

Short Note

2,5-Bis((*E*)-2-ferrocenylvinyl)-*N,N,N',N'*-tetrapropylbenzene-1,4-diamine

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Abstract: The synthesis and spectroscopic investigation of an acidochromic phenylenevinylene dye with two ferrocene groups is presented.

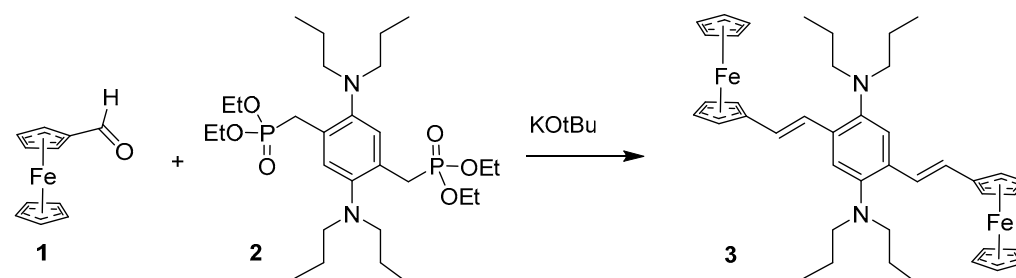
Keywords: ferrocene; acidochromism; cyclic voltammetry; crystal structure

1. Introduction

Conjugated oligomers and polymers of the arylenevinylene type are in the focus of functional materials for organic electronics [1–6]. In addition to the typical units composed of vinylene groups, benzene rings and heterocycles such as thiophene or pyridine, building blocks with heavier atoms [7–9] and even transition metals [10] are used to alter the optical and electronic properties. Especially for redox-active materials, ferrocene is a prime candidate and has been incorporated into larger π -conjugated materials [11–14]. Several methods are useful for the synthesis of oligo (arylenevinylene)s containing ferrocene, e.g., metathesis reactions or Wittig olefination [15–17]. In addition to the exchange of building blocks in order to change electrical and optical properties, and the incorporation of acidic or basic sites into the π -system to allow tuning, these materials may also be used as sensors for environmental properties. Especially, pyridine-type heterocycles and aniline units are of prime interest [18–23]. This paper presents the synthesis and some optical and electrical properties of an acidochromic dye with two ferrocene units. Furthermore, structural and theoretical investigations are added.

2. Synthesis

Among the different methods to synthesize 1,2-diarylethenes, the Horner olefination [23] has received broad attention due to the ease of performance in combination with high yields and high *E*-selectivity, especially in the field of conjugated oligomers [24–26]. The synthesis of the title compound was performed from a central aminoaniline with two phosphonate groups **2** and two ferrocene carboxaldehyde **1** as shown in Scheme 1. Bisphosphonate **2** was prepared from the corresponding diol [27] via chlorination with thionyl chloride and the Michaelis–Arbuzov reaction [28].



Scheme 1. Synthesis of the title compound **3** via Horner olefination.



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Compound **3** was prepared from **2** (80 mg, 0.14 mmol) and 72 mg (0.34 mmol) of ferrocene carbaldehyde in 3 mL of dry DMF. The compounds were mixed under nitrogen in a Schlenk flask and freshly sublimed potassium *t*-butylate (47 mg) was added in small portions while stirring in an ice-water bath. Thereafter, the mixture was allowed to reach ambient temperature. Stirring was continued for 48 h and 0.5 mL water and 10 mL of acetonitrile were added. Suction filtration and washing of the filter cake with acetonitrile (20 mL) gave a red crystalline solid (27 mg, 44%). Melting point: 207–212 °C. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ (ppm): 7.27–7.25 (2H phenylene, 1H vinylene, superimposed by CHCl_3); 6.72 (d, $^3J = 16.51$ Hz, 2H, CH vinylene); 4.52 (“s”, 2H, ferrocene 1); 4.29 (“s”, 2H, ferrocene 1); 4.16 (“s”, 4H, ferrocene 2 integration for 1H too small); 3.00 (t, $^3J = 7.33$ Hz, 8H, N-CH_2); 1.57 (m, CH_2 , superimposed by water); 0.94 (t, $^3J = 7.33$ Hz, 12H, CH_3). $^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz): δ (ppm) = 145.18 (C_q , C1, C4 phenylene); 133.48 (C_q , C2, C5 phenylene); 124.62 (CH, vinylene); 124.42 (CH, vinylene); 118.97 (CH, C3, C6 phenylene); 84.67 (C_q , ferrocene 1); 69.12 (5CH, ferrocene 2); 68.70 (2CH, ferrocene 1); 66.75 (2CH, ferrocene 1); 56.23 (NCH_2); 20.52 (CH_2); 11.91 (CH_3). IR (KBr): ν (cm^{-1}) = 2962 w, 2794 w, 1734 w, 1684 m, 1627 w, 1559 w, 1507 m, 1495 m, 1456 s, 1377 m, 1302 m, 1206 m, 1165 w, 1104 s, 1028 m, 964 s, 892 w, 817 s, 760 w, 662 w. MS (APCI): 695 (13%), 697 (100%), 698 (53%); HR-MS: found: 697.2900, calcd. for ($\text{C}_{42}\text{H}_{52}\text{Fe}_2\text{N}_2 + \text{H}^+$) 697.2908. (see Supplementary Materials).

3. Optical Spectroscopy

Compound **3** is soluble in chlorinated solvents such as chloroform, but insoluble in cyclohexane or ethanol. Optical spectroscopy was performed with 10^{-6} M solutions in dichloromethane and dichloromethane with an increasing concentration of trifluoroacetic acid (Figure 1). The main absorption band appears at $\lambda_{\text{max}} = 339$ nm and a slightly weaker maximum at $\lambda^2 = 385$ nm, typical for distyrylbenzenes with a *p*-aminoaniline center [29]. The long wavelength maximum ($\lambda^3 = 455$ nm) cannot only be attributed to transitions in the ferrocene part, since the extinction coefficient of $\log \epsilon^1 = 4.71$ is much larger than of ferrocene ($\lambda_{\text{max}} = 440$ nm, $\epsilon = 90$ L/mol cm [30]), all maximas being listed in Table 1. Upon addition of TFA to this solution, the high-energy maxima collapses to a single maximum at ca. 355 nm and the long-wavelength shoulder is intensified and shifted to the red. Only with a TFA concentration of 0.01 M does this shoulder vanish and the double maximum structure in the UV is reestablished, but shifted about more than 20 nm to higher energies.

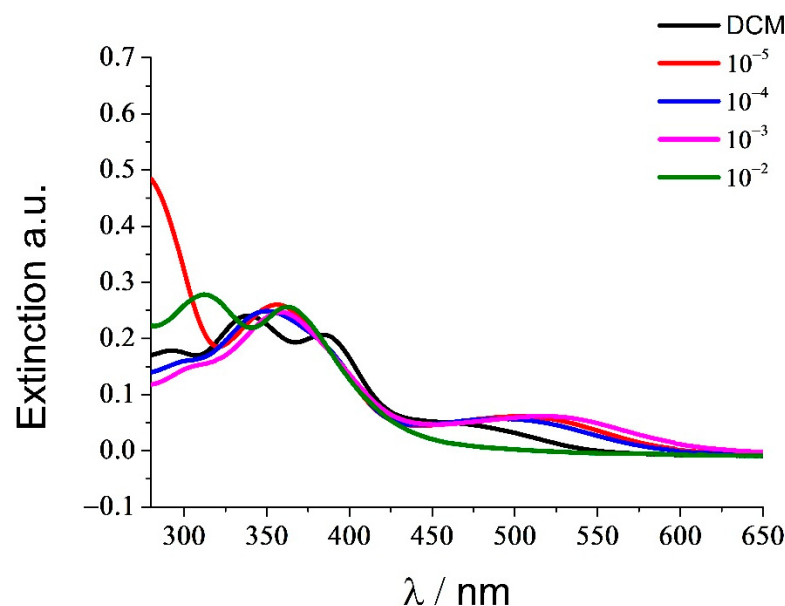


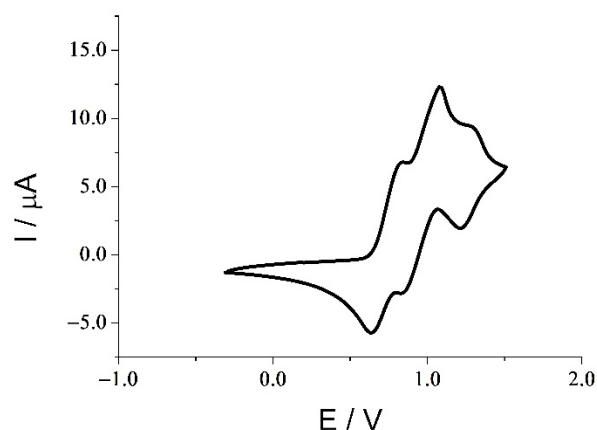
Figure 1. Optical spectra of **3** in dichloromethane and in the presence of acid.

Table 1. Optical data of **3** in dichloromethane and with TFA.

Entry	TFA /mol L	λ^1 /nm	$\log \epsilon^1$	λ^2 /nm	$\log \epsilon^2$	λ^3 /nm	$\log \epsilon^3$
1	DCM	455	4.71	385	5.31	339	5.38
2	10^{-5}	505	4.79	-		355	5.41
3	10^{-4}	497	4.75	-		350	5.46
4	10^{-3}	515	4.79	-		358	5.39
5	10^{-2}	-		362	5.41	312	5.44

4. Electrochemistry

Cyclic voltammetry of **3** was performed in THF with tetrabutylammonium hexafluorophosphate (0.1M) conducting salt and a glassy carbon working electrode using counter electrode Pt wire and reference electrode silver wire. The cyclovoltammogram was calibrated in a subsequent experiment using ferrocene $I_{1/2} = 0.624$ V as a standard [31]. Figure 2 shows the cyclovoltammogram of **3** at 100 mV/s and averaged over four scans. Three fully reversible oxidation waves appear, the first wave at 0.72 V and a second at 1.05 V, followed by the third at 1.26 V. A comparison with a related distyryl-diaminoaniline allows to attribute the redox wave at 1.05 V to an oxidation of the aminoaniline unit, whereas the two ferrocenes are oxidized separately, indicating an effective coupling of these units via conjugation; thus, **3** can be attributed to a Robin–Day class 3 complex.

**Figure 2.** Cyclic voltammogram of **3** in THF.

5. DFT Calculation Mechanics

The molecular structure was preoptimized using MM3, and thereafter, calculated with Scigress Suite, DGauss B88LYP/6-31G (d,p). Lacking minima in the Hesse matrix, subsequent treatment with Orca 5.0.1, B3LYP/def2svp (def2/J auxiliary basis, defgrid 2, resolution of identity chain of spheres exchange approximation) gave optimization to a minimum as was proven via frequency analysis, giving the structure shown in Figure 3, as well as the frontier orbitals from Figures 4 and 5. Pictures in figure CCC were generated with the open-source software AVOGADRO (orca enhanced, V1.2.0, and QT Ver. 4.8.6) [32–38].

Contrary to the crystal structure, the gas-phase-optimized structure shows a lack of structural symmetry regarding the angles of the vinylene groups. In spite of the reduced orbital overlap due to torsion, the conjugation of both ferrocenyl groups over the complete molecule is effective. This is substantiated by the contribution of the hole molecule to the frontier orbitals (Figures 4 and 5).

According to the results of the DFT calculations, the central diaminobenzene dominates the highly occupied orbitals HOMO and HOMO-1 (Figure 4). Whereas HOMO extends nearly exclusively over the divinyl diaminoaniline part, ferrocene has only small

contributions to this MO. However, coefficients on the ferrocene units increase in the orbitals of lower energy (e.g., HOMO-2) and vanish on the central part in HOMO-3 and HOMO-4. Despite their broken molecular symmetry, the coefficients increase on both ion cores similarly.

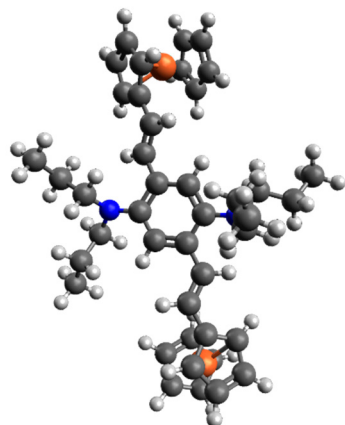


Figure 3. Molecular structure of 3 as result of Orca calculation.

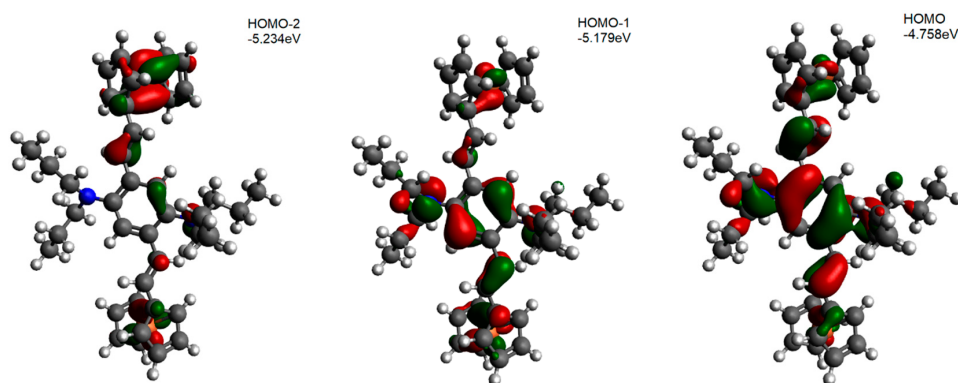


Figure 4. Occupied frontier orbitals: HOMO-2, HOMO-1 and HOMO.

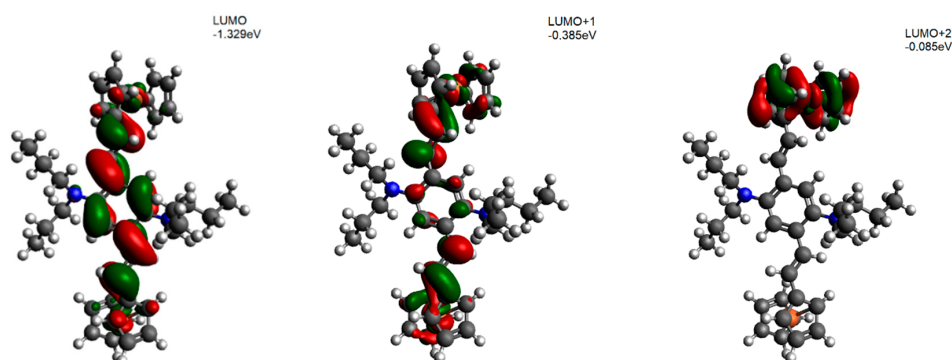


Figure 5. Unoccupied frontier orbitals: LUMO, LUMO+1 and LUMO+2.

Like the HOMO, the LUMO coefficients are concentrated on the divinyl diaminobenzene part (Figure 5). In the orbitals of higher energy, the ferrocene parts increasingly become the sites for larger MO coefficients.

A comparison of the energy differences between these orbitals and the UV spectrum shows energetic similarities of HOMO–LUMO (3.329 eV, 372 nm) with the band at $\lambda = 384$ nm, HOMO-1–LUMO (3.850 eV, 283 nm) with the band at $\lambda = 293$ nm and HOMO–LUMO+1 (4.373 eV, 283 nm) with the band at $\lambda = 293$ nm.

6. Crystal Structure

Slow evaporation of a chloroform solution of the title compound gives a conglomerate of red and brownish needles (Figure 6).

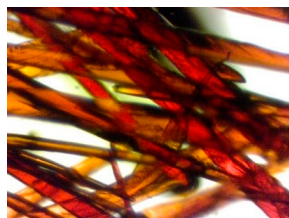


Figure 6. Microphotograph of crystalline 3.

X-ray analysis of the two crystals reveals a monoclinic shape and nearly identical structures of 3 in these crystals. One crystal structure belongs to the space group $P2_1/c$, the other to $P2_1/n$. The main differences are the conformations of the dipropylamino groups and the staggered ($P2_1/n$) and eclipsed ($P2_1/c$) conformations of the ferrocene units.

The molecular structures are depicted in Figure 7. As the two conformers are very similar, only the one forming red needles is discussed in detail. Here, 3 adopts a centrosymmetric conformation in these crystals and the π -system is only weakly distorted. According to the neighboring dipropylamino group, the torsion angle between phenylene and vinylene shows the largest deviation from coplanarity: $163.8(3)^\circ$ (C2-C3-C11-C12), which is only 1.6° more than between vinylene and ferrocene (C14-C13-C12-C11, $-165.4(3)^\circ$). The torsion angle of the vinylene moiety amounts to $171.7(3)^\circ$. This leads to a dihedral angle between phenylene and the cyclopentadiene ring of $16.86(4)^\circ$. The propyl groups in the dipropylamino moiety adopt gauche conformation with torsion angles $N4-C5-C6-C7 = -56.8(3)^\circ$ and $N4-C8-C9-C10 = -56.4(3)^\circ$. The ferrocene shows a staggered conformation with nearly identical distances between iron cyclopentadiene centroids (Fe-C18-C22: $1.6523(17)\text{\AA}$; Fe-C13-C17: $1.6497(13)\text{\AA}$) and the distance between the iron atoms is $13.3447(10)\text{\AA}$. In the crystal, the molecules are arranged in layers in the ab -plane with a parallel offset of $\frac{1}{2}$.

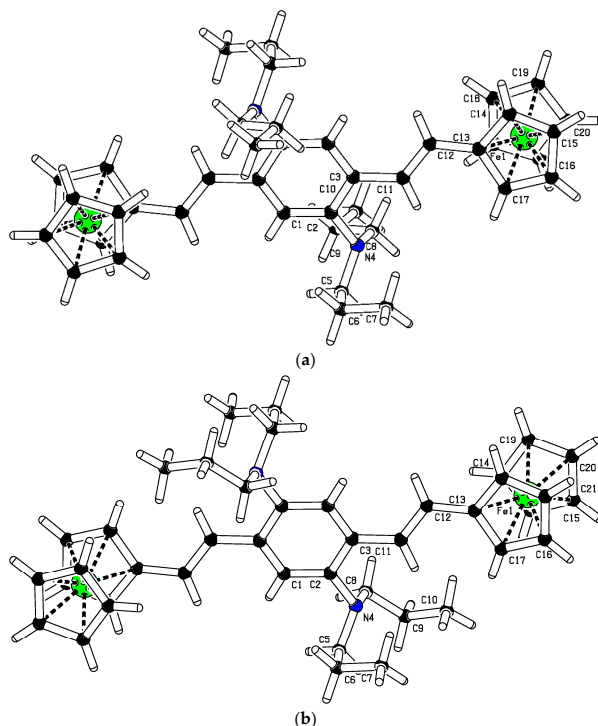


Figure 7. Molecular structure of 3 in the eclipsed (a) form with Fe as the inversion center of two Cp-rings, and staggered (b) conformer, with congruent Cp-rings.

The brown crystals are built from molecules with eclipsed conformations of the cyclopentadienes and a gauche ($N4-C5-C6-C7 = -57.6$) and an anti-periplanar ($N4-C8-C9-C10 = 177.8(1)$) configured propylamino chain. The entire molecule is less distorted; though the torsion angle $C2-C3-C11-C12 = 164.3(3)$ is slightly larger, the vinylene unit $C3-C11-C12-C13$ ($176.8(3)$) and $C14-C13-C12-C11$ ($177.0(3)^\circ$) are nearly planar.

For ferrocene, the staggered or eclipsed conformation had been a highly discussed problem [39,40], as this compound renders both conformers, double staggered and double eclipsed, as a conglomerate; a mixed conformer, staggered and eclipsed, is still missing.

7. Discussion

Three functional units were combined to a redox-active, acidochromic dye. Additionally, for the synthesis of conjugated oligomers incorporating ferrocene, the Horner olefination was an efficient method. Two very similar conformers crystallized from chloroform, the π -conjugated path was nearly planar in the solid state but for the gas phase and torsion along the arylenevinylene path was visible. Nevertheless, cyclic voltammetry and DFT calculations proved a strong conjugation and the complex belongs to the Robin–Day class 3.

8. Conclusions

Horner olefination is a suitable route to synthesize arylenevinylene oligomers to incorporate ferrocene. The ferrocene units are conjugated and the optical properties are tunable by protonation of the central aminoaniline unit.

9. Materials and Methods

NMR spectra were prepared using an Avance II 400 with a 5 mm BBFO-head with a z-gradient and ATM. TLC plates used were ALUGRAM SIL G/UV₂₅₄ from Macherey-Nagel. Melting points: Tottoli apparatus (Büchi) and Electrothermal IA9100. IR spectra: JASCO FT/IR-4100 (ATR). MS: Agilent 6545 Q-TOF-MS, ESI modus. UV/Vis spectra: PerkinElmer Lambda 16. Cyclic voltammetry: Potentiostat Autolab, GPES software. THF was distilled over sodium.

Supplementary Materials: The following supporting information are available online, containing crystallographic information and NMR spectra of 3.

Author Contributions: Conceptualization, H.D.; methodology, I.P.; X-ray analysis, D.S.; calculations, M.J. and I.P.; resources, H.D.; writing—original draft preparation, H.D.; writing—review and editing, M.J. and H.D.; visualization, M.J.; supervision, H.D.; project administration, H.D.; funding acquisition, H.D. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compound 1, 2 and 3 are available from the authors.

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