)—C(1)—C(2)	121·1 (3)	121·4 (3)	119·9 (5)	120·5 (2)	120·6 (2)	121·2 (6)	121·2 (6)	119·9 (2)	119·7 (2)
C(12)—C(7)—C(8)	121·1 (3)	121·2 (3)	121·5 (5)	120·2 (2)	120·5 (2)	121·2 (6)		121·1 (2)	120·9 (2)
C(1)—C(6)—C(12)	89·8 (3)	89·9 (3)	89·5 (5)	90·6 (1)	90·7 (2)	90·7 (5)	91·0 (6)	90·2 (1)	90·2 (1)
C(7)—C(12)—C(6)	90·0 (3)	89·8 (3)	91·0 (5)	90·4 (1)	90·4 (2)	90·4 (5)		90·4 (1)	90·6 (1)
C(2)—C(1)—C(7)	148·7 (3)	148·4 (4)	149·6 (4)	150·1 (2)	150·0 (2)	149·0 (6)	149·8 (7)	150·6 (2)	150·9 (2)
C(8)—C(7)—C(1)	148·8 (4)	148·6 (4)	149·4 (4)	150·2 (2)	150·0 (2)	149·7 (6)		149·0 (2)	149·2 (2)
H(O1)—O(1)—C(2)	112·2 (26)	108·8 (24)	112·5 (30)	112·9 (16)	115·8 (19)	113·0 (37)	130·4 (51)		
H(O2)—O(2)—C(8)	111·3 (31)	109·5 (23)	112·6 (34)	114·0 (14)	111·2 (17)	110·3 (35)			
O(1)—H(O1)···O(3)			167·6 (48)	175·6 (29)	176·9 (33)	167·3 (59)	144·6 (64)		
O(2)—H(O2)···O(3)			172·4 (46)	177·7 (28)	173·9 (28)	172·0 (57)			
O(1)···O(3)···O(2)			107·1 (4)	112·0 (2)	114·8 (2)	112·7 (4)	113·4 (8)		
O(3)—C(13)—C(14)				122·2 (2)	121·6 (2)	121·6 (7)	121·8 (5)		
C(14)—C(13)—C(17)				116·2 (2)	116·1 (2)	114·5 (6)	116·4 (10)		
C(13)—C(14)—C(15)				120·6 (2)	121·7 (2)	120·4 (6)	121·3 (9)		
C(13)—C(17)—C(16)				120·3 (2)	121·7 (3)	122·9 (6)			
C(14)—C(15)—O(4)				121·3 (2)		122·4 (6)			
C(17)—C(16)—O(4)				121·6 (2)		120·5 (6)			
C(15)—O(4)—C(16)				120·2 (2)		119·3 (5)			
C(18)—C(15)—O(4)				111·4 (2)		110·7 (6)			
C(19)—C(16)—O(4)				111·5 (2)		111·3 (6)			
C(14)—C(15)—N(4)					120·1 (2)		120·8 (8)		
C(17)—C(16)—N(4)					120·0 (2)				
C(15)—N(4)—C(16)					120·4 (2)		119·0 (8)		
C(18)—C(15)—N(4)					118·8 (2)		118·9 (7)		
C(19)—C(16)—N(4)					118·8 (2)				
C(15)—N(4)—C(20)					119·7 (2)		120·5 (5)		
O(3)—P—N(1)			109·4 (2)						
O(3)—P—N(2)			109·3 (2)						
O(3)—P—N(3)			113·3 (2)						
N(1)—P—N(2)			108·9 (2)						
N(1)—P—N(3)			106·8 (2)						
N(2)—P—N(3)			109·0 (2)						
P—N(1)—C(1N1)			119·2 (3)						
P—N(1)—C(2N1)			126·5 (3)						
C(1N1)—N(1)—C(2N1)			112·1 (4)						
P—N(2)—C(1N2)			120·2 (5)						
P—N(2)—C(2N2)			122·3 (5)						
C(1N2)—N(2)—C(2N2)			116·0 (5)						
P—N(3)—C(1N3)			124·3 (4)						
P—N(3)—C(2N3)			119·8 (4)						
C(1N3)—N(3)—C(2N3)			114·9 (4)						
C(4)—C(5)—N(5)						119·2 (7)			
C(12)—C(11)—N(6)						122·5 (6)			
C(5)—N(5)—O(5)						117·6 (6)			
C(11)—N(6)—O(7)						118·4 (6)			
O(5)—N(5)—O(6)						123·8 (7)			
O(7)—N(6)—O(8)						123·1 (6)			
C(2)—C(3)—C(21)							121·4 (8)		
C(23)—O(1)—C(2)								115·3 (2)	115·2 (1)
C(24)—O(2)—C(8)								117·4 (2)	117·7 (2)

* (1A) and (1B) and (7A) and (7B) are the crystallographically nonequivalent molecules of (1) and (7).

† The crystallographic mirror plane contains the C(20), N(4), C(13) and O(3) atoms, and bisects the C(1)—C(7) and C(6)—C(12) bonds.

common labeling scheme has been used throughout in order to facilitate comparisons among the structures.

Discussion. These seven structures display various kinds of hydrogen-bonding interactions which may be classified as follows: 1,8-biphenylenediol (1) contains intermolecular (O—H···O) hydrogen bonds, each of the five adducts [(1.4), (1.5), (1.6), (2.5) and (3.6)] forms a double-hydrogen-bonded system where both hydroxy groups of the diol are hydrogen bonded to the same O atom of the base, and 1,8-dimethoxybiphenylene (7) contains intramolecular (C—H···O) hydrogen bonds. The double-hydrogen-bonded system of the adducts is of primary interest here since there are few reports of this type of structure (Hine *et al.*, 1984). The formation of double hydrogen bonds has several effects on the geometry of the 1,8-biphenylenediol component of each adduct and these effects can be assessed by comparison with the structure of (1) alone.

1,8-*Biphenylenediol* (1). Each O atom is involved in two intermolecular hydrogen bonds and these bonds are between molecules *A* and *B*. In one of these

Table 3. *Bond distances* (Å) *in* 1,8-*biphenylenediol and related compounds*

	(1A)*	(1B)*	(1.4)	(1.5)	(1.6)	(2.5)	(3.6)†	(7A)*	(7B)*
O(1)—C(2)	1·381 (4)	1·379 (5)	1·338 (5)	1·350 (2)	1·351 (3)	1·341 (7)	1·347 (8)	1·361 (2)	1·362 (2)
O(2)—C(8)	1·381 (5)	1·381 (4)	1·337 (6)	1·350 (2)	1·353 (3)	1·340 (6)		1·364 (2)	1·365 (2)
C(1)—C(2)	1·359 (5)	1·363 (4)	1·383 (6)	1·371 (2)	1·374 (3)	1·373 (7)	1·346 (8)	1·363 (2)	1·365 (2)
C(7)—C(8)	1·356 (4)	1·366 (5)	1·367 (6)	1·376 (2)	1·369 (3)	1·365 (7)		1·372 (2)	1·370 (2)
C(2)—C(3)	1·412 (4)	1·413 (5)	1·400 (6)	1·418 (2)	1·424 (3)	1·416 (8)	1·405 (10)	1·418 (3)	1·411 (2)
C(8)—C(9)	1·418 (5)	1·416 (4)	1·420 (6)	1·411 (3)	1·423 (3)	1·434 (7)		1·411 (2)	1·409 (2)
C(3)—C(4)	1·376 (5)	1·371 (6)	1·362 (8)	1·372 (3)	1·371 (4)	1·366 (8)	1·409 (10)	1·367 (3)	1·377 (3)
C(9)—C(10)	1·378 (5)	1·386 (6)	1·365 (9)	1·372 (3)	1·372 (3)	1·356 (7)		1·372 (2)	1·376 (3)
C(4)—C(5)	1·417 (5)	1·411 (5)	1·380 (8)	1·408 (3)	1·416 (3)	1·403 (7)	1·415 (10)	1·415 (3)	1·414 (3)
C(10)—C(11)	1·422 (4)	1·406 (5)	1·376 (9)	1·412 (3)	1·414 (3)	1·391 (7)		1·405 (2)	1·406 (3)
C(5)—C(6)	1·362 (4)	1·375 (5)	1·363 (8)	1·367 (2)	1·366 (3)	1·374 (7)	1·342 (8)	1·358 (2)	1·358 (2)
C(11)—C(12)	1·358 (5)	1·366 (4)	1·378 (8)	1·361 (3)	1·353 (3)	1·368 (6)		1·363 (2)	1·361 (2)
C(1)—C(6)	1·428 (5)	1·412 (5)	1·413 (6)	1·421 (2)	1·419 (3)	1·409 (7)	1·409 (9)	1·424 (2)	1·427 (2)
C(7)—C(12)	1·428 (5)	1·415 (5)	1·411 (6)	1·422 (2)	1·422 (3)	1·424 (7)		1·413 (2)	1·415 (2)
C(1)—C(7)	1·514 (4)	1·504 (4)	1·505 (6)	1·522 (2)	1·528 (3)	1·520 (7)	1·554 (14)	1·520 (2)	1·520 (2)
C(6)—C(12)	1·520 (4)	1·512 (4)	1·493 (8)	1·496 (2)	1·502 (3)	1·494 (7)	1·504 (14)	1·504 (2)	1·502 (2)
O(1)—H(O1)	0·84 (4)	0·85 (3)	0·88 (4)	0·92 (3)	1·02 (3)	0·90 (5)	0·78 (6)		
O(2)—H(O2)	0·78 (5)	0·90 (4)	0·76 (4)	0·96 (3)	0·90 (3)	0·97 (6)			
O(1)···O(2)	3·923 (4)	3·835 (4)	4·193 (6)	4·290 (2)	4·290 (3)	4·261 (7)	4·271 (13)	4·075 (2)	4·083 (2)
H(O1)···O(3)			1·73 (5)	1·67 (3)	1·53 (4)	1·66 (6)	1·88 (6)		
H(O2)···O(3)			1·86 (4)	1·63 (3)	1·65 (3)	1·61 (6)			
O(1)···O(3)			2·601 (5)	2·585 (2)	2·545 (3)	2·546 (7)	2·554 (7)		
O(2)···O(3)			2·613 (5)	2·589 (2)	2·548 (3)	2·573 (6)			
O(3)—C(13)				1·262 (2)	1·286 (3)	1·255 (6)	1·298 (12)		
C(13)—C(14)				1·422 (3)	1·407 (3)	1·434 (7)	1·397 (8)		
C(13)—C(17)				1·426 (3)	1·404 (4)	1·428 (8)			
C(14)—C(15)				1·339 (3)	1·358 (3)	1·331 (7)	1·360 (9)		
C(16)—C(17)				1·341 (3)	1·361 (4)	1·318 (8)			
C(15)—O(4)				1·361 (2)		1·361 (6)			
C(16)—O(4)				1·355 (2)		1·369 (6)			
C(15)—C(18)				1·480 (3)	1·499 (4)	1·502 (7)	1·480 (9)		
C(16)—C(19)				1·480 (3)	1·498 (4)	1·485 (8)			
C(15)—N(4)					1·367 (3)		1·368 (9)		
C(16)—N(4)					1·368 (3)				
N(4)—C(20)					1·476 (3)		1·503 (12)		
P—O(3)			1·488 (3)						
P—N(1)			1·614 (3)						
P—N(2)			1·622 (4)						
P—N(3)			1·624 (4)						
N(1)—C(1N1)			1·453 (5)						
N(1)—C(2N1)			1·435 (6)						
N(2)—C(1N2)			1·450 (7)						
N(2)—C(2N2)			1·449 (8)						
N(3)—C(1N3)			1·445 (6)						
N(3)—C(2N3)			1·451 (6)						
C(5)—N(5)						1·448 (7)			
C(11)—N(6)						1·450 (7)			
N(5)—O(5)						1·224 (6)			
N(6)—O(7)						1·218 (5)			
N(5)—O(6)						1·209 (6)			
N(6)—O(8)						1·230 (5)			
C(3)—C(21)							1·542 (9)		
O(1)—C(23)								1·426 (2)	1·422 (2)
O(2)—C(24)								1·427 (2)	1·428 (2)

* (1A) and (1B) and (7A) and (7B) are the crystallographically nonequivalent molecules of (1) and (7).
† The crystallographic mirror plane contains the C(20), N(4), C(13) and O(3) atoms, and bisects the C(1)—C(7) and C(6)—C(12) bonds.

interactions the O atom is a hydrogen-bond donor; in the other it is a hydrogen-bond acceptor. As a result, the two O atoms in a given diol molecule are involved in hydrogen bonding with an O atom in each of four other different diol molecules. The hydrogen bonds form a set of infinite chains which lie approximately parallel to the direction of the *b* axis. The set of chains composes a plane which is roughly perpendicular to the *c* axis.

The hydrogen bonds in (1) are longer and therefore presumably weaker than those in the adducts of (1) with (4), (5) and (6). They range in O—O distance from 2·752 (3) to 2·828 (3) Å for the four crystallographically nonequivalent hydrogen bonds as shown in Table 11. Such weaker hydrogen bonds would be expected since the O atoms of (1) are more weakly

basic than those in (4), (5) and (6). The O—H···O angles range from 168 (3) to 174 (4)°. The O—H bonds in (1), O(1)—H and O(2)—H, are at dihedral angles of 20 (3) and 133 (4)°, respectively, with the C(2)—C(3) and C(8)—C(9) bonds in molecule *A*, so that both O—H bonds point roughly along the same direction; in molecule *B* these bonds form dihedral angles of 20 (3) and 23 (3)°, respectively, with the C(2)—C(3) and C(8)—C(9) bonds, so that these O—H bonds point in opposite directions. An ORTEP drawing of *A* is shown in Fig. 1(*a*); since *B* looks essentially the same, except for the differing direction of the O(2)—H bond as described above, it is not shown in this figure.

A stereo drawing of the packing in the unit cell is shown in Fig. 2. There is a pseudo-inversion center

Table 4. *Final positional parameters for* (1)

E.s.d.'s in the least significant figures are given in parentheses in this and all subsequent tables. $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1A)	0·1579 (2)	0·5516 (4)	0·3763	1·89 (9)
O(2A)	−0·0386 (2)	−0·0054 (4)	0·3927 (1)	2·02 (9)
C(1A)	0·1283 (2)	0·3675 (6)	0·4658 (2)	1·6 (1)
C(2A)	0·1762 (2)	0·5416 (6)	0·4324 (2)	1·5 (1)
C(3A)	0·2462 (2)	0·7036 (6)	0·4580 (2)	1·6 (1)
C(4A)	0·2646 (2)	0·6896 (6)	0·5140 (2)	1·6 (1)
C(5A)	0·2154 (2)	0·5073 (6)	0·5490 (2)	1·6 (1)
C(6A)	0·1481 (2)	0·3528 (6)	0·5237 (2)	1·6 (1)
C(7A)	0·0516 (2)	0·1553 (6)	0·4722 (2)	1·5 (1)
C(8A)	−0·0161 (2)	−0·0020 (6)	0·4484 (2)	1·5 (1)
C(9A)	−0·0638 (2)	−0·1872 (6)	0·4836 (2)	1·7 (1)
C(10A)	−0·0436 (2)	−0·2017 (6)	0·5394 (2)	1·8 (1)
C(11A)	0·0259 (2)	−0·0340 (6)	0·5649 (2)	1·8 (1)
C(12A)	0·0712 (2)	0·1393 (6)	0·5301 (2)	1·6 (1)
O(1B)	0·2223 (2)	1·0489 (4)	0·3353 (1)	1·91 (9)
O(2B)	0·4143 (2)	0·5035 (4)	0·35026 (9)	1·99 (9)
C(1B)	0·2933 (2)	0·8649 (6)	0·2536 (2)	1·5 (1)
C(2B)	0·2312 (2)	1·0381 (6)	0·2785 (2)	1·5 (1)
C(3B)	0·1769 (2)	1·2044 (6)	0·2429 (2)	1·8 (1)
C(4B)	0·1857 (2)	1·1911 (6)	0·1864 (2)	1·8 (1)
C(5B)	0·2490 (2)	1·0108 (6)	0·1601 (2)	1·7 (1)
C(6B)	0·3018 (2)	0·8521 (6)	0·1953 (2)	1·6 (1)
C(7B)	0·3698 (2)	0·6546 (6)	0·2595 (2)	1·5 (1)
C(8B)	0·4226 (2)	0·4917 (6)	0·2933 (2)	1·5 (1)
C(9B)	0·4862 (2)	0·3109 (6)	0·2670 (2)	1·8 (1)
C(10B)	0·4944 (2)	0·3026 (6)	0·2098 (2)	1·9 (1)
C(11B)	0·4399 (2)	0·4691 (6)	0·1748 (2)	1·8 (1)
C(12B)	0·3789 (2)	0·6411 (6)	0·2012 (2)	1·5 (1)

Table 5. *Final positional parameters for* (1.4)

	x	y	z	$B_{eq}(\text{Å}^2)$
P	0·2214 (1)	0·04247 (8)	0·28288 (7)	4·61 (5)
O(3)	0·3853 (3)	0·0748 (2)	0·2785 (2)	5·7 (2)
N(1)	0·2221 (4)	−0·0407 (2)	0·3490 (2)	5·5 (2)
N(2)	0·1153 (5)	0·1211 (3)	0·3193 (3)	7·2 (2)
N(3)	0·1392 (5)	0·0087 (3)	0·1892 (3)	6·6 (2)
C(1N1)	0·3086 (6)	−0·0340 (3)	0·4346 (3)	7·2 (3)
C(2N1)	0·1134 (8)	−0·1134 (4)	0·3438 (4)	9·8 (4)
C(1N2)	0·1397 (9)	0·2122 (4)	0·2938 (5)	11·8 (4)
C(2N2)	−0·0278 (9)	0·1035 (6)	0·3605 (5)	13·4 (5)
C(1N3)	0·0069 (7)	0·0519 (4)	0·1413 (3)	8·9 (3)
C(2N3)	0·2164 (8)	−0·0581 (4)	0·1403 (4)	8·9 (3)
O(1)	0·5312 (4)	0·1638 (2)	0·4063 (2)	5·8 (2)
O(2)	0·5283 (5)	0·1082 (3)	0·1386 (2)	7·0 (2)
C(1)	0·6627 (4)	0·2554 (3)	0·3053 (3)	5·0 (2)
C(2)	0·6198 (5)	0·2330 (3)	0·3872 (3)	4·8 (2)
C(3)	0·6797 (6)	0·2874 (4)	0·4562 (4)	7·0 (3)
C(4)	0·7739 (8)	0·3583 (4)	0·4441 (6)	9·7 (4)
C(5)	0·8166 (7)	0·3826 (4)	0·3628 (6)	9·6 (4)
C(6)	0·7588 (6)	0·3302 (4)	0·2952 (5)	7·5 (3)
C(7)	0·6626 (5)	0·2348 (3)	0·2093 (3)	5·2 (2)
C(8)	0·6171 (6)	0·1812 (4)	0·1398 (3)	6·1 (3)
C(9)	0·6735 (7)	0·2053 (5)	0·0589 (4)	8·9 (4)
C(10)	0·7698 (9)	0·2766 (6)	0·0512 (5)	11·6 (6)
C(11)	0·8141 (8)	0·3310 (5)	0·1211 (6)	10·7 (5)
C(12)	0·7592 (6)	0·3094 (4)	0·2001 (5)	7·7 (3)

Table 6. *Final positional parameters for* (1.5)

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0·2480 (2)	0·7947 (1)	0·6611 (2)	2·82 (5)
O(2)	0·7658 (2)	0·9605 (1)	0·8025 (2)	2·84 (5)
C(1)	0·4587 (2)	0·7091 (1)	0·7494 (2)	1·75 (5)
C(2)	0·3004 (2)	0·7102 (1)	0·6977 (3)	1·98 (6)
C(3)	0·1766 (2)	0·6099 (1)	0·6786 (3)	2·29 (6)
C(4)	0·2103 (2)	0·5167 (1)	0·7058 (3)	2·37 (6)
C(5)	0·3722 (2)	0·5148 (1)	0·7542 (3)	2·24 (5)
C(6)	0·4911 (2)	0·6118 (1)	0·7746 (3)	1·89 (5)
C(7)	0·6422 (2)	0·7679 (1)	0·7940 (2)	1·80 (5)
C(8)	0·7716 (2)	0·8611 (1)	0·8188 (3)	2·10 (5)
C(9)	0·9292 (2)	0·8511 (1)	0·8665 (3)	2·46 (6)
C(10)	0·9549 (2)	0·7554 (2)	0·8852 (3)	2·47 (7)
C(11)	0·8230 (2)	0·6593 (1)	0·8601 (3)	2·23 (6)
C(12)	0·6715 (2)	0·6695 (1)	0·8169 (3)	1·93 (5)
O(3)	0·4765 (2)	0·9761 (1)	0·7388 (2)	3·60 (6)
C(13)	0·4550 (3)	1·0644 (1)	0·7312 (3)	2·55 (6)
C(14)	0·2966 (3)	1·0737 (1)	0·6970 (3)	2·49 (6)
C(15)	0·2785 (2)	1·1689 (1)	0·6912 (3)	2·31 (6)
O(4)	0·4099 (2)	1·25913 (9)	0·7177 (2)	2·37 (4)
C(16)	0·5629 (3)	1·2538 (1)	0·7493 (3)	2·29 (6)
C(17)	0·5890 (2)	1·1610 (1)	0·7558 (3)	2·46 (7)
C(18)	0·1231 (3)	1·1920 (2)	0·6539 (3)	3·15 (8)
C(19)	0·6881 (3)	1·3602 (2)	0·7746 (3)	2·87 (7)

Table 7. *Final positional parameters for* (1.6)

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0·6132 (3)	0·04686 (8)	0·6752 (2)	2·37 (8)
O(2)	0·5614 (3)	0·14154 (8)	1·0702 (2)	2·21 (8)
C(1)	0·4635 (3)	0·1440 (1)	0·7007 (2)	1·61 (9)
C(2)	0·5231 (3)	0·0951 (1)	0·6253 (3)	1·8 (1)
C(3)	0·4864 (3)	0·0959 (1)	0·4766 (3)	2·1 (1)
C(4)	0·3953 (4)	0·1418 (1)	0·4118 (3)	2·3 (1)
C(5)	0·3309 (4)	0·1918 (1)	0·4892 (3)	2·1 (1)
C(6)	0·3686 (3)	0·1908 (1)	0·6314 (3)	1·8 (1)
C(7)	0·4441 (3)	0·1774 (1)	0·8416 (3)	1·63 (9)
C(8)	0·4744 (3)	0·1809 (1)	0·9850 (3)	1·7 (1)
C(9)	0·4060 (3)	0·2331 (1)	1·0532 (3)	2·0 (1)
C(10)	0·3134 (3)	0·2769 (1)	0·9817 (3)	2·0 (1)
C(11)	0·2823 (3)	0·2733 (1)	0·8336 (3)	1·9 (1)
C(12)	0·3494 (3)	0·2238 (1)	0·7698 (3)	1·7 (1)
O(3)	0·6497 (2)	0·04450 (8)	0·9442 (2)	2·29 (8)
C(13)	0·7348 (3)	0·0005 (1)	1·0014 (3)	1·73 (9)
C(14)	0·8020 (3)	−0·0472 (1)	0·9194 (3)	1·9 (1)
C(15)	0·8996 (3)	−0·0921 (1)	0·9786 (3)	2·0 (1)
N(4)	0·9332 (3)	−0·09219 (9)	1·1216 (2)	2·09 (9)
C(16)	0·8678 (3)	−0·0475 (1)	1·2063 (3)	2·1 (1)
C(17)	0·7691 (3)	−0·0025 (1)	1·1481 (3)	2·0 (1)
C(18)	0·9773 (4)	−0·1410 (1)	0·8890 (3)	2·9 (1)
C(20)	1·0402 (4)	−0·1410 (1)	1·1849 (3)	3·2 (1)
C(19)	0·9123 (4)	−0·0482 (1)	1·3617 (3)	3·0 (1)

which relates the non-H atoms of molecule (1A) to those of molecule (1B) and is probably responsible for the centric nature of the intensity statistics. However, this pseudo-inversion center does not fit into the unit cell to make the centrosymmetric space group choice feasible. Also, since the O—H bonds point in different directions for (1A) and (1B), these two molecules are truly different so that the presence of an inversion center relating them is not possible.

The adducts. In each of the five adducts both hydroxy groups of the diol are hydrogen bonded to the same O atom of the base. This basic O atom is within 0·45 Å of the least-squares plane of the biphenylene ring in all cases, so that the O(1)—C(2)—C(1)—C(7)—C(8)—O(2) arch of the diol opens up. The largest changes are in the O(1)—C(2)—C(1) and O(2)—C(8)—C(7) angles. These angles increase from an average 122·3 (21)° in (1), whose two hydroxylic H atoms are not hydrogen-bonded to the same O atom, to an average 128·1 (8)° in the five adducts whose structures were determined. The angles C(2)—C(1)—C(7) and C(8)—C(7)—C(1), which are strongly buttressed by the ring system, are much less affected: they increase from an average 148·6 (4)° in (1) to an average 150·0 (7)° for the five adducts. The combined changes are accompanied by an increase in the O(1)···O(2) distance from an average 3·88 (6) in (1) to an average 4·28 (4) Å in the adducts.

The bond distances, for which the force constants are larger, are much less affected by this spreading apart of the hydroxy groups. The average of the

Table 8. *Final positional parameters for* (2.5)

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0·5402 (4)	0·6732 (6)	1·0946 (3)	5·1 (3)
O(2)	0·4012 (4)	0·8406 (5)	0·8496 (3)	4·8 (2)
C(1)	0·3627 (5)	0·5921 (6)	1·0064 (4)	3·5 (3)
C(2)	0·4479 (5)	0·5911 (7)	1·0769 (4)	3·8 (3)
C(3)	0·4376 (6)	0·4888 (8)	1·1400 (4)	5·4 (4)
C(4)	0·3468 (6)	0·4010 (7)	1·1352 (4)	5·3 (4)
C(5)	0·2582 (5)	0·4081 (7)	1·0644 (4)	4·1 (3)
C(6)	0·2693 (5)	0·5004 (7)	1·0001 (4)	3·5 (3)
C(7)	0·3134 (4)	0·6527 (7)	0·9192 (4)	3·5 (3)
C(8)	0·3208 (5)	0·7445 (7)	0·8545 (4)	3·9 (3)
C(9)	0·2297 (5)	0·7398 (6)	0·7824 (4)	4·2 (3)
C(10)	0·1429 (5)	0·6466 (6)	0·7768 (3)	3·8 (3)
C(11)	0·1387 (4)	0·5496 (6)	0·8419 (4)	3·5 (3)
C(12)	0·2220 (5)	0·5550 (6)	0·9130 (4)	3·4 (3)
N(5)	0·1574 (5)	0·3266 (7)	1·0644 (4)	5·5 (4)
O(5)	0·1633 (4)	0·2259 (5)	1·1146 (3)	6·9 (3)
O(6)	0·0726 (4)	0·3620 (6)	1·0156 (3)	7·6 (3)
N(6)	0·0500 (5)	0·4424 (7)	0·8303 (3)	4·5 (3)
O(7)	0·0738 (4)	0·3171 (5)	0·8520 (3)	7·0 (3)
O(8)	−0·0448 (3)	0·4807 (5)	0·7959 (3)	6·4 (3)
O(3)	0·5606 (3)	0·8569 (5)	0·9814 (3)	5·6 (2)
C(13)	0·6436 (5)	0·9360 (7)	0·9808 (4)	4·0 (3)
C(14)	0·7394 (5)	0·9352 (7)	1·0492 (4)	4·1 (3)
C(15)	0·8281 (5)	1·0163 (7)	1·0457 (4)	3·9 (3)
O(4)	0·8328 (3)	1·1017 (4)	0·9780 (3)	4·4 (2)
C(16)	0·7434 (6)	1·1057 (7)	0·9110 (4)	4·7 (4)
C(17)	0·6531 (5)	1·0294 (7)	0·9123 (4)	4·6 (4)
C(18)	0·9349 (5)	1·0261 (7)	1·1112 (4)	5·7 (3)
C(19)	0·7652 (5)	1·2620 (7)	0·8432 (4)	6·4 (4)

Table 9. *Final positional parameters for* (3.6)

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0·1042 (3)	0·4112 (8)	0·4042 (3)	5·4 (4)
C(1)	0·0379 (3)	0·5490 (9)	0·3359 (3)	3·5 (4)
C(2)	0·0947 (4)	0·500 (1)	0·3584 (3)	4·0 (4)
C(3)	0·1530 (4)	0·545 (1)	0·3322 (4)	4·8 (5)
C(4)	0·1496 (4)	0·643 (1)	0·2847 (3)	5·0 (5)
C(5)	0·0901 (4)	0·6971 (9)	0·2613 (3)	4·5 (4)
C(6)	0·0367 (3)	0·6438 (9)	0·2876 (3)	3·7 (4)
C(21)	0·2200 (3)	0·492 (1)	0·3551 (3)	6·0 (5)
O(3)	0·0	0·346 (1)	0·4567 (3)	5·5 (5)
C(13)	0·0	0·260 (1)	0·5015 (4)	4·0 (6)
C(14)	0·0579 (4)	0·214 (1)	0·5272 (3)	4·5 (4)
C(15)	0·0575 (4)	0·1148 (9)	0·5723 (3)	4·1 (4)
N(4)	0·0	0·062 (1)	0·5949 (3)	4·1 (5)
C(18)	0·1197 (4)	0·057 (1)	0·5967 (3)	6·9 (6)
C(20)	0·0	−0·047 (2)	0·6447 (4)	6·0 (7)

Table 10. *Final positional parameters for* (7)

	x	y	z	$B_{eq}(\text{Å}^2)$
O(2A)	0·37100 (8)	0·49676 (9)	0·6606 (1)	2·60 (5)
O(1A)	0·34700 (8)	0·2416 (1)	0·4469 (1)	2·75 (5)
C(7A)	0·5032 (1)	0·4262 (1)	0·6292 (2)	1·84 (7)
C(8A)	0·4635 (1)	0·4990 (1)	0·6819 (2)	2·04 (6)
C(9A)	0·5239 (1)	0·5724 (1)	0·7573 (2)	2·37 (7)
C(10A)	0·6169 (1)	0·5709 (1)	0·7770 (2)	2·53 (7)
C(11A)	0·6582 (1)	0·4970 (1)	0·7229 (2)	2·36 (7)
C(12A)	0·5991 (1)	0·4263 (1)	0·6506 (2)	1·97 (6)
C(1A)	0·4929 (1)	0·3305 (1)	0·5500 (2)	1·90 (6)
C(2A)	0·4394 (1)	0·2563 (1)	0·4769 (2)	2·22 (7)
C(3A)	0·4846 (1)	0·1844 (1)	0·4238 (2)	2·66 (7)
C(4A)	0·5773 (1)	0·1879 (1)	0·4449 (2)	2·75 (8)
C(5A)	0·6341 (1)	0·2637 (1)	0·5221 (2)	2·45 (7)
C(6A)	0·5895 (1)	0·3322 (1)	0·5713 (2)	2·01 (7)
C(24A)	0·3349 (2)	0·5697 (2)	0·7264 (3)	3·36 (10)
C(23A)	0·3015 (1)	0·3107 (2)	0·5046 (2)	2·79 (8)
O(1B)	0·10740 (8)	0·24143 (9)	0·5609 (1)	2·50 (5)
O(2B)	0·08647 (9)	0·00702 (9)	0·7899 (1)	2·73 (5)
C(1B)	−0·0356 (1)	0·1489 (1)	0·5329 (2)	1·93 (6)
C(2B)	0·0162 (1)	0·2208 (1)	0·5012 (2)	2·13 (7)
C(3B)	−0·0291 (1)	0·2835 (1)	0·3947 (2)	2·39 (7)
C(4B)	−0·1220 (1)	0·2749 (1)	0·3267 (2)	2·63 (8)
C(5B)	−0·1773 (1)	0·2019 (1)	0·3593 (2)	2·49 (7)
C(6B)	−0·1318 (1)	0·1416 (1)	0·4609 (2)	2·12 (7)
C(7B)	−0·0450 (1)	0·0620 (1)	0·6177 (2)	2·00 (7)
C(8B)	−0·0056 (1)	−0·0006 (1)	0·7210 (2)	2·18 (6)
C(9B)	−0·0654 (1)	−0·0692 (1)	0·7502 (2)	2·72 (7)
C(10B)	−0·1580 (1)	−0·0735 (1)	0·6793 (2)	2·93 (8)
C(11B)	−0·1991 (1)	−0·0095 (1)	0·5731 (2)	2·60 (8)
C(12B)	−0·1404 (1)	0·0562 (1)	0·5458 (2)	2·17 (7)
C(23B)	0·1528 (1)	0·1811 (2)	0·6713 (2)	2·64 (8)
C(24B)	0·1227 (2)	−0·0543 (2)	0·9029 (2)	3·48 (10)

C(1)—C(2) and the C(7)—C(8) bond lengths increases from 1·361 (5) in (1) to 1·371 (10) Å in the five adducts. The C(1)—C(7) distance increases from an average 1·509 (7) in (1) to 1·523 (18) Å in the five adducts. In (1) the C(1)—C(7) bond length is slightly, but not significantly, smaller than the C(6)—C(12) bond length. In the adducts the C(1)—C(7) bond is always longer than the C(6)—C(12) bond by amounts varying from 0·01 to 0·05 Å. The average of the O(1)—C(2) and O(2)—C(8) distances decreases from 1·381 (5) in (1) to 1·349 (8) Å in the five adducts, presumably because of the greater amount of phenoxide character in the diol parts of the adducts.

The bond lengths within the diol in the adducts, as well as in (1) and (7), display the same marked alternation in length as observed in the X-ray crystal structure of biphenylene (Fawcett & Trotter, 1966) and in its gas-phase electron diffraction study (Yokozeki, Wilcox & Bauer, 1974). This alternating

pattern keeps the double-bond character out of the four-membered ring so that the valence-bond structure shown for (1)–(3) is the more important one.

The average length of the hydrogen bonds, that is, the O—O distances in the O—H···O bonds, in the five adducts is 2·58 (3) Å. These distances increase from 2·546 (3) in (1.6) to 2·587 (3) in (1.5) to 2·607 (9) Å in (1.4). The proton basicities of the three bases vary in the order (6) > (5) > (4), but the hydrogen-bonding basicities are (6) > (4) > (5). Thus the hydrogen bonds become shorter as the proton basicities increase. Analogously, the average hydrogen-bond length in (2.5) is 2·562 (19) Å, which is shorter than the length in (1.5), in which the acid is weaker and the base is the same. It is interesting to note that of the five adducts only (2.5) shows a significant difference between the two O—H···O distances.

In (2.5), the nitro groups are twisted out of the plane of the biphenylene ring by 20·5 (4) and 42·9 (4)°. The C—O single-bond lengths in (2.5) average 1·341 (7) Å compared with 1·350 (2) Å for (1.5); the C(1)—C(6) and C(7)—C(12) bonds in (2.5) average 1·416 (11) and those in (1.5) average 1·422 (2) Å; and the C(3)—C(4) and C(9)—C(10) bonds in (2.5) average 1·360 (8) compared with 1·372 (3) Å for (1.5). This suggests some double-bond character in the C—O bonds and greater double-bond character in the C(1)—C(6), C(7)—C(12), C(3)—C(4) and C(9)—C(10) bonds of (2.5), arising from resonance interaction with the nitro groups *para* to the C—O bonds to give quinonoid character to the ring. These differences in

the bond lengths between (2.5) and (1.5) are much smaller than the corresponding differences between the bond lengths in phenol (Gillier-Pandrand, 1967) and *p*-nitrophenol (Coppens & Schmidt, 1965). At least part of this relatively decreased resonance observed with our compounds must arise from the noncoplanarity of the two nitro groups with the biphenylene ring.

A comparison of the (1.6) and (3.6) adducts shows that these O—H⋯O distances are not significantly different. As a result any steric restrictions imposed by the *ortho* methyl substituents of the (3) diol are assumed to be negligible.

All these O—O distances seem to be slightly smaller than the O—O distances in single-hydrogen-bonded complexes that might be expected to have hydrogen bonds of about the same strength. For example, the O—O distance in the adduct of pentafluorophenol, whose acidity (pK_a 5·53) (Birchall & Haszeldine, 1959) is comparable to that of (2)
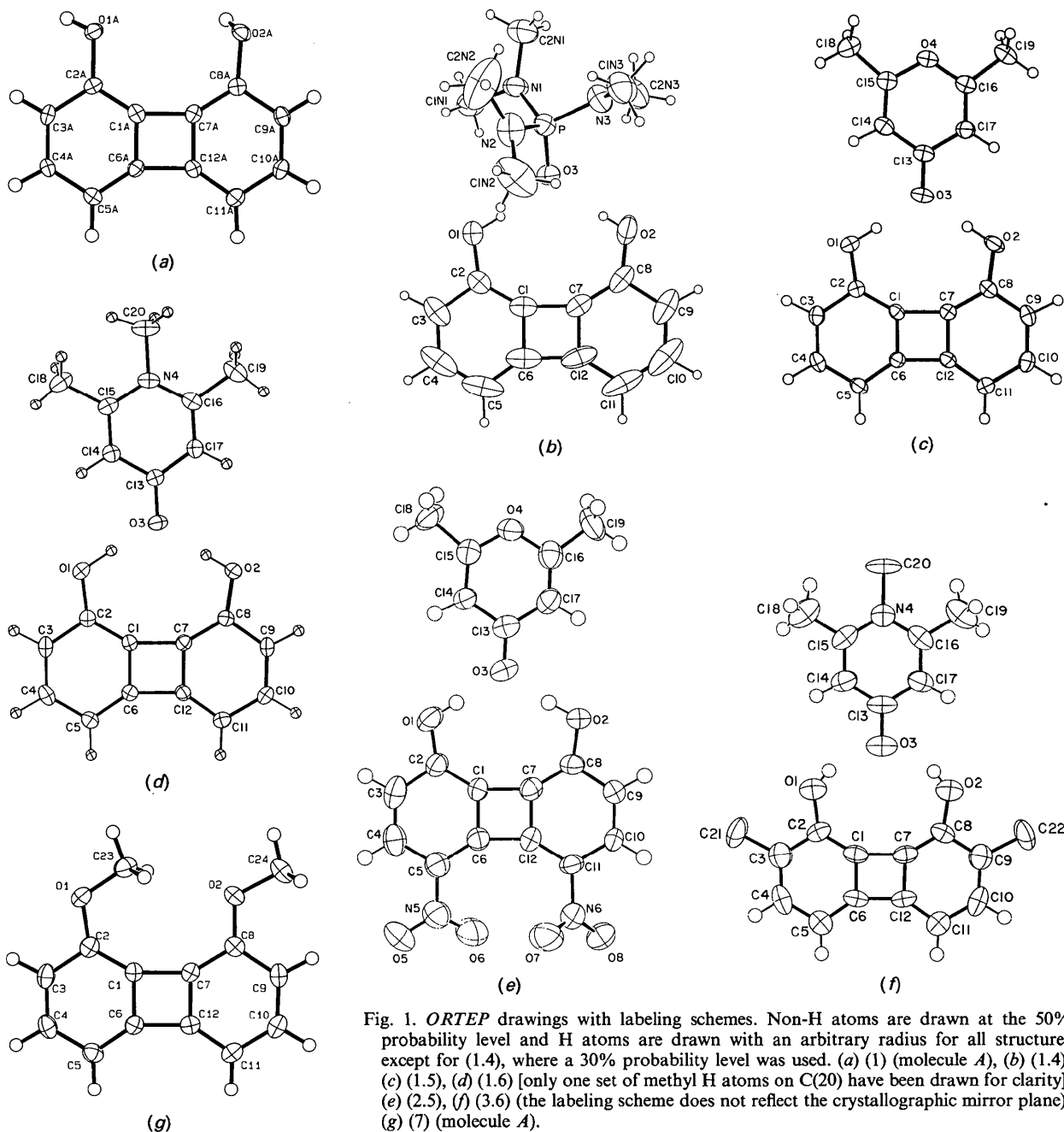
Fig. 1. *ORTEP* drawings with labeling schemes. Non-H atoms are drawn at the 50% probability level and H atoms are drawn with an arbitrary radius for all structures except for (1.4), where a 30% probability level was used. (*a*) (1) (molecule *A*), (*b*) (1.4), (*c*) (1.5), (*d*) (1.6) [only one set of methyl H atoms on C(20) have been drawn for clarity], (*e*) (2.5), (*f*) (3.6) (the labeling scheme does not reflect the crystallographic mirror plane), (*g*) (7) (molecule *A*).

Table 11. *Hydrogen-bond distances* (Å) *and angles* (°)
for 1,8-*biphenylenediol* (1)

O(1*A*)—H(O1*A*)	0·84 (4)	O(2*A*)···H(O2*B*ⁱⁱ)	1·86 (4)
O(1*B*)···H(O1*A*)	1·96 (4)	O(2*B*)—H(O2*B*)	0·90 (4)
O(1*A*)···O(1*B*)	2·804 (3)	O(2*A*)···O(2*B*ⁱⁱ)	2·752 (3)
O(1*A*)···H(O1*B*ⁱ)	1·99 (3)	O(2*A*)—H(O2*A*)	0·78 (5)
O(1*B*)—H(O1*B*)	0·85 (3)	O(2*B*ⁱⁱⁱ)···H(O2*A*)	1·99 (5)
O(1*A*)···O(1*B*ⁱ)	2·828 (3)	O(2*A*)···O(2*B*ⁱⁱⁱ)	2·769 (3)

O(1*A*)—H(O1*A*)···O(1)*B*	174·2 (37)	O(2*A*)···H(O2*B*ⁱⁱ)—O(2*B*ⁱⁱ)	173·2 (58)
O(1*A*)···H(O1*B*ⁱ)—O(1*B*ⁱ)	168·5 (29)	O(2*A*)—H(O2*A*)···O(2*B*ⁱⁱⁱ)	172·8 (34)

Symmetry code: (i) *x, y* − 1, *z*; (ii) *x* − ½, −*y, z*; (iii) *x* − ½, 1 − *y, z*.

Fig. 2. Stereo drawing of the unit cell for (1).

(pK_a 5·61) (Hine *et al.*, 1987*b*), with triphenylphosphine oxide, whose hydrogen-bonding basicity (Taft, Gurka, Joris, Schleyer & Rakshys, 1969) is approximately the same as that of (4), is 2·645 (2) Å (Gramstad, Husebye & Maartmann-Moe, 1986). The O—O distance in the adduct of pentafluorophenol with dioxane, whose hydrogen-bonding basicity is less than that of any of the bases used here, is about the same, 2·647 (1) Å (Gramstad, Husebye & Maartmann-Moe, 1985). The O—O distance in the adduct of phenol with another triarylphosphine oxide, namely 5-methyl-10-phenyl-5,10-dihydrodibenzo[1,4]phosphazine 10-oxide, is 2·68 Å (Gusev, Gurkova, Bel'skii, Zavodnik & Yagodina, 1979). All of the double hydrogen bonds reported here meet Emsley's bond-distance criterion for very strong hydrogen bonds in that they are smaller than the sum of the van der Waals radii by more than 0·3 Å (Emsley, 1980). They are not as short, however, as some of the hydrogen bonds in which a proton ties together two identical oxygen bases. The H(NO₃)₂⁻ anion, for example, has an O—O distance of 2·46 Å (Roziere, Lehmann & Potier, 1979).

The (5) and (6) parts of these adducts show the difference in molecular geometry that would be expected from the greater ability of an N atom than an O atom to share its unshared pair of electrons and thus give aromatic character to the ring in which it is located. Thus the O(3)—C(13), C(14)—C(15) and C(16)—C(17) bonds have shorter lengths and hence more double-bond character in (1.5) and (2.5) than in (1.6) and (3.6). Correspondingly, the C(13)—C(14) and C(13)—C(17) bonds have more single-bond character in the adducts of (5) than in the adducts of (6).

1,8-*Dimethoxybiphenylene* (7). An *ORTEP* drawing of the structure of molecule *A* of (7) is shown in Fig. 1(*g*). Both of the methoxy groups are essentially coplanar with the aromatic ring. The angles between the C—O(methoxy) vector and the least-squares plane of the diol portion of the molecule (minus the methyl C atoms) are 3·4 (3) and 4·4 (3)° in one and 2·2 (3) and 5·1 (3)° in the other of the two nonequivalent molecules in the asymmetric unit. For both molecules one of these methoxy
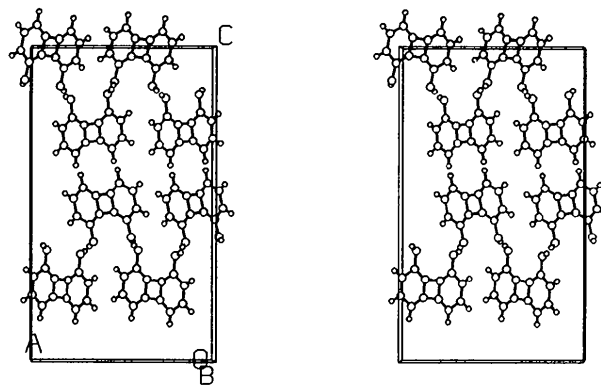
groups is oriented *syn* and the other one *anti* to the O atom of the other methoxy group. The O(2)···C(23) distance is 2·999 (3) for molecule *A* and 3·000 (3) Å for molecule *B*. This is smaller than the sum of the van der Waals radii by more than 0·2 Å. It is interesting that the methyl group and the O atom should get this close together when rotation around the C(2)—O(1) bond could make the distance much larger, especially since a 180° rotation would keep the methoxy group coplanar with the ring. One contributing factor may be the formation of two attractive C—H···O contacts between the methyl C atom of one methoxy group and the O atom of the second methoxy group. The geometry of these interactions is such that they may be described as C—H···O hydrogen bonds (Taylor & Kennard, 1982). A second contributing factor may be the larger amount of double-bond character in the C(1)—C(2) and C(7)—C(8) bonds than in the C(2)—C(3) and C(8)—C(9) bonds, as evidenced by the significantly shorter bond distances characteristic of bonds of the former type. The same factor that causes one of the C—H bonds of a methyl group in propene or acetaldehyde to eclipse the adjacent double bond may cause the methoxy C—O bond in (7) to eclipse the C(1)—C(2) bond in preference to the C(2)—C(3) bond.

References

BAKER, W., BARTON, J. W. & McOMIE, J. F. W. (1958). *J. Chem. Soc.* pp. 2658–2665.

BIRCHALL, J. M. & HASZELDINE, R. N. (1959). *J. Chem. Soc.* p. 3653.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.

COPPENS, P. & SCHMIDT, G. M. J. (1965). *Acta Cryst.* **18**, 62–67, 654–663.

DUCHAMP, D. J. (1964). *CRYM Crystallographic Computing System.* Programs and Abstracts, American Crystallographic Association Meeting, Bozeman, MT, 1964; modified by G. G. CHRISTOPH at The Ohio State University.

EMSLEY, J. (1980). *Chem. Soc. Rev.* **9**, 91–124.

FAWCETT, J. K. & TROTTER, J. (1966). *Acta Cryst.* **20**, 87–93.

GILLIER-PANDRAND, H. (1967). *Bull. Soc. Chim. Fr.* **25**, 1988–1995.

GRAMSTAD, T., HUSEBYE, S. & MAARTMANN-MOE, K. (1985). *Acta Chem. Scand. Ser. B*, **39**, 767–771.

GRAMSTAD, T., HUSEBYE, S. & MAARTMANN-MOE, K. (1986). *Acta Chem. Scand. Ser. B*, **40**, 26–30.

GUSEV, A. I., GURKOVA, S. N., BEL'SKII, V. K., ZAVODNIK, V. E. & YAGODINA, L. A. (1979). *J. Struct. Chem. (Engl. Transl.)*, **20**, 537–541; *Zh. Strukt. Khim.* **20**, 632–637.

HINE, J. & AHN, K. (1987*a*). *J. Org. Chem.* **52**, 2083–2086.

HINE, J. & AHN, K. (1987*b*). *J. Org. Chem.* **52**, 2089–2091.

HINE, J., AHN, K., GALLUCCI, J. C. & LINDEN, S.-M. (1984). *J. Am. Chem. Soc.* **106**, 7980–7981.

HINE, J., HAHN, S. & MILES, D. E. (1986). *J. Org. Chem.* **51**, 577–584.

HINE, J., HAHN, S., MILES, D. E. & AHN, K. (1985). *J. Org. Chem.* **50**, 5092–5096.

HINE, J., LINDEN, S.-M. & KANAGASABAPATHY, V. M. (1985*a*). *J. Am. Chem. Soc.* **107**, 1082–1083.

HINE, J., LINDEN, S.-M. & KANAGASABAPATHY, V. M. (1985*b*). *J. Org. Chem.* **50**, 5096–5099.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2*B*. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

ROZIERE, J., LEHMANN, M. S. & POTIER, J. (1979). *Acta Cryst.* **B35**, 1099–1102.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TAFT, R. W., GURKA, D., JORIS, L., SCHLEYER, P. VON R. & RAKYSHYS, J. W. (1969). *J. Am. Chem. Soc.* **91**, 4801–4808.

TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

YOKOZEKI, A., WILCOX, C. F. JR & BAUER, S. H. (1974). *J. Am. Chem. Soc.* **96**, 1026–1032.

Structure of 5-[(2,3-Epoxy-3-methyl)butoxy]furo[3,2-g]coumarin

BY IRENA WOLSKA, TERESA BOROWIAK* AND MARIAN GAWRON

Department of Crystallography, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Abstract. $C_{16}H_{14}O_5$, $M_r = 286.28$, triclinic, $P\bar{1}$, $a = 8.485$ (1), $b = 11.054$ (2), $c = 7.868$ (1) Å, $\alpha = 103.31$ (1), $\beta = 94.97$ (1), $\gamma = 105.88$ (1)°, $V = 681.8$ (2) Å^3, $Z = 2$, $D_x = 1.394$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1.54178$ Å, $\mu = 0.775$ mm^{-1}, $F(000) = 300$, room temperature, $R = 0.050$ for 1490 observed reflections. The furocoumarin system is not strictly planar. The pyran ring adopts a very flattened boat conformation. The orientation of the (2,3-epoxy-3-methyl)butoxy substituent is determined by a weak intramolecular C—H···O hydrogen bond.

Introduction. Coumarin compounds have a wide spectrum of biological activity including antithrombotic effects, vasodilating effects on coronary vessels, a tonic influence on capillary blood vessels, reduction in blood pressure, and antispastic and photosensitizing effects. The mechanism of coumarin biological activity is, in most cases, unknown.

---

* To whom correspondence should be addressed.

This paper presents results of a structural study of 5-[(2,3-epoxy-3-methyl)butoxy]furo[3,2-g]coumarin (oxypeucedanin), a compound extracted from the roots and fruits of *Angelica archangelica* L. and *Angelica silvestris* L. (Cisowski, 1986), and is part of a systematic study of coumarins and flavonoids extracted from plants of the *Umbelliferae* family.

Experimental. Poor-quality single crystals were grown, with great difficulty, by slow evaporation from acetone; crystal system and approximate cell dimensions were determined from oscillation and Weissenberg photographs; crystal specimen 0·35 × 0·20 × 0·05 mm; Syntex *P*2₁ four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation, θ–2θ scan mode, background and intensity of reflections determined by peak-profile analysis (Lehmann & Larsen, 1974; Jaskólski, 1982); accurate cell parameters refined from setting angles of 15 reflections with $29.7 \le 2\theta \le 45.0°$, maximum $(\sin\theta/\lambda) = 0.509$ Å^{-1}, $0 \le h \le 10$, $-13 \le k \le 13$, $-10 \le l \le 10$,