Nygaard, L., Hansen, R. L., Nielsen, J. T., Andersen, J. R., Sorensen, G. O. & Steiner, P. A. (1972). *J. Mol. Struct.* **12**, 56–69.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2303–2305

4,4′-Bis(2,4,6-trimethylbenzenesulfonamido)diphenylmethane

M. FEIGEL,[a]*† TH. STRASSNER,[a]‡ J. MANERO[a]§ AND E. WECKERT[b]

[a]*Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, 90154 Erlangen, Germany, and* [b]*Institut für Kristallographie, Universität Karlsruhe (TH), Kaiserstrasse 12, 76128 Karlsruhe, Germany*

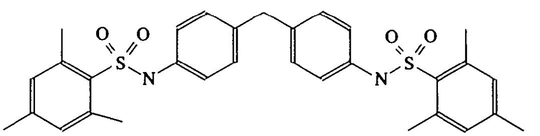
(*Received 6 November 1995; accepted 24 April 1996*)

Abstract

The crystal structure of the title compound, $C_{31}H_{32}N_2O_4S_2$, has been determined at 293 K. The structure of the central diphenylmethane moiety can be described as nearly C_2 symmetrical. The central bond angle at the CH_2 group has a value of 112.1 (8)° and the dihedral angles between the planes of the central aromatic rings and the central plane, defined by C_{ar}—CH_2—C_{ar}, are 53.8 (8) and 57.9 (6)°, respectively.

Comment

The molecular geometry at the central atom of compounds of the type aryl—*X*—aryl with different *X* groups [*e.g.* *X* = O, CH_2, diphenylether (DPE) and diphenylmethane (DPM)] has been discussed for several years now (Le Fèvre & Saxby, 1966; Montaudo, Caccamese & Finocchiaro, 1971; Barnes, Paton, Damewood & Mislow, 1981; Naik, Parsons, McGrail & MacKenzie, 1991). One of the reasons for this interest is the occurrence of the aryl—*X*—aryl structural unit in many important natural compounds and another arises from the growing importance of polymeric materials, where the aryl—*X*—aryl unit seems to account for their extraordinary properties (Dominghaus, 1988). There are some published X-ray structures of diphenylmethane compounds, but most are substituted in the *ortho* position and therefore free rotation is restricted. We are looking for *para*-substituted compounds where no steric interaction of substituents influences the conformational behaviour. In the course of an experimental and theoretical study on the usefulness of diphenylmethane compounds as a constituent unit of host–guest compounds, several compounds were synthesized for comparison. During this research, we obtained crystals of the title compound, (I), of suitable quality for diffraction studies and we now report its structure.



(I)

Fig. 1 shows the molecular geometry and atom labelling scheme. The dihedral angles between the planes of the central aromatic rings and the central plane, defined by C13,C16,C17, are 53.8 (8) and 57.9 (6)°, so the structure of the central diphenylmethane moiety is nearly C_2 symmetrical.

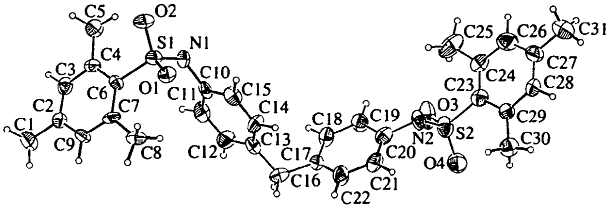


Fig. 1. *CRYSTAN88* (Burzlaff & Rothammel, 1989) plot of (I). Displacement ellipsoids are drawn at the 50% level.

The geometry of compound (I) is similar to the X-ray structure of diphenylmethane (DPM) where the dihedral angles are 63.9 and 71.9°. Significantly larger bond angles have been reported in the crystal structures of other substituted diphenylmethane derivatives (Barnes, Paton, Damewood & Mislow, 1981). The central bond angle of 112.5° in DPM is in good agreement with the value of 112.1 (8)° for the title compound.

Experimental

Compound (I) was prepared by reaction of 4,4′-diaminodiphenylmethane with 2,4,6-trimethylbenzenesulfonyl chloride in pyridine and recrystallization from EtOH following standard procedures for the synthesis of sulfonamides. Crystals suitable for X-ray study were obtained from an EtOH solution by slow evaporation of solvent.

Crystal data

$C_{31}H_{32}N_2O_4S_2$	Cu $K\alpha$ radiation
$M_r = 560.73$	$\lambda = 1.5418$ Å

---

† Present address: Ruhr-Universität Bochum, Fakultät für Chemie, 44780 Bochum, Germany.

‡ Present address: Institut für Organische Chemie, Technische Universität Dresden, Mommsenstrasse 13, 01062, Dresden, Germany.

§ Present address: Hoechst AG, Geschäftseinheit Forschungsprodukte, LCD-Materialien, 65926 Frankfurt, Germany.

Monoclinic
$P2_1/n$
$a = 21.330\,(1)$ Å
$b = 5.4002\,(1)$ Å
$c = 26.232\,(2)$ Å
$\beta = 112.447\,(9)°$
$V = 2792$ Å^3
$Z = 4$
$D_x = 1.333$ Mg m^{-3}
D_m not measured

Cell parameters from 20 reflections
$\theta = 15–33°$
$\mu = 2.003$ mm^{-1}
$T = 293$ K
Prism
0.6 × 0.5 × 0.4 mm
Colourless

Data collection

Huber four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.32$, $T_{\max} = 0.45$
11813 measured reflections
3140 independent reflections

1658 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.047$
$\theta_{\max} = 52°$
$h = -21 \rightarrow 21$
$k = -5 \rightarrow 5$
$l = -26 \rightarrow 26$
3 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.051$
$wR = 0.054$
$S = 1.66$
1658 reflections
353 parameters
$w = 1/[\sigma(|F|)^2 + 0.0002|F|^2]$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Extinction correction: Larson (1970)
Extinction coefficient: 203 (10)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, 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	$U_{\rm eq}$
S(1)	0.3152 (1)	0.1531 (5)	0.8223 (1)	0.0389
S(2)	0.6801 (2)	−0.0829 (6)	0.5784 (1)	0.0510
N(1)	0.3490 (4)	−0.033 (1)	0.7901 (3)	0.0392
N(2)	0.6381 (3)	0.122 (1)	0.6013 (3)	0.0380
O(1)	0.3465 (3)	0.393 (1)	0.8278 (2)	0.0436
O(2)	0.2432 (3)	0.135 (1)	0.7918 (2)	0.0437
O(3)	0.6545 (3)	−0.326 (1)	0.5831 (2)	0.0573
O(4)	0.7524 (3)	−0.053 (1)	0.6060 (2)	0.0613
C(1)	0.3830 (4)	−0.302 (2)	1.0501 (3)	0.0563
C(2)	0.3657 (5)	−0.186 (2)	0.9944 (4)	0.0393
C(3)	0.3119 (5)	−0.267 (2)	0.9489 (4)	0.0404
C(4)	0.2940 (4)	−0.169 (2)	0.8967 (4)	0.0329
C(5)	0.2329 (5)	−0.280 (2)	0.8517 (4)	0.0473
C(6)	0.3354 (5)	0.030 (2)	0.8904 (3)	0.0274
C(7)	0.3907 (4)	0.113 (2)	0.9358 (4)	0.0326
C(8)	0.4384 (4)	0.317 (2)	0.9328 (3)	0.0432
C(9)	0.4044 (4)	0.007 (2)	0.9875 (4)	0.0375
C(10)	0.4211 (5)	−0.014 (2)	0.8005 (4)	0.0340
C(11)	0.4654 (6)	−0.198 (2)	0.8282 (4)	0.0439
C(12)	0.5333 (5)	−0.191 (2)	0.8330 (4)	0.0515
C(13)	0.5578 (5)	0.002 (2)	0.8115 (4)	0.0393
C(14)	0.5133 (5)	0.187 (2)	0.7847 (4)	0.0446
C(15)	0.4461 (5)	0.180 (2)	0.7787 (3)	0.0416
C(16)	0.6316 (5)	0.002 (2)	0.8162 (4)	0.0530
C(17)	0.6370 (5)	0.029 (2)	0.7607 (4)	0.0401
C(18)	0.6057 (5)	−0.137 (2)	0.7201 (5)	0.0477
C(19)	0.6056 (6)	−0.115 (2)	0.6672 (4)	0.0467
C(20)	0.6406 (5)	0.084 (2)	0.6566 (4)	0.0431
C(21)	0.6738 (5)	0.248 (2)	0.6981 (4)	0.0443
C(22)	0.6717 (5)	0.223 (2)	0.7500 (4)	0.0509
C(23)	0.6515 (5)	0.009 (2)	0.5083 (4)	0.0404
C(24)	0.5934 (5)	−0.090 (2)	0.4687 (5)	0.0500
C(25)	0.5482 (5)	−0.283 (2)	0.4793 (4)	0.0721
C(26)	0.5741 (5)	−0.011 (2)	0.4143 (5)	0.0583
C(27)	0.6097 (6)	0.173 (2)	0.3992 (4)	0.0502
C(28)	0.6655 (5)	0.268 (2)	0.4397 (5)	0.0458
C(29)	0.6896 (5)	0.201 (2)	0.4948 (4)	0.0399
C(30)	0.7507 (5)	0.334 (2)	0.5342 (4)	0.0526
C(31)	0.5855 (5)	0.259 (2)	0.3405 (4)	0.0785

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

S(1)—N(1)	1.645 (7)	C(4)—C(5)	1.51 (1)
S(1)—O(1)	1.439 (6)	C(4)—C(6)	1.44 (1)
S(1)—O(2)	1.439 (5)	C(6)—C(7)	1.39 (1)
S(1)—C(6)	1.798 (8)	C(7)—C(8)	1.52 (1)
S(2)—N(2)	1.674 (7)	C(7)—C(9)	1.40 (1)
S(2)—O(3)	1.443 (6)	C(10)—C(11)	1.37 (1)
S(2)—O(4)	1.441 (6)	C(10)—C(15)	1.39 (1)
S(2)—C(23)	1.774 (9)	C(11)—C(12)	1.41 (1)
N(1)—C(10)	1.46 (1)	C(12)—C(13)	1.38 (1)
N(2)—C(20)	1.45 (1)	C(13)—C(14)	1.37 (1)
C(1)—C(2)	1.50 (1)	C(13)—C(16)	1.53 (1)
C(2)—C(3)	1.37 (1)	C(14)—C(15)	1.38 (1)
C(2)—C(9)	1.38 (1)	C(16)—C(17)	1.51 (1)
C(3)—C(4)	1.38 (1)		
O(1)—S(1)—N(1)	108.9 (4)	O(2)—S(1)—N(1)	104.9 (4)
O(2)—S(1)—O(1)	118.1 (4)	C(6)—S(1)—N(1)	107.4 (4)
C(6)—S(1)—O(1)	108.0 (4)	C(6)—S(1)—O(2)	109.1 (4)
O(3)—S(2)—N(2)	107.4 (4)	O(4)—S(2)—N(2)	111.2 (4)
O(4)—S(2)—O(3)	115.3 (5)	C(23)—S(2)—N(2)	99.7 (4)
C(23)—S(2)—O(3)	110.5 (5)	C(23)—S(2)—O(4)	111.5 (4)
C(10)—N(1)—S(1)	119.9 (6)	C(20)—N(2)—S(2)	116.4 (6)
C(3)—C(2)—C(1)	121.8 (10)	C(9)—C(2)—C(1)	120.4 (9)
C(9)—C(2)—C(3)	117.8 (9)	C(4)—C(3)—C(2)	124.4 (9)
C(5)—C(4)—C(3)	117.1 (10)	C(6)—C(4)—C(3)	116.8 (8)
C(6)—C(4)—C(5)	126.1 (9)	C(4)—C(6)—S(1)	117.8 (8)
C(7)—C(6)—S(1)	122.1 (8)	C(7)—C(6)—C(4)	120.8 (8)
C(8)—C(7)—C(6)	123.8 (9)	C(9)—C(7)—C(6)	119.3 (8)
C(9)—C(7)—C(8)	116.9 (9)	C(7)—C(9)—C(2)	121.6 (9)
C(11)—C(10)—N(1)	120.7 (10)	C(15)—C(10)—N(1)	121.1 (10)
C(15)—C(10)—C(11)	117.9 (9)	C(12)—C(11)—C(10)	120.2 (9)
C(13)—C(12)—C(11)	121.7 (10)	C(14)—C(13)—C(12)	117.6 (9)
C(16)—C(13)—C(12)	120.5 (10)	C(16)—C(13)—C(14)	121.9 (10)
C(15)—C(14)—C(13)	121.5 (9)	C(14)—C(15)—C(10)	121.1 (9)
C(17)—C(16)—C(13)	112.1 (8)	C(18)—C(17)—C(16)	119.6 (10)
C(13)—C(16)—C(17)—C(18)	−57.4 (13)		
C(14)—C(13)—C(16)—C(17)	−53.1 (14)		

The structure was solved by direct methods (*SIR*92; Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). All non-H atoms were refined anisotropically using full-matrix least-squares techniques (*CRYSTALS*; Watkin, Carruthers & Betteridge, 1985) based on $|F|$. All H-atom positions were calculated. The H-atom displacement factors were set to 1.1 times the $U_{\rm eq}$ value of the corresponding C atom. Molecular graphics were obtained using *ATARI CRYSTAN*88 (Burzlaff & Rothammel, 1989).

TS wishes to thank the 'Studienstiftung des deutschen Volkes' for financial support. JM thanks the 'Konrad-Adenaur-Stiftung' for a scholarship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1212). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Barnes, J. C., Paton, J. D., Damewood, J. R. Jr & Mislow, K. (1981). *J. Org. Chem.* **46**, 4975–4979.

Burzlaff, H. & Rothammel, W. (1989). *ATARI CRYSTAN88*. Proceedings of the 3rd Workshop *Computer in der Chemie*, edited by G. Gauglitz. Berlin: Springer Verlag.

Domininghaus, H. (1988). *Die Kunststoffe und ihre Eigenschaften*, 3rd edition, pp. 549–561. Düsseldorf: VDI-Verlag.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 281, expression (22). Copenhagen: Munksgaard.

Le Fèvre, R. J. W. & Saxby, J. D. (1966). *J. Chem. Soc. B*, pp. 1064–1066.

Montaudo, G., Caccamese, S. & Finocchiaro, P. (1971). *J. Am. Chem. Soc.* **93**, 4202–4213.

Naik, H. A., Parsons, I. W., McGrail, P. T. & MacKenzie, P. D. (1991). *Polymer*, **32**, 140–145.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, University of Oxford, England.

Acta Cryst. (1996). C**52**, 2305-2307

Diethyl 5-Bis(diphenylphosphinoyl)methyl-2-hydroxy-3-*tert*-butylphenylphosphonate Hydrate at 173 K

MATTHIAS RAMM[a] AND BURKHARD COSTISELLA[b]

[a]*Freie Universität, Institut für Kristallographie, Takustrasse 6, D-14195 Berlin, Germany, and* [b]*Institut für Angewandte Chemie, D-12484 Berlin, Germany. E-mail: ramm@chemie.fu-berlin.de*

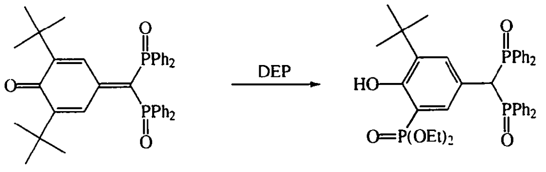
(*Received 29 January 1996; accepted 18 March 1996*)

Abstract

The title compound, $C_{39}H_{43}O_6P_3.H_2O$, shows an intramolecular hydrogen bond between the O1 and O2 atoms. It interacts *via* two further intermolecular hydrogen bonds involving one water molecule.

Comment

The addition of diethylphosphite (DEP) to phosphinoxidoquinonmethide, (1), by splitting off isobutene, led to the phosphorylated aromatic product, (2). The structure of (2) was proven by detailed NMR studies (Gross, Keitel & Costisella, 1991). Surprisingly, the ^{1}H NMR signal of the OH group was shifted strongly to lower field compared with very similar compounds (Gross, Keitel & Costisella, 1991). The shift to lower field can be explained by the neighbourhood of the electron-withdrawing phosphonate group and the possibility of an intramolecular hydrogen bond between the OH proton and the phosphoryl O atom of the phosphonate group. The aim of the present structure analysis was therefore to prove whether the presumed intramolecular hydrogen bond exists or not.



(1) (2)

Previous X-ray structure analyses of related compounds at room temperature (Ramm & Schulz, 1990; Ramm, 1993) showed that due to high thermal motion the positions of the O—C_2H_5 groups could not be determined accurately. The data collection was therefore performed at 173 K. The P atoms form distorted tetrahedra. They are coordinated either by three O atoms and one C atom (P1) or by one O atom and three C atoms (P2 and P3). The tetrahedral angles around P2 and P3 show the same systematic deviations from the ideal value. The three angles enclosing the P=O double bond are larger, the other three being smaller. This corresponds to other phosphorus-containing compounds (Kulpe & Seidel, 1979; Ramm, Costisella & Gross, 1995). Only the O2—P1—O3 bond angle deviates from this array. This can be attributed to the participation of the O2 atom in an intramolecular hydrogen bond with O1 resulting in a six-membered ring [O1···O2

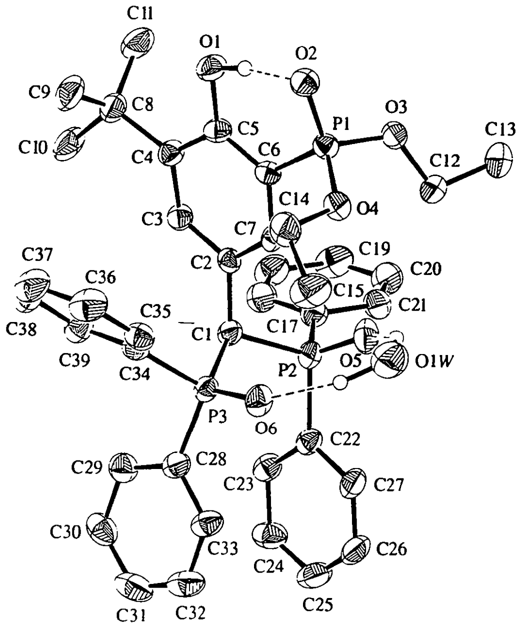


Fig. 1. *ORTEP*II (Johnson, 1971) drawing of the asymmetric unit of the title compound showing 50% probability displacement ellipsoids. Only H atoms participating in hydrogen bonds are drawn. Dashed lines represent hydrogen bonds.