

1,2,4,5-Tetrakis(diazidomethyl)-
benzeneMarcel Wieland,^a Kuan-Jen Su,^a Gerald Wagner,^a Udo H.
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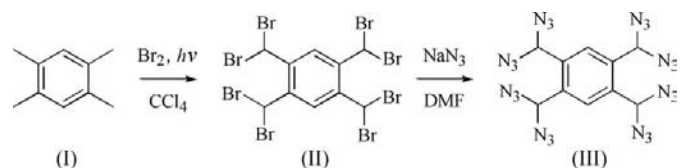
The molecule of the title compound, C₁₀H₆N₂₄, lies on a crystallographic inversion centre located in the middle of the benzene ring. Steric overcrowding by the bulky N₃ groups is avoided by the tendency of four azide entities to be arranged parallel to the benzene ring and the other four azide groups to be arranged alternately above and below the benzene plane in a skeletal C_i symmetry. The compound is of interest for high-energy research and as a precursor for the synthesis of carbon nanotubes, nanospheres or high-nitrogen carbon nitrides with great potential for biological and technological applications.

Comment

Some 80 years ago, Mills and Nixon (Mills & Nixon, 1930) put forward the interesting question of whether strain could lead to a localization of aromatic double bonds. Since then, for compounds comprising three- or four-membered rings annulated onto the benzene nucleus, a strain-induced bond localization has been discussed (Collins *et al.*, 1990; Baldrige & Siegel, 1992; Siegel, 1994; Stanger *et al.*, 1997; Bürgi *et al.*, 2005) but it remains controversial. The X-ray diffraction study of a compound containing a benzene ring connected to a spiro-pentane moiety, however, shows indeed a minor bond alternation that is caused by the spiro-pentane subunit working as a tensile spring. Thus, while the annulated bond is expanded, the other C–C bonds of the benzene ring show alternating distances leaning toward one Kekule structure (Boese *et al.*, 1989).

We were interested in investigating whether a similar effect can be observed by introducing eight azide groups into the tetramethylbenzene system. Although molecules with two, three or even four azide groups at one C atom are now available (Nishiyama & Yamaguchi, 1988; Nishiyama *et al.*, 1987; Petrie *et al.*, 1997; Lyssenko *et al.*, 2005), a survey of the Cambridge Structural Database (Allen, 2002) revealed the absence of X-ray diffraction structures of benzene derivatives with geminal diazide groups. The photobromination of 1,2,4,5-

tetramethylbenzene, (I), afforded 1,2,4,5-tetrakis(dibromomethyl)benzene, (II), in 90% yield (Soyer *et al.*, 1975; Schrievers & Brinker, 1988). Compound (II) reacts with NaN₃ to give 1,2,4,5-tetrakis(diazidomethyl)benzene, (III), in 91% yield (Gilbert, 1987). We report here the results of the investigation of the crystal structure of the fourfold geminal diazide, (III), by X-ray crystallography.



The 1,2,4,5-tetrakis(diazidomethyl)benzene molecule (Fig. 1) lies on a crystallographic inversion centre located in the middle of the benzene ring. There is then half a molecule within the asymmetric unit. Two of the unique azide groups tend to remain in the plane of the benzene ring, with the torsion angles showing deviation from planarity [$\Theta(\text{C}2-\text{C}3-\text{C}4-\text{N}10)$ and $\Theta(\text{C}3-\text{C}2-\text{C}1-\text{N}4)$ of 164.47 (12) and 159.73 (12)°, respectively]. Both azide groups oriented nearly parallel to the benzene ring are almost linear, with N4–N5–N6 and N10–N11–N12 angles of 173.42 (15) and 171.35 (14)°, respectively. The other two unique azide groups (N1–N2–N3 and N7–N8–N9) are also nearly linear, with corresponding angles of 174.32 (15) and 173.37 (16)°, and adopt an opposite orientation above and below the benzene ring with torsion angles $\Theta(\text{C}2-\text{C}3-\text{C}4-\text{N}7)$ and $\Theta(\text{C}3-\text{C}2-\text{C}1-\text{N}1)$ of -72.40 (16) and -77.85 (15)°, respectively. The average C–N _{α} –N _{β} angle of 112.9 (5)° deviates by more than 3° from the ideal tetrahedral value. Such an arrangement of the geminal diazide groups avoids steric overcrowding.

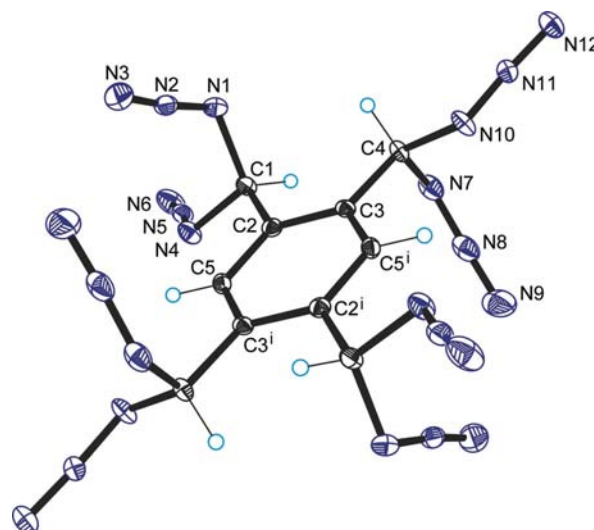


Figure 1

The molecular structure of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.]

The endocyclic angles at C2 and C3 are only slightly smaller than the exocyclic angles (Table 1), but very close to the ideal value. The maximal deviation from 120° does not exceed 0.84° . A more significant deviation of exocyclic angles ($>3^\circ$) from 120° was observed for 1,2,4,5-tetrakis(bromomethyl)benzene (Wang *et al.*, 2006). The distribution of the electron density over the benzene ring expressed by the corresponding bond lengths quoted in Table 1 differs from that observed earlier in a benzene-bridged spiro-pentane (Boese *et al.*, 1989).

Despite the presence of a large number of N atoms, with lone pairs potentially available for hydrogen-bond formation as proton acceptors, there are no C—H \cdots N contacts in the crystal structure of (III) (Fig. 2), which might be classified as a typical hydrogen bond (mean statistical parameters: H \cdots N = 2.38 Å and C—H \cdots N = 155°) (Mascal, 1998). The shortest contacts between adjacent molecules are 2.984 Å and can be described as van der Waals interactions (Bondi, 1964; Nyburg & Faerman, 1985; Pauling, 1942).

We noticed that the melting point (379–381 K) and the density of (III) (1.602 Mg m^{-3}) are within the ranges observed for polyazidopyrimidines (225–403 K and $1.55\text{--}1.72 \text{ Mg m}^{-3}$, respectively) and are due to inefficient packing caused by the azidomethyl groups. Polyazidopyrimidines and other organic polyazide-substituted compounds are characterized by high heats of formation and, therefore, are of particular interest for high-energy research (Petrie *et al.*, 1997). The endothermicity of a hydrocarbon increases upon addition of one azide group by about 87 kcal mol^{-1} , while the melting point is lowered

significantly upon addition of an azidomethyl group with no change or only a slight decrease in thermal stability. All these properties are crucial for the preparation of energetic ionic liquids (Ye *et al.*, 2006). Moreover, these compounds with little or no hydrogen content have also been reported to be excellent precursors for the synthesis of carbon nanotubes (Ye *et al.*, 2006), carbon nanospheres and carbon nitrides (Huynh *et al.*, 2004). Carbon nitrides are superhard materials with great potential for biological and technological applications. Their properties are determined to a large extent by the shape and size of these nanoparticles, but also by the relative nitrogen content. By using different heating protocols or special catalytic detonation procedures for explosive precursors, nanoparticles of different size ranges and morphologies have been prepared in high yields (Ye *et al.*, 2006; Huynh *et al.*, 2004).

In summary, the first crystal structure of a geminal diazide has been reported. The compound, 1,2,4,5-tetrakis(diazidomethyl)benzene, (III), proved to be more stable in the solid state than expected. The arrangement of the azide groups adopted by the molecule means that steric clashes are avoided. The compound is of potential interest as a precursor for the synthesis of carbon nanoparticles and/or nanosized carbon nitrides.

Experimental

For the preparation of (II) (see scheme in *Comment*), bromine (140 ml, 5.6 mol) was added dropwise over a period of 3–3.5 h to a solution of (I) (43.75 g, 0.325 mol) in CCl_4 (1.75 l) in a 2 l three-necked flask, equipped with a dropping funnel and a reflux condenser with a gas outlet, under mechanical stirring and under reflux. During the addition and for the total reaction time under reflux, the reaction mixture was irradiated with two 500 W halogen lamps. After 3 d, the white solid which formed was filtered off, washed with hot chloroform (250 ml) and dried *in vacuo* overnight (yield 224 g, 90%).

Caution: the operations listed below were performed under the safety conditions normally used for potentially explosive substances. For the preparation of (III), NaN_3 (0.2 g, 3.08 mmol) was added to a vigorously stirred solution of (II) (196 mg, 0.26 mmol) in dimethylformamide (15 ml) at room temperature. The light-protected mixture was heated to 343 K for 4 h. After cooling to room temperature, the turbid solution was poured into cold water (250 ml) and extracted with dichloromethane ($3 \times 100 \text{ ml}$). The combined organic layers were washed with water ($3 \times 100 \text{ ml}$) and then dried with anhydrous MgSO_4 . The solvent was removed under reduced pressure to give the crude product as colourless crystals, which were recrystallized from acetone (yield 109 mg, 91%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.90 (s, 2ArH), 6.09 (s, 4ArCH). Crystals of (III) of X-ray diffraction quality were grown from hexane at 249 K over a period of 4–5 h.

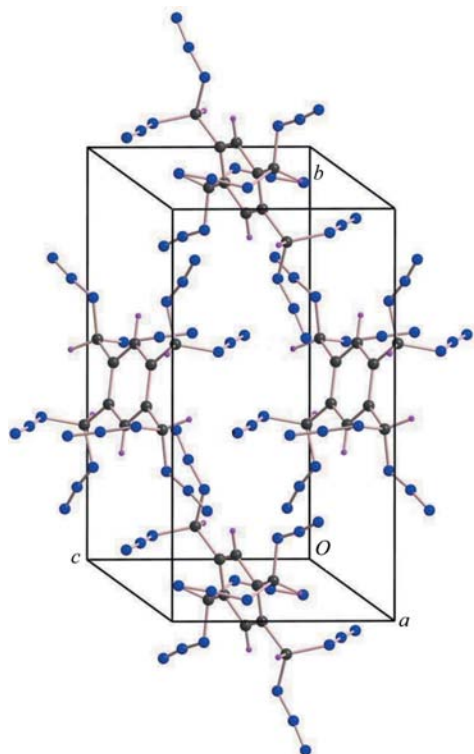


Figure 2
A view of the packing of (III), showing the contents of the unit cell.

Crystal data

$\text{C}_{10}\text{H}_6\text{N}_4$	$V = 954.40 (14) \text{ \AA}^3$
$M_r = 462.39$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.2393 (9) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 14.3799 (13) \text{ \AA}$	$T = 100 \text{ K}$
$c = 7.5145 (5) \text{ \AA}$	$0.35 \times 0.10 \times 0.10 \text{ mm}$
$\beta = 107.069 (2)^\circ$	

Data collection

Bruker X8 APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.948$, $T_{\max} = 0.978$

7716 measured reflections
2788 independent reflections
2019 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.110$
 $S = 1.02$
2788 reflections

154 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C2—C5	1.3939 (19)	C3—C5 ⁱ	1.3924 (18)
C2—C3	1.4020 (19)		
C5—C2—C3	119.56 (12)	C5 ⁱ —C3—C2	119.16 (12)
C5—C2—C1	120.11 (12)	C5 ⁱ —C3—C4	120.70 (12)
C3—C2—C1	120.24 (12)	C2—C3—C4	120.07 (12)

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

H atoms were placed at calculated positions and refined using a riding model, with C—H distances of 0.95 (aromatic) and 1.00 \AA (methine), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3112). Services for accessing these data are described at the back of the journal.

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