Refinement

Refinement on F^2
$R(F) = 0.0594$
$wR(F^2) = 0.1653$
$S = 1.028$
2174 reflections
155 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0888P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: none
Scattering factors from
    International Tables for
    Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

P—C11	1.7722 (15)	B3—B4	1.763 (6)
P—C21	1.777 (4)	B3—B8	1.780 (6)
B1—B2	1.741 (8)	B4—B8	1.758 (7)
B1—B3	1.758 (6)	B4—B9	1.764 (6)
B1—B4	1.763 (7)	B4—B4^i	1.776 (10)
B2—B3	1.751 (5)	B7—B8	1.856 (6)
B2—B7	1.761 (6)	B7—B7^i	1.895 (8)
B3—B7	1.751 (6)	B8—B9	1.883 (6)
C11^i—P—C11	112.5 (2)	B8—B4—B9	64.6 (3)
C11—P—C21	110.29 (9)	B1—B4—B4^i	59.8 (2)
B2—B1—B3	60.1 (2)	B9—B4—B4^i	59.8 (2)
B3—B1—B4	60.1 (2)	B3—B7—B2	59.8 (2)
B4^i—B1—B4	60.5 (4)	B3—B7—B8	59.0 (2)
B1—B2—B3	60.5 (2)	B2—B7—B7^i	57.4 (2)
B3—B2—B7	59.8 (2)	B8—B7—B7^i	107.4 (2)
B7^i—B2—B7	65.1 (3)	B4—B8—B3	59.8 (2)
B2—B3—B7	60.4 (3)	B3—B8—B7	57.6 (2)
B2—B3—B1	59.5 (3)	B4—B8—B9	57.9 (3)
B1—B3—B4	60.1 (3)	B7—B8—B9	109.6 (3)
B7—B3—B8	63.4 (2)	B4—B9—B4^i	60.4 (4)
B4—B3—B8	59.5 (2)	B4—B9—B8	57.5 (2)
B8—B4—B3	60.7 (2)	B8^i—B9—B8	105.9 (4)
B1—B4—B3	59.8 (2)		

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

The structure was solved by Patterson methods (*SHELX*76; Sheldrick, 1976) for the P atom and by difference Fourier syntheses (*SHELXL*93; Sheldrick, 1993) for B and C atoms, and for the phosphonium and borane H atoms. The C atoms of the wholly crystallographically-independent phenyl ring were constrained to be a rigid planar hexagon (C—C 1.39 Å) and all phenyl H atoms were set riding in idealized positions (C—H 0.93 Å), with an isotropic displacement parameter equal to 1.5 times the equivalent isotropic displacement parameter of the corresponding C atom. Terminal borane H atoms were positionally refined subject to a common B—H distance [1.15 (3) Å at convergence]; the positions of the *endo* and bridging borane H atoms H11 and H100 were fixed after their location. [Attempts to refine the positions of H11 and H100 were unsuccessful, resulting in their migration to chemically non-sensible positions away from the borane face (with B···H > 2 Å) and the reappearance of electron-density peaks in the difference Fourier map close to the original apparent positions of these atoms.] The parameters of the phosphonium H atom were successfully refined to a final P—H distance of 1.37 (4) Å. All non-H atoms were ultimately refined with anisotropic displacement parameters; all non-phenyl H atoms were assigned a common (refined) isotropic displacement parameter [$U_{iso} = 0.081$ (4) Å^2 at convergence].

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CADABS* (Gould & Smith, 1986). Program used to refine structure: *SHELXL*93. Molecular graphics: *ORTEX* (McArdle, 1994).

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Tetrakis(*p*-dimethylaminophenyl)ethylene Hemibenzene Solvate

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## Abstract

The crystal structure of the title compound, ethylene-tetrayltetrakis[dimethyl(4-phenyl)amine] hemibenzene solvate, $C_{34}H_{40}N_4 \cdot 0.5C_6H_6$, has been determined by X-ray diffraction at 200 K. The molecular halves of the tetrasubstituted ethylene subunit are twisted by 12.0 (2)°

around the ethylene C=C bond. Two of the *p*-dimethyl-amino groups are pyramidal and twisted by 21.3 (2) and 20.8 (3)° out of the planes of the attached phenyl rings, whereas the other two are almost coplanar with their attached phenyl rings. All structural parameters support an extensive electron delocalization over at least two of the four *p*-dimethylaminophenyl substituents.

Comment

Arising from our interest in the structural changes of organic molecules during one- or two-electron redox reactions to their molecular cations or anions (Bock *et al.*, 1992), we have synthesized and structurally characterized both tetrakis(*p*-dimethylaminophenyl)ethylene and its dication (Bock, Näther & Havlas, 1995). The two structures differ significantly and the changes observed can be rationalized by quantum-mechanical calculations. In addition, our crystallization experiments yielded a pseudo-polymorphic form of tetrakis(*p*-dimethyl-aminophenyl)ethylene containing benzene solvent molecules, (I).
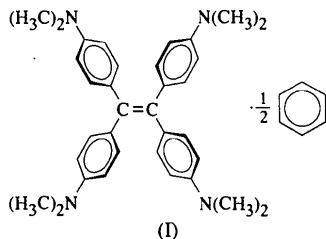
In the crystal structure of the title compound, (I) (Fig. 1), the molecules are stacked along the *a* axis. Between these stacks, channels are formed which contain slightly disordered benzene molecules located on a centre of inversion. There are no significant short contacts between the guest and host molecules.

In tetrakis(*p*-dimethylaminophenyl)ethylene (Fig. 2), the molecular halves are twisted by 12.0 (2)° around the central ethylene bond of 1.361 (2) Å. The Ph—C—Ph angles are close to 114.62 (13) and 115.31 (13)°. As a result of steric repulsion between the bulky *p*-dimethylaminophenyl groups, the six-membered rings are twisted out of an idealized plane calculated through
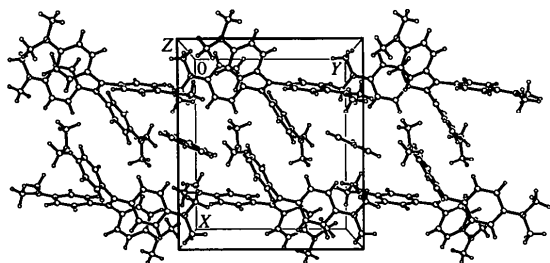

Fig. 1. The crystal structure of tetrakis(*p*-dimethylaminophenyl)ethyl-ene hemibenzene solvate viewed along the *c* axis.
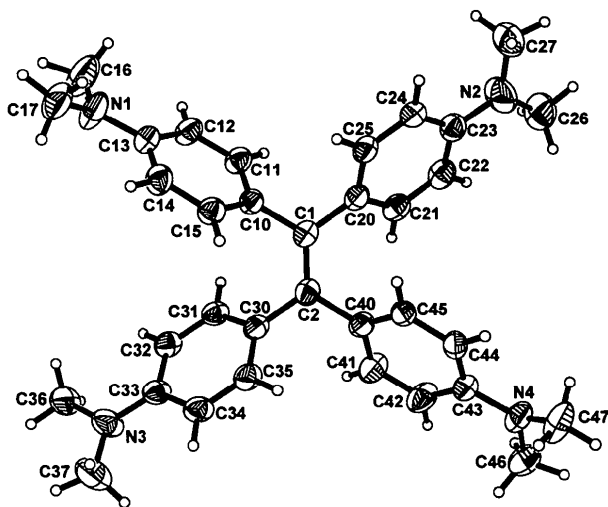

Fig. 2. The molecular structure of tetrakis(*p*-dimethylaminophenyl)-ethylene with the atomic labelling. Displacement ellipsoids are drawn at the 50% probability level.

atoms C1, C2, C10, C20, C30 and C40 by 56.7 (2), 49.1 (2), 46.5 (2) and 49.7 (2)°. Two of the four di-methylamino groups are pyramidal, with the sums of angles around the N1 atom 356.7 (2)° and around the N4 atom 355.2 (2)°. The interplanar angles between these two groups and the phenyl rings amount to 21.3 (2) and 20.8 (2)°. The distances N1—C13 and N4—C43 are 1.397 (2) and 1.393 (2) Å, respectively, with phenyl *ipso*-angles C12—C13—C14 of 116.94 (15) and C42—C43—C44 of 116.49 (14)°. In contrast, the other two di-methylamino groups are nearly planar with angle sums of 359.8 (2) and 359.0 (2)° around atoms N2 and N3, respectively, and are nearly coplanar with their attached six-membered rings; the interplanar angle between the N2, C26, C27 and C20–C25 planes is 7.5 (2)°, and between the N3, C36, C37 and C30–C35 planes is 11.5 (2)°. The C—N bond lengths are only slightly shorter than those of the pyramidal dimethylamino groups [N2—C23 1.383 (2) and N3—C33 1.387 (2) Å] and the phenyl *ipso*-angles C22—C23—C24 and C32—C33—C34 are 117.0 (2) and 116.89 (15)°, respectively. All of these structural changes indicate an extensive π interaction between the *p*-dimethylamino and phenyl groups.

Most of the structural parameters in the benzene solvate are comparable to those in the solvent-free compound (Bock, Näther & Havlas, 1995). One notable difference is the twist angle between the molecular halves, which decreases from 19° in the solvent-free compound to 12°. A search of the literature revealed three compounds possessing a tetraphenylethylene core. In tetraphenylethylene (Hoekstra & Vos, 1975), the twist angle is 8.9°, whereas the sterically overcrowded tetra-mesitylethylene (Blount, Mislow & Jacobus, 1972) is twisted by only 4.4°. For 1,1,2-tris(4-methoxyphenyl)-1-

(4-chlorophenyl)ethylene (Mahato, Mandal, Pal, Maitra, Lehmann & Inger, 1988), another derivative with donor substituents in the *p*-phenyl position, a twist angle of 8° was observed. In the extremely electron-rich parent molecule tetrakis(dimethylamino)ethylene, the molecular halves are twisted by 28° (Bock, Borrmann, Havlas, Oberhammer, Ruppert & Simon, 1991). These results suggest that the twisting of the ethylene bond originates from the superposition of both the packing and stereo-electronic effects of the donor substituents.

Experimental

Tetrakis(*p*-dimethylaminophenyl)ethylene was synthesized following the published procedure of Willstätter & Goldman (1906). Single crystals of the benzene solvate were obtained on recrystallization from benzene.

Crystal data

$C_{34}H_{40}N_4.0.5C_6H_6$	Mo $K\alpha$ radiation
$M_r = 543.75$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 88
$P2_1/c$	reflections
$a = 13.8538(11)$ Å	$\theta = 12.5–18.0°$
$b = 12.0498(8)$ Å	$\mu = 0.067$ mm^{-1}
$c = 19.0800(12)$ Å	$T = 200(2)$ K
$\beta = 91.068(7)°$	Prism
$V = 3184.6(4)$ Å^3	$0.6 \times 0.5 \times 0.5$ mm
$Z = 4$	Light green
$D_x = 1.134$ Mg m^{-3}	
D_m not measured	

Data collection

Stoe AED-II diffractometer	$\theta_{max} = 25.02°$
ω/θ scans	$h = -16 \rightarrow 16$
Absorption correction: none	$k = 0 \rightarrow 14$
6284 measured reflections	$l = 0 \rightarrow 22$
5613 independent reflections	4 standard reflections
4210 reflections with	frequency: 60 min
$I > 2\sigma(I)$	intensity decay: none
$R_{int} = 0.0356$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.336$ e Å^{-3}
$R(F) = 0.0427$	$\Delta\rho_{min} = -0.132$ e Å^{-3}
$wR(F^2) = 0.1200$	Extinction correction:
$S = 1.044$	SHELXL93
5613 reflections	Extinction coefficient:
379 parameters	0.0095(7)
$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2$	Scattering factors from
$+ 0.8189P]$	International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)
$(\Delta/\sigma)_{max} < 0.001$	

Table 1. *Selected geometric parameters* (Å, °)

C1—C2	1.361(2)	C23—C24	1.401(2)
C1—C20	1.487(2)	C24—C25	1.381(2)
C1—C10	1.496(2)	N3—C33	1.387(2)
C2—C30	1.486(2)	N3—C37	1.426(2)
C2—C40	1.498(2)	N3—C36	1.441(2)
N1—C13	1.397(2)	C30—C35	1.388(2)
N1—C16	1.416(3)	C30—C31	1.397(2)
N1—C17	1.439(3)	C31—C32	1.380(2)
C10—C15	1.390(2)	C32—C33	1.402(2)
C10—C11	1.390(2)	C33—C34	1.399(2)
C11—C12	1.380(2)	C34—C35	1.378(2)
C12—C13	1.395(2)	N4—C43	1.393(2)
C13—C14	1.396(2)	N4—C47	1.440(3)
C14—C15	1.382(2)	N4—C46	1.446(2)
N2—C23	1.383(2)	C40—C45	1.389(2)
N2—C27	1.438(3)	C40—C41	1.392(2)
N2—C26	1.440(3)	C41—C42	1.379(2)
C20—C25	1.395(2)	C42—C43	1.395(2)
C20—C21	1.400(2)	C43—C44	1.397(2)
C21—C22	1.378(2)	C44—C45	1.379(2)
C22—C23	1.401(3)		
C2—C1—C20	123.24(13)	C22—C23—C24	117.0(2)
C2—C1—C10	122.14(14)	C25—C24—C23	120.9(2)
C20—C1—C10	114.62(13)	C24—C25—C20	122.34(15)
C1—C2—C30	122.46(13)	C33—N3—C37	120.42(15)
C1—C2—C40	122.15(14)	C33—N3—C36	120.08(14)
C30—C2—C40	115.31(13)	C37—N3—C36	118.5(2)
C13—N1—C16	120.2(2)	C35—C30—C31	116.01(15)
C13—N1—C17	119.1(2)	C35—C30—C2	121.12(14)
C16—N1—C17	117.4(2)	C31—C30—C2	122.86(14)
C15—C10—C11	116.54(14)	C32—C31—C30	121.97(15)
C15—C10—C1	121.90(14)	C31—C32—C33	121.31(14)
C11—C10—C1	121.52(14)	N3—C33—C34	121.42(15)
C12—C11—C10	122.12(15)	N3—C33—C32	121.69(14)
C11—C12—C13	121.2(2)	C34—C33—C32	116.89(15)
C12—C13—C14	116.94(14)	C35—C34—C33	120.7(2)
C12—C13—N1	121.8(2)	C34—C35—C30	122.98(15)
C14—C13—N1	121.2(2)	C43—N4—C47	120.0(2)
C15—C14—C13	121.22(15)	C43—N4—C46	118.8(2)
C14—C15—C10	121.92(15)	C47—N4—C46	116.4(2)
C23—N2—C27	120.6(2)	C45—C40—C41	116.16(14)
C23—N2—C26	120.5(2)	C45—C40—C2	121.82(13)
C27—N2—C26	118.6(2)	C41—C40—C2	121.96(14)
C25—C20—C21	116.40(15)	C42—C41—C40	122.0(2)
C25—C20—C1	120.88(13)	C41—C42—C43	121.7(2)
C21—C20—C1	122.71(14)	N4—C43—C42	122.11(15)
C22—C21—C20	121.9(2)	N4—C43—C44	121.4(2)
C21—C22—C23	121.43(15)	C42—C43—C44	116.49(14)
N2—C23—C22	121.5(2)	C45—C44—C43	121.25(15)
N2—C23—C24	121.4(2)	C44—C45—C40	122.41(14)

The data were corrected for Lorentz and polarization effects. All C atoms were refined with anisotropic displacement parameters and all H atoms were located from a difference map, but positioned with idealized geometry and refined with fixed individual isotropic displacement parameters [$U_{iso} = 1.2U_{eq}(C_{aromatic})$ or $1.5U_{eq}(C_{methyl})$] using a riding model with the parameters C—H(aromatic) 0.93 and C—H(methyl) 0.96 Å. The benzene molecule exhibits unusually high anisotropic displacement parameters indicating static or dynamic disorder. Refinement using a split model was not successful.

Data collection: *DIF4* (Stoe & Cie, 1991*a*). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXL93*. Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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α,β-Trehalose Monohydrate

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Abstract

The structure of α,β-trehalose (α-D-glucopyranosyl-β-D-glucopyranoside) monohydrate, $C_{12}H_{22}O_{11}.H_2O$, was determined in order to compare it with the molecular structures of the stereoisomers α,α-trehalose and β,β-trehalose. Both hexopyranosyl rings have $^4C_1$ conformations. In the glycosidic linkage, the torsion angles about the α-anomeric C—O bond are close to those observed in α,α-trehalose, but the torsion angles about the β-anomeric C—O bond deviate from those in β,β-trehalose and other β-pyranosides. This conformation is stabilized by an intramolecular hydrogen bond between the O(6) hydroxyl groups of the two glucopyranosyl residues. The hydrogen-bond system in the crystal structure consists of infinite and finite chains cross-linked by the water molecule.

Comment

α,β-Trehalose is one of the three stereoisomers about the 1–1 glycosidic linkage of the non-reducing disaccha-ride consisting of two D-glucopyranosyl residues. α,α-Trehalose is widely distributed in nature (Birch, 1963), while α,β- and β,β-trehaloses are its synthetic isomers (Fischer & Delbrück, 1909; Helferich & Weis, 1956). α,α-Trehalose is attracting a great deal of attention as an efficient protecting agent for maintaining the struc-tural integrity of the cytoplasm (Wiemken, 1990), and its structure has been extensively studied. The crystal struc-tures of α,α-trehalose dihydrate (Brown et al., 1972; Taga, Senma & Osaki, 1972), anhydrous α,α-trehalose (Jeffrey & Nanni, 1985), α,α-trehalose calcium bromide monohydrate (Cook & Bugg, 1973) and several α,α-trehalose derivatives (Williams, Lavallee, Hanssian & Brisse, 1979; Lee, Koh, Xu & Linden, 1994; Linden & Lee, 1994, 1995) have been reported so far. Little has been reported of the synthetic isomers, only the crystal structure of β,β-trehalose tetrahydrate (Lee & Koh, 1993) having been published previously. The β,β-trehalose molecule has exact C2 symmetry in the crystal structure, while the title α,β-trehalose, (I), has an asym-metric configuration about the glycosidic linkage. The object of this study was to compare the molecular struc-ture of asymmetric α,β-trehalose with the structures of other symmetric isomers.

(I)
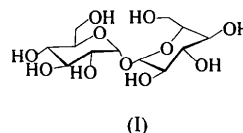
A perspective view of the molecular structure of (I) is given in Fig. 1. Both glucopyranosyl rings adopt chair $^4C_1$ conformations denoted by the Cremer & Pople (1975) puckering parameters $Q = 0.53$ Å and $\theta = 7.1°$ for the α-pyranosyl ring, and $Q = 0.59$ Å and $\theta = 5.8°$ for the β-pyranosyl ring. The torsion angles about the glycosidic C(1)—O(1) bond [O(5)—C(1)—O(1)—C(1′) 68.8 (6) and C(2)—C(1)—O(1)—C(1′) −169.3 (4)°]
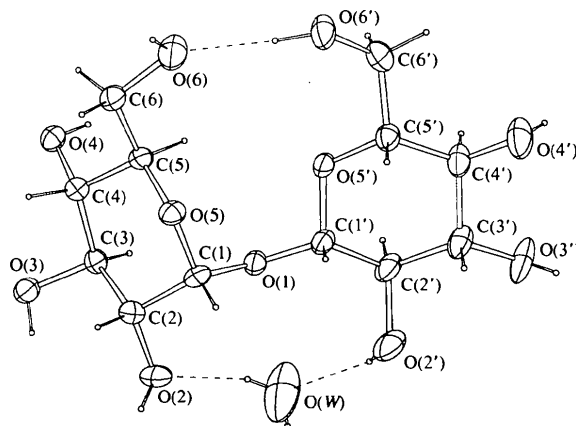

Fig. 1. The structure of α,β-trehalose monohydrate showing 50% probability displacement ellipsoids.