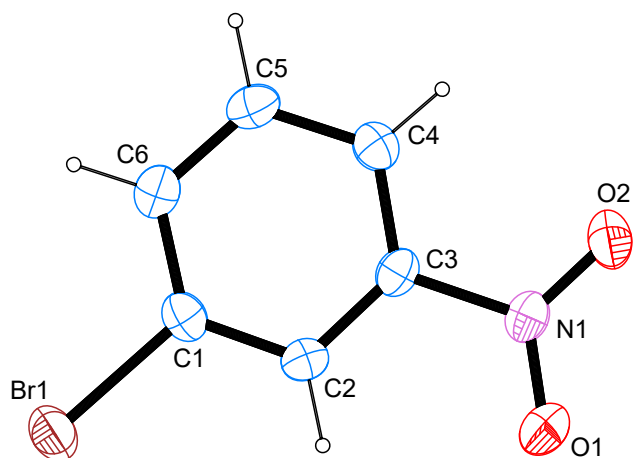


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Redetermination of the crystal structure of 3-bromonitrobenzene at 200 K, $C_6H_4BrNO_2$ – temperature effects on cell constants



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Abstract

$C_6H_4BrNO_2$, orthorhombic, $Pna2_1$ (no. 33), $a = 21.3992(17)$ Å, $b = 5.9311(4)$ Å, $c = 5.2923(4)$ Å, $V = 671.70(9)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0284$, $wR_{ref}(F^2) = 0.0708$, $T = 200(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Sigma–Aldrich). Crystals suitable for the diffraction study were taken directly from the provided product.

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Table 1: Data collection and handling.

Crystal:	Colorless rod
Size:	0.50 × 0.26 × 0.14 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	6.05 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ _{max} , completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	3459, 1595, 0.024
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1364
$N(param)_{refined}$:	91
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U_{eq}(C)$.

Comment

Benzene is among the most important synthons in chemistry. Via electrophilic substitution reactions a vast variety of functionalized derivatives is readily available. The interplay between activating and deactivating substituents as well as the competition and synergism between inductive and mesomeric effects allows for the seemingly endless functionalization of the respective archetype hydrocarbon scaffold. The latter gives rise to a large toolbox of new synthons that can be applied for the production of dyes, medications, catalysts and ligands for novel coordination compounds. Several simple and fundamental derivatives of benzene are powerful and versatile reagents themselves and have entered the preparative chemist's toolbox decades ago. One notable example for the latter statement is *meta*-bromo nitrobenzene which is readily available upon bromination of nitrobenzene and offers a wealth of follow up reactions. During the preparation of a number of functionalized derivatives of boronic and borinic acids the title compound – which is commercially available – was used as a starting material. To prevent

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Br1	0.26427 (2)	0.54725 (8)	0.08920 (17)	0.03670 (16)
O1	0.41907 (19)	0.3645 (6)	0.8493 (7)	0.0377 (9)
O2	0.48054 (18)	0.6513 (6)	0.9122 (6)	0.0361 (8)
N1	0.4384 (2)	0.5550 (6)	0.7983 (7)	0.0260 (9)
C1	0.3322 (2)	0.6846 (7)	0.2633 (9)	0.0265 (10)
C2	0.3589 (2)	0.5715 (7)	0.4644 (9)	0.0251 (10)
H2	0.343943	0.428412	0.517733	0.030*
C3	0.40832 (18)	0.6756 (6)	0.5840 (12)	0.0236 (7)
C4	0.4313 (2)	0.8848 (8)	0.5151 (9)	0.0281 (10)
H4	0.465486	0.951069	0.602372	0.034*
C5	0.4026 (3)	0.9953 (8)	0.3131 (10)	0.0295 (11)
H5	0.417025	1.139877	0.262316	0.035*
C6	0.3530 (2)	0.8950 (8)	0.1857 (9)	0.0284 (10)
H6	0.333674	0.969520	0.047468	0.034*

accidentally characterizing the title compound instead of the sought-after ligands by means of diffraction studies based on single crystals and in continuation of our own studies into the structural aspects of core-halogenated derivatives of benzene [7–12] the crystallographic data for the substrate was sought. The molecular and crystal structure of the title compound has been reported earlier [13], however, the hydrogen atoms were not included in the refinement. A later structure determination conducted at room temperature (295 K) took the latter atoms into account [14]. Furthermore, the molecular and crystal structures of several other multi-halogenated and nitrated derivatives of benzene have been reported earlier [15, 16].

The structure solution shows the title compound to be a derivative of nitrobenzene bearing a bromo substituent in *meta* position to the nitro group. The C–Br bond length was measured at 1.904(5) Å while the C–N bond length was found at 1.488(7) Å. N–O resonance is indicated by the pertaining bond lengths determined to be almost identical with values of 1.226(5) and 1.233(5) Å, respectively. The latter values are in good agreement with pertaining values for comparable compounds whose metrical parameters have been deposited with the Cambridge Structural Database [17]. C–C–C angles cover a range of 117.0(4)–123.6(5)° with the smallest angle found on the carbon atom in between the two functionalized ring atoms while the largest value is located on the carbon atom bearing the nitro group. In comparison to the corresponding metrical parameters apparent for the structure at room temperature [14] a slight increase to longer bond distances at 200 K is observed. The molecule is essentially planar with the least-squares plane engulfing all non-hydrogen atoms featuring one of the two oxygen atoms deviating most with a value of only 0.046(4) Å. The extension of mesomeric

effects to the pnictogen-based substituent is further corroborated by the angle of only 3.0(5)° enclosed by the least-squares planes as defined by the carbon atoms of the phenyl ring on the one hand and the nitrogen and oxygen atoms of the NO₂ group on the other hand.

In the crystal, C–H···O contacts are observed whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. These contacts are supported by the hydrogen atom in two-fold *meta*-orientation to both substituents as donor and one of the two oxygen atoms of the nitro group as acceptor and connect the molecules to chains along [0 1 1]. In terms of graph-set analysis [18, 19], these contacts require a C₁(6) descriptor on the unary level. Furthermore, a C–Br···π interaction can be observed which precludes the formation of π stacking with the shortest distance in between two centers of gravity measured at 5.292(3) Å. Although the qualitative mode of packing in this low-temperature study is in agreement with the picture obtained at room temperature [14], an interesting increase for the distance between two centers of gravity is apparent that was measured at 5.342(2) Å in the latter case. While this trend of an increase in bond distance is in contrast to the otherwise invariably smaller/shorter values found at room temperature (see above), this finding might explain why the *a* and *c* axes reported for the compound's unit cell at 295 K show a marked lengthening. The latter would reflect the more “lofty” packing of the molecules.

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