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RESEARCH ARTICLE

Design, Synthesis and Photophysical Properties of New 2,6-Dicyanoanilines Based on Isophthalaldehyde and Terephthalaldehyde Skeleton

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Abstract: A novel series of 2, 6-dicyanoanilines based on isophthalaldehyde and terephthalaldehyde were designed, synthesized and characterized by spectral methods. The new chemical entities thus synthesized were studied for their photophysical properties.

Keywords: Isophthalaldehyde, Terephthalaldehyde, Dicyanoanilines, Malanonitrile

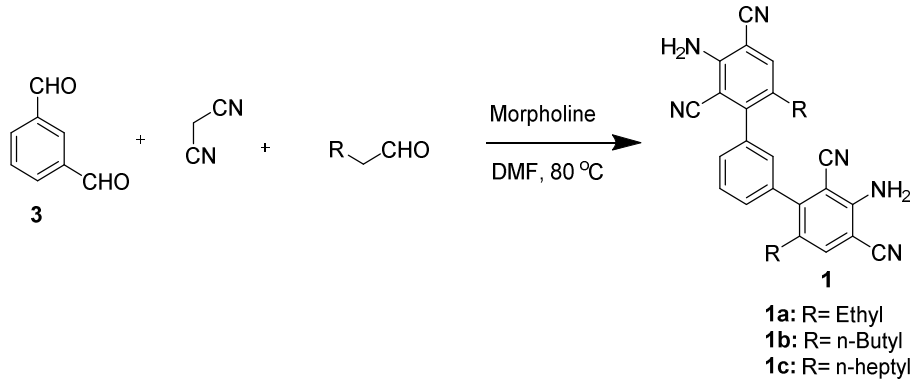
Introduction

The 2,6-dicyanoanilines and their analogues are known for their significant fluorescent properties[1] and have been studied and exploited in many different areas of science like non-linear optical materials[2], molecular electronic devices[3] and have been reported to exhibit biological activities like antileishmanial[4] and antifungal[5] activity. Also, the flexibility of conversion of cyano and amino groups in to other functional groups makes these compounds versatile for utilization as intermediates in the preparation of many diverse substrates for comprehensive use. There are number of such compounds and methods of their preparations are reported in the literature[6,7]**.** Most of the reported 2,6-dicyanoanilines and their related compounds are based on single Acceptor-Donor-Acceptor (A-D-A) moiety on the aromatic skeleton except for a few synthetic strategies reported for tri-substituted 2,6-dicyanoanilines by Klebe[8], Webster *et al.,*[9] and Wallenfels *et al.,*[10] where single aromatic ring bears two A-D-A systems.

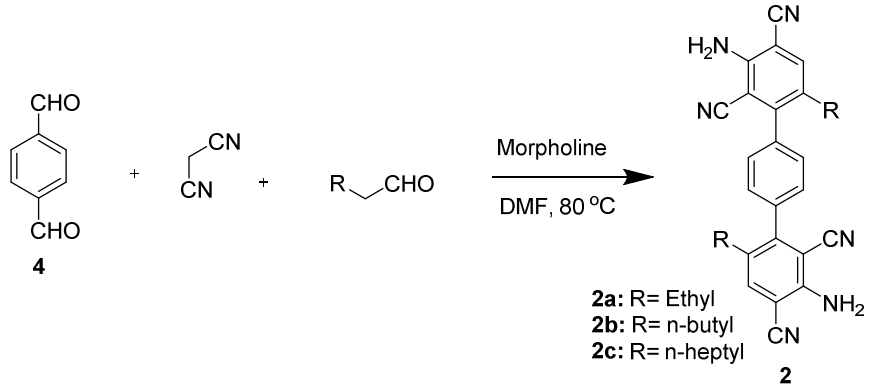
To the best of our knowledge, there is no report on the multicomponent reaction of aromatic di-aldehyde (phthalaldehyde, isophthalaldehyde or terephthalaldehyde) with malononitrile and aliphatic aldehyde in the presence of base which can deliver a number of very interesting new chemical entities and the structure and property, relationship of this type of molecules can be studied. H. B. Borate and group[11] reported the multicomponent reaction of aromatic aldehyde, aliphatic aldehyde and malononitrile in the presence of morpholine in dimethylformamide to give 3-aryl,4-alkyl-2,6-dicyanoanillnes in good yield.

Experimental

We designed molecules based on the same synthetic strategy to build up new chemical entities bearing two A-D-A systems (Scheme 1 and 2, Table 1). Accordingly, we performed multicomponent reactions of isophthalaldehyde or terephthalaldehyde with malononitrile and aliphatic aldehyde (butanal or hexanal or nonanal) in the presence of morpholine in dimethylformamide at 80 ^{o}C for 8 h and results are presented herein. As expected, the reaction gave mixture of a number of products and it was difficult to isolate the desired compound by column chromatography. The desired products were obtained by recrystallization of crude product followed by column chromatography. All the products were characterized by ^{1}H NMR, ^{13}C NMR, IR and mass spectroscopy. These compounds were found to be soluble in DMF and DMSO and sparingly soluble in methanol, acetonitrile, chloroform, acetone, dichloromethane, ethyl acetate *etc*.



Scheme 1. Synthesis of dicyanoanilines based on isophthalaldehyde skeleton



Scheme 2. Synthesis of dicyanoanilines based on terephthalaldehyde skeleton

Table 1. Synthesis of new 2,6-dicyanoanilines (**1a-1c** and **2a-2c**)

Entry	Aliphatic aldehyde	Aromatic aldehyde	Product	Yeild[a]
1	Butanal	3	1a	35
2	Hexanal	3	1b	43
3	Nonanal	3	1c	50
4	Butanal	4	2a	45
5	Hexanal	4	2b	48
6	Nonanal	4	2c	53

[a]*The yields given are for isolated products*

*Representative procedure for the preparation of 3,3''-diamino-6,6''-diheptyl-[1,1':3',1''-terphenyl]-2,2'',4,4''-tetracarbonitrile (**1c**)*

To a mixture of isophthalaldehyde (0.500 g, 0.003727 mol), nonanal (1.272 g, 0.008946 mol) and malononitrile (1.08 g, 0.01639) in dry DMF taken in a round bottom flask and equipped with reflux condenser and guard tube, morpholine (1.55 g, 0.01788 mol) was added at 0 ^{o}C and the mixture was allowed to cool to room temperature and stirred at 80 ^{o}C for 8 h. Progress of the reaction was checked by the TLC. (Solvent system- Petroleum ether: Ethyl acetate (80:20)). After completion of reaction, the reaction mixture was allowed to cool to room temperature and water was added, then extracted with excess of ethyl acetate (250 mL), dried over sodium sulphate and concentrated on rotavapour. Ethyl acetate (10 mL) was added and the solution of reaction mixture was added slowly drop by drop to 100 mL petroleum ether for recrystallization. After settlement of the precipitate in the beaker, the supernatant solution was decanted in other beaker. The precipitate thus obtained was washed with 10% ethyl acetate and petroleum ether mixture. The residue thus obtained was chromatographed on silica gel (60-120 mesh) using 15-20% ethyl acetate in petroleum ether to afford 3,3''-diamino-6,6''-diheptyl-[1,1':3',1''-terphenyl]-2,2'',4,4''-tetracarbonitrile as off-white flappy solid (1.03 g 50%) mp: 190 ^{o}C. UV (In DMF): 361nm. IR (Neat): 1270, 1470, 1556, 1591, 1643, 2218, 2853, 2923, 2953, 3243, 3336, 3442, 3476 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 0.46-0.73 (m, 6H), 0.77-1.28 (m, 20H), 1.99-2.28 (m, 4H), 4.95 and 5.08 (2 s, 4H), 6.90 (s, 1H), 7.14 (d, 2H), 7.30 (s, 2H), 7.42 (t, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): 14.01(2C), 22.51(2C), 28.86(4C), 30.79(2C), 31.59(2C), 31.90(2C), 96.66(2C), 98.80(2C), 115.18(2C), 115.95(2C), 128.43, 128.91(2C), 129.17(2C), 131.52, 137.25 (2C), 137.42(2C), 149.26(2C), 149.53(2C). MS (ESI) *m/z*: 579.2 (M+Na). HRMS Obtained $C_{36}H_{41}N_6$ 557.3400 (M+H), Calculated $C_{36}H_{41}N_6$ 557.3393 (M+H). (In case of **1a** and **2a** the amount of base (Morpholine) used was 3.0 equivalent)

*3,3''-Diamino-6,6''-dibutyl-[1,1':3',1''-terphenyl]-2,2'',4,4''-tetracarbonitrile (**1b**)*

Off-white flappy solid (0.709 g 43%) mp: 212 ^{o}C. UV (In DMF): 361 nm. IR (Neat): 1269, 1477, 1664, 2164, 2218, 2870, 2929, 2956, 3243, 3336, 3443, 3480 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$+DMSO-d_6): 0.62-0.77 (m, 6H), 0.98-1.15 (m, 4H), 2.20-2.37 (m, 4H), 6.60 (s, 4H), 7.20 (s, 1H), 7.38-7.47 (m, 2H), 7.62-7.70 (m, 1H), 7.75 (s, 1H), 7.76 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): 13.58 (2C), 21.66 (2C), 30.90 (2C), 32.41 (2C), 95.65 (2C), 97.71 (2C), 115.47 (2C), 116.47 (2C), 128.37 (1C), 128.64 (2C), 128.94 (1C), 129.31 (2C), 137.45 (2C), 138.41 (2C), 149.33 (1C), 149.61 (1C), 150.61 (1C), 150.76 (1C). HRMS Obtained $C_{30}H_{29}N_6$ 473.2457 (M+H), $C_{30}H_{29}N_6$ Calculated 473.2355(M+H)).

*3,3''-Diamino-6,6''-diethyl-[1,1':3',1''-terphenyl]-2,2'',4,4''-tetracarbonitrile (**1a**)*

Off-white flappy solid (0.542 g, 35%) mp: 222 ^{o}C. UV (DMSO): 361 nm. IR (Neat): 1273, 1469, 1550, 1594, 1647, 2220, 2857, 2924, 2953, 3242, 3334, 3442, 3445 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6): 0.04-0.16 (m, 6H), 1.39-1.56 (m, 4H), 5.25 (s, 4H), 6.27 (s, 1H), 6.45-6.54 (m, 2H), 6.68 (s, 2H), 6.73-6.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): 13.80 (2C), 23.55 (2C), 94.89 (2C), 96.77 (2C), 114.03 (2C), 114.94 (2C), 127, 127.12 (2C), 127.51 (2C), 129.28, 135.73 (2C), 136.17 (2C), 147.48, 147.73, 149.18, 149.29. HRMS Obtained $C_{26}H_{21}N_6$ 417.1822 (M+H), Calculated $C_{26}H_{21}N_6$ 417.1829 (M+H).

*3,3''-Diamino-6,6''-diheptyl-[1,1':4',1''-terphenyl]-2,2'',4,4''-tetracarbonitrile (**2c**)*

Off-white flappy solid (1.09 g, 53%) mp: decomposition around 240-243 ^{o}C. UV (DMF): 361 nm. IR (Neat): 1267, 1466, 1644, 2219, 2851, 2921, 2952, 3226, 3324, 3378, 3444, 3469 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 0.84 (t, 6H), 1.03-1.47 (m, 20H), 2.37 (t, 4H), 5.15 (bs, 4H), 7.39(s, 4H), 7.53(s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$+DMSO-d_6): 13.72 (2C), 21.99 (2C), 28.23, 28.37 (2C), 28.47, 28.62, 30.34, 30.44, 31.09, 31.14, 31.48, 95.85 (2C), 97.68, 97.93, 115.08 (2C), 116.04 (2C), 128.31 (2C), 128.35 (2C), 129.30, 129.48, 137.09, 137.13, 137.35, 137.43, 148.89, 149.13, 150.33, 150.46. HRMS Obtained $C_{36}H_{41}N_6$ 557.3397 (M+H) $C_{36}H_{41}N_6$ Calculated 557.3394 (M+H).

*3,3''-Diamino-6,6''-dibutyl-[1,1':4',1''-terphenyl]-2,2'',4,4''-tetracarbonitrile (**2b**)*

Off-white flappy solid (0.792 g, 48 %) mp: decomposition around 267-270 ^{o}C. UV (DMF): 361 nm. IR (Neat): 1266, 1466, 1632, 2216, 2865, 2928, 2953, 3237, 3358, 3477 cm^{-1}. 1H NMR (500 MHz, DMSO-d_6): 0.70 (bs, 6H), 1.06 (bs, 4H), 1.24 (bs, 4H), 2.27 (bs, 4H), 6.62 (bs, 4H), 7.44 (bs, 4H), 7.78 (bs, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 13.48 (2C), 21.69 (2C), 30.95 (2C), 32.48 (2C), 95.64 (2C), 97.47, 97.71, 115.43 (2C), 116.48 (2C), 128.62 (2C), 128.71 (2C), 129.09, 129.20, 137.19, 137.32, 138.53 (2C), 149.57, 149.83, 150.81, 150.70. MS (ESI) *m/z*: 495.2 (M+Na). HRMS Obtained $C_{30}H_{29}N_6$**:** 473.2448 (M+H), Calculated $C_{30}H_{29}N_6$**:** 473.2455 (M+H).

*3,3''-Diamino-6,6''-diethyl-[1,1':4',1''-terphenyl]-2,2'',4,4''-tetracarbonitrile (**2a**)*

Off-white flappy solid (0.697 g, 45%) mp: decomposition around 277-278 ^{o}C. UV (DMF): 361 nm. IR (Neat): 1267, 1463, 1632, 2215, 2863, 2930, 2951, 3238, 3358, 3478 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): 0.81-1.00 (m, 6H), 2.20-2.37 (m, 4H), 6.63 (s, 4H), 7.45 and 7.46 (2s, 4H), 7.79 and 7.80 (2s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 14.87, 15.02, 24.59, 24.67, 95.77 (2C), 97.44, 97.58, 115.50 (2C), 116.49 (2C), 128.63 (2C), 128.68 (2C), 128.76, 129.54, 137.14, 137.30, 138.00 (2C), 149.39, 149.59, 150.73, 150.84. HRMS Obtained $C_{26}H_{21}N_6$ 417.1822 (M+H), Calculated $C_{26}H_{21}N_6$ 417.1829 (M+H)).

Results and Discussion

Photophysical properties

The photophysical properties of synthesized compounds were studied as they show strong fluorescence under UV. The UV-Visible absorption and fluorescence spectra of synthesized compounds were recorded in dimethyl formamide and are presented in Figure 1 and 2. The wavelength of maximum absorption (λ_{max}) in the UV was observed at ~360 nm while the wavelength of maximum emission ($\lambda_{max.emi}$) for the compounds was observed at ~412 nm. The fluorescence spectra of the target compounds were recorded at fixed UV absorption of 0.1 optical densities.

Table 2. UV and fluorescence observations of **1a-1c** and **2a-2c**

Compd. No.	UV absorption maximum at 361 nm	Fluorescence maximum at 412 nm	Length of carbon chain
1a	0.1021	34.32	Two
1b	0.1000	36.83	Four
1c	0.1030	33.39	Seven
2a	0.1078	20.21	Two
2b	0.1068	27.61	Four
2c	0.1035	25.37	Seven

The compound **1b** showed maximum fluorescence and the compound **2a** showed minimum fluorescence while all other entities showed intermediate fluorescence. The values for fluorescence maxima of compounds with various chains are given in Table 2 and it is observed that between the two isomers of phthalaldehyde used in present study, the compound obtained from the isophthalaldehyde with four carbon chain shows maximum fluorescence.

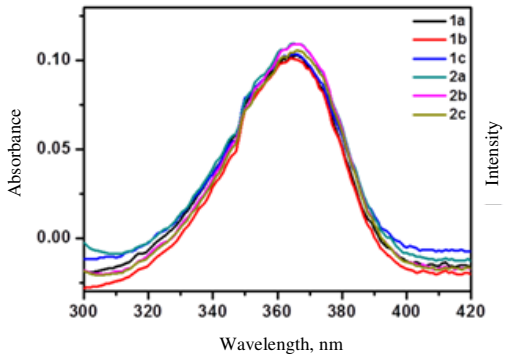


Figure 1. UV Abosorption Spectra of compound **1a-c, 2a-c**

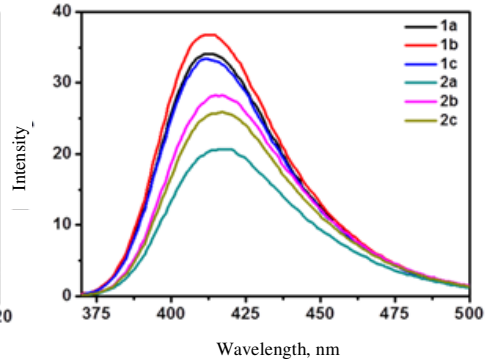


Figure 2. Fluorescence spectra of compounds **1a-c, 2a-c**

Conclusion

This work describes the preliminary results about synthesis of novel 2,6-dicyanoanilines obtained from aromatic dialdehydes, isophthalaldehyde and terephthalaldehyde and their fluorescence properties. These compounds can be modified to obtain a variety of useful compounds and can be screened for various applications. Based on these results, we are planning to synthesize compounds with long hydrophobic aliphatic chains and polar groups in the molecule and to screen these molecules in different forensic applications like finding adulteration in the vegetable oil and staining the fingerprints *etc*.

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