

## Complex stabilization of sesquifulvalene derivatives

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### Abstract

Template syntheses of sesquifulvalenes (**1**) and (**2**) lead to air-stable complexes [(**1**)Mn(CO)<sub>3</sub>]BF<sub>4</sub> (**6**) and [(**2**)Mn(CO)<sub>3</sub>]BF<sub>4</sub> (**9**) as potential candidates for non-linear optical applications; the X-ray structure of **6** is reported.

**Keywords:** Sesquifulvalenes; Manganese; Non-linear Optics; Crystal structure

### 1. Introduction

The development and synthesis of new materials with large optical non-linearities has become an important area of research [1]. With a few exceptions [2], the majority of organic compounds exhibiting large second harmonic generation (SHG) efficiencies are polarizable dipolar molecules with a  $\pi$ -conjugated electron donor/acceptor arrangement. These requirements are fulfilled by aromatic sesquifulvalene (**1**), and substantial hyperpolarizabilities have been predicted for sesquifulvalene derivatives based on theoretical calculations [3]. However, the instability [4] of **1** does prevent applications in optical device technology, and to our knowledge experimental studies of the non-linear optical properties of **1** and derivatives have not been undertaken. In contrast, complexation of **1** by transition metal fragments should lead to new organometallic compounds, which are currently receiving considerable attention in the field of non-linear optics [5]. We have therefore initiated a program to synthesize stable organometallic complexes of sesquifulvalene (**1**) and its cumulogous and vinylogous derivatives **2** and **3** (Fig. 1) as potential candidates for non-linear optical applications.

As early as 1967 Cais and Eisenstadt reported on the synthesis of metal complexes of the sesquifulvalene and calicene systems and isolated stable and intensely coloured complexes such as [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(**1**)]BF<sub>4</sub> by

reacting ferrocene with tropylium fluoroborate [6]. Independently of our approach, Heck et al. have recently synthesized ferrocene derivatives of **1**, **2** and **3** and have already measured very promising first molecular hyperpolarizabilities [7]. Our first efforts were directed towards the development of cymantren derivatives and here we wish to report on the template syntheses of **1** and **2** at the Mn(CO)<sub>3</sub> metal fragment.

### 2. Results and discussion

CpMn(CO)<sub>3</sub> (**4**) reacts with *tert*-butyllithium at –78 °C to give ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Li)Mn(CO)<sub>3</sub> [8], which easily adds to the tropylium ring upon treatment with (C<sub>7</sub>H<sub>7</sub>)BF<sub>4</sub>. Complex **5** is obtained after chromatographic work-up as yellow crystals. Hydride abstraction is best achieved with triphenylcarbenium tetrafluoroborate, (Ph<sub>3</sub>C)BF<sub>4</sub>, and complex [(**1**)Mn(CO)<sub>3</sub>]BF<sub>4</sub> (**6**) is formed almost instantly in CH<sub>2</sub>Cl<sub>2</sub> solution (Scheme 1).

As shown in Scheme 2, the synthesis of the Mn(CO)<sub>3</sub> complex of the higher cumulog follows the same route employing ( $\eta^5$ -HC≡CC<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>3</sub> (**7**) instead of CpMn(CO)<sub>3</sub>. Lithiation and consecutive reaction with tropylium tetrafluoroborate yields complex **8**, which is converted into cationic **9** by loss of one hydride (Scheme 2).

The IR spectra of **5** and **6** (in CH<sub>2</sub>Cl<sub>2</sub>) exhibit two CO absorptions which can be assigned to the symmetric (A<sub>1</sub>) and asymmetric (E) stretching modes expected for local C<sub>3v</sub> symmetry at the metal centre (Table 1). Calculation of the CO force constants by the method of

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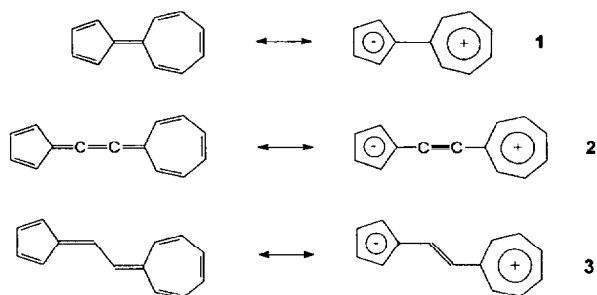
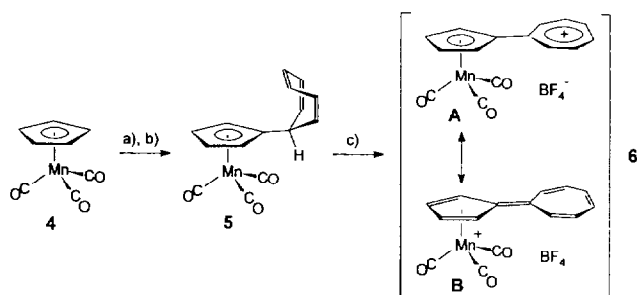


Fig. 1. Canonical presentations for sesquifulvalene derivatives.

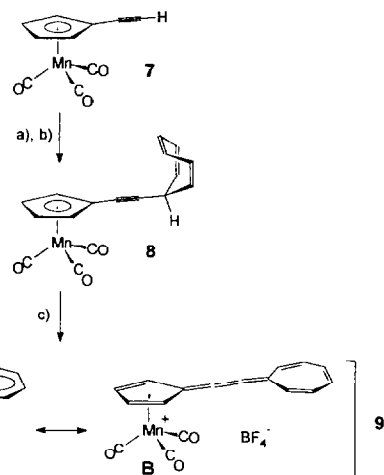
Cotton and Kraihanzel [9] ( $5$   $k(\text{CO}) = 1555 \text{ N m}^{-1}$ ;  $6$   $k(\text{CO}) = 1596 \text{ N m}^{-1}$ ) clearly shows that the sesquifulvalene ligand in **6** is a far better  $\pi$ -acceptor than the substituted cyclopentadienyl ring in **5**, thus indicating the formation of a  $\pi$ -conjugated ligand system in **6**. Comparison of the IR data of complexes **8** and **9** follows the same trend although the increase in  $k(\text{CO})$  is less pronounced (Table 1).

Complexes **6** and **9** are air-stable, intensely coloured compounds. They show strong solvatochromic behaviour and their ultraviolet visible spectra are markedly affected by varying the solvent, which is usually a good indication of possible NLO activity [5,10]. All spectra exhibit three strong absorptions, with the lowest energy band  $\lambda_{\text{max}}$  (Table 1) being most strongly shifted upon changing the solvent from methylene chloride to acetonitrile ( $\Delta\tilde{\nu}(\mathbf{6}) = -1090 \text{ cm}^{-1}$ ,  $\Delta\tilde{\nu}(\mathbf{9}) = -2230 \text{ cm}^{-1}$ ). Owing to these hypsochromic shifts (negative solvatochromic behaviour) we assign the lowest energy transition in these systems to the  $\pi$  to  $\pi^*$  CT transition [11], which is *approximately* (!) represented by the canonical forms **A** (ground state) and **B** (excited state) shown in Scheme 1 for **6** and Scheme 2 for **9**. Usually, extension of the conjugation path between an electron donor and acceptor increases the polarizability significantly [1,5], which is in agreement with the observation that **9** has a stronger solvatochromic behaviour than **6**.

The X-ray crystal structure of  $\mathbf{6} \cdot 0.5\text{CH}_2\text{Cl}_2$  is depicted in Fig. 2. The asymmetric unit contains two independent molecules. The Cp rings are not exactly coplanar with the seven-membered rings (dihedral an-



Scheme 1. (a)  $^1\text{BuLi}$ , THF,  $-78^\circ\text{C}$ , 30 min; (b)  $(\text{C}_7\text{H}_7)\text{BF}_4$ , THF,  $-78^\circ\text{C}$ – $20^\circ\text{C}$ , 90 min; (c)  $(\text{PH}_3\text{C})\text{BF}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ , 45 min.



Scheme 2. (a)  $^1\text{BuLi}$ , THF,  $-78^\circ\text{C}$ , 30 min; (b)  $(\text{C}_7\text{H}_7)\text{BF}_4$ , THF,  $-78^\circ\text{C}$ – $20^\circ\text{C}$ , 90 min; (c)  $(\text{PH}_3\text{C})\text{BF}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ , 60 min.

gles of  $10.2(2)$  and  $2.1(1)^\circ$ ) with inter-ring bond distances of  $1.466(6)$  and  $1.456(6) \text{ \AA}$ , slightly shorter than expected for a  $\text{C}(\text{sp}^2)\text{--}\text{C}(\text{sp}^2)$  single bond [12]. The intra-ring  $\text{C--C}$  bond distances do not alternate significantly, thus indicating that the solid state structure is best described as a cymantrenyltropylium salt by the canonical form **A** (Scheme 1).

On the basis of our results  $\text{Mn}(\text{CO})_3$  stabilized sesquifulvalene derivatives are promising candidates with potentially large first molecular hyperpolarizabilities. Furthermore, this system offers the possibility of tuning the electronic and optical properties, for instance by introducing phosphine ligands, which is easily achieved by carbonyl substitution reactions. This will

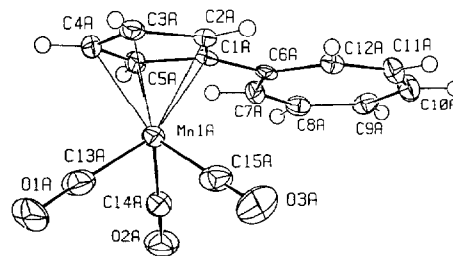


Fig. 2. ORTEP drawing of one cation of **6**. The asymmetric unit contains two independent molecules of **6** and one molecule of methylene chloride. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): molecule A [molecule B]  $\text{Mn1--C1}$  2.126(4) [2.135(4)],  $\text{Mn1--C2}$  2.128(5) [2.135(3)],  $\text{Mn1--C3}$  2.147(5) [2.150(4)],  $\text{Mn1--C4}$  2.135(4) [2.145(5)],  $\text{Mn1--C5}$  2.128(3) [2.126(5)],  $\text{Mn1--C13}$  1.800(6) [1.784(5)],  $\text{Mn1--C14}$  1.790(5) [1.800(4)],  $\text{Mn1--C15}$  1.793(4) [1.792(5)],  $\text{C1--C2}$  1.432(5) [1.431(6)],  $\text{C1--C5}$  1.442(6) [1.453(5)],  $\text{C1--C6}$  1.466(6) [1.456(6)],  $\text{C2--C3}$  1.414(7) [1.411(7)],  $\text{C3--C4}$  1.418(5) [1.413(6)],  $\text{C4--C5}$  1.389(6) [1.404(7)],  $\text{C6--C7}$  1.408(5) [1.408(6)],  $\text{C6--C12}$  1.409(6) [1.416(5)],  $\text{C7--C8}$  1.371(6) [1.381(7)],  $\text{C8--C9}$  1.392(7) [1.393(6)],  $\text{C9--C10}$  1.376(6) [1.371(6)],  $\text{C10--C11}$  1.390(6) [1.394(7)],  $\text{C11--C12}$  1.377(7) [1.378(7)],  $\text{C13--O1}$  1.140(7) [1.152(6)],  $\text{C14--O2}$  1.155(6) [1.148(5)],  $\text{C15--O3}$  1.152(5) [1.147(6)]; internal ring angles  $\text{C}_5$   $106.2(4)$ – $108.8(4)$  [ $105.8(4)$ – $109.1(3)$ ],  $\text{C}_7$   $124.3(4)$ – $130.7(4)$  [ $124.2(4)$ – $130.2(4)$ ].

Table 1  
IR and UV/vis data for Mn(CO)<sub>3</sub> complexes

Compound	$\bar{\nu}(\text{CO}) (\text{cm}^{-1})$		$k(\text{CO}) (\text{N m}^{-1})$	$\lambda_{\text{max}} (\text{nm})$		$\Delta\bar{\nu} (\text{cm}^{-1})$
	A <sub>1</sub>	E		CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN	
<b>5</b>	2020	1933	1555			
<b>6</b>	2035	1964	1596	540	510	1090
<b>8</b>	2025	1938	1563			
<b>9</b>	2030	1952	1580	550	490	2230

increase the electron density at the metal centre with the cymantrenyl side becoming a stronger electron donor. The use of readily available chiral phosphines will lead to optically active compounds which crystallize in non-centrosymmetric space groups and thus fulfill a crucial requirement for the observation of macroscopic NLO effects [13].

### 3. Experimental details

All operations were performed in an atmosphere of dry argon using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on a Bruker AM 250 (250 MHz) instrument. Infrared spectra were taken on a Perkin-Elmer 983 instrument in KBr. Elemental analyses (C, H, N) were performed at the Freie Universität Berlin on a Heraeus CHN-Rapid elemental analyzer. Mass spectra were recorded on a Varian MAT 711 instrument and UV/vis spectra on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer.

**7** was prepared according to the method of Stille [14].

#### 3.1. [(2,4,6-Cycloheptatrien-1-yl)- $\eta^5$ -cyclopentadienyl]tricarbonyl-manganese(I) (**5**)

A solution of **4** (2.00 g, 9.8 mmol) in 20 ml of THF was treated dropwise with *tert*-butyllithium (6.0 ml of a 1.7 M solution in cyclohexane, 10.2 mmol) at  $-78^\circ\text{C}$ . After stirring for 30 min cycloheptatrienylium tetrafluoroborate (1.75 g, 9.8 mmol) was added as a solid to the orange solution. The mixture was allowed to warm to room temperature and stirring was continued for 1 h. The reaction mixture was then refluxed for an additional 45 min. After removal of the solvent in vacuo, the crude product was purified chromatographically on silica (4% H<sub>2</sub>O) with petrolether. Evaporation of the solvent afforded **5** as a yellow solid, 1.50 g (52%), m.p. 39–41  $^\circ\text{C}$ . Anal. Found: C, 60.99; H, 3.69. C<sub>15</sub>H<sub>11</sub>MnO<sub>3</sub> Calc.: C, 61.24; H, 3.77%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  6.68 (t, 2H, C<sub>7</sub> CH); 6.24 (dm, 2H, C<sub>7</sub> CH); 5.24 (m, 2H, C<sub>7</sub> CH); 4.86 (t, 2H, C<sub>5</sub> CH); 4.76 (t, 2H, C<sub>5</sub> CH); 2.48 (t, 1H, C<sub>7</sub> CH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.90 MHz):  $\delta$  224.8 (CO); 131.2 (C<sub>7</sub> CH); 125.0 (C<sub>7</sub> CH); 124.4 (C<sub>7</sub> CH); 108.4 (C<sub>5</sub> C-1); 81.8 (C<sub>5</sub> CH); 81.7 (C<sub>5</sub> CH); 37.7 (C<sub>7</sub> C-1) ppm. IR

(CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2020 (s, CO); 1933 (vs, CO) cm<sup>-1</sup>. MS (EI, 70 ev): *m/z* (%) 294 (8) [M<sup>+</sup>]; 210 (100) [(M-3CO)<sup>+</sup>]; 155 (15) [(M-3CO-Mn)<sup>+</sup>]; 132 (47) [(M-3CO-C<sub>6</sub>H<sub>6</sub>)<sup>+</sup>]; 55 (38) [Mn<sup>+</sup>].

#### 3.2. Cymantrenylcycloheptatrienylium tetrafluoroborate (**6**)

To a solution of **5** (1.0 g, 3.4 mmol) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> was added triphenylcarbenium tetrafluoroborate (1.12 g, 3.40 mmol) as a solid. The solution immediately turned red and stirring was continued for 30 min. After addition of 100 ml of diethyl ether the red crystalline precipitate was isolated by filtration and washed with diethyl ether. Crystallization from methylene chloride afforded **6** as red–purple crystals, 640 mg (50%), m.p. 191–193  $^\circ\text{C}$ . Unsatisfactory elemental analyses were obtained due to partial loss of solvent from crystalline **6**·0.5CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 250 MHz):  $\delta$  8.92 (m, 2H, C<sub>7</sub> CH); 8.78 (m, 4H, C<sub>7</sub> CH); 6.12 (t, 2H, C<sub>5</sub> CH); 5.44 (t, 2H, C<sub>5</sub> CH) ppm. <sup>13</sup>C NMR (CD<sub>3</sub>CN, 62.90 MHz):  $\delta$  223.2 (CO); 167.1 (C<sub>7</sub> C-1); 153.0 (C<sub>7</sub> CH); 149.2 (C<sub>7</sub> CH); 93.4 (C<sub>5</sub> C-1); 89.4 (C<sub>5</sub> CH); 88.8 (C<sub>5</sub> CH) ppm. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2035 (s, CO); 1964 (vs, CO) cm<sup>-1</sup>. MS (FAB, positive ions): *m/z* (%) 293 (84) [M<sup>+</sup>]; 209 (35) [(M-3CO)<sup>+</sup>]; 55 (49) [Mn<sup>+</sup>]. UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  (log  $\epsilon$ ) 265 (4.2); 356 (4.0); 540 (3.1) nm. UV/vis (CH<sub>3</sub>CN):  $\nu$  (log  $\epsilon$ ) 260 (4.2); 346 (4.0); 510 (3.7) nm.

#### 3.3. {[(2,4,6-Cycloheptatrien-1-yl)ethynyl]- $\eta^5$ -cyclopentadienyl}tricarbonyl-manganese(I) (**8**)

A solution of **7** (2.44 g, 10.7 mmol) in 20 ml of THF was treated dropwise with *tert*-butyllithium (7.0 ml of a 1.55 M solution in cyclohexane, 10.9 mmol) at  $-78^\circ\text{C}$ . After stirring for 30 min cycloheptatrienylium tetrafluoroborate (1.93 g, 10.9 mmol) was added as a solid to the orange solution. The mixture was allowed to warm to room temperature and stirring was continued for 90 min. The reaction mixture was then refluxed for an additional 60 min.

After removal of the solvent in vacuo, the crude product was purified chromatographically on silica (4% H<sub>2</sub>O) with petrolether. Evaporation of the solvent afforded **5** as a yellow solid, 1.1 g (33%), m.p. 53  $^\circ\text{C}$ .

Anal. Found: C, 64.37; H, 3.45.  $C_{17}H_{11}MnO_3$  Calc.: C, 64.17; H, 3.48%.  $^1H$  NMR ( $CDCl_3$ , 250 MHz):  $\delta$  6.68 (t, 2H,  $C_7$  CH); 6.20 (dm, 2H,  $C_7$  CH); 5.36 (m, 2H,  $C_7$  CH); 4.98 (t, 2H,  $C_5$  CH); 4.70 (t, 2H,  $C_5$  CH); 2.64 (t, 1H,  $C_7$  CH) ppm.  $^{13}C$  NMR ( $CDCl_3$ , 62.90 MHz):  $\delta$  224.3 (CO); 131.0 ( $C_7$  CH); 124.9 ( $C_7$  CH); 122.3 ( $C_7$  CH); 91.0 ( $C_5$  C-1); 85.8 ( $C_5$  CH); 83.6 ( $C\equiv C$ ); 81.9 ( $C_5$  CH); 72.7 ( $C\equiv C$ ); 30.8 ( $C_7$  C-1) ppm. IR ( $CH_2Cl_2$ ):  $\nu$  2025 (s, CO); 1938 (vs, CO)  $cm^{-1}$ . MS (EI, 70 ev):  $m/z$  (%) 318 (31) [ $M^+$ ]; 262 (21) [( $M-2CO$ ) $^+$ ]; 234 (100) [( $M-3CO$ ) $^+$ ]; 179 (16) [( $M-3CO-Mn$ ) $^+$ ]; 156 (80) [( $M-3CO-C_6H_6$ ) $^+$ ]; 55 (31) [ $Mn^+$ ].

### 3.4. (Cymantrenylethynyl)cycloheptatrienylium tetrafluoroborate (9)

To a solution of **8** (0.45 g, 1.4 mmol) in 5 ml of  $CH_2Cl_2$  was added triphenylcarbenium tetrafluoroborate (0.46 g, 1.4 mmol) as a solid. The solution immediately turned red and stirring was continued for 45 min. After addition of 50 ml of diethyl ether the red crystalline precipitate was isolated by filtration and washed with diethyl ether. Crystallization from methylene chloride afforded **6** as red–purple crystals, 420 mg (74%), m.p. 97–99 °C. Anal. Found: C, 51.22; H, 3.87.  $C_{17}H_{10}BF_4MnO_3$  Calc.: C, 50.54; H, 2.50%.  $^1H$  NMR ( $CD_3CN$ , 250 MHz):  $\delta$  8.93 (m, 6H,  $C_7$  CH); 5.62 (t, 2H,  $C_5$  CH); 5.12 (t, 2H, CH) ppm.  $^{13}C$  NMR ( $CD_3CN$ , 62.90 MHz):  $\delta$  224.8 (CO); 156.2 ( $C_7$  CH); 155.2 ( $C_7$  CH); 154.0 ( $C_7$  CH); 152.7 ( $C_7$  C-1); 107.2 ( $C_5$  C-1); 92.3 ( $C\equiv C$ ); 92.2 ( $C_5$  CH); 86.3 ( $C_5$  CH); 75.4 ( $C\equiv C$ ) ppm. IR ( $CH_2Cl_2$ ):  $\nu$  2030 (s, CO); 1952 (vs, CO)  $cm^{-1}$ . MS (FAB, positive ions):  $m/z$  (%) 317 (50) [ $M^+$ ]; 233 (33) [( $M-3CO$ ) $^+$ ]; 55 (56) [ $Mn^+$ ]. UV/vis ( $CH_2Cl_2$ ):  $\nu$  (log( $\epsilon$ )) 268 (4.2); 390 (4.1); 550 (3.8) nm. UV/vis ( $CH_3CN$ ):  $\nu$  (log( $\epsilon$ )) 278 (3.7); 384 (3.6); 490 (3.4) nm.

### 3.5. X-ray crystal structure of $6 \cdot 0.5CH_2Cl_2$ [15]

Red–purple crystals were obtained by crystallization from dichloromethane at  $-26$  °C. Selected crystallographic details:  $C_{15}H_{10}BF_4MnO_3 \cdot 0.5CH_2Cl_2$ ,  $M = 422.45$ , triclinic, space group  $P\bar{1}$  (No. 2),  $a = 9.850(1)$ ,  $b = 13.521(4)$ ,  $c = 14.338(3)$  Å,  $\alpha = 105.97(2)$ ,  $\beta = 104.77(1)$ ,  $\gamma = 103.90(2)^\circ$ ,  $V = 1673.3(7)$  Å $^3$ ,  $Z = 4$ ,  $D_c = 1.68$  g  $cm^{-3}$ , Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). 5854 unique diffraction data collected on a CAD-4 four-circle diffractometer at  $-135(3)$  °C in the  $2\theta$ -range between 2 and 46°. Positional parameters for all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic

parameters ( $B_H = B_{eq,C}$ ).  $R = 4.2$ ,  $R_w = 3.2$  for 3845 reflections [ $F_o \geq 2\sigma(F_o)$ ] and 526 variables.

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### References and notes

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