Accepted Manuscript

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PII: S0022-2860(16)30221-6

DOI: 10.1016/j.molstruc.2016.03.026

Reference: MOLSTR 22337

To appear in: Journal of Molecular Structure

Received Date: 4 February 2016

Revised Date: 8 March 2016

Accepted Date: 9 March 2016

Please cite this article as: T.-H. Doan, I. Talbi, J.-F. Lohier, S. Touil, C. Alayrac, B. Witulski, Synthesis, crystal structure, optical, electrochemical and thermal properties of the ynamide: Bis-(*N*-4-methylbenzenesulfonyl, *N*-*n*-butyl)-1,3-butadiyne-1,4-diamide, *Journal of Molecular Structure* (2016), doi: 10.1016/j.molstruc.2016.03.026.

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Synthesis, crystal structure, optical, electrochemical and thermal properties of the ynamide: Bis-(N-4-methylbenzenesulfonyl, N-n-butyl)-1,3-butadiyne-1,4diamide

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HIGHLIGHTS

- The novel ynamide **3**, having a 1,3-butadiyne-1,4-diamide moiety was prepared.
- First characterization of a 1,3-butadiyne-1,4-diamide by x-ray diffraction.
- The helical twisted molecular structure of diynamide 3 implies helical twisted MOs.
- The HOMO-LUMO energies of **3** were determined by optical and electrochemical methods.

ABSTRACT

Probable topochemical ynamide polymerization was investigated.

ARTICLE INFO

Article history:	The novel ynamide compound, bis-(N-4-methylbenzenesulfonyl, N-n-
Received	butyl)-1,3-butadiyne-1,4-diamide (3), was synthesized and
Accepted	characterized by single crystal x-ray diffraction, ¹ H and ¹³ C NMR,
Available online	UV-fluorescence spectroscopy, cyclic voltammetry, TGA and DSC
Tryunable onnine	techniques. This first reported x-ray structure of a 1,3-butadiyne-1,4-
	diamide revealed that the amido substituents of 3 adopt a twisted
Keywords:	conformation in the crystal with a torsion angle of 76.6° resulting in a
Diacetylenes	molecule with axial chirality. The crystal structure of compound 3 is
Ynamides	stabilized by intermolecular CH- π interactions that give pairs of
x-ray crystal structure	stacked bis-alkyne-3 units. HOMO/LUMO energy levels of 3 were
HOMO/LUMO energy levels	experimentally determined by means of electrochemical and optical
Polymerization of ynamides	methods to be -5.87/-1.98 eV respectively. The solid state
Holical twisted MOs	polymerization of the title compound was investigated by differential
Theme at twisted WOS	scanning calorimetry (DSC) revealing that polymerization proceeded
	simultaneously to the phase transition assigned to the melting of 3 .
	The solid state polymerization of 3 is discussed of being a
	topochemically initiated polymer chain reaction that proceeds with a
	non-topochemical chain growth.

1. Introduction

Functionalized acetylenes are versatile building blocks displaying widespread reactivity patterns that result in a plethora of useful synthetic transformations and many of them found application in the synthesis of natural products or material oriented research [1-6]. Especially nitrogen functionalized alkynes, such as the electron-rich ynamines [7, 8], or their electron deficient and

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therefore more stable variants - the ynamides (1-alkynylamides) [9-13] - gained considerable interest in recent years. Since our first report of a reliable and up-scalable synthesis of ynamides, [14] these versatile acetylenes found widespread use in organic chemistry. Particularly, transition metal catalyzed transformations such as the Pauson-Khand reaction [15, 16], Ni(0)-, Rh(I)- and Ru(II) catalyzed [4+2], [3+2] and [2+2+2] cycloadditions [17-22], as well as ring-closing metathesis [23] and Au(I)-catalyzed reactions [24-27], highlighted the applicability of ynamides as building blocks in organic synthesis. Many other reported transformations of ynamides took likewise benefit of the slightly polarized alkyne moiety. Notably, first applications of the chemistry of ynamides in step- and atom economic syntheses of natural products appeared [18, 20, 28-31]. In contrast to the chemistry of ynamides with just one alkyne moiety, only a small number of examples exist with ynamides having a 1,3-diyne or larger conjugated alkyne skeleton [32-39]. As a part of our efforts on the synthesis of ynamides with a conjugated oligoyne structure that are of interest for non-linear optical materials [34] or as molecular wire for organic electronics, we became interested in the study of symmetrical 1,3-diyne-1,4 amides.

Symmetrical amino alkynes of the type R_2N -(C=C)_n-NR₂ (n = 1, 2, 3, ...) are less well described although the parent compound with n = 1 was already reported by Viehe in the 60s [40]. However, detailed molecular properties including x-ray structure were only revealed by Tamm recently [41]. Similar counts for the next higher homologues with n = 2 whose syntheses have been reported by Ficini and Himbert [42-46] but a detailed molecular structure analysis was only disclosed for two examples the *N*,*N*,*N*,*N*-tetraphenylbutadien-1,3-diyne-1,4-diamine **1** [47], and the electronically more conjugated derivative, the bis(1-carbazolyl)buta-1,3-diyne **2** [48] (Figure 1). Both molecular structures belong to the electron-rich ynamine family. Here, we report on the synthesis, the molecular structure and properties of the 1,3-buta-1,4-diynamide **3** – the electron deficient and therefore more stable ynamide variant of **1** and **2**.



Figure 1. The electron rich 1,3-butadiyne-1,4-diamines 1 and 2, and the here reported electron deficient ynamide variant 3.

Extended conjugated oligoynes like the title compound 3 are proposed to have axial chirality due to a twisted conformation, like the one found in the allene family. The axial chirality has furthermore impact on the topology of the frontier orbitals that resemble extended helices

displaying non-linear π -interactions throughout the conjugated carbon rod. Such a helical twist of conjugated frontier orbitals should have implications for structure stability, spectroscopy and principle reaction pathways, as recently discussed by Aron Walsh et al. on the basis of quantum chemical calculations [49]. Furthermore, 1,3-butadiynes gain considerable interest as monomers in topochemical polymerization reactions as introduced by Wegner [50-52]. However, to the best of our knowledge, the polymerization of ynamides or diynamides have not yet been reported.

2. Experimental

2.1.1. General procedure

Toluene was purified by an Innovative Technology Pure Solv. Device (activated alumina column containing a copper catalyst and molecular sieves). Chromatographic purifications were performed using Merck silica gel Si 60 (40-63 µm) and TLC were developed on silica gel 60-F254 plates (0.1 mm) with UV detection. ¹H and ¹³C NMR spectra were recorded on a BRUKER AVANCE III 400 or 500 spectrometer. ¹H and ¹³C NMR chemical shifts are given in ppm using the TMS signal (0 ppm) and the residual peak of chloroform-d (77.16 ppm) respectively as internal reference. Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, quint = quintuplet, sext = sextuplet, m = multiplet, br = broad. Infrared (IR) spectra were recorded either on a "Perkin Elmer Spectrum One" spectrometer equipped with an ATR device, or with a Perkin Elmer FT-IR Spectrometer 16PC and only the strongest or structurally most important peaks are listed. Mass Spectrometry was performed with a QTOF Micro WATERS spectrometer (ESI), or with a Finnigan MAT 90 for EI (70eV). CHN analyses were performed with a Perkin-Elmer Elemental Analyzer EA 240 or with a Perkin Elmer analyser 2400 CHN. Melting points (mp) were measured with a melting point microscope not corrected. The amide 4 and are was obtained from 4methylbenzenesulfonylchloride and *n*-butylamine in dichloromethane and the alkynyliodonium salts 5a and 5b were synthesized by literature proceedings [53].

2.1.2. Preparation of N-n-Butyl-N-trimethylsilanylethynyl-4-methylbenzenesulfonylamide (6)

<u>Procedure A:</u> To a solution of N-*n*-butyl-4-methylbenzenesulfonylamide (**4**) (690 mg, 3.04 mmol) in dry toluene (50 mL) was added *n*-BuLi (3.29 mmol; 2.19 mL of a 1.5 M solution in hexane) at -78 °C. The solution was brought slowly to 0 °C and alkynyliodonium salt **5a** (1.485 g, 3.30 mmol) was added. The resulting solution was stirred at room temperature for 12-14 h. After completion of the reaction (TLC indicated complete consumption of **4**) the solvents were removed in vacuum and the remaining residue chromatographed on silica gel (SiO₂, hexanes / diethyl ether = 8:2 (v/v)) to give ynamide **6** (800 mg, 2.48 mmol, 82% yield); R_f: 0.6 (SiO₂, hexanes / ethyl acetate = 7:3 (v/v)); colorless crystals with mp. 54-55 °C (chloroform/pentane, -

20 °C). ¹H NMR (400 MHz, CDCl₃) δ = 7.78 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.60 (m, 2H), 1.33 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.16 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 144.4 (s), 134.7 (s), 129.5 (d), 127.7 (d), 95.3 (s), 73.0 (s), 50.9 (t), 29.7 (t), 21.5 (q), 19.3 (t), 13.4 (q). IR (KBr) v 2961, 2873, 2162, 1596, 1492, 1492, 1469, 1364, 1292, 1248, 1188, 1172, 1089, 1016, 985, 927 cm⁻¹. MS (EI, 70 eV), m/z (%): 323 (100) [M⁺], 308 (55), 252 (26), 155 (21), 112 (18), 91 (33), 75 (38). C,H,N analysis for C₆H₂₅NO₂SSi (323.53); calc: C 59.40, H 7.79, N 4.33; found C 59.83, H 7.60, N 4.17. HRMS for C₁₆H₂₅NO₂SSi (323.53); calc. 323.1375; found 323.1380.

2.1.3 Desilylation of ynamide 6

To a solution of **6** (1.24 g, 3.83 mmol) in oxygen-free wet THF (145 mL) was slowly added a 1M solution of TBAF in THF (4.72 mL, 1.2 equiv.) at 0 °C. After stirring for 15 min at 0 °C, TLC indicated total consumption of **6** and the solvent was removed in vacuum. To the residue were added CH_2Cl_2 and brine. After separation of the layers the organic phase was dried over MgSO₄ and filtered. The solvents were removed in vacuum and the remaining residue was purified by column chromatography on silica gel (SiO₂, pentane / ethyl acetate = 95:5 (v/v)) to give ynamide **7** (710 mg, 2.82 mmol, 74% yield).

2.1.4 Preparation of N-n-Butyl-N-ethynyl-4-methylbenzenesulfonylamide (7)

Procedure B: To a solution of *N*-*n*-butyl-4-methylbenzenesulfonylamide (**4**) (300 mg, 1.30 mmol) in dry toluene (30 mL) was added *n*-BuLi (1.43 mmol; 0.95 mL of 1.5 M solution in hexane) at -78 °C. The solution was brought slowly to 0 °C and alkynyliodonium salt **5b** (570 mg, 1.51 mmol) was added. The resulting solution was stirred at room temperature for 12-14 h. After completion of the reaction (TLC indicated complete consumption of **4**) the solvents were removed in vacuum and the remaining residue chromatographed on silica gel (SiO₂, hexanes/diethyl ether = 8:2 (v/v)) to give ynamide **7** (250 mg, 1.00 mmol, 77% yield); R_f: 0.4 (SiO₂, hexanes/ethyl acetate = 8:2 (v/v)); colorless crystals with mp. 43-45 °C (chloroform / pentane, -20 °C). ¹H NMR (500 MHz, CDCl₃) δ = 7.80 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 3.30 (t, *J* = 7.2 Hz, 2H), 2.72 (s, 1H), 2.45 (s, 3H), 1.63 (m, 2H), 1.34 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ = 144.8 (s), 134.7 (s), 129.9 (d), 127.8 (d), 76.2 (s), 59.1 (d), 51.0 (t), 29.8 (t), 21.8 (q), 19.5 (t), 13.7 (q). IR (KBr) v 2961, 2875, 2133, 1595, 1303, 1169, 1120, 1089, 1026, 1016, 973, 939 cm⁻¹. MS (EI, 70 eV), m/z (%) = 251 (8) [M⁺], 195 (22), 186 (27), 155 (36), 131 (45), 91 (100). C,H analysis C₁₃H₁₇NO₂S: 251.0980; found 251.0972.

2.1.5. Preparation of bis-(N-4-methylbenzenesulfonyl, N-n-butyl)-1,3-butadiyne-1,4-diamide (3) To a suspension of CuI (36 mg, 0.19 mmol, 10 mol%) in dry acetone (10 mL) was added TMEDA (58 µL, 0.19 mmol, 20 mol%). After 15 min of stirring at rt and under air condition a solution of ynamide 7 (495 mg, 1.97 mmol) in dry acetone (10 mL) was added and the mixture was vigorously stirred until complete consumption of the starting material (4 h, TLC monitoring). The solvent was removed in vacuo and the residue was purified by silica gel column chromatography using Pentane/EtOAc 8:2 as eluent to give the 1,3-butadiyne-1,4-diamide 3 in 92% yield (453 mg) as a white solid. Colorless crystals. Mp 109-110 °C (CHCl₃/Pentane). $R_f =$ 0.44 (Pentane/EtOAc 8:2 (v/v)). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 8.2 Hz, 4H, H-14/H-18), 7.37 (d, J = 8.2 Hz, 4H, H-15/H-17), 3.34 (t, J = 7.3 Hz, 4H, H-5), 2.47 (s, 6H, H-19), 1.62 (quint, J = 7.4 Hz, 4H, H-6), 1.32 (sext, J = 7.4 Hz, 4H, H-7), 0.90 (t, J = 7.4 Hz, 6H, H-8). ¹³C NMR (100 MHz, CDCl₃) δ 145.0 (C_q, C-16), 134.8 (C_q, C-13), 130.0 (CH, C-15/C-17), 127.7 (CH, C-14/C-18), 75.4 (C_s, C-1), 59.6 (C_s, C-2), 51.6 (C_t, C-5), 30.0 (C_t, C-6), 21.8 (C_q, C-19), 19.6 (Ct, C-7), 13.7 (Cq, C-8). IR (ATR) v 2960, 2933, 2874, 2169, 1596, 1492, 1456, 1361, 1184, 1163, 1087, 921, 811, 706 cm⁻¹. HRMS (ESI) Calcd for C₂₆H₃₂N₂O₄NaS₂ [M+Na]⁺: 523.1701. Found: 523.1717.

2.2 Physical measurements

UV absorption spectra in solution were recorded with a JASCO V-660 spectrometer and emission spectra with a Perkin Elmer LS55 fluorescence spectrometer. Absolute photoluminescence quantum yields in solution were recorded with the Hamamatsu CC9920 integration sphere set-up at room temperature. For quantum yield measurements solutions of **3** were purged with argon prior to measurement. Electrochemical studies were carried out at room temperature using a GAMRY Ref600 potentiostat. The working electrode was a platinum electrode, and the auxiliary electrode a platinum wire. The reference electrode was an aqueous saturated (KCl) calomel electrode. Under the conditions used, the reversible potential for the ferrocenium/ferrocene couple at 298 K is +0.46 V in CH₂Cl₂. A 10^{-3} M solution of **3** in a $1x10^{-1}$ M Bu₄NPF₆ /CH₂Cl₂ electrolyte solution was used. TGA measurements were recorded on a Perkin Elmer Thermogravimetric Analyser TGA7. Differential Scanning Calorimetry measurements were performed on a Perkin Elmer DSC7 analyser.

2.3 X-ray diffraction data for compound 3

Single crystals of ynamide **3** were grown by slow diffusion of pentane into a solution of **3** in chloroform at room temperature. X-ray crystallographic data of the single crystals of **3** were collected at 150 K on a Bruker Apex II Kappa CCD single-crystal diffractometer working with monochromatic Mo K α radiation and equipped with an area detector. The crystal structure was

solved by direct methods with SHELXS-97 [54] and refined against F^2 with SHELXL-2014 [55], with anisotropic thermal parameters for all non-hydrogen atoms. Idealized geometries were assigned to the hydrogen atoms. Crystal data and refinement details for compound **3** are summarized in Table 1.

Crystal system	Triclinic	Ζ	2
Crystal size	$0.32 \times 0.30 \times 0.27$	$Dx (Mg/m^3)$	1.251
Crystal color	Colorless	$\mu (\mathrm{mm}^{-1})$	0.23 (Μο Κα)
Space group	<i>P</i> -1	Theta range for data collection (°)	2.3–30.5
<i>a</i> (Å)	11.3148(4)	Limiting indices	$\begin{array}{l} -16\leqslant h\leqslant 16, -16\leqslant k\leqslant 15,\\ -18\leqslant l\leqslant 17 \end{array}$
<i>b</i> (Å)	11.4384(4)	Reflections collected/unique	$30969/8091 \ (R_{int} = 0.023)$
<i>c</i> (Å)	12.8115(5)	Reflections with $I > 2\sigma(I)$	6566
<i>a</i> (°)	64.9887(16)	Refined parameters/restrains	331/0
β (°)	73.5519(16)	Goodness of fit on <i>F</i> ²	1.04
g (°)	62.8724(15)	R_1, wR_2	0.062, 0.185
$V(\text{\AA}^3)$	1328.90(9)	Largest diff. peak and hole $(e^{A^{-3}})$	1.10 and -0.68

 $\label{eq:constant} \textbf{Table 1}. Crystal \ data \ and \ refinement \ details \ for \ ynamide \ \textbf{3} \ with \ Formula \ Sum \ C_{26}H_{32}N_2O_4S_2 \ and \ Formula \ Weight \ \textbf{500.67} \ g \ mol^{-1}.$

3. Results and discussion

3.1 Synthesis of bis-(N-4-methylbenzenesulfonyl, N-n-butyl)-1,3-butadiyne-1,4-diamide (3) The synthesis of the title **3** was achieved by two complementary routes using alkynyliodonium salts for a direct N-ethynylation following our previous procedure (Scheme 1) [14, 56].



Scheme 1. Synthesis of bis-(*N*-4-methylbenzenesulfonyl, *N*-*n*-butyl)-1,3-butadiyne-1,4-diamide (3).

Accordingly, tosylamide **4** was deprotonated with *n*-butyl lithium in dry toluene and the resulting amide was treated with the readily available silylated alkynyliodonium salt **5a** to give ynamide **6** in 82% yield after work-up and column chromatography (Procedure A, Scheme 1). Thereafter, **6** was converted into the terminal ynamide **7** by desilylation with tetrabutyl ammonium fluoride (TBAF) to give **7** in 74% yield. Alternatively, the terminal ynamide **7** was accessible by *N*-ethynylation with the alkynyliodonium salt **5b** (Procedure B, Scheme 1). This gave **7** in 77% yield through an even more straightforward synthetic transformation. Finally, the oxidative homo-coupling of ynamide **7** mediated by copper catalysis in acetone yielded title compound **3** in 92% yield after its isolation by column chromatography on silica gel as a colorless, air and moisture stable solid.

3.2¹H and ¹³C NMR studies

With the aim to achieve the full assignment of the ¹H and ¹³C NMR signals characterizing ynamide **3**, the ¹H and ¹³C NMR spectra were measured together with more detailed 2D NMR analyses including ¹H-¹H Cosy, HSQC and HMBC experiments. All NMR spectra were recorded in CDCl₃ solution at room temperature. The HMBC cross peaks and their assignment are shown in Figure 2.



Figure 2. HMBC spectra of bis-(N-4-methylbenzenesulfonyl, N-n-butyl)-1,3-butadiyne-1,4-diamide (3).

In the HMBC spectrum, the tosyl methyl group (H-19, 2.47 ppm) correlates with the quaternary carbon atom at 145.0 ppm and is therefore assigned to C-16. Consequently, the signal at 134.8 ppm can be appointed to C-13, the other aromatic quaternary carbon atom. The ¹³C NMR signal at 130.0 ppm can be endorsed to C-15 and C-17 because of its correlation with the ¹H NMR signal of H-19. Accordingly, the ¹³C NMR signal at 127.7 ppm corresponds to C-14 and C-18. The assignment of the ¹H NMR signals of H-14/H-18 and H-15/H-17 at 7.79 and 7.37 ppm respectively can then be deduced from the analysis of the HSQC spectrum (see, supplement material). Finally, the relaxation of the acetylenic carbon atoms C-1 and C-2 occurred at 75.4 and 59.6 ppm respectively, based on the HMBC spectrum analysis. Indeed a correlation spot is observed between the triplet ¹H NMR signal corresponding to H-5 at 3.34 ppm and the ¹³C NMR peak at 75.4 ppm.

3.3 Molecular structure in the single crystal

Single crystals of diynamide **3** were obtained by slow diffusion of *n*-pentane into a chloroform (**3**) solution through the vapor phase. The molecular structure of **3** as the result of a single crystal x-ray analysis is shown in Figure 3 together with a listing of bond lengths and bond angles.

The amido substituents in **3** adopt a twisted orientation along the 1,3-diyne carbon rod resulting in a molecule with axial chirality. The bond lengths of N1-C1 and N2-C4 are 1.345(4) Å and 1.348(3) Å, respectively, which are consistent with the reported lengths of the related compounds **1** and **2** [47, 48]. The distances of C1-C2, C2-C3 and C3-C4 are 1.199(4) Å, 1.365(4) Å and 1.199(4) Å, showing a clear bond alternation. The C1-C2/C3-C4 bond length is with 1.199(4) Å

in agreement with the presence of a C-C triple bond – albeit it is slightly longer than C-C triple bonds reported for **1** and **2** with respectively 1.193(6) and 1.188(3) Å. This might be due to a more favorable electronic conjugation along the 1,3-butadiyne-1,4-diamide moiety in **3**. This gains further support by the slightly shorter C2-C3 bond length of **3** with 1.365(4), compared to those of **1** and **2** with 1.376(6) and 1.373(4) respectively.



Figure 3. Asymmetric unit of 3 and table of bond length and angles. Displacement ellipsoids are drawn at the 50% probability level.

The 1,3-butadiyne moiety curves slightly, where the angles of N1-C1-C2, C1-C2-C3, C2-C3-C4 and C3-C4-N2 are 179.0(2), 178.5(2), 177.7(2) and 177.2(2)°, respectively. The nitrogen atoms have a trigonal planar environment as evidenced by both, the sum of the bond angles at N1/N2 =358.7°/354.3° as well as the plane r.m.s. (root-mean-square) deviation of 0.0437 Å and 0.0899 Å for the N1/C1/C5/S1 and the N2/C4/C9/S2 plane, respectively. Such a planar environment around the nitrogen atoms is also due to the effective conjugation of the nitrogen lone pair with the adjacent carbon-carbon triple bond. The torsion angle between the mean planes of N1/C1/C5/S1 and N2/C4/C9/S2 is 76.6° underlining an orthogonal arrangement of the two amide moieties throughout the spacing 1,3-butadiyne carbon rod (Figure S9 in supplementary material). This orthogonal or twisted arrangement should not be solely understood as a conformation that is stabilized by the crystal lattice - it is also reasoned by effective conjugations of the nitrogen lone pairs with the adjacent 1,3-butadiyne moiety. The latter should be interpreted as being the origin for extended helices of frontier molecular orbitals displaying non-linear π -interactions. Similar twisted amino groups attached to a conjugated 1,3-divne unit can be found in the 1,3-butadivne-1,4-diamines 1 and 2 with torsion angles of 60.2° and 85.2°, respectively. With 76.6° the torsion angle of ynamide $\mathbf{3}$ is also in very good agreement with ab initio molecular geometry calculations of a related diynamide, where a calculated torsion angle of 66.74° was reported [49].

The crystal packing of diynamide **3** is shown in Figure 4 and 5. The molecular packing of **3** is stabilized by weak CH- π intermolecular interaction: the distance between hydrogen H24 and Cg1 (Cg1 is centroid of C13-C19 benzene ring at 1-x, -y, -z symmetry code) is 2.914 Å (Figure 4).



Figure 4. CH- π intermolecular interaction within dimer units of 3 in the single crystal.

This interaction aligns molecules of **3** to pairs with an intermolecular spacing of 4.62 Å for the shortest intermolecular distance between two 1,3-diyne units within these pairs – and about 7.89 Å for the translational distance between the two 1,3-diynes of adjacent pairs. Each pair of **3** consists of a right- and left-handed axial chiral carbon rod. The intermolecular distance of 4.62 Å for two alkyne rods within such a pair is in the range to favor topochemical reactions; whereas the spacing of the diyne pairs will make a topochemical chain polymerization less likely [57-60]. For example, for the topochemical chain polymerization of 1,3-diacetylenes the steric requirements are one-dimensional stacking of the diacetylene units to translational positions around 4.9 Å and inclination angles of the diacetylene axes to the packing axis about 45° [61].



Figure 5. Crystal packing of diynamide 3.

Within the crystal packing of **3**, there are short contacts (i.e. the distance between the atoms involved is less than the sum of the van der Waals radii of these atoms) between protons H22 and H25 of a benzene ring and the O atoms of the sulfonyl groups of adjacent molecules (Figure 5 and Table 2, and Figure S10 in supplementary material): 2.48 Å (CHO angle = 157°) and 2.60 Å (CHO angle = 102°), respectively. These distances suggest the existence of relatively unusual C-H...O hydrogen bonds.

Table 2. Hydrogen-bonding geometry (A, °).					
D—H…A	D—H [Å]	H…A [Å]	D…A [Å]	D—H…A [°]	
$C(22)-H(22)\cdots O(2)^{i}$	0.95	2.48	3.380(3)	157	
$C(25)H(25)\cdots O(4)^{ii}$	0.95	2.60	2.952(3)	102	
Symmetry code (i) : 1-x, 1-y, -z (ii) : -x, -y, -z					

3.4 Photophysical and electrochemical properties

The photophysical properties of diynamide **3** were examined using UV-vis and fluorescence spectroscopy in diluted (10^{-5} M) THF, CH₂Cl₂ and CH₃CN solutions at room temperature. The corresponding spectra are illustrated in Figure 6.



Figure 6. UV-vis absorption spectra of 3 in THF (black), CH₂Cl₂ (red), and CH₃CN (blue).

In agreement with the symmetrical molecular structure of diynamide **3**, the solvatochromism is negligible and the UV-vis spectra are almost identical in solvents of different polarity. The UV-vis spectra have an onset value of $\lambda_{onset} = 319$ nm and shoulders at 295, 277, and 254 nm. Photoluminescene measurements with 10⁻⁵ M solutions of diynamide **3** in THF, CH₂Cl₂ and CH₃CN at excitation wavelength of $\lambda_{ex} = 270$, 280 and 290 nm respectively revealed that the compound is non-emissive in these solvents and with our experimental setup.

Cyclic voltammetry experiments with **3** were carried out in the presence of Bu_4NPF_6 (0.1 M in CH_2Cl_2) and with Fc/Fc⁺ (0.46 V vs SCE) [62] as the internal standard. Within the

solvent/electrolyte window diynamide **3** showed a non-reversible oxidation potential $E_{1/2}^{ox} = 1.51$ V with a well pronounced oxidation half-wave at $E^{ox} = 1.54$ V, respectively (Figure 7).



Figure 7. Cyclic voltammetry study of compound **3** (10^{-3} M in CH₂Cl₂/0.1 M nBu ${}_{4}PF_{0}$) at room temperature measured versus SCE. Scan rate 100 mV/s, values are corrected vs internal ferrocene (Fc/Fc⁺= 0.46 V vs SCE).

From the onset of the oxidation half-wave $E^{ox}_{onset} = 1.23$ V, the energy level of the highest occupied molecular orbital (HOMO) of **3** was estimated to $E_{HOMO} = -5.87$ eV; with $E_{HOMO} = -(E_{onset, ox vs Fc/Fc+} + 5.10)$ (eV) for measurements in dichloromethane solution with 0.1 M Bu₄NPF₆ as the supporting electrolyte. We choose -5.10 eV as the formal potential of the Fc+/Fc redox couple in the Fermi scale as suggested by Bazan et al. and not the often used value of -4.8 eV for 0.0 V, because the calibration scale of -5.10 eV is based on a set of empirically obtained electrochemical data and reflects best the stability of the redox species involved [63]. The energy level of the lowest unoccupied molecular orbital (LUMO) was thereafter estimated by adding the value of the optical band gap taken from the onset of the absorption spectra of **3** in CH₂Cl₂ ($\lambda_{onset} = 319$ nm, 3.89 eV) providing $E_{LUMO} = -1.98$ eV with $E_{LUMO} = E_{HOMO} + {}^{Gap}E_{opt}$. The results of the photophysical and electrochemical investigation of diynamide **3** are summarized in Table 3.

$\lambda_{onset} (nm)$	^{Gap} E _{opt} (eV)	$E^{ox}(V)$	$E_{1/2}^{ox}(V)$	E ^{ox} onset (V)	HOMO (eV)	LUMO (eV)
319	3.89	1.54	1.51	1.23	-5.87	-1.98

Table 3. Experimental determination of the HOMO-LUMO energy levels of diynamide 3.

3.5 Thermal properties

The thermal properties of compound **3** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) which are shown in Figure 8. Based on the TGA analysis decomposition with mass loss proceeded slowly at 198 $^{\circ}$ C and the following decomposition process was completed when the temperature was raised above 545 $^{\circ}$ C.



Figure 8. Thermogravimetric analysis (TGA) [left] and Differential Scanning Calorimetry (DSC) [right] of diynamide 3.

A more detailed picture of the thermal transitions of diynamide 3 were obtained from DSC analysis (Figure 8). The small endotherm transition at 98 °C can be assigned to an "alkyl chain melting" process of the n-butyl groups of diynamide 3 in the crystal. This weakly endotherm transition is followed by the endothermic melting with a maximum at 113 °C. Notably, simultaneous to the melting of 3, an exothermic reaction was observed with a maximum at 137 °C that proceeded during the heating period of 110-180 °C and that is synonymous with a chain polymerization. The occurrence of a polymerization reaction of $\mathbf{3}$ was furthermore verified by the following cooling and a second heating scan. In the latter case, neither "alkyl chain melting" nor the melting of 3 could be observed certainly demonstrating that discrete molecules of diynamide **3** were absent. This was sustained by the observation of film formation during continuous increase of temperature during the heating process above the melting point. Based on the DSC analysis, the spontaneous thermal polymerization of diynamide 3 in the solid state is less likely of the sole topochemical type as it proceeds simultaneously with or shortly after the endothermic phase transition assigned to melting. However, as the closest distances between the alkyne rods of 3 in the single crystal are in the range of a topochemical reaction and the polymerization process proceeds simultaneously to the disruptor of the regular crystal lattice, the results presented here might be best interpreted as a topochemical initiated polymerization that is induced by closely packed dimers of 3 in the crystal and that is continued by a non-topochemical polymer chain growth of these dimers during the process of melting. Notably, the resulting polymer gains thermal stability up to 198 °C without any mass loss by polymer fragmentation as evidenced by TGA.

4. Conclusion

The new ynamide bis-(N-4-methylbenzenesulfonyl, N-n-butyl)-1,3-butadiyne-1,4-diamide (3) was synthesized by direct N-ethynylation using alkynyliodonium salts followed by a subsequent oxidative Glaser coupling. The molecular properties of the title compound **3** were characterized

by single crystal x-ray diffraction, 1- and 2D ¹H and ¹³C NMR, UV-vis and fluorescence spectroscopy, as well as cyclic voltammetry. The HOMO/LUMO energy levels of the diynamide **3** were experimentally estimated to be -5.87/-1.98 eV respectively by means of photophysical and electrochemical investigations. In the single crystal, the amido substituents of **3** adopt a twisted orientation with a torsion angle of 76.6°. Such a twist results in a molecule with axial chirality where the lone-pairs of the nitrogen atoms conjugate effectively with the adjacent π -systems of the alkyne motifs. Therefore, ynamide **3** is an example of a conjugated linear molecule displaying helical frontier molecular orbitals with non-linear π -interactions. Intermolecular CH- π interactions align molecules of **3** into pairs within the crystal lattice and as a result, the intermolecular spacing of the 1,3-diyne units is with 4.62 Å in the range to favor topochemical reactions. Based on TGA and DSC analyses, the thermally initiated solid state polymerization of **3** might be best described as a topochemical initiated polymer chain reaction that proceeds with a non-topochemical chain growth.

Further studies on polymerization reactions of ynamides, diynamides and related alkynes including polymerization in confined spaces are under investigation in our laboratory and will be reported in due course.

Acknowledgement

Financial support of this work from the French Agence National de la Recherche (ANR) through the program "Investissements d'Avenir" (ANR-10-LABEX-09-01) - EMC3 (energy materials and clean combustion center) - and from the Ministère de l'Enseignement Supérieur et de la Recherche of France for T.-H. Doan are gratefully acknowledged. I. Talbi is indebted to the Ministry of Higher Education and Scientific Research of Tunisia for a scholarship allowing her two short-term research stays at the LCMT in France.

Appendix A. Supplementary material

The supplementary crystallographic data for diynamide **3** have been deposited with the Cambridge Crystallography Data Centre, 12 Union road, Cambridge CB22 1EZ, UK (Fax: +44 1223 336 033); E-mail: <u>deposit@ccdc.cam.ac.uk</u> or <u>http://www.ccdc.cam.ac.uk</u> and are available free of charge on request quoting the deposition Number CCDC 1449990. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/XX.XXX.

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Graphical Abstract

Synthesis, crystal structure, optical, electrochemical and thermal properties of the ynamide: Bis-(*N*-4-methylbenzenesulfonyl, *N*-*n*-butyl)-1,3-butadiyne-1,4-diamide

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