

STUDY OF THE REACTIVITY OF SUBSTITUTED PHTHALIC ACIDS AND ANHYDRIDES IN CONDENSATION REACTIONS WITH N-CARBOXYMETHYLPYRIDINIUM SALTS AND THE SYNTHESIS OF NOVEL N-(1H-INDENE- 1,3(2H)-DION-2-YL)PYRIDINIUM BETAINES

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Reaction of substituted phthalic acids or their anhydrides (including pyromellitic dianhydride) with salts of N-carboxymethylpyridinium and substituted N-carboxymethylpyridinium in the presence of acetic anhydride and triethylamine in acetonitrile or acetic acid solutions gave a series of novel N-(1H-indene-1,3(2H)-dion-2-yl)pyridinium betaines. Electron acceptor substituents in the phthaloyl and pyridine rings were found to increase and electron donor substituents – to decrease the reactivity.

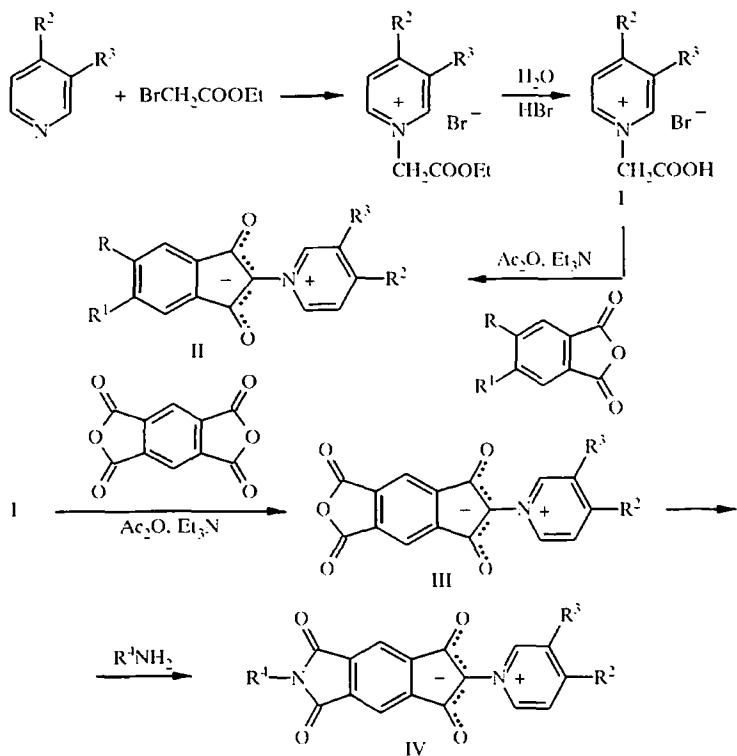
N-(1H-Indene-1,3(2H)-dion-2-yl)pyridinium betaines (II) are of interest as the basis for synthesizing photoconductive materials [1] and monomolecular layers with non-linear optical properties (generators of secondary harmonics) [2, 3].

In this work, our aim was to develop the methods for synthesis of novel indanedionylpyridinium betaine derivatives which contain substituents in the phthaloyl ring, for use in the anhydride condensation reaction first discovered in 1967 [4, 5]. Reaction of phthalic anhydride with N-carboxymethylpyridinium salts in the presence of acetic anhydride and triethylamine was subsequently used several times for preparing aza derivatives of such betaines [6], analogs containing imidazole ring [7], and amphiphilic derivatives which contain a long, unbranched hydrocarbon substituent in the phthaloyl ring [3].

In our work we have basically used the following phthalic acids or anhydrides with electron-acceptor substituents: 4-nitro-, 4-bromo, 4-iodo, and 4,5-dibromophthalic acids and pyromellitic acid dianhydride. With the aim of comparing the reactivity towards condensation, 4-*tert*-butyl- and 4-acetamidophthalic anhydrides also attracted interest. Active methylene group components were represented by N-carboxymethylpyridinium bromide, N-carboxymethyl-4-dimethylaminopyridinium- and N-carboxymethylisoquinolinium bromides, betaine of N-carboxymethylpyridinium-3-carboxylic acid, and N-carboxymethyl-4-cyanopyridinium bromide (general structure I) and these were synthesized by alkylation of the corresponding pyridine using ethyl bromoacetate and hydrolysis of N-carbethoxymethylpyridinium bromide with hydrobromic acid or by the reaction of nicotinic acid or 4-cyanopyridine with bromoacetic acid (see Scheme 1). In contrast to previous anhydride condensation experiments [3, 6], in agreement with data in publication [8], acetonitrile or acetic acid were used as solvents. 4-Nitrophthalic acid was found to react remarkably readily in acetonitrile solution to give the corresponding betaines II [9] in high yields. 4-Nitrophthalic acid gave better results than the previously prepared 4-nitrophthalic anhydride. 4,5-Dibromophthalic acid also gives a good yield of the betaines but 4-bromo- and 4-iodophthalic acids were poorer. The lowest yield was found for 4-*tert*-butyl- and 4-acetamidophthalic acids.

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Scheme 1



I a R² = R³ = H; b R² = N(CH₃)₂, R³ = H; c R² = NH₂, R³ = H; d R² = CN, R³ = H;
 e R², R³ = CH=CH-CH=CH; f R² = H, R³ = COO⁻, Br⁻ - absent. II a R = NO₂, R¹ = R² = R³ = H;
 b R = NO₂, R¹ = R³ = H, R² = 4-nitrophthalimido; c R = NO₂, R¹ = R³ = H, R² = N(CH₃)₂;
 d R = NO₂, R¹ = R² = H, R³ = COOH; e R = NO₂, R¹ = H, R², R³ = CH=CH-CH=CH; f R = I,
 R¹ = R² = R³ = H; g R = Br, R¹ = R² = R³ = H; h R = Br, R¹ = R³ = H, R² = N(CH₃)₂; i R = R¹ = Br, R² = R³ = H;
 j R = C(CH₃)₃, R¹ = R² = R³ = H; k R = NHCOCH₃, R¹ = R² = R³ = H; l R = R¹ = R³ = H; R² = CN.
 III a R² = R³ = H; b R² = N(CH₃)₂, R³ = H. IV a R² = R³ = R⁴ = H; b R² = R³ = H, R⁴ = C₁₈H₃₇;
 c R² = R³ = H, R⁴ = t-Bu; d R² = R³ = H, R⁴ = NH₂(CH₂)₆; e R² = R³ = H, R⁴ = HOOCCH₂; f R² = N(CH₃)₂,
 R³ = H, R⁴ = C₁₈H₃₇; g R² = N(CH₃)₂, R³ = H, R⁴ = HOOCCH₂

The reaction of pyromellitic anhydride with carboxymethylpyridinium bromide is a special case. Pyromellitic anhydride contains two active anhydride groupings but the reaction in acetic acid solution involves only one of the groups and gives a good yield of the novel compound N-(5,6-dicarboxy-1H-indene-1,3(2H)-dion-2-yl)pyridinium betaine anhydride (III). A similar reaction occurs with N-carboxymethyl-4-dimethylaminopyridinium bromide.

Synthesis of the novel betaines has shown that the reaction can be successfully carried out using solvents, that substituted phthalic acids instead of anhydrides can be used, and that electronic effects of substituents in the phthaloyl ring have a remarkable effect. They can be arranged in a series according to the betaine yield: (CO)₂O > NO₂ > Br > I > H > t-Bu > AcNH > (CO)₂C⁻. At the same time, introduction of donor substituents into position 4 of the pyridinium ring lowers the product yield. This is possibly due to the electron donor effect of the substituent which lowers the CH-acidity of N-carboxymethyl-substituted pyridine. Removal of the proton from it by basic catalyst, creating a nucleophilic center, is hindered in the same way.

The reactivity of anhydride III was studied with the aim to study the possibility of use of the anhydride group transformations in the synthesis of novel betaine derivatives. It was found that the anhydride grouping in compound III has a markedly lower reactivity when compared with phthalic anhydride.

TABLE I. Spectral Characteristics for Compounds IIa-f and IIIa,b

Compound	IR spectrum, ν , cm^{-1}	UV spectrum, λ_{max} , nm (ϵ)	^1H NMR spectrum, δ , ppm	Solvent
IIa	1615, 1573, 1545, 1510	305, 319, 332, 406* (dioxane)	7.95 (H, d, 7-H); 8.31 (H, d, 7-H); 8.48 (1H, dd, 6-H); 8.71 (3H, m, 3'-H, 4'-H, 5'-H); 9.71 (2H, d, 2'-H, 6-H)	DMSO- d_6
IIb	1733, 1688, 1661, 1586, 1547, 1510	300, 407, 423* (dioxane)	*2	
IIc	1673, 1652, 1637, 1614	372, 386, 404* (dioxane)	*2	
IId	1582, 1561, 1520	296, 320, 414* (dioxane)	—	
IIe	1740, 1726, 1711, 1673, 1625, 1580, 1516	304 (15300), 372 (8700), 435 (28600) (dioxane)	7.17 (1H, d, 7-H); 7.66 (1H, d, 4-H); 7.87 (1H, dd, 6-H); 8.02 (3H, m, 3'-H, 4'-H, 5'-H); 9.71 (2H, d, 2'-H, 6-H)	DMSO- d_6
IIf	1612, 1570, 1546, 1521, 1508	318 (5000), 338 (2600), 410 (19800) (dioxane)	7.33 (1H, d, 7-H); 7.37 (1H, d, 4-H); 7.48 (1H, dd, 6-H); 7.8 (3H, m, 3'-H, 4'-H, 5'-H); 10.15 (2H, d, 2'-H, 6'-H)	CDCl_3
IIg	1660, 1620, 1576	243 (29000), 253 (20700), 304 (5000), 392 (20700) (alcohol)	3.20 (6H, s, Me); 6.21 (1H, d, 7-H); 7.21-7.60 (4H, m, 4'-H, 6-H, 3'-H, 5'-H); 8.95 (2H, d, 2'-H, 6-H)	CDCl_3
IIh	1650, 1620, 1571, 1528	213 (16800), 264 (13800), 316 (94600), 358 (13200), 380 (8800), 420 (1400) (alcohol)	*2	
IIi	1620, 1574, 1555, 1519	306 (2300), 315 (2700), 408 (17000) (dioxane)	—	
IIf	1621, 1582, 1545	208 (18000), 242 (39200), 251 (48000), 257 (18400), 302 (5600), 314 (6400), 394 (20000), (alcohol)	2.9 (1H, s, <i>t</i> -Bu); 6.92 (1H, d, 7-H); 7.18 (1H, d, 4-H); 7.64-7.71 (4H, m, 6-H, 3'-H, 4'-H, 5'-H); 8.99 (2H, d, 2'-H, 6'-H)	DMSO- d_6
IIk	3364, 3297, 3114, 1707, 1661, 1634, 1598, 1551	271 (18400), 278 (15200), 312 (6800), 324 (7200), 401 (26400), 417 (21200) (alcohol)	2.11 (3H, s, Me); 7.12 (1H, d, 7-H); 7.50-7.97 (5H, m, 4-H, 6-H, 3'-H, 4'-H, 5'-H); 9.6 (1H, s, NH); 10.15 (2H, d, 2'-H, 6'-H)	CDCl_3
III	3048, 2248, 1616, 1562	245 (16000), 313 (1800), 450 (22400) (alcohol)	7.46 (4H, m, 4-H, 5-H, 6-H, 7-H); 7.60 (2H, m, 3'-H, 5'-H); 10.17 (2H, d, 2'-H, 6'-H)	CDCl_3
IIa	3064, 1842, 1766, 1688, 1618, 1585	—	7.62 (2H, s, 4-H, 7-H); 8.11 (3H, m, 3'-H, 4'-H, 5'-H); 9.69 (2H, d, 2'-H, 6'-H)	DMSO- d_6
IIb	3074, 1768, 1656, 1616, 1574	—	2.41 (6H, s, $\text{N}(\text{CH}_3)_2$); 7.10 (2H, d, 3'-H, 5'-H); 7.55 (2H, c, 4-H, 7-H); 8.62 (2H, d, 2'-H, 6'-H)	CDCl_3

* Difficultly soluble for UV.

*² Insoluble for PMR.

TABLE 2. Spectral Characteristics for Imides IVa-g

Compound	IR spectrum, ν , cm^{-1}	UV spectrum, λ_{max} , nm (ϵ)	^1H NMR spectrum, δ , ppm	Solvent
IVa	3188, 1774, 1722, 1632, 1560	403 (10668) (chloroform)	7.12 (1H, s, NH); 7.66 (2H, s, 4-H, 7-H); 7.88-8.40 (3H, m, 3'-H, 4'-H, 5'-H); 9.73 (2H, d, 2'-H, 6'-H)	DMSO-d ₆
IVb	2920, 2845, 1760, 1710, 1620, 1580	405 (29420) (chloroform)	0.88 (3H, t, CH_2CH_2); 1.26 (30H, s, $(\text{CH}_2)_{15}$); 1.60 (2H, m, CH_2); 3.64 (2H, t, CH_2); 7.77 (3H, m, 3'-H, 4'-H, 5'-H); 7.93 (2H, s, 4-H, 7-H); 10.17 (2H, d, 2'-H, 6'-H)	CDCl_3
IVc	2918, 2850, 1770, 1710, 1618, 1586	405 (14953) (methanol)	*	
IVd	3420, 2934, 2858, 1768, 1710, 1642, 1618, 1586	—	2.89 (8H, m, $(\text{CH}_2)_4$); 3.64 (2H, m, CH_2); 3.83 (2H, t, CH_2); 4.12 (2H, m, NH ₂); 7.86 (3H, m, 3'-H, 4'-H, 5'-H); 8.02 (2H, s, 4-H, 7-H); 10.06 (2H, d, 2'-H, 6'-H)	CDCl_3
IVe	3080, 1765, 1715, 1620, 1590	405 (14356) (chloroform)	4.28 (2H, s, CH_2); 7.56 (2H, s, 4-H, 7-H); 8.16 (3H, m, 3'-H, 4'-H, 5'-H); 9.71 (2H, d, 2'-H, 6'-H)	DMSO-d ₆
IVf	2920, 2852, 1774, 1720, 1616, 1572	—	*	
IVg	2924, 1776, 1716, 1640, 1626, 1558	379 (22304), 405 (17960) (chloroform)	3.23 (6H, s, $\text{N}(\text{CH}_3)_2$); 4.32 (2H, s, CH_2); 7.14 (2H, d, 3'-H, 5'-H); 7.63 (2H, s, 4-H, 7-H); 8.63 (2H, d, 2'-H, 6'-H)	DMSO-d ₆

* Substance insoluble.

Hydrolysis of anhydride of 5,6-dicarboxylic acid betaine III gives the corresponding dicarboxylic acid, but interaction with various amines leads to formation of imides. Reaction with the amines was carried out in acetic acid or dimethyl formamide solutions with the exception of compound IVc. In latter case it was necessary to use more drastic conditions – heating at 120°C without solvent. The UV spectra of the obtained imides show a “charge transfer” type absorption band in the region of 405 nm; in the case of carboxymethylimide of N-(5,6-dicarboxy-1H-indene-1,3(2H)-dion-2-yl)-4-dimethylaminopyridinium betaine (IVg) a second, more intense absorption maximum appears which is hypsochromically shifted. The strongest absorption was recorded for octadecylimide of N-(5,6-dicarboxy-1H-indene-1,3(2H)-dion-2-yl)pyridinium betaine IVb

Parameters for the compounds prepared are given in Tables 1 and 2.

EXPERIMENTAL

IR spectra were taken on a Specord M-80 instrument in paraffin oil or in hexachlorobutadiene. PMR spectra were recorded on a Bruker WH-90/DS instrument using CDCl_3 or DMSO-d₆ solvent and TMS internal standard. UV spectra were taken on a Specord M-40 instrument in alcohol, dioxane, or chloroform solutions.

Synthesis of the Active Methylene Components. N-Carboxymethylpyridinium Bromide (Ia). Solution of pyridine (8.15 ml, 0.1 mol) in acetone (70 ml) was added to solution of ethyl bromoacetate (12.3 ml, 0.11 mol) in acetone (15 ml) and refluxed for 1 h. The white needles which separated after cooling (20.2 g) were filtered off and then dissolved in water (15 ml) with the addition of concentrated HBr (7.8 ml). The product was refluxed for 1 h and the crystals which formed upon cooling were filtered off and washed with ether. Yield 3.99 g (90%); mp 183-187°C (alcohol). Found, %: C 38.57; H 3.64; N 6.42; Br 36.71. $\text{C}_7\text{H}_8\text{BrNO}_2$. Calculated, %: C 38.53; H 3.67; N 6.42; Br 36.69.

N-Carboxymethyl-4-dimethylaminopyridinium Bromide (Ib). Solution of 4-dimethylaminopyridine (3.36 g, 0.03 mol) in acetone (80 ml) was added with stirring to solution of ethyl bromoacetate (3.29 ml, 0.032 mol) in acetone (15 ml) and refluxed for 1 h. The white needles which precipitated after cooling (8.30 g) were filtered off and washed with acetone or ether. N-Carbethoxy-4-dimethylaminopyridinium bromide formed (8.08 g, 0.027 mol) was dissolved in water (65 ml), concentrated HBr (16 ml) was added, and the product was refluxed for 2 h. Then it was cooled and evaporated to dryness in *vacuo*. The precipitated, white crystals were washed with acetone. Yield 7.0 g (96%); mp 241–243°C (ethanol–ethyl acetate, 3: 2). Found, %: C 40.95; H 5.19; N 10.98; Br 30.45. $C_9H_{13}BrN_2O_2$. Calculated, %: C 41.40; H 5.02; N 10.73; Br 30.60.

4-Amino-N-carboxymethylpyridinium Bromide (Ic). Ethyl bromoacetate (12.3 ml, 0.11 mol) was added to solution of 4-aminopyridine (9.41 g, 0.1 mol) in acetone (70 ml) and refluxed for 1 h. The precipitated crystals (23.24 g) were filtered, washed on the filter with acetone, and crystallized from alcohol. 4-Amino-N-carbethoxypyridinium bromide (6.7 g, 0.0257 mol) formed was then dissolved in distilled water (30 ml), concentrated HBr (10 ml) added, and refluxed for 1 h. The product was cooled to room temperature and evaporated to dryness in *vacuo*. The white crystals formed were treated with acetone (50 ml) and filtered. Yield 5.74 g (96%); mp 256–257°C (alcohol). Found, %: C 36.10; H 3.97; N 12.11; Br 34.36. $C_7H_9BrN_2O_2$. Calculated, %: C 36.07; H 3.89; N 12.02; Br 34.28.

N-Carboxymethyl-4-cyanopyridinium Bromide (Id). Solution of bromoacetic acid (1.53 g, 0.01 mol) and cyanopyridine (1.04 g, 0.01 mol) in acetonitrile (10 ml) was heated for 1 h and the precipitated white crystals were filtered off. Yield 3 g (84%); mp 218–220°C (alcohol). Found, %: C 39.49; H 2.90; N 11.56; Br 32.92. $C_8H_7BrN_2O_2$. Calculated, %: C 39.51; H 2.87; N 11.52; Br 32.92.

N-Carboxymethylisoquinolinium Bromide (Ie). Solution of isoquinoline (11.7 ml, 0.1 mol) in acetone (100 ml) was added with stirring to ethyl bromoacetate (13.4 ml, 0.12 mol), stirred at ~ 20°C for 1 h, then for 15 min. The precipitated crystals (21.02 g) were filtered off and washed on the filter with acetone and ether. Solution of N-carbethoxymethylisoquinolinium bromide (16 g, 0.054 mol) in water (100 ml) was then treated with concentrated HBr (25 ml) and refluxed for 1 h. After cooling to room temperature and evaporation to dryness it was treated with acetone (200 ml). The white crystals formed on cooling were filtered off. Yield 14.08 g (97%); mp 185–187°C (alcohol). Found, %: C 49.29; H 3.92; N 4.48; Br 29.70. $C_{11}H_{10}BrNO_2$. Calculated, %: C 49.28; H 3.76; N 5.22; Br 29.80.

N-Carboxymethyl-3-carboxypyridinium Betaine (If)·NaBr. Nicotinic acid (2.11 g, 0.017 mol) was suspended in water (25 ml). An equimolar amount of sodium hydroxide solution was added with stirring. The precipitate dissolved. Solution of bromoacetic acid (2.79 g, 0.02 mol) in water (15 ml) was added with stirring, the solution was heated to reflux, stirred for 1 h, and evaporated to give a viscous liquid. It was then treated with ethanol (60 ml), cooled, and the precipitate filtered and washed with acetone and ether. Yield 2.5 g (52%) as mixture of betaine If and sodium bromide (1:1). The mixture was used in the subsequent syntheses without separation and purification. Found, %: Br 28.72. $C_8H_7NO_4\cdot NaBr$. Calculated, %: Br 28.13.

Synthesis of Betaines by Anhydride Condensation. N-(5-Nitro-1H-indene-1,3(2H)-dion-2-yl)-pyridinium Betaine (IIa). Acetonitrile (25 ml) was added to mixture of 4-nitrophthalic acid (2.53 g, 0.012 mol) and N-carboxymethylpyridinium bromide (2.18 g, 0.01 mol). With stirring, acetic anhydride (3.3 ml, 0.035 mol) and triethylamine (5.6 ml, 0.04 mol) were then added. Stirring was continued and the mixture was heated to reflux and heating was continued for 1 h. The mixture was cooled and water (25 ml) was added after several hours. The red violet, crystalline betaine was filtered off, washed with water, and then with acetone. The crystals were dried at 110–130°C. Yield 2.47 g (92%); mp 287–289°C (75% aqueous DMF). Found, %: C 62.85; H 3.00; N 10.59. $C_{14}H_8N_2O_4$. Calculated, %: C 62.69; H 3.01; N 10.44.

N-(5-Nitro-1H-indene-1,3(2H)-dion-2-yl)-4'-(4-nitrophthalimido)pyridinium Betaine (IIb). Mixture of acetonitrile and acetic acid (50 ml, 2:3) was added to mixture of 4-nitrophthalic acid (13 g, 0.062 mol) and 4-amino-N-carboxymethylpyridinium bromide (5 g, 0.021 mol) and the product was heated to reflux with stirring. Triethylamine (70 ml, 0.5 mol) and acetic anhydride (14 ml, 0.148 mol) were added and reflux was continued for 45 min. After cooling, the dark yellow precipitate was filtered off and washed on the filter with water and acetone, and dried at 120°C. The product obtained was virtually insoluble in organic solvents and was used without purification. Yield 8.63 g (88%).

N-(5-Nitro-1H-indene-1,3(2H)-dion-2-yl)-(4'-dimethylamino)pyridinium Betaine (IIc). Acetonitrile (25 ml) was added to mixture of 4-nitrophthalic acid (1.66 g, 0.0079 mol) and N-carboxymethyl-4-dimethylaminopyridinium bromide (1.71 g, 0.0065 mol). Triethylamine (13.7 ml, 0.099 mol) was then added under stirring. Stirring was continued for 5 min and then acetic anhydride (2.2 ml, 0.023 mol) was added. With continued stirring, the product was refluxed on a water bath for 1 h. After cooling for several hours, water (25 ml) was added. The dark red crystalline precipitate was filtered off and washed on the filter with water, then acetone, and dried at 100-130°C. Yield 1.13 g (56%); mp above 450°C (DMF). Found, %: C 61.72; H 4.20; N 13.67. $C_{16}H_{13}N_3O_4$. Calculated %: C 61.73; H 4.20; N 13.49.

N-(5-Nitro-1H-indene-1,3(2H)-dion-2-yl)-(3-carboxy)pyridinium Betaine (IId). Mixture of acetonitrile and acetic acid (50 ml, 3: 2) was added to mixture of 4-nitrophthalic acid (2.23 g, 0.0106 mol) and N-carboxymethyl-3-carboxypyridinium betaine and sodium bromide mixture (1.59 g), (the mixture contained approximately 0.0056 moles of the betaine). Triethylamine (14.7 ml, 0.106 mol) and acetic anhydride (5.0 ml, 0.053 mol) were added with stirring. With continued stirring, the product was refluxed on a water bath for 2 h. After cooling to room temperature, the product was evaporated in vacuo and then treated with water (100 ml). The dark orange precipitate was filtered off and washed with water. Yield 0.99 g (57%); mp 304-305°C (50% AcOH). Found, %: C 57.00; H 2.67; N 8.64. $C_{15}H_8N_2O_6$. Calculated, %: C 57.70; H 2.58; N 8.97.

N-(5-Nitro-1H-indene-1,3(2H)-dion-2-yl)isoquinolinium Betaine (IIe). Acetonitrile (25 ml) was added to mixture of 4-nitrophthalic acid (2.53 g, 0.012 mol) and N-carboxymethylisoquinolinium bromide (2.68 g, 0.01 mol). Triethylamine (7 ml, 0.05 mol) was then added under stirring. Stirring was continued for 5 min and acetic anhydride (3.3 ml, 0.035 mol) was added. With continued stirring, the product was refluxed on a water bath for 1 h. After cooling for several hours, water (25 ml) was added. The red crystalline precipitate was filtered off and washed on the filter with water and then acetone, and dried at 110-130°C. Yield 2.08 g (65%); mp 316-318°C (88% aqueous DMF). Found, %: C 68.01; H 3.03; N 8.73. $C_{18}H_{10}N_2O_4$. Calculated, %: C 67.9; H 3.10; N 8.80.

N-(5-Iodo-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine (IIf). Acetonitrile (30 ml) was added to mixture of 4-iodophthalic acid (3.24 g, 0.011 mol) and N-carboxymethylpyridinium bromide (2.62 g, 0.012 mol). Triethylamine (9.2 ml, 0.066 mol) was then added under stirring. Stirring was continued for 5 min and acetic anhydride (9.2 ml, 0.097 mol) was added. With continued stirring, the product was refluxed on a water bath for 1 h. After cooling for several hours, water (25 ml) was added. The orange yellow crystalline precipitate was filtered off and washed on the filter with water, then acetone, and dried at 80°C. The product was recrystallized from ethanol with addition of aluminium oxide. Yield 2.59 g (65%); mp 240-242°C. Found, %: C 48.10; H 2.55; N 4.08; I 36.56. $C_{14}H_8INO_2$. Calculated, %: C 48.16; H 2.31; N 4.01; I 36.35.

N-(5-Bromo-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine (IIf). Acetonitrile (30 ml) was added to mixture of 4-bromophthalic acid (2.94 g, 0.012 mol) and N-carboxymethylpyridinium bromide (2.181 g, 0.01 mol). Triethylamine (5.6 ml, 0.04 mol) and acetic anhydride (3.3 ml, 0.035 mol) were then added. With continued stirring, the product was refluxed on a water bath for 45 min. After cooling for several hours, water (25 ml) was added. The precipitated bright orange crystals were filtered off and washed on the filter with water and then acetone. Yield 1.67 g (55%); mp 244-245°C. Found, %: C 55.15; H 2.97; N 4.29; Br 26.20. $C_{14}H_8BrNO_2$. Calculated, %: C 55.66; H 2.67; N 4.64, Br 26.45.

N-(5-Bromo-1H-indene-1,3(2H)-dion-2-yl)-(4-dimethylamino)pyridinium Betaine (IIh). Acetonitrile (30 ml) was added to mixture of 4-bromophthalic acid (2.94 g, 0.012 mol) and N-carboxymethyl-4-dimethylaminopyridinium bromide (2.61 g, 0.01 mol). With continued stirring and refluxing, triethylamine (5.6 ml, 0.04 mol) and acetic anhydride (3.3 ml, 0.035 mol) were added and the product was stirred under reflux for 30 min. After cooling for several hours, water (50 ml) was added and the orange yellow crystalline betaine was filtered off, washed on the filter with water and then acetone. Yield 1.21 g (35%); mp 319-320°C (60% aqueous DMF). Found, %: C 55.05; H 3.97; N 7.82; Br 23.01. $C_{16}H_{13}BrN_2O_2$. Calculated, %: C 55.66; H 3.80; N 8.12; Br 23.15.

N-(4,5-Dibromo-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine (IIIi). Acetonitrile (25 ml) was added to mixture of 4,5-dibromophthalic acid (4.57 g, 0.012 mol) and N-carboxymethylpyridinium bromide (2.18 g, 0.01 mol). With stirring, triethylamine (5.6 ml, 0.04 mol) and acetic anhydride (3.3 ml, 0.035 mol) were added and stirring was continued with reflux on a water bath for 30 min. After cooling for several hours, water (25 ml) was

added and the bright yellow crystalline betaine was filtered off and washed on the filter with water and then acetone. Yield 3.6 g (94%); mp 115°C (DMF). Found, %: C 43.65; H 2.06; N 3.50; Br 42.17. $C_{14}H_7Br_2NO_2$. Calculated, %: C 44.13; H 1.85; N 3.68; Br 41.94.

N-(5-tert-Butyl-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine (IIj). Acetonitrile (50 ml) was added to mixture of 4-tert-butylphthalic acid (4.085 g, 0.02 mol) and N-carboxymethylpyridinium bromide (3.361 g, 0.02 mol). With stirring and refluxing, triethylamine (28 ml, 0.20 mol) and acetic anhydride (6.6 ml, 0.07 mol) were added. Stirring and refluxing were continued for 5 min. Solvent was then evaporated to half the original volume, hot water (100 ml) was added, and the dark yellow crystalline betaine was filtered. The precipitate was dried and then dissolved in acetone (600 ml) and chromatographed on a column with aluminum oxide (150 g). Yield 2.19 g (39%); mp 205-207°C (ethanol-hexane, 3:7). Found, %: C 77.66; H 6.49; N 5.19. $C_{18}H_{17}NO_2$. Calculated, %: C 77.40; H 6.50; N 5.01.

N-(5-Acetamido-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine (IIk). Triethylamine (10 ml, 0.072 mol) and acetic anhydride (10 ml, 0.106 mol) were added with stirring to solution of 4-acetamidophthalic acid (2.52 g, 0.0123 mol) and double salt of N-carboxymethylpyridinium betaine chloride (2.29 g, 0.0074 mol) in acetic acid (20 ml). Stirring was continued and the solution was refluxed for 5 min. After cooling for several hours, water (25 ml) and then concentrated NaOH solution to basic reaction were added. After cooling, the precipitated orange crystals were filtered off, washed on the filter with water, and dried at 110-120°C. Yield 1.10 g (32%); mp 300-304°C (water). Found, %: C 68.10; H 4.53; N 9.7. $C_{16}H_{12}N_2O_3$. Calculated, %: C 68.56; H 4.32; N 9.99.

N-(1H-Indene-1,3(2H)-dion-2-yl)cyanopyridinium Betaine (II l). Mixture of phthalic anhydride (0.2 g, 0.0013 mol) and compound Id (0.3 g, 0.0013 mol) was stirred at 75°C in the presence of triethylamine (1.4 ml, 0.101 mol) and acetic anhydride (0.33 ml, 0.003 mol). After cooling, the mixture was evaporated and the oil formed was triturated with alcohol. The dark yellow crystals formed were filtered off. Yield 0.22 g (65%); mp 258-260°C (ethanol-hexane, 3:7). Found, %: C 72.60; H 3.18; N 11.71. $C_{15}H_8N_2O_2$. Calculated, %: C 72.58; H 3.23; N 11.29.

N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine Anhydride (IIIa). Solution of pyromellitic acid dianhydride (4.36 g, 0.02 mol) and N-carboxymethylpyridinium bromide (4.13 g, 0.02 mol) in acetic acid (40 ml) was refluxed for 15 min in the presence of triethylamine (19.9 ml, 0.143 mol) and acetic anhydride (7.78 ml, 0.082 mol). The red crystals formed on cooling were filtered off and washed on the filter with ether. Yield 3.40 g; (58%); mp 360-370°C (DMF-Ac₂O, 14:1). Found, %: C 65.42; H 2.45; N 4.62. $C_{16}H_7NO_5$. Calculated, %: C 65.54; H 2.41; N 4.78.

N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)-4'-dimethylaminopyridinium Betaine Anhydride (IIIb). Mixture of pyromellitic acid dianhydride (2.00 g, 0.009 mol), N-carboxymethyl-4-dimethylaminopyridinium bromide (1.28 g, 0.009 mol) and acetic acid (25 ml) together with triethylamine (33.6 ml, 0.026 mol) and acetic anhydride (9.0 ml, 0.095 mol) was refluxed for 15 min. After cooling, the red crystals were filtered off and washed on the filter with ether. Yield 1.7 g (63%); mp 358-360°C (DMF-Ac₂O, 14:1). Found, %: C 64.11; H 3.59; N 8.43. $C_{18}H_{12}N_2O_5$. Calculated, %: C 64.28; H 3.57; N 8.33.

Synthesis of Imides. N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine Imide (IVa). Solution of urea (0.06 g, 1 mmol) and anhydride IIIa (0.3 g, 1 mmol) was refluxed for 1 h in DMF (15 ml). The dark yellow crystals were filtered off and crystallized from DMF-acetonitrile mixture (2:1). Yield 0.17 g (58.2%); mp 243-245°C (with decomp.). Found, %: C 65.14; H 2.83; N 9.99. $C_{16}H_8N_2O_4$. Calculated, %: C 65.75; H 2.74; N 9.59.

N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine Octadecylimide (IVb). Solution of octadecylamine (0.21 g, 0.8 mmol) and compound IIIa (0.23 g, 0.8 mmol) in acetic acid (15 ml) was refluxed for 12 h. The dark red crystals obtained upon cooling were crystallized from mixture of ethanol and nitromethane (4:1). Yield 0.22 g (50%); mp 200°C. Found, %: C 74.33; H 8.02; N 4.99. $C_{34}H_{44}N_2O_4$. Calculated, %: C 75.02, H 8.15; N 5.15.

N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine *tert*-Butylimide (IVc). Mixture of compound IIIa (0.1 g, 0.3 mmol) and excess of *tert*-butylamine was heated on a Wood's alloy bath at 120°C. Unreacted amine was distilled off to give red orange crystals (0.07 g, 60%); mp 160-165°C (alcohol). Found, %: C 68.91; H 4.97; N 7.99. $C_{20}H_{16}N_2O_4$. Calculated, %: C 68.96; H 4.59; N 8.05.

N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine 6-Aminohexylimide (IVd). Solution of hexamethylenediamine (0.12 g, 1 mmol) and compound IIIa (0.3 g, 1 mmol) in acetic acid (30 ml) was refluxed for 5 h. The bright orange crystals formed were crystallized from ethanol–nitromethane mixture (4:1). Yield 0.26 g (65%); mp 265–267°C. Found, %: C 67.05; H 5.50; N 10.24. $C_{22}H_{21}N_3O_4$. Calculated, %: C 67.52; H 5.41; N 10.74.

N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)pyridinium Betaine Carboxymethylimide (IVe). Solution of aminoacetic acid (0.05 g, 0.67 mmol) and compound IIIa (0.2 g, 0.68 mmol) in DMF was refluxed for 20 min. The red crystals formed upon cooling were crystallized from ethanol. Yield 0.2 g (80%); decomposition temperature above 360°C. Found, %: C 62.03; H 3.07; N 8.25. $C_{18}H_{16}N_2O_6$. Calculated, %: C 61.83; H 2.88; N 8.01.

N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)-4'-dimethylaminopyridinium Betaine Octadecylimide (IVf). Solution of octadecylamine (0.39 g, 1.5 mmol) and compound IIIb (0.5 g, 1.5 mmol) in acetic acid (15 ml) was refluxed for 2 h. The violet brown crystals formed on cooling were crystallized from ethanol–ethyl acetate mixture (3:7). Yield 0.5 g (57.5%); mp 130–135°C. Found, %: C 73.72; H 8.06; N 7.13. $C_{36}H_{49}N_3O_4$. Calculated, %: C 73.61; H 8.41; N 7.15.

N-(5,6-Dicarboxy-1H-indene-1,3(2H)-dion-2-yl)-4'-dimethylaminopyridinium Betaine Carboxymethylimide (IVg). Mixture of aminoacetic acid (0.05 g, 0.67 mmol) and compound IIIb (0.2 g, 0.60 mmol) was dissolved in acetic acid (10 ml) with the addition of anhydrous sodium acetate (0.05 g) and refluxed for 2 h. The solution became turbid, the precipitated brown solid was filtered off and crystallized from water. The recrystallized residue was dissolved in water and HBr was added to acid reaction. The solution turbidified and a red solid was formed which was then recrystallized from acetonitrile–DMF mixture (1:2). Yield 0.15 g (65%); mp above 300°C. Found, %: C 60.45; H 3.93; N 10.57. $C_{20}H_{15}N_3O_6$. Calculated, %: C 61.16; H 3.86; N 10.69.

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