

Table I. Characterization Data of 1-Amino-4-anilinoanthraquinone 2-Ethers (Dyes III)

compd	R ¹	R ²	synthesis method and recryst solv ^a	crude prod yield, %	$\lambda_{\max}$ (log ϵ) in C ₆ H ₅ Cl ^b	mp, °C
IIIa	H	H			454 s (3.93), 573 (4.11), 610 (4.12)	
IIIb	Br	H			584 (4.12), 621 (4.11)	
IIIc	OC ₆ H ₅	H	1A	75.7	528 s (3.96), 536 (4.18), 600 (4.19)	189-190
IIId	OC ₆ H ₄ CH ₃ - <i>p</i>	H	1A	73.8	530 s (3.93), 562 (4.15), 600 (4.16)	168
IIIe	OC ₆ H ₄ OCH ₃ - <i>p</i>	H	1A	94.5	534 s (4.02), 562 (4.20), 600 (4.21)	184
IIIf	OOCH ₃ - <i>m</i>	H	2A	69.0	534 s (3.92), 564 (4.12), 600 (4.13)	120
IIIg	OC ₆ H ₄ OH- <i>p</i>	H	1A	80.3	534 s (3.94), 562 (4.14), 600 (4.14)	220
IIIh	OC ₆ H ₄ NH ₂ - <i>p</i>	H	1A	128.0	534 s (3.94), 561 (4.15), 600 (4.16)	202
IIIi	OC ₆ H ₄ C(CH ₃) ₂ - <i>p</i> -C ₆ H ₄ OH- <i>p</i>	H	1A	54.7	536 s (3.90), 564 (4.15), 600 (4.16)	110
IIIj	OCH ₃	H	3B	126.0	530 s (4.00), 552 (4.18), 582 (4.20)	165
IIIk	OCH ₃	CH ₃	3C	111.0	530 s (4.00), 554 (4.19), 5.93 (4.21)	118
IIIl	OC ₆ H ₅	CH ₃	1B	87.4	568 (3.15), 604 (4.15)	148
IIIm	OC ₆ H ₄ CH ₃ - <i>p</i>	CH ₃	1C	85.7	566 (4.16), 602 (4.18)	194
IIIn	OC ₆ H ₄ OCH ₃ - <i>p</i>	CH ₃	1C	81.8	534 s (3.91), 565 (4.16), 602 (4.18)	200
IIIo	OCH ₃	OCH ₃	1A	103.0	530 s (3.90), 556 (4.09), 592 (4.11)	118
IIIp	OC ₆ H ₅	OCH ₃	1A	82.5	536 s (3.98), 568 (4.18), 600 (4.18)	128
IIIq	OC ₆ H ₄ CH ₃ - <i>p</i>	OCH ₃	1A	94.3	536 s (3.98), 602 (4.18), 602 (4.18)	182
IIIr	OC ₆ H ₄ OCH ₃ - <i>p</i>	OCH ₃	1C	86.4	536 s (4.00), 568 (4.18), 600 (4.18)	204

^a A = acetone. B = ethanol. C = toluene. ^b S = shoulder.

g), mp 165-166 °C. The compound was confirmed by mass spectrometry and elemental analysis.

The other bands were also isolated and their structures confirmed by mass spectrometry. Similarly prepared from appropriate bromoaryl compounds were other dyes (III) listed in Table I.

Registry No. I (X = Br), 81-49-2; II (R = H, X = CH₃O), 2872-48-2; IIIa, 4395-65-7; IIIb, 1564-71-2; IIIc, 86397-46-8; IIId, 90791-31-4; IIIe, 90791-32-5; IIIf, 90791-33-6; IIIg, 90791-34-7; IIIh, 90791-35-8; IIIi, 90791-36-9; IIIj, 90791-37-0; IIIk, 90791-38-1; IIIl, 90822-50-7; IIIm, 90791-39-2; IIIn, 90791-40-5; IIIo, 90791-41-6; IIIp, 90791-42-7;

IIIq, 90791-43-8; IIIr, 90791-44-9; C₆H₅NH₂, 62-53-3; C₆H₅OH, 108-95-2; *m*-CH₃OC₆H₄OH, 150-19-6; C₆H₅Br, 108-86-1.

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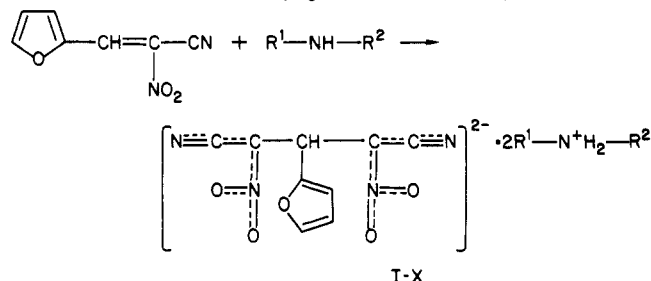
Synthesis of Some Bis(ammonium) Salts of 2,4-Dinitro-3-(2-furyl)glutarodinitrile

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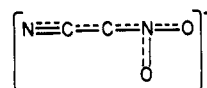
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A number of bis(ammonium) salts of 2,4-dinitro-3-(2-furyl)glutarodinitrile are synthesized from 1-nitro-1-cyano-2-(2-furyl)ethene via reaction with aliphatic and alicyclic amines. The structure of the products is supported by IR and NMR spectra.

In continuation of our investigations on the reaction of cyanonitroalkenes with amines (1-4), we carried out the reaction of 1-nitro-1-cyano-2-(2-furyl)ethene (5) with aliphatic and alicyclic amines and obtained the corresponding bis(ammonium) salts of 2,4-dinitro-3-(2-furyl)glutarodinitrile (I-X).



The structures of the compounds follow from elemental analyses, spectroscopic data (Table I), and some chemical reactions. There are several absorption bands in the IR spectra in the region 1470-1080 cm⁻¹ and a band at 2210-2195 cm⁻¹ which correspond to the vibrations of the conjugated anionic system (1-4, 6, 7)



This anion is also confirmed by the presence of the three furyl protons at δ 7.40, 6.24, and 5.96 and one proton at δ 5.40 in NMR spectra. The presence of ammonium counterion is proved by the broad absorption band at 3300-2600 cm⁻¹ in IR spectra (6, 8), by a signal at δ 7.76 or 8.40 (D₂O exchanged) in NMR spectra, and also by acidification of the salts with excess hydrobromic acid, when the respective ammonium bromides were obtained quantitatively.

All salts are crystalline solids, easily soluble in water and polar solvents, insoluble in ether, benzene, chloroform, tetrachloromethane, and petroleum ether. They must be kept in dark

Table I. Bis(ammonium) Salts of 2,4-Dinitro-3-(2-furyl)glutarodinitrile^a

no.	R ¹	R ²	yield, %	mp, °C	IR (in KBr) ν , cm ⁻¹		
					N≡C	⁺ NH _n	[NC≡C≡NOC] ⁻
I	H	n-C ₃ H ₇	98.0	117-118	2205	3300-2700	1460, 1310, 1230, 1080
II	H	n-C ₄ H ₉	95.9	108-109	2195	3200-2700	1470, 1310, 1230, 1080
III	H	C(CH ₃) ₃	60.0	155-167	2205	3300-2700	1440, 1330, 1245, 1090
IV	H	C ₆ H ₁₁	80.3	138-139	2200	3200-2800	1460, 1320, 1240, 1100
V	H	C ₈ H ₁₇	70.9	119-120	2210	3300-2800	1480, 1320, 1230, 1080
VI	H	C ₁₂ H ₂₅	71.0	118-119	2210	3300-2700	1470, 1320, 1230, 1080
VII	H	C ₁₆ H ₃₃	71.0	121-122	2210	3300-2800	1470, 1320, 1240, 1080
VIII	H	C ₁₇ H ₃₅	73.3	108-110	2210	3300-2800	1470, 1320, 1240, 1080
IX	C ₂ H ₅	C ₂ H ₅	75.3	129-130	2195	3200-2700	1465, 1320, 1225, 1090
X	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \quad \quad \\ \text{CH}_2-\quad -\text{CH}_2 \end{array}$		82.9	129-130	2195	3100-2600	1460, 1310, 1210, 1100

NMR δ

no.	R ¹	R ²	CH ₃	CH ₂	CH		⁺ NH _n
III	H	C(CH ₃) ₃	1.22 (s, 18 H)		5.40 (s, 1 H)	5.96 (d, 1 H) 6.24 (t, 1 H) 7.40 (d, 1 H)	7.76 (s, 6 H)
IX	C ₂ H ₅	C ₂ H ₅	1.16 (t, 12 H)	2.88 (q, 8 H)	5.40 (s, 1 H)	5.96 (d, 1 H) 6.24 (t, 1 H) 7.40 (d, 1 H)	8.40 (s, 4 H)

^a Elemental analyses (C, H, N) in agreement with theoretical values have been obtained and were submitted for review.

containers at 0-5 °C, because of their decomposition at room temperature in daylight.

Experimental Section

A solution of 1-nitro-1-cyano-2-(2-furyl)ethene (0.01 mol) in dioxane is added in drops to the solution of freshly distilled amine (0.01 mol) in 60 cm³ of diethyl ether and 10 cm³ of methanol at room temperature with vigorous stirring. About 10 min after, the precipitate separated is filtered and washed with diethyl ether. The obtained bis(ammonium) salts of 2,4-dinitro-3-(2-furyl)glutarodinitrile are purified through reprecipitation with ether from methanolic solution.

Registry No. I, 81548-95-0; II, 81548-96-1; III, 81548-97-2; IV, 81548-98-3; V, 91328-21-1; VI, 91328-22-2; VII, 91328-23-3; VIII, 91328-24-4; IX, 81548-99-4; X, 81549-00-0; 1-nitro-1-cyano-2-(2-furyl)ethene, 67075-62-1; 1-propanamine, 107-10-8; 1-butanamine, 109-73-9; 2-methyl-2-propanamine, 75-84-9; cyclohexylamine, 108-91-8; 1-octan-

amine, 111-86-4; 1-dodecanamine, 124-22-1; 1-hexadecanamine, 143-27-1; 1-heptadecanamine, 4200-95-7; N-ethylethanamine, 109-89-7; piperidine, 110-89-4.

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Correction

Densities of the Molten Salt System Cesium Bromide-Cuprous Bromide. Gert J. Lamprecht* and G. D. Peckham, *J. Chem. Eng. Data* **1977**, *22*, 329.

This paper was originally published with a single author. G. D. Peckham should have been cited as a coauthor.