Crystal structure of benzyl (2,6-diisocyano-4-methyl)phenyl ether, $C_{16}H_{12}N_2O$

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Source of material: Crystals of the title compound were obtained by recrystallization from CH_2Cl_2 /hexane. The title compound was synthesized by the following sequence: reaction of 4-methylhydroxybenzene with fuming nitric acid, reduction of the formed 2,5-dinitro-4-methylhydroxybenzene with hydrazine, conversion of the primary amines into formamide functions by refluxing with phenylformate in ethanol, protection of the hydroxyl function with benzylbromide and finally conversion of the formamide functions into isocyanides with diphosgene according to the method of Ugi (see ref. 1). The isocyanide formation is not possible with the free hydroxy compound. The overall yield is 25 % based on 4-methylhydroxybenzene.

We reported recently on an effective way for the synthesis of *N,O*-heterocarbene complexes using the intramolecular nucleophilic attack of the hydroxy group of coordinated 2-hydroxyphenylisocyanide (see ref. 2). This reaction is reversible and the reaction product depends on the electronic situation at the metal center (see ref. 3). The title compound features two isocyanides, which upon coordination to different metals will compete for the hydroxyl group liberated after *O*-benzyl bond cleavage. It will therefore allow for a direct comparison of the carbene formation tendency of two different metal centers under otherwise completely identical reaction conditions. Bond lengths and angles in

the compound are normal. The $N\equiv C$ separations in the isocyanide groups of 1.141(3) Å and 1.145 Å fall in the range observed previously for functionalized arylisocyanides (see refs. 4–6).

$C_{16}H_{12}N_2O$, monoclinic, $P12_1/c1$ (No. 14), $a=4.238(4)$ Å, $b=12.276(2)$ Å, $c=26.218(9)$ Å, $\beta=93.84(5)^\circ$, $V=1360.9$ Å³, $Z=4$, $\rho_m=1.218$ g·cm⁻³, $R(F)=0.043$, $R_w(F^2)=0.117$.

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

Crystal:	colorless needle, size 0.12 x 0.14 x 0.42 mm
Wavelength:	Mo $K\alpha$ radiation (0.71069 Å)
μ :	0.77 cm ⁻¹
Diffractometer:	Enraf-Nonius CAD4
Scan mode:	$\omega/2\theta$
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	45°
$N(hkl)_{\text{unique}}$:	1766
Criterion for I_0 :	$I_0 > 2\sigma(I_0)$
$N(\text{param})_{\text{refined}}$:	208
Programs:	SHELXS-86, SHELXL-93, MolEN, ZORTEP

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

Atom	Site	x	y	z	U_{iso}
H(3)	4e	0.806(6)	0.391(2)	-0.0178(9)	0.087
H(5)	4e	0.351(6)	0.106(2)	-0.0228(9)	0.090
H(7A)	4e	0.572(8)	0.286(3)	-0.105(1)	0.123
H(7B)	4e	0.657(8)	0.166(3)	-0.097(1)	0.123
H(7C)	4e	0.877(9)	0.234(3)	-0.089(1)	0.123
H(10A)	4e	0.737(7)	0.302(2)	0.157(1)	0.095
H(10B)	4e	0.570(7)	0.180(2)	0.158(1)	0.095
H(12)	4e	0.430(7)	0.453(2)	0.200(1)	0.111
H(13)	4e	0.181(9)	0.503(3)	0.275(1)	0.141
H(14)	4e	0.027(9)	0.371(3)	0.329(1)	0.144
H(15)	4e	0.073(9)	0.182(3)	0.304(1)	0.139
H(16)	4e	0.312(7)	0.134(3)	0.228(1)	0.112

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}
O(1)	4e	0.3243(3)	0.2914(1)	0.11845(5)	0.0476(8)	0.085(1)	0.0533(9)	0.0106(7)	0.0016(7)	-0.0011(7)
N(1)	4e	0.1554(5)	0.1057(2)	0.06585(8)	0.061(1)	0.073(1)	0.087(1)	-0.001(1)	-0.001(1)	-0.003(1)
N(2)	4e	0.7074(5)	0.4437(2)	0.07492(7)	0.073(1)	0.066(1)	0.068(1)	0.001(1)	0.004(1)	-0.001(1)
C(1)	4e	0.4271(5)	0.2748(2)	0.07129(8)	0.047(1)	0.066(1)	0.053(1)	0.011(1)	-0.001(1)	0.001(1)
C(2)	4e	0.6077(5)	0.3514(2)	0.04756(8)	0.056(1)	0.065(1)	0.057(1)	0.009(1)	-0.002(1)	-0.001(1)
C(3)	4e	0.6903(6)	0.3381(2)	-0.00193(9)	0.059(2)	0.081(2)	0.060(2)	0.008(1)	0.006(1)	0.005(1)
C(4)	4e	0.5948(6)	0.2474(2)	-0.03000(9)	0.063(1)	0.084(2)	0.057(1)	0.015(1)	0.001(1)	-0.003(1)

Table 3. (Continued)

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(5)	4e	0.4194(6)	0.1703(2)	-0.00656(9)	0.060(2)	0.076(2)	0.070(2)	0.011(1)	-0.010(1)	-0.013(1)
C(6)	4e	0.3369(5)	0.1840(2)	0.04309(9)	0.049(1)	0.068(1)	0.066(1)	0.006(1)	-0.002(1)	-0.001(1)
C(7)	4e	0.6779(9)	0.2345(3)	-0.0841(1)	0.100(2)	0.124(3)	0.061(2)	0.031(2)	0.006(2)	-0.010(2)
C(8)	4e	0.0029(8)	0.0441(3)	0.0856(1)	0.085(2)	0.091(2)	0.125(2)	-0.013(2)	0.008(2)	0.002(2)
C(9)	4e	0.7889(8)	0.5185(3)	0.0983(1)	0.112(3)	0.079(2)	0.104(2)	-0.003(2)	0.003(2)	-0.009(2)
C(10)	4e	0.5397(6)	0.2586(2)	0.16064(9)	0.060(2)	0.102(2)	0.057(1)	0.016(2)	-0.000(1)	0.008(1)
C(11)	4e	0.3925(5)	0.2876(2)	0.20851(8)	0.046(1)	0.088(2)	0.053(1)	0.003(1)	-0.002(1)	0.003(1)
C(12)	4e	0.3547(7)	0.3944(3)	0.2222(1)	0.077(2)	0.098(2)	0.082(2)	-0.005(2)	0.015(2)	-0.007(2)
C(13)	4e	0.2187(8)	0.4218(3)	0.2664(1)	0.100(2)	0.131(3)	0.096(2)	0.007(2)	0.013(2)	-0.028(2)
C(14)	4e	0.1206(8)	0.3427(5)	0.2968(1)	0.090(2)	0.172(4)	0.071(2)	0.003(3)	0.009(2)	-0.004(2)
C(15)	4e	0.1511(8)	0.2367(4)	0.2854(1)	0.093(2)	0.151(4)	0.078(2)	-0.010(2)	0.006(2)	0.036(2)
C(16)	4e	0.2905(7)	0.2082(3)	0.2402(1)	0.080(2)	0.104(2)	0.075(2)	0.004(2)	0.000(2)	0.013(2)

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