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2,2'-Biphenol–1,4-diazabicyclo[2.2.2]octane (2/1), a three-dimensional framework built from O—H···O, O—H···N, N—H···O and C—H···π(arene) hydrogen bonds

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Abstract

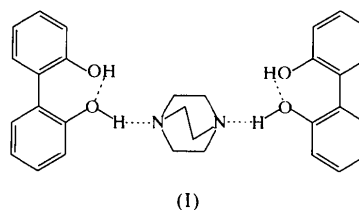
In the 2:1 adduct of 2,2'-biphenol and 1,4-diazabicyclo[2.2.2]octane, 2C₁₂H₁₀O₂·C₆H₁₂N₂, there are eight molecules of the biphenol and four molecules of the amine in the asymmetric unit, and several of these components exhibit orientational disorder even at 100 K. Each biphenol unit contains an intramolecular O—H···O hydrogen bond [O···O range for the ordered components 2.594 (6) to 2.668 (5) Å]. Each of the amines is hydrogen bonded to two biphenol units [O···N range for the ordered components 2.521 (7) to 2.594 (6) Å], so forming four independent three-molecule aggregates. These aggregates are further linked by an extensive

series of C—H···π(arene) interactions into a continuous three-dimensional framework.

Comment

The bis-tertiary amine 1,4-diazabicyclo[2.2.2]octane, (DABCO), is a strong acceptor of hydrogen bonds which readily forms adducts with phenols and bis-phenols. With simple mono-phenols, which can act as donors forming just one hydrogen bond per molecule, 1:2 adducts (DABCO)-2(phenol) are formed whose structures are built from finite three-molecule aggregates, which are held together by two O—H···N hydrogen bonds (Mak *et al.*, 1984; Takama *et al.*, 1988). Rather similar adducts can be formed with tertiary alcohols (Yasui *et al.*, 1989). In 1:1 adducts, bis-phenols which can act as double donors of hydrogen bonds form continuous chains with DABCO (Mak *et al.*, 1984; Ferguson, Coupar & Glidewell, 1997; Ferguson *et al.*, 1998), and where the bis-phenol has little or no conformational flexibility, the resulting chains are essentially rigid with no coiling (Mak *et al.*, 1984; Ferguson *et al.*, 1998). It has been suggested (Ferguson, Bell *et al.*, 1997) that chain-coiling controlled largely by the soft (Braga *et al.*, 1995) hydrogen bonds is likely to occur where one or other of the components in such a chain exhibits conformational flexibility.

In 2,2'-biphenol, HOC₆H₄—C₆H₄OH, there is no real restriction to rotation about the central C—C bond, so that a wide range of conformations is accessible. In the crystal structure of the pure substance, intramolecular O—H···O hydrogen bonds are present (Byrne *et al.*, 1998), but in its hydrate (Chen *et al.*, 1996) and in its adducts with 4,4'-bipyridyl (Lavender *et al.*, 1999) and hexamethylenetetramine (MacLean *et al.*, 1999), 2,2'-biphenol forms only intermolecular hydrogen bonds. We have therefore sought to prepare, and structurally characterize, a 1:1 adduct of 2,2'-biphenol with DABCO, in the expectation of observing highly coiled chains. In the event, co-crystallization of the two molecular components in various proportions consistently yielded the 2:1 adduct 2C₁₂H₁₀O₂·C₆H₁₂N₂, (I), whose structure consists of finite aggregates, but which is nonetheless crystallographically interesting.



The diffraction intensities for compound (I) pointed strongly towards the centrosymmetric space group *P4/m*. However, repeated and robust attempts at structure solution in *P4/m* were all dismally unsuccessful, but the structure was solved very easily in the

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non-centrosymmetric space group $P\bar{4}$ to reveal eight independent 2,2'-biphenol molecules and four independent DABCO molecules (Figs. 1 and 2). Two of the DABCO units, those containing N3 and N5, are disordered, and each was modelled using two sets of sites. For the N3/N4 molecules the site occupancy factors refined to 0.736(4) and 0.264(4), while for the N5/N6 molecule the refined site occupancy factors are 0.839(4) and 0.161(4).

Fully ordered DABCO molecules in general positions appear to be rather unusual in DABCO-phenol adducts. In the adducts of DABCO with hydroquinone (1/1) (Mak *et al.*, 1984), *p*-cresol (2/1) (Takama *et al.*, 1988) and $\text{Me}_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$ (1/1) (Ferguson, Coupar & Glidewell, 1997) the DABCO units lie on twofold axes; in the adducts with $\text{S}(\text{C}_6\text{H}_4\text{OH})_2$ (2/1) (Ferguson, Coupar & Glidewell, 1997) and with 4,4'-biphenol (1/1) (Ferguson *et al.*, 1998), the DABCO units are disordered across centres of inversion; in the 1:1 adduct with $\text{S}(\text{C}_6\text{H}_4\text{OH})_2$ (Ferguson, Coupar & Glidewell, 1997) the DABCO units exhibit rotational disorder about the $\text{N}\cdots\text{N}$ vector with the two equally populated orientations separated by a rotation of $37.1(2)^\circ$; and in the 1:1 adduct with $\text{O}(\text{C}_6\text{H}_4\text{OH})_2$ (Ferguson, Coupar & Glidewell, 1997), there are two unequally populated orientations, separated by a rotation of $48(3)^\circ$. Only in the 2:1 adduct with phenol itself (Mak *et al.*, 1984) are the DABCO units fully ordered in general positions. For both of the disordered DABCO units in compound (I), the alternative N sites for the two orientations (N3, N3A, *etc.*) are not quite coincident: hence it is not possible to define or determine rigorously the rotational separation between the two orientations. Nonetheless it is clear that this separation is *ca* 50° in both units, close to full staggering between the two orientations. The frequently observed orientational disorder is doubtless a consequence of the near-cylindrical profile of the van der Waals surface in DABCO; moreover, it is at least possible that in some systems of this type the disordered sites modelled from X-ray diffraction data represent, not static disorder, but rather the well-populated local minima in the rapid rotation of the DABCO units about the $\text{N}\cdots\text{N}$ vectors.

In the biphenol unit containing O41 and O42, the ring carrying O42 showed marked anisotropy and was modelled using two sets of sites, labelled O42, C421–C426 and O43, C431–C436, having equal occupancy. In all of the 2,2'-biphenol units there is an intramolecular $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bond, and each 2,2'-biphenol is hydrogen-bonded to a DABCO unit (Table 1). In three of the hydrogen-bonded $\text{O}\cdots\text{N}$ pairs involving N1, N4 and N8, difference maps showed that the H atoms were disordered over two sites, one adjacent to O and one adjacent to N, having equal occupancy, so forming a disordered mixture of $\text{O}\cdots\text{H}\cdots\text{N}$ and $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds. Each DABCO unit is thus linked to two biphenol units (Table 1) and the molecular components

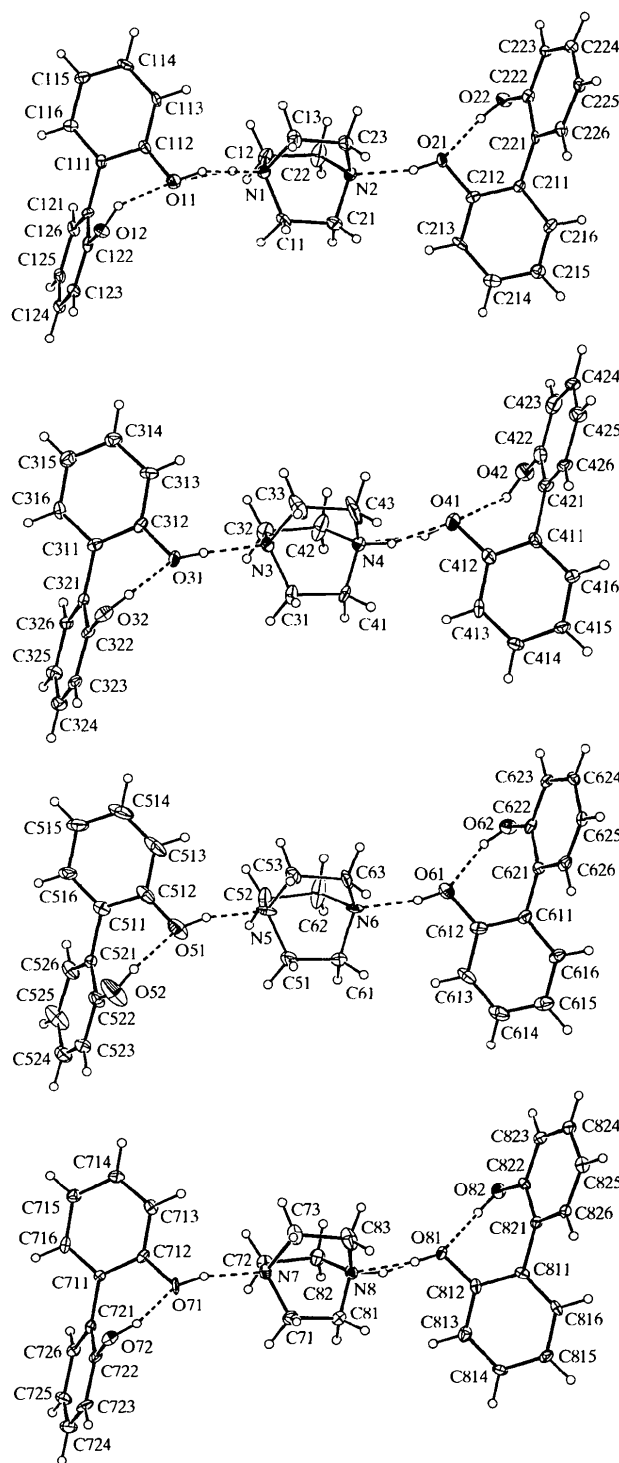


Fig. 1. The molecular components of compound (I) showing the atom-labelling scheme: in the biphenol units, C atoms are labelled $C(npq)$ where n (1–8) defines the molecule, p (1 or 2) defines the ring and q (1–6) defines the atom; atoms $O(np)$ are bonded to $C(np2)$. For the sake of clarity, the minor orientations of the disordered DABCO units are omitted; similarly the ring O42, C421–C426 is shown but O43, C431–C436 is omitted. Displacement ellipsoids are drawn at the 30% probability level.

are linked into four similar, but independent, three-molecule aggregates: (2,2'-biphenol)–(DABCO)–(2,2'-biphenol) (Fig. 1). The resulting Z' value of four is unusually high for the tetragonal system; indeed Z' values above two are rare in all systems other than triclinic and monoclinic (Wilson, 1993; Brock & Dunitz, 1994). The four independent hydrogen-bonded aggregates are so arranged that in projection down [001] the asymmetric unit is very close to having fourfold rotational symmetry, and the corresponding projection of the entire structure closely mimics the square plane group $p4$ with a unit cell one quarter the size of the real cell. It is interesting to note that the mean $\langle E^2 - 1 \rangle$ value is much higher for the $hk0$ reflections than for either $h0l$ or $0kl$ or for the data as a whole. However, the z coordinates of the centroids of the four independent DABCO molecules indicate that, in three dimensions, the asymmetric unit does not have even approximate rotational symmetry (Fig. 2).

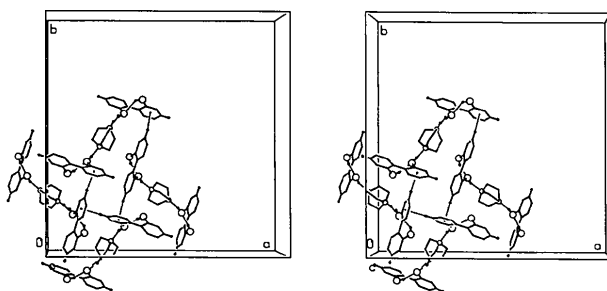


Fig. 2. Stereoview of part of the crystal structure of (I), showing the components of the asymmetric unit linked by O—H...N, N—H...O and C—H... π (arene) hydrogen bonds.

The O...O distances in the O—H...O hydrogen bonds show a reasonable correlation with the dihedral angles between the two aryl rings of the biphenol units (Tables 1 and 2): all of the O—H...N and N—H...O hydrogen bonds are short (Table 1), but there is no clear association of particularly short O...N distances with partially ionic components. In addition to the hard O—H...N and N—H...O hydrogen bonds linking the components in the three-molecule aggregates, there is an extensive range of soft C—H... π (arene) interactions which serve to link the three-molecule aggregates into a three-dimensional continuum (Table 1). In each such interaction the bond C n p4—H n p4 ($n = 1-8$; $p = 1$ or 2) in one aryl ring (that *para* to the inter-ring bond in the biphenyl) acts as hydrogen-bond donor to the π -system of an aryl ring in a neighbouring biphenol unit. Of the 16 independent C n p4 atoms, only C224, C624 and C824 do not participate as donors in these interactions, and of the 16 independent rings only the rings C221–C226, C621–C626 and C821–C826 do not act as acceptors. The interactions involving C g (r) for $r = 1, 5, 8$ and 13 link together all four aggregates within the asymmetric unit (Fig. 2); those for $r = 3, 9-11$ and 15, when propagated by the symmetry operators of the

space group, link together all the asymmetric units in the (001) plane forming a two-dimensional net; and those for $r = 2, 6, 7$ and 14 link all the (001) nets into a three-dimensional framework.

The highest possible molecular symmetry for a neutral DABCO molecule is D_{3h} ($\bar{6}m2$), but this requires fully eclipsed CH₂ groups within each NCH₂CH₂N fragment. Relief of the steric strain induced by this eclipsing can be achieved by an internal twist about the N...N vector, which reduces the molecular symmetry to D_3 (32). For isolated, gas-phase molecules the internal dynamics indicated a very broad potential well for the twisting motion, best fitted by a harmonic quartic potential function having an energy minimum corresponding to a twist of *ca* 10° from the D_{3h} geometry (Yokozeki & Kuchitsu, 1971). By contrast, in a neutron diffraction study of the hexagonal crystalline phase of DABCO it was found that the molecules were ordered on sites of D_{3h} symmetry (Nimmo & Lucas, 1976). In compound (I), excluding the minor components, the N—C—C—N torsion angles (Table 3) range between 6.5 (8) and 13.6 (9)°, with a mean value which is very close, possibly by chance, to the gas-phase energy minimum (Yokozeki & Kuchitsu, 1971). In adducts of DABCO with hydroquinone (Mak *et al.*, 1984) and with 4,4'-isopropylidenediphenol and 4,4'-oxodiphenol (Ferguson, Coupar & Glidewell, 1997) there are also clear indications of significant twists away from the D_{3h} conformation.

Despite the partial protonation of N1, N4 and N8, there is no significant difference between the C—N bond lengths involving these N atoms and those to the remaining N atoms (Table 4): in general, protonated DABCO (C₆H₁₃N₂)⁺ shows a very clear difference in the two types of C—N bond, with those to protonated N typically longer by 0.03 to 0.04 Å (Baksi *et al.*, 1994; Zhao *et al.*, 1996; Bock *et al.*, 1997; Henschel *et al.*, 1997; Meehan *et al.*, 1997; Jiang *et al.*, 1998).

Examination of the structure with PLATON (Spek, 1999) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

Equimolar quantities of 2,2'-biphenol and DABCO were separately dissolved in methanol. These solutions were mixed, and the mixture was set aside to crystallize, producing compound (I). Analysis: found C 73.4, H 6.4, N 5.7%; 2C₁₂H₁₀O₂·C₆H₁₂N₂ requires C 74.3, H 6.7, N 5.8%. The same material was produced using other molar ratios of 2,2'-biphenol to DABCO in the range 2:1 to 1:2. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

2C₁₂H₁₀O₂·C₆H₁₂N₂
 $M_r = 484.58$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Tetragonal
 $P4$
 $a = 27.9391$ (8) Å
 $c = 12.7565$ (4) Å
 $V = 9957.6$ (5) Å³
 $Z = 16$
 $D_x = 1.293$ Mg m⁻³
 D_m not measured

Data collection

KappaCCD diffractometer
 φ and ω scans with κ offsets
Absorption correction:
multi-scan (*DENZO-SMN*;
Otwinowski & Minor,
1997)
 $T_{\min} = 0.975$, $T_{\max} = 0.990$
27 924 measured reflections
11 817 independent
reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.162$
 $S = 1.009$
11817 reflections
1325 parameters
H-atom parameters
constrained

Cell parameters from 11817
reflections
 $\theta = 2.61$ – 27.49°
 $\mu = 0.086$ mm⁻¹
 $T = 100$ (1) K
Plate
 $0.30 \times 0.25 \times 0.12$ mm
Colourless

6435 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$
 $\theta_{\text{max}} = 27.49^\circ$
 $h = 0 \rightarrow 36$
 $k = -25 \rightarrow 25$
 $l = 0 \rightarrow 16$
Intensity decay: negligible

$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.026$
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Symmetry codes: (i) $-x, -y, z$; (ii) $-x, 1 - y, z$; (iii) $1 - x, 1 - y, z$;
(iv) $1 - y, x, -z$; (v) $1 - x, -y, z$; (vi) $y, -x, 1 - z$; (vii) $1 - y, x, 1 - z$;
(viii) $-y, x, 1 - z$.

† Aryl rings Cn11–Cn16 and Cn21–Cn26 ($n = 1$ –8) have centroids
 $Cg(2n-1)$ and $Cg(2n)$, respectively.

Table 2. Selected dihedral angles ($^\circ$)

| n | (Cn11–Cn16) [^] (Cn21–Cn26)† | n | (Cn11–Cn16) [^] (Cn21–Cn26) |
|-----|---------------------------------------|-----|--------------------------------------|
| 1 | 50.4 (2) | 5 | 44.1 (2) |
| 2 | 43.8 (2) | 6 | 42.2 (2) |
| 3 | 50.2 (2) | 7 | 48.7 (2) |
| 4 | 53.1 (3) | 8 | 41.6 (2) |

† Atom numbering as in Fig. 1.

Table 3. Selected torsion angles ($^\circ$)

| n | Nn–Cn1–Cm1–Nm† | Nn–Cn2–Cm2–Nm | Nn–Cn3–Cm3–Nm |
|-----|----------------|---------------|---------------|
| 1 | 9.4 (8) | 6.5 (8) | 6.7 (8) |
| 3 | 7.0 (11) | 7.1 (11) | 7.5 (13) |
| 5 | 13.1 (9) | 10.3 (10) | 13.6 (9) |
| 7 | 13.6 (8) | 11.3 (7) | 11.8 (8) |

† Atom numbering as in Fig. 1; $m = n + 1$.

Table 4. Selected bond lengths (Å)

| n | Nn–Cn1† | Nn–Cn2 | Nn–Cn3 | On1–Cn12 | On2–Cn22 |
|-----|------------|------------|------------|-----------|-----------|
| 1 | 1.473 (7) | 1.453 (7) | 1.466 (7) | 1.362 (7) | 1.389 (7) |
| 2 | 1.497 (7) | 1.460 (7) | 1.473 (7) | 1.374 (6) | 1.386 (5) |
| 3 | 1.457 (10) | 1.472 (9) | 1.478 (10) | 1.369 (6) | 1.363 (6) |
| 4 | 1.449 (10) | 1.486 (11) | 1.470 (11) | 1.357 (5) | 1.373 (3) |
| 5 | 1.467 (8) | 1.456 (9) | 1.448 (8) | 1.350 (6) | 1.351 (6) |
| 6 | 1.527 (8) | 1.474 (8) | 1.464 (8) | 1.367 (7) | 1.383 (6) |
| 7 | 1.490 (7) | 1.502 (7) | 1.469 (7) | 1.376 (6) | 1.363 (6) |
| 8 | 1.427 (7) | 1.486 (7) | 1.463 (7) | 1.361 (7) | 1.360 (6) |

† Atom numbering as in Fig. 1.

Table 1. Hydrogen-bond parameters (Å, $^\circ$)

| D—H...A | D—H | H...A | D...A | D—H...A |
|----------------------------------|------|-------|------------|---------|
| N1—H1...O11 | 0.93 | 1.69 | 2.596 (6) | 164 |
| N4—H4...O41 | 0.93 | 1.74 | 2.628 (10) | 159 |
| N8—H8...O81 | 0.93 | 1.71 | 2.594 (6) | 157 |
| O11—H11...N1 | 0.84 | 1.82 | 2.596 (6) | 154 |
| O12—H12...O11 | 0.84 | 1.97 | 2.667 (5) | 140 |
| O21—H21...N2 | 0.84 | 1.80 | 2.606 (6) | 160 |
| O22—H22...O21 | 0.84 | 1.83 | 2.616 (5) | 155 |
| O31—H31...N3 | 0.84 | 1.75 | 2.578 (9) | 171 |
| O32—H32...O31 | 0.84 | 1.90 | 2.668 (5) | 151 |
| O41—H41...N4 | 0.84 | 1.87 | 2.628 (10) | 149 |
| O42—H42...O41 | 0.84 | 2.12 | 2.786 (10) | 136 |
| O43—H43...O41 | 0.84 | 1.78 | 2.558 (10) | 152 |
| O51—H51...N5 | 0.84 | 1.72 | 2.521 (7) | 159 |
| O52—H52...O51 | 0.84 | 1.83 | 2.602 (7) | 152 |
| O61—H61...N6 | 0.84 | 1.76 | 2.585 (7) | 168 |
| O62—H62...O61 | 0.84 | 1.82 | 2.594 (6) | 152 |
| O71—H71...N7 | 0.84 | 1.77 | 2.586 (6) | 165 |
| O72—H72...O71 | 0.84 | 1.90 | 2.639 (5) | 146 |
| O81—H81...N8 | 0.84 | 1.78 | 2.594 (6) | 163 |
| O82—H82...O81 | 0.84 | 1.84 | 2.617 (5) | 153 |
| C114—H114...Cg(5)† | 0.95 | 2.65 | 3.565 | 162 |
| C514—H514...Cg(13) | 0.95 | 2.71 | 3.588 | 154 |
| C524—H524...Cg(8) | 0.95 | 2.97 | 3.707 | 135 |
| C714—H714...Cg(1) | 0.95 | 2.58 | 3.509 | 165 |
| C214—H214...Cg(15 [†]) | 0.95 | 2.68 | 3.532 | 149 |
| C414—H414...Cg(3 [†]) | 0.95 | 2.68 | 3.551 | 153 |
| C424—H424...Cg(10 [†]) | 0.95 | 2.81 | 3.582 | 139 |
| C614—H614...Cg(9 [†]) | 0.95 | 2.85 | 3.633 | 140 |
| C814—H814...Cg(11 [†]) | 0.95 | 2.72 | 3.538 | 145 |
| C124—H124...Cg(2 [†]) | 0.95 | 2.68 | 3.495 | 144 |
| C314—H314...Cg(7 [†]) | 0.95 | 2.60 | 3.508 | 160 |
| C324—H324...Cg(14 [†]) | 0.95 | 2.70 | 3.516 | 145 |
| C724—H724...Cg(6 [†]) | 0.95 | 2.67 | 3.497 | 146 |

Compound (I) crystallized in the tetragonal system, Laue group $4/m$ with $Z = 16$. There were no systematic absences in the diffraction data, allowing the space groups $P4$, $P4$ and $P4/m$. The E statistics strongly indicated that the structure was centrosymmetric but, despite this, structure solution was possible only in $P4$. Space group $P4$ is non-centrosymmetric with no atom having significant $\Delta f''$ anomalous dispersion contributions. The Friedel pairs were merged before refinement. The biphenol unit containing O41 and O42 was markedly anisotropic and one of the rings was modelled using two sets of sites with equal occupancy, all refined anisotropically; all rings in this molecule were constrained to be regular hexagons with C—C distances of 1.390 Å. The biphenol containing O51 and O52 exhibited very large displacement parameters consistent with a rocking motion of the entire molecule, approximately about the mid-point of the C511—C521 bond; attempts to model this as two sets of sites were unsuccessful, but it was again necessary to constrain the rings to be regular hexagons, as above. For the disordered DABCO molecules, the major components were refined anisotropically and the minor components were refined isotropically with appropriate distance restraints.

Data collection: *KappaCCD Server Software* (Nonius, 1997). Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997). Data reduction: *DENZO-SMN*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *NRCVAX96* (Gabe *et al.*, 1989) and *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1999). Software used to prepare material for publication: *NRCVAX96*,

SHELXL97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC (Canada). RMG thanks EPSRC (UK) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1331). Services for accessing these data are described at the back of the journal.

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Network of C—H···O interactions in 4-benzyloxy-3-methoxybenzaldehyde (vanillin benzyl ether)

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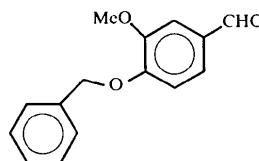
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Abstract

The title aldehyde, C₁₅H₁₄O₃, crystallized in the centrosymmetric space group *P2₁/c* with one molecule in the asymmetric unit. Six significant intermolecular C—H···O interactions have C···O distances ranging from 3.405 (2) to 3.802 (2) Å and C—H···O angles ranging from 121 to 162°. These six intermolecular interactions link a molecule directly to six neighbors and form a three-dimensional network. The dihedral angle between the best-fit planes of the benzene rings within a molecule is 78.1 (1)°. The dihedral angle between the carboxaldehyde-group plane and the best-fit plane of the ring to which it is attached is 3 (1)°.

Comment

This report on the title aldehyde, (I), is one of a series on hydrogen bonding in organic solids. It follows our reports on two other aldehydes with additional O atoms as potential acceptors, dibenzofuran-4-carboxaldehyde (Fitzgerald *et al.*, 1991) and 2,2'-dihydroxy-5,5'-dimethoxybiphenyl-3,3'-dicarboxaldehyde [hereafter, (II)] (Gerkin, 1999). (I) crystallized in the centrosymmetric space group *P2₁/c* with one molecule in the asymmetric unit. The refined molecule and the labeling scheme are shown in Fig. 1. Six intermolecular C—H···O interactions have parameter values falling well within



(I)

the criteria of Taylor & Kennard (1982) for significantly attractive interactions; a recent comprehensive analysis of such interactions is given by Steiner & Desiraju (1998). Geometric details for these are given in Table 2. Altogether these interactions link a molecule directly to six neighbors; in (II), 11 intermolecular interactions link a molecule directly to eight neighbors. The results