Bock, H., Arad, C., Näther, C. & Göbel, I. (1996). *Helv. Chim. Acta*, **79**, 92–100.
Bock, H., Havlas, Z., Rauschenbach, A., Näther, C. & Kleine, M. (1996). *J. Chem. Soc. Chem. Commun.* pp. 1529–1530.
Bock, H., Rauschenbach, A., Näther, C., Kleine, M. & Bats, J. W. (1996). *Phosphorus Sulfur Silicon.* In the press.
Bock, H., Seitz, W., Sievert, M., Kleine, M. & Bats, J. W. (1996). *Angew. Chem.* **108**, 2382–2384; *Angew. Chem. Int. Ed. Engl.* **35**, 2244–2246.
Bock, H., Sievert, M., Schödel, H. & Kleine, M. (1996). *Z. Naturforsch. Teil B.* In the press.
Bock, H., Ziemer, K., Näther, C., Schödel, H., Kleine, M. & Sievert, M. (1996). *Z. Naturforsch. Teil B.* In the press.
Duesler, E. N., Engelmann, J. H., Curtin, D. Y. & Paul, I. C. (1978). *Cryst. Struct. Commun.* **7**, 449–453.
Hanson, A. W. (1965). *Acta Cryst.* **19**, 19–26.
Herbstein, F. H. (1971). *Perspectives in Structural Chemistry*, Vol. IV, edited by J. D. Dunitz & J. A. Ibers, pp. 166–395. New York: John Wiley.
Herbstein, F. H. & Kaftory, M. (1975). *Acta Cryst.* B**31**, 60–67.
Herbstein, F. H. & Kaftory, M. (1976). *Acta Cryst.* B**32**, 387–396.
Kovats, E., Günthard, H. H. & Plattner, P. A. (1955). *Helv. Chim. Acta*, **38**, 1912–1919.
Robertson, J. M., Shearer, H. M. M., Sim, G. A. & Watson, D. G. (1962). *Acta Cryst.* **15**, 1–8.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XSCANS. X-ray Single Crystal Analysis Software.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Soriano-Garcia, M., Srikrishan, T. & Parthasarathy, R. (1978). *Acta Cryst.* A**34**, 114–117.
Soriano-Garcia, M., Srikrishan, T. & Parthasarathy, R. (1980). *Z. Kristallogr.* **151**, 317–319.
Wong, H. N. C., So, K. P. & Mak, T. C. W. (1984). *Z. Kristallogr.* **169**, 117–125.
Yamaguchi, S., Goto, M., Takayanagi, H. & Ogura, H. (1988). *Bull. Chem. Soc. Jpn*, **61**, 1026–1028.

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N,N′-Bis(4-methylbenzoyl)-*p*-phenylenediamine at 200 K

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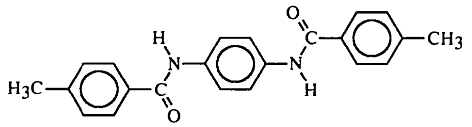
Abstract

The title compound, *N,N′-p*-phenylenebis(4-methylbenzamide), $C_{22}H_{20}N_2O_2$, crystallizes with an almost linear arrangement of the three benzene units, but both outer benzene ring planes are twisted relative to the plane of the central ring by 58.03 (6)°. N—H···O=C hydrogen bonds perpendicular to the long axis of the molecules connect them into ribbons parallel to the *a* axis.

Comment

The structure of the title compound, (I), has been determined as part of a study on the structures and properties of *N,N′*-di- and *N,N,N′,N′*-tetrasubstituted *p*-phenylenediamines (Bock, Göbel, Näther, Havlas, Gavezzotti & Filippini, 1993; Bock, Meuret, Näther & Krynitz, 1994). The derivative *N,N′*-ditosyl-*p*-phenylenediamine, with two sulfonamide instead of two amide subunits, has the ability to include a large variety of solvents on crystallization. The inclusion compounds with one molecular equivalent of acetone, cyclopentanone, cyclopent-2-en-1-one, tetrahydrofuran, 2,5-dihydrofuran and dioxolane are isostructural, whereas a second type of isostructural inclusion compound includes one molar equivalent of a less polar solvent such as benzene or furan (Nagel, 1993; Näther, 1994). In addition, hydrogen-bonded 2:1 adducts crystallize from solutions containing strong hydrogen-bond acceptors such as dimethyl sulfoxide (DMSO) (Nagel, Näther & Bock, 1995) and *N,N*-dimethylformamide (DMF). In both types of isostructural inclusion compound, only one O atom of each sulfonamide group is involved in hydrogen bonding. We therefore became interested in the inclusion properties of (I).



(I)

Crystallization experiments on (I), however, proved it to be almost insoluble in most organic solvents and no solvates could be crystallized. Solvent-free crystals suitable for single-crystal X-ray structure analysis were obtained from DMF. The compound crystallizes in space group $P\bar{1}$ with half a molecule in the asymmetric unit. The geometric parameters correspond to values found in similar compounds (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1994). The molecules are located around crystallographic centres of inversion and their conformation can thus be characterized by the torsion along the three bonds C1—N1, N1—C4 and C4—C10 (Fig. 1). The torsion angles ω(C2—C1—N1—C4) of −30.7 (2), ω(C1—N1—C4—C10) of 179.29 (13) and ω(N1—C4—C10—C11) of −29.1 (2)° confirm that the H1N—N1—C4=O1 amide subunit is fixed in an antiperiplanar conformation and that the H1N and O1 atoms are both twisted out of the planes of their adjacent benzene subunits by about 30°. The position of the refined hydrogen bound to N1 indicates that the substituted nitrogen centre is almost planar, in contrast to the analogous compound with sulfonamide subunits,

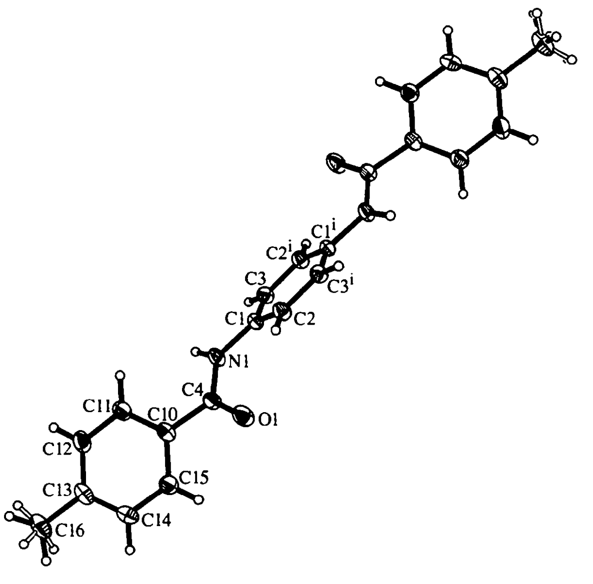


Fig. 1. View of the anisotropic displacement ellipsoids (50% probability) for the C, N and O atoms of (I) and the numbering scheme.

in which the nitrogen centres are pyramidally substituted (Nagel, 1993; Näther, 1994; Nagel, Näther & Bock, 1995).

In the crystal structure of compound (I), each molecule exhibits four symmetry-equivalent N—H···O═C hydrogen bonds; N···O(1 + x, y, z) 3.127 (2), (N)H···O 2.29 (2) Å and N1—H1N···O1 158.4 (15). The molecules, which are connected by hydrogen bonds perpendicular to the long molecular axis, form ribbons parallel to the a axis (Fig. 2). Between the ribbons, only C—H···π (Nishio, Umezawa, Hirota & Takeuchi, 1995; Hunter, 1994; Hobza, Selzle & Schlag, 1994) and van der Waals interactions are present.

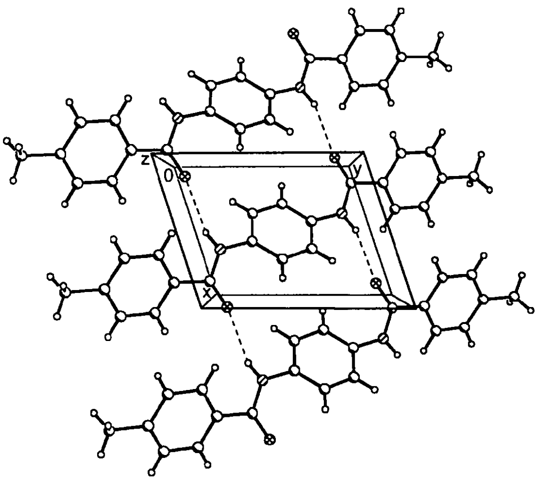


Fig. 2. Crystal packing of (I) with a view on the ab plane.

Experimental

1,4-Phenylenediamine dihydrochloride (0.1 mol, 18.1 g) was dissolved in 100 ml pyridine and 4-methylbenzoyl chloride (0.2 mol, 27.4 ml) was added dropwise to the stirred cooled solution, whereupon a white powder started to precipitate. After addition of toluoyl chloride, the suspension was poured into ice water, filtered and the precipitate washed with water, hot ethanol and diethyl ether. Yield of the residue, dried *in vacuo*: 27.5 g (79.8%); elemental analysis: calculated C 76.72, H 5.85, N 8.13%; found C 76.02, H 6.05, N 8.02%. The compound neither melts nor decomposes when heated to 600 K. Single crystals were obtained by recrystallization from DMF.

Crystal data

$C_{22}H_{20}N_2O_2$
M_r = 344.40
Triclinic
$P\bar{1}$
a = 5.3243 (7) Å
b = 6.9487 (11) Å
c = 12.1489 (14) Å
α = 83.429 (11)°
β = 87.055 (9)°
γ = 71.914 (9)°
V = 424.40 (10) Å^3
Z = 1
D_x = 1.348 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 58 reflections
θ = 10–18°
μ = 0.087 mm^{-1}
T = 200 (2) K
Plate
0.7 × 0.4 × 0.1 mm
Colourless

Data collection

Siemens $P4$ four circle diffractometer
ω scans
Absorption correction: none
1803 measured reflections
1609 independent reflections
1340 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.0294
$\theta_{\rm max}$ = 26.49°
h = 0 → 6
k = −8 → 8
l = −15 → 15
3 standard reflections monitored every 100 reflections
intensity decay: negligible

Refinement

Refinement on F^2
$R(F)$ = 0.0399
$wR(F^2)$ = 0.1094
S = 1.061
1609 reflections
123 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.1474P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.298 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.180 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 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	0.5825 (2)	0.5552 (2)	0.14596 (10)	0.0335 (3)
N1	0.1389 (3)	0.6206 (2)	0.12930 (10)	0.0236 (3)
C1	0.0771 (3)	0.8119 (2)	0.06326 (12)	0.0208 (3)
C2	0.2154 (3)	0.9495 (2)	0.06950 (12)	0.0229 (3)
C3	−0.1378 (3)	0.8634 (2)	−0.00634 (12)	0.0221 (3)

C4	0.3813 (3)	0.5068 (2)	0.16646 (12)	0.0230 (3)
C10	0.3888 (3)	0.3119 (2)	0.23590 (12)	0.0227 (3)
C11	0.1773 (3)	0.2861 (2)	0.30087 (13)	0.0284 (4)
C12	0.1998 (3)	0.1016 (2)	0.36339 (13)	0.0318 (4)
C13	0.4302 (3)	−0.0611 (2)	0.36167 (13)	0.0290 (4)
C14	0.6399 (3)	−0.0330 (2)	0.29695 (13)	0.0294 (4)
C15	0.6214 (3)	0.1514 (2)	0.23510 (13)	0.0264 (4)
C16	0.4486 (4)	−0.2635 (3)	0.4268 (2)	0.0411 (5)

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

O1—C4	1.225 (2)	C10—C15	1.386 (2)
N1—C4	1.356 (2)	C10—C11	1.388 (2)
N1—C1	1.425 (2)	C11—C12	1.388 (2)
C1—C2	1.386 (2)	C12—C13	1.388 (2)
C1—C3	1.389 (2)	C13—C14	1.383 (2)
C2—C3^{i}	1.386 (2)	C13—C16	1.511 (2)
C4—C10	1.502 (2)	C14—C15	1.387 (2)
C4—N1—C1	126.32 (13)	N1—C4—C10	115.04 (13)
C2—C1—C3	119.50 (13)	C15—C10—C11	118.94 (13)
C2—C1—N1	122.67 (13)	C15—C10—C4	117.62 (14)
C3—C1—N1	117.77 (13)	C11—C10—C4	123.43 (14)
O1—C4—N1	123.78 (13)	C4—O1—H1N^{ii}	164.2 (4)
O1—C4—C10	121.18 (13)		
C4—N1—C1—C2	−30.7 (2)	O1—C4—C10—C15	−28.2 (2)
C4—N1—C1—C3	151.96 (15)	N1—C4—C10—C15	151.60 (14)
C1—N1—C4—O1	−0.9 (3)	O1—C4—C10—C11	151.1 (2)
C1—N1—C4—C10	179.29 (13)	N1—C4—C10—C11	−29.1 (2)

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

All C-, N- and O-atom positions were refined with anisotropic displacement parameters. All C—H hydrogens were located from the difference map, placed in idealized positions and refined with fixed isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ at the phenyl rings and $U_{iso}(H) = 1.5U_{eq}(C)$ at the methyl groups, using a riding model with C—H distances of 0.95 and 0.98 Å, respectively. The position and isotropic displacement parameter of the H atom bound to nitrogen were refined. The methyl hydrogens were found disordered over two positions and were placed accordingly, with fixed site-occupation factors of 0.5.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1219). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bock, H., Göbel, I., Näther, C., Havlas, Z., Gavezzotti, A. & Filippini, G. (1993). *Angew. Chem.* **105**, 1823–1825; (1993) *Angew. Chem. Int. Ed. Engl.* **32**, 1755–1757.

Bock, H., Meuret, J., Näther, C. & Krynitz, U. (1994). *Chem. Ber.* **127**, 55–65.

Hobza, P., Selzle, H. L. & Schlag, E. W. (1994). *Chem. Rev.* **94**, 1767–1785.

Hunter, C. A. (1994). *Chem. Soc. Rev.* pp. 101–109.

Nagel, N. (1993). Masters thesis, University of Frankfurt, Germany.

Nagel, N., Näther, C. & Bock, H. (1995). *Acta Cryst.* **C51**, 1935–1937.

Näther, C. (1994). PhD thesis, University of Frankfurt, Germany.

Nishio, M., Umezawa, Y., Hirota, M. & Takeuchi, Y. (1995). *Tetrahedron*, **51**, 8665–8701.

Orpen, A. G., Brammer, L., Allen, F. A., Kennard, O., Watson, D. G. & Taylor, R. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi & J. D. Dunitz, appendix A, pp. 751–784. Weinheim: VCH Publishers.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1994). *XSCANS. X-ray Single Crystal Analysis Software*. Version 2.10. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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A Tetrameric Macrocycle with 2,5-Dithio-1,3,4-thiadiazole Subunits

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Abstract

The centrosymmetric molecule 40<[OS(2,5)1,3,4-thiadiazolo,S]$_4$-coronand-16> (alternative name: 10,11,21,22,32,33,43,44-octaaza-5,16,27,38-tetraoxa-2,8,13,19,24,30,35,41,45,46,47,48-dodecathiapentacyclo[40.2.1.$1^{9,12}$.$1^{20,23}$.$1^{31,34}$]octatetracontane), $C_{24}H_{32}N_8O_4S_{12}$, has its 40-membered ring, in which no cavity exists, in an extended conformation, with its maximum dimension approximately three times that of its minimum. Linkage of one of the two independent thiadiazole rings to the remainder of the molecule is *syn* to nitrogen on both sides, with N—C—S—C torsion-angle magnitudes of 0.8 (3) and 13.6 (4)°. The other thiadiazole ring has one linkage *syn* to nitrogen and one *anti* to nitrogen, with torsion-angle magnitudes of 31.3 (3) and 177.9 (3)°.

Comment

We have reported previously the structures of monomeric and dimeric macrocycles containing the 2,5-dithio-1,3,4-thiadiazole subunit, and also the structures of several of their transition metal complexes (Evans *et al.*, 1988; Cho, Fronczek, Taylor & Watkins, 1988; Bonomo, Bottino, Fronczek, Mamo & Pappalardo, 1989). The