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

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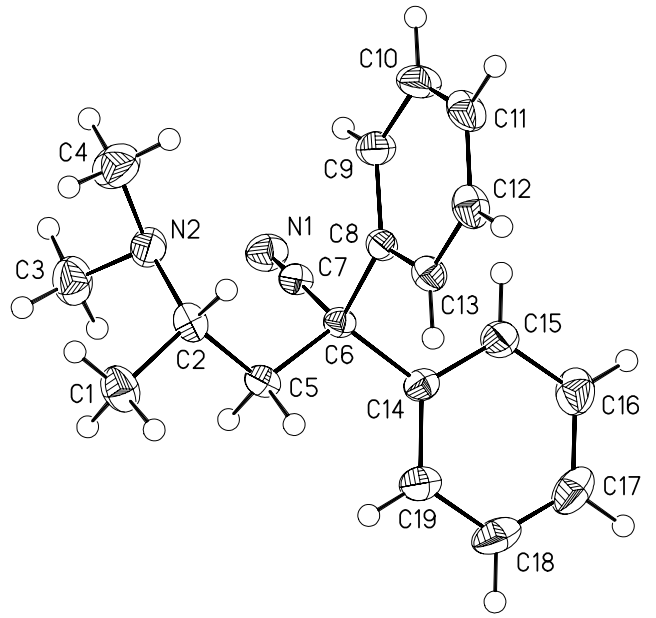

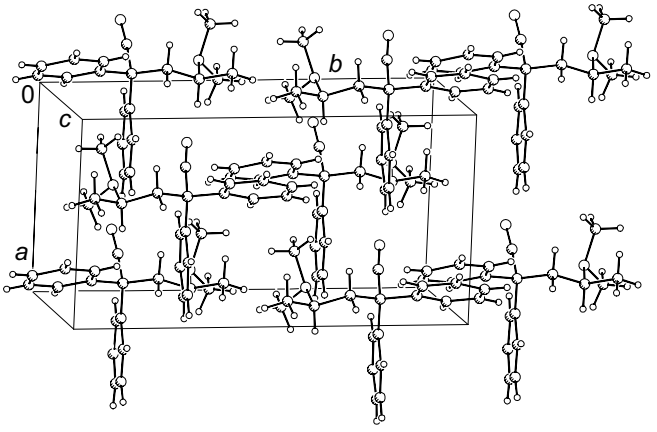

Abstract

$C_{19}H_{22}N_2$, monoclinic, *C*1*c*1 (no. 9), a = 8.636(1) Å, b = 15.162(2) Å, c = 12.807(2) Å, β = 106.599(3)°, V = 1607.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.088, T = 120 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-chloropropane 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°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7566, 2322
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2073
$N(param)_{refined}$:	190
Programs:	SHELXTL [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*a*	0.6016	0.5007	0.1346	0.055
H(1B)	4*a*	0.5759	0.4373	0.0345	0.055
H(1C)	4*a*	0.7485	0.4487	0.1162	0.055
H(2A)	4*a*	0.4838	0.3664	0.1631	0.033
H(3A)	4*a*	0.8705	0.4138	0.4096	0.063
H(3B)	4*a*	0.8437	0.4656	0.2999	0.063
H(3C)	4*a*	0.9019	0.3673	0.3083	0.063
H(4A)	4*a*	0.6130	0.4403	0.4203	0.070
H(4B)	4*a*	0.4599	0.4103	0.3280	0.070
H(4C)	4*a*	0.5580	0.4934	0.3108	0.070
H(5A)	4*a*	0.7689	0.2873	0.1448	0.029
H(5B)	4*a*	0.5977	0.2768	0.0615	0.029
H(10A)	4*a*	0.5099	0.2019	0.3779	0.035
H(11A)	4*a*	0.2459	0.1963	0.3895	0.044
H(12A)	4*a*	0.0309	0.1935	0.2333	0.043
H(13A)	4*a*	0.0778	0.1981	0.0643	0.039
H(14A)	4*a*	0.3403	0.2006	0.0515	0.031
H(16A)	4*a*	0.5707	0.0344	0.2447	0.038
H(17A)	4*a*	0.6073	–0.0991	0.1665	0.047
H(18A)	4*a*	0.7066	–0.1009	0.0159	0.048
H(19A)	4*a*	0.7716	0.0291	–0.0533	0.047
H(20A)	4*a*	0.7365	0.1632	0.0245	0.037

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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)	4*a*	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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