Crystal Structure of 1,4-Bis(2-iodo-4,5-dimethylphenyl)-1,3-butadiyne

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1,4-Bis(2-iodo-4,5-dimethylphenyl)-1,3-butadiyne has been synthesized and structurally characterized by X-ray crystallography. Its crystal structure is triclinic with the space group $P\bar{1}$ and $Z = 1$. The cell parameters are $a = 7.387(4)\text{\AA}$, $b = 7.832(4)\text{\AA}$, $c = 9.408(5)\text{\AA}$, $\alpha = 66.32(2)^\circ$, $\beta = 78.75(3)^\circ$, $\gamma = 64.38(3)^\circ$, and $V = 449.3(4)\text{\AA}^3$. The substituents between the terminal benzene rings have a coplanar *transoid*-configuration. The packing diagram shows the intermolecular van der Waals interactions of type I...I.

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In recent years, conjugated hydrocarbons, such as phenyleneethynylene oligomers and polymers, have received attention because they possess attractive electrical, optical, and nonlinear optical properties for molecular electronics.¹ Syntheses of acyclic and cyclic analogues with well-established cross-coupling reactions have been reported by many groups. For these reasons, our group began to synthesize various phenyleneethynylene derivatives. Here, we report on the synthesis and crystal structure of 1,4-bis(2-iodo-4,5-dimethylphenyl)-1,3-butadiyne (**1**).

1-(Trimethylsilylethynyl)-2-iodo-4,5-dimethylbenzene (0.95 mmol), prepared from 1,2-diiodo-4,5-dimethylbenzene,² was treated with sodium methoxide to give 1-ethynyl-2-iodo-4,5-dimethylbenzene (0.86 mmol). The oxidative homo-coupling of the ethynylbenzene with $\text{Cu}(\text{OAc})_2$ produced the title compound **1** as a pale tan solid (0.27 mmol). The chemical structure is shown in Fig. 1.

Single crystals for X-ray crystallography were obtained by slow evaporation from a toluene-THF solution at room temperature. The data were collected using a Rigaku/MS C Mercury CCD diffractometer at 296 K. The linear absorption coefficient (μ) for Mo K_α radiation was 35.0 cm^{-1} . A numerical absorption correction was applied, which resulted in transmission factors ranging from 0.35 to 0.58. The data were corrected for Lorentz and polarization effects. The structure determination was carried out using the program SIR92.³ All of the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated geometrically and were not refined. All calculations were performed using the teXsan program package.⁴ Crystal and experimental data are listed in Table 1. In Figs. 2 and 3, the molecule structure and a

Fig. 1 Chemical structure of the title compound.

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Table 1 Crystal and experimental data

Formula: $\text{C}_{20}\text{H}_{16}\text{I}_2$
Formula weight = 510.16
Crystal color, habit: colorless, prism
Crystal size: $0.45 \times 0.25 \times 0.15\text{ mm}$
Crystal system: triclinic
Space group: $P\bar{1}$ $Z = 1$
$T = 296\text{ K}$
$a = 7.387(4)\text{\AA}$
$b = 7.832(4)\text{\AA}$
$c = 9.408(5)\text{\AA}$
$\alpha = 66.32(2)^\circ$
$\beta = 78.75(3)^\circ$
$\gamma = 64.38(3)^\circ$
$V = 449.3(4)\text{\AA}^3$
$D_{\text{calc}} = 1.885\text{ g/cm}^3$
No. of reflections used = 1803 ($I > 2.00\sigma(I)$)
$2\theta_{\text{max}} = 55.0^\circ$ with Mo $K_\alpha(0.71069\text{ \AA})$
$R, R_w = 0.050, 0.148$
$(\Delta/\sigma)_{\text{max}} = 0.002$
$(\Delta\rho)_{\text{max}} = 1.24\text{ e\AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.94\text{ e\AA}^{-3}$
Measurement: Rigaku/MS C Mercury CCD
Program system: teXsan
Structure determination: direct method (SIR92)
Refinement: full-matrix least-squares

Fig. 2 ORTEP drawing of the title compound with atom labeling. The thermal ellipsoids are drawn at the 50% probability level. The spheres of the hydrogen atoms are drawn in an arbitrary scale. Symmetry operation: (*) $-x-1, -y-1, -z+2$.

Fig. 3 Packing diagram of the title compound. The I...I van der Waals interactions are shown by the dashed lines.

Table 2 Atomic coordinates and equivalent isotropic thermal parameters (B_{eq})

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
I(1)	0.02188(4)	-0.33283(4)	0.77288(3)	3.99(1)
C(1)	-0.1594(6)	-0.2803(6)	0.6001(4)	2.84(7)
C(2)	-0.3336(6)	-0.3193(6)	0.6399(5)	3.06(7)
C(3)	-0.4447(6)	-0.2828(7)	0.5190(5)	3.39(8)
C(4)	-0.3884(7)	-0.2078(6)	0.3627(5)	3.33(8)
C(5)	-0.2125(7)	-0.1699(6)	0.3261(5)	3.22(8)
C(6)	-0.0988(6)	-0.2097(6)	0.4462(5)	3.19(8)
C(7)	-0.3995(7)	-0.3968(7)	0.7962(5)	3.43(9)
C(8)	-0.4633(7)	-0.4629(7)	0.9263(5)	3.41(9)
C(9)	-0.5174(7)	-0.1677(7)	0.2377(6)	4.5(1)
C(10)	-0.1417(9)	-0.0927(8)	0.1605(5)	4.3(1)

$$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha).$$

Table 3 Selected bond lengths ($\text{\AA}$), bond angles ($^\circ$) and torsion angles ($^\circ$)

Atom	Atom	Distance	Atom	Atom	Distance
I(1)	C(1)	2.107(4)	C(1)	C(2)	1.396(6)
C(1)	C(6)	1.386(5)	C(2)	C(3)	1.395(6)
C(2)	C(7)	1.424(5)	C(3)	C(4)	1.400(6)
C(4)	C(5)	1.404(7)	C(4)	C(9)	1.507(7)
C(5)	C(6)	1.392(6)	C(5)	C(10)	1.505(5)
C(7)	C(8)	1.210(6)	C(8)	C(8*)	1.374(8)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
I(1)	C(1)	C(2)	120.9(3)	I(1)	C(1)	C(6)	118.2(3)
C(2)	C(1)	C(6)	121.0(4)	C(1)	C(2)	C(3)	117.5(4)
C(1)	C(2)	C(7)	123.1(4)	C(3)	C(2)	C(7)	119.3(4)
C(2)	C(3)	C(4)	122.4(4)	C(3)	C(4)	C(5)	118.8(4)
C(3)	C(4)	C(9)	119.8(4)	C(5)	C(4)	C(9)	121.4(4)
C(4)	C(5)	C(6)	119.1(4)	C(4)	C(5)	C(10)	121.5(4)
C(6)	C(5)	C(10)	119.5(4)	C(1)	C(6)	C(5)	121.2(4)
C(2)	C(7)	C(8)	176.7(5)	C(7)	C(8)	C(8*)	179.7(7)

Atom	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Atom	Angle
I(1)	C(1)	C(2)	C(3)	-179.3(3)	I(1)	C(1)	C(2)	C(7)	-0.4(6)
I(1)	C(1)	C(6)	C(5)	-179.4(3)	C(1)	C(2)	C(3)	C(4)	-0.7(7)
C(1)	C(2)	C(7)	C(8)	-177.0(9)	C(1)	C(6)	C(5)	C(4)	-1.8(7)
C(1)	C(6)	C(5)	C(10)	179.8(4)	C(2)	C(1)	C(6)	C(5)	1.9(7)
C(2)	C(3)	C(4)	C(5)	0.7(7)	C(2)	C(3)	C(4)	C(9)	-178.7(4)
C(3)	C(2)	C(1)	C(6)	-0.6(6)	C(3)	C(2)	C(7)	C(8)	1.0(9)
C(3)	C(4)	C(5)	C(6)	0.6(7)	C(3)	C(4)	C(5)	C(10)	178.9(4)
C(4)	C(3)	C(2)	C(7)	-179.6(4)	C(6)	C(1)	C(2)	C(7)	178.4(4)
C(6)	C(5)	C(4)	C(9)	180.0(4)	C(9)	C(4)	C(5)	C(10)	-1.7(7)

Symmetry operation: (*) $-x-1, -y-1, -z+2$

packing diagram are shown. The final positional parameters are given in Table 2, and selected bond lengths, bond angles and torsion angles are listed in Table 3.

This X-ray analysis reveals that half of the formula unit is crystallographically independent, and that **1** has a planar conformation with a maximum deviation of 0.04 $\text{\AA}$ for C(8) among all non-hydrogen atoms. The diyne unit shows linearity with the $\text{C}\equiv\text{C}-\text{C}$ angles [$\text{C}(2)-\text{C}(7)-\text{C}(8) = 176.7(5)^\circ$ and $\text{C}(7)-\text{C}(8)-\text{C}(8^*)(-x-1, -y-1, -z+2) = 179.7(7)^\circ$]. The bond lengths of $\text{C}(2)-\text{C}(7)$, $\text{C}(7)-\text{C}(8)$, and $\text{C}(8)-\text{C}(8^*)(-x-1, -y-1, -z+2)$ are 1.424(5), 1.210(6), and 1.374(8) $\text{\AA}$, respectively. They are typical bond lengths for 1,4-bis(aryl)-1,3-butadiyne.⁵ The other bond lengths and bond angles are within the expected ranges. Interestingly, the configuration of the substituents between the terminal benzene rings is *transoid*. The array would be led by intermolecular interactions. Thus, in the packing diagram, the neighboring molecules are packed close to each other by van der Waals interactions [$\text{I}(1)\cdots\text{I}(1^*)(-x, -y-1, -z+2) = 4.0529(5)\text{\AA}$]. The molecules almost form a plane. We could not observe effective $\pi-\pi$ interactions between the layers [$\text{C}(2)\cdots\text{C}(4)(-x-1, -y, -z+1) = 3.725(6)\text{\AA}$].

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References

1. Y. Geerts, G. Klärner, and K. Müllen, "Hydrocarbon Oligomers", in "Electronic Materials: The Oligomer Approach", ed. K. Müllen and G. Wegner, **1998**, Wiley-VCH, Weinheim, 1.
2. H. Suzuki, K. Nakamura, and R. Goto, *Bull. Chem. Soc. Jpn.*, **1966**, 39, 128.
3. A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, and G. Polidori, *J. Appl. Cryst.*, **1994**, 27, 435.
4. Crystal Structure Analysis Package, Molecular Structure Corporation, **1985 & 1999**.
5. M. M. Haley, M. L. Bell, J. J. English, C. A. Johnson, and T. J. R. Weakley, *J. Am. Chem. Soc.*, **1997**, 119, 2956.