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N^2-(2,6-Dibromo-4-nitrophenyl)-N^1,N^1-diethyl-2-(triisopropylsilyl)ethanamidine

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Key indicators

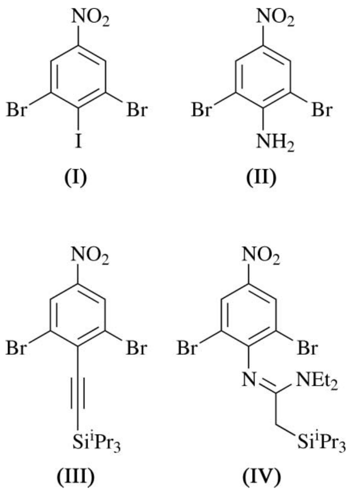
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.022
wR factor = 0.022
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Molecules of the title compound, $C_{21}H_{35}Br_2N_3O_2Si$, form dimers by virtue of O(nitro)$\cdots$H(isopropyl) interactions [O$\cdots$H = 2.55 Å, O$\cdots$C = 3.545 (3) Å and O$\cdots$H—C = 171°].

Comment

We have recently become interested in the synthesis of star-shaped molecules and dendrimers containing multiple alkyne functionalities (Constable *et al.*, 2006, and references therein). During these studies, we have developed routes to a number of alkyne-containing building blocks containing mixed halo substituents to facilitate preferential alkyne-coupling at specific sites under Sonogashira conditions (Sonogashira *et al.*, 1975; Sonogashira, 2002). A key building block is (I) (see scheme), which is prepared from 2,6-dibromo-4-nitroaniline, (II) (Senear *et al.* 1946). In the reaction of a crude sample of (I) containing (II) with ^{i}Pr$_3$SiCCH under Sonogashira conditions, we isolated a single crystal of (IV) in addition to the expected alkyne (III). Attempts to repeat the preparation of (IV) were unsuccessful. Compound (IV) is an amidine and is derived from a molecule of (II), ^{i}Pr$_3$SiCCH and an Et$_2$N unit originating from triethylamine. The structure of (IV) is shown in Fig. 1.



The 2,6-dibromo-4-nitrophenyl substituent is planar and has no unusual features. The geometrical parameters for the remaining aryl substituent are consistent with the formation of a substituted acetamidine. Atom C8 has a trigonal planar environment, and the C8—N7 and C8—N9 bond lengths of 1.305 (2) and 1.353 (2) Å [compared to N—C distances in the NEt$_2$ unit of 1.474 (3) and 1.467 (3) Å] are consistent with π-delocalization. Consistent with this is the fact that N9 is in a trigonal planar environment (sum of bond angles = 360°) and that N7 can be considered to be sp^2-hybridized [C1—N7—C8

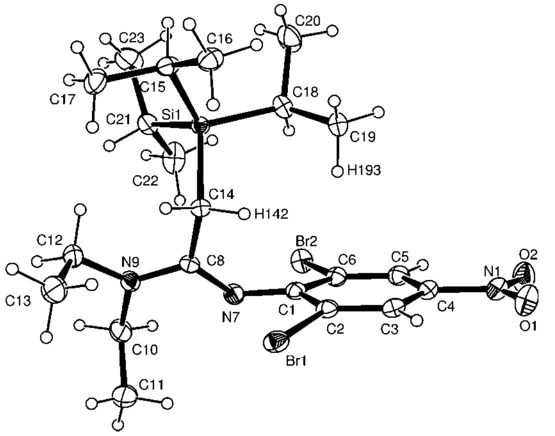


Figure 1
The molecular structure of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

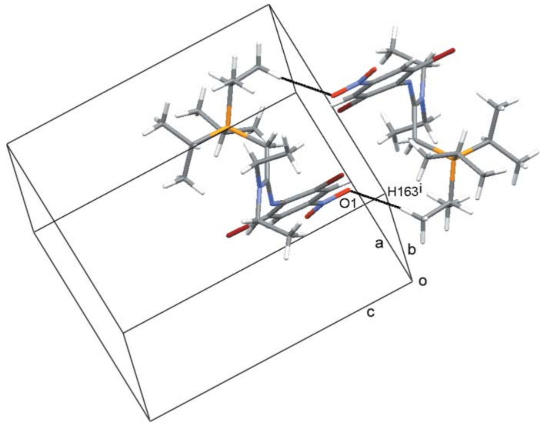


Figure 2
A dimer of (IV) in the solid state. Intermolecular interactions are shown as black lines. [Symmetry code: (i) $1 - x$, $1 - y$, $-z$.]

= 125.59 (16)°]. The C8—C14 bond [1.498 (2) Å], formally a single bond, originates from the triple bond in ^{i}Pr$_3$SiCCH, confirming that reduction of this unit has occurred during the formation of (IV). There are two intramolecular short contacts. The first is between Br1 and H142 [Br1···H142 = 2.84 Å, C14···Br1 = 3.4191 (18) Å and C14—H142···Br1 = 118°]. The second involves one ^{i}Pr group which is oriented so that H193 points towards the aromatic cloud of the aryl ring (H193···centroid = 2.72 Å and C19—H193···centroid = 154°). Such C—H···π interactions are well documented (Nishio, 2004).

Compound (IV) crystallizes in the space group $P\overline{1}$, and there are no significant attractive interactions between symmetry-related pairs of molecules in the unit cell. Molecules of (IV) form dimers (Fig. 2) in which one nitro group interacts with a CH group of the ^{i}Pr substituent of a second molecule [O1···H163^i = 2.55 Å, O1···C16^i = 3.545 (3) Å and O1···H163^i—C16^i = 171°; symmetry code: (i) $1 - x$, $1 - y$, $-z$].

Experimental

For the preparation of compounds (III) and (IV), 3,5-dibromo-4-iodonitrobenzene, (I), was prepared from 2,6-dibromo-4-nitroaniline, (II) (Senear *et al.*, 1946). (I) (1.50 g, 3.69 mmol), CuCl (54.5 mg, 0.55 mmol) and [Pd(PPh$_3$)$_2$Cl$_2$] (381 mg, 0.54 mmol) were dissolved in Et$_3$N (50 ml) under argon. ^{i}Pr$_3$SiCCH (4.90 ml, 22.1 mm l) was added and the reaction mixture was stirred at 318 K for 17 h. The solvent was then removed and the residue extracted with CH$_2$Cl$_2$/hexanes (10% CH$_2$Cl$_2$, total volume 100 ml). The dark mixture was filtered and the volume of the filtrate was reduced. Column chromatography (alumina, hexanes followed by hexanes–CH$_2$Cl$_2$ 3:1) gave one major fraction, spectroscopic characterization of which was consistent with (III); details are given in the CIF. Part of this sample was redissolved in CHCl$_3$, and from it, a single crystal of (IV) was isolated.

Crystal data

$C_{21}H_{35}Br_2N_3O_2Si$
$M_r = 549.42$
Triclinic, $P\overline{1}$
$a = 9.5058$ (2) Å
$b = 10.5180$ (2) Å
$c = 12.7195$ (2) Å
$\alpha = 84.5138$ (9)°
$\beta = 88.4554$ (8)°
$\gamma = 78.6724$ (8)°

$V = 1241.19$ (4) Å^3
$Z = 2$
$D_x = 1.470$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 3.34$ mm^{-1}
$T = 173$ K
Block, orange
0.20 × 0.16 × 0.10 mm

Data collection

Nonius Kappa CCD diffractometer
φ and ω scans
Absorption correction: multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)
$T_{\min} = 0.55$, $T_{\max} = 0.72$

11254 measured reflections
5691 independent reflections
4137 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\max} = 27.5$°

Refinement

Refinement on F
$R[F > 2\sigma(F)] = 0.022$
$wR(F) = 0.022$
$S = 1.02$
4137 reflections
263 parameters
H-atom parameters constrained

Modified Chebychev polynomial (Watkin, 1994, Prince, 1982) with the coefficients 0.109 −0.105 −0.0515 −0.0758
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: Larson (1970) equation 22
Extinction coefficient: 59.1 (20)

All H atoms were treated as riding atoms, with C—H distances of 1.00 Å and isotropic U values set at 1.2 times the $U_{\rm eq}$ value of the adjacent bonded atom.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK*; data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CRYSTALS*.

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