

1-[(*E*)-3-*sec*-Butyl-4-(4'-ethoxy-3,5-diethylbiphenyl-4-yl)diazenyl]phenoxy]hexadecaneMina R. Han,^{a*} Daisuke Hashizume^b and Masahiko Hara^a^aLocal Spatio-Temporal Functions Laboratory, Frontier Research System, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan, and^bMolecular Characterization Team, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Correspondence e-mail: minahjp@riken.jp

Key indicators

Single-crystal X-ray study

T = 90 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

Disorder in main residue

R factor = 0.047

wR factor = 0.128

Data-to-parameter ratio = 24.5

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

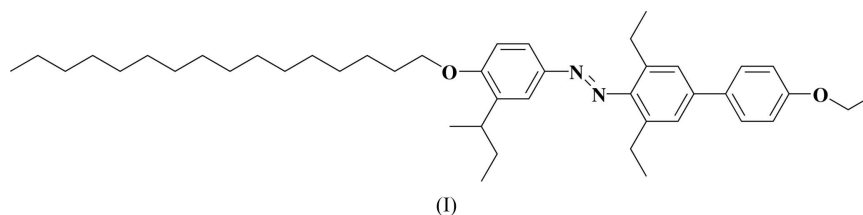
A Suzuki coupling reaction produced the title compound, $\text{C}_{44}\text{H}_{66}\text{N}_2\text{O}_2$, which consists of a photoisomerizable azobenzene unit coupled to a biphenyl group and a long alkyl chain. The molecule has a *trans* configuration with respect to the azo ($-\text{N}=\text{N}-$) group, and the long alkyl chain adopts a well ordered zigzag arrangement.

Received 15 June 2006

Accepted 19 June 2006

Comment

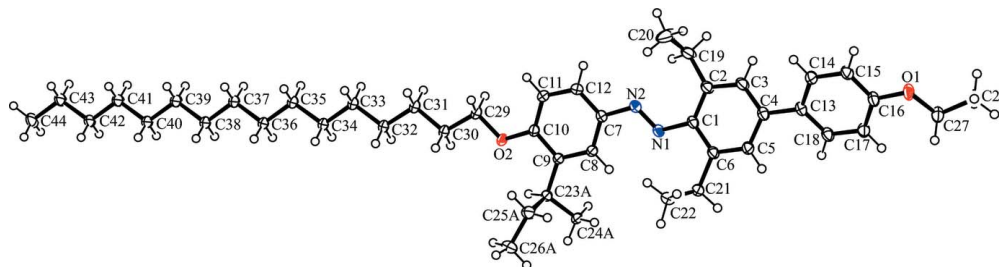
The title compound, (I), was prepared as part of our ongoing investigation (Han & Hara, 2005, 2006; Han *et al.*, 2006) of light-driven self-assembled aggregates of azobenzene derivatives. The spontaneous formation of spherical aggregates displayed unusual fluorescence enhancement, even though the isolated monomer itself was not fluorescent in dilute solution at ambient temperature. The X-ray crystallographic analysis of an azobenzene derivative can be of significance for understanding molecular and stacking structures in the solid state.



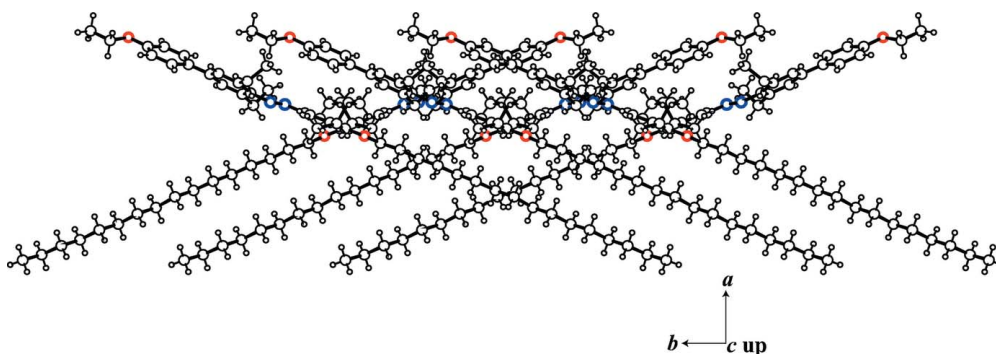
In the molecule of (I), the two benzene rings, C1–C6 and C7–C12, have a *trans* configuration with respect to the azo ($-\text{N1}=\text{N2}-$) functional group (Fig. 1). Selected bond distances and angles are given in Table 1. The N1–C1 and N2–C7 bond lengths are typical of significant single-bond character. The N1=N2 bond length is indicative of an acceptable double-bond length (Rau, 1973; Brown, 1966; Dickson & Ibers, 1972). The bond angles C12–C7–N2, O2–C10–C11, C2–C1–N1 and O1–C16–C17 deviate by 4–6° from the ideal value (120°) for sp^2 carbon. Similar deviation has been observed in many *trans*-azobenzene derivatives (Bouwstra *et al.*, 1983; Okuyama *et al.*, 1986). The *sec*-butyl group is disordered over two sites with occupancies of 0.633 (2) and 0.367 (2) for the major and minor components. The long alkyl chain adopts a *trans* zigzag conformation. The molecules stack along the *c* axis by the *c*-glide operation, forming a crossed layer structure parallel to the *bc* plane (Fig. 2).

Experimental

The precursor [4-(4'-bromo-2',6'-diethyl-phenylazo)-3-*sec*-butylphenoxy]hexadecane, of (I) was synthesized using the well known


Figure 1

A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The minor component of the *sec*-butyl group has been omitted for clarity.


Figure 2

The layer structure of (I) parallel to the *bc* plane.

diazonium coupling and subsequent Williamson reaction (Smith & March, 2001; Han & Hara, 2005). Compound (I) was prepared from the Suzuki coupling reaction of the precursor in the presence of palladium(0) catalyst (Miyaura & Suzuki, 1995). A catalytic amount of tetrakis(triphenylphosphine)palladium(0) was added to a solution of the precursor (2.46 g, 0.004 mol) in degassed DMF (50 ml). 4-Ethoxyphenylboronic acid (1.00 g, 0.006 mol), a solution of NaHCO₃ (1.68 g, 0.020 mol) in distilled water (30 ml) and toluene (20 ml) were added to the mixture solution. The reaction mixture was heated under reflux for 28 h with vigorous stirring. After the mixture was cooled to room temperature, water (50 ml) and ethyl acetate (50 ml) were added to the solution. The organic layer was separated and purified by silica gel column chromatography using hexane–dichloromethane (6:1) as eluent to afford (I) as an orange solid (yield 0.47 g, 18%). The crystals were obtained by slow evaporation of a dichloromethane–hexane solution (10:1) at ambient temperature.

Crystal data

C ₄₄ H ₆₆ N ₂ O ₂	<i>Z</i> = 4
<i>M_r</i> = 654.99	<i>D_x</i> = 1.086 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 22.0464 (3) Å	<i>μ</i> = 0.07 mm ⁻¹
<i>b</i> = 9.9446 (1) Å	<i>T</i> = 90 K
<i>c</i> = 18.8628 (3) Å	Needle, orange
<i>β</i> = 104.3701 (5)°	0.40 × 0.15 × 0.04 mm
<i>V</i> = 4006.14 (9) Å ³	

Data collection

Rigaku AFC-8 diffractometer with Saturn 70 CCD detector	11745 independent reflections
<i>ω</i> scans	9044 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: none	<i>R</i> _{int} = 0.025
22050 measured reflections	<i>θ</i> _{max} = 30.1°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.047
wR(*F*²) = 0.128
S = 1.03
 11745 reflections
 480 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 1.1001P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$$

Table 1

Selected geometric parameters (Å, °).

O1–C16	1.3734 (13)	N1–N2	1.2610 (12)
O1–C27	1.4334 (14)	N1–C1	1.4255 (13)
O2–C10	1.3642 (12)	N2–C7	1.4209 (13)
O2–C29	1.4344 (12)	C4–C13	1.4848 (14)
C10–O2–C29	118.82 (8)	C12–C7–N2	116.01 (9)
N2–N1–C1	115.39 (8)	O2–C10–C11	123.86 (9)
C2–C1–N1	125.85 (9)	O1–C16–C17	124.16 (10)
C1–N1–N2–C7	−178.05 (8)	C29–O2–C10–C9	−178.00 (9)
N2–N1–C1–C6	156.32 (9)	C3–C4–C13–C18	−146.73 (11)
N1–N2–C7–C12	−171.40 (10)	C5–C4–C13–C14	−148.69 (11)

H atoms, except for those in the *sec*-butyl group, were located in a difference map and were treated as riding atoms, with C–H = 1.00, 0.99, 0.98 and 0.95 Å for methyl, methylene, methine and aromatic groups, respectively, and with *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(methyl C). The *sec*-butyl group was found to be disordered over two sites, with occupancies of 0.633 (2) and 0.367 (2) for the major and minor components, respectively. Each C–C bond distance in the disordered *sec*-butyl group was restrained to be 1.530 (3) Å. The intramolecular

contact distances were also restrained to be 2.42 (1) and 2.55 (1) Å for C24A···C25A/C24B···C25B and C23A···C26A/C23B···C26B, respectively.

Data collection: *CrystalClear SM* (Rigaku/MSI Inc., 2005); cell refinement: *HKL2000* (Otwinowski & Minor, 1997); data reduction: *HKL2000*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bouwstra, J. A., Schouten, A. & Kroon, J. (1983). *Acta Cryst.* **C39**, 1121–1123.
- Brown, C. J. (1966). *Acta Cryst.* **21**, 146–152.
- Dickson, R. S. & Ibers, J. A. (1972). *J. Am. Chem. Soc.* **94**, 2988–2993.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Han, M. & Hara, M. (2005). *J. Am. Chem. Soc.* **127**, 10951–10955.
- Han, M. & Hara, M. (2006). *New J. Chem.* **30**, 223–227.
- Han, M. R., Hirayama, Y. & Hara, M. (2006). *Chem. Mater.* **18**, 2784–2786.
- Miyaura, N. & Suzuki, A. (1995). *Chem. Rev.* **95**, 2457–2483.
- Okuyama, K., Watanabe, H., Shimomura, M., Hirabayashi, K., Kunitake, T., Kajiyama, T. & Yasuoka, N. (1986). *Bull. Chem. Soc. Jpn.* **59**, 3351–3356.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
- Rau, H. (1973). *Angew. Chem. Int. Ed. Engl.* **12**, 224–235.
- Rigaku/MSI Inc. (2005). *CrystalClear SM*. Version 1.3.6. Rigaku/MSI Inc., 9009 New Trails Drive, The Woodlands, Texas, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Smith, M. B. & March, J. (2001). *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed. Hoboken, NJ: Wiley-Interscience.