

5,8-Diethynyl-2,3-diphenylquinoxaline

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Key indicators

Single-crystal X-ray study
 $T = 170$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.035
 wR factor = 0.081
Data-to-parameter ratio = 7.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{24}\text{H}_{14}\text{N}_2$, is a rigid-rod terminal dialkyne exhibiting extended π -conjugation through the heteroaromatic linker unit in the backbone. There is an intermolecular $\text{C}-\text{H}\cdots\text{N}$ close contact between one of the terminal alkyne groups and one of the N atoms, with a $\text{C}\cdots\text{N}$ distance of 3.374 (3) Å. Intermolecular interactions are also present between the alkynyl H atoms and $\text{C}\equiv\text{C}$ groups.

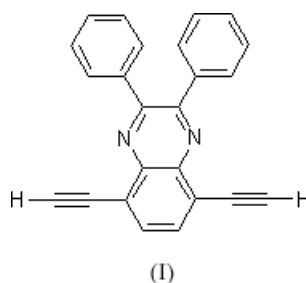
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Comment

In this paper, we report the structural characterization of the title compound, (I), which is the precursor of the platinum(II) diyne species, *trans*-[(Et_3P)₂(Ph)Pt— $\text{C}\equiv\text{C}$ —*R*— $\text{C}\equiv\text{C}$ —Pt(Ph)(Et_3P)₂] (*R* is 2,3-diphenyl-quinoxaline-5,8-diyl; Khan *et al.*, 2002). Such diplatinum compounds form the building blocks for the rigid-rod organometallic polymer species, *trans*-[(Bu_3P)₂Pt— $\text{C}\equiv\text{C}$ —*R*— $\text{C}\equiv\text{C}$ —]_∞ (*R* is an aromatic or heteroaromatic linker unit), which are of interest due to the high level of conjugation exhibited along the polymer backbone, and the optical emission properties to which this gives rise (Wittmann *et al.*, 1994; Beljonne *et al.*, 1996; Younus *et al.*, 1998; Chawdhury *et al.*, 1998, 1999; Wilson *et al.*, 2000, 2001, 2002). The monomers and precursors to these species are studied as models of the molecular and electronic properties and structure–property relationships in the polyynes.



The structure of (I) exhibits three intermolecular contacts of interest. A $\text{C}-\text{H}\cdots\text{N}$ close contact between alkynyl atom H42 and N2 is found with a $\text{C42}\cdots\text{N2}$ distance of 3.374 (3) Å (Table 2). Also found are two contacts between the alkynyl H atoms and $\text{C}\equiv\text{C}$ triple bonds. The first involves the $\text{C71}\equiv\text{C72}$ triple bond and H72. The intermolecular distance between H72 and the $\text{C71}\equiv\text{C72}$ centroid (Cg1) is 2.73 Å, and the angle $\text{C72}-\text{H72}\cdots\text{Cg1}$ is 148°. The second interaction is longer and involves the $\text{C41}\equiv\text{C42}$ triple bond and H42. The intermolecular distance between H42 and the $\text{C41}\equiv\text{C42}$ centroid (Cg2) is 3.01 Å, and the angle $\text{C42}-\text{H42}\cdots\text{Cg2}$ is 147°.

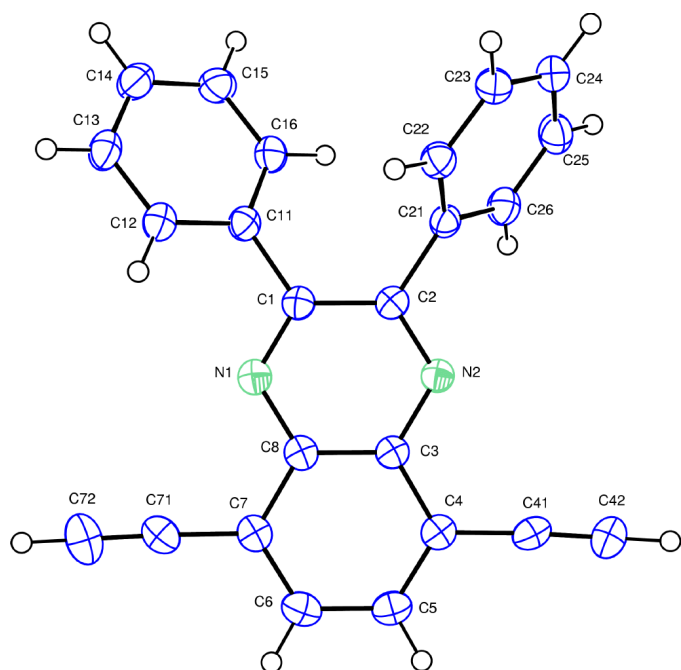


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The TMS-protected compound, 2,3-diphenyl-5,8-bis(trimethylsilyl)ethynylquinoxaline was synthesized by the following procedure. Catalytic amounts of CuI (10 mg, 0.05 mmol), Pd(OAc)₂ (10 mg, 0.04 mmol) and PPh₃ (30 mg, 0.11 mmol) were added to a solution of 2,3-diphenyl-5,8-diiodoquinoxaline (2.00 g, 3.74 mmol) in ^tPr₂NH/THF (50 ml, 1:4 v/v) under nitrogen. The solution was stirred for 0.5 h at room temperature, and then trimethylsilylethyne (0.92 g, 9.36 mmol) was added at room temperature to the vigorously stirred solution; during the addition, a white precipitate formed. The reaction mixture was stirred at reflux for 2 h and the completion of the reaction was determined by silica TLC and IR spectroscopy. After cooling to room temperature, the mixture was filtered to eliminate the ammonium salt and the solvent mixture was removed under vacuum. The residue was purified by silica column chromatography, eluting with dichloromethane–hexane (2:1 v/v), to yield an off-white solid. Recrystallization from hexane–dichloromethane led to snow-white crystals of the target compound in 78% yield (1.39 g).

The title compound was synthesized by the following procedure. 2,3-Diphenyl-5,8-bis(trimethylsilyl)ethynylquinoxaline (1.00 g, 2.1 mmol, see above) was proto-desilylated in THF/methanol (50 ml, 4:1 v/v), using KOH (0.26 g, 4.6 mmol). The reaction mixture was stirred for 2 h at room temperature, during which period IR and TLC showed that all the starting material had been deprotected. The solvent mixture was removed and the residue, dissolved in CH₂Cl₂, was subjected to silica column chromatography. The desired colourless band was collected with the aid of hexane–dichloromethane (1:1 v/v), to afford the target compound (0.63 g, 90% yield) as a colourless microcrystalline solid.

Crystal data

C₂₄H₁₄N₂
M_r = 330.37
Monoclinic, P2₁
a = 9.870 (3) Å
b = 5.8527 (9) Å
c = 14.888 (3) Å
β = 93.924 (9)°
V = 858.0 (3) Å³
Z = 2

D_x = 1.279 Mg m⁻³
Mo Kα radiation
Cell parameters from 3933 reflections
θ = 2.9–25.0°
μ = 0.08 mm⁻¹
T = 170 (2) K
Plate, colourless
0.23 × 0.09 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ and ωscans
2838 measured reflections
1654 independent reflections
1400 reflections with I > 2σ(I)

R_{int} = 0.025
θ_{max} = 25.1°
h = -11 → 11
k = -6 → 5
l = -17 → 17

Refinement

Refinement on F²
R[F² > 2σ²(F_o²) + (0.0417P)² + 0.0338P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.16 e Å⁻³
Δρ_{min} = -0.15 e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.041 (5)

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.323 (3)	C4—C41	1.436 (3)
N1—C8	1.365 (3)	C5—C6	1.396 (3)
N2—C2	1.324 (3)	C6—C7	1.382 (3)
N2—C3	1.367 (3)	C7—C8	1.428 (3)
C1—C2	1.441 (3)	C7—C71	1.437 (3)
C3—C8	1.406 (3)	C41—C42	1.191 (3)
C3—C4	1.431 (3)	C71—C72	1.177 (3)
C4—C5	1.379 (3)		
C42—C41—C4	177.4 (2)	C72—C71—C7	177.4 (3)
C8—N1—C1—C11	175.23 (17)	C2—N2—C3—C4	177.20 (18)
C3—N2—C2—C21	176.27 (18)	C1—N1—C8—C7	-176.81 (19)
C11—C1—C2—C21	8.5 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C42—H42...N2 ⁱ	0.95	2.64	3.374 (3)	135

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

Both aromatic and alkynyl H atoms were constrained as riding atoms fixed to the parent atoms, with distances of 0.95 Å in both cases. The isotropic displacement parameters were fixed at 1.2U_{eq} of that of the parent atom. Friedel pairs were merged for the final refinement, as the value of the absolute structure parameter (Flack, 1983) obtained upon refinement with Friedel pairs was -3 (3) using 2841 reflections.

Data collection: COLLECT (Nonius, 1997); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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