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One-pot multicomponent synthesis of piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4-diones): NMR spectroscopic and X-ray structure characterization

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Abstract: A facile synthesis of piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4-dione) analogs as organic salts is described by the one-pot pseudo-four-component reaction between 2-hydroxy-1,4-naphthoquinone, aromatic aldehydes, and piperidine. The single-crystal X-ray diffraction analysis of these systems confirms that the stabilized predominant interactions are N-H...O and O-H...O hydrogen bonds. Mild and clean reaction conditions, high atom economy, and operational simplicity of this one-pot multicomponent reaction coupled with excellent yields and no need for column chromatography have transformed this procedure to be a superior synthetic route for the efficient formation of families of naphthoquinone-derived compounds.

Key words: Organic salts, 2-hydroxy-1,4-naphthoquinone, crystal structure, hydrogen bonds

1. Introduction

Quinones and naphthoquinones are remarkable structural motifs that are found abundantly in numerous natural products and designed molecules of biological significance. 2-Hydroxy-1,4-naphthoquinone (HNQ), commonly known as lawsone and found naturally in the leaves of the henna plant (*Lawsonia inermis*), jewelweed (*Impatiens balsamica*),[1] and endophytic fungus (*Gibberella moniliformis*),[2] is a popular red-orange compound ubiquitous in numerous cosmetic targets (hair dye, body paint, and tattoo dye).

3,3'-(Arylmethylene) bis (2-hydroxynaphthalene-1,4-diones) are one class of HNQ-containing compounds. Recently, these dimeric compounds derived from lawsone have been reported to be active against influenza neuraminidase of the H5N1 virus.[3] These compounds have been recognized as suitable candidates for anticancer drugs via the induction of reactive oxygen species.[4] The antioxidant and antifungal activities of these naphthoquinone derivatives have also been proved.[5] Piperidine and its derivatives have been ubiquitously used in the synthesis of pharmaceuticals and fine chemicals. These notable building blocks are found in commercial drugs such as paroxetine,[6] morphine and derivatives,[7] risperidone,[8] pethidine,[9] mesoridazine,[10] ethylphenidate,[11] and many others.

In medicine, half of all drug molecules are provided as salts. Therefore, the selection of a suitable salt for a drug target is a main step in the preclinical phase of drug development. On the other hand, salt

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formation has blossomed dramatically in the pharmaceutical industry for improving the physical properties of active pharmaceutical ingredients.[12,13] The most useful and reliable intermolecular interaction that often holds salts together is hydrogen bonding interaction. So far, this main steering force, owing to its existence in many drug-like motifs, its strength, and its directionality properties, has been known as the most important interaction in designing crystal packing and solid state organic synthesis, biomaterials, ionic conductors, and organic semiconductors. Additionally, it has been explored in the organic crystal engineering of commercial significant pigments.[14–17]

Multicomponent reactions have emerged as efficient synthetic strategies for preparing assemblage libraries of diverse drug-like chemical architectures by virtue of their simple execution, high degree of atom economy, flexibility, efficiency, and convergence in one-pot operations.[18–20]

Few studies have been reported for the preparation of organic salts including naphthoquinone cores.[21,22] Therefore, following our investigations of important organic conversions,[23–27] here we report the synthesis of a new class of organic salts, namely piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4- diones), in a one-pot, pseudo-four-component route via the reaction between 2-hydroxy-1,4-naphthoquinone **1**, aromatic aldehydes **2**, and piperidine **3** (Figure 1). The combination of readily available substrates with a one-pot multicomponent feature would offer an attractive route to assemble a library of organic salts including a naphthoquinone core.

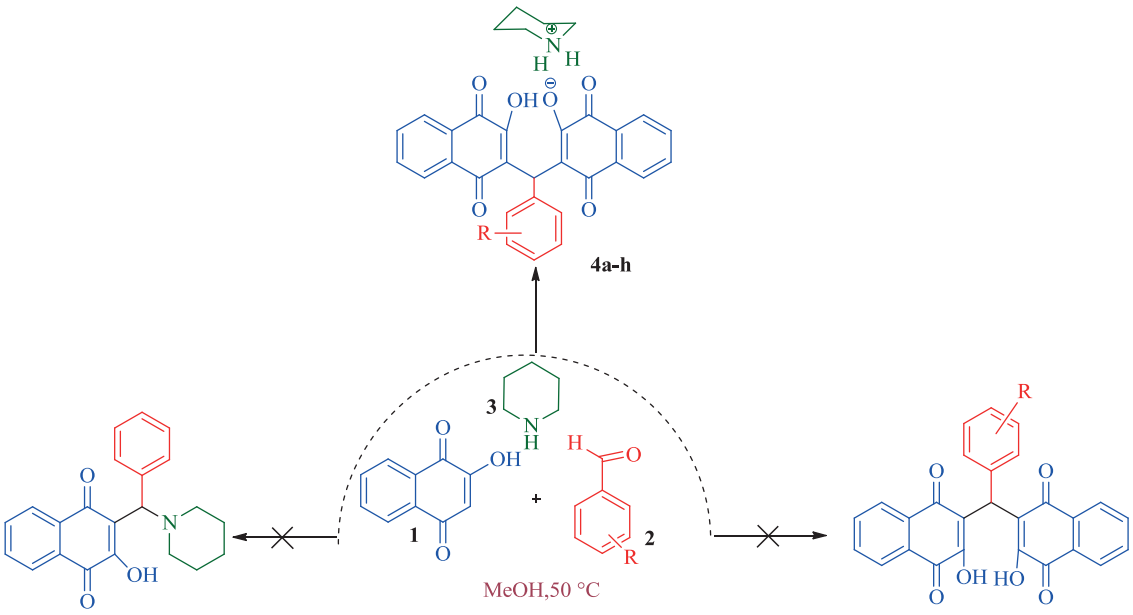


Figure 1. Synthesis of piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4-dione) derivatives.

2. Results and discussion

There are several methods available in the literature that describe the reliable synthesis of 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4- diones).[28–31] In this context, and in line with our interest in one-pot multicomponent synthesis of these versatile compounds, we planned to employ piperidine as a substrate for condensation with 2-hydroxy-1,4-naphthoquinone and aromatic aldehydes to produce related naphthoquinone (Figure 1). However, when the reaction was conducted in the presence of piperidine in MeOH at 50 °C, an orange powdery

product was obtained with spectral data inconsistent with our expected structures. Indeed, the data were in acceptable agreement with the formation of an unprecedented product with good symmetric properties including piperidine in which the single-crystal X-ray diffraction analysis confirmed the formation of the crystal structure of piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4- diones) (Figure 2).

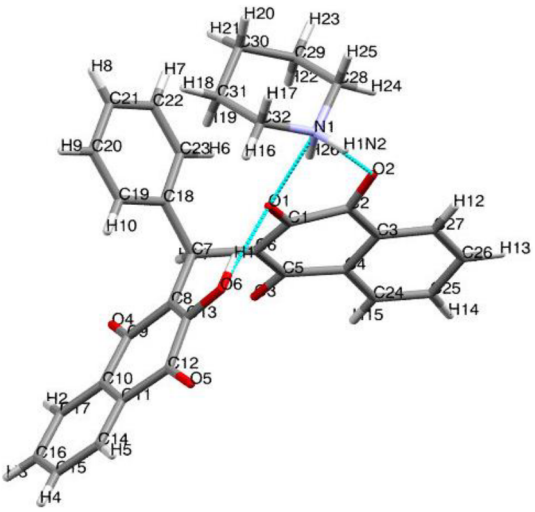


Figure 2. The molecular structure and hydrogen bonds of **4a**.

The ^{1}H NMR spectrum of compound **4c** showed a multiplet (δ 1.49–1.59) related to six protons of piperidine, a triplet (δ 2.97, J = 6.0 Hz) related to four protons of piperidine, and a singlet observed at 6.57 ppm related to the proton of CH. Chemical shift values and coupling constants of aromatic protons have shown the presence of twelve protons related to aromatic protons. A broad peak was observed at 8.39 and 15.69 ppm related to the NH and OH protons (Figure 3). The ^{13}C NMR spectrum of compound **4c** exhibited eighteen signals in line with the suggested motifs.

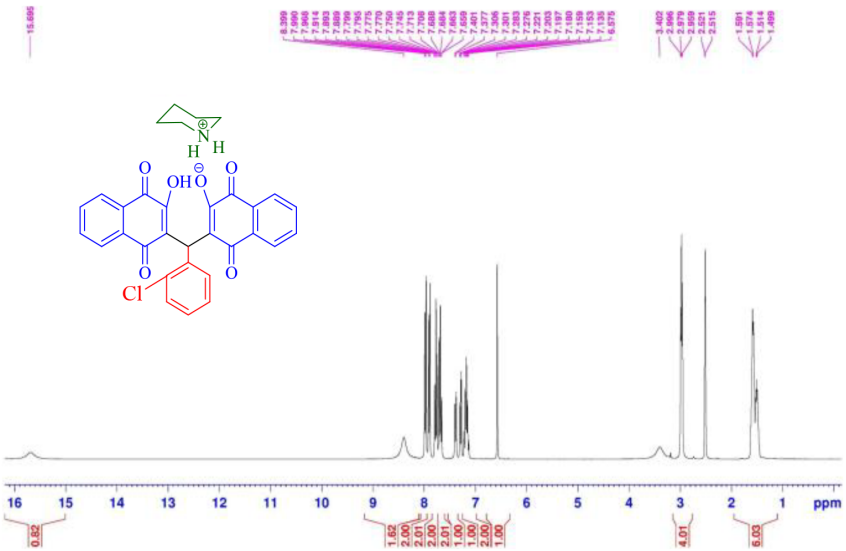
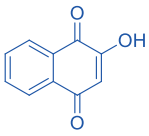
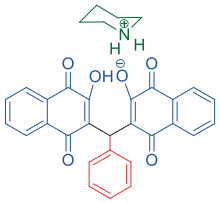


Figure 3. ^{1}H NMR spectrum of compound **4c**.

As shown in Figure 1, the products are formed from the condensation of two equimolar amounts of lawsone and one equimolar amount of aldehyde. One equimolar amount of piperidine has been located beside the formatted products of 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4-dione) with strong hydrogen bonding.

For the optimized conditions, first the reaction between 2-hydroxy-1,4-naphthoquinone (2.0 mmol), benzaldehyde (1.0 mmol), and piperidine (1.0 mmol) was selected as a model reaction and the temperature factor was evaluated, as shown in Table 1. A test reaction was accomplished at room temperature. In these conditions, the desired product was not afforded after 24 h (Table 1, entry 1). Then the reaction temperature was varied from 40 to 60 °C to investigate its effects. It was found that 50 °C was an efficient temperature (Table 1, entry 3). The role of piperidine was also seen as in the absence of piperidine, the reaction did not progress even after 24 h. Therefore, using piperidine is essential for the condensation of the substrates (Table 1, entry 5).

Table 1. Optimization of reaction conditions.

Substrate	Product	Entry	Temperature (°C)	Time (h)	Isolated Yield (%)
$C_5H_{11}N$ C_6H_5CHO 		1	r.t	24	N.R.
		2	40	5	78
		3	**50**	**3**	**92**
		4	60	3	93
		5/No Piperidine	50	24	Trace

For further evaluation of the feasibility of this strategy, a variety of arylaldehydes were selected. As shown in Figure 4, the reactions tolerated both electron-withdrawing and electron-donating groups on the aldehyde aromatic rings, including ortho-, meta-, and para-substituted groups with the corresponding products in satisfying yields.

The proposed mechanism for the synthesis of these compounds is portrayed in Figure 5. The nucleophilic attack of active lawsone by piperidine to the aldehyde led to intermediate product **A** (Knoevenagel-type condensation reaction) and Michael addition to another lawsone gave species **B**, followed by its tautomerization to piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4-dione) salts (**4a**–**4h**).

In conclusion, with the aim of achieving important organic synthesis, we have developed a one-pot, pseudo-four-component synthesis of new piperidinium 3,3'-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione) salts from the reaction between 2-hydroxy-1,4-naphthoquinone, piperidine, and aromatic aldehydes. The formation of salts was characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR analysis. The X-ray crystal structure analysis confirmed the existence of hydrogen bonding interactions in the crystal structure.

3. Experimental

3.1. General

Melting points and IR spectra of all compounds were determined by an Electrothermal 9100 apparatus and FT-IR-JASCO-460 plus spectrometer, respectively. The ^{1}H and ^{13}C NMR spectra of known compounds were

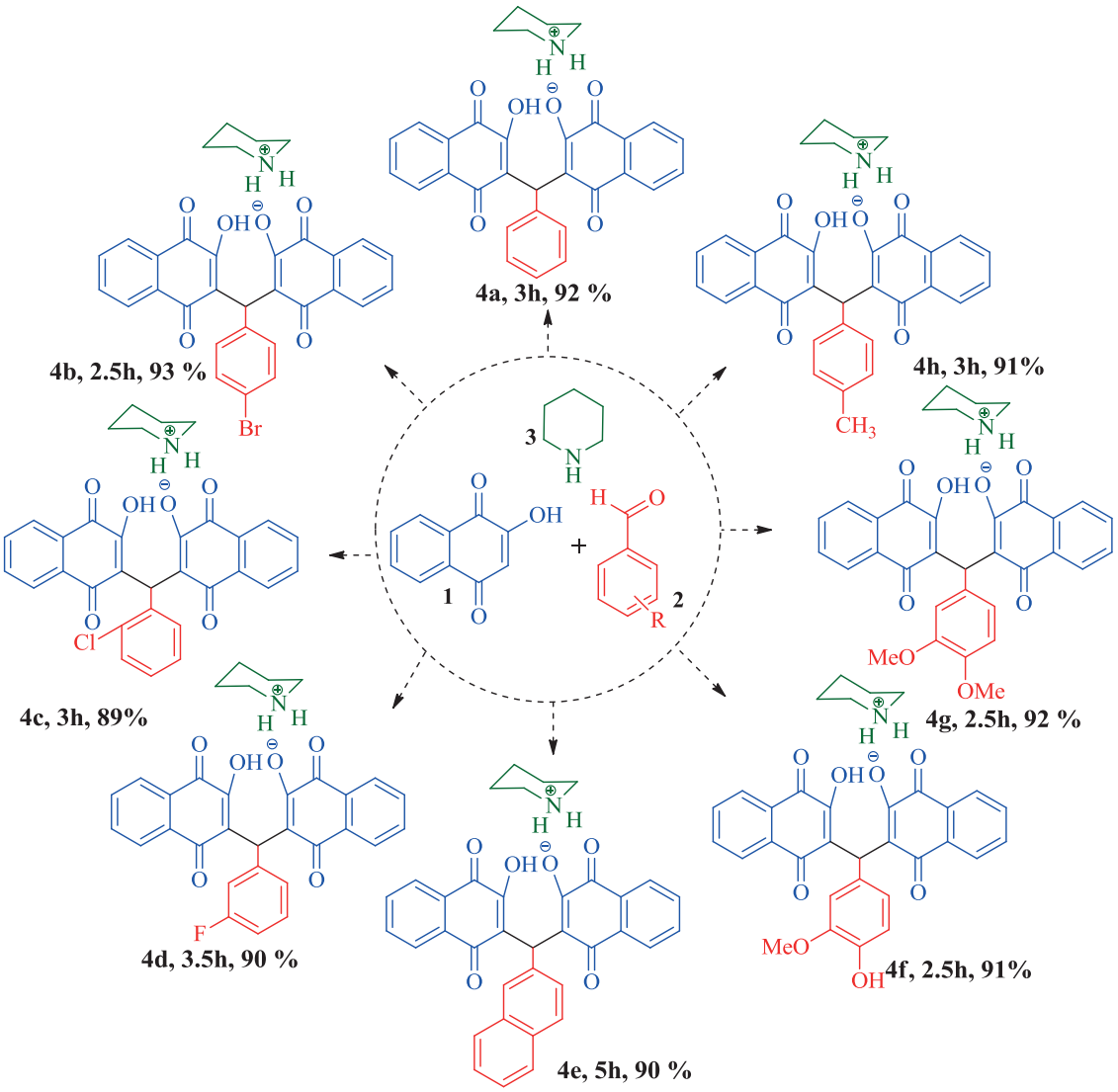


Figure 4. Synthesis of piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4-dione) derivatives.

recorded on a Bruker Avance DRX-400 instrument in $CDCl_3$ and DMSO at 300 MHz. All chemicals were provided from chemical producers Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland) and used without further purification.

3.2. General procedure for preparing piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4- dione) salts

A mixture of 2-hydroxy-1,4-naphthoquinone (2.0 mmol, 0.348 mg), aromatic aldehydes (1.0 mmol), and piperidine (1.0 mmol, 0.085 mg) was heated to 50 °C in MeOH. The progress of the reaction was monitored by TLC. Then the reaction mixture was cooled down to room temperature. The mixture was washed with MeOH for separating the product. Finally, the crude product was recrystallized from MeOH to afford the pure naphthoquinone derivatives.

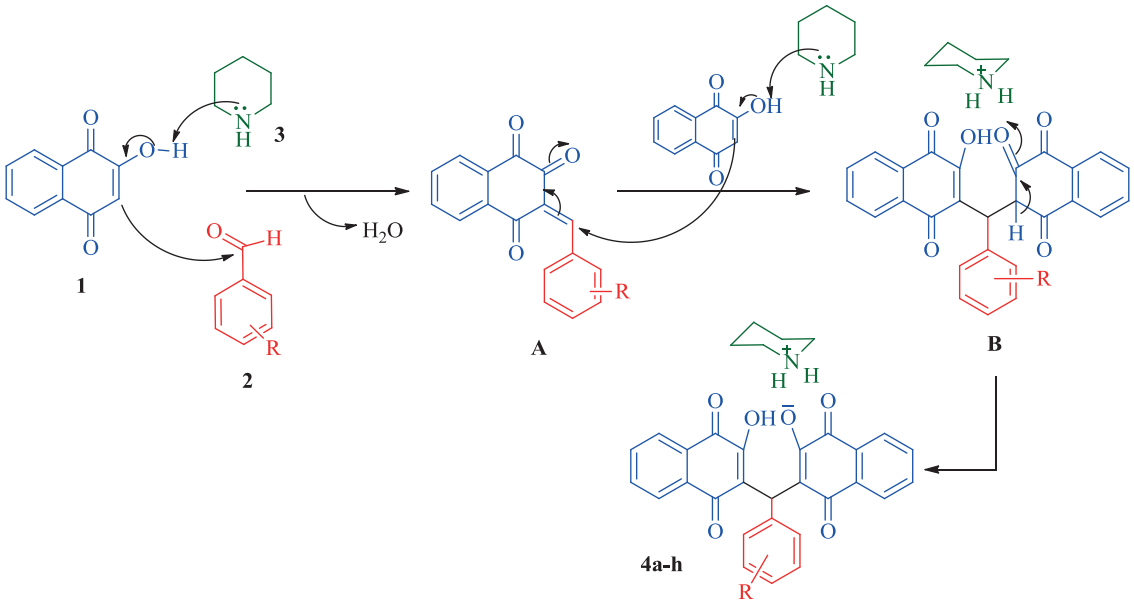


Figure 5. The proposed mechanism for the synthesis of piperidinium 3,3'-(arylmethylene) bis (2-hydroxynaphthalene-1,4-dione) salts.

3.3. Characterization data of selected compounds

3.3.1. Piperidinium 3,3'-(phenylmethylene) bis (2-hydroxynaphthalene-1,4-dione) (4a)

Red-orange solid; yield 92%; mp 213–215 °C; IR (KBr) ν: 3464, 3059, 3022, 2947, 1679, 1636, 1598, 1536, 1356, 1278, 731; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.39 (6H, br, CH_2), 2.83, (4H, br, N-CH_2), 6.84 (1H, s, CH), 7.00 (1H, t, J = 6.9 Hz, ArH), 7.10 (2H, d, J = 7.2 Hz, ArH), 7.20 (2H, d, J = 8.1 Hz, ArH), 7.50 (2H, td, J = 7.5 Hz, J = 1.2 Hz, ArH), 7.59 (2H, td, J = 7.5 Hz, J = 1.2 Hz, ArH), 7.79 (2H, d, J = 6.9 Hz, ArH), 8.10 (2H, d, J = 7.5 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75.65 MHz) δ: 22.15, 30.94 (2C), 33.75, 44.93 (2C), 124.09 (2C), 125.08 (2C), 125.39 (2C), 126.91 (2C), 127.21 (2C),127.83 (2C), 130.27 (2C), 131.85 (2C), 133.46 (2C), 134.01 (2C), 140.91, 162.44, 183.96 (2CO), 185.46 (2CO). MS m/z (%): 77.1 (100), 84.1 (23), 105.1 (88), 174.1 (30), 264.1 (39), 327.2 (31), 404.2 (46).

3.3.2. Piperidinium 3,3'-((4-bromophenyl)methylene) bis (2-hydroxynaphthalene-1,4-dione) (4b)

Red-orange solid; yield 93%; mp 247–249 °C; IR (KBr) νmax/cm^{-1}: 3435, 3051, 3020, 2940, 1675, 1635, 1597, 1567, 1355, 1261, 733; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.54–1.61 (6H, m, CH_2), 3.00 (4H, s, N-CH_2), 6.66 (1H, s, CH), 7.11 (2H, d, J = 8.1 Hz, ArH), 7.35 (2H, d, J = 8.4 Hz, ArH), 7.69 (1H, t, J = 7.2 Hz, ArH), 7.78 (2H, t, J = 7.2 Hz, ArH), 7.90 (2H, d, J = 7.2 Hz, ArH), 7.98 (2H, d, J = 7.5 Hz, ArH), 8.33 (2H, br, NH_2), 15.88 (1H, br, OH); ^{13}C NMR ($CDCl_3$, 75.65 MHz) δ: 22.09, 22.62 (2C), 33.18, 44.22 (2C), 118.26 (2C), 122.51 (2C), 125.64 (2C), 126.23 (2C), 129.68 (2C),131.02 (2C), 131.41 (2C), 132.45 (2C), 133.66 (2C), 134.32 (2C), 141.48, 164.87, 182.86 (2CO), 184.01 (2CO). MS m/z (%): 76.1 (100), 84.2 (39), 105.1 (95), 174.1 (69), 233.2 (37), 312.2 (24), 417.2 (16), 498.2 (15).

3.3.3. Piperidinium 3,3'-((2-chlorophenyl)methylene) bis (2-hydroxynaphthalene-1,4-dione) (4c)

Red-orange solid; yield 92%; mp 218–220 °C IR (KBr) ν: 3525, 3245, 3061, 2952, 1671, 1645, 1647, 1596, 1567, 1351, 1273, 960, 742, 728; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.49–1.59 (6H, m, 3CH_2), 2.97 (4H, m, 2N-CH_2), 6.57 (1H, s, CH), 7.13–7.22 (2H, m, ArH), 7.29 (2H, dd, J= 7.2 Hz, J= 2.1 Hz, ArH), 7.38 (2H, d, J= 7.2 Hz, ArH), 7.68 (2H, td, J= 7.5 Hz, J= 1.2 Hz, ArH), 7.77 (2H, td, J= 7.2 Hz, J= 1.2 Hz, ArH), 7.90 (2H, dd, J= 6.9 Hz, J= 1.2 Hz, ArH), 7.98 (2H, d, J= 6.6 Hz, ArH), 8.39 (2H, br, NH_2), 15.69 (1H, br, OH); ^{13}C NMR ($CDCl_3$, 75.65 MHz) δ: 22.0, 22.6 (2C), 33.8, 44.2 (2C), 122.2 (2C), 125.6 (2C), 126.2 (2C), 126.6, 127.6 (2C), 129.8 (2C), 131.0, 131.4 (2C), 132.5 (2C), 132.9, 133.5, 134.3, (2C), 139.7, 164.5, 182.6 (2CO), 184.0 (2CO). MS m/z (%): 76.1 (61), 84.1 (30), (105.1 (55), 174.1 (31), 233.1 (100), 261.1 (17), 389.2 (7), 435.2 (32).

3.3.4. Piperidinium 3,3'-((3-fluorophenyl)methylene) bis (2-hydroxynaphthalene-1,4-dione) (4d)

Red-orange solid; yield 90%; mp 228–230 °C; IR (KBr) ν: 3525, 3172, 3057, 2942, 1676, 1612, 1596, 1569, 1357, 1275, 973, 732; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.56–1.54 (6H, m, CH_2), 3.01 (4H, br, N-CH_2), 6.70 (1H, s, CH), 6.89–7.25 (4H, m, ArH), 7.69 (2H, t, J= 7.5 Hz, J= 1.2 Hz, ArH), 7.77 (2H, t, J= 7.3 Hz, J= 1.5 Hz, ArH), 7.90 (2H, d, J= 7.5 Hz, J= 0.9 Hz, ArH), 7.98 (2H, d, J= 7.5 Hz, J= 0.9 Hz, ArH), 8.28 (2H, br, NH_2), 15.69 (1H, br, OH); ^{13}C NMR ($CDCl_3$, 75.65 MHz) δ: 22.0, 22.6 (2C), 33.4, 44.2 (2C), 112.1 (d, $^2J_{FC}$ = 21.18 Hz, C_6H_4F), 113.9 (d, $^2J_{FC}$ = 20.42 Hz, C_6H_4F), 122.4 (2C), 123.3 (2C), 125.6 (2C),126.2 (2C), 129.8 (d, $^4J_{FC}$ = 8.3 Hz, C_6H_4F), 131.4 (2C), 132.4 (2C), 133.6 (2C), 134.3 (2C), 145.2 (d, $^3J_{FC}$ = 6.8 Hz, C_6H_4F), 162.8 (d, $^1J_{FC}$ = 241.3 Hz, C_6H_4F), 164.9, 182.8 (2CO), 184.0 (2CO). MS m/z (%): 44.1 (38), 84.1 (100), 105.1 (43), 174.1 (24), 251.1 (31).

3.3.5. Piperidinium 3,3'-(naphthalen-2-ylmethylene) bis (2-hydroxynaphthalene-1,4-dione) (4e)

Red-orange solid; yield 90%; mp 247–249 °C; IR (KBr) ν: 3436, 3140, 2958, 1679, 1648, 1598, 1569, 1359, 1279, 922, 728; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.46–1.56 (6H, m, CH_2), 2.96 (4H, m, N-CH_2), 6.85 (1H, s, CH), 7.3–7.82 (10H, m, ArH), 7.93 (2H, d, J= 7.2 Hz, ArH), 8.01 (2H, d, J= 7.2 Hz, ArH), 8.31 (2H, br, NH_2), 15.78 (1H, br, OH); ^{13}C NMR ($CDCl_3$, 75.65 MHz) δ: 22.0, 22.5 (2C), 33.8, 44.1 (2C), 122.8, 124.8, 125.2 (2C), 125.6 (2C), 125.9 (2C), 126.2 (2C), 126.7 (2C), 127.5 (2C), 127.6 (2C), 127.9, 131.5 (2C), 131.8 (2C), 132.4 (2C), 133.5, 133.7, 134.3 (2C), 139.5, 165.0, 182.9 (2CO), 184.1 (2CO). MS m/z (%): 56.1 (44), 84.1 (76), 105.1 (99), 174.1 (79), 226.1 (41), 283.1 (100).

3.3.6. Piperidinium 3,3'-((4-hydroxy-3-methoxyphenyl) methylene) bis (2-hydroxynaphthalene-1,4-dione) (4f)

Red-orange solid; yield 91%; mp 207–209 °C; IR (KBr) ν: 3522, 3116, 2951, 1676, 1642, 1596, 1569, 1356, 1278, 958, 741; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.46 (6H, s, CH_2), 2.97 (4H, s, N-CH_2), 3.67 (3H, s, OCH_3), 5.83 (1H, br, ArOH), 6.67 (1H, d, J= 8.1 Hz, ArH), 6.73 (1H, d, J= 8.1 Hz, ArH), 6.76 (1H, s, CH), 7.29 (1H, s, ArH), 7.43 (2H, t, J= 7.5 Hz, ArH), 7.58 (2H, t, J= 7.5 Hz, ArH), 7.75 (2H, d, J= 7.5 Hz, ArH), 8.09 (2H, d, J= 7.8 Hz, ArH), 8.93 (2H, br, NH_2), 15.97 (1H, br, OH); ^{13}C NMR ($CDCl_3$, 75.65 MHz) δ: 22.1, 30.9 (2C), 33.7, 44.9 (2C), 110.3, 113.8, 119.8, 124.0 (2C), 125.4 (2C), 126.7 (2C), 130.8 (2C), 131.8 (2C), 132.4 (2C), 133.4 (2C), 133.9 (2C), 143.4, 146.5, 163.0, 184.1 (2CO), 185.1 (2CO). MS m/z (%): 50.1 (51), 84.1 (61), 105.1 (100), 174.1 (72), 209.1 (10), 249.1 (21), 310.2 (29).

3.3.7. Piperidinium 3,3'-(3,4-dimethoxyphenyl) bis (2-hydroxynaphthalene-1,4-dione) (4g)

Red-orange solid; yield 92%; mp 247–248 °C; IR (KBr) ν: 3435, 3122, 2950, 1672, 1642, 1570, 1511, 1363, 1244, 741; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.54–1.61 (6H, m, 3CH_2), 3.00 (4H, s, N-CH_2), 3.57 (3H, s, OCH_3), 3.69 (3H, s, OCH_3), 6.63–6.77 (4H, m, CH and ArH), 7.68 (2H, t, J= 7.5 Hz, ArH), 7.77 (2H, t, J= 7.5 Hz, ArH), 7.89 (2H, d, J= 6.9 Hz, ArH), 7.98 (2H, d, J= 7.5 Hz, ArH), 8.35 (2H, br, NH_2); ^{13}C NMR ($CDCl_3$, 75.65 MHz) δ: 22.0, 22.6 (2C), 33.1, 44.2 (2C), 55.9 (2OMe), 111.8, 111.9, 119.4, 123.2 (2C), 125.5 (2C), 126.2 (2C), 131.3 (2C), 132.3 (2C), 133.7 (2C), 134.2 (2C), 147.0 (2C), 148.8, 164.8, 182.9 (2CO), 184.2 (2CO). MS m/z (%): 50.1 (50), 84.2 (63), 105.1 (100), 174.1 (59), 251.1 (16), 294.1 (64), 322.2 (31).

Table 2. Crystal data and structure refinement for piperidinium 3,3'-(phenylmethylene) bis (2-hydroxynaphthalene-1,4-dione).

Empirical formula	$C_{27}H_{15}O_6$, $C_5H_{12}N$
Formula weight	521.55
Temperature (K)	293
Crystal system	Monoclinic
Space group	P21/n (No. 14)
Unit cell dimensions	a= 10.188 (2) Å
	b = 20.132 (4) Å
	c = 12.829 (3) Å
	$\alpha = 90°$
	$\beta = 102.54(3)°$
	$\gamma = 90°$
Volume	2568.5(10) Å^3
Z	4
Density (calculated)	1.349
μ/mm^{-1}	0.093
F(000)	4704
Crystal Size	0.20 × 0.30 × 0.50 mm^3
θ range for data collection	2.6 to 25.0
Observed Data [$I > 2\sigma$ (I)]	1804
Dataset	–12: 12 ; –23: 21 ; –15: 11
Data collected	9933
Unique data, R(int)	4375, 0.073
Parameters	356
R, wR_2, S	0.0468, 0.1306, 0.78
Max, Min [e·Å^{-3}]	–0.20, 0.21
CCDC	1552866

w = 2[(FO2) + (0.0598P)2], P = (FO2 + 2FC2)/3'.

3.3.8. Piperidinium 3,3'-(*p*-tolylmethylene) bis (2-hydroxynaphthalene-1,4-dione) (4h)

Red-orange solid; yield 91%; mp 226–228 °C; IR (KBr) ν: 3448, 3154, 3065, 2953, 1676, 1646, 1595, 1575, 1355, 1276, 962, 740; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.42 (6H, s, 3CH_2), 2.22 (3H, s, CH_3), 2.88, (4H, br, 2N-CH_2), 6.83 (1H, s, CH), 6.96 (2H, d, J= 8.1 Hz, ArH), 7.14 (2H, d, J= 7.8 Hz, ArH), 7.48 (2H, td, J= 7.8 Hz, J= 0.9 Hz, ArH), 7.62 (2H, td, J= 7.6 Hz, J= 0.9 Hz, ArH), 7.82 (2H, d, J= 7.2 Hz, ArH), 8.14 (2H, d, J= 7.5 Hz, ArH), 8.35 (2H, br, NH_2); ^{13}C NMR ($CDCl_3$, 75.65 MHz) δ: 20.8, 22.1, 22.2 (2C), 33.4, 44.9 (2C), 124.1, 125.3 (2C), 126.8 (2C), 127.1 (2C), 128.5 (2C), 130.8 (2C),131.8 (2C), 133.4 (2C), 133.9 (2C), 134.2 (2C), 137.6 (2C), 140.9, 162.4, 184.0 (2CO), 185.3 (2CO). MS m/z (%): 76.1 (100), 84.1 (31), 105.1 (78), 174.1 (61), 276.2 (33), 433.2 (17).

3.4. Crystallographic data

The molecular salt **4a**, which crystallized as orange crystals in the monoclinic space group P21/n with cell parameters a = 10.188 (2) Å, b = 20.132 (4) Å, c = 12.829 (3) Å, α = 90 °, β = 102.54(3) °, γ = 90 °, V = 2568.5(10) Å^3, D_{calc} = 1.349 g cm^{-3}, and Z = 4, consists of one monoprotonated piperidine and one monoanion of 3,3'-(phenylmethylene) bis (2-hydroxynaphthalene-1,4- dione) (Figure 2). The final Rvalue is 0.0468 for 9933 reflections. Crystallographic data and the refinement procedures for **4a** are given in Table 2 and the relevant hydrogen bond parameters are provided in Table 3.

Table 3. Hydrogen bond metrics for piperidinium 3,3'-(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione).

D–H···A (deg)	D···A (Å)	H···A (Å)	D–H (Å)	D–H···A (Å)
168.00	2.502	1.5700	0.9400	O6–H1···O1
115(5) 4_455	3.070(4)	2.54(7)	0.96(8)	N1–H1N2···O3
156.00	2.768(4)	1.9200	0.9100	N1–H26···O1
128.00	3.056(4)	2.4100	0.9100	N1–H26···O2
157.00 3_655	3.466(5)	2.5900	0.9300	C20–H9···O6
108.00	2.829(4)	2.3600	0.9800	C7–H11···O3
113.00	2.795(4)	2.2700	0.9800	C7–H11···O4
153.00	3.365(5)	2.5100	0.9300	C26–H13···O3
145.00 4_455	3.362(4)	2.5600	0.9300	C25–H14···O6
119.00	3.074(5)	2.4900	0.9700	C28–H24···O2

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