molbank

MDPI

Short Note

Ethyl 4-((11-(Hexylamino)-11-oxoundecyl)oxy)benzoate

Jorge Jesús Montes-Patiño [1], Nancy Patricia Díaz-Zavala [1,*], Samuel Zapién-Castillo [2], Philippe J. Mésini [3], Jessica Ismalé Lozano-Navarro [1], Lorena Margarita Salas-Ordaz [1] and Marco Antonio Aguirre-Lam [1]

[1] Centro de Investigación en Petroquímica División de Estudios de Posgrado e Investigación, Tecnológico Nacional de México-Instituto Tecnológico de Ciudad Madero, Altamira 89600, Mexico; jorgemontes95@hotmail.com (J.J.M.-P.); yukino_85@hotmail.com (J.I.L.-N.); lorena.so@cdmadero.tecnm.mx (L.M.S.-O.); marco.al@cdmadero.tecnm.mx (M.A.A.-L.)
[2] Instituto de Estudios Superiores de Tamaulipas, Altamira 89605, Mexico; samuel.zapien@iest.edu.mx
[3] Institut Charles Sadron, Université de Strasbourg, CNRS, 23 Rue du Loess, F-67000 Strasbourg, France; mesini@ics-cnrs.unistra.fr
* Correspondence: nancy.dz@cdmadero.tecnm.mx

Abstract: Ethyl 4-((11-(hexylamino)-11-oxoundecyl)oxy)benzoate was synthesized using 11-bromoundecanoic acid hexylamide and commercially available ethyl 4-hydroxybenzoate through a Williamson etherification synthesis. The structural characterization was performed using UV-Vis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, and HRMS.

Keywords: benzoate; bifunctional groups; monoamide

check for updates

Citation: Montes-Patiño, J.J.; Díaz-Zavala, N.P.; Zapién-Castillo, S.; Mésini, P.J.; Lozano-Navarro, J.I.; Salas-Ordaz, L.M.; Aguirre-Lam, M.A. Ethyl 4-((11-(Hexylamino)-11-oxoundecyl)oxy)benzoate. *Molbank* **2024**, *2024*, M1829. https://doi.org/10.3390/M1829

Academic Editor: Nicholas Leadbeater

Received: 24 April 2024
Revised: 17 May 2024
Accepted: 19 May 2024
Published: 27 May 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Oil spills are frequent, particularly due to the intensive use of petroleum products in our daily lives. They have been occurring regularly for almost 75 years. Among the various techniques to remove oil spills at sea, the use of organogelators is the most promising [1,2]. An organogel is a viscoelastic system considered to be a semi-solid preparation, in which an external, generally non-polar, liquid phase is immobilized [3,4].

Since 2005, several organic compounds have been synthesized to form organogelators for removing oil spills in aqueous media. These molecules contain a diversity of functional groups such as alkanes, cycloalkanes, ethers, alcohols, aromatic compounds, carboxylic acids, amides, imines, etc., which provide intermolecular forces capable of trapping oil away from water. The most common intermolecular forces involved are hydrogen bonding, Van der Waals interactions, π-π stacking, and dipole–dipole interactions [5–12].

This work demonstrates the synthesis and characterization of ethyl 4-((11-(hexylamino)-11-oxoundecyl)oxy)benzoate (OAM2) (Figure 1), synthesized from 11-bromoundecanoic acid hexylamide and ethyl 4-hydroxybenzoate. This compound has the potential to be an effective organogelator for removing oil spills due to the presence of functional groups that facilitate the necessary intermolecular forces.

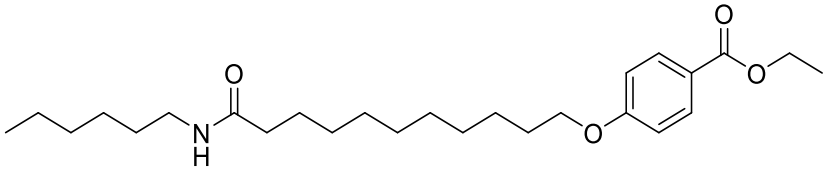


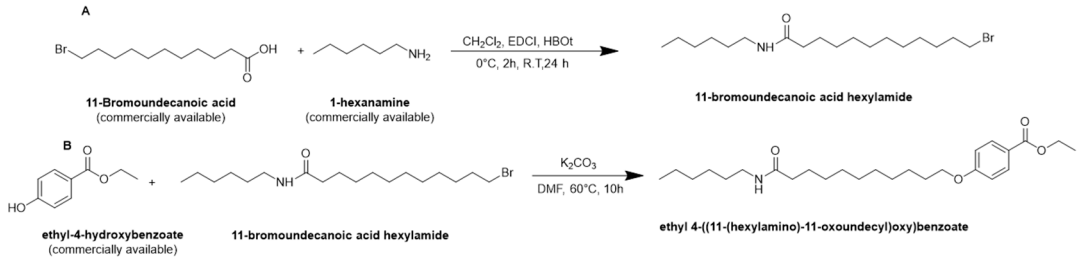
Figure 1. Chemical structure of ethyl 4-((11-(hexylamino)-11-oxoundecyl)oxy)benzoate (OAM2).

2. Results

Synthesis of Ethyl 4-((11-(Hexylamino)-11-oxoundecyl)oxy)benzoate (OAM2)

OAM2 was synthesized in two steps. First, 11-bromoundecanoic acid hexylamide was prepared according to a method identified in the literature (Scheme 1A) [13,14]. This

starting material was then used for Williamson etherification with commercially available ethyl 4-hydroxybenzoate (Scheme 1B).



Scheme 1. (**A**) Synthesis of 11-bromoundecanoic acid hexylamide via a procedure identified in the literature [13]; (**B**) synthesis of ethyl 4-((11-(hexylamino)-11-oxoundecyl)oxy)benzoate.

OAM2 was recrystallized via evaporation in acetonitrile. The product was analyzed using FT-IR, high-resolution ESI-MS, UV-Vis, and ^{1}H and ^{13}C-NMR (for the spectra, see Supplementary Materials, Figures S1–S6).

3. Materials and Methods

3.1. Generals

11-bromoundecanoic acid (95%), silica gel (high purity grade) tetrabutylammonium bromide (95%), N-(3-dimethylamino-propyl)-N′-ethylcarboiimide hydrochloride (EDCI, ≥98%), 1-hydroxybenzotriazole (HBOt, ≥98%), hydrochloric acid (37%), ethyl-4-hydroxybenzoate (99%), and dichloromethane (CH_2CI_2, 99.5%) were purchased from Sigma-Aldrich; sodium bicarbonate (99.7%) was purchased from BDH. 11-bromoundecanoic acid hexylamide was synthesized as previously described in the literature [13,14]. The ^{1}H and ^{13}C NMR analyses were performed using a Bruker ASCEND™ 400 MHz AVANCE III at 400 MHz and 100 MHz, respectively. Tetramethylsilane (TMS) was used as the standard, and deuterated chloroform ($CDCl_3$) was used as the solvent. Melting point analysis was conducted using a Fisher-Johns melting point apparatus. The FT-IR analyses were conducted on a PerkinElmer Spectrum One spectrophotometer. UV-Vis absorption studies were performed on a UV-Vis Cintra 303 GBC. High-resolution mass spectra (HRMS) were recorded with a microTOF II spectrometer obtained from Bruker Daltonics (Bremen, Germany) with an electrospray ionization (ESI) source. The solvent used was chloroform.

3.2. Synthesis

A mixture of ethyl 4-hydroxybenzoate (0.7745 g, 4.66 mmol), 11-bromoundecanoic acid hexylamide (1.757 g, 5.215 mmol), potassium carbonate (1.820 g, 13.1717 mmol), and tetrabutylammonium bromide (0.34 g, 1.053 mmol) were dissolved in DMF (70 mL). The blend was agitated at 650 rpm and heated at 65 ± 5 °C for 10 h. The reaction mixture was poured into cold, deionized water (600 mL), and the pH level was adjusted to 1–2 using aqueous HCl (10% w/w). A white solid precipitated and was collected by vacuum filtration using a glass Büchner funnel. The wet product was then placed in a desiccator over 3 Å molecular sieves for 1–2 weeks. If the DMF signal persisted, repeated washes with cold deionized water were performed, followed by recrystallization in acetonitrile. Yield: 67.33% (1.34 g); mp: 80–90 °C. UV (ethanol) λ_{max} 256 nm, (cyclohexane) λ_{max} 253 nm, (n-hexane) λ_{max} 253 nm, (acetonitrile) λ_{max} 255 nm. FTIR (ATR-diamond) υ_{max} (cm^{-1}): 3302 (νN–H), 2921 (ν as C–H), 2854 (ν C–H), 1710 (ester νC=O), 1633 (amide I), 1541 (amide II), 1251 (ν as (ar)C-O–C(al)), 1174 (ester as νC–O), 1108 (ester sy νC–O), 1015 (ν (ar)C–O–C(al)), 843 (fpp Ar C–H), 768 (fpp Ar sust1,4), 696 (γ–$(CH_2)_n$–). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ [ppm] 7.98 (d, J = 8.3 Hz, 2H, COO-(Ar)CCH), 6.90 (d, J = 9.0 Hz, 2H, O-(Ar)CCH), 5.51 (s, 1H, NH), 4.34 (q, J = 7.6 Hz, 2H, $COOCH_2$), 4.04–3.95 (m, 2H, Ar-O-CH_2), 3.23 (q, J = 7.1 Hz, 2H, $CONHCH_2$), 2.15 (t, J = 7.7 Hz, 2H, $NHCOCH_2$), 1.80 (dd, J = 15.1, 7.6 Hz, 3H, $COOCH_2CH_3$), 1.62 (t, J = 7.6 Hz, 2H, $CONCH_2CH_2$), 1.46 (dt, J = 14.5, 7.1 Hz,

4H, Ar-O(CH_2)$_2$$CH_2$, NHCO$CH_2$$CH_2$), 1.33 (m, 18H, CH_2), 0.88 (t, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ [ppm]: 173.11 (NHCO), 166.52 (COO), 162.87 (O-(Ar)C), 131.53 (OOC-(Ar)CCH), 122.60 (OO-(Ar)C), 114.00 (C3,5, O-(Ar)CCH), 68.16 (Ar-OCH_2), 60.65 (COOCH_2), 39.51 (CONHCH_2), 36.96 (NHCOCH_2), 31.51 (CONH(CH_2)$_3$$CH_2$), 29.66 (CONC$H_2$$CH_2$), 29.50 (Ar-O$CH_2$$CH_2$), 29.42 (Ar-O-($CH_2$)$_2$$CH_2$), 29.38 (Ar-O($CH_2$)$_3$$CH_2$), 29.35 (Ar-O($CH_2$)$_4$$CH_2$), 29.32 (NHCO($CH_2$)$_4$$CH_2$), 29.12 (NHCO($CH_2$)$_3$$CH_2$), 26.62 (NHCO($CH_2$)$_2$$CH_2$), 25.98 (NHCO$CH_2$$CH_2$), 25.86 (CONH($CH_2$)$_2$$CH_2$), 22.60 (CONH($CH_2$)$_4$$CH_2$), 14.42 (CONH($CH_2$)$_5$$CH_3$), 14.07 (COO$CH_2$$CH_3$). HRMS (ESI+): m/z 434.3276 $[M + H]^+$ $C_{26}H_{43}NO_4$ requires: 434.3265.

4. Conclusions

A new molecule, ethyl 4-((11-(hexylamino)-11-oxoundecyl)oxy)benzoate (OAM2), was synthesized with a good yield from 11-bromoundecanoic acid hexylamide and commercially available ethyl 4-hydroxybenzoate. This compound was characterized using various spectroscopic methods. OAM2 shows potential as a gelator for oil and fuels, indicating its possible application in oil/fuel-spill remediation. Further research is suggested.

Supplementary Materials: Figure S1: FT-IR of OAM2; Figure S2: ESI-MS spectra of OAM2; Figure S3: ESI HRMS mass spectra of OAM2 (top: experimental; bottom: simulated); Figure S4: UV-vis absorption spectra at 25 °C of OAM2 in (●) ethanol, (▲) cyclohexane, (■) n-hexane and (**x**) acetonitrile; Figure S5: ^{1}H-NMR of OAM2 in $CDCl_3$; Figure S6: ^{13}C-DEPT-135 spectra of OAM2 in $CDCl_3$. References [13,15] are cited in the supplementary materials.

Author Contributions: Conceptualization, N.P.D.-Z. and P.J.M.; methodology, J.J.M.-P.; formal analysis, L.M.S.-O.; investigation, S.Z.-C.; writing—original draft preparation, writing—review and editing, visualization, supervision, N.P.D.-Z. and J.J.M.-P.; funding acquisition, N.P.D.-Z.; analysis results, J.I.L.-N. and M.A.A.-L.; writing—review and editing, J.I.L.-N. All authors have read and agreed to the published version of the manuscript.

Funding: We would like to acknowledge the Consejo Nacional de Humanidades, Ciencias y Tecnologías (CONAHCYT) for the scholarship to J.J.M.-P.

Data Availability Statement: Not applicable.

Acknowledgments: We would like to thank Tecnológico Nacional de México (13265.21-P project).

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

References

1. Motta, F.L.; Stoyanov, S.R.; Soares, J.B.P. Application of Solidifiers for Oil Spill Containment: A Review. *Chemosphere* **2018**, *194*, 837–846. [CrossRef]
2. George, M.; Tan, G.; John, V.T.; Weiss, R.G. Urea and Thiourea Derivatives as Low Molecular-Mass Organogelators. *Chem. A Eur. J.* **2005**, *11*, 3243–3254. [CrossRef]
3. Sahoo, S.; Kumar, N.; Bhattacharya, C.; Sagiri, S.S.; Jain, K.; Pal, K.; Ray, S.S.; Nayak, B. Organogels: Properties and Applications in Drug Delivery. *Des. Monomers Polym.* **2011**, *14*, 95–108. [CrossRef]
4. Prathap, A.; Sureshan, K.M. A Mannitol Based Phase Selective Supergelator Offers a Simple, Viable and Greener Method to Combat Marine Oil Spills. *Chem. Commun.* **2012**, *48*, 5250. [CrossRef]
5. De Loos, M.; Friggeri, A.; Van Esch, J.; Kellogg, R.M.; Feringa, B.L. Cyclohexane Bis-Urea Compounds for the Gelation of Water and Aqueous Solutions. *Org. Biomol. Chem.* **2005**, *3*, 1631. [CrossRef]
6. Ghosh, S.; Praveen, V.K.; Ajayaghosh, A. The Chemistry and Applications of π-Gels. *Annu. Rev. Mater. Res.* **2016**, *46*, 235–262. [CrossRef]
7. Isare, B.; Petit, L.; Bugnet, E.; Vincent, R.; Lapalu, L.; Sautet, P.; Bouteiller, L. The Weak Help the Strong: Low-Molar-Mass Organogelators Harden Bitumen. *Langmuir* **2009**, *25*, 8400–8403. [CrossRef]
8. Mukherjee, S.; Shang, C.; Chen, X.; Chang, X.; Liu, K.; Yu, C.; Fang, Y. N-Acetylglucosamine-Based Efficient, Phase-Selective Organogelators for Oil Spill Remediation. *Chem. Commun.* **2014**, *50*, 13940–13943. [CrossRef]
9. Bhardwaj, V.; Patel, A.M.; Ballabh, A. Stimuli Responsive Gelation of Tert-Butylacetic Acid Based LMOGs—Applications in Remediation of Marine Oil Spills, Dye Removal and Heavy Metal Sensing. *Soft Matter* **2023**, *19*, 8595–8603. [CrossRef]
10. Sosa-Sevilla, J.E.; Brachetti-Sibaja, S.B.; Pérez-Sánchez, J.F.; Lozano-Navarro, J.I.; Díaz-Zavala, N.P. Alkoxybenzoate Derivatives: Design and Gelation Effect on Organic Solvents, Fuels, and Oils. *Water Air Soil Pollut.* **2021**, *232*, 239. [CrossRef]

11. Das, A.; Naskar, S.; Dhar, M.; Manna, U. Rapid and Scalable Synthesis of a Vanillin-Based Organogelator and Its Durable Composite for a Comprehensive Remediation of Crude-Oil Spillages. *ACS Appl. Mater. Interfaces* **2021**, *13*, 46803–46812. [CrossRef] [PubMed]
12. Su, T.; Hong, K.H.; Zhang, W.; Li, F.; Li, Q.; Yu, F.; Luo, G.; Gao, H.; He, Y.-P. Scaleable Two-Component Gelator from Phthalic Acid Derivatives and Primary Alkyl Amines: Acid–Base Interaction in the Cooperative Assembly. *Soft Matter* **2017**, *13*, 4066–4073. [CrossRef] [PubMed]
13. Zapién-Castillo, S.; Díaz-Zavala, N.P.; Melo-Banda, J.A.; Schwaller, D.; Lamps, J.-P.; Schmutz, M.; Combet, J.; Mésini, P.J. Structure of Nanotubes Self-Assembled from a Monoamide Organogelator. *Int. J. Mol. Sci.* **2020**, *21*, 4960. [CrossRef] [PubMed]
14. Thuo, M.M.; Reus, W.F.; Simeone, F.C.; Kim, C.; Schulz, M.D.; Yoon, H.J.; Whitesides, G.M. Replacing $-CH_2CH_2-$ with $-CONH-$ Does Not Significantly Change Rates of Charge Transport through Ag^{TS}-SAM//Ga_2O_3/EGaIn Junctions. *J. Am. Chem. Soc.* **2012**, *134*, 10876–10884. [CrossRef] [PubMed]
15. Zapien, S.; Perez-Sanchez, J.F.; Díaz, N.; Melo-Banda, J.A. Qualitative determination of an amide of unknown fragmentation pattern using Gas Chromatography—Mass Spectrometry. *AJER* **2020**, *9*, 242–246.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.