

# Molecular structure and optical nonlinearity of 1,8-bis(ferrocenyl)-3-*t*-butyl-oct-3-ene-1,5,7-triynes

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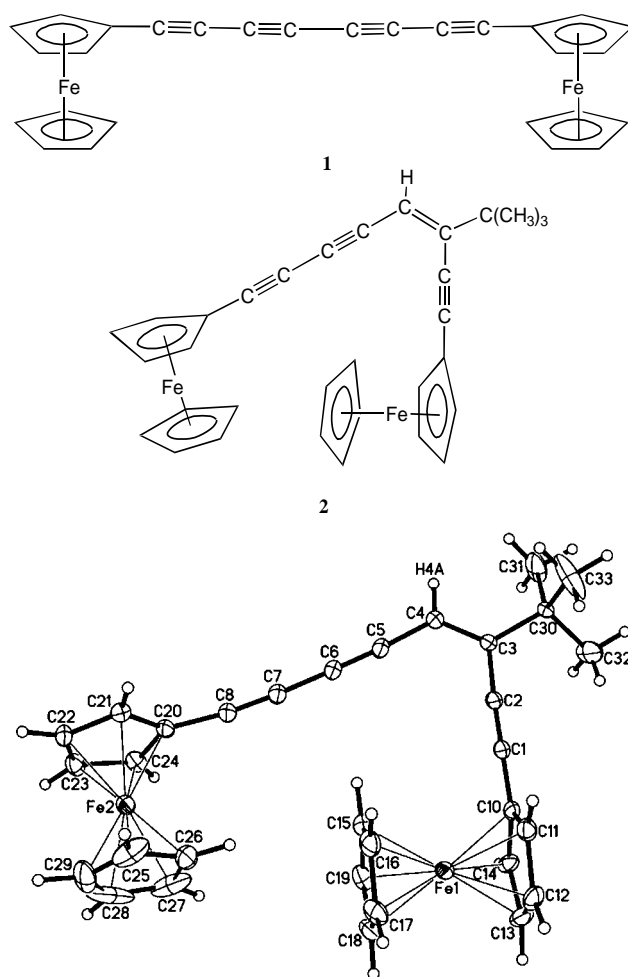
Interaction of 1,8-bis(ferrocenyl)-octatetrayne **1** with one equiv. of *t*-butyl lithium followed by treatment with water gave 1,8-bis(ferrocenyl)-3-*t*-butyl-oct-3-ene-1,5,7-triynes **2**. The solid-state structure of **2**, containing a bent carbon chain between two ferrocenes, has been determined. The nonlinear optical properties of **2** were also investigated.

**Keywords:** crystal structures, polyynes, enynes, ferrocenes, optical nonlinearity

Ferrocene is a well-known redox active material and it can be incorporated into metal polynyl complexes and polymers as a redox-active centre.<sup>1</sup> Research into these compounds has been developed as a key area of organometallic chemistry.<sup>2</sup> The polyynes with two end-capping ferrocenes usually have rigid-rod architectures and conjugated backbones which make them useful materials in the fields of linear and non-linear optics, liquid crystallinity and photovoltaic cells.<sup>3</sup> Synthetic routes to symmetrical ferrocenyl polyynes and related metal complexes have been extensively reported in recent years, however, of unsymmetrical compounds few have appeared in the literature.<sup>4</sup> Herein, we describe an addition reaction of **1**, 8-bis(ferrocenyl)-octatetrayne to give an unsymmetrical **2**, 8-bis(ferrocenyl)-3-*t*-butyl-oct-3-ene-1,5,7-triynes. The crystal structure and optical nonlinearity of the title compound are reported for the first time in this paper.

Treatment of 1,8-bis(ferrocenyl)-octatetrayne<sup>4</sup> (**1**) with an equivalent of *t*-butyl-lithium in hexane, followed by hydrolysis with a little water, resulted in the isolation of 1,8-bis(ferrocenyl)-3-*t*-butyl-oct-3-ene-1,5,7-triynes (**2**) in 35% yield after chromatography. Efforts to isolate other addition products in a few close bands were unsuccessful. The obvious absorption bands at 2202 and 2210 cm<sup>-1</sup> in the solution IR spectrum of **2** in CH<sub>2</sub>Cl<sub>2</sub> are attributed to the characteristic C≡C triple bond vibrations. The FAB mass spectrum of **2** displays molecular ion peak corresponding to [M - 1]<sup>+</sup>. A single crystal structure analysis showed a bent carbon-chain turned at a C=C double bond formed by *cis*-addition of a *t*-butyl group and a hydrogen atom. The ORTEP drawing of **2** is shown in Fig. 1. The two angles at carbons of the C=C double bond are 120.1(3) and 124.0(4)° for C2–C3–C4 and C3–C4–C5, respectively. The formal bond C3–C4 has a distance of 1.336(5) Å, which is typical for a double bond. The average length of the three triple bonds is 1.193(5) Å, as would be expected for an isolated –C≡C– length.<sup>5</sup> The C6–C7 single bond is 1.376(6) Å, which is in the range normally observed for *sp*-hybridised carbon–carbon distance; comparably, two single bonds relating with the formal double bond in the bend chain [C4–C5 = 1.425(6) Å and C2–C3 = 1.420(5) Å] are compared to the expected value 1.42 Å for a single bond between *sp*- and *sp*<sup>2</sup>-hybridised carbon atoms.<sup>6</sup> Similarly, the single bond C3–C30 has a relatively long distance of 1.533(5) Å due to the two *sp*<sup>2</sup>- and *sp*<sup>3</sup>-hybridised carbon atoms. The Fe1 ferrocenyl group has an almost perfectly eclipsed geometry with its rings inclined by *ca* 0.5°, whilst that for Fe2 has *ca* 15° stagger with rings inclined by *ca* 2°. The separation between two iron atoms is 7.057 Å.

Compound **2** was dissolved in toluene with a non-saturation concentration of 2.2 × 10<sup>-3</sup> mol/dm<sup>3</sup> and put in a 1 mm thick glass cell for optical limiting measurements. The linear transmissivity of the sample is 78% at 532 nm, corresponding



**Fig. 1** Molecular structure of the title compound (**2**). Displacement ellipsoids are drawn at the 50% probability level.

**Table 1** Selected bond lengths and angles in compound **2**

Bond	Length (Å)	Bonds	Angle (°)
Fe1–C (Cp)	2.029(3)*	C10–C1–C2	179.8(4)
Fe2–C (Cp)	2.015(5)*	C1–C2–C3	176.8(4)
C10–C1	1.433(5)	C2–C3–C4	120.1(3)
C1–C2	1.192(5)	C3–C4–C5	124.0(4)
C2–C3	1.420(5)	C4–C5–C6	176.2(5)
C3–C4	1.336(5)	C5–C6–C7	179.0(5)
C4–C5	1.425(6)	C6–C7–C8	177.1(5)
C5–C6	1.194(6)	C7–C8–C20	173.9(5)
C6–C7	1.376(6)	C4–C3–C30	122.6(3)
C7–C8	1.193(5)	C2–C3–C30	117.2(3)
C8–C20	1.428(6)		
C3–C30	1.533(5)		

\*Mean value.

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to a ground-state absorption cross section of  $1.68 \times 10^{-18} \text{ cm}^2$ . For comparison, a solution of  $\text{C}_{60}$  in toluene solution with the same linear transmissivity was measured under the same experimental conditions.<sup>7</sup> To obtain the nonlinear optical parameters we employed a  $z$  scan theory that considers effective nonlinearity of third-order nature only:  $\alpha = \alpha_0 + \alpha_2 I$  and  $n = n_0 + n_2 I$ , where  $\alpha_0$  and  $\alpha_2$  are the linear and nonlinear absorption coefficient;  $n_0$  and  $n_2$  are the linear and nonlinear refractive index, respectively; and  $I$  is the irradiance of the laser beam within the sample.<sup>8</sup> The peak fluence for  $z$  scan is about  $1.5 \text{ J/dm}^2$  both in ns  $z$  scans. The  $\alpha_2$  and  $n_2$  value extracted from 7 ns experimental data are  $124 \text{ cm/GW}$  and  $6.53 \times 10^{-5} \text{ cm}^2/\text{GW}$ , respectively. Fig. 2 represents the observed variation of output fluence with input fluence for the title compound and  $\text{C}_{60}$  in toluene. It is clear that the optical limiting capability of the title compound is compatible to that of  $\text{C}_{60}$  with the same linear transmissivity. The optical limiting threshold, defined as the input fluence at which that transmissivity is 78% of the linear transmissivity, is about  $0.54 \text{ J/cm}^2$  for the ferrocene-polyynes compound and about  $0.50 \text{ J/cm}^2$  for  $\text{C}_{60}$ .<sup>9</sup>

In summary, a unsymmetrical ferrocene-polyynes compound, 1,8-bis(ferrocenyl)-3-tert-butyl-oct-3-ene-1,5,7-triynes has been isolated and structurally characterized by X-ray diffraction. With nanosecond-duration laser pulses, the limiting threshold for the title compound is comparable to that of  $\text{C}_{60}$ , which makes ferrocene-polyynes promising candidates for optical limiting application.

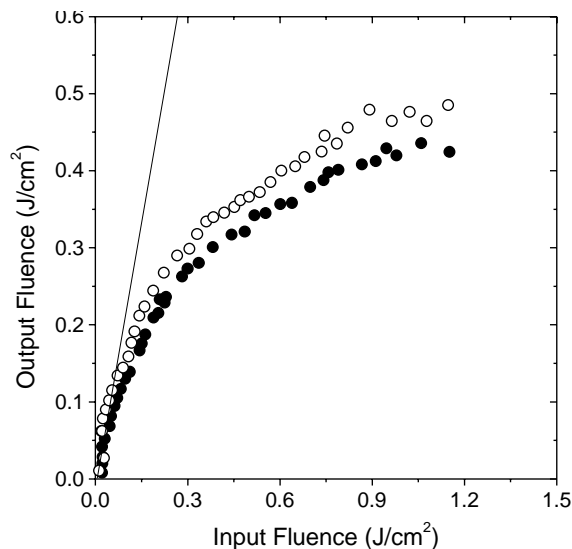
## Experimental

Infrared spectrum was recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, mass spectrum on a Finnigan TSQ 7000 spectrometer. NMR spectrum was recorded on a Bruker ALX 300 spectrometer operating at 300 MHz for  $^1\text{H}$ . Chemical shifts ( $\delta$ , ppm) were reported with reference to  $\text{SiMe}_4$ .

To 1,8-bis(ferrocenyl)octatetrayne<sup>4</sup> (**1**) (22.0 mg, 0.0472 mmol) in hexane (10 ml) at  $-40^\circ\text{C}$  was added one equiv. of *t*-butyl lithium in hexane (1.6 mmol/ml, 0.03 ml). The mixture was stirred for 1 h and then half a drop of water was added. The solution was allowed to warm to room temperature after 2 h. The crude product was chromatographed on an alumina column using hexane/diethyl ether (4:1) as the eluting solvent. The bright orange-brown crystalline product of **2** was isolated from hexane as the first band in 35 % yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  1.18 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 4.16 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.21 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.49 (t, 4H,  $\text{C}_5\text{H}_4$ ), 4.53 (t, 4H,  $\text{C}_5\text{H}_4$ ), 5.72 (s, 1H, CH). MS (FAB):  $m/z$  523 ( $\text{M}^+ - 1$ ). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{C})$ , 2202 (w), 2210 (w). Anal. Calcd. for  $\text{C}_{32}\text{H}_{28}\text{Fe}_2$ : C, 73.3; H, 5.34%. Found: C, 72.8; H, 5.31%.

Orange crystals suitable for X-ray crystallography were isolated by evaporation of a hexane solution of the title compound in air at  $4^\circ\text{C}$ . Intensity data were collected at 296 K on a Bruker SMART Apex CCD diffractometer for a plate  $0.30 \times 0.15 \times 0.04 \text{ mm}^3$ . Crystal data:  $\text{C}_{32}\text{H}_{28}\text{Fe}_2$ ,  $M = 524.24$ , triclinic,  $P-1$ ,  $a = 10.8336(6)$ ,  $b = 10.9552(6)$ ,  $c = 12.9320(7) \text{ \AA}$ ,  $\alpha = 67.591(1)^\circ$ ,  $\beta = 84.480(1)^\circ$ ,  $\gamma = 64.053(1)^\circ$ ,  $U = 1271.29(12) \text{ \AA}^3$ ,  $Z = 2$ ,  $F(000) = 544$ ,  $\mu = 1.159 \text{ mm}^{-1}$ ,  $D_c = 1.37 \text{ g cm}^{-3}$ , 4478 data ( $\theta_{\text{max}} = 25.02^\circ$ ), refinement converged to  $R1 = 0.080$ ,  $wR2 = 0.129$ , and  $S = 0.996$  for all 4478 reflections and 307 parameters; for the 3057 independent reflections with  $I \geq 2.0\sigma(I)$ ,  $R1 = 0.051$ . Programs used: SAINT,<sup>10</sup> SADABS,<sup>11</sup> SHELXTL-97.<sup>12</sup> CCDC deposition number: 234030.

A toluene solution of  $2.2 \times 10^{-3} \text{ mol dm}^{-3}$  of **2** was placed in a 1 mm quartz cell for optical measurements. The optical limiting characteristics along with nonlinear absorption and refraction was investigated with a linearly polarised laser light ( $\lambda = 532 \text{ nm}$ , pulse width = 7 ns) generated from a Q-switched and frequency-doubled Nd:YAG laser. The spatial profiles of the optical pulses were nearly Gaussian. The laser beam was focused with a 25 cm focal length focusing mirror. The radius of the laser beam waist was measured to



**Fig. 2** Comparison of optical limiting properties of the title compound **2** (○) and  $\text{C}_{60}$  (●) in toluene with the same linear transmissivity of 78% at 532 nm.

be  $30 \pm 5 \mu\text{m}$  (half-width at  $1/e^2$  maximum in irradiance). The incident and transmitted pulse energy were measured simultaneously by two Laser Precision detectors (RJP-735 energy probes) communicating to a computer via an IEEE interface,<sup>8,13</sup> while the incident pulse energy was varied by a Newport Com. Attenuator. The interval between the laser pulses was chosen to be 1 s to avoid the influence of thermal and long-term effects.<sup>14</sup>

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