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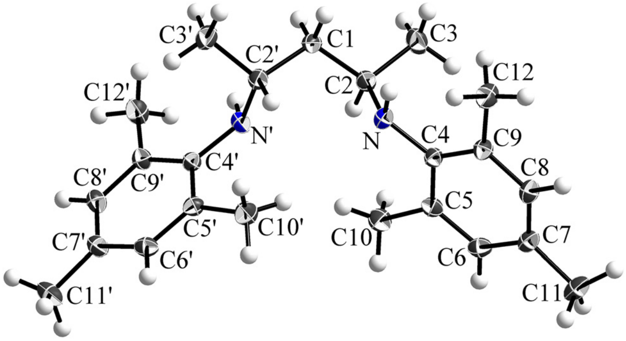
Crystal structure of N^2,N^4-dimesitylpentane-2,4-diamine, $C_{23}H_{34}N_2$



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Abstract

$C_{23}H_{34}N_2$, monoclinic, $C2/c$ (no. 15), a = 15.2448(11) Å, b = 8.2189(5) Å, c = 16.7350(16) Å, β = 103.133(7)°, V = 2042.0(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0438, $wR_{ref}(F^2)$ = 0.1277, T = 150 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reactions were performed under ambient conditions. N^2,N^4-dimesitylpentane-2,4-diamine (**1**; mesityl=2,4,6-trimethylphenyl) was obtained as a by-product during the preparation and crystallization of NacNac$^{\text{Mes}}$H [*N*,*N*′-di(2,4,6-trimethylphenyl)-*β*-diketiminate] [5]. The NacNac$^{\text{Mes}}$H ligand was prepared according to a modified literature procedure [6]. Acetylacetone (Merck), 2,4,6-trimethylaniline (Alfa Aesar), and *p*-toluenesulfonic acid (Merck) were used without further purification. Acetylacetone (5 g, 50 mmol) and 2,4,6-trimethylaniline (13.5 g, 100 mmol) were dissolved in toluene (200 mL) and cooled in an ice bath. Subsequently, *p*-toluenesulfonic acid (8.6 g, 50 mmol) was added to the flask. After stirring the reaction mixture for 15 h at 110 °C, the solvent was removed under reduced pressure. The solid precipitate was dissolved in dichloromethane (100 mL) and the organic phase was extracted with a saturated potassium carbonate solution. The aqueous phase was re-extracted twice with dichloromethane and the solvent was removed from the combined organic phases under vacuum. The crude product was recrystallized from methanol. Few colorless crystals of **1** were obtained as a by-product besides the main product NacNac$^{\text{Mes}}$H.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.20 × 0.10 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.06 mm^{-1}
Diffractometer, scan mode:	STOE StadiVari, *ω*
$\theta_{\max}$, completeness:	30.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int}:	34,500, 2983, 0.043
Criterion for I_{obs}, $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\ \sigma(I_{\text{obs}})$, 2179
$N(param)_{\text{refined}}$:	122
Programs:	X-Area [1], SHELX [2, 3], Diamond [4]

Experimental details

The single crystal of **1** was selected under a microscope equipped with a light source in an Ar-filled glove box. Subsequently, the crystal was transferred under Ar to the diffractometer (STOE StadiVari) equipped with a PILATUS 300K detector (DECTRIS) and a Mo *Kα* radiation source (λ = 0.71073 Å). For the data collection the crystal was cooled in a 150 K cold stream of dry nitrogen. The single crystal structure was solved by direct methods using the program SHELXS-97 [2]. Structure refinements were performed by full-matrix least-squares calculations against F^2

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$).

Atom	x	y	z	$U_{iso}*/U_{eq}$
C1	0.5000	0.64420 (18)	0.2500	0.0228 (3)
H1A[a]	0.4481	0.7154	0.2266	0.027*
H1B[a]	0.5519	0.7154	0.2734	0.027*
C2	0.52311 (7)	0.54381 (13)	0.18010 (7)	0.0238 (2)
H2	0.4696	0.4754	0.1552	0.029*
C3	0.54380 (9)	0.65475 (16)	0.11294 (8)	0.0356 (3)
H3A	0.5923	0.7302	0.1372	0.053*
H3B	0.4897	0.7167	0.0875	0.053*
H3C	0.5626	0.5883	0.0711	0.053*
N	0.59849 (6)	0.43451 (11)	0.21606 (6)	0.0235 (2)
H1	0.6455 (11)	0.499 (2)	0.2479 (11)	0.044 (4)*
C4	0.63402 (7)	0.32711 (12)	0.16458 (6)	0.0202 (2)
C5	0.58201 (7)	0.19841 (13)	0.12242 (7)	0.0223 (2)
C6	0.62219 (8)	0.08763 (13)	0.07811 (7)	0.0246 (2)
H6	0.5864	0.0026	0.0490	0.030*
C7	0.71248 (8)	0.09742 (13)	0.07514 (7)	0.0251 (2)
C8	0.76200 (7)	0.22660 (14)	0.11607 (7)	0.0253 (2)
H8	0.8235	0.2370	0.1139	0.030*
C9	0.72504 (7)	0.34183 (13)	0.16031 (7)	0.0223 (2)
C10	0.48513 (8)	0.17106 (15)	0.12607 (8)	0.0311 (3)
H10A	0.4457	0.2356	0.0833	0.047*
H10B	0.4765	0.2044	0.1800	0.047*
H10C	0.4703	0.0554	0.1173	0.047*
C11	0.75574 (10)	−0.03149 (16)	0.03248 (8)	0.0360 (3)
H11A	0.8068	0.0158	0.0141	0.054*
H11B	0.7115	−0.0729	−0.0151	0.054*
H11C	0.7770	−0.1210	0.0707	0.054*
C12	0.78280 (8)	0.47986 (16)	0.20280 (8)	0.0322 (3)
H12A	0.8428	0.4731	0.1910	0.048*
H12B	0.7882	0.4721	0.2621	0.048*
H12C	0.7549	0.5840	0.1828	0.048*

[a] Occupancy: 0.5.

(SHELXL-2014) [3]. A riding model was used to calculate and refine the positions of hydrogen atoms, except for the hydrogen atom bound to nitrogen which was located from the difference Fourier map and was refined with free positional and isotropic displacement parameters. Other elements than hydrogen were refined with anisotropic displacement parameters.

Comment

N^2,N^4-dimesitylpentane-2,4-diamine (**1**) crystallizes in the monoclinic space group $C2/c$ with four molecules per unit cell and all atoms at general $8f$ Wyckoff positions except for C1 at a $4e$ site which lies on a twofold axis, defining one molecule half as asymmetric unit. It represents the fully reduced congener to the organic compound $\mathrm{NacNac^{Mes}H}$ (**2**), which serves as a ligand in e.g. magnesium organyls [7, 8]. However, due to the absence of any reducing agent in the reaction mixture the formation of compound **1** cannot be explained in a straightforward way. Structurally similar compounds like N^2,N^4-di(*iso*-propylphenyl)-3,3-dimethylpentane-2,4-diamine (**3**) have been reported before [9, 10], some of which were prepared by the reduction of the corresponding aryl-diimines with $LiAlH_4$ [11]. Diamines obtained via this route have been applied as ligands for the generation of nickel complexes, which are used as catalytic species in the polymerization of polyethylene [11].

The presence of amine moieties was corroborated not only by evaluating the difference Fourier electron density map, revealing hydrogen atoms adjacent to the nitrogen atoms, but also by comparing the C–C and C–N bond lengths of **1** to the compounds **2** and **3** [8, 9]. The backbone of compound **1** comprises solely C–C and N–C single bonds [C1–C2 = 1.5364(13) Å, N–C2 = 1.4749(14) Å, N–C4 = 1.4237(13) Å] in analogy to molecule **3**. In contrast, the backbone of the unsaturated compound **2** reveals shortened C=C and N=C double bonds of 1.397 and 1.324 Å (mean values), respectively [8]. The NH groups form neither intramolecular nor intermolecular hydrogen bonds of relevant strength, also no π–π interactions between the mesityl residues indicated by parallel orientation of the aryl rings are present. Only weak C–H···π interactions are found in the crystal of compound **1** (C12–H12b···C6(π)′, symmetry operation is 1.5-x,0.5+y,0.5-z; H···C(π) = 2.87 Å, C–H···C(π) = 147°).

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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