Table 1. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
N16—H16···O11^{i}	0.92 (3)	2.25 (3)	166 (2)
C3—H3···O11^{ii}	0.90 (2)	2.69 (2)	176 (2)
C8—H8···O1^{i}	0.95 (2)	2.51 (2)	161 (2)
C15—H15*A*···F3^{iii}	0.91 (3)	2.53 (3)	138 (2)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 2-z$; (iii) $x-1, y, z-1$.

Compound (II)

Crystal data

$C_{15}H_{14}F_3NO_2$
$M_r = 297.3$
Monoclinic
$P2_1/n$
$a = 9.756$ (4) Å
$b = 12.613$ (4) Å
$c = 22.443$ (4) Å
$\beta = 92.45$ (2)°
$V = 2759.1$ (15) Å^3
$Z = 8$
$D_x = 1.431$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 36.79$–$42.39°$
$\mu = 0.1154$ mm^{-1}
$T = 296$ K
Prism
0.6 × 0.5 × 0.3 mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
ω scans with profile analysis
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.938$, $T_{\max} = 1.000$
5158 measured reflections
4856 independent reflections

2236 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = -26 \rightarrow 26$
3 standard reflections every 150 reflections intensity decay: 0.41%

Refinement

Refinement on F^2
$R(F) = 0.055$
$wR(F^2) = 0.127$
$S = 1.17$
4850 reflections
389 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 1.0311P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1988); program(s) used to solve structures: *MITHRIL* (Gilmore, 1984); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *TEXSAN GRAPHICS*; software used to prepare material for publication: *TEXSAN FINISH*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1297). Services for accessing these data are described at the back of the journal.

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1,4-Bis(triphenylmethoxy)-2-butyne, Rhombohedral with $Z' = \frac{7}{6}$

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Abstract

The title compound, $C_{42}H_{34}O_2$, crystallizes in the space group $R\bar{3}$ with one molecule disordered at a crystallographic $\bar{3}$ site and another in a general position. The conformation of the linkage of the trityl groups to the central butyne group is such that the O—C···C—O grouping forms a torsion angle of magnitude 87.2 (2)°. The C≡C length in the ordered molecule is 1.176 (3) Å.

Comment

The ditritylated title compound, (1), was isolated as a minor side-product during the synthesis of 4-tri-

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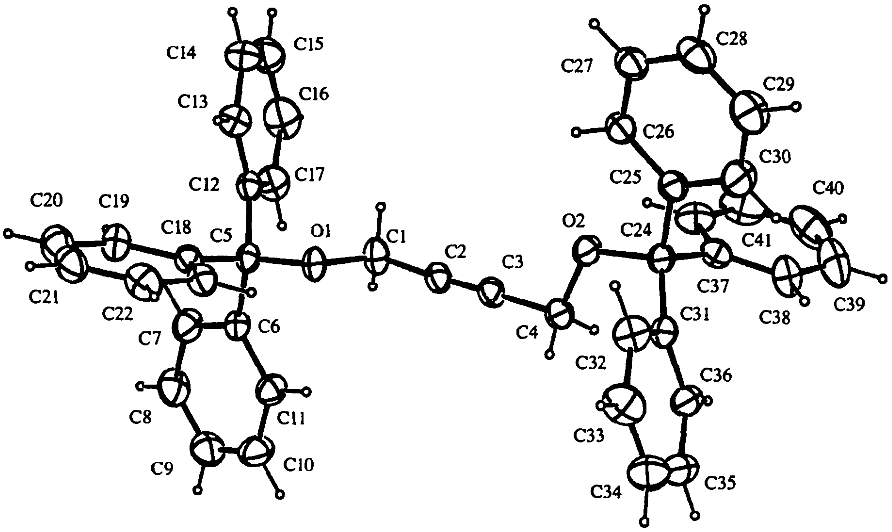
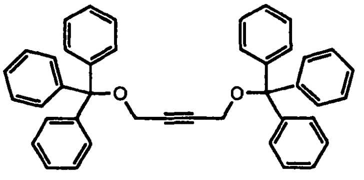


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the ordered molecule of (1), with 30% probability ellipsoids and H atoms of arbitrary radii.

phenylmethoxy-2-butyn-1-ol from 2-butyne-1,4-diol. The structure determination was carried out in order to confirm its identity.



(1)

Compound (1) crystallizes in the rhombohedral space group $R\bar{3}$, with the uncommon value of $Z = 21$ ($Z' = \frac{7}{6}$). There are two independent molecules in the asymmetric unit, one lying in a general position (Fig. 1) and another disordered at a crystallographic $\bar{3}$ site rendering geometric parameters for this (disordered) molecule unreliable. The triply-bonded C atom (C2*A*) and the central C atom of the trityl group (C3*A*) doubtless also exhibit unresolved disorder, rendering geometric parameters for this molecule unreliable. The conformation of the central O—C—C≡C—C—O group of the ordered molecule is non-planar, with the O1, C1, C2 and O2, C4, C3 planes almost perpendicular to one another, forming a dihedral angle of 87.2 (2)°. Similar conformations have been observed in 2-butyne-1,4-diol and its inclusion compound with α-cyclodextrin (Steiner, 1996), in which the corresponding dihedral angles are 94.7 (3) and 83°, respectively. The angles involving the C≡C bond (C1—C2—C3 and C2—C3—C4) are close to linearity. The *O*-trityl groups are *anti* with respect to the C1—C2 and C3—C4 bonds [C5—O1—C1—C2 torsion angle −169.62 (13) and C24—O2—C4—C3 −170.5 (2)°]. The phenyl rings in the trityl groups do not present a symmetrical propeller conformation as does triphenylmethanol (Ferguson *et al.*, 1992), but a less symmetric arrangement, with the O1—C5—C—C and O2—C24—C—C torsion angles having magnitudes in the range 5.2 (3)–78.8 (2)°. The C(trityl)—O bond lengths (C5—O1 and C24—O2) are within the range observed for the equivalent C—O bonds in triphenylmethanol (1.44 Å), tris(4-methoxyphenyl)methanol [1.441 (3)–1.459 (3) Å; Ferguson *et al.*, 1996] and substituted diphenylmethanols [1.421 (4)–1.462 (4) Å; Ferguson *et al.*, 1995].

A search of the Cambridge Structural Database (Allen & Kennard, 1993; Version of April 1997; *ca* 168 000 entries) for $Z = 21$ yielded but three hits, all of which are rhombohedral. CCl_4 at 229 K (Rudman & Post, 1968) is reported to be rhombohedral with $Z = 21$, but the space group is unknown. Tris(tricyclohexylphosphine)platinum heptane solvate (Immirzi *et al.*, 1977) is reported to be ordered in space group $R3$. The lone precedent for $R\bar{3}$ with $Z = 21$ is dodecamethylcyclotetrasilazane (Edwards *et al.*, 1976), which also has one ordered molecule in a general position and one disordered on a $\bar{3}$ site.

Experimental

The title compound was prepared by treatment of triphenylmethyl chloride with a large excess of 2-butyne-1,4-diol in the presence of catalytic amounts of 4-dimethylaminopyridine in CH_2Cl_2. Purification by flash chromatography (hexane–ethyl acetate 1:1) afforded compound (1) as a minor side-product in 2% yield. Crystals were grown by layering a CH_2Cl_2 solution of (1) with CH_3OH.

Crystal data

$C_{42}H_{34}O_2$
$M_r = 570.74$
Trigonal
$R\bar{3}$
$a = 36.120\,(2)$ Å
$c = 14.787\,(1)$ Å
$V = 16\,707\,(2)$ Å^3
$Z = 21$
$D_x = 1.191$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 22$–$38°$
$\mu = 0.52$ mm^{-1}
$T = 295$ K
Fragment
0.40 × 0.25 × 0.23 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min} = 0.86$, $T_{\max} = 0.89$
8031 measured reflections
7651 independent reflections

5705 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 75°$
$h = -45 \rightarrow 0$
$k = 0 \rightarrow 39$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 0.8%

Refinement

Refinement on F^2
$R(F) = 0.057$
$wR(F^2) = 0.059$
$S = 1.206$
5705 reflections
476 parameters
H atoms calculated
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o{}^4]$
$(\Delta/\sigma)_{\max} = 0.008$

$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.06$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $5.4\,(2) \times 10^{-7}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
O1	0.24736 (3)	0.04764 (4)	0.49284 (8)	0.0455 (6)
O2	0.24019 (4)	0.08196 (4)	0.14049 (8)	0.0445 (6)
C1	0.21143 (5)	0.04739 (6)	0.4529 (1)	0.0564 (9)
C2	0.21407 (5)	0.04435 (5)	0.3544 (1)	0.0461 (8)
C3	0.21516 (5)	0.04302 (5)	0.2751 (1)	0.0452 (8)
C4	0.21575 (6)	0.03997 (5)	0.1764 (1)	0.0498 (9)
C5	0.24599 (5)	0.04299 (5)	0.5904 (1)	0.0414 (8)
C6	0.21343 (5)	−0.00324 (5)	0.6162 (1)	0.0427 (8)
C7	0.19888 (6)	−0.01427 (6)	0.7044 (1)	0.054 (1)
C8	0.17303 (7)	−0.05648 (7)	0.7286 (1)	0.064 (1)
C9	0.16119 (7)	−0.08843 (7)	0.6663 (2)	0.067 (1)
C10	0.17497 (7)	−0.07812 (6)	0.5793 (2)	0.064 (1)
C11	0.20085 (6)	−0.03597 (6)	0.5543 (1)	0.053 (1)
C12	0.23771 (5)	0.07703 (5)	0.6316 (1)	0.0490 (8)
C13	0.27090 (6)	0.11882 (6)	0.6394 (2)	0.067 (1)
C14	0.26350 (8)	0.15115 (7)	0.6664 (2)	0.088 (1)
C15	0.22331 (8)	0.14286 (7)	0.6851 (2)	0.103 (1)
C16	0.18956 (7)	0.10185 (7)	0.6768 (2)	0.099 (1)
C17	0.19702 (6)	0.06897 (6)	0.6511 (1)	0.071 (1)
C18	0.29026 (5)	0.04992 (5)	0.6156 (1)	0.0430 (8)
C19	0.30282 (6)	0.05430 (6)	0.7057 (1)	0.059 (1)
C20	0.34193 (6)	0.05946 (7)	0.7297 (2)	0.069 (1)
C21	0.36969 (6)	0.06074 (6)	0.6652 (2)	0.067 (1)
C22	0.35778 (6)	0.05617 (6)	0.5759 (2)	0.065 (1)
C23	0.31829 (5)	0.05049 (6)	0.5510 (1)	0.0525 (9)
C24	0.23833 (5)	0.08529 (5)	0.0430 (1)	0.0426 (8)
C25	0.27306 (5)	0.13131 (5)	0.0208 (1)	0.0460 (9)
C26	0.29582 (5)	0.16071 (5)	0.0869 (1)	0.0488 (9)
C27	0.32768 (6)	0.20173 (6)	0.0645 (2)	0.057 (1)
C28	0.33666 (6)	0.21369 (6)	−0.0233 (2)	0.064 (1)
C29	0.31397 (8)	0.18517 (7)	−0.0901 (2)	0.077 (1)
C30	0.28240 (8)	0.14416 (7)	−0.0686 (1)	0.065 (1)
C31	0.24876 (5)	0.05304 (5)	0.0008 (1)	0.0456 (8)
C32	0.29102 (6)	0.06225 (6)	−0.0012 (1)	0.061 (1)
C33	0.30133 (6)	0.03191 (7)	−0.0276 (2)	0.084 (1)
C34	0.26972 (7)	−0.00803 (6)	−0.0528 (2)	0.089 (1)
C35	0.22802 (7)	−0.01777 (6)	−0.0502 (2)	0.078 (1)
C36	0.21716 (6)	0.01243 (6)	−0.0238 (1)	0.059 (1)
C37	0.19514 (5)	0.08063 (5)	0.0161 (1)	0.0486 (9)
C38	0.17984 (6)	0.07211 (7)	−0.0716 (1)	0.070 (1)
C39	0.14273 (7)	0.07270 (8)	−0.0941 (2)	0.096 (1)
C40	0.12077 (7)	0.08174 (7)	−0.0306 (2)	0.094 (1)
C41	0.13527 (7)	0.08924 (7)	0.0558 (2)	0.085 (1)
C42	0.17208 (6)	0.08910 (6)	0.0792 (2)	0.063 (1)
O1*A*†	0.01588 (9)	0.0043 (2)	0.1890 (2)	0.060 (2)
C1*A*†	−0.0011 (2)	0.0192 (2)	0.1308 (4)	0.070 (4)
C2*A*	0	0	0.0379 (2)	0.0655 (8)
C3*A*	0	0	0.2871 (2)	0.0620 (8)
C4*A*	0.04568 (6)	0.03162 (7)	0.3199 (1)	0.068 (1)
C5*A*	0.05367 (8)	0.05933 (9)	0.3898 (2)	0.086 (2)
C6*A*	0.09442 (9)	0.0859 (1)	0.4232 (3)	0.105 (2)
C7*A*	0.12747 (9)	0.0857 (1)	0.3879 (3)	0.117 (2)
C8*A*	0.12252 (7)	0.0587 (1)	0.3205 (2)	0.134 (2)
C9*A*	0.08113 (8)	0.03132 (9)	0.2854 (2)	0.131 (2)

† Site occupancy = 0.33.

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.422 (3)	C1—C2	1.467 (3)
O1—C5	1.450 (2)	C2—C3	1.176 (3)
O2—C4	1.422 (2)	C3—C4	1.463 (3)
O2—C24	1.451 (2)		
C1—O1—C5	115.7 (1)	C1—C2—C3	176.7 (3)
C4—O2—C24	115.5 (1)	C2—C3—C4	178.3 (2)
O1—C1—C2	108.6 (2)	O2—C4—C3	108.5 (1)
C5—O1—C1—C2	−169.6 (1)	O1—C5—C12—C13	−78.8 (2)
C1—O1—C5—C18	−173.2 (1)	O1—C5—C18—C23	−12.4 (2)
C24—O2—C4—C3	−170.5 (2)	O2—C24—C25—C26	−5.2 (3)
C4—O2—C24—C25	−170.0 (2)	O2—C24—C31—C32	−76.3 (2)
O1—C5—C6—C11	20.9 (3)	O2—C24—C37—C42	22.3 (2)

The H atoms on the disordered C1*A* atom were not located. Atoms C1*A* and O1*A* were assigned a population of $\frac{1}{3}$. For the calculation of H-atom positions, a C—H distance of 0.95 Å was assumed. Isotropic displacement parameters for H atoms were assigned as $B_{\rm iso} = 1.3B_{\rm eq}$ of the bonded C atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN*. Software used to prepare material for publication: *BTABLE PTABLE CIF IN* in *MolEN*.

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge. Improvements to the LSU X-ray Crystallography Facility were supported by Grant No. LEQSF(1996–97)-ENH-TR-10, administered by the Louisiana Board of Regents.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1398). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 415–417

Stereochemistry of Anti-Inflammatory Drugs. VI. Piperazinium 2-(2,6-Dichlorophenylamino)phenylacetate Dihydrate, $(H_2PZ)D_2.2H_2O$

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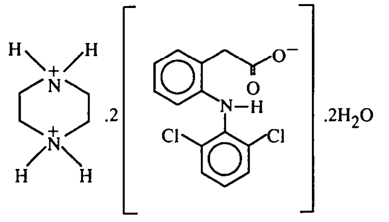
Abstract

The asymmetric unit of the title compound, $C_4H_{12}N_2^{2+}.2C_{14}H_{10}Cl_2NO_2^-.2H_2O$, consists of two piperazinium dications located around two non-equivalent centers of symmetry, two 2-(2,6-dichlorophenylamino)phenylacetate anions in general positions and two water molecules. The solid-state structure is strongly hydrogen bonded.

Comment

The structure of the title salt has been investigated by X-ray diffraction as a part of a systematic study (Castellari & Sabatino, 1994, 1996; Castellari & Ottani, 1995, 1996, 1997) of diclofenac [2-(2,6-dichlorophenylamino)phenylacetic acid] salts, an important group of nonsteroidal anti-inflammatory drugs. Alterations in solubility and chemical stability have important pharmaceutical consequences since they can modify the bioavailability of a drug. Such alterations depend on the presence of polymorphic forms, crystalline stoichiometry and water molecules in the solid. Thus, the successful design of a dosage form of the drug depends strongly on knowledge of its solid-state chemistry. The asymmetric unit of the title compound, $(H_2PZ)D_2.2H_2O$ [where H_2PZ is the piperazinium dication and D is the 2-(2,6-dichlorophenylamino)phenylacetate anion] is shown in Fig. 1.



$(H_2PZ)D_2.2H_2O$

The asymmetric unit contains two bivalent piperazinium cations located around the symmetry centers $(0,0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, two 2-(2,6-dichlorophenylamino)phenylacetate anions and two water molecules. The structure is characterized by the presence of several hydrogen bonds (Table 2). The cations, anions and water molecules are connected by intermolecular hydrogen bonds to form a two-dimensional network in the *ab* plane. No short contact is detected along the **c** direction of the cell. The carboxylate groups, cations and water molecules are arranged along the [010] direction to form a hydrophilic tunnel. Water molecules interact with both H_2PZ and D ions, but not with each other.

The H_2PZ cations form salt bridges with the carboxylate groups. The N···O distances are short, as expected for hydrogen bonds in which both donor and acceptor atoms carry a formal charge. However, while both the ammonium H atoms (H11 and H12) at each end of the cation at $(0,0,\frac{1}{2})$ interact with carboxylate O atoms, only one H atom (H12*A*) from each end of the cation at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ forms a salt bridge. As detailed in Table 2, the other ammonium H atom (H11*A*) is strongly bonded to the O3 water molecule. As a consequence, O3 is more closely packed than the O3*A* water molecule [mean contact distances 2.853 (2) and 2.994 (2) Å for O3 and O3*A*, respectively]. This feature is probably related to the simultaneous donor and acceptor character of O3 in the hydrogen-bonding