

Crystal Engineering Using Bisphenols. Chains, Ladders and Sheets Formed by the Adducts of 1,4-Diazabicyclo[2.2.2]octane with Bisphenols: Structures of Adducts with 4,4'-Isopropylidenediphenol (1/1), 4,4'-Oxodiphenol (1/1) and 4,4'-Thiodiphenol (1/1 and 2/1)

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Abstract

4,4'-Isopropylidenediphenol–1,4-diazabicyclo[2.2.2]octane (1/1), (1), C₁₅H₁₆O₂.C₆H₁₂N₂, monoclinic, *P2₁/a*, *a* = 11.385 (2), *b* = 6.5565 (12), *c* = 13.076 (2) Å, β = 96.240 (11)°, with *Z* = 2; the two components of the adduct, which each lie across twofold axes, are joined into simple chains *via* O—H···N hydrogen bonds in a motif with graph set C₂²(17). 4,4'-Oxodiphenol–1,4-diazabicyclo[2.2.2]octane (1/1), (2), C₁₂H₁₀O₃.C₆H₁₂N₂, orthorhombic, *P2₁2₁2₁*, *a* = 9.4222 (11), *b* = 11.1886 (15), *c* = 15.694 (2), with *Z* = 4; the diamine component is disordered by rotation about the N···N vector, having two orientations [populations 0.76 (1) and 0.24 (1)] rotated by 48 (3)° from coincidence: the components are joined into chains *via* O—H···N hydrogen bonds in a motif with graph set C₂²(17); pairs of these chains are joined into ladders by C—H···O hydrogen bonds in a motif of graph set R₂²(22). 4,4'-Thiodiphenol–1,4-diazabicyclo[2.2.2]octane (1/1), (3), C₁₂H₁₀O₂S.C₆H₁₂N₂, isomorphous, *a* = 9.5785 (11), *b* = 11.4525 (13), *c* = 15.759 (2) Å (and *ipso facto* isostructural), with (2); the diamine disorder is characterized by two equally populated orientations related by a rotation about the N···N vector of 37.1 (2)° and pairs of chains are now joined into ladders by C—H···S hydrogen bonds. 4,4'-Thiodiphenol–1,4-diazabicyclo[2.2.2]octane (2/1), (5), (C₁₂H₁₀O₂S)₂.C₆H₁₂N₂, monoclinic, *P2₁/n*, *a* = 8.3198 (9), *b* = 11.4006 (13), *c* = 15.056 (2) Å, β = 104.955 (8)°, with *Z* = 2; the diamine component of the adduct is disordered across a centre of inversion, and the bisphenol components are linked into chains by O—H···O hydrogen bonds in a motif with graph set C(12). These chains form cross-links *via* the diamine component by means of O—H···N hydrogen bonds in a C₃³(19) motif to yield sheets within which are large hydrogen-bonded rings described by the unusual graph set R₈⁸(62).

1. Introduction

The cage-like diamine 1,4-diazabicyclo[2.2.2]octane, N(CH₂CH₂)₃N (DABCO), forms adducts with both

phenol and hydroquinone having stoichiometric ratios of phenol:amine of 2:1 and 1:1, respectively (Mak, Yip & Book, 1984): in each of these adducts the components are linked by O—H···N hydrogen bonds to give finite aggregates in the phenol adduct and infinite chains in the hydroquinone adduct. Similar chains have been observed in the 1:1 DABCO adduct with (2,6-dihydroxyphenylisocyanide)pentacarbonylchromium (Hahn, Tamm & Lügger, 1994). As part of a wide-ranging study of the use of bisphenols and trisphenols as building blocks in crystal engineering, we have studied the interactions of bisphenols with a range of polybasic organic amines, and using DABCO and a series of bisphenols of the type X(C₆H₄OH)₂ we have isolated crystalline adducts (1)–(4) having 1:1 stoichiometry when X = Me₂C, O, S or CO, respectively, and an adduct (5) having 2:1 phenol:amine stoichiometry in the case of X = S. Here we report the structures of adducts (1), (2), (3) and (5). In principal, if the DABCO component utilizes both N atoms as hydrogen-bond acceptors and the bisphenol component uses both hydroxyl groups as donors, simple chains may be expected to result, provided that there are no other significant hydrogen-bond donors or acceptors in the system. Where there is an excess of hydrogen-bond acceptors *E*, the formation of hydrogen bonds of the type C—H···*E* may be expected (Hunter, 1991).

2. Experimental

2.1. Synthesis

Adducts (1)–(5) were prepared by co-crystallizing the diamine with the appropriate bisphenol from solutions in methanol. Analyses: (1) found: C 74.3, H 8.5, N 8.4%; C₂₁H₂₈N₂O₂ requires: C 74.1, H 8.3, N 8.2%; (2) found: C 68.8, H 7.3, N 8.9%; C₁₈H₂₂N₂O₃ requires: C 68.8, H 7.1, N 8.9%; (3) found: C 65.4, H 7.0, N 8.6%; C₁₈H₂₂N₂O₂S requires: C 65.4, H 6.7, N 8.5%; (4) found: C 69.9, H 6.9, N 8.7%; C₁₉H₂₂N₂O₃ requires: C 69.9, H 6.8, N 8.6%; (5) found: C 65.8, H 6.0, N 5.1; C₃₀H₃₂N₂O₄S₂ requires: C 65.7, H 5.9, N 5.1%. Crystals of adducts (1), (2), (3) and (5) suitable for single-

crystal X-ray diffraction were selected directly from the analytical samples: no suitable crystals of adduct (4) could be obtained.

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 ($h0l$ absent if $h = 2n + 1$) permit the space group to be either Pa or $P2_1/a$; $P2_1/a$ was chosen and confirmed by analysis. For (2) and (3) the space group $P2_12_12_1$ was uniquely determined by the systematic absences ($h00$ absent if $h = 2n + 1$, $0k0$ absent if $k = 2n + 1$, $00l$ absent if $l = 2n + 1$). For (5) the space group $P2_1/n$ was uniquely determined by the systematic absences ($h0l$ absent if $h + l = 2n + 1$, $0k0$ absent if $k = 2n + 1$). All structures were solved by direct methods (Gabe, Le Page, Charland, Lee & White, 1989). A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed to reduce statistical bias (Wilson, 1976). In the structures of (2) and (3) it became clear early in the anisotropic refinement that the C atoms of the DABCO molecule were markedly anisotropic, consistent with their being disordered over closely adjacent sites; allowance for this was made using the restraints and constraints available in *SHELXL93* (Sheldrick, 1993) to derive a disordered model in which two sets of diamine C atoms were effectively rotated, relative to one another about the N··N axis of the diamine, by $48(3)^\circ$ in (2) and $37.1(2)^\circ$ in (3). In the structure of (5) the DABCO component is disordered across an inversion centre. H atoms bonded to carbon were positioned on geometric grounds (C—H, 0.95 Å) and initial coordinates for hydroxyl H atoms were obtained from difference maps; all H atoms were included in the refinements as riding atoms. We attribute the R value of 0.072 in (3) to the disorder in the crystal and to the crystal decay during data collection decay of intensity (6% fall in the intensity of three standard reflections, corrected for by linear scaling). Examination of all 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 fractional coordinates are presented in Table 2 and selected dimensions in Table 3.*

3. Results and discussion

3.1. Structures and molecular packing

Adduct (1), $\text{Me}_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2 \cdot \text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$, crystallizes in the monoclinic space group $P2_1/a$ with both the

* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: AB0360). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bisphenol and the diamine components lying on twofold axes (Fig. 1). The two components of the adduct are linked by O—H···N hydrogen bonds: the O atom of the bisphenol lying across the twofold axis at $(\frac{1}{4}, y, 0)$ acts as a donor to the N atom of the diamine lying across the twofold axis at $(\frac{3}{4}, y, \frac{1}{2})$. These hydrogen bonds thus generate an infinite chain of alternating bisphenol and diamine units in the $[10\bar{1}]$ direction (Fig. 2): the action of the inversion centres is to generate an infinite bundle of parallel chains, but there are no hydrogen-bonding interactions between neighbouring chains. In this respect the structure of (1) has some resemblance to that of the hydroquinone–DABCO adduct (Mak, Yip & Book, 1984).

Although in general the occupancy of special positions on twofold rotation axes is neither especially favoured or disfavoured, in space group $P2_1/c$ the majority of the known examples have $Z' = 0.5$, with the twofold sites occupied (Brock & Dunitz, 1994). It has been pointed out (Brock & Dunitz, 1994) that twofold axes are effective for bringing into close contact molecules with partially concave surfaces: 4,4'-isopropylidenediphenol is such a molecule and in the structure of (1) the molecules of this component are stacked in register along the short b axis; the DABCO molecules are stacked similarly. The chain structure adopted by (1), with both components lying on twofold rotation axes, is the simplest structure which can be

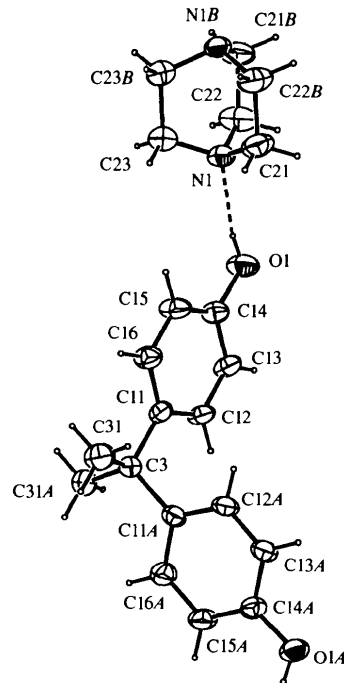


Fig. 1. View of the two components of adduct (1), showing the atom-numbering scheme; the atom labels A and B refer to atoms in the equivalent positions $(\frac{1}{2} - x, y, -z)$ and $(\frac{3}{2} - x, y, 1 - z)$, respectively. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. *Experimental details*

	(1)	(2)	(3)	(5)
Crystal data				
Chemical formula	C ₁₅ H ₁₆ O ₂ ·C ₆ H ₁₂ N ₂	C ₁₂ H ₁₀ O ₃ ·C ₆ H ₁₂ N ₂	C ₁₂ H ₁₀ O ₂ ·S·C ₆ H ₁₂ N ₂	2(C ₁₂ H ₁₀ O ₂ S)·C ₆ H ₁₂ N ₂
Chemical formula weight	340.45	314.38	330.44	548.70
Cell setting	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P2₁/a</i>	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P2₁/n</i>
<i>a</i> (Å)	11.385 (2)	9.4222 (11)	9.5785 (11)	8.3198 (9)
<i>b</i> (Å)	6.5565 (12)	11.1886 (15)	11.4525 (1.3)	11.4006 (13)
<i>c</i> (Å)	13.076 (2)	15.694 (2)	15.759 (2)	15.056 (2)
β (°)	96.240 (11)			104.955 (8)
<i>V</i> (Å ³)	970.3 (3)	1654.5 (4)	1728.7 (3)	1379.7 (3)
<i>Z</i>	2	4	4	2
<i>D_c</i> (Mg m ⁻³)	1.165	1.262	1.270	1.321
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107
No. of reflections for cell parameters	25	25	25	25
θ range (°)	10.01–17.01	8.70–13.76	6.30–12.02	8.22–14.82
μ (mm ⁻¹)	0.075	0.086	0.198	0.232
Temperature (K)	294 (1)	294 (1)	294 (1)	294 (1)
Crystal form	Block	Plate	Block cut from a larger fragment	Plate
Crystal size (mm)	0.40 × 0.32 × 0.28	0.36 × 0.30 × 0.15	0.43 × 0.43 × 0.35	0.41 × 0.39 × 0.13
Crystal colour	Colourless	Colourless	Colourless	Colourless
Data collection				
Diffractometer	Enraf–Nonius CAD-4	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	$\theta/2\theta$ scans
Absorption correction	None	None	None	None
No. of measured reflections	2215	1676	3018	3162
No. of independent reflections	2117	1676	2710	3055
No. of observed reflections	838	989	1324	1500
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
<i>R</i> _{int}	0.014	–	0.045	0.016
θ _{max} (°)	27	25	25	27.1
Range of <i>h, k, l</i>	–14 → <i>h</i> → 14 0 → <i>k</i> → 8 0 → <i>l</i> → 16	0 → <i>h</i> → 11 0 → <i>k</i> → 13 0 → <i>l</i> → 18	–11 → <i>h</i> → 11 –13 → <i>k</i> → 13 –18 → <i>l</i> → 18	–10 → <i>h</i> → 10 0 → <i>k</i> → 14 0 → <i>l</i> → 19
No. of standard reflections	3	3	3	3
Frequency of standard reflections (min)	120	120	120	120
Intensity decay (%)	No decay, variation 1.2	No decay, variation 1.1	6.0	No decay, variation 1.1
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
$R[F^2 > 2\sigma(F^2)]$	0.0587	0.0582	0.0724	0.0638
$wR(F^2)$	0.1707	0.1340	0.1762	0.1526
<i>S</i>	0.928	0.951	0.973	0.939
No. of reflections used in refinement	2117	1676	2710	3055
No. of parameters used	115	267	228	204
H-atom treatment	Riding (C—H 0.93–0.97, O—H 0.82 Å)	Riding (C—H 0.93–0.97, O—H 0.82 Å)	Riding (C—H 0.93–0.97, O—H 0.82 Å)	Riding (C—H 0.93–0.97, O—H 0.82 Å)
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000	–0.001	0.014	0.001
$\Delta\rho_{\max}$ (e Å ⁻³)	0.219	0.145	0.252	0.236
$\Delta\rho_{\min}$ (e Å ⁻³)	–0.144	–0.184	–0.266	–0.276
Extinction method	None	<i>SHELXL93</i> (Sheldrick, 1993)	None	<i>SHELXL93</i> (Sheldrick, 1993)
Extinction coefficient	–	0.0075 (20)	–	0.0163 (23)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs				
Data collection	CAD-4 (Enraf–Nonius, 1989)	CAD-4 (Enraf–Nonius, 1989)	CAD-4 (Enraf–Nonius, 1989)	CAD-4 (Enraf–Nonius, 1989)
Cell refinement	<i>SET4</i> and <i>CELDIM</i> (Enraf–Nonius, 1992)	<i>SET4</i> and <i>CELDIM</i> (Enraf–Nonius, 1992)	<i>SET4</i> and <i>CELDIM</i> (Enraf–Nonius, 1992)	<i>SET4</i> and <i>CELDIM</i> (Enraf–Nonius, 1992)
Data reduction	<i>DATRD2</i> in <i>NRCVAX94</i> (Gabe, Le Page, Charland, Lee & White, 1989)	<i>DATRD2</i> in <i>NRCVAX94</i> (Gabe, Le Page, Charland, Lee & White, 1989)	<i>DATRD2</i> in <i>NRCVAX94</i> (Gabe, Le Page, Charland, Lee & White, 1989)	<i>DATRD2</i> in <i>NRCVAX94</i> (Gabe, Le Page, Charland, Lee & White, 1989)
Structure solution	<i>SHELXS86</i> (Sheldrick, 1985)	<i>SHELXS86</i> (Sheldrick, 1985)	<i>SHELXS86</i> (Sheldrick, 1985)	<i>SHELXS86</i> (Sheldrick, 1985)
Structure refinement	<i>NRCVAX94</i> and <i>SHELXL93</i> (Sheldrick, 1993)	<i>NRCVAX94</i> and <i>SHELXL93</i> (Sheldrick, 1993)	<i>NRCVAX94</i> and <i>SHELXL93</i> (Sheldrick, 1993)	<i>NRCVAX94</i> and <i>SHELXL93</i> (Sheldrick, 1993)
Preparation of material for publication	<i>NRCVAX94</i> , <i>SHELXL93</i> and <i>WordPerfect</i> macro PREPCIF	<i>NRCVAX94</i> , <i>SHELXL93</i> and <i>WordPerfect</i> macro PREPCIF	<i>NRCVAX94</i> , <i>SHELXL93</i> and <i>WordPerfect</i> macro PREPCIF	<i>NRCVAX94</i> , <i>SHELXL93</i> and <i>WordPerfect</i> macro PREPCIF

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
(1)				
O1	0.4357 (2)	0.7810 (3)	0.33702 (15)	0.0773 (7)
C11	0.3048 (2)	0.4157 (4)	0.0890 (2)	0.0484 (7)
C12	0.2439 (2)	0.5814 (5)	0.1217 (2)	0.0573 (8)
C13	0.2875 (2)	0.6996 (5)	0.2039 (2)	0.0599 (8)
C14	0.3965 (2)	0.6579 (5)	0.2565 (2)	0.0540 (8)
C15	0.4581 (3)	0.4941 (5)	0.2262 (2)	0.0663 (9)
C16	0.4127 (2)	0.3741 (5)	0.1440 (2)	0.0637 (8)
C3	1/4	0.2816 (6)	0.0000	0.0592 (11)
C31	0.3439 (3)	0.1443 (5)	-0.0422 (3)	0.0967 (13)
N1	0.6511 (2)	0.7095 (4)	0.4424 (2)	0.0578 (7)
C21	0.7425 (3)	0.8107 (6)	0.3908 (2)	0.0865 (11)
C22	0.6385 (3)	0.8076 (6)	0.5402 (2)	0.0923 (12)
C23	0.6912 (3)	0.5009 (5)	0.4649 (2)	0.0772 (10)
(2)				
O12	0.3179 (4)	0.4764 (3)	0.3319 (2)	0.0830 (11)
O1	0.7317 (4)	0.3937 (5)	0.0892 (2)	0.0980 (14)
O2	0.3771 (4)	0.2743 (3)	0.6510 (2)	0.0803 (11)
C11	0.4226 (5)	0.4516 (4)	0.2720 (3)	0.0554 (13)
C12	0.5201 (5)	0.3616 (4)	0.2810 (3)	0.0658 (13)
C13	0.6191 (5)	0.3429 (5)	0.2183 (3)	0.0706 (14)
C14	0.6237 (5)	0.4123 (5)	0.1468 (3)	0.0640 (13)
C15	0.5226 (6)	0.4996 (4)	0.1378 (3)	0.0730 (14)
C16	0.4222 (5)	0.5187 (4)	0.1999 (3)	0.0676 (14)
C21	0.3349 (6)	0.4272 (5)	0.4137 (3)	0.0666 (14)
C22	0.2482 (6)	0.3350 (5)	0.4379 (3)	0.0704 (14)
C23	0.2646 (5)	0.2863 (4)	0.5185 (3)	0.0662 (14)
C24	0.3664 (6)	0.3291 (4)	0.5737 (3)	0.0620 (13)
C25	0.4513 (6)	0.4219 (5)	0.5492 (3)	0.072 (2)
C26	0.4361 (6)	0.4721 (5)	0.4689 (3)	0.076 (2)
N1	0.6498 (4)	0.3824 (3)	-0.0737 (2)	0.0580 (10)
N2	0.5497 (4)	0.3436 (4)	-0.2235 (2)	0.0612 (11)
C1A	0.6328 (10)	0.4967 (5)	-0.1171 (4)	0.076 (2)
C2A	0.7465 (9)	0.3088 (9)	-0.1246 (4)	0.089 (3)
C3A	0.5140 (8)	0.3206 (9)	-0.0682 (4)	0.078 (3)
C4A	0.5657 (8)	0.4745 (5)	-0.2054 (4)	0.070 (2)
C5A	0.6894 (7)	0.2928 (7)	-0.2147 (4)	0.073 (2)
C6A	0.4561 (7)	0.2990 (7)	-0.1565 (3)	0.067 (2)
C1B	0.523 (3)	0.454 (3)	-0.0939 (16)	0.114 (11)
C2B	0.753 (2)	0.409 (4)	-0.1402 (11)	0.119 (11)
C3B	0.610 (4)	0.2558 (12)	-0.0860 (12)	0.097 (8)
C4B	0.452 (2)	0.420 (3)	-0.1773 (14)	0.115 (11)
C5B	0.6956 (19)	0.388 (4)	-0.2298 (14)	0.128 (11)
C6B	0.558 (3)	0.2290 (12)	-0.1763 (11)	0.097 (9)
(3)				
S1	0.3316 (2)	0.5240 (2)	0.34696 (11)	0.0841 (7)
O1	0.7419 (5)	0.3702 (5)	0.0875 (2)	0.090 (2)
O2	0.4282 (5)	0.2285 (4)	0.6477 (3)	0.086 (2)
C11	0.4509 (6)	0.4713 (5)	0.2699 (3)	0.056 (2)
C12	0.5463 (7)	0.3840 (5)	0.2846 (4)	0.060 (2)
C13	0.6410 (7)	0.3509 (5)	0.2227 (4)	0.063 (2)
C14	0.6396 (6)	0.4043 (5)	0.1446 (4)	0.054 (2)
C15	0.5428 (8)	0.4882 (6)	0.1292 (4)	0.074 (2)
C16	0.4483 (7)	0.5226 (6)	0.1905 (4)	0.072 (2)
C21	0.3641 (7)	0.4350 (5)	0.4365 (4)	0.060 (2)
C22	0.2813 (7)	0.3415 (6)	0.4535 (4)	0.075 (2)
C23	0.3012 (7)	0.2742 (6)	0.5245 (4)	0.080 (2)
C24	0.4079 (7)	0.2983 (5)	0.5803 (4)	0.063 (2)
C25	0.4931 (6)	0.3934 (5)	0.5636 (3)	0.057 (2)
C26	0.4694 (7)	0.4612 (5)	0.4933 (4)	0.065 (2)
N1	0.6693 (5)	0.3530 (4)	-0.0747 (3)	0.0550 (12)
N2	0.5881 (5)	0.3003 (4)	-0.2247 (3)	0.0571 (13)
C1A	0.6458 (14)	0.4609 (9)	-0.1225 (7)	0.092 (2)
C2A	0.7749 (12)	0.2823 (10)	-0.1196 (7)	0.083 (2)
C3A	0.5383 (10)	0.2889 (12)	-0.0705 (8)	0.097 (2)
C4A	0.5942 (14)	0.4302 (8)	-0.2121 (7)	0.093 (2)
C5A	0.7244 (11)	0.2512 (10)	-0.2085 (7)	0.080 (2)
C6A	0.4895 (12)	0.2600 (12)	-0.1599 (7)	0.095 (2)
C1B	0.5590 (11)	0.4300 (11)	-0.1067 (7)	0.092 (2)
C2B	0.7816 (12)	0.3593 (11)	-0.1375 (6)	0.083 (2)
C3B	0.6102 (15)	0.2346 (8)	-0.0775 (8)	0.097 (2)

Table 2 (cont.)

	x	y	z	U_{eq}
C4B	0.5085 (12)	0.3987 (10)	-0.1957 (7)	0.093 (2)
C5B	0.7372 (10)	0.3268 (10)	-0.2270 (7)	0.080 (2)
C6B	0.5598 (15)	0.2033 (9)	-0.1667 (7)	0.095 (2)
(5)				
S1	0.71379 (13)	-0.12588 (8)	-0.34733 (8)	0.0579 (3)
O1	0.2990 (3)	0.1207 (2)	-0.1396 (2)	0.0585 (7)
O2	1.0318 (3)	0.2577 (2)	-0.5039 (2)	0.0640 (8)
C11	0.5886 (4)	-0.0473 (3)	-0.2886 (2)	0.0403 (8)
C12	0.5796 (4)	0.0732 (3)	-0.2845 (2)	0.0429 (8)
C13	0.4807 (4)	0.1270 (3)	-0.2354 (2)	0.0448 (8)
C14	0.3899 (4)	0.0613 (3)	-0.1890 (2)	0.0410 (8)
C15	0.3974 (4)	-0.0599 (3)	-0.1926 (2)	0.0485 (9)
C16	0.4956 (4)	-0.1128 (3)	-0.2422 (2)	0.0493 (9)
C21	0.8093 (4)	-0.0128 (3)	-0.3957 (2)	0.0442 (8)
C22	0.7330 (4)	0.0318 (3)	-0.4819 (2)	0.0542 (10)
C23	0.8056 (4)	0.1216 (3)	-0.5191 (2)	0.0541 (10)
C24	0.9565 (4)	0.1673 (3)	-0.4705 (2)	0.0449 (9)
C25	1.0367 (4)	0.1211 (3)	-0.3862 (2)	0.0506 (9)
C26	0.9626 (4)	0.0322 (3)	-0.3492 (2)	0.0487 (9)
N1	0.1027 (3)	0.0204 (3)	-0.0493 (2)	0.0514 (8)
C1A	-0.0349 (9)	0.0974 (8)	-0.0752 (6)	0.062 (2)
C2A	0.0331 (11)	-0.1041 (6)	-0.0738 (6)	0.065 (2)
C3A	0.1901 (9)	0.0161 (10)	0.0441 (4)	0.071 (3)
C1B	-0.0659 (8)	0.0088 (10)	-0.1008 (5)	0.064 (2)
C2B	0.1568 (10)	-0.0720 (8)	0.0175 (6)	0.067 (3)
C3B	0.0905 (10)	0.1273 (7)	0.0143 (6)	0.068 (2)

envisaged for a two-component system in which one component acts as a bis-donor of hydrogen bonds and the other as a bis-acceptor. In other examples containing similar bis-donors and -acceptors more complex structures are observed (Coupar, Glidewell & Ferguson, 1997), consequent upon the folding and twisting of the chains. The simplicity in (1) arises partly

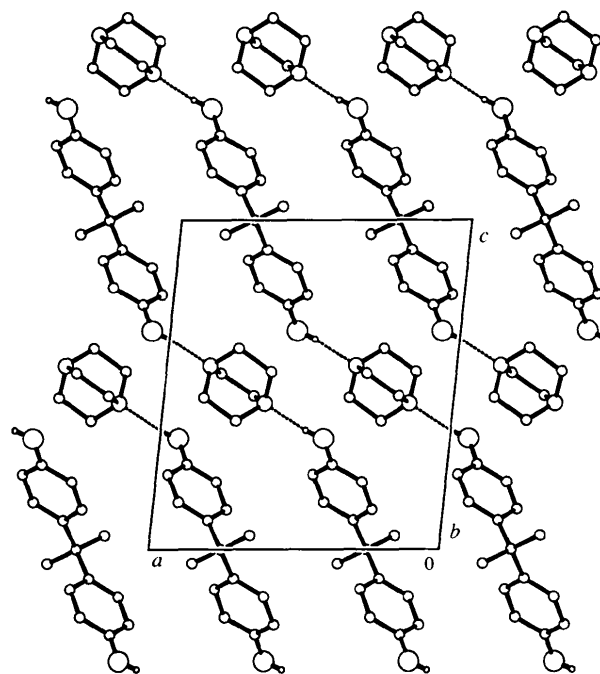


Fig. 2. Packing diagram of the crystal structure of adduct (1), viewed along the b axis; H atoms bonded to carbon are omitted.

Table 3. Selected molecular dimensions (\AA , $^\circ$)

(1)			
O1—C14	1.362 (3)	C11 ⁱ —C3—C11—C12	45.4 (2)
N1—N21	1.460 (4)	C21—C22 ⁱⁱ	1.544 (4)
N1—C22	1.452 (4)	C23—C23 ⁱⁱⁱ	1.539 (6)
N1—C23	1.461 (4)		
N1—C21—C22 ⁱⁱ —N1 ⁱⁱ	-1.4 (4)	N1—C23—C23 ⁱⁱⁱ —N1 ⁱⁱⁱ	-1.4 (3)
O1...N1	2.720 (3)	O1—H1...N1	166
(2)			
O1—C14	1.377 (5)	O2—C24	1.363 (5)
O12—C11	1.390 (5)	O12—C21	1.407 (5)
C11—O12—C21	117.3 (4)		
C21—O12—C11—C12	16.1 (6)	C11—O12—C21—C22	-107.9 (5)
N1—C1A	1.458 (6)	N1—C1B	1.471 (10)
N1—C2A	1.465 (6)	N1—C2B	1.460 (10)
N1—C3A	1.456 (6)	N1—C3B	1.477 (10)
N2—C4A	1.500 (6)	N2—C4B	1.449 (10)
N2—C5A	1.440 (6)	N2—C5B	1.466 (10)
N2—C6A	1.461 (6)	N2—C6B	1.484 (10)
C1A—C4A	1.543 (7)	C1B—C4B	1.518 (10)
C2A—C5A	1.525 (7)	C2B—C5B	1.526 (10)
C3A—C6A	1.508 (6)	C3B—C6B	1.528 (10)
N1—C1A—C4A—N2	-4.9 (9)	N1—C1B—C4B—N2	-13 (4)
N1—C2A—C5A—N2	-5.7 (10)	N1—C2B—C5B—N2	-1 (4)
N1—C3A—C6A—N2	0.5 (10)	N1—C3B—C6B—N2	-6 (3)
O1...N1	2.673 (5)	O1—H1...N1	167
O2...N2 ⁱⁱⁱ	2.668 (5)	O2—H2...N2 ⁱⁱⁱ	158
C4B...O12 ^v	2.80 (2)	C4B—H4B1...O12 ^v	107
(3)			
O1—C14	1.386 (7)	O2—C24	1.344 (6)
S1—C11	1.773 (6)	S1—C21	1.768 (6)
C11—S1—C21	103.7 (3)		
C21—S1—C11—C12	-2.4 (6)	C11—S1—C21—C22	-98.3 (5)
N1—C1A	1.465 (8)	N1—C1B	1.466 (8)
N1—C2A	1.476 (8)	N1—C2B	1.463 (8)
N1—C3A	1.455 (8)	N1—C3B	1.470 (8)
N2—C4A	1.502 (8)	N2—C4B	1.435 (8)
N2—C5A	1.444 (8)	N2—C5B	1.461 (8)
N2—C6A	1.465 (8)	N2—C6B	1.464 (8)
C1A—C4A	1.537 (9)	C1B—C4B	1.526 (9)
C2A—C5A	1.523 (8)	C2B—C5B	1.519 (8)
C3A—C6A	1.521 (9)	C3B—C6B	1.528 (9)
N1—C1A—C4A—N2	-1.9 (14)	N1—C1B—C4B—N2	-1.1 (14)
N1—C2A—C5A—N2	0.6 (13)	N1—C2B—C5B—N2	1.4 (14)
N1—C3A—C6A—N2	1.9 (15)	N1—C3B—C6B—N2	1.3 (15)
O1...N1	2.656 (6)	O1—H1...N1	154
O2...N2 ⁱⁱⁱ	2.658 (6)	O2—H2...N2 ⁱⁱⁱ	163
C4B...S1 ^{iv}	3.442 (12)	C4B—H4B1...S1 ^{iv}	139
(5)			
O1—C14	1.369 (4)	O2—C24	1.368 (4)
S1—C11	1.774 (3)	S1—C21	1.767 (3)
C11—S1—C21	102.75 (15)		
C21—S1—C11—C12	-1.1 (4)	C11—S1—C21—C22	-88.9 (3)
N1—C1A	1.416 (6)	N1—C1B	1.424 (6)
N1—C2A	1.542 (6)	N1—C2B	1.445 (7)
N1—C3A	1.406 (7)	N1—C3B	1.569 (7)
C1A—C2B ^v	1.524 (7)	C1B—C3A ^v	1.527 (7)
C2A—C3B ^v	1.551 (7)	C2B—C1A ^v	1.524 (7)
C3A—C1B ^v	1.527 (7)	C3B—C2A ^v	1.551 (7)
N1—C1A—C2B ^v —N1 ^v	1.1 (11)	N1—C1B—C3A ^v —N1 ^v	0.6 (11)
N1—C2A—C3B ^v —N1 ^v	-0.2 (11)	N1—C2B—C1A ^v —N1 ^v	-1.1 (11)
N1—C3A—C1B ^v —N1 ^v	-0.6 (11)	N1—C3B—C2A ^v —N1 ^v	0.2 (11)
O1...N1	2.640 (4)	O1—H1...N1	158
O2...O1 ^{vi}	2.794 (4)	O2—H2...O1 ^{vi}	161

Symmetry codes: (i) $\frac{1}{2} - x, y, -z$; (ii) $\frac{3}{2} - x, y, 1 - z$; (iii) $x, y, 1 + z$; (iv) $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$; (v) $-x, -y, -z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

from the geometric constraints applied by the axial sites of the hydrogen-bond acceptors in the DABCO component.

Adducts (2), (3) and (5) differ from (1) in that the central atom of the bisphenol component, oxygen in (2) and sulfur in (3) and (5), is in each case a potential acceptor of hydrogen bonds.

The adducts (2) and (3) are amorphous in space group $P2_12_12_1$. In adducts (2), $O(C_6H_4OH)_2 \cdot N(CH_2CH_2)_3N$, and (3), $S(C_6H_4OH)_2 \cdot N(CH_2CH_2)_3N$, the bisphenol and diamine components are again linked by $O-H \cdots N$ hydrogen bonds into infinite chains of alternating bisphenol and diamine units parallel to the c direction (Figs. 3–6). Although the hydroxyl H atoms are fully ordered, there is disorder in the orientation of the DABCO cage in each of (2) and (3) with two orientations differing by a rotation about the $N \cdots N$ vector of some 48° in (2) and 37° in (3): in (2) the site-occupation factors for the two orientations refined to 0.76 (1) and 0.24 (1), while in (3) the disorder was best modelled by assigning site-occupation factors of 0.50 to all the disordered C atoms. In addition to the $O-H \cdots N$ hydrogen bonds there are short $C-H \cdots O$ hydrogen bonds in (2) and $C-H \cdots S$ hydrogen bonds in (3), involving the $C4B-H4B1$ bond in the diamine at (x, y, z) acting as a donor and the O12 atom, in (2), or the S1 atom, in (3), of the bisphenol at $(\frac{1}{2} - x, 1 - y, z - \frac{1}{2})$ as an acceptor. The $C4B-H4B1$ bond in the diamine at $(\frac{1}{2} - x, 1 - y, z - \frac{1}{2})$ in turn acts as a donor to either O12 or S1 at $(x, y, z - 1)$. The effect of these $C-H \cdots O$ or $C-H \cdots S$ interactions is to cross-link

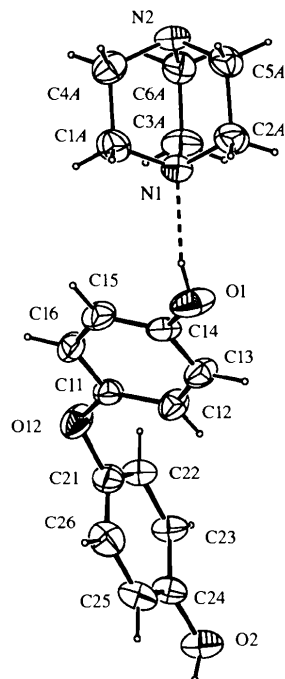


Fig. 3. View of the asymmetric unit of (2), showing only one orientation of the disordered DABCO component; atoms are depicted as in Fig. 1.

the pair of parallel chains related by the screw axis at $(\frac{1}{4}, \frac{1}{2}, z)$ into a ladder: there are no hydrogen bonds between adjacent ladders.

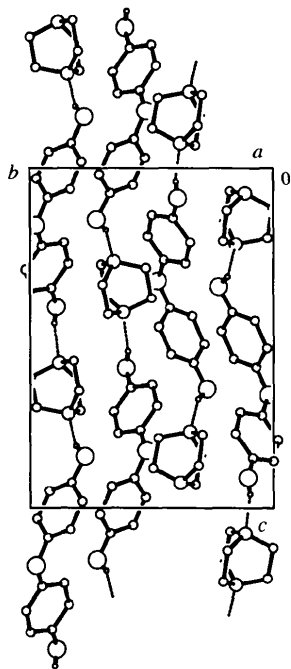


Fig. 4. Packing diagram of the structure of adduct (2), viewed along the *a* axis; H atoms bonded to carbon are omitted.

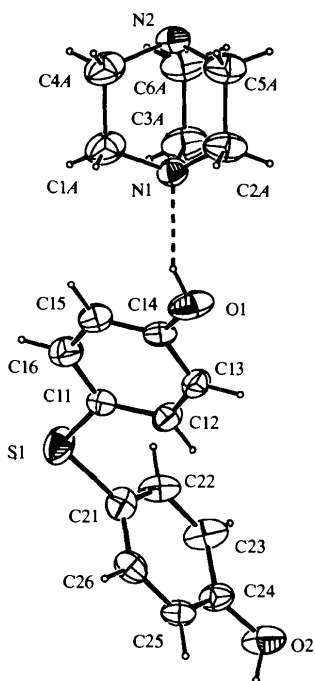


Fig. 5. View of the asymmetric unit of (3), showing only one orientation of the disordered DABCO component; atoms are depicted as in Fig. 1.

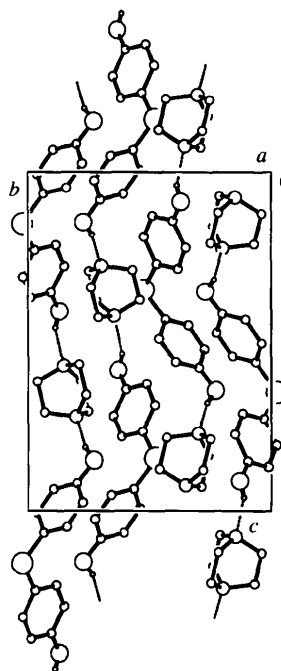
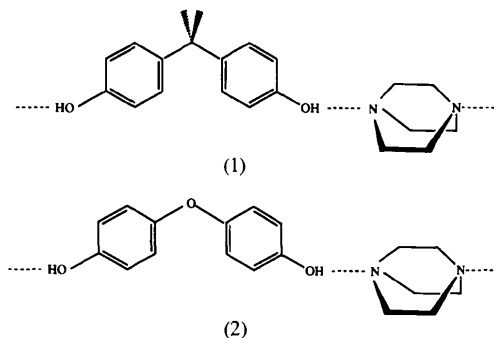
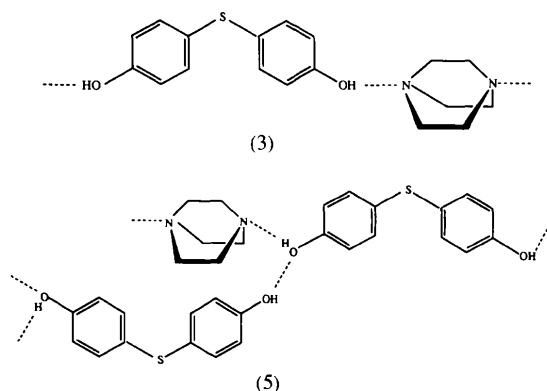


Fig. 6. Packing diagram of the structure of adduct (3), viewed along the *a* axis; H atoms bonded to carbon are omitted.

Compound (5), the 2:1 adduct $[\text{S}(\text{C}_6\text{H}_4\text{OH})_2]_2 \cdot \text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$, crystallizes in the monoclinic space group $P2_1/n$ with two formula units per cell (Figs. 7 and 8). The bisphenol units lie in general positions, while the diamines lie across inversion centres and so are disordered, with two equally populated orientations inter-related by a rotation of 180° about the $\text{N} \cdots \text{N}$ vector. The bisphenol units are linked by $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds into chains generated by the glide planes: the O2 atom of the bisphenol at (x, y, z) acts as a hydrogen-bond donor to O1 in the bisphenol at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. This chain formation utilizes only one hydroxyl hydrogen per bisphenol unit and the remaining O1 atom of each bisphenol acts as a donor to the N atom of the diamine in the same asymmetric unit. In this way the parallel chains of bisphenol units are cross-linked into continuous two-dimensional sheets normal to the $[100]$ direction: while the O1 atom acts as both a donor and an acceptor of hydrogen bonds, O2 acts as only a donor.





Hence, the hydrogen bonding in adduct (1) generates simple chains; in (2) and (3) it gives rise to ladders; in (5) it generates sheets.

3.2. Molecular conformations and dimensions

Each of the bisphenol components in adducts (1), (2), (3) and (5) could in principle adopt conformations in which the symmetry of the heavy atom skeleton is C_{2v} or any of its sub-groups (C_2 , C_s or C_1). In adduct (1) C_2 symmetry is crystallographically imposed, but the conformation is nonetheless very far from C_{2v} symmetry (Table 3). In adducts (2) and (3) the conformation adopted has only C_1 symmetry and the planes of the two independent aryl rings are almost orthogonal (Table 3). In (5) again the conformation of the bisphenol has

only C_1 symmetry with the two independent phenyl rings almost orthogonal.

The conformational properties of the DABCO molecule have been extensively investigated, both in the solid state (Weiss, Parkes, Nixon & Hughes, 1964; Nimmo & Lucas, 1976; Mak, Yip & Book, 1984) and in the gas phase (Yokozeki & Kuchitsu, 1971). The principal point of interest is the extent of any twist of the molecule from ideal D_{3h} symmetry by internal rotation about the N···N vector: in the D_{3h} conformation the neighbouring CH_2 groups are all eclipsed. For isolated molecules in the gas phase (Yokozeki & Kuchitsu, 1971) the internal dynamics indicated a very broad potential well for the twist motion, best fitted by an harmonic-quartic potential function having an energy minimum corresponding to a twist of *ca* 10° from the D_{3h} geometry. A very similar conclusion was reached concerning the internal motion of the [2.2.2]bicyclooctane cage in [2.2.2]bicyclooctane-1,4-dicarboxylic acid (Ermer & Dunitz, 1969). On the other hand, a neutron diffraction study (Nimmo & Lucas, 1976) of the hexagonal phase II of pure DABCO concluded that the space group was $P6_3/m$, which with $Z = 2$ indicates that the molecules in that phase lie on sites having D_{3h} symmetry and that the molecules are ordered, so that the N—C—N torsion angles must be identically zero. In the 2:1 adduct of phenol with DABCO the N—C—N torsional angles were found to range from $2.7(6)$ to $4.0(6)^\circ$, while those in the 1:1 adduct of hydroquinone with DABCO ranged from $-0.5(6)$ to $3.1(6)^\circ$ (Mak, Yip & Book, 1984): these values indicate a small but real distortion from

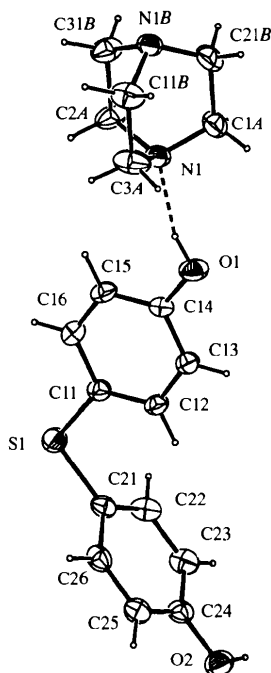


Fig. 7. View of the two components in adduct (5), showing only one orientation of the DABCO molecule; atoms are depicted as in Fig. 1.

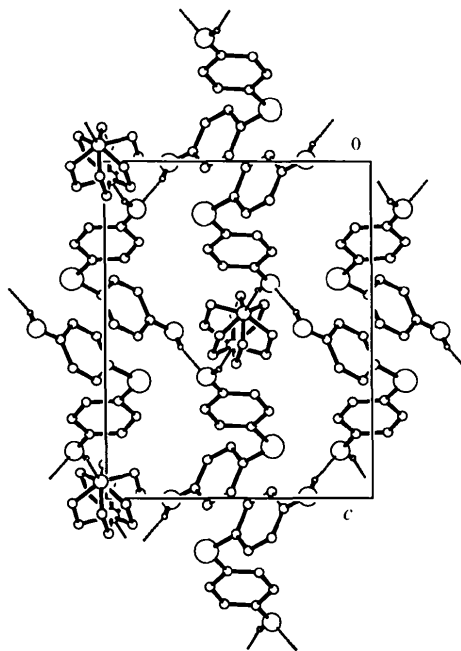


Fig. 8. Packing diagram of the crystal structure of adduct (5), viewed along the a axis; H atoms bonded to carbon are omitted.

the fully eclipsed conformation in these adducts. In adduct (1) the N—C—C—N torsional angles (Table 3) consistently show a slight twist. In adducts (2), (3) and (5) the orientational disorder of the DABCO molecules renders judgement about the conformation more tentative: however, in (2) there is clear evidence from the major orientation [atoms C_nA (*n* = 1–6), Table 3] of a significant distortion of the molecule from ideal *D*_{3h} symmetry, while no significant distortion is apparent in the DABCO component of adducts (3) and (5).

The only unusual feature of the bond lengths observed for the bisphenol components is the discrepancy between the two independent C—O distances in adduct (3): these differ by *ca* 0.04 and both lie beyond the range defined by the upper and power quartile values for C(aryl)—O bonds in phenols (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The other distances in the bisphenol units are typical of their types. The different structure determinations for pure DABCO, although yielding very similar values for the C—N bond length [solid state 1.470 (7) (Nimmo & Lucas, 1976), gas phase 1.472 (7) Å (Yokozeki & Kuchitsu, 1971)], give rather different values for the C—C distance [solid state 1.513 (5), gas phase 1.562 (9) Å]. The mean C—N and C—C distances found for the DABCO components in adducts (1), (2), (3) and (5) (Table 3) are all very close to the values found for pure DABCO.

3.3. Hydrogen-bonding motifs

The chain-forming hydrogen-bond motif in adduct (1) has graph set *C*₂²(17) (Etter, 1990; Etter, MacDonald & Bernstein, 1990; Bernstein, Davis, Shimoni & Chang, 1995). This same graph set describes the principal O—H...N hydrogen-bonded chain motif in both (2) and (3) also, while the ladder-forming cross-linking motif in (3) has graph set *R*₂²(22). In adduct (5) the bisphenol chains give rise to a hydrogen-bond motif with graph set *C*(12), while the cross-linking chains containing alternating DABCO and bisphenol units give a motif with graph set *C*₃³(19): the sheet-forming interaction of these two motifs gives rise to a large ring-forming motif, describing a Z-shaped ring, with graph set *R*₈⁸(62). These graph sets serve to indicate the unusual structural features exhibited by the adducts (2), (3) and (5).

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