Crystal structure of *N,N,N',N',N'',N''*-hexakis(2-methylallyl)-[1,3,5]-triazin-2,4,6-triamine, $C_{27}H_{42}N_6$

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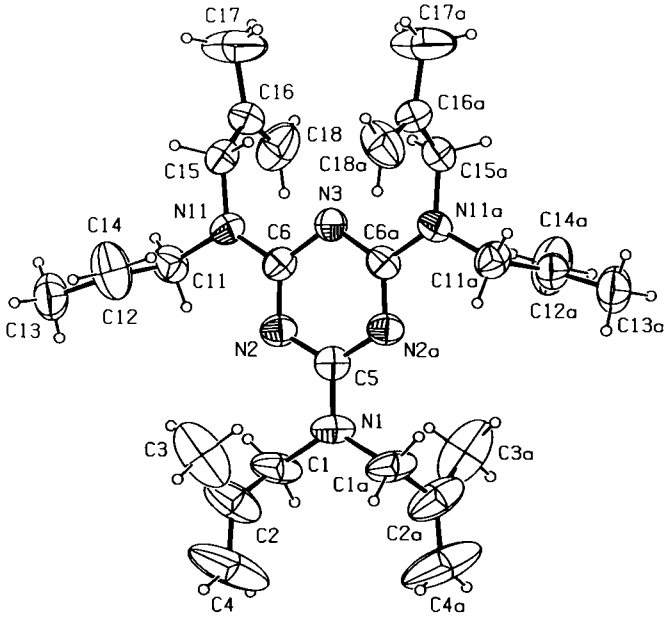

Abstract

$C_{27}H_{42}N_6$, tetragonal, $P4_32_12$ (no. 96), a = 9.779(1) Å, c = 30.975(4) Å, V = 2961.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.081, T = 291 K.

Source of material

The title compound was prepared according to [1]. To 11.41 g (457.20 mmol) sodium hydride was added 200 ml DMF at 273 K. 5.00 g (39.60 mmol) melamine was added and stirred for further 10 min. Subsequently 43.03 g (475.20 mmol) methylallylchloride was added dropwise to this suspension over a period of 30 min at room temperature. After 24 hours stirring at room temperature, the suspension was hydrolyzed with icy water following by extraction with diethyl ether. The organic phase was dried over $MgSO_4$, filtered, evaporated and dried with an oil pump (yield 11.08 g). *N,N,N',N',N'',N''*-Hexakis-(2-methyl-allyl)-[1,3,5]-triazin-2,4,6-triamine (24.58 mmol, 62 %) was obtained as a colorless oil, which forms colorless crystals after standing for some weeks in a refrigerator. ^{1}H NMR, ^{13}C NMR, IR and MS data are available in the CIF.

Discussion

The melamine unit can function as a rigid core inside the title compound. The six methallyl fragments are used for dendrimer synthesis by hydroaminomethylation [2], a multi step reaction with hydroformylation as the initial step. The hydroformylation reaction, the most important homogeneously catalyzed reaction, produces a mixture of linear and branched aldehydes from olefins, carbon monoxide and hydrogen [3]. The title compound was found to react in a sixfold hydroaminomethylation reaction of morpholine [4].

The title compound crystallizes with half a molecule in the asymmetric unit. The molecule resides on a twofold axis with the atoms N1, N3 and C5 along the axis. There are no short intermolecular contacts. The 2-methylallyl group containing the atoms C2, C3 and C4 is disordered.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.04 × 0.10 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.61 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, ω (κ offset)
$2\theta_{max}$:	50.68°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15255, 1655
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 337
$N(param)_{refined}$:	151
Programs:	SHELXS-97 [5], SHELXL-97 [6], PARST95 [7], PLATON [8], SHELXTL-Plus [9]

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

Atom	Site	x	y	z	U_{iso}
H(1B)	8*b*	−0.5135	0.5088	0.0447	0.194
H(1C)	8*b*	−0.3684	0.5490	0.0621	0.194
H(3C)	8*b*	−0.2003	0.2636	0.0117	0.435
H(3D)	8*b*	−0.1682	0.3886	0.0417	0.435
H(3E)	8*b*	−0.2049	0.4125	−0.0070	0.435
H(4A)	8*b*	−0.4314	0.1772	0.0254	0.442
H(4B)	8*b*	−0.5477	0.2854	0.0392	0.442
H(11A)	8*b*	−0.1563	0.7195	0.1098	0.153
H(11B)	8*b*	−0.0433	0.8061	0.1328	0.153
H(13A)	8*b*	0.0914	0.4872	0.1530	0.268
H(13B)	8*b*	−0.0583	0.5374	0.1618	0.268
H(13C)	8*b*	0.0660	0.6314	0.1736	0.268
H(14A)	8*b*	0.1488	0.4957	0.0823	0.251
H(14B)	8*b*	0.0911	0.6139	0.0510	0.251
H(15A)	8*b*	0.0967	0.9380	0.0386	0.146
H(15B)	8*b*	0.1443	0.8836	0.0836	0.146
H(17A)	8*b*	0.1365	1.2368	0.1015	0.401
H(17B)	8*b*	0.1963	1.1619	0.0609	0.401
H(17C)	8*b*	0.2291	1.1072	0.1074	0.401
H(18A)	8*b*	−0.0945	1.1912	0.1103	0.228
H(18B)	8*b*	−0.1554	1.0431	0.0982	0.228

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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*	–0.3973(9)	x	0	0.125(5)	U_{11}	0.121(8)	–0.049(6)	0.026(5)	$-U_{13}$
N(2)	8*b*	–0.2226(7)	0.7141(6)	0.0355(2)	0.112(5)	0.108(5)	0.106(4)	–0.011(4)	0.004(4)	–0.014(4)
N(3)	4*a*	–0.1029(5)	x	0	0.110(4)	U_{11}	0.091(5)	–0.005(5)	–0.005(3)	$-U_{13}$
N(11)	8*b*	–0.0444(7)	0.8307(6)	0.0688(2)	0.107(5)	0.112(5)	0.116(5)	–0.013(4)	–0.019(5)	–0.007(5)
C(1)	8*b*	–0.4170(8)	0.5116(9)	0.0375(2)	0.211(8)	0.173(9)	0.101(5)	–0.095(8)	0.052(5)	–0.004(6)
C(2)	8*b*	–0.367(2)	0.367(1)	0.0293(3)	0.41(2)	0.13(1)	0.118(6)	–0.08(1)	0.049(9)	–0.018(8)
C(3)	8*b*	–0.223(1)	0.357(1)	0.0179(3)	0.47(2)	0.20(1)	0.208(8)	0.09(1)	0.12(1)	0.029(7)
C(4)	8*b*	–0.458(1)	0.2666(9)	0.0315(3)	0.73(3)	0.20(1)	0.181(6)	–0.25(1)	0.12(1)	–0.055(7)
C(5)	4*a*	–0.302(1)	x	0	0.111(7)	U_{11}	0.096(9)	0.000(8)	0.011(5)	$-U_{13}$
C(6)	8*b*	–0.1271(8)	0.8103(8)	0.0342(2)	0.100(7)	0.116(8)	0.090(6)	0.001(6)	0.000(6)	–0.012(5)
C(11)	8*b*	–0.0617(7)	0.7486(9)	0.1080(2)	0.160(8)	0.130(7)	0.094(5)	–0.008(6)	0.003(5)	0.009(5)
C(12)	8*b*	0.0271(9)	0.6260(9)	0.1105(2)	0.149(8)	0.116(8)	0.133(7)	–0.004(6)	–0.037(7)	0.013(7)
C(13)	8*b*	0.0320(6)	0.5654(6)	0.1534(2)	0.166(7)	0.209(9)	0.161(6)	0.028(6)	–0.010(5)	0.065(6)
C(14)	8*b*	0.0956(8)	0.5735(8)	0.0781(2)	0.28(1)	0.190(9)	0.160(7)	0.100(7)	0.028(7)	0.008(6)
C(15)	8*b*	0.0683(7)	0.925(1)	0.0683(2)	0.109(8)	0.130(8)	0.126(5)	–0.002(7)	–0.024(5)	0.002(5)
C(16)	8*b*	0.0404(9)	1.063(1)	0.0878(2)	0.139(9)	0.100(8)	0.159(6)	–0.016(7)	–0.020(7)	0.010(6)
C(17)	8*b*	0.1608(8)	1.1495(8)	0.0896(3)	0.179(9)	0.160(9)	0.46(1)	–0.071(7)	0.050(9)	–0.063(8)
C(18)	8*b*	–0.0816(8)	1.1029(8)	0.1000(2)	0.151(9)	0.21(1)	0.213(7)	0.042(8)	–0.038(7)	–0.048(6)

References

1. Saito, Y.; Imanaka, Y.; Nakamatsu, H.; Iwata, K.; Horiie, A.: Production of Hexaarylmelamine. Japan Pat. Appl. JP 54100388 (1979).
2. Eilbracht, P.; Bärfacker, L.; Buss, C.; Hollmann, C.; Kitsos-Rzychon, B. E.; Kranemann, C. L.; Rische, T.; Roggenbuck, R.; Schmidt, A.: Tandem Reaction Sequence Under Hydroformylation Conditions: New Synthetic Applications of Transition Metal Catalysis. Chem. Rev. (1999) 3329-3365.
3. Claver, C.; van Leeuwen, P. W. N. M.: Rhodium Catalyzed Hydroformylation. Kluwer Academic Publishers, Dordrecht 2000.
4. Koç, F.: Synthese von Dendrimeren durch Hydroaminomethylierung und ihre Anwendung. Dissertation, Universität Dortmund, Germany 2004.
5. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
6. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
7. Nardelli, M.: PARST: A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analyses. J. Appl. Crystallogr. **28** (1995) 659.
8. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.
9. Sheldrick, G. M.: SHELXTL-Plus. Structure Determination Software Suite. Version 4.1. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA 1991.