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The 1:1 Molecular Complex of *N,N'*-Bis(4-methoxybenzylidene)ethylenediamine and Hydroquinone†

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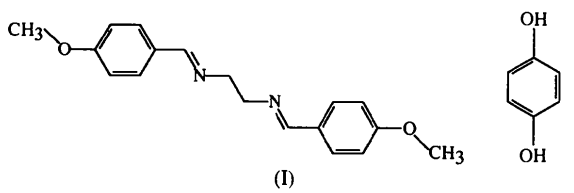
Abstract

The present X-ray diffraction study establishes the molecular structure of the title complex, $C_{18}H_{20}N_2O_2.C_6H_6O_2$. There are two half molecules in the asymmetric unit. The crystal structure is stabilized by an intermolecular O—H···N hydrogen bond and a C—H···N and two C—H···O intermolecular interactions. The O—H···N hydrogen bond favours the formation of the complex, thus forming the supramolecule with a linear array along the *c* axis.

Comment

Crystal engineering or solid-state supramolecular synthesis has been motivated in recent times by aesthetic (symmetry, topology and network properties) or utilitarian (non-linear optics, ferromagnets, molecular electronics and nanostructures) considerations, and in this respect is important to supramolecular chemistry (Thalladi, Panneerselvam, Carrell, Carrell & Desiraju, 1995) and biological systems (Engels, Bashford & Ghadiri, 1995). We have studied the supramolecular properties in the molecular complex of *meso*-1,2-diphenyl-1,2-ethanediol and bis-imines (Reyes-Arellano, Boese, Steller & Sustmann, 1995). As a continuation of these studies, we prepared the complex formed between *N,N'*-bis(4-methoxybenzylidene)ethylenediamine and hydroquinone, (I), and the X-ray study of this complex is presented here.



(I)

The asymmetric unit comprises half of an *N,N'*-bis(4-methoxybenzylidene)ethylenediamine (*A*) molecule and half of a hydroquinone (*B*) molecule, with the other half related by the centre of symmetry coinciding with C9—C9′ for *A* and the centre of the ring for *B* (Fig. 1). Bond lengths and angles are normal compared with values reported in the literature (Panneerselvam, Soriano-García, Reyes-Arellano, Tamariz-Mascarúa & Mendoza-Sánchez, 1996). The average C—C bond length for the phenyl rings is 1.398 (3) and 1.390 (3) Å for molecules *A* and *B*, respectively. Both phenyl rings are planar within the maximum deviations of 0.006 (1) and 0.010 (1) Å. There is clear evidence of a double bond [1.271 (2) Å] localized between the C8 and N1 atoms, accompanied by a single C9—N1 bond of 1.472 (2) Å. The conformation around the C9—C9′ bond is *trans* (N1—C9—C9′—N1′ 180.0°).

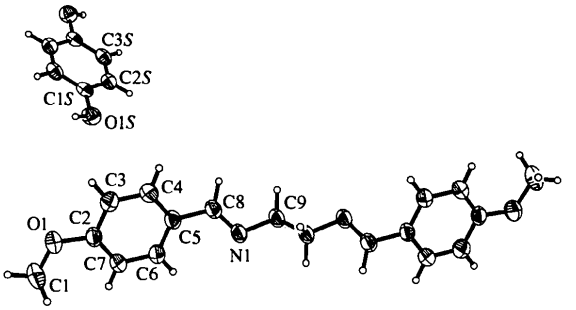


Fig. 1. The molecular structure of the title compound with the atom-labelling scheme and 50% probability displacement ellipsoids.

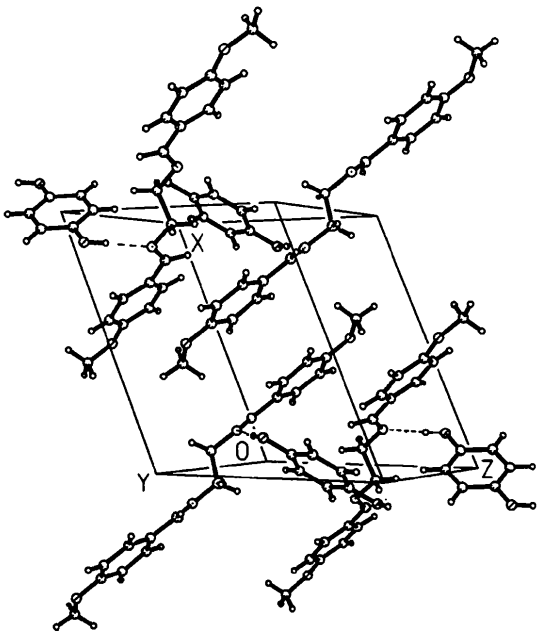


Fig. 2. A drawing of the packing arrangement (down the *b* axis). Dashed lines indicate the O—H···N hydrogen bonds.

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The molecular arrangement, consisting of layers of alternate *A* and *B* molecules along the *c* axis, is shown in Fig. 2. The hydroxy group of the hydroquinone molecule participates in an O—H···N hydrogen bond with the N atom of molecule *A*, with O1*S*···N1($1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) 2.836 (2) Å [H1*SO*···N1 1.93 (3) Å and O1*S*—H1*SO*···N1 177 (2)°] (Allen, Kennard & Taylor, 1983). In addition to the hydrogen bond mentioned above, there are three intermolecular contacts, the non-H atom contacts being C3*S*···N1($x+1$, $\frac{1}{2}-y$, $z-\frac{1}{2}$) 3.461 (2) Å [H3*S*···N1 2.78 (2) Å and C3*S*—H3*S*···N1 129 (1)°], C7···O1($1-x$, $y+\frac{1}{2}$, $\frac{3}{2}-z$) 3.584 (2) Å [H7···O1 2.70 (2) Å and C7—H7···O1 157 (2)°] and C6···O1*S*($1-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$) 3.325 (2) Å [H6···O1*S* 2.65 (2) Å and C6—H6···O1*S* 126 (1)°] (Desiraju, 1991). It should be mentioned that the O—H···N hydrogen bonds form a linear array (Fig. 2) in forming the supramolecule.

Experimental

A 1:1 molar ratio of *N*,*N'*-bis(4-methoxybenzylidene)ethylenediamine and hydroquinone were dissolved in EtOAc. The mixture was crystallized from hexane.

Crystal data

$C_{18}H_{20}N_2O_2.C_6H_6O_2$
M_r = 406.46
Monoclinic
$P2_1/c$
a = 11.929 (3) Å
b = 9.357 (3) Å
c = 10.434 (3) Å
β = 113.32 (2)°
V = 1069.5 (5) Å^3
Z = 2
D_x = 1.262 Mg m^{-3}
D_m = 1.260 Mg m^{-3}
D_m measured by flotation in benzene/chloroform solution

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 20–40°
μ = 0.699 mm^{-1}
T = 293 (2) K
Colourless
0.24 × 0.24 × 0.18 mm
Rectangular

Data collection

*P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1513 measured reflections
1420 independent reflections
1275 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0628

θ_{max} = 56.67°
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 11$
3 standard reflections monitored every 100 reflections
intensity decay: 1.0%

Refinement

Refinement on F^2
$R(F)$ = 0.0350
$wR(F^2)$ = 0.0952
S = 1.098
1420 reflections
188 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.2935P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.008
$\Delta\rho_{max}$ = 0.117 e Å^{-3}
$\Delta\rho_{min}$ = −0.155 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)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C1	0.5870 (2)	0.2245 (3)	0.8116 (2)	0.0674 (6)
C2	0.4328 (1)	0.1870 (2)	0.5828 (2)	0.0420 (5)
C3	0.3675 (2)	0.0901 (2)	0.4788 (2)	0.0490 (5)
C4	0.2902 (2)	0.1384 (2)	0.3488 (2)	0.0456 (5)
C5	0.2731 (1)	0.2837 (2)	0.3203 (2)	0.0399 (4)
C6	0.3375 (2)	0.3795 (2)	0.4260 (2)	0.0456 (5)
C7	0.4173 (2)	0.3327 (2)	0.5564 (2)	0.0463 (5)
C8	0.1904 (1)	0.3303 (2)	0.1796 (2)	0.0415 (5)
C9	0.0641 (2)	0.4832 (2)	0.0050 (2)	0.0430 (5)
N1	0.1450 (1)	0.4550 (2)	0.1513 (1)	0.0422 (4)
O1	0.5104 (1)	0.1288 (1)	0.7065 (1)	0.0585 (4)
C1*S*	0.9351 (2)	0.0644 (2)	0.0711 (2)	0.0415 (5)
C2*S*	0.9302 (2)	0.1199 (2)	−0.0549 (2)	0.0442 (5)
C3*S*	0.9948 (2)	0.0568 (2)	−0.1250 (2)	0.0444 (5)
O1*S*	0.8719 (1)	0.1345 (1)	0.1380 (1)	0.0548 (4)

Table 2. *Geometric parameters (Å, °)*

C1—O1	1.431 (3)	C8—N1	1.271 (2)
C2—O1	1.370 (2)	C9—N1	1.472 (2)
C2—C7	1.389 (3)	C9—C9^i	1.524 (3)
C2—C3	1.391 (3)	C1*S*—O1*S*	1.379 (2)
C3—C4	1.381 (3)	C1*S*—C3*S*^{ii}	1.389 (3)
C4—C5	1.389 (3)	C1*S*—C2*S*	1.393 (2)
C5—C6	1.392 (2)	C2*S*—C3*S*	1.387 (3)
C5—C8	1.474 (2)	C3*S*—C1*S*^{ii}	1.389 (3)
C6—C7	1.387 (3)		
O1—C2—C7	124.4 (2)	N1—C8—C5	123.9 (2)
O1—C2—C3	115.9 (2)	N1—C9—C9^i	109.6 (2)
C7—C2—C3	119.7 (2)	C8—N1—C9	116.7 (1)
C4—C3—C2	120.2 (2)	C2—O1—C1	117.5 (2)
C3—C4—C5	121.0 (2)	O1*S*—C1*S*—C3*S*^{ii}	123.1 (2)
C4—C5—C6	118.2 (2)	O1*S*—C1*S*—C2*S*	118.2 (2)
C4—C5—C8	119.1 (2)	C3*S*^{ii}—C1*S*—C2*S*	118.6 (2)
C6—C5—C8	122.7 (2)	C3*S*—C2*S*—C1*S*	121.0 (2)
C7—C6—C5	121.5 (2)	C2*S*—C3*S*—C1*S*^{ii}	120.4 (2)
C6—C7—C2	119.3 (2)		

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

Data collection: *P*4 diffractometer software. Cell refinement: *XSCANS* (Siemens, 1992). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990). Software used to prepare material for publication: *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: KA1210). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.

Engels, M., Bashford, D. & Ghadiri, M. R. (1995). *J. Am. Chem. Soc.* **117**, 9151–9158.

Panneerselvam, K., Soriano-García, M., Reyes-Arellano, A., Tamariz-Mascarúa, J. & Mendoza-Sánchez, R. I. (1996). *Anal. Sci.* In the press.

Reyes-Arellano, A., Boese, R., Steller, I. & Sustmann, R. (1995). *Struct. Chem.* **6**, 391–395.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1990). *SHELXTL-Plus.* Release 4.0. 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 (1992). *XSCANS Users Manual.* Version 2.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Thalladi, V. R., Panneerselvam, K., Carrell, C. J., Carrell, H. J. & Desiraju, G. R. (1995). *J. Chem. Soc. Chem. Commun.* pp. 341–342.

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6-Ammonio-(1*H*$^+$)-1,4,8,11-tetraazacyclotridecane-5,7-dione Dichloride Methanol Solvate: an Amino-Pendant Tetraazacyclotridecane Derivative

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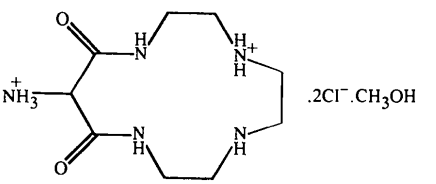
Abstract

The structure of a new aminotetraazacycloalkane derivative, 6-amino-1,4,8,11-tetraazacyclotridecane-5,7-dione, has been determined in its diprotonated form. Charge balance is supplied by two chloride anions and the lattice also contains a methanol solvate to give the formula $C_9H_{21}N_5O_2^{2+}.2Cl^-.CH_3OH$.

Comment

The attachment of metal ions to proteins such as monoclonal antibodies can create new tools for use in biology (Meares & Wensel, 1984) and medicine (Sundberg, Meares, Goodwin & Diamanti, 1974). The reagents used for such attachment are normally referred to as bifunctional chelating agents because they incorporate a strong metal-chelating group and a chemically reactive group. Such agents are most often used to endow biological molecules with the nuclear (Sundberg, Meares, Goodwin & Diamanti, 1974), physical (Leung & Meares, 1977) or chemical (Dreyer & Dervan, 1985) properties of the chelated metal ions. In the last few years, substantial progress has been made in the application of such reagents to problems such as cancer therapy and diagnosis (Scheinberg, Strand & Gansow, 1982; Hnatowich, Layne, Childs, Lanteigne, Davis & Griffin, 1983), clinical immunoassays (Siitari, Hemmila, Sioni, Lorgen & Koisteinen, 1983) and DNA fingerprinting (Van Dyke & Dervan, 1983).

The properties of the chelated metal ions play a major role in the application of the bifunctional chelates. Radioisotopes of copper such as ^{67}Cu have been shown to be potentially useful in radioimmunotherapy (DeNardo, Jungerman, DeNardo, Lagunas-Solar, Cole & Meares, 1985). We have undertaken the development of new bifunctional chelates containing ^{67}Cu which, when conjugated to antitumour monoclonal antibodies, will serve as tumour-imaging and tumour-therapeutic agents. For this application, it is essential that the radioactive copper ion remains attached to the antibody for several days in a living system. Cu^{II} is a very labile metal ion and to counteract this, we have prepared the title compound (I), a ligand specially designed to form a kinetically inert complex with Cu^{II} and to provide a side chain for attachment to a protein.



(I)

Our single-crystal X-ray study of (I) represents a complete structural determination for a tetraazacycloalkanedione compound. Previous IR, NMR and mass spectroscopic studies (Kimura, Koike, Machida, Nagai & Kodama, 1984; Kimura, Haruta *et al.*, 1993) of the analogous amino-pendant dioxocyclam were consistent with the existence of a dioxotetraazacycloalkane molecule. However, no structural conclusions regarding the packing of the dioxocyclam molecules or related species could be drawn from the NMR data recorded in solution. It was only possible to establish that the amino-dioxocyclam existed in a protonated form. Our structure determination confirms the protonation of the amino[13]ane-N_4-dione to give the [amino[13]ane-N_4-dione]$^{2+}.2Cl^-$, (I), shown in Fig. 1. The facile location and stable refinement of all the H atoms in the structure leave no doubt as to the identity of the protonated sites at N1 and N6. This is confirmed by the C6—