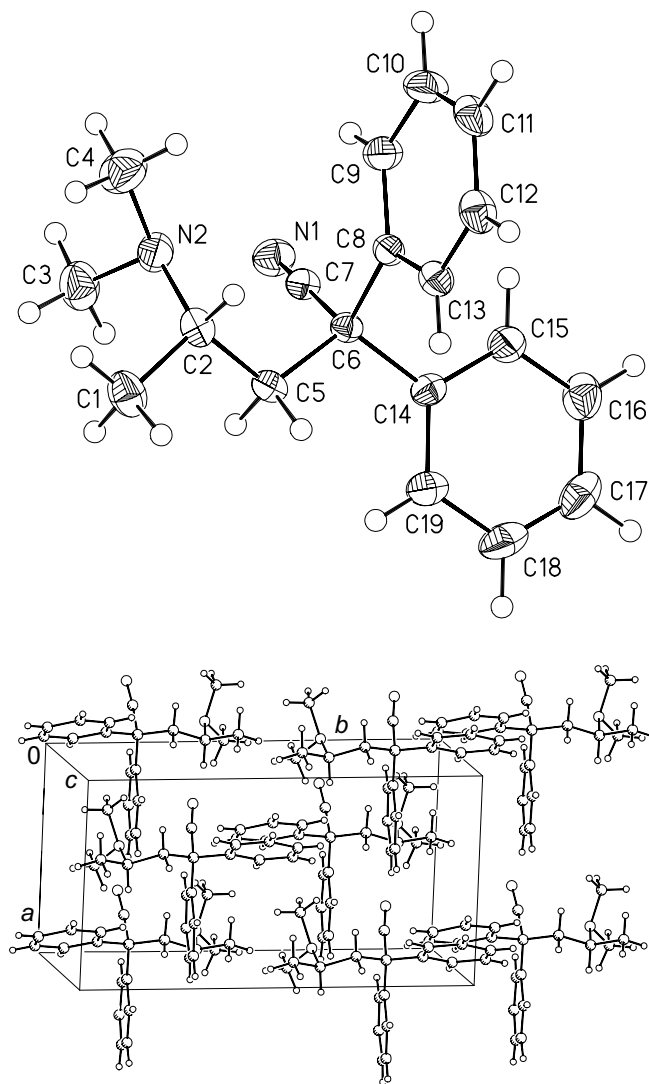


Crystal structure of 2,2-diphenyl-4-dimethylaminopentanenitrile, $C_{19}H_{22}N_2$

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Abstract

$C_{19}H_{22}N_2$, monoclinic, $C1c1$ (no. 9), $a = 8.636(1) \text{ \AA}$, $b = 15.162(2) \text{ \AA}$, $c = 12.807(2) \text{ \AA}$, $\beta = 106.599(3)^\circ$, $V = 1607.1 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.044$, $wR_{\text{ref}}(F^2) = 0.088$, $T = 120 \text{ K}$.

Source of material

The title compound was synthesized by reaction of 1-dimethylamino-2-chloropropane hydrochloride and diphenylacetonitrile in the presence of NaOH as a base. 1-dimethylamino-2-chloro-

propane was obtained from the reaction of thionyl chloride and 1-dimethylamino-2-propanol whose preparation was described previously [1]. In a typical procedure, a 50 % w/v solution of sodium hydroxide in water (12.5 ml, 0.32 mol) was added to a mechanically stirred suspension of diphenylacetonitrile (15.0 g, 0.08 mol) and dibenzo-18-crown-6 (0.5 g, cat.) in dimethylsulfoxide (12.5 ml). The color rapidly deepened to an orange/brown. 1-Dimethylamino-2-chloropropane hydrochloride (15 g, 0.095 mol) was added in portions over 30 min, this caused the temperature to rise to 30 °C. After the addition was completed the mixture was warmed to 45–50 °C (water bath) and stirred for one hour. The reaction mixture was then allowed to cool to room temperature, poured into ice/water (250 ml) and extracted with ethyl acetate (3 × 150 ml). The combined extracts were dried ($MgSO_4$), filtered and evaporated down to 100 ml. The product was extracted into 1 N HCl (100 ml + 50 ml) and then again washed with ethyl acetate. The aqueous solution was basified with 2 M sodium hydroxide and extracted into ethyl acetate (3 × 100 ml). The extracts were washed with saturated NaCl solution (70 ml), dried ($MgSO_4$), and evaporated down to a yellow oil. This was chilled and titrated with cold hexane (50 ml) to give the title compound (yield 39 %). Recrystallization from hexane gave crystals suitable for X-ray analysis (m.p. 91–92 °C).

Discussion

Racemic methadone, 6-dimethylamino-4,4-diphenyl-3-heptanone, is used as a maintenance drug in the treatment of heroin addiction and severe pain symptoms. It also helps to combat the spread of HIV by reducing injection of heroin [2]. These and other unique properties of methadone led us to synthesize the methadone. In a multi-step preparation of methadone, the synthesis of 2,2-diphenyl-4-dimethyl aminopentanenitrile is a very important step in which we gained a series of crystals.

The crystal structure of the title compound is built up by only the $C_{19}H_{22}N_2$ molecules within which all bond lengths are almost in normal ranges (figure, top). C6 atom is substituted with two phenyl groups and the C8–C6–C14 angle is 108.2(4)°. The C7–C6–C14 angle of 104.3(2)° and C2–C1–C16 angle of 110.8(2)° deviate slightly from the ideal value of 109.5°. The other bond angle around C6 are C5–C6–C7 (108.6(2)°), C5–C6–C8 (111.0(2)°) and C5–C6–C14 (112.8(2)°), which shows small steric strains between the substituents. The cyanide group twists very slightly out of the line of C1–C2 as seen by the C6–C7–N1 angle of 173.4(2)°. The planes of the two phenyl rings on C6 are oriented differently to each other with one in a horizontal and the other in a vertical manner. The arrangement of two molecules in the unit cell is in a fashion that intermolecular π - π stacking interactions between two horizontal phenyl groups are achieved. These interactions were not observed for the vertical phenyl groups (figure, bottom).

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Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.6 × 0.4 × 0.4 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.67 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{\max}$:	60.06°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	7566, 2322
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2073
$N(\text{param})_{\text{refined}}$:	190
Programs:	SHELXTL [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	4a	0.6016	0.5007	0.1346	0.055
H(1B)	4a	0.5759	0.4373	0.0345	0.055
H(1C)	4a	0.7485	0.4487	0.1162	0.055

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2A)	4a	0.4838	0.3664	0.1631	0.033
H(3A)	4a	0.8705	0.4138	0.4096	0.063
H(3B)	4a	0.8437	0.4656	0.2999	0.063
H(3C)	4a	0.9019	0.3673	0.3083	0.063
H(4A)	4a	0.6130	0.4403	0.4203	0.070
H(4B)	4a	0.4599	0.4103	0.3280	0.070
H(4C)	4a	0.5580	0.4934	0.3108	0.070
H(5A)	4a	0.7689	0.2873	0.1448	0.029
H(5B)	4a	0.5977	0.2768	0.0615	0.029
H(10A)	4a	0.5099	0.2019	0.3779	0.035
H(11A)	4a	0.2459	0.1963	0.3895	0.044
H(12A)	4a	0.0309	0.1935	0.2333	0.043
H(13A)	4a	0.0778	0.1981	0.0643	0.039
H(14A)	4a	0.3403	0.2006	0.0515	0.031
H(16A)	4a	0.5707	0.0344	0.2447	0.038
H(17A)	4a	0.6073	-0.0991	0.1665	0.047
H(18A)	4a	0.7066	-0.1009	0.0159	0.048
H(19A)	4a	0.7716	0.0291	-0.0533	0.047
H(20A)	4a	0.7365	0.1632	0.0245	0.037

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
N(1)	4a	0.8505(2)	0.1877(1)	0.3866(2)	0.030(1)	0.039(1)	0.0257(9)	0.0018(8)	0.0064(8)	0.0001(8)
N(2)	4a	0.6674(3)	0.3796(1)	0.2967(2)	0.035(1)	0.0275(9)	0.0297(9)	-0.0027(8)	0.0080(8)	-0.0022(8)
C(1)	4a	0.6350(3)	0.4463(2)	0.1095(2)	0.037(1)	0.031(1)	0.039(1)	-0.004(1)	0.007(1)	0.009(1)
C(2)	4a	0.6015(3)	0.3699(2)	0.1781(2)	0.025(1)	0.026(1)	0.031(1)	-0.0018(8)	0.0071(9)	0.0029(9)
C(3)	4a	0.8352(3)	0.4091(2)	0.3316(2)	0.042(2)	0.042(1)	0.037(1)	-0.011(1)	0.002(1)	0.001(1)
C(4)	4a	0.5658(4)	0.4357(2)	0.3429(3)	0.059(2)	0.038(1)	0.046(2)	0.007(1)	0.021(1)	-0.005(1)
C(5)	4a	0.6544(3)	0.2836(1)	0.1382(2)	0.0212(9)	0.029(1)	0.0224(9)	-0.0009(8)	0.0073(8)	0.0033(8)
C(7)	4a	0.7481(3)	0.1966(1)	0.3077(2)	0.026(1)	0.025(1)	0.023(1)	-0.0007(8)	0.0102(8)	0.0001(8)
C(8)	4a	0.6242(2)	0.2000(1)	0.1998(2)	0.0181(9)	0.0227(9)	0.0204(8)	0.0002(7)	0.0064(7)	0.0004(7)
C(9)	4a	0.4528(2)	0.2007(1)	0.2134(2)	0.0221(9)	0.0192(9)	0.0251(9)	0.0000(8)	0.0099(8)	0.0004(8)
C(10)	4a	0.4238(3)	0.2002(2)	0.3147(2)	0.031(1)	0.033(1)	0.027(1)	0.0002(9)	0.0116(9)	-0.0012(9)
C(11)	4a	0.2648(3)	0.1973(2)	0.3216(2)	0.039(1)	0.040(1)	0.041(1)	0.001(1)	0.026(1)	-0.001(1)
C(12)	4a	0.1362(3)	0.1959(2)	0.2283(2)	0.026(1)	0.031(1)	0.056(2)	0.000(1)	0.022(1)	-0.001(1)
C(13)	4a	0.1643(3)	0.1980(2)	0.1273(2)	0.023(1)	0.030(1)	0.043(1)	0.0000(9)	0.008(1)	0.001(1)
C(14)	4a	0.3221(3)	0.1999(1)	0.1197(2)	0.023(1)	0.027(1)	0.029(1)	-0.0009(8)	0.0083(8)	0.0010(9)
C(15)	4a	0.6494(2)	0.1133(1)	0.1429(2)	0.0195(9)	0.028(1)	0.0216(9)	0.0021(8)	0.0050(7)	-0.0027(8)
C(16)	4a	0.6112(3)	0.0337(2)	0.1848(2)	0.035(1)	0.027(1)	0.037(1)	0.0013(9)	0.017(1)	-0.002(1)
C(17)	4a	0.6328(3)	-0.0466(2)	0.1378(3)	0.037(1)	0.028(1)	0.055(2)	0.002(1)	0.015(1)	-0.004(1)
C(18)	4a	0.6927(3)	-0.0476(2)	0.0479(2)	0.031(1)	0.041(2)	0.045(2)	0.005(1)	0.005(1)	-0.018(1)
C(19)	4a	0.7310(3)	0.0301(2)	0.0066(2)	0.032(1)	0.054(2)	0.032(1)	0.007(1)	0.011(1)	-0.012(1)
C(20)	4a	0.7099(3)	0.1110(2)	0.0534(2)	0.029(1)	0.040(1)	0.026(1)	0.002(1)	0.0096(9)	-0.002(1)

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