

Formation of One-Dimensional Chains, Two-Dimensional Bilayers and a Three-Dimensional Diamondoid Architecture in Hydrogen-Bonded Adducts of 4,4'-Biphenol with 1,4-Diazabicyclo[2.2.2]octane and 1,2-Diaminoethane

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(Received 28 April 1997; accepted 11 July 1997)

Abstract

In 4,4'-biphenol–1,4-diazabicyclo[2.2.2]octane (1/1), C₁₂H₁₀O₂·C₆H₁₂N₂ (1), monoclinic, C2/c, *a* = 12.1510 (9), *b* = 6.3202 (4), *c* = 21.051 (2) Å, β = 98.875 (10)° with *Z* = 4, the biphenol units lie across twofold rotation axes and the diamine units are disordered across centres of inversion. The molecular components are linked by means of O–H···N hydrogen bonds into zigzag chains with graph set C₂²(16) running parallel to the [201] direction; the chains are not coiled and there are no interactions between neighbouring chains. In 4,4'-biphenol–1,2-diaminoethane–methanol (2/1/1), (C₁₂H₁₀O₂)₂·C₂H₈N₂·CH₄O (2), triclinic, P1̄, *a* = 9.4592 (7), *b* = 10.6311 (10), *c* = 12.2085 (14) Å, α = 91.812 (9), β = 93.091 (6), γ = 90.652 (6)° with *Z* = 2, there are seven independent hydrogen bonds of O–H···O, O–H···N and N–H···O types and each oxygen and each nitrogen acts as a single donor and single acceptor of hydrogen bonds. The four independent components are linked by means of O–H···O and O–H···N hydrogen bonds into a linear aggregate, and further O–H···N and O–H···O hydrogen bonds generate chains in the [011] direction containing alternating biphenol and diamine units, and in the [021] direction containing methanol and pairs of biphenol molecules. These two types of chain intersect to form a continuous two-dimensional net, graph set R₁₀¹⁰(62), with biphenol molecules at the nodes: pairs of these nets are linked into bilayers by N–H···O hydrogen bonds, but the nets are not interwoven. In 4,4'-biphenol–1,2-diaminoethane (1/1), C₁₂H₁₀O₂·C₂H₈N₂ (3), monoclinic, P2₁/a, *a* = 8.2121 (5), *b* = 5.3401 (3), *c* = 14.6014 (9) Å, β = 99.962 (7)° with *Z* = 2, each of the components lies across a centre of inversion. The O atoms act as single donors and double acceptors of hydrogen bonds and the N atoms as double donors and single acceptors, so that both oxygen and nitrogen are effectively four-coordinate; all the hydrogen bonds are of O–H···N or N–H···O type. Chains built from N–H···O and O–H···N hydrogen bonds run parallel to [100] and [010] and the intersection of these gives two-dimensional nets built from R₆⁶(12) rings: these nets

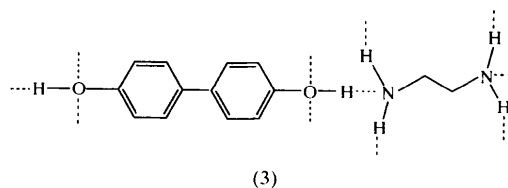
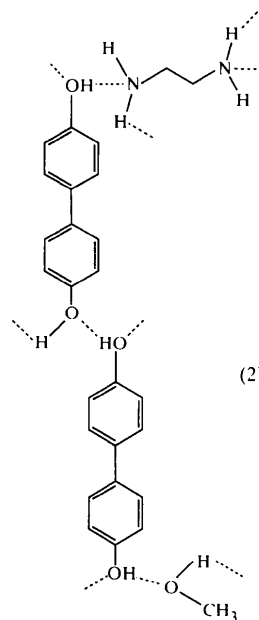
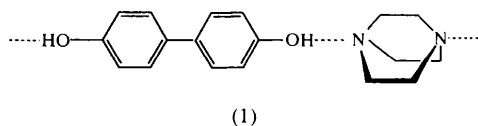
are linked by the –C₆H₄C₆H₄– and –CH₂CH₂– spacer units into a continuous three-dimensional diamondoid structure.

1. Introduction

Hydrogen bonds of the type O–H···O, O–H···N and N–H···O are some of the most robust and versatile synthons of supramolecular chemistry (Desiraju, 1995). In hydrogen-bonded adducts of bis-phenols and tris-phenols with di-tertiary amines, it is generally found that all the hydroxy groups of the phenol component act as hydrogen-bond donors; for adducts of bis-phenols with di-tertiary amines, the predominant mode of aggregation is the formation of chains built from O–H···N hydrogen bonds (Coupar *et al.*, 1996a; Ferguson, Coupar & Glidewell, 1997; Coupar *et al.*, 1997; Ferguson, Bell *et al.*, 1997). Where both the bis-phenol and the diamine have some degree of conformational flexibility, the chains can coil, sometimes giving multiple helices, while in other examples the overall structure is controlled by soft hydrogen bonds (Coupar *et al.*, 1997): the suggestion has been made (Ferguson, Bell *et al.*, 1997) that soft hydrogen bonds will be of little significance when the conformational flexibility of the chain components is reduced to a minimum, leading to a prediction of quasi-linear chains of extreme simplicity in such cases. In adducts of poly-phenols with secondary amines the N–H bonds can themselves also act as hydrogen-bond donors, as in the piperazine adducts with 4,4'-thiodiphenol, where there are hydrogen bonds of N–H···π(arene) type (Coupar *et al.*, 1996b) and with 4,4'-sulfonyldiphenol and 1,1,1-tris(4-hydroxyphenyl)ethane, in both of which there are N–H···O hydrogen bonds (Coupar *et al.*, 1996c; Ferguson, Bell *et al.*, 1997). Similarly, in the adducts of piperazine and of 2,5-dimethylpiperazine with phenol itself (Loehlin *et al.*, 1994) the N–H bonds of the amine components act as donors in N–H···O hydrogen bonds.

When NH₂ groups are present, considerable structural complexity can result: in the adduct of the bis-primary amine 1,2-diaminoethane with phenol, of

composition $(C_6H_5OH)_2 \cdot H_2NCH_2CH_2NH_2$ and containing equal numbers of NH_2 and OH groups, each NH_2 and each OH group act as both a single donor and a single acceptor of hydrogen bonds, and the resulting structure is built from two-dimensional hydrogen-bonded sheets (Loehlin *et al.*, 1994). The hydroquinone-aniline adduct $C_6H_4(OH)_2 \cdot (C_6H_5NH_2)_2$ again contains equal numbers of NH_2 and OH groups, but the NH_2 groups act as double donors and single acceptors of hydrogen bonds, while the OH groups act as single donors and double acceptors (Loehlin *et al.*, 1994): the resulting quasi-tetrahedral coordination at both nitrogen and oxygen leads to the formation of two-dimensional sheets, built from hexagonal $R_6^6(12)$ rings (Etter, 1990; Bernstein *et al.*, 1995), and the presence of two hydroxy groups in the hydroquinone components leads to the pairwise linking of these sheets, with the $-C_6H_4-$ units as linkers. If both components contain two functional groups, OH or NH_2 , and each of these adopts a quasi-tetrahedral coordination of covalent and hydrogen bonds, then continuous three-dimensional diamondoid structures result, as in the 1:1 adducts formed between hydroquinone or 4,4'-biphenol, on the one hand, and *p*-phenylenediamine or benzidine (4,4'-diaminodiphenol), on the other (Ermer & Eling, 1994). It was suggested (Ermer & Eling, 1994) that in such systems 1:1 stoichiometry was especially favoured, because of the complementarity of the OH and NH_2 groups for maximal hydrogen bonding, while framework units smaller than $-C_6H_4-$ groups would be more likely to promote the formation of finite, possibly polyhedral, aggregates rather than continuous super-diamondoid structures. In this paper, we report the preparation and structures of three adducts formed by 4,4'-biphenol, a 1:1 adduct (1) with 1,4-diazabicyclo[2.2.2]octane (DABCO) and two adducts with 1,2-diaminoethane: one is a methanol-solvated 2:1 adduct $(HOC_6H_4C_6H_4OH)_2 \cdot H_2NCH_2CH_2NH_2 \cdot MeOH$ (2) and the other a 1:1 adduct (3): adduct (1) forms simple chains which are neither folded nor coiled, adduct (2) forms two-dimensional bilayers and adduct (3) forms a three-dimensional diamondoid structure. These structures illustrate the rather easy transformation from extreme simplicity of supramolecular architecture in (1), *via* (2), to the complexity of a continuous three-dimensional diamondoid structure in (3), all produced by self-assembly from extremely simple molecular components: at the same time, they indicate that equal numbers of OH and NH_2 groups are not necessary for compound formation between poly-phenols and primary amines.



2. Experimental

2.1. Synthesis

Samples of (1), (2) and (3) were obtained by recrystallization of methanol solutions containing 4,4'-biphenol (0.005 mol) with stoichiometric quantities of the amine. Analysis: (1) found C 72.0, H 7.9, N 9.6%; $C_{18}H_{22}N_2O_2$ requires C 72.5, H 7.4, N 9.4%; (2) found C 70.4, H 7.2, N 6.2%; $C_{27}H_{32}N_2O_5$ requires C 69.8, H 6.9, N 6.0%; (3) found C 68.1, H 7.4, N 11.3%; $C_{14}H_{18}N_2O_2$ requires C 68.3, H 7.4, N 11.4%. Samples of (1)–(3) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. Data collection, structure solution and refinement

Details of cell data, data collection and refinement are summarized in Table 1. For (1), the systematic absences (hkl absent if $h + k = 2n + 1$; $h0l$ absent if $l = 2n + 1$) permitted the space group to be Cc or $C2/c$: the intensity statistics suggested a centrosymmetric space group and $C2/c$ was selected and confirmed by successful analysis. Compound (2) is triclinic and the space group $P\bar{1}$ was chosen and confirmed by analysis; for (3) the systematic absences ($h0l$ absent if $h = 2n + 1$; $0k0$ absent if $k = 2n + 1$) permitted the space group to

Table 1. *Experimental details*

| | (1) | (2) | (3) |
|--|--|--|---|
| Crystal data | | | |
| Chemical formula | C ₁₈ H ₂₂ N ₂ O ₂ | C ₂₇ H ₃₂ N ₂ O ₅ | (C ₁₂ H ₁₀ O ₂).(C ₂ H ₈ N ₂) |
| Chemical formula weight | 298.38 | 464.55 | 246.30 |
| Cell setting | Monoclinic | Triclinic | Monoclinic |
| Space group | C2/c | P $\bar{1}$ | P2 ₁ /a |
| a (Å) | 12.1510 (9) | 9.4592 (7) | 8.2121 (5) |
| b (Å) | 6.3202 (4) | 10.6311 (10) | 5.3401 (3) |
| c (Å) | 21.051 (2) | 12.2085 (14) | 14.6014 (9) |
| α (°) | | 91.812 (9) | |
| β (°) | 98.875 (10) | 93.091 (6) | 99.962 (7) |
| γ (°) | | 90.652 (6) | |
| V (Å ³) | 1597.3 (2) | 1225.2 (2) | 630.67 (7) |
| Z | 4 | 2 | 2 |
| D _x (Mg m ⁻³) | 1.241 | 1.259 | 1.297 |
| Radiation type | Mo K α | Mo K α | Mo K α |
| Wavelength (Å) | 0.7107 | 0.7107 | 0.7107 |
| No. of reflections for cell parameters | 25 | 25 | 25 |
| θ range (°) | 10.94–20.49 | 20.11–26.72 | 13.07–21.73 |
| μ (mm ⁻¹) | 0.081 | 0.087 | 0.088 |
| Temperature (K) | 294 (1) | 294 (1) | 294 (1) |
| Crystal form | Block | Block | Lath |
| Crystal size (mm) | 0.42 × 0.32 × 0.17 | 0.41 × 0.41 × 0.35 | 0.42 × 0.21 × 0.10 |
| Crystal colour | Colourless | Colourless | Colourless |
| Data collection | | | |
| Diffractometer | Enraf–Nonius CAD-4 | Enraf–Nonius CAD-4 | Enraf–Nonius CAD-4 |
| Data collection method | $\theta/2\theta$ scans | $\theta/2\theta$ scans | $\theta/2\theta$ scans |
| Absorption correction | None | None | None |
| No. of measured reflections | 2058 | 5695 | 1703 |
| No. of independent reflections | 1822 | 5609 | 1438 |
| No. of observed reflections | 1133 | 4230 | 784 |
| Criterion for observed reflections | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| R _{int} | 0.030 | 0.019 | 0.018 |
| θ_{\max} (°) | 27.35 | 27.45 | 27.40 |
| Range of h, k, l | -15 → h → 15 0 → k → 8 0 → l → 27 | -12 → h → 12 0 → k → 13 -15 → l → 15 | -10 → h → 10 0 → k → 6 0 → l → 18 |
| No. of standard reflections | 3 | 3 | 3 |
| Frequency of standard reflections (min) | 120 | 120 | 60 |
| Intensity decay (%) | No decay, variation 0.7 | No decay, variation 1.0 | 4.9, allowed for by scaling |
| Refinement | | | |
| Refinement on | F ² | F ² | F ² |
| R[F ² > 2 σ (F ²)] | 0.0433 | 0.0427 | 0.0478 |
| wR(F ²) | 0.1081 | 0.1266 | 0.1446 |
| S | 1.022 | 1.070 | 1.017 |
| No. of reflections used in refinement | 1822 | 5609 | 1438 |
| No. of parameters used | 144 | 348 | 85 |
| H-atom treatment | H parameters constrained | H parameters constrained | Riding (C–H 0.93–0.97, N–H 0.89, O–H 0.82 Å) |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.1241P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.1612P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0786P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| (Δ/σ) _{max} | 0.000 | -0.011 | 0.000 |
| $\Delta\rho_{\max}$ (e Å ⁻³) | 0.143 | 0.240 | 0.208 |
| $\Delta\rho_{\min}$ (e Å ⁻³) | -0.113 | -0.185 | -0.199 |
| Extinction method | SHELXL93 (Sheldrick, 1993) | SHELXL93 (Sheldrick, 1993) | SHELXL93 (Sheldrick, 1993) |
| Extinction coefficient | 0.0120 (13) | 0.0642 (42) | 0.157 (17) |
| Source of atomic scattering factors | <i>International Tables for Crystallography</i> (1992, Vol. C) | <i>International Tables for Crystallography</i> (1992, Vol. C) | <i>International Tables for Crystallography</i> (1992, Vol. C) |
| Computer programs | | | |
| Data collection | CAD-4 (Enraf–Nonius, 1992) | CAD-4 (Enraf–Nonius, 1992) | CAD-4 (Enraf–Nonius, 1992) |

Table 1 (cont.)

| | (1) | (2) | (3) |
|---|---|---|---|
| Cell refinement | SET4 and CELDIM (Enraf-Nonius, 1992) | SET4 and CELDIM (Enraf-Nonius, 1992) | SET4 and CELDIM (Enraf-Nonius, 1992) |
| Data reduction | DATRD2 in NRCVAX96 (Gabe <i>et al.</i> , 1989) | DATRD2 in NRCVAX96 (Gabe <i>et al.</i> , 1989) | DATRD2 in NRCVAX94 (Gabe <i>et al.</i> , 1989) |
| Structure solution | SOLVER in NRCVAX96 | SOLVER in NRCVAX96 | SOLVER in NRCVAX94 |
| Structure refinement | NRCVAX96 and SHELXL93 (Sheldrick, 1993) | NRCVAX96 and SHELXL93 (Sheldrick, 1993) | NRCVAX94 and SHELXL93 (Sheldrick, 1993) |
| Preparation of material for publication | NRCVAX96, SHELXL93 and WordPerfect macro PREPCIF97 (Ferguson, 1997) | NRCVAX96, SHELXL93 and WordPerfect macro PREPCIF97 (Ferguson, 1997) | NRCVAX94, SHELXL93 and WordPerfect macro PREPCIF97 (Ferguson, 1997) |

be uniquely assigned as $P2_1/a$. The structures were solved by direct methods (Gabe *et al.*, 1989). A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed to reduce statistical bias (Wilson, 1976). H atoms bonded to carbon were positioned on geometric grounds (C—H 0.93–0.97 Å) and coordinates for H atoms bonded to N or O were obtained from difference maps. In (1) the DABCO components are disordered across centres of inversion; in (2) it became clear from an early stage that the two C atoms of the diamine component were disordered over two sets of sites, whose site occupation factors (s.o.f.'s) refined to 0.874 (4) and 0.126 (4). Similarly, the methyl H atoms in the methanol components of (2) were disordered and this disorder was modelled by means of six sites each with $\frac{1}{2}$ occupancy. All H atoms were included in the refinements as riding atoms. Examination of the structures using PLATON (Spek, 1995a) showed that there were no solvent-accessible voids in the lattices. The diagrams were prepared using ORTEPII (Johnson, 1976), as implemented in PLATON, and with PLUTON (Spek, 1995b). Final refined coordinates are presented in Table 2 and selected dimensions in Table 3.†

3. Results and discussion

3.1. Structures and molecular packing

3.1.1. *Compound (1)*. The DABCO molecules are disordered across centres of inversion, just as found in the structure of the 2:1 adduct formed between 4,4'-thiodiphenol and DABCO (Ferguson, Coupar & Glidewell, 1997), while the 4,4'-biphenol molecules lie across twofold axes. The centre of the N...N vector in the DABCO molecule is slightly displaced from the centre of inversion, so that the sites for the two N2 and N3 atoms do not coincide (Fig. 1). The structural description is based upon a single orientation of the

disordered DABCO component, but since the principal effect of the disorder is the switching of the two nitrogen sites, with only a slight positional displacement, this disorder of the DABCO components does not materially affect the chain formation. Within the molecular aggregate (Fig. 2), O1 at (x, y, z) , which is in the same biphenol molecule as atom O1A at $(1 - x, y, \frac{1}{2} - z)$, acts as a donor to N2, while N3 in the same DABCO unit acts as an acceptor from O1 at $(-x, -y, -z)$, in a second biphenol molecule. The other O atom in this latter diphenol molecule, at $(-1 + x, -y, -\frac{1}{2} + z)$, acts as a donor to N2 at $(-1 + x, -y, -\frac{1}{2} + z)$, while N3 of the same DABCO acts as an acceptor from O1 at $(-1 - x, y, -\frac{1}{2} - z)$: repetition of these hydrogen bonds leads to the generation of chains running parallel to the [201] direction. The formation of such a chain utilizes only one molecule each of 4,4'-biphenol and DABCO per unit cell; hence, with $Z = 4$, there must be four such chains running through each cell. The individual chains are related to one another by the action of the screw axes parallel to the [010] direction and hence the chains all run in a parallel direction (Fig. 3). The only conformational degrees of freedom in these chains are those provided by the non-linearity of the C—O—H and O—H...N fragments, and it is these which give rise

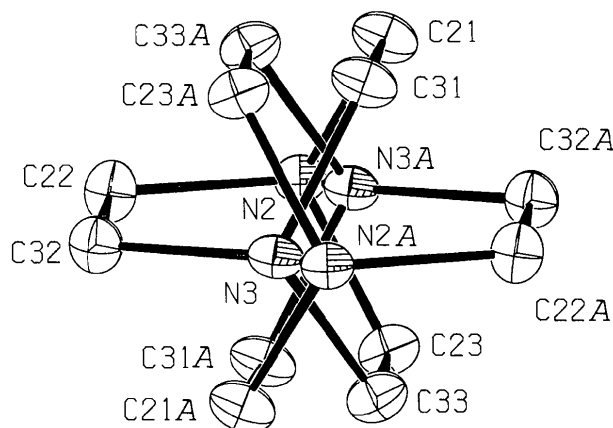


Fig. 1. The disordered DABCO component in (1). Displacement ellipsoids are drawn at the 30% probability level.

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: AB0381). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates and anisotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | U_{eq} |
|------|---------------|---------------|---------------|-------------|
| (1)† | | | | |
| O1 | 0.13241 (9) | 0.4631 (2) | 0.11503 (6) | 0.0773 (4) |
| C11 | 0.23480 (12) | 0.4500 (2) | 0.15215 (7) | 0.0533 (4) |
| C12 | 0.27293 (11) | 0.6245 (2) | 0.18857 (7) | 0.0553 (4) |
| C13 | 0.37586 (16) | 0.6201 (2) | 0.22670 (6) | 0.0512 (4) |
| C14 | 0.44423 (10) | 0.4425 (2) | 0.22984 (6) | 0.0453 (3) |
| C15 | 0.40352 (11) | 0.2677 (2) | 0.19350 (6) | 0.0513 (4) |
| C16 | 0.30048 (11) | 0.2710 (2) | 0.15525 (6) | 0.0538 (4) |
| N2 | 0.0446 (6) | 0.1521 (13) | 0.0411 (4) | 0.0529 (15) |
| C21 | 0.0706 (3) | -0.0641 (5) | 0.0646 (2) | 0.0696 (10) |
| C22 | -0.0759 (2) | 0.1862 (5) | 0.0389 (2) | 0.0676 (9) |
| C23 | 0.0704 (3) | 0.1678 (6) | -0.0247 (2) | 0.0666 (10) |
| C31 | -0.0001 (3) | -0.2260 (5) | 0.0215 (2) | 0.0699 (10) |
| C32 | -0.1437 (2) | 0.0273 (5) | -0.0074 (2) | 0.0671 (9) |
| C33 | 0.0044 (3) | 0.0028 (6) | -0.0688 (2) | 0.0667 (9) |
| N3 | -0.0679 (6) | -0.1196 (12) | -0.0329 (3) | 0.052 (2) |
| (2)‡ | | | | |
| O11 | 0.16094 (11) | 0.81937 (9) | 0.04727 (8) | 0.0495 (3) |
| O12 | 0.18831 (12) | 0.14813 (9) | -0.52356 (9) | 0.0534 (3) |
| C111 | 0.16192 (13) | 0.72988 (11) | -0.03565 (10) | 0.0374 (3) |
| C112 | 0.04277 (14) | 0.65805 (13) | -0.06772 (12) | 0.0458 (3) |
| C113 | 0.04860 (14) | 0.56743 (13) | -0.15102 (12) | 0.0454 (3) |
| C114 | 0.17263 (13) | 0.54459 (11) | -0.20422 (10) | 0.0352 (3) |
| C115 | 0.29135 (13) | 0.61766 (12) | -0.17079 (10) | 0.0373 (3) |
| C116 | 0.28632 (14) | 0.70950 (12) | -0.08798 (10) | 0.0393 (3) |
| C121 | 0.18158 (14) | 0.24650 (11) | -0.44937 (11) | 0.0393 (3) |
| C122 | 0.29968 (14) | 0.27312 (12) | -0.37992 (11) | 0.0429 (3) |
| C123 | 0.29684 (13) | 0.36944 (12) | -0.30162 (11) | 0.0406 (3) |
| C124 | 0.17733 (13) | 0.44369 (11) | -0.29093 (10) | 0.0356 (3) |
| C125 | 0.06094 (14) | 0.41703 (12) | -0.36316 (11) | 0.0426 (3) |
| C126 | 0.06183 (14) | 0.31981 (13) | -0.44091 (11) | 0.0449 (3) |
| O21 | 0.32033 (15) | -0.06088 (11) | -0.42529 (9) | 0.0669 (3) |
| O22 | 0.32269 (13) | -0.78230 (10) | -0.95248 (9) | 0.0568 (3) |
| C211 | 0.3231 (2) | -0.16064 (13) | -0.49901 (11) | 0.0453 (3) |
| C212 | 0.3008 (2) | -0.14631 (13) | -0.61024 (11) | 0.0462 (3) |
| C213 | 0.29978 (15) | -0.25017 (12) | -0.68103 (11) | 0.0437 (3) |
| C214 | 0.32480 (12) | -0.37115 (11) | -0.64440 (10) | 0.0354 (3) |
| C215 | 0.3485 (2) | -0.38247 (13) | -0.53179 (11) | 0.0482 (3) |
| C216 | 0.3473 (2) | -0.27935 (15) | -0.45992 (12) | 0.0550 (4) |
| C221 | 0.32546 (13) | -0.68637 (12) | -0.87457 (11) | 0.0417 (3) |
| C222 | 0.3178 (2) | -0.70604 (12) | -0.76392 (12) | 0.0470 (3) |
| C223 | 0.31786 (15) | -0.60472 (12) | -0.68962 (10) | 0.0443 (3) |
| C224 | 0.32673 (12) | -0.48079 (11) | -0.72330 (10) | 0.0354 (3) |
| C225 | 0.33662 (14) | -0.46434 (12) | -0.83564 (11) | 0.0413 (3) |
| C226 | 0.33546 (15) | -0.56458 (13) | -0.91052 (11) | 0.0445 (3) |
| N1 | -0.08408 (14) | 0.83597 (12) | 0.14393 (11) | 0.0555 (3) |
| C1 | -0.1153 (2) | 0.9637 (2) | 0.1845 (2) | 0.0506 (5) |
| C2 | 0.0007 (2) | 1.0075 (2) | 0.2667 (2) | 0.0495 (5) |
| N2 | -0.0216 (2) | 1.13231 (14) | 0.31822 (12) | 0.0638 (4) |
| O3 | 0.35215 (11) | -1.00660 (9) | -0.86609 (11) | 0.0617 (3) |
| C3 | 0.4936 (2) | -1.0411 (2) | -0.8438 (2) | 0.0704 (5) |
| C11 | -0.0706 (19) | 0.9246 (9) | 0.2384 (6) | 0.073 (5) |
| C22 | -0.0142 (15) | 1.0528 (9) | 0.2185 (6) | 0.052 (4) |
| (3) | | | | |
| O1 | 0.0549 (2) | 0.0142 (3) | -0.33168 (9) | 0.0483 (4) |
| C11 | 0.0439 (2) | 0.0146 (4) | -0.23889 (12) | 0.0364 (5) |
| C12 | -0.0451 (3) | -0.1745 (4) | -0.20540 (13) | 0.0423 (5) |
| C13 | -0.0616 (3) | -0.1796 (4) | -0.11318 (13) | 0.0412 (5) |
| C14 | 0.0098 (2) | 0.0013 (4) | -0.04973 (11) | 0.0317 (4) |
| C15 | 0.1014 (3) | 0.1868 (4) | -0.08521 (13) | 0.0414 (5) |

Table 2 (cont.)

| | x | y | z | U_{eq} |
|-----|------------|------------|---------------|------------|
| C16 | 0.1181 (2) | 0.1937 (4) | -0.17770 (12) | 0.0431 (5) |
| N1 | 0.1591 (2) | 0.4610 (3) | -0.39278 (10) | 0.0443 (5) |
| C1 | 0.0895 (3) | 0.5035 (6) | -0.49116 (15) | 0.0589 (7) |

† In (1) atoms N2, N3, C21, C22, C23, C31, C32 and C33 all have s.o.f. = 0.50 (see text). ‡ In (2) atoms C1 and C2 have s.o.f. = 0.874 (4) and C22 has s.o.f. = 0.126 (4).

Table 3. Selected molecular dimensions (\AA , °)

| | | | |
|-------------------------|------------|-----------------------------|-----------|
| (1) | | | |
| O1—C11 | 1.366 (2) | C14—C14 ⁱ | 1.484 (2) |
| N2—C21 | 1.471 (7) | N3—C31 | 1.467 (7) |
| N2—C22 | 1.474 (7) | N3—C32 | 1.468 (7) |
| N2—C23 | 1.469 (7) | N3—C33 | 1.464 (7) |
| C21—C31 | 1.540 (4) | C22—C32 | 1.546 (4) |
| C23—C33 | 1.538 (4) | | |
| N2—C21—C31—N3 | 3.5 (5) | N2—C22—C32—N3 | 3.2 (4) |
| N2—C23—C33—N3 | 1.6 (5) | | |
| O1...N2 | 2.629 (8) | O1—H1...N2 | 161 |
| O1...N3 ⁱⁱ | 2.810 (7) | O1—H1...N3 ⁱⁱ | 170 |
| (2) | | | |
| O11—C111 | 1.368 (1) | O21—C211 | 1.370 (2) |
| O12—C121 | 1.366 (2) | O22—C221 | 1.371 (2) |
| C114—C124 | 1.486 (2) | C214—C224 | 1.489 (2) |
| N1—C1 | 1.469 (2) | N1—C11 | 1.465 (1) |
| N2—C2 | 1.472 (2) | N2—C22 | 1.465 (1) |
| C1—C2 | 1.507 (2) | C11—C22 | 1.490 (1) |
| C3—O3 | 1.406 (1) | | |
| N1—C1—C2—N2 | -177.0 (2) | N1—C11—C22—N2 | 174.2 (1) |
| N1...O22 ⁱⁱⁱ | 3.194 (2) | N1—H1A...O22 ⁱⁱⁱ | 169 |
| N2...O21 ^{iv} | 3.268 (2) | N2—H2A...O21 ^{iv} | 159 |
| O3...O11 ^v | 2.722 (2) | O3—H3...O11 ^v | 164 |
| O11...N1 | 2.662 (2) | O11—H11...N1 | 172 |
| O12...N2 ^{vi} | 2.694 (2) | O12—H12...N2 ^{vi} | 171 |
| O21...O12 | 2.830 (2) | O21—H21...O12 | 169 |
| O22...O3 | 2.649 (2) | O22—H22...O3 | 173 |
| (3) | | | |
| O1—C11 | 1.373 (2) | C14—C14 ⁱⁱ | 1.489 (3) |
| N1—C1 | 1.469 (3) | C1—C1 ^{vii} | 1.448 (4) |
| O1...N1 | 2.736 (2) | O1—H1...N1 | 173 |
| N1...O1 ^{viii} | 3.221 (2) | N1—H1A...O1 ^{viii} | 165 |
| N1...O1 ^{ix} | 3.243 (2) | N1—H1B...O1 ^{ix} | 155 |

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $-x, -y, -z$; (iii) $-x, -y, -1 - z$; (iv) $-x, 1 - y, -z$; (v) $x, -2 + y, -1 + z$; (vi) $x, -1 + y, -1 + z$; (vii) $-x, 1 - y, -1 - z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (ix) $x, 1 + y, z$.

to the zigzag arrangement of each chain (Fig. 3). Owing to the very limited conformational flexibility, there is no coiling of the chains: this contrasts with the 1:1 adduct formed between 4,4'-isopropylidenediphenol, $\text{Me}_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$, and hexamethylenetetramine, $(\text{CH}_2)_6\text{N}_4$

(HMTA), where the chains are coiled to form a double helix (Coupar *et al.*, 1997), and with the 1:2 adduct formed between 1,1,1-tris(4-hydroxyphenyl)ethane and HMTA, where a triple helix is formed (Coupar *et al.*, 1997): in each of these adducts, the HMTA units provide the conformational flexibility required for chain-coiling. There are no significant interactions between the neighbouring chains in (1).

3.1.2. *Compound (2)*. The asymmetric unit consists of one molecule of 1,2-diaminoethane, two molecules of 4,4'-biphenol and one molecule of methanol (Fig. 4). Within the asymmetric unit, O11, O21 and O22 act as hydrogen-bond donors to N1, O12 and O3, respectively; these interactions utilize three of the five hydroxyl donors, but none of the amino-group N—H bonds. Of the remaining hydroxyl donors, O12 in the unit at (x, y, z) acts as a donor to N2 in the unit at $(x, -1 + y, -1 + z)$ and repetition of this, along with the O11—H11···N1 interaction, generates a chain of alternating diphenol and diamine units running parallel to the [011] direction. In this chain the biphenol acts as a bis-donor of hydrogen bonds and the diamine as a bis-acceptor, so that all the hydrogen bonds are of O—H···N type.

O3 in the unit at (x, y, z) acts as a hydrogen-bond donor to O11 in the unit at $(x, -2 + y, -1 + z)$: together with the O21—H21···O12 and O22—H22···O3 interactions, this generates a second chain, running parallel to the [021] direction. In these [021] chains, where all the hydrogen bonds are of the O—H···O type, the

methanol molecules are both donors and acceptors of hydrogen bonds, biphenol molecule 1 (containing O11 and O12) acts as a bis-acceptor of hydrogen bonds and biphenol molecule 2 acts as a bis-donor. These two sets of chains, parallel to [011] and [021], have the biphenol molecule 1 as the common component; the intersection of these chains thus generates continuous two-dimensional networks (Fig. 5), with biphenol molecule 1 at the nodes, and an entire network can be generated from the asymmetric unit at (x, y, z) simply by translations along the [010] and [001] directions. Such a network, built from O—H···O and O—H···N hydrogen bonds only, utilizes only half of the contents of the unit cell and, in fact, the network derived from the asymmetric unit at (x, y, z) lies predominantly in that half of the cell having $0 < x < \frac{1}{2}$. An entirely similar network, related to the first by the centres of inversion lying in the bc plane, lies in the adjacent cell, predominantly in that half of the cell having $-\frac{1}{2} < x < 0$: these two networks are cross-linked by N—H···O hydrogen bonds. One hydrogen only of each amino group acts as a donor towards an O atom in the adjacent network: N1 in the unit at (x, y, z) acts as a donor, *via* H1A, to O22 in the diphenol at $(-x, -y, -1 - z)$, while N2 acts as a donor, *via* H2A to O21 in the unit at $(-x, 1 - y, -z)$; the other two amino H atoms, H1B and H2B, play no part in the hydrogen-bonding scheme. An equivalent, but more helpful description of the N—H···O interactions is in terms of the diamine unit at $(-x, 1 - y, -z)$: N2 acts as a donor

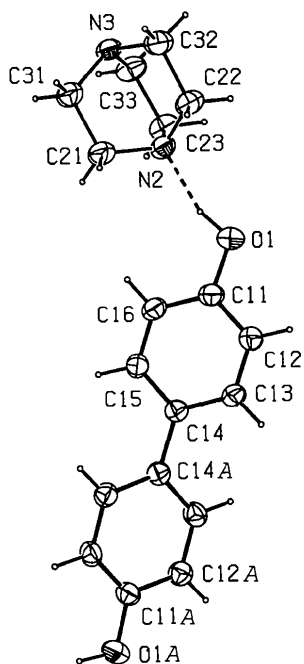


Fig. 2. The molecular aggregate in (1), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms as small spheres of arbitrary size.

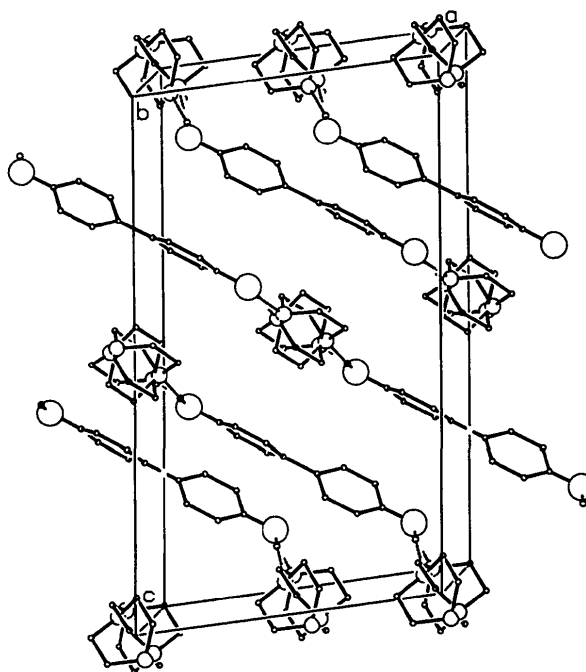


Fig. 3. View of part of the crystal structure of (1), approximately along the [010] direction, showing the $C_2^2(16)$ chains running parallel to [201].

to O21 at (x, y, z) , while N1 acts as a donor to O22 at $(x, 1 + y, 1 + z)$, so that the effect of these interactions is to link pairs of biphenol molecules of type 2 which are separated by a unit translation along $[011]$, thus generating a further set of chains running parallel to $[011]$. These chains consist of alternating biphenol and diamine units and contain only N—H···O hydrogen bonds (Fig. 5).

The diamine units in each sheet act as hydrogen-bond donors to O atoms in one neighbouring sheet, such that the sheets are linked together in pairs to form bilayers in which the two components are related by centres of inversion. The N—H···O hydrogen bonds together with the $[021]$ chains generate two ring motifs, each involving only one type of N atom. N2 at (x, y, z) acts as a hydrogen-bond donor to O21 at $(-x, 1 - y, -z)$, which in turn acts as a donor to O12, also at $(-x, 1 - y, -z)$: this atom is a donor to N2 at $(-x, 2 - y, 1 - z)$ and repetition of these interactions, starting from N2 at $(-x, 2 - y, 1 - z)$, generates a centrosymmetric ring, centred at $(0, 1, \frac{1}{2})$ and containing two each of N—H···O, O—H···O and O—H···N hydrogen bonds (Fig. 6). N1 in the unit at (x, y, z) acts as a donor to O22 at $(-x, -y, -1 - z)$, which itself is donor to O3 also at $(-x, -y, -1 - z)$; this atom, in turn, acts as a donor to O11 at $(-x, 2 - y, -z)$, which then acts as a donor to N1 at $(-x, 2 - y, -z)$. Repetition of this sequence, starting from N1 at $(-x, 2 - y, -z)$, generates a centrosymmetric ring centred at $(0, 1, 0)$, which contains

four O—H···O, two O—H···N and two N—H···O hydrogen bonds (Fig. 7).

3.1.3. *Compound (3)*. The asymmetric unit consists of half a molecule of each component: the biphenol molecule lies across the centre of inversion at the origin and the diamine lies across that at $(0, \frac{1}{2}, -\frac{1}{2})$, i.e. the components occupy the two Wyckoff (*a*) sites. The two components within the asymmetric unit are linked: the O atom of the biphenol forms an O—H···N hydrogen bond with the N atom of the diamine (Fig. 8). Repetition of this motif, combined with the action of the centres of inversion, produces a chain running in the $[01\bar{1}]$ direction in which all the hydrogen bonds are of O—H···N type. In addition, each of the independent N—H bonds acts as a hydrogen-bond donor to O atoms in other asymmetric units. The N atom at (x, y, z) acts, via H1A, as a hydrogen-bond donor to the O atom in the unit at $(\frac{1}{2} + x, \frac{1}{2} - y, z)$, while the N atom in this second unit acts as a donor to the O atom at $(1 + x, y, z)$: the glide plane thus generates a chain in the $[100]$ direction containing both N—H···O and O—H···N hydrogen bonds. By means of the second hydrogen of the amino group, H1B, the N atom at (x, y, z) acts as a donor to the O atom at $(x, 1 + y, z)$, forming another chain, this time running parallel to the $[010]$ direction and containing both N—H···O and O—H···N hydrogen bonds. The O atom at (x, y, z) thus acts as a hydrogen-bond donor to the nitrogen at (x, y, z) and as an acceptor from the two N atoms at $(-\frac{1}{2} + x, \frac{1}{2} - y, z)$ and $(x, -1 + y, z)$.

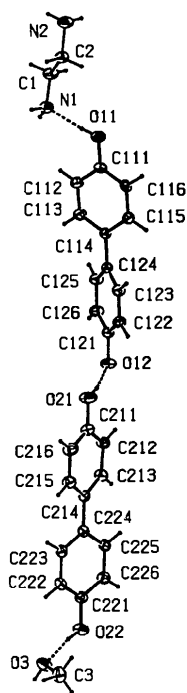


Fig. 4. The asymmetric unit of (2), showing the atom-numbering scheme. Atoms are depicted as in Fig. 2.

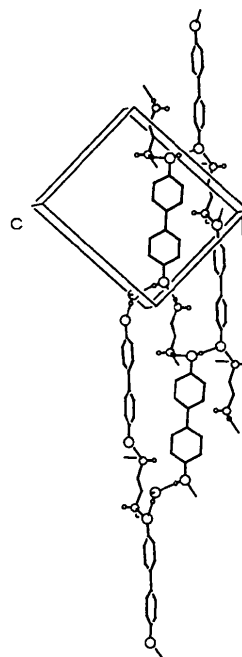


Fig. 5. View of part of the crystal structure of (2), showing the $[021]$ chains, the two types of $[011]$ chains, and the $R_6^s(36)$, $R_8^s(40)$ and $R_{10}^s(62)$ rings.

The intersection of the [100] and [010] chains gives rise to the formation of a continuous two-dimensional net, normal to the [001] direction, built up from puckered 12-membered rings each of the form $\cdots\text{H}-\text{N}-\text{H}\cdots\text{O}-\text{H}\cdots\text{N}-\text{H}\cdots\text{O}-\text{H}\cdots\text{N}-\text{H}\cdots\text{O}\cdots$ and containing only $\text{O}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Fig. 9). The non-H atoms alternate around these rings and each $(\text{ON})_3$ system has a chair conformation. Each of the N and O atoms is therefore four-coordinate, counting both the covalent bonds and the hydrogen bonds, and the hydrogen-bonded nets consist of *trans*-fused cyclohexane-type rings, giving the entire net a topology similar to that observed in rhombohedral arsenic (Bradley, 1924; Schiferl & Barrett, 1969). A single organic fragment occupies each of the axial sites in the $(\text{ON})_3$ rings and the biphenol units are directed essentially along the *c* direction. The biphenol units all lie on one side of a given ring and the diamine units on the other (Fig. 10), and these serve as linkers joining the nets into a continuous three-dimensional diamondoid array. There are two types of linking units between the hydrogen-bonded nets: long, rigid linear $-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-$ units and short, flexible zigzag $-\text{CH}_2\text{CH}_2-$ units, so that the nets occur in closely adjacent pairs, for example, on either side of the $z = 0.5$ plane (Fig. 10).

Similar hydrogen-bonded rings have been observed in the 1:2 adduct of hydroquinone and aniline (Loehlin *et al.*, 1994), giving a bilayer structure, while continuous three-dimensional arrays containing such rings were

observed in the 1:1 adducts formed by 4,4'-biphenol with both *p*-phenylenediamine and benzidine (Ermer & Eling, 1994). However, the structure of (3) demonstrates it is not necessary either to include rigid aromatic spacer units in both components or to have two spacer units of similar size and shape: the constitution and structure of (2) suggests that donor-acceptor complementarity of the NH_2 and OH groups is not an overwhelming structural determinant, since (2) crystallizes with very different numbers of OH and NH_2 groups in the asymmetric unit. In the crystal structure of the cubic diamondoid adduct $[\text{Mn}(\text{CO})_3(\mu_3\text{-OH})]_4(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2$, where the OH groups cannot act as hydrogen-bond acceptors, the components are linked together only by $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds, while the NH_2 groups do not act as hydrogen-bond donors (Copp *et al.*, 1992).

3.2. Hydrogen-bond motifs and dimensions

In (1) the two types of $\text{O}-\text{H}\cdots\text{N}$ hydrogen-bond motif (Table 3) can be described by their graph sets $N_1 = DD$, $N_2 = C_2^2(16)$ (Bernstein *et al.*, 1995): in the 1:1 DABCO adducts with the bis-phenols $X(\text{C}_6\text{H}_4\text{OH})_2$, where $X = \text{Me}_2\text{C}$, O or S , the chain-forming motif has binary graph set $N_2 = C_2^2(17)$ (Ferguson, Coupar & Glidewell, 1997).

Compound (2) contains a number of chain- and ring-forming hydrogen-bond motifs. There are seven inde-

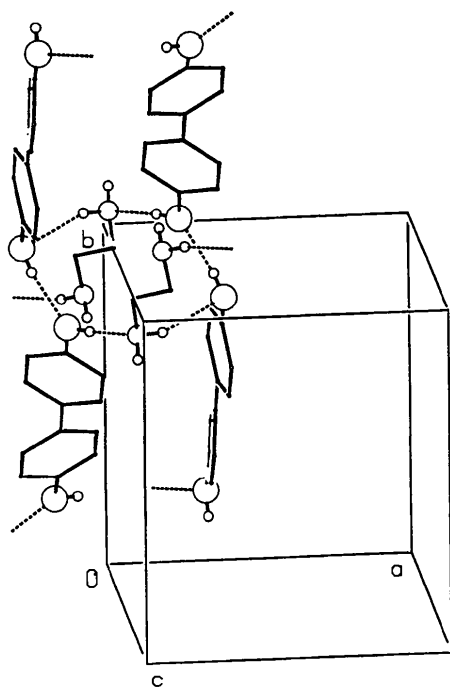


Fig. 6. View of the 12-membered ring formed in (2) by interaction of the diamine atom N2 with the [021] chains.

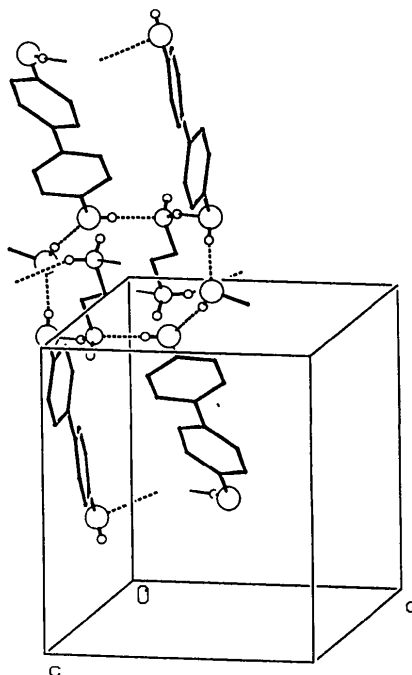


Fig. 7. View of the 16-membered ring formed in (2) by interaction of the diamine atom N1 with the [021] chains.

pendent hydrogen-bond types in the crystal structure, comprising $O-H \cdots O$, $O-H \cdots N$ and $N-H \cdots O$, but not $N-H \cdots N$ types: each O atom and each N atom acts as a single donor and single acceptor of hydrogen bonds. There is a chain of alternating biphenol and diamine units running parallel to [011] and containing only $O-H \cdots N$ hydrogen bonds which has $N_1 = DD$, $N_2 = C_2^2(16)$, just as in (1), while the [021] chain built from one methanol and two biphenol molecules contains only $O-H \cdots O$ hydrogen bonds, and has $N_1 = DDD$, $N_2 = C_3^3(24)$. The nets resulting from the intersection of these two types of chain are characterized by the binary graph set $R_{10}^{10}(62)$, where the $R(62)$ rings include contributions from six molecules of the biphenol and two molecules each of methanol and the diamine. It is interesting to note the occurrence of $R_8^8(62)$ rings in the solvent-free 2:1 adduct formed by 4,4'-thiodiphenol and DABCO, $[S(C_6H_4OH)_2]_2 \cdot C_6H_{12}N_2$ (Ferguson, Coupar & Glidewell, 1997), where the $R(62)$ rings again include contributions from six molecules of the bis-phenol and two of the diamine: the absence of the two methanol molecules reduces the numbers of donors and acceptors from ten to eight, but the incorporation into the ring of four complete $S(C_6H_4OH)_2$ molecules in place of four complete $HOC_6H_4C_6H_4OH$ units maintains the overall ring size. There is a further chain of alternating biphenol and diamine units running parallel to the [011] direction, containing only $N-H \cdots O$ hydrogen bonds; this again has graph set $N_1 = DD$, $N_2 = C_2^2(16)$: in each such chain,

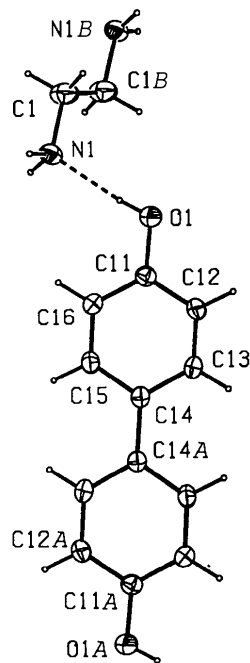


Fig. 8. The molecular aggregate in compound (3), showing the atom-numbering scheme. Atoms are depicted as in Fig. 2.

the two components belong to different sheets, of opposite hand. These chains effectively cross-brace the $R_{10}^{10}(62)$ rings, by dividing them into two smaller rings with binary graph sets $R_6^6(36)$ and $R_8^8(40)$. The smaller rings arising from the interactions of the atoms N2 and N1 with the [021] chains (Figs. 6 and 7) have graph sets $N_1 = DDD$, $N_2 = R_6^6(12)$ and $N_1 = DDDD$, $N_2 = R_8^8(16)$, respectively.

Only $N-H \cdots O$ and $O-H \cdots N$ hydrogen bonds are present in (3). The [100] and [010] chains are both characterized by the graph set $C_2^2(4)$, while the chains in the $[01\bar{1}]$ direction have the now-familiar binary graph set $C_2^2(16)$. The rings formed upon the intersection of the [100] and [010] chains have binary graph set $R_6^6(12)$ and it is possible to trace an almost infinite number of other ring patterns within the continuous three-dimensional structure. For example, the two biphenol molecules containing O atoms at (x, y, z) and $(-x, -y, -z)$, and $(\frac{1}{2} + x, \frac{1}{2} - y, z)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, -z)$, respectively, together with the amino groups at (x, y, z) and $(\frac{1}{2} - x, \frac{1}{2} + y, -z)$, describe a cyclic motif containing three $N-H \cdots O$ and one $O-H \cdots N$ hydrogen bonds and characterized by graph set $N_1 = DDDD$, $N_2 = R_4^4(26)$.

The dimensions of the hydrogen bonds are summarized in Table 3. In the $O-H \cdots O$ and $O-H \cdots N$ hydrogen bonds the donor-acceptor distances span very similar ranges: these, and the corresponding distances in the $N-H \cdots O$ hydrogen bonds, are typical of such distances in bis-phenols and their amine adducts (Jackisch *et al.*, 1990; Goldberg *et al.*, 1991; Loehlin *et al.*, 1994; Ermer & Eling, 1994; Coupar *et al.*, 1996a; Glidewell & Ferguson, 1996; Ferguson & Glidewell,

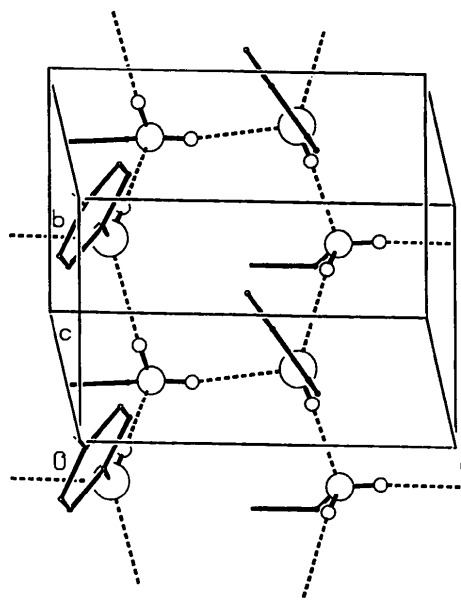


Fig. 9. The 12-membered rings formed in (3) by the intersection of the [100] and [010] chains.

1996; Coupar *et al.*, 1997; Ferguson, Coupar & Glidewell, 1997). The O1...N2 distance in (1) is less than, while the O1...N3 distance is greater than, the corresponding O...N distances observed in 1:1 adducts of DABCO with several other bis-phenols [range 2.656 (6)–2.720 (3) Å (Ferguson, Coupar & Glidewell, 1997)], while the O(–H)...N distances in (2) and (3) are all less than the O...N distance, 2.774 (8) Å, in [Mn(CO)₃(μ₃-OH)]₄·(H₂NCH₂CH₂NH₂)₂ (Copp *et al.*, 1992). None of the hydrogen bonds in (1)–(3) can be regarded as strong, but it is the collective and cooperative effect of all the many hydrogen bonds which accounts for the coherence of the supramolecular architectures.

3.3. Molecular conformations and dimensions

The DABCO and biphenol components in (1) lie across a centre of inversion and a twofold rotation axis, respectively, and the DABCO is therefore disordered. It is interesting to observe that the DABCO molecule could readily lie on a twofold axis without any orientational disorder, while 4,4'-biphenol could lie across a centre of inversion, as found in the pure substance (Jackisch *et al.*, 1990), or even on a site of $2/m$ (C_{2h}) symmetry. In the event, each component in (1) adopts a crystallographic site more appropriate to the other: the orientation of the DABCO units is such that the local twofold axes of this component are not parallel to the crystallographic rotation axes.

The most striking structural feature in pure 4,4'-biphenol (Jackisch *et al.*, 1990) is the internal angle of the aromatic ring at the site *ipso* to the other ring: in the pure biphenol the value of this angle is 116.9 (1)° and similarly small angles are found in the biphenol components in each (1)–(3); this is doubtless related to the relative electronegativities of the two ring substi-

tuents (Domenicano *et al.*, 1975). Although the 4,4'-biphenol could adopt molecular symmetry as high as C_{2h} or C_{2v} , in (1)–(3) the symmetry is never higher than C_2 or C_i . In (1), where it has C_2 symmetry, the dihedral angle between the aromatic rings is 40.5 (2)°, while in (2), where neither molecule of the biphenol exhibits any symmetry, the inter-plane angles in the two molecules are 35.9 (1) and 15.1 (1)°. In (3) the centrosymmetric biphenol molecules depart from C_{2h} symmetry only inasmuch as the torsional angle H1–O1–C11–C16 is –13 (2)° rather than zero.

The 1,2-diaminoethane component of (3) lies across a centre of inversion and therefore adopts a *trans*-planar configuration, precisely as found in the pure compound at –60° (Jamet-Delcroix, 1973): in (2), although no symmetry is imposed upon the diamine component, the major orientational form has a torsional angle N1–C1–C2–N2 of –177.0 (2)°, so that the conformation is clearly *trans*, and almost planar.

The other bond lengths and angles are all typical of their types (Allen *et al.*, 1987).

4. General comments and conclusions

The crystal structures of (1)–(3), with hydrogen bonding generating one-, two- and three-dimensional structures, illustrate the range of supramolecular architectures, from simplicity to complexity, which can be attained by self-assembly from very simple molecular building blocks, in this case the simplest possible biphenol and two very simple diamines. As usual, the 4,4'-biphenol acts always as a double donor of hydrogen bonds, but in the adducts (2) and (3) with 1,2-diaminoethane the biphenol also acts as an acceptor: each molecule of the biphenol in (2) acts as a bis-acceptor, while in (3) the biphenol molecule is an acceptor of four hydrogen

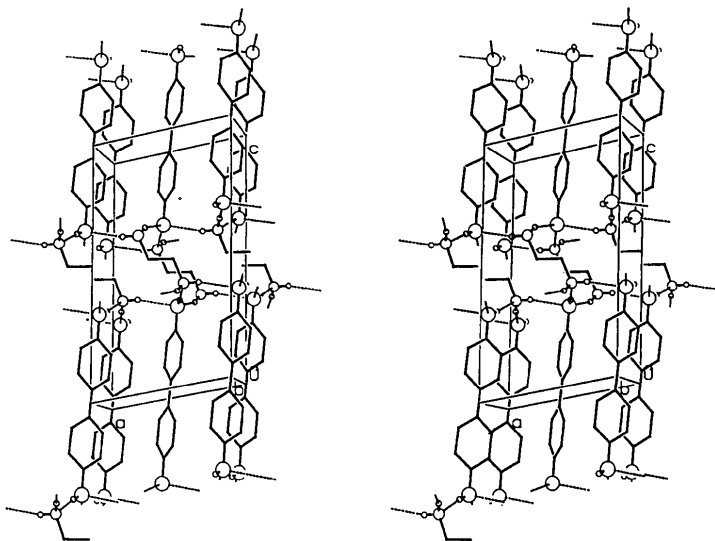


Fig. 10. Stereoview of part of the crystal structure of (3).

bonds. It is noteworthy that in none of the adducts formed between bis-phenols and either primary or secondary amines reported here and elsewhere (Loehlin *et al.*, 1994; Ermer & Eling, 1994; Coupar *et al.*, 1996*b,c*) are there any N—H...N hydrogen bonds, even in examples such as (3) where the number of N—H bonds in the asymmetric unit is double the number of O—H bonds. In some 1,2-diaminoethane adducts, such as (2) or (C₆H₅OH)₂·H₂NCH₂CH₂NH₂ (Loehlin *et al.*, 1994), half of the N—H bonds take no part in the hydrogen bonding, while in [Mn(CO)₃(μ₃-OH)]₄·(H₂NCH₂CH₂NH₂)₂ (Copp *et al.*, 1992) none of the N—H bonds participate in hydrogen bonding. Again in the 1:1 adduct of 4,4'-thiodiphenol and piperazine (Coupar *et al.*, 1996*b*) there are N—H...π(arene), but not N—H...N, hydrogen bonds. An extreme example of this tendency to avoid the formation of N—H...N hydrogen bonds is provided by the isoelectronic and isosteric pair Ph₃COH and Ph₃CNH₂; Ph₃COH forms tetrahedral tetrameric aggregates in which the molecules are held together by O—H...O hydrogen bonds (Ferguson *et al.*, 1992), while in the structure of Ph₃CNH₂ there is no hydrogen bonding at all (Glidewell & Ferguson, 1994*a*). A counter-example is however provided by a second isoelectronic and isosteric pair: in Ph₃CONH₂, pairs of molecules are connected into R₂²(4) dimers by pairs of N—H...N rather than N—H...O hydrogen bonds, while in Ph₃CSNH₂, N—H...S hydrogen bonds generate R₂²(6) dimers (Glidewell & Ferguson, 1994*b*).

Although the presence of equal numbers of OH and NH₂ groups can, when the OH acts as a single donor and a double acceptor and the NH₂ groups acts as a double donor and a single acceptor, provide a beautiful example of structural complementarity (Ermer & Eling, 1994), this phenomenon does not appear to be, in general, a significant determinant either of self-assembled stoichiometry or of crystal architecture. Although in (3), and in the adducts of 4,4'-biphenol with *p*-phenylenediamine and with benzidine (Ermer & Eling, 1994), the OH and NH₂ groups are present in the numerical ratio 1:1, (2) has a 5:2 ratio, while the recently characterized adduct of 1,2-diaminoethane and 1,1,1-tris(4-hydroxyphenyl)ethane of stoichiometry [CH₃C(C₆H₄OH)₃]₂·H₂NCH₂CH₂NH₂ has a 3:1 ratio of these groups (Ferguson *et al.*, 1998)

GF thanks NSERC (Canada) for research grants; RMG thanks EPSRC (UK) for financial support.

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