Crystal structure of 2,4,6-tri-*tert*-butylphenylazide, (C₄H₉)₃C₆H₂N₃

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Source of material: The title compound was prepared, according to ref. 1–3, by conversion of 2,4,6-tri-*tert*-butylaniline with an excess of gaseous nitric oxide into the diazonium nitrate (see ref. 4) followed by treatment with hydrazine hydrate. Introduction of nitric oxide in a stream of argon into a solution of the aniline in ether at 273 K – 278 K yielded a pale yellow precipitate which was not isolated. Addition of hydrazine hydrate to the suspension after 0.5 h, followed by stirring at 293 K – 298 K for 4 h and evaporation of the solvent yielded a green, solid product (melting point range 388 K – 396 K) consisting of the title compound, 1,3,5-tri-*tert*-butylbenzene, and mainly 2,4,6-tri-*tert*-butylnitrosobenzene. Flash chromatography on silica gel with petroleum ether separated the nitroso compound (39% yield, mp 440 K, see ref. 5). Cyclic medium pressure liquid chromatography of the remaining two-component mixture on silica gel with petroleum ether (6 repetitive cycles) separated 1,3,5-tri-*tert*-butylbenzene (8% yield, mp 400 K – 401 K) and the title compound (8% yield) which gave colorless crystals, mp 395 K – 396 K, on recrystallization from petroleum ether.

Separation of the title compound from 1,3,5-tri-*tert*-butylbenzene, which inevitably arises in similar amounts, is very difficult, and the melting point (401 K – 402 K), reported in ref. 3 for the title compound, is actually that of 1,3,5-tri-*tert*-butylbenzene.

The unit cell of the title compound contains two pairs of different molecules which are distinguished by slightly different torsional angles. Due to the *tert*-butyl groups at the ortho positions, the azido group adopts a perpendicular conformation relative to the ring plane.

C₁₈H₂₉N₃, triclinic, $P\bar{1}$ (No. 2), $a = 11.745(4)$ Å, $b = 17.113(5)$ Å, $c = 9.983(3)$ Å, $\alpha = 97.86(2)^\circ$, $\beta = 107.96(2)^\circ$, $\gamma = 98.67(2)^\circ$, $V = 1850.7$ Å³, $Z = 4$, $R(F) = 0.085$, $R_w(F) = 0.079$.

Table 1. Parameters used for the X-ray data collection

Crystal:	colorless plate, size 0.4 x 0.8 x 0.2 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.60 cm ⁻¹
Diffractometer:	Siemens R3m/V
Scan mode:	Wyckoff
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{unique}}$:	8499
Criterion for F_o :	$F_o > 3 \sigma(F_o)$
$N(\text{param})_{\text{refined}}$:	434
Program:	SHELXTL-plus

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{iso}
H(13)	2i	0.3026(3)	0.3431(2)	-0.0503(3)	0.08
H(15)	2i	0.2428(2)	0.5664(2)	-0.0803(3)	0.08
H(12A)	2i	0.3629(3)	0.4010(2)	0.4084(4)	0.08
H(12B)	2i	0.4567(3)	0.3795(2)	0.3338(4)	0.08
H(12C)	2i	0.3942(3)	0.3150(2)	0.4004(4)	0.08
H(12D)	2i	0.1369(3)	0.3210(2)	0.2854(4)	0.08
H(12E)	2i	0.1794(3)	0.2394(2)	0.2589(4)	0.08
H(12F)	2i	0.1012(3)	0.2719(2)	0.1287(4)	0.08
H(12G)	2i	0.2674(5)	0.2372(2)	0.0315(4)	0.08
H(12H)	2i	0.3388(5)	0.2200(2)	0.1817(4)	0.08
H(12I)	2i	0.4024(5)	0.2835(2)	0.1143(4)	0.08
H(14A)	2i	0.1907(4)	0.3272(3)	-0.3037(4)	0.08
H(14B)	2i	0.2098(4)	0.3673(3)	-0.4294(4)	0.08
H(14C)	2i	0.1194(4)	0.3943(3)	-0.3538(4)	0.08
H(14D)	2i	0.4227(3)	0.3702(3)	-0.1832(4)	0.08
H(14E)	2i	0.4807(3)	0.4625(3)	-0.1453(4)	0.08

Table 2. (Continued)

Atom	Site	x	y	z	U_{iso}
H(14F)	2i	0.4323(3)	0.4166(3)	-0.3055(4)	0.08
H(14G)	2i	0.2178(4)	0.5366(2)	-0.3154(4)	0.08
H(14H)	2i	0.3122(4)	0.5074(2)	-0.3824(4)	0.08
H(14I)	2i	0.3579(4)	0.5593(2)	-0.2266(4)	0.08
H(16A)	2i	0.0572(3)	0.5750(2)	0.2294(5)	0.08
H(16B)	2i	0.0244(3)	0.5860(2)	0.0694(5)	0.08
H(16C)	2i	0.0593(3)	0.6615(2)	0.1934(5)	0.08
H(16D)	2i	0.2879(4)	0.6143(2)	0.3822(4)	0.08
H(16E)	2i	0.2791(4)	0.7001(2)	0.3467(4)	0.08
H(16F)	2i	0.3775(4)	0.6559(2)	0.3126(4)	0.08
H(16G)	2i	0.1644(4)	0.6618(2)	-0.0151(4)	0.08
H(16H)	2i	0.3055(4)	0.6856(2)	0.0681(4)	0.08
H(16I)	2i	0.2161(4)	0.7295(2)	0.1235(4)	0.08
H(23)	2i	0.9028(3)	0.1638(2)	0.5424(3)	0.08
H(25)	2i	0.7651(3)	-0.0585(2)	0.5824(3)	0.08
H(22A)	2i	0.7038(5)	0.0986(3)	0.0840(4)	0.08
H(22B)	2i	0.8457(5)	0.1257(3)	0.1589(4)	0.08
H(22C)	2i	0.7694(5)	0.1865(3)	0.0899(4)	0.08
H(22D)	2i	0.5788(4)	0.1749(2)	0.1970(5)	0.08
H(22E)	2i	0.6599(4)	0.2611(2)	0.2264(5)	0.08
H(22F)	2i	0.6299(4)	0.2273(2)	0.3525(5)	0.08

Table 2. (Continued)

Atom	Site	x	y	z	U_{iso}
H(22G)	2i	0.8584(4)	0.2694(3)	0.4473(5)	0.08
H(22H)	2i	0.8745(4)	0.2799(3)	0.3002(5)	0.08
H(22I)	2i	0.9442(4)	0.2227(3)	0.3898(5)	0.08
H(24A)	2i	0.9109(5)	0.1601(4)	0.8115(4)	0.08
H(24B)	2i	0.9760(5)	0.1185(4)	0.9361(4)	0.08
H(24C)	2i	0.8368(5)	0.0866(4)	0.8478(4)	0.08
H(24D)	2i	1.0734(4)	0.1588(6)	0.7045(6)	0.08
H(24E)	2i	1.0619(4)	0.0658(6)	0.6592(6)	0.08
H(24F)	2i	1.1320(4)	0.1092(6)	0.8190(6)	0.08
H(24G)	2i	0.8949(7)	-0.0354(3)	0.7753(6)	0.08
H(24H)	2i	1.0350(7)	-0.0095(3)	0.8632(6)	0.08
H(24I)	2i	0.9909(7)	-0.0353(3)	0.6956(6)	0.08
H(26A)	2i	0.4262(3)	-0.0707(2)	0.2629(5)	0.08
H(26B)	2i	0.4521(3)	-0.0771(2)	0.4244(5)	0.08
H(26C)	2i	0.3925(3)	-0.1543(2)	0.3035(5)	0.08
H(26D)	2i	0.5504(4)	-0.1177(2)	0.1234(4)	0.08
H(26E)	2i	0.5237(4)	-0.2018(2)	0.1653(4)	0.08
H(26F)	2i	0.6590(4)	-0.1574(2)	0.1981(4)	0.08
H(26G)	2i	0.5985(4)	-0.1542(2)	0.5208(5)	0.08
H(26H)	2i	0.6991(4)	-0.1718(2)	0.4547(5)	0.08
H(26I)	2i	0.5672(4)	-0.2256(2)	0.3905(5)	0.08

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(11)	2i	0.2105(2)	0.4745(2)	0.3090(2)	0.063(2)	0.067(2)	0.045(1)	0.012(1)	0.024(1)	0.012(1)
N(12)	2i	0.1055(3)	0.4561(2)	0.3072(3)	0.078(2)	0.081(2)	0.063(2)	0.027(2)	0.037(2)	0.029(1)
N(13)	2i	0.0129(3)	0.4405(2)	0.3210(4)	0.092(3)	0.150(3)	0.130(3)	0.045(2)	0.071(2)	0.071(3)
C(11)	2i	0.2319(2)	0.4671(2)	0.1721(3)	0.045(2)	0.051(2)	0.033(1)	0.009(1)	0.014(1)	0.006(1)
C(12)	2i	0.2637(2)	0.3967(2)	0.1201(3)	0.052(2)	0.049(2)	0.042(2)	0.014(1)	0.016(1)	0.011(1)
C(13)	2i	0.2826(3)	0.3915(2)	-0.0112(3)	0.061(2)	0.054(2)	0.046(2)	0.021(1)	0.018(1)	0.004(1)
C(14)	2i	0.2738(2)	0.4534(2)	-0.0885(3)	0.044(2)	0.062(2)	0.038(1)	0.012(1)	0.014(1)	0.007(1)
C(15)	2i	0.2476(2)	0.5229(2)	-0.0287(3)	0.044(2)	0.052(2)	0.044(2)	0.008(1)	0.015(1)	0.013(1)
C(16)	2i	0.2275(2)	0.5335(2)	0.1032(3)	0.041(2)	0.045(2)	0.041(1)	0.007(1)	0.011(1)	0.004(1)
C(120)	2i	0.2828(3)	0.3266(2)	0.2038(3)	0.079(2)	0.056(2)	0.060(2)	0.028(2)	0.025(2)	0.021(2)
C(121)	2i	0.3828(3)	0.3590(2)	0.3509(4)	0.090(3)	0.096(3)	0.074(2)	0.034(2)	0.021(2)	0.045(2)
C(122)	2i	0.1637(3)	0.2870(2)	0.2215(4)	0.103(3)	0.062(2)	0.098(3)	0.014(2)	0.037(2)	0.033(2)
C(123)	2i	0.3264(5)	0.2608(2)	0.1245(4)	0.156(4)	0.081(3)	0.098(3)	0.069(3)	0.056(3)	0.041(2)
C(140)	2i	0.2958(3)	0.4423(2)	-0.2329(3)	0.058(2)	0.081(2)	0.040(2)	0.018(2)	0.022(1)	0.012(2)
C(141)	2i	0.1952(4)	0.3764(3)	-0.3397(4)	0.093(3)	0.134(4)	0.047(2)	0.001(3)	0.027(2)	-0.003(2)
C(142)	2i	0.4188(3)	0.4205(3)	-0.2149(4)	0.081(3)	0.146(4)	0.059(2)	0.042(3)	0.037(2)	0.017(2)
C(143)	2i	0.2936(4)	0.5183(2)	-0.2954(4)	0.124(3)	0.120(3)	0.060(2)	0.041(3)	0.054(2)	0.030(2)
C(160)	2i	0.2050(3)	0.6153(2)	0.1652(3)	0.057(2)	0.043(2)	0.053(2)	0.009(1)	0.018(1)	0.003(1)
C(161)	2i	0.0751(3)	0.6092(2)	0.1667(5)	0.075(3)	0.056(2)	0.130(3)	0.024(2)	0.041(2)	0.010(2)
C(162)	2i	0.2958(4)	0.6487(2)	0.3159(4)	0.098(3)	0.059(2)	0.077(2)	0.009(2)	0.018(2)	-0.009(2)
C(163)	2i	0.2261(4)	0.6791(2)	0.0781(4)	0.137(4)	0.050(2)	0.097(3)	0.021(2)	0.057(3)	0.017(2)
N(21)	2i	0.5721(3)	0.0231(2)	0.1813(3)	0.069(2)	0.082(2)	0.059(2)	0.018(2)	0.003(1)	0.015(1)
N(22)	2i	0.4730(3)	0.0432(2)	0.1770(3)	0.080(2)	0.073(2)	0.083(2)	0.016(2)	0.009(2)	0.019(2)
N(23)	2i	0.3768(3)	0.0578(2)	0.1547(5)	0.079(3)	0.119(3)	0.184(4)	0.042(2)	0.016(3)	0.042(3)
C(21)	2i	0.6655(3)	0.0345(2)	0.3214(3)	0.051(2)	0.052(2)	0.043(2)	0.010(1)	0.010(1)	0.009(1)
C(22)	2i	0.7534(3)	0.1065(2)	0.3714(3)	0.055(2)	0.048(2)	0.052(2)	0.011(1)	0.019(1)	0.013(1)
C(23)	2i	0.8425(3)	0.1145(2)	0.5045(3)	0.052(2)	0.051(2)	0.057(2)	0.004(1)	0.017(1)	0.004(1)
C(24)	2i	0.8482(3)	0.0541(2)	0.5856(3)	0.049(2)	0.067(2)	0.044(2)	0.018(2)	0.016(1)	0.007(1)
C(25)	2i	0.7615(3)	-0.0161(2)	0.5283(3)	0.058(2)	0.056(2)	0.055(2)	0.016(2)	0.021(2)	0.020(1)
C(26)	2i	0.6684(2)	-0.0291(2)	0.3955(3)	0.049(2)	0.049(2)	0.051(2)	0.009(1)	0.017(1)	0.011(1)
C(220)	2i	0.7581(3)	0.1750(2)	0.2854(4)	0.078(2)	0.056(2)	0.075(2)	0.015(2)	0.030(2)	0.028(2)
C(221)	2i	0.7691(5)	0.1428(3)	0.1408(4)	0.169(4)	0.106(3)	0.102(3)	0.058(3)	0.081(3)	0.064(3)
C(222)	2i	0.6469(4)	0.2135(2)	0.2652(5)	0.118(3)	0.063(2)	0.118(3)	0.034(2)	0.041(3)	0.036(2)
C(223)	2i	0.8698(4)	0.2426(3)	0.3628(5)	0.112(4)	0.091(3)	0.150(4)	-0.008(3)	0.033(3)	0.069(3)
C(240)	2i	0.9476(3)	0.0662(2)	0.7313(3)	0.054(2)	0.088(2)	0.046(2)	0.022(2)	0.008(1)	0.009(2)
C(241)	2i	0.9149(5)	0.1097(4)	0.8429(4)	0.122(4)	0.261(7)	0.049(2)	0.102(4)	-0.003(2)	-0.019(3)
C(242)	2i	1.0642(4)	0.1079(6)	0.7346(6)	0.083(4)	0.62(2)	0.109(5)	-0.086(7)	-0.037(3)	0.147(7)
C(243)	2i	0.9727(7)	-0.0084(3)	0.7751(6)	0.31(1)	0.206(8)	0.136(5)	0.152(8)	-0.138(6)	-0.037(5)
C(260)	2i	0.5781(3)	-0.1113(2)	0.3379(3)	0.060(2)	0.048(2)	0.073(2)	0.005(1)	0.020(2)	0.011(2)
C(261)	2i	0.4502(3)	-0.1039(2)	0.3325(5)	0.082(3)	0.071(2)	0.139(4)	-0.003(2)	0.050(3)	0.007(2)
C(262)	2i	0.5783(4)	-0.1502(2)	0.1930(4)	0.102(3)	0.069(3)	0.108(3)	-0.010(2)	0.037(3)	-0.015(2)
C(263)	2i	0.6136(4)	-0.1720(2)	0.4336(5)	0.131(4)	0.057(3)	0.145(4)	-0.010(3)	0.008(3)	0.033(3)

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