

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Editors: **W. Clegg** and **D. G. Watson**

1,1'-Methylenebis(naphthalen-2-amine) methanol solvate

Andrew B. Mahon, Donald C. Craig and Andrew C. Try

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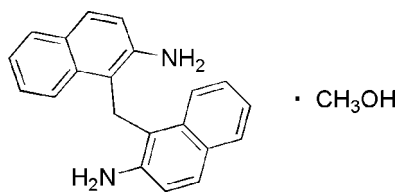
ISSN 1600-5368

1,1'-Methylenebis(naphthalen-2-amine)
methanol solvateAndrew B. Mahon,^a Donald C. Craig^b and Andrew C. Try^{a*}^aDepartment of Chemistry and Biomolecular Sciences, Building F7B, Macquarie University, Sydney, NSW 2109, Australia, and ^bSchool of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia
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Received 26 September 2007; accepted 12 October 2007

Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; H-atom completeness 82%; disorder in solvent or counterion; R factor = 0.049; wR factor = 0.065; data-to-parameter ratio = 6.1.In the title compound, $\text{C}_{21}\text{H}_{18}\text{N}_2 \cdot \text{CH}_4\text{O}$, the two naphthyl ring systems are arranged almost orthogonal to one another, with a dihedral angle of 89.8 (1)°.

Related literature

For related literature, see: Farrar (1964); Gibson *et al.* (1996); Ibers & Hamilton (1974); Miyahara *et al.* (1999); Morgan & Jones (1923); Partridge & Vipond (1962); Tálas *et al.* (1998).

Experimental

Crystal data

 $\text{C}_{21}\text{H}_{18}\text{N}_2 \cdot \text{CH}_4\text{O}$ $M_r = 330.4$ Orthorhombic, $C_{cc}2$ $a = 13.020$ (4) Å $b = 26.448$ (7) Å $c = 4.978$ (2) Å $V = 1714.2$ (9) Å³ $Z = 4$ Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹ $T = 294$ K
 $0.30 \times 0.12 \times 0.10$ mm

Data collection

Enraf-Nonius CAD-4
diffractometer
Absorption correction: none
851 measured reflections
851 independent reflections720 reflections with $I > 2\sigma(I)$
1 standard reflections
frequency: 30 min
intensity decay: none

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.065$
 $S = 1.34$
720 reflections118 parameters
H-atom parameters not refined
 $\Delta\rho_{\text{max}} = 0.26$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³Data collection: *CAD-4 Software* (Schagen *et al.*, 1989); cell refinement: *CAD-4 Software*; data reduction: local program; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *RAELS* (Rae, 1996); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: local programs.

The authors thank the Australian Research Council for a Discovery Project Grant to ACT (No. DP0345180), and Macquarie University for the award of a Macquarie University Research Development Grant to ACT and the award of a PhD scholarship to ABM.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2306).

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supplementary materials

Acta Cryst. (2007). E63, o4341 [doi:10.1107/S1600536807050131]

1,1'-Methylenebis(naphthalen-2-amine) methanol solvate

A. B. Mahon, D. C. Craig and A. C. Try

Comment

The syntheses of methylene bridged aromatic amines have been the subject of over 40 patents during the past 40 years, however, to the best of our knowledge the synthesis of (I) has not been previously reported. Compound (I) was obtained as an unexpected by-product in the removal of the apical methylene strap from naphthalene Tröger's base (Farrar, 1964; Tálas *et al.*, 1998) using trifluoroacetic anhydride (Miyahara *et al.*, 1999) as outlined in Fig. 2. Dinitrated analogues of (I), and various isomers thereof, have been reported (Morgan & Jones, 1923) and benzo analogues (Partridge & Vipond, 1962) have been used in the synthesis of organometallic complexes (Gibson *et al.*, 1996) The asymmetric unit contains one half molecule of (I) and one half molecule of methanol, *i.e.*, it is a 1:1 composition. The two naphthalene rings of (I) are oriented at almost 90 ° with respect to one another, and they are aligned in an anti-parallel fashion, such that the the two amino substituents are projected in opposite directions.

The molecular structure of (I) is shown in Fig. 1.

Experimental

Naphthalene Tröger's base (100 mg, 0.311 mmol) was suspended in a mixture of trifluoroacetic anhydride (TFAA) (0.5 ml) and dichloromethane (1 ml) and stirred at room temperature in a closed vessel. The reaction was monitored by TLC. After 3 h all starting material had been consumed and the reaction was quenched with ice and basified with saturated sodium hydrogen carbonate solution. The cloudy mixture was extracted with dichloromethane (2 x 30 ml) and the organic layers were combined before being washed with brine, dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure, affording a colourless transparent solid. The residue (assumed to be the di-trifluoroacetylated dissecondary amine) was dissolved in a mixture of ethanol (5 ml) and sodium hydroxide (100 mg) and stirred at room temperature for 12 h. Ethanol was removed under vacuum and the residue was taken up in a mixture of water (20 ml) and dichloromethane (20 ml). The organic layer was separated and the aqueous layer extracted with dichloromethane (20 ml). The combined organic layers were then washed with brine, dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. The residue was chromatographed (silica gel, dichloromethane) to afford (I) (35 mg, 38%) as a white solid (the first major band eluted), m.p: 172.06 °C (DSC). Single crystals of (I) were grown by slow evaporation of a dichloromethane/methanol solution.

Refinement

Refinement on F was by full-matrix least squares (RAELS) using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were included in geometrically idealized positions calculated each cycle, with C—H distances of 1.00 Å, and were assigned thermal parameters equal to those of the parent atom. The NH protons were included in idealized positions after location in a difference fourier. The methanol was located in a difference fourier, and included as two independent anisotropic atoms. The H atoms were not located. This space group has a floating origin in the *z* direction, so to avoid a singular situation the *z* coordinate of one atom (N1) is fixed.

Figures

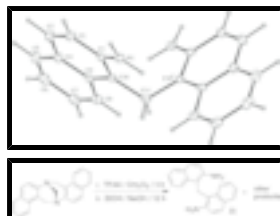


Fig. 1. ORTEP (Johnson, 1976) plot of the title compound, with ellipsoids at the 10% probability level. H atoms are drawn as spheres of arbitrary radius. Symmetry code is: $i\ 1/2 - x, 1/2 - y, z$.

1,1'-Methylenebis(naphthalen-2-amine) methanol solvate

Crystal data

$C_{21}H_{18}N_2 \cdot CH_4O$

$M_r = 330.4$

Orthorhombic, $Ccc2$

$a = 13.020$ (4) Å

$b = 26.448$ (7) Å

$c = 4.978$ (2) Å

$V = 1714.2$ (9) Å³

$Z = 4$

$F_{000} = 704.0$

$D_x = 1.28$ Mg m⁻³

Melting point: 445 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 11 reflections

$\theta = 11\text{--}13^\circ$

$\mu = 0.08$ mm⁻¹

$T = 294$ K

Prism, colourless

$0.30 \times 0.12 \times 0.10$ mm

Data collection

Enraf-Nonius CAD-4
diffractometer

ω - 2θ scans

Absorption correction: none

851 measured reflections

851 independent reflections

720 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = ?$

$\theta_{\text{max}} = 25^\circ$

$h = 0 \rightarrow 15$

$k = 0 \rightarrow 31$

$l = 0 \rightarrow 5$

1 standard reflections

every 30 min

intensity decay: none

Refinement

Refinement on F

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.065$

$S = 1.34$

720 reflections

118 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.26$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.4225 (2)	0.2517 (1)	0.6709	0.0515 (7)	
C1	0.3632 (2)	0.2076 (1)	0.6484 (8)	0.0462 (8)	
C2	0.3936 (2)	0.1656 (1)	0.8030 (9)	0.0564 (9)	
C3	0.3454 (3)	0.1203 (1)	0.7752 (10)	0.064 (1)	
C4	0.2654 (2)	0.1137 (1)	0.5882 (10)	0.0574 (9)	
C5	0.2174 (3)	0.0660 (1)	0.5540 (12)	0.072 (1)	
C6	0.1411 (3)	0.0597 (2)	0.3746 (13)	0.080 (1)	
C7	0.1081 (3)	0.1006 (2)	0.2175 (12)	0.073 (1)	
C8	0.1523 (3)	0.1472 (1)	0.2473 (9)	0.062 (1)	
C9	0.2335 (2)	0.1558 (1)	0.4327 (9)	0.0491 (8)	
C10	0.2820 (2)	0.2038 (1)	0.4677 (8)	0.0441 (7)	
C11	0.2500	0.2500	0.3067 (11)	0.051 (1)	
C1Me	0.5000	0.0000	0.046 (6)	0.168 (7)	
O1Me	0.4580 (6)	0.0183 (3)	0.296 (4)	0.216 (9)	0.5
H1N1	0.4835	0.2524	0.7930	0.052	
H2N1	0.4038	0.2824	0.5648	0.052	
HC2	0.4512	0.1691	0.9346	0.056	
HC3	0.3671	0.0912	0.8898	0.064	
HC5	0.2405	0.0366	0.6650	0.072	
HC6	0.1079	0.0258	0.3534	0.080	
HC7	0.0519	0.0957	0.0830	0.073	
HC8	0.1269	0.1760	0.1354	0.062	
H1C11	0.1906	0.2400	0.1907	0.051	0.5
H2C11	0.3094	0.2600	0.1907	0.051	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.047 (1)	0.063 (2)	0.044 (2)	-0.003 (1)	-0.002 (1)	0.000 (1)
C1	0.042 (1)	0.060 (2)	0.038 (2)	0.006 (1)	0.005 (1)	-0.005 (2)
C2	0.054 (2)	0.068 (2)	0.047 (2)	0.006 (2)	-0.002 (2)	0.006 (2)
C3	0.065 (2)	0.066 (2)	0.062 (2)	0.012 (2)	0.000 (2)	0.012 (2)
C4	0.059 (2)	0.057 (2)	0.056 (2)	0.005 (2)	0.009 (2)	-0.001 (2)
C5	0.070 (2)	0.060 (2)	0.086 (3)	0.000 (2)	0.015 (3)	-0.002 (2)
C6	0.081 (3)	0.065 (2)	0.093 (3)	-0.013 (2)	0.021 (3)	-0.021 (3)
C7	0.072 (2)	0.084 (2)	0.065 (3)	-0.011 (2)	-0.002 (2)	-0.023 (2)
C8	0.063 (2)	0.077 (2)	0.047 (2)	-0.005 (2)	-0.004 (2)	-0.007 (2)
C9	0.047 (2)	0.061 (2)	0.039 (2)	0.001 (1)	0.008 (2)	-0.008 (2)
C10	0.047 (2)	0.053 (2)	0.032 (2)	0.005 (1)	0.005 (1)	-0.002 (2)
C11	0.058 (2)	0.063 (3)	0.032 (2)	-0.001 (2)	0.0000	0.0000
C1Me	0.141 (9)	0.096 (7)	0.267 (9)	0.009 (7)	0.0000	0.0000
O1Me	0.145 (9)	0.139 (9)	0.363 (9)	-0.001 (7)	-0.002 (9)	0.017 (9)

supplementary materials

Geometric parameters (Å, °)

N1—C1	1.402 (4)	C6—C7	1.404 (7)
N1—H1N1	1.000	C6—HC6	1.000
N1—H2N1	1.000	C7—C8	1.368 (5)
C1—C2	1.408 (4)	C7—HC7	1.000
C1—C10	1.392 (4)	C8—C9	1.422 (4)
C2—C3	1.359 (5)	C8—HC8	1.000
C2—HC2	1.000	C9—C10	1.427 (4)
C3—C4	1.407 (5)	C10—C11	1.520 (4)
C3—HC3	1.000	C11—C10 ⁱ	1.520 (4)
C4—C5	1.418 (5)	C11—H1C11	1.000
C4—C9	1.420 (5)	C11—H2C11	1.000
C5—C6	1.346 (7)	C1Me—O1Me	1.443 (17)
C5—HC5	1.000		
C1—N1—H1N1	120.0	C5—C6—HC6	120.1
C1—N1—H2N1	120.0	C7—C6—HC6	120.1
H1N1—N1—H2N1	120.0	C6—C7—C8	120.4 (4)
N1—C1—C2	117.3 (3)	C6—C7—HC7	119.8
N1—C1—C10	122.0 (3)	C8—C7—HC7	119.8
C2—C1—C10	120.6 (3)	C7—C8—C9	121.9 (4)
C1—C2—C3	120.7 (3)	C7—C8—HC8	119.1
C1—C2—HC2	119.7	C9—C8—HC8	119.1
C3—C2—HC2	119.7	C4—C9—C8	116.5 (3)
C2—C3—C4	121.2 (3)	C4—C9—C10	120.1 (3)
C2—C3—HC3	119.4	C8—C9—C10	123.4 (3)
C4—C3—HC3	119.4	C1—C10—C9	118.7 (3)
C3—C4—C5	121.1 (4)	C1—C10—C11	119.4 (2)
C3—C4—C9	118.7 (3)	C9—C10—C11	121.9 (3)
C5—C4—C9	120.2 (3)	C10—C11—C10 ⁱ	116.4 (4)
C4—C5—C6	121.1 (4)	C10—C11—H1C11	107.7
C4—C5—HC5	119.4	C10—C11—H2C11	107.7
C6—C5—HC5	119.4	H1C11—C11—H2C11	109.5
C5—C6—C7	119.9 (4)		

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

Fig. 1

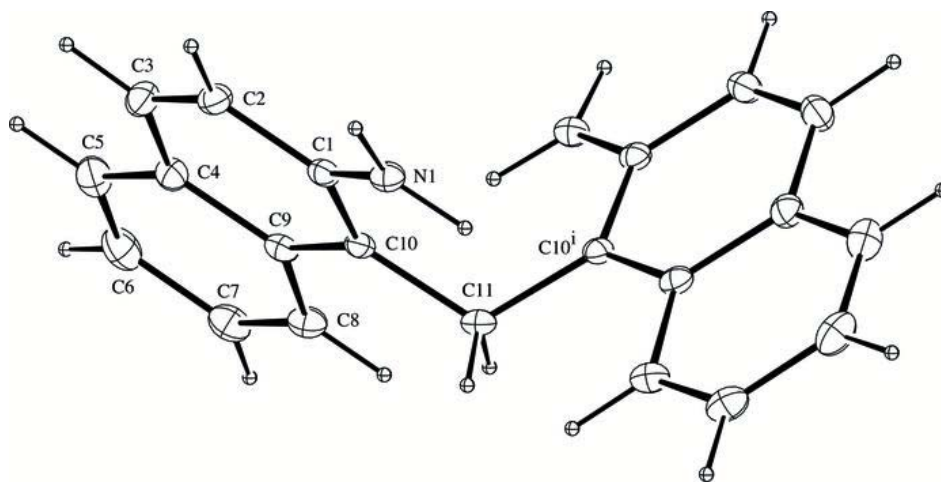


Fig. 2

