

Synthesis of a new furan-bearing triazine dichloride compound

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Abstract:

Due to their strong electron affinity and symmetrical structure, triazine and its derivatives are widely recognized as electron-deficient units with good electrical and optical characteristics. When triazine-based molecular acceptor units are used in organic solar cell architectures, various positive impacts on device performance result, including increased crystallinity, increased charge transport mobility, and increased absorption. Good mechanical and thermostable qualities are only a couple of the special benefits that organic materials with an s-triazine ring in their backbone also enjoy. According to additional study, triazine-based polymers are used as a starting point for dyes, crosslinking agents, and flame-retardant compounds. Additionally, it has been demonstrated that polymers containing conjugated triazine rings offer outstanding optoelectronic characteristics for organic light-emitting diodes. Donor-acceptor compounds have been receiving increased attention lately, especially in opto-electronic applications. In this work, a novel compound named triazine-furan, comprised of a triazine acceptor moiety and a furan donor side group, was designed and synthesised for the first time. The influences of temperature and the feeding proportion of cyanuric chloride to furfurylamine were investigated to optimise the reaction yield and purification process. The synthesised compound was characterised using thin-layer chromatography (TLC), Fourier-transform infrared spectroscopy (FTIR), and proton nuclear magnetic resonance (¹H-NMR) spectroscopy.

Keywords: compound, conjugated diene, cyanuric chloride, triazine.

Classification numbers: 2.1, 2.3

1. Introduction

Triazine and its derivatives are well known as electron-deficient units that possess excellent electronic and photonic properties owing to their high electron affinity and symmetrical structure [1-3]. The use of triazine-based molecular acceptor units in organic solar cell structures give rise to many beneficial effects on device performance such as higher crystallinity, charge transport mobility, as well as broadened absorption [4]. Organic materials with an s-triazine ring in their backbone also benefit from unique advantages such as good mechanical and thermostable properties [5]. Other research indicates that triazine-based polymers are employed as a precursor to flame-retardant materials, dyes, and crosslinking agents [6, 7]. Besides, polymers containing conjugated triazine rings have been shown to possess excellent optoelectronic properties for organic light-emitting diodes [8].

Indeed, donor-acceptor (D-A) organic materials have attracted substantial interest in opto-electronic applications such as organic solar cells, thin-film transistors, and organic light-emitting diodes [9, 10]. It has been reported in the literature that incorporating donor groups into the triazine moiety results in donor-acceptor systems with interesting characteristics such as a two-photon absorbing cross-section [11]. Several units, including ferrocenyl, phenyl, and thiophene, have been

combined with triazine in donor-acceptor systems [12-14].

Therefore, in this work, a novel compound named triazine-furan (TF), comprised of a triazine acceptor moiety and a furan donor side group, was designed and synthesised for the first time.

The authors use cyanuric chloride and furfurylamine as reaction agents with N, N-diisopropylethylamine (DIPEA) as the catalyst to synthesize the compound. Factors including temperature and molar ratio between cyanuric chloride and furfurylamine are controlled over the reaction to optimize the reaction yield and product purity. The authors use chemical analytical techniques such as proton nuclear magnetic (¹H-NMR), Fourier-transform infrared spectroscopy (FTIR), and thin-layer chromatography (TLC) to identify the purity and reaction yield of the synthesised compounds.

2. Materials and methods

2.1. Materials

The materials used were cyanuric chloride (CyC, Sigma Aldrich, 99%), furfurylamine (FuA, Sigma Aldrich, 99%), and N,N-diisopropylethylamine (DIPEA, Sigma Aldrich, 99%). All the solvents were purchased from Fisher Chemicals.

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2.2. Instrumentation

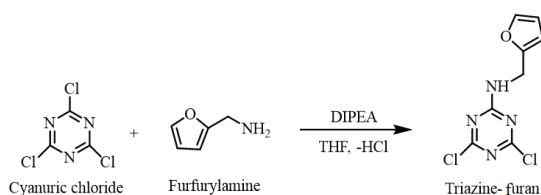
Proton nuclear magnetic resonance (^1H -NMR) spectra were recorded in a deuterated chloroform solvent (CDCl_3), with TMS as an internal reference, on a Bruker Avance 500 MHz spectrometer. FTIR spectra were collected as an average of 524 scans with a resolution of 4 cm^{-1} on an FT-IR Tensor 27 spectrometer. Thin-layer chromatography plates were purchased from Sigma-Aldrich.

2.3. Synthesis of TF compound

The preparation of triazine-furan (TF) was carried out in a round-bottomed flask, the concentration of the reaction solution was 4 M in dried tetrahydrofuran (THF). In a dilute solution of cyanuric chloride in dried THF, a mixture of furfurylamine and DIPEA was dissolved in dried THF and added dropwise at the various temperatures (various values from -20°C to room temperature). The reaction was continuously stirred at the designed temperature for 4 h and then followed by TLC. After the reaction was stopped, the obtained mixture was washed with distilled water, dried over K_2CO_3 , then purified by flash chromatography (hexane/ethyl acetate, 5:1 (v/v)) to yield TF.

3. Results and discussion

The synthesis pathway of triazine-furan (TF) from cyanuric chloride (CyC) and furfurylamine (FuA) is shown in Scheme 1. The conversion of FuA ($R_f=0$) and CyC ($R_f=0.85$) to TF ($R_f=0.7$) was followed by TLC (hexane/ethyl acetate=5/1 (v/v)).



Scheme 1. Synthesis of the TF compound.

After the purification process, the final product was structurally characterised by ^1H -NMR and the result is shown in Fig. 1 with δ (ppm): 6.57 (a, 1H, NH), 4.67 (b, 2H, N-CH₂), 6.31-6.34 (c, d, 2H, -CH=), and 7.37 (e, 1H, O-CH=). The product was also analysed by FTIR (Fig. 2), which illustrated the characteristic vibration of the triazine ring as evidenced by the absorption bands at 1604.71 and 1591.21 cm^{-1} and the band of 790.78 cm^{-1} that is attributed to the C-Cl stretching vibration. Besides, the bands at 3249.92-3120.70 cm^{-1} and 790.78 cm^{-1} are assigned to the secondary amine and furan groups, respectively. Thus, the resulting spectrum contributes to the confirmation of the intended chemical structure of the title compound.

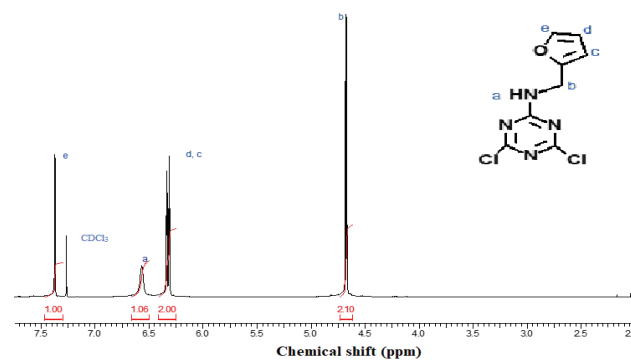


Fig. 1. ^1H -NMR spectrum of the TF product.

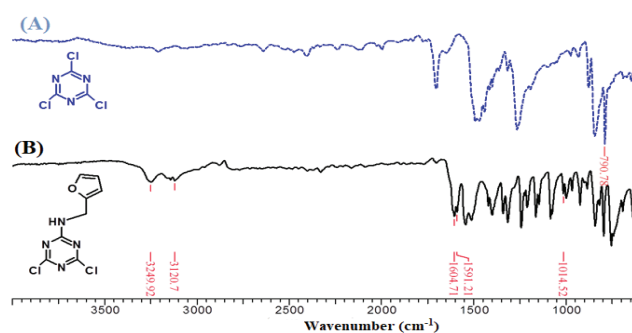


Fig. 2. FTIR spectrum of (A) cyanuric chloride and (B) the triazine-furan product.

3.1. Effect of temperature

Because the reactivity of cyanuric chloride is strongly influenced by temperature, we studied the temperature dependence of the reaction. With the use of equimolar amounts of cyanuric chloride and furfurylamine, the reactions were carried out at various temperatures from -20 to 30°C (room temperature). The reaction was followed by TLC and the yields obtained were compared. The results of the comparison are shown in Fig. 3, which indicates a nearly double increase in yields from 21% at 30°C to 40% at 0°C . When the reaction was carried out at -10°C , the yield increased to 63%, but the yield remained the same value as the temperature was cooled down further to -20°C . Therefore, a temperature of -10°C was chosen to perform this reaction.

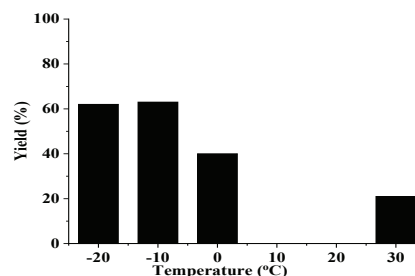


Fig. 3. Synthesis yield of TF at various reaction temperatures.

3.2. Effect of feeding molar ratio of cyanuric chloride/furfurylamine

For further study, the reaction yield was expected to increase by shifting the reaction equilibrium. The reaction was carried out with various feeding molar ratios of CyC/FuA from 1 to 2. As shown in Table 1, by fixing the temperature at -10°C and increasing the molar ratio of CyC/FuA from 1.00 to 1.25 and 1.5, the yield increased and reached a maximum of 92% at a feeding molar ratio of 1.5.

Table 1. Data summary of triazine furan (TF) preparation.

Entry	[CyC] ₀ : [FuA] ₀ : [DIPEA] ₀	Temperature (°C)	Yield (%)
1	1.0/1.0/1.0	-20	62
2	1.0/1.0/1.0	-10	63
3	1.0/1.0/1.0	0	40
4	1.0/1.0/1.0	30	21
5	1.0/1.0/1.0	-10	63
6	1.25/1.0/1.25	-10	77
7	1.5/1.0/1.5	-10	92
8	2.0/1.0/2.0	-10	81

However, when a higher molar ratio was examined, the TF product was obtained at a lower yield. The use of a large excess of CyC in the higher molar ratio may cause a product loss during purification, which may explain the low yield with a molar ratio above 1.5. Thus, a feeding molar ratio of 1.5 for CyC/FuA and a temperature of -10°C were chosen as the optimum conditions for synthesis of the compound.

4. Conclusions

The new furan-bearing triazine dichloride compound, so called triazine-furan (TF), was successfully prepared via a direct coupling reaction between cyanuric chloride and furfurylamine in the presence of DIPEA. It was found that the feeding molar ratio of 1.5 for CyC/FuA and temperature of -10°C are the optimum conditions for the preparation of TF, which resulted in a yield of 92%.

CRediT author statements

Thi Thuy Dung Phung, Thu Thuy Truong: Conceptualization, Methodology, Data curation, Formal analysis, Writing - Review & Editing; Thanh Luan Nguyen, Tran Ha Nguyen: Conceptualization, Methodology, Writing - Original draft preparation, Writing - Review & Editing.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] I. Nenner, G.J. Schulz (1975), "Temporary negative ions and electron affinities of benzene and *N*-heterocyclic molecules: Pyridine, pyridazine, pyrimidine, pyrazine, and *s*-triazine", *J. Chem. Phys.*, **62**, pp.1747-1758, DOI: 10.1063/1.430700.
- [2] R. Fink, C. Frenz, M. Thelakkat, et al. (1997), "Synthesis and characterization of aromatic poly(1,3,5-triazine-ether)s for electroluminescent devices", *Macromolecules*, **30**, pp.8177-8181, DOI: 10.1021/ma970528x.
- [3] H. Meier, E. Karpuk, H.C. Holst (2006), "Star-shaped pushpull compounds having 1,3,5-triazine cores", *Eur. J. Org. Chem.*, **2003**(21), pp.2609-2617, DOI: 10.1002/ejoc.200300132.
- [4] Y. Duan, X. Xu, H. Yan, et al. (2017), "Pronounced effects of a triazine core on photovoltaic performance - Efficient organic solar cells enabled by a pdi trimer-based small molecular acceptor", *Adv. Mater.*, **29**(7), DOI: 10.1002/adma.201605115.
- [5] S.M. Osman, S.N. Khattab, E.S.A. Aly, et al. (2017), "1,3,5-triazine-based polymer: Synthesis, characterization and application for immobilization of silver nanoparticles", *J. Polym. Res.*, **24**, DOI: 10.1007/s10965-017-1385-2.
- [6] J.X. Jiang, A. Trewin, F. Su, et al. (2009), "Microporous poly(tri(4-ethynylphenyl)amine) networks: Synthesis, properties, and atomistic simulation", *Macromolecules*, **42**(7), pp.2658-2666, DOI: 10.1021/ma802625d.
- [7] J.X. Jiang, F. Su, A. Trewin, et al. (2008) "Synthetic control of the pore dimension and surface area in conjugated microporous polymer and copolymer networks", *J. Am. Chem. Soc.*, **130**(24), pp.7710-7720, DOI: 10.1021/ja8010176.
- [8] N. Chakravarthi, U.K. Aryal, K. Gunasekar, et al. (2017), "Triazine-based polyelectrolyte as an efficient cathode interfacial material for polymer solar cells", *ACS Appl. Mater. Interfaces*, **9**(29), pp.24753-24762, DOI: 10.1021/acsami.7b03187.
- [9] H.A.M. Mullekom, J.A.J.M. Vekemans, E.E. Havinga, et al. (2001), "Developments in the chemistry and band gap engineering of donor-acceptor substituted conjugated polymers", *Materials Science and Engineering: R: Reports*, **32**(1), pp.1-40, DOI: 10.1016/S0927-796X(00)00029-2.
- [10] Z.G. Zhang, J. Wang (2012), "Structures and properties of conjugated donor-acceptor copolymers for solar cell applications", *J. Mater. Chem.*, **22**(10), pp.4178-4187, DOI: 10.1039/C2JM14951F.
- [11] C. Y. Zhi, F. Qi, X. Gang, et al. (2005), "Cooperative enhancement of two-photon absorption of multibranched compounds with vinylenes attaching to the *s*-triazine core", *Chem. Lett.*, **34**(5), pp.644-645, DOI: 10.1246/cl.2005.644.
- [12] R. Maragani, R. Misra (2013), "Donor-acceptor ferrocenyl triazines: Synthesis and properties", *Tetrahedron Lett.*, **54**(39), pp.5399-5402, DOI: 10.1016/j.tetlet.2013.07.119.
- [13] R. Misra, P. Gautam, R. Sharma, et al. (2013), "Donor- π -acceptor- π -donor ferrocenyl benzothiadiazoles: Synthesis, structure, and properties", *Tetrahedron Lett.*, **54**(5), pp.381-383, DOI: 10.1016/j.tetlet.2012.11.016.
- [14] R. Maragani, T. Jadhav, S.M. Mobin, et al. (2012), "Synthesis, structure, photophysical, and electrochemical properties of donor-acceptor ferrocenyl derivatives", *Tetrahedron Lett.*, **68**(36), pp.7302-7308, DOI: 10.1016/j.tet.2012.06.094.