

Acta Cryst. (1996). **C52**, 2009–2014

Host–Guest Complexes of Furan-2,5-diylbis(diphenylmethanol): Structures of the 2:1 Adducts with Dimethylformamide, Dimethyl Sulfoxide and Pyridine

GEORGE FERGUSON,^a CHRISTOPHER GLIDEWELL^b AND CHOUDHURY M. ZAKARIA^c

^a*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1,* ^b*School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, Scotland,* and ^c*Department of Chemistry, University of Rajshahi, Rajshahi 6205, Bangladesh. E-mail: cg@st-andrews.ac.uk*

(Received 26 January 1996; accepted 4 March 1996)

Abstract

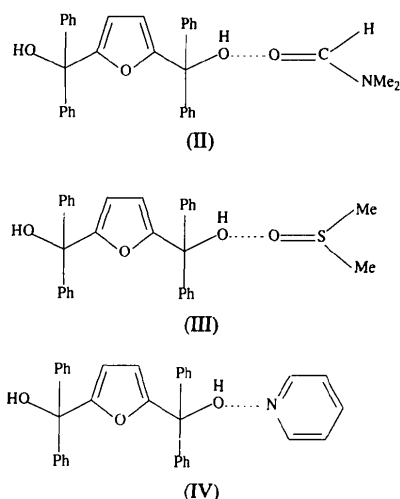
In the isomorphous 2:1 adducts of furan-2,5-diylbis(diphenylmethanol) with dimethylformamide (DMF), [2(C₃₀H₂₄O₃):1(C₃H₇NO)] (II), and with dimethyl sulfoxide (DMSO), [2(C₃₀H₂₄O₃):1(C₂H₆OS)] (III), the centrosymmetric molecular aggregate consists of two molecules of the diol, linked *via* O—H···O hydrogen bonds involving only the hydroxyl O atoms, and one molecule of either DMF or DMSO disordered across other centres of inversion and linked to the diol dimer by O—H···O hydrogen bonds. In the 2:1 adduct with pyridine, [2(C₃₀H₂₄O₃):1(C₅H₅N)] (IV), the molecular aggregate is similar in structure to those in (II) and (III), but with detailed differences in the hydrogen-bonding scheme within the diol dimer.

Comment

Organic diols of type [RR'C(OH)]₂X, where *R* and *R'* represent phenyl or other large aryl substituents and *X* represents a spacer group of limited flexibility, are versatile hosts for the capture of a wide range of guest molecules, and in most cases the guest is bound to the host by hydrogen bonds. We have recently investigated the structural behaviour of a range of such host–guest adducts formed by ferrocene-1,1'-diylbis(diphenylmethanol), Fe[C₅H₄CPh₂OH]₂ (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*; Glidewell, Ferguson, Lough & Zakaria, 1994). This diol itself crystallizes as hydrogen-bonded dimers, in which the hydroxyl H atoms appear from the X-ray diffraction to be disordered (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*) but are found from solid-state NMR to be mobile (Aliev, Harris, Shannon, Glidewell, Zakaria & Schofield, 1995). The unsolvated parent diol of the compounds described here, furan-2,5-diylbis(diphenylmethanol), C₄H₂O(CPh₂OH)₂ (I), also crystallizes as

hydrogen-bonded dimers, but with the O atom in the furan spacer group participating in the hydrogen-bonding in addition to the hydroxyl groups (Glidewell, Zakaria & Ferguson, 1996).

The diol (I) has now been found to form adducts having host–guest ratios of 2:1 with dimethylformamide (II), dimethyl sulfoxide (III), pyridine (IV) and 1,4-dioxan (V), and a 1:1 adduct (VI) with methanol (see Experimental section); here we report the structures of the adducts (II)–(IV).



Crystals of (II) and (III) are isostructural; views of the asymmetric units are given in Figs. 1 and 3. In each compound, the molecular aggregate (Figs. 2 and 4) consists of two molecules of the diol and one of the guest molecule, DMF or DMSO. In each of (II) and (III), the hydroxyl H atom on O1 is disordered over two sites with equal occupancy, while that on O2 is ordered. The guest molecules are disordered across the centre of inversion at (0, 1/2, 1/2); the diols are linked across the

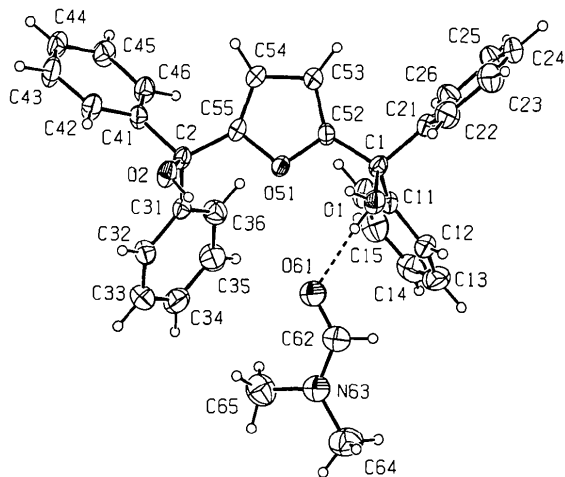


Fig. 1. A view of the asymmetric unit of (II) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

inversion centre at $(1/2, 1/2, 1/2)$ into hydrogen-bonded dimers with the H atom on O2 acting as donor to O1 of the molecule at $(1 - x, 1 - y, 1 - z)$, giving a motif whose graph set (Etter, 1990; Etter, MacDonald & Bernstein, 1990; Bernstein, Davis Shimoni & Chang, 1995) is $R_2^2(16)$ (Figs. 2 and 4). The disordered H atoms

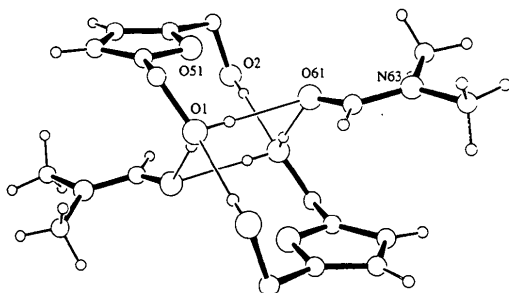


Fig. 2. A view of a hydrogen-bonded dimer with the dimethylformamide molecules. For clarity, all phenyl ring atoms have been omitted and only one of the two possible orientations of the disordered dimethylformamide molecule is shown.

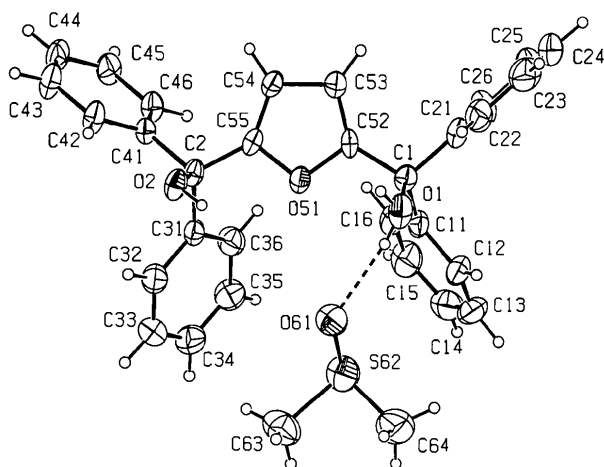


Fig. 3. A view of the asymmetric unit of (III) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

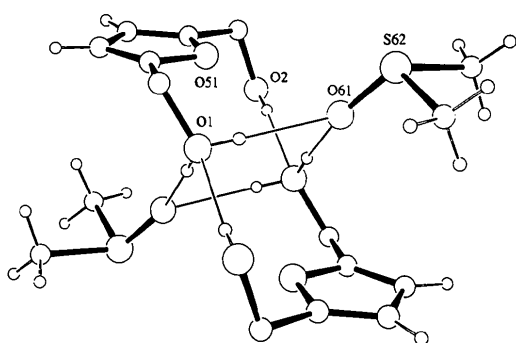


Fig. 4. A view of a hydrogen-bonded dimer with dimethyl sulfoxide molecules. Phenyl rings are omitted for clarity and only one of the two possible orientations of the disordered dimethyl sulfoxide molecule is shown.

on O1 act (Table 4) as hydrogen-bond donors to the oxygen O61 of the guest molecules: H1A acts as donor towards the guest at (x, y, z) , and H1B as donor towards the guest at $(1 - x, 1 - y, 1 - z)$; each motif has graph set D . Within the cyclic motif defined by O1 and O61 in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, there is no necessary correlation between the orientation of the two types of hydrogen bond. In this respect, the hydrogen bonding in (II) and (III) differs from that in the dimers of ferrocene-1,1'-diyl-bis(diphenylmethanol) (Ferguson, Gallagher, Glidewell & Zakaria, 1993b). Finally, the orientational disorder of the guest molecules serves to link the diol dimer units into chains parallel to the a direction.

The asymmetric unit of compound (IV) is shown in Fig. 5 and although it is not isomorphous with (II) and (III), it too contains centrosymmetric molecular aggregates (Fig. 6) with pyridine molecules disordered over the inversion centres at $(0, 1/2, 1/2)$ and the hydroxyl H atom on O1 disordered over two equally

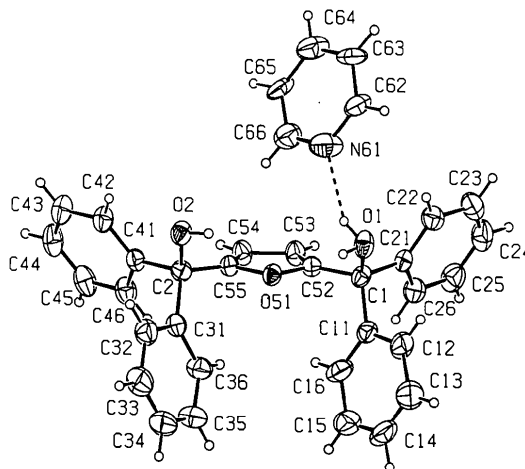


Fig. 5. A view of the asymmetric unit of (IV) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

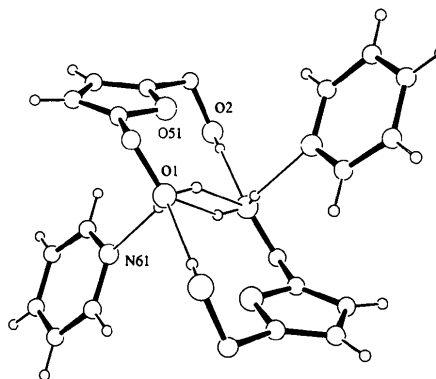


Fig. 6. A view of a hydrogen-bonded dimer with pyridine. Phenyl rings are removed for clarity and only one of the two possible orientations of the disordered pyridine molecule is shown.

populated sites. The diol components are linked across the inversion centre at (1/2, 1/2, 1/2) to form hydrogen-bonded dimers (Fig. 6, Table 3) containing both an $R_2^2(16)$ motif involving H2 on O2 and an $R_2^2(4)$ motif involving H1A on O1; there are, in addition, weak intramolecular hydrogen bonds involving O51 as acceptor, similar to those observed in the structure of (I) (Glidewell, Zakaria & Ferguson, 1996), so that these dimers differ significantly from those in (II) and (III). H1B on O1 acts as donor towards N61 of the pyridine guest in a motif having graph set *D*, and the orientational disorder of the guest molecules serves to link the dimer units into chains parallel to *a*.

The principal differences between (II) and (III) on the one hand and (IV) on the other, arise simply because the O atoms in DMF and DMSO in (II) and (III) each have two lone pairs to participate as acceptors in O—H...O hydrogen bonding whereas the pyridine in (IV) has only one lone pair available.

The dimensions and conformations of the diol components in (II)–(IV) (Figs. 1,3,5, Table 5) are all similar to those found in the free diol (I) (Glidewell, Zakaria & Ferguson, 1996). In every case, the conformation of the diol approaches C_s (*m*) mirror symmetry; it is possible that this conformation, which makes (I) an ideal host molecule for the formation of host–guest adducts, is dominated by the steric requirements of the phenyl groups.

Experimental

Adducts were prepared by crystallizing the diol (I) (Glidewell, Zakaria & Ferguson, 1996) from the appropriate guest as solvent. Analyses: (II), found C 81.5, H 6.1, N 1.5; $C_{63}H_{55}NO_4$ requires C 80.7, H 5.9, N 1.5%; (III), found: C 79.8, H 5.9; $C_{62}H_{54}SO_4$ requires C 79.0, H 5.7%; (IV), found: C 82.5, H 5.5, N 1.5; $C_{65}H_{53}NO_4$ requires C 82.7, H 5.6, N 1.5%; (V), found: C 79.9, H 5.9; $C_{64}H_{56}O_8$ requires C 80.6, H 5.9%; (VI), found: C 79.9, H 5.9; $C_{31}H_{28}O_4$ requires C 80.2, H 5.9%. The 1H and ^{13}C NMR spectra of each adduct in CD_2Cl_2 solution were each the sum of the spectra of the individual components, in the appropriate molar ratio.

Compound (II)

Crystal data

$C_{30}H_{24}O_3 \cdot 0.5C_3H_7NO$

$M_r = 469.04$

Triclinic

$P\bar{1}$

$a = 8.7825$ (13) Å

$b = 11.6787$ (10) Å

$c = 13.194$ (2) Å

$\alpha = 81.142$ (10)°

$\beta = 71.847$ (10)°

$\gamma = 85.672$ (8)°

$V = 1270.1$ (3) Å³

$Z = 2$

$D_x = 1.226$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25 reflections

$\theta = 9.9$ – 19.7 °

$\mu = 0.079$ mm⁻¹

$T = 294$ (1) K

Block cut from a larger piece

$0.39 \times 0.35 \times 0.31$ mm

Colourless

Data collection

Enraf–Nonius CAD-4

diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

5499 measured reflections

5499 independent reflections

2526 observed reflections

$[I > 2\sigma(I)]$

$\theta_{\max} = 26.90$ °

$h = -11 \rightarrow 11$

$k = 0 \rightarrow 14$

$l = -16 \rightarrow 16$

3 standard reflections

frequency: 120 min

intensity decay: 3.0%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0585$

$wR(F^2) = 0.1971$

$S = 0.876$

5499 reflections

346 parameters

H atoms riding (SHELXL93

defaults, C—H 0.93–0.96,

O—H 0.82 Å)

$w = 1/[\sigma^2(F_o^2) + (0.1216P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.261$ e Å⁻³

$\Delta\rho_{\min} = -0.294$ e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.020 (4)

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)

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

	x	y	z	U_{eq}
O1	0.4570 (3)	0.40730 (15)	0.63226 (15)	0.0535 (5)
O2	0.7575 (2)	0.45806 (14)	0.22549 (14)	0.0529 (5)
O51	0.6079 (2)	0.31384 (14)	0.43915 (13)	0.0427 (5)
C1	0.5026 (3)	0.2863 (2)	0.6341 (2)	0.0423 (6)
C2	0.7339 (3)	0.3352 (2)	0.2446 (2)	0.0424 (6)
C11	0.3567 (3)	0.2201 (2)	0.6389 (2)	0.0480 (7)
C12	0.2073 (4)	0.2472 (3)	0.7064 (2)	0.0621 (8)
C13	0.0754 (4)	0.1857 (4)	0.7151 (3)	0.0833 (12)
C14	0.0885 (5)	0.0968 (4)	0.6567 (4)	0.0883 (13)
C15	0.2361 (5)	0.0684 (3)	0.5887 (3)	0.0837 (11)
C16	0.3678 (4)	0.1293 (3)	0.5796 (3)	0.0635 (9)
C21	0.5570 (3)	0.2446 (2)	0.7335 (2)	0.0479 (7)
C22	0.5999 (4)	0.3213 (3)	0.7874 (3)	0.0721 (10)
C23	0.6471 (5)	0.2833 (4)	0.8778 (3)	0.0900 (13)
C24	0.6522 (5)	0.1685 (5)	0.9151 (3)	0.0926 (14)
C25	0.6120 (5)	0.0911 (4)	0.8622 (3)	0.0898 (13)
C26	0.5623 (4)	0.1275 (3)	0.7725 (3)	0.0678 (9)
C31	0.5753 (3)	0.3095 (2)	0.2305 (2)	0.0457 (7)
C32	0.5149 (4)	0.3808 (3)	0.1563 (2)	0.0587 (8)
C33	0.3756 (5)	0.3565 (4)	0.1394 (3)	0.0767 (10)
C34	0.2901 (4)	0.2594 (4)	0.1956 (3)	0.0781 (11)
C35	0.3496 (4)	0.1883 (3)	0.2684 (3)	0.0740 (10)
C36	0.4894 (4)	0.2116 (3)	0.2857 (3)	0.0603 (8)
C41	0.8697 (3)	0.2814 (2)	0.1597 (2)	0.0437 (6)
C42	0.9733 (4)	0.3505 (3)	0.0759 (2)	0.0573 (8)
C43	1.0892 (4)	0.3013 (3)	−0.0044 (2)	0.0689 (10)
C44	1.1072 (4)	0.1837 (3)	−0.0007 (2)	0.0658 (9)
C45	1.0072 (4)	0.1137 (3)	0.0835 (2)	0.0589 (8)
C46	0.8884 (4)	0.1625 (2)	0.1624 (2)	0.0533 (7)
C52	0.6393 (3)	0.2725 (2)	0.5334 (2)	0.0399 (6)
C53	0.7884 (3)	0.2254 (2)	0.5124 (2)	0.0473 (7)
C54	0.8541 (3)	0.2372 (2)	0.3980 (2)	0.0471 (7)
C55	0.7424 (3)	0.2896 (2)	0.3562 (2)	0.0395 (6)
O61†	0.2754 (5)	0.4662 (4)	0.4963 (4)	0.0677 (12)
C62†	0.1333 (8)	0.4910 (5)	0.5377 (6)	0.064 (2)
N63†	0.0206 (9)	0.5148 (8)	0.4899 (5)	0.064 (2)
C64†	−0.1432 (9)	0.5531 (8)	0.5429 (8)	0.100 (3)
C65†	0.0629 (11)	0.5014 (8)	0.3761 (6)	0.093 (2)

† Site occupancy = 0.50.

Compound (III)*Crystal data*C₃₀H₂₄O₃.0.5C₂H₆OS $M_r = 471.56$

Triclinic

 $P\bar{1}$ $a = 8.802$ (3) Å $b = 11.707$ (3) Å $c = 13.162$ (4) Å $\alpha = 80.170$ (12)° $\beta = 72.074$ (14)° $\gamma = 84.187$ (13)° $V = 1269.8$ (7) Å³ $Z = 2$ $D_x = 1.233$ Mg m⁻³ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.7107$ Å

Cell parameters from 25

reflections

 $\theta = 7.6$ – 15.3 ° $\mu = 0.119$ mm⁻¹ $T = 294$ (1) K

Block cut from a larger

piece

 $0.38 \times 0.37 \times 0.30$ mm

Colourless

C31	0.5679 (5)	0.3100 (3)	0.2285 (3)	0.0490 (10)
C32	0.5070 (6)	0.3810 (4)	0.1543 (3)	0.0682 (12)
C33	0.3669 (7)	0.3575 (5)	0.1368 (4)	0.0847 (14)
C34	0.2852 (6)	0.2623 (5)	0.1937 (4)	0.0873 (15)
C35	0.3431 (6)	0.1903 (4)	0.2677 (4)	0.0856 (14)
C36	0.4840 (6)	0.2135 (4)	0.2844 (3)	0.0693 (12)
C41	0.8619 (4)	0.2815 (3)	0.1574 (3)	0.0441 (10)
C42	0.9623 (5)	0.3502 (3)	0.0729 (3)	0.0654 (12)
C43	1.0798 (5)	0.3004 (4)	-0.0061 (3)	0.0768 (14)
C44	1.1028 (5)	0.1829 (4)	-0.0015 (3)	0.0728 (13)
C45	1.0033 (5)	0.1138 (3)	0.0831 (3)	0.0647 (12)
C46	0.8836 (5)	0.1626 (3)	0.1607 (3)	0.0555 (11)
C52	0.6382 (5)	0.2705 (3)	0.5311 (3)	0.0470 (10)
C53	0.7844 (5)	0.2198 (3)	0.5107 (3)	0.0570 (11)
C54	0.8476 (5)	0.2323 (3)	0.3961 (3)	0.0539 (11)
C55	0.7367 (5)	0.2888 (3)	0.3538 (3)	0.0448 (10)
O61†	0.2615 (6)	0.4739 (5)	0.4845 (4)	0.084 (2)
S62†	0.1024 (4)	0.4281 (2)	0.4889 (2)	0.0967 (9)
C63†	0.0423 (17)	0.5009 (13)	0.3736 (7)	0.117 (6)
C64†	-0.0627 (16)	0.4956 (14)	0.5835 (10)	0.151 (6)

† Site occupancy = 0.50.

Data collection

Enraf–Nonius CAD-4

diffractometer

 $\theta/2\theta$ scans

Absorption correction:

none

2367 measured reflections

2367 independent reflections

1463 observed reflections

 $[I > 2\sigma(I)]$ $\theta_{\max} = 20$ ° $h = -8 \rightarrow 8$ $k = 0 \rightarrow 11$ $l = -12 \rightarrow 12$

3 standard reflections

frequency: 120 min

intensity decay: 3.0%

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.0426$ $wR(F^2) = 0.1093$ $S = 0.999$

2367 reflections

336 parameters

H atoms riding (*SHELXL93*)

AFIX defaults, C—H 0.93,

O—H 0.82 Å)

 $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.329$ e Å⁻³ $\Delta\rho_{\min} = -0.160$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O1	0.4568 (4)	0.4084 (2)	0.6286 (2)	0.0730 (9)
O2	0.7473 (3)	0.4569 (2)	0.2221 (2)	0.0586 (8)
O51	0.6045 (3)	0.3150 (2)	0.4368 (2)	0.0512 (7)
C1	0.5019 (5)	0.2873 (3)	0.6313 (3)	0.0507 (10)
C2	0.7273 (4)	0.3347 (3)	0.2428 (3)	0.0465 (10)
C11	0.3558 (5)	0.2242 (4)	0.6375 (3)	0.0570 (11)
C12	0.2086 (7)	0.2523 (4)	0.7048 (3)	0.0819 (15)
C13	0.0761 (7)	0.1924 (6)	0.7151 (4)	0.103 (2)
C14	0.0887 (7)	0.1024 (6)	0.6591 (5)	0.102 (2)
C15	0.2359 (8)	0.0718 (4)	0.5901 (4)	0.093 (2)
C16	0.3672 (5)	0.1328 (4)	0.5810 (3)	0.0723 (13)
C21	0.5567 (5)	0.2432 (4)	0.7313 (3)	0.0580 (11)
C22	0.6007 (5)	0.3197 (4)	0.7839 (4)	0.0806 (14)
C23	0.6486 (6)	0.2811 (6)	0.8752 (5)	0.097 (2)
C24	0.6544 (6)	0.1662 (7)	0.9146 (4)	0.099 (2)
C25	0.6140 (6)	0.0891 (5)	0.8626 (4)	0.096 (2)
C26	0.5632 (5)	0.1270 (4)	0.7719 (3)	0.0753 (13)

Compound (IV)*Crystal data*C₃₀H₂₄O₃.0.5C₅H₅N $M_r = 472.04$

Triclinic

 $P\bar{1}$ $a = 8.9789$ (13) Å $b = 11.814$ (3) Å $c = 13.329$ (3) Å $\alpha = 96.55$ (2)° $\beta = 109.47$ (2)° $\gamma = 102.40$ (2)° $V = 1275.1$ (4) Å³ $Z = 2$ $D_x = 1.229$ Mg m⁻³ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.7107$ Å

Cell parameters from 25

reflections

 $\theta = 10.1$ – 17.4 ° $\mu = 0.078$ mm⁻¹ $T = 294$ (1) K

Block cut from a larger

piece

 $0.39 \times 0.39 \times 0.35$ mm

Colourless

Data collection

Enraf–Nonius CAD-4

diffractometer

 $\theta/2\theta$ scans

Absorption correction:

none

4465 measured reflections

4465 independent reflections

1808 observed reflections

 $[I > 2\sigma(I)]$ $\theta_{\max} = 24.94$ ° $h = -10 \rightarrow 10$ $k = 0 \rightarrow 14$ $l = -15 \rightarrow 15$

3 standard reflections

frequency: 120 min

intensity decay: 6.3%

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.0412$ $wR(F^2) = 0.1278$ $S = 0.879$

4465 reflections

354 parameters

H atoms riding (*SHELXL93*)

defaults, C—H 0.93, O—

H 0.82 Å)

 $w = 1/[\sigma^2(F_o^2) + (0.0694P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.023$ $\Delta\rho_{\max} = 0.264$ e Å⁻³ $\Delta\rho_{\min} = -0.160$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (IV)

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

	x	y	z	U_{eq}
O1	0.3995 (3)	0.41886 (14)	0.38461 (13)	0.0645 (5)
O2	0.5665 (2)	0.44829 (14)	0.77902 (13)	0.0611 (5)
O51	0.4623 (2)	0.31118 (13)	0.56416 (12)	0.0485 (4)
C1	0.3603 (3)	0.2916 (2)	0.3692 (2)	0.0496 (6)
C2	0.5492 (3)	0.3237 (2)	0.7583 (2)	0.0520 (7)
C11	0.5030 (3)	0.2523 (3)	0.3536 (2)	0.0567 (7)
C12	0.5780 (4)	0.3035 (3)	0.2899 (2)	0.0859 (10)
C13	0.6995 (5)	0.2684 (5)	0.2694 (3)	0.1178 (14)
C14	0.7518 (4)	0.1795 (5)	0.3120 (3)	0.1097 (15)
C15	0.6821 (5)	0.1237 (4)	0.3781 (3)	0.1094 (13)
C16	0.5539 (4)	0.1620 (3)	0.3981 (2)	0.0824 (9)
C21	0.2052 (3)	0.2397 (2)	0.2678 (2)	0.0506 (6)
C22	0.1128 (3)	0.3090 (3)	0.2148 (2)	0.0677 (8)
C23	-0.0240 (4)	0.2601 (4)	0.1208 (3)	0.0813 (9)
C24	-0.0714 (4)	0.1423 (4)	0.0806 (2)	0.0874 (10)
C25	0.0169 (4)	0.0709 (3)	0.1324 (2)	0.0809 (9)
C26	0.1558 (3)	0.1201 (3)	0.2247 (2)	0.0666 (8)
C31	0.7163 (3)	0.3023 (2)	0.7685 (2)	0.0548 (7)
C32	0.8588 (4)	0.3774 (3)	0.8462 (2)	0.0740 (8)
C33	1.0092 (4)	0.3566 (4)	0.8587 (3)	0.0950 (11)
C34	1.0198 (4)	0.2617 (4)	0.7944 (3)	0.0971 (11)
C35	0.8812 (4)	0.1874 (3)	0.7177 (3)	0.0870 (10)
C36	0.7290 (4)	0.2065 (3)	0.7045 (2)	0.0710 (8)
C41	0.4939 (3)	0.2731 (2)	0.8441 (2)	0.0512 (6)
C42	0.4692 (3)	0.3442 (3)	0.9229 (2)	0.0664 (8)
C43	0.4180 (4)	0.2968 (3)	1.0001 (2)	0.0812 (9)
C44	0.3914 (4)	0.1791 (3)	0.9993 (2)	0.0820 (10)
C45	0.4160 (4)	0.1069 (3)	0.9217 (3)	0.0782 (9)
C46	0.4683 (3)	0.1541 (2)	0.8448 (2)	0.0660 (8)
C52	0.3334 (3)	0.2581 (2)	0.4681 (2)	0.0488 (6)
C53	0.2162 (3)	0.1855 (2)	0.4892 (2)	0.0614 (7)
C54	0.2737 (3)	0.1933 (2)	0.6045 (2)	0.0617 (7)
C55	0.4223 (3)	0.2696 (2)	0.6470 (2)	0.0500 (6)
N61†	0.1742 (7)	0.4888 (5)	0.4721 (5)	0.104 (2)
C62†	0.0848 (8)	0.5539 (5)	0.4137 (5)	0.091 (2)
C63†	-0.0558 (8)	0.5708 (6)	0.4255 (6)	0.110 (3)
C64†	-0.1087 (9)	0.5198 (7)	0.4999 (7)	0.102 (3)
C65†	-0.0198 (10)	0.4532 (6)	0.5605 (6)	0.082 (2)
C66†	0.1197 (9)	0.4397 (5)	0.5445 (5)	0.105 (3)

† Site occupancy = 0.50.

Table 4. Hydrogen-bonding geometry (\AA , $^\circ$) for compounds (II), (III) and (IV)

	D—H...A	D—H	H...A	D...A	D—H...A
(II)					
O1—H1A...O61	0.82	1.92	2.733 (5)	176	
O1—H1B...O61 ¹	0.82	1.99	2.802 (5)	170	
O2—H2...O1 ¹	0.82	1.99	2.793 (3)	167	
(III)					
O1—H1A...O61	0.82	2.10	2.895 (6)	171	
O1—H1B...O61 ¹	0.82	2.01	2.825 (6)	173	
O2—H2...O1 ¹	0.82	2.00	2.808 (4)	169	
(IV)					
O1—H1A...O1 ¹	0.82	2.46	3.140 (2)	141	
O1—H1B...N61	0.82	2.13	2.865 (7)	149	
O2—H2...O1 ¹	0.82	2.08	2.887 (2)	167	
O1—H1A...O51	0.82	2.51	2.787 (2)	101	
O2—H2...O51	0.82	2.49	2.865 (2)	109	

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

Table 5. Selected bond lengths (\AA) and torsion angles ($^\circ$) for compounds (II), (III) and (IV)

	(II)	(III)	(IV)
O1—C1	1.439 (3)	1.430 (4)	1.442 (3)
O2—C2	1.437 (3)	1.429 (4)	1.431 (3)
O51—C52	1.366 (3)	1.369 (4)	1.374 (3)
O51—C55	1.383 (3)	1.379 (4)	1.379 (3)

C1—C11	1.525 (4)	1.521 (5)	1.520 (3)
C1—C21	1.532 (4)	1.530 (5)	1.527 (3)
C1—C52	1.508 (3)	1.511 (5)	1.498 (3)
C2—C31	1.519 (4)	1.534 (5)	1.539 (3)
C2—C41	1.530 (3)	1.524 (4)	1.522 (3)
C2—C55	1.510 (3)	1.493 (5)	1.501 (3)
C52—C53	1.344 (4)	1.329 (5)	1.336 (3)
C53—C54	1.428 (4)	1.424 (5)	1.434 (3)
C54—C55	1.335 (4)	1.333 (4)	1.333 (3)
C52—C1—C11—C12	-161.5 (2)	-162.7 (3)	-160.4 (2)
C52—C1—C21—C22	100.1 (3)	100.3 (4)	109.3 (3)
C55—C2—C31—C32	152.9 (2)	153.2 (3)	156.6 (2)
C55—C2—C41—C42	-125.8 (3)	-126.2 (4)	-118.4 (3)
O1—C1—C52—O51	-57.0 (3)	-56.3 (4)	-55.4 (3)
C11—C1—C52—O51	61.6 (3)	62.7 (4)	63.2 (3)
C21—C1—C52—O51	-176.0 (2)	-175.6 (3)	-173.9 (2)
O2—C2—C55—O51	75.7 (3)	74.2 (4)	62.1 (2)
C31—C2—C55—O51	-46.3 (3)	-47.5 (4)	-58.6 (3)
C41—C2—C55—O51	-167.4 (2)	-168.5 (3)	179.7 (2)

None of the crystals diffracted significantly at θ values $> 20^\circ$. Data collection for (III) was terminated at $\theta = 20^\circ$ when it became obvious that no significant reflections were being measured. In all three compounds, the solvate molecules lie disordered (with 0.5 occupancy) about inversion centres. In the initial refinements, the solvate occupancies were allowed to refine, but as they did not move significantly from 0.5 values, the occupancies were fixed at 0.5 in subsequent refinement cycles. In each case the disorder of the solvate was allowed for by appropriate constraints and restraints during the *SHELXL93* (Sheldrick, 1993) refinement. For each compound, difference map sections normal to the relevant C—O bonds were calculated with the *COFOUR* option in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White 1989) and showed that the hydroxyl H atom on O1 was disordered over two sites while that on O2 was ordered; these H atoms were allowed for in the *SHELXL93* refinement using the *AFIX* commands. Examination of the structures with *PLATON* showed that there were no solvent-accessible voids in the crystal lattices.

For all compounds, data collection: *CAD-4/PC* (Enraf-Nonius, 1992); cell refinement: *SET4* and *CELDIM* (Enraf-Nonius, 1992); data reduction: *DATRD2* (*NRCVAX94*; Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *NRCVAX94*, *SHELXL93* (Sheldrick, 1993); molecular graphics: *NRCVAX94*, *PLATON* (Spek, 1995a), *PLUTON* (Spek 1995b); software used to prepare material for publication: *NRCVAX94*, *SHELXL93* and *PREPCIF* in *WordPerfect*.

GF thanks NSERC (Canada) for Research Grants.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1360). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2014–2017

1-[3,5-Bis(trifluoromethyl)phenyl]-8-(4-methoxyphenyl)naphthalene: a Novel Three-Dimensional Non-Linear Optical Chromophore

ANDRÉ BAHL,^a WALTER GRAHN^a AND PETER G. JONES^{b*}

^aInstitut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany, and ^bInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

(Received 21 May 1996; accepted 11 June 1996)

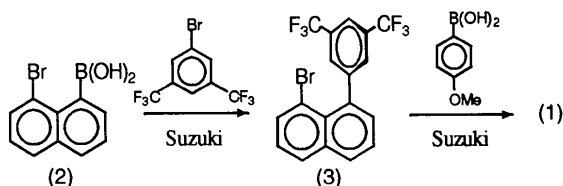
Abstract

There are two molecules of C₂₅H₁₆F₆O in the asymmetric unit. The interplanar angles between the naphthalene moiety and the phenyl substituents are 51.7, 52.5(1)° in the first molecule and 59.8, 58.1(1)° in the second for the trifluoromethyl- and methoxy-substituted rings, respectively. Calculations indicate that these are 'soft' parameters.

Comment

As part of our continuing efforts to design materials for frequency doubling of diode laser sources, we are especially interested in donor(D)–acceptor(A)-substituted diarylnaphthalenes (Bahl *et al.*, 1995) such as the title compound (1). According to the classification introduced by Nalva, Watanabe & Miyata (1995) (one- and two-dimensional non-linear optical chromophores),

these molecules represent a novel three-dimensional type. The three-dimensional chromophoric system is constituted by two non-conjugated biphenylene subunits and a potential through-space charge–transfer (CT) subchromophore. To estimate the effectiveness of these interactions, which depend strongly on the inter-aryl angles and distances, and also to determine whether the substances crystallize in non-centrosymmetric space groups (a prerequisite for frequency doubling), we have embarked on a series of X-ray structure determinations (Jones, Grahn, Bahl & Reisner, 1995).



Compound (1) crystallizes in a centrosymmetric space group, which renders the crystals unsuitable for applications of quadratic non-linear optical effects. The two independent molecules, (1a) and (1b) [(1a) is shown in Fig. 1], display different conformations, the differences arising mostly from the relative orientation of the ring systems.

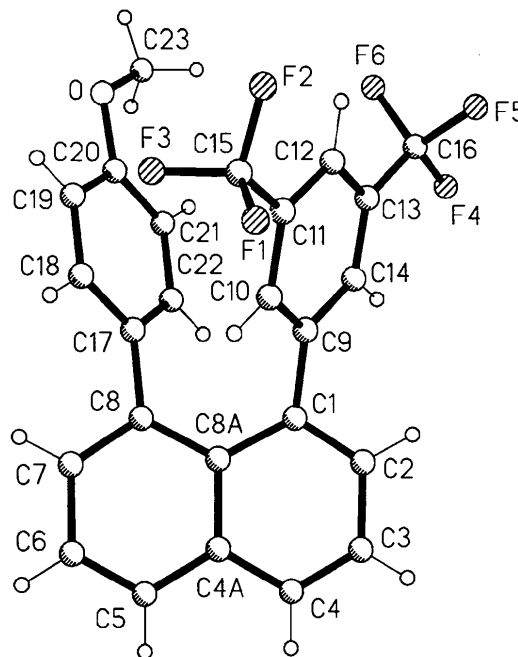


Fig. 1. One of the two independent molecules of the title compound in the crystal. Radii are arbitrary.

As is known from X-ray structures of other 1,8-diarylnaphthalenes (Clough, Kung, Marsh & Roberts 1976; Wahl, Krieger, Schweitzer & Staab, 1984; Jones *et al.*, 1995; Tsuji *et al.*, 1993), the steric strain