Quinonic Enaminones; Synthesis of New Dialkylaminovinyl and Bis(dialkylaminovinyl) Derivatives of Quinones

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Abstract: The reaction of halogenated quinones with a variety of secondary amines in the presence of acetaldehyde proceeds via intermediate formation of enamines and produces mono quinonic enaminones. The use of two equivalents of enamine results in both symmetrical and nonsymmetrical bis-derivatives.

Key words: quinones, enamines, quinonic enaminones

Donor/acceptor substituted organic molecules exhibit interesting optical and electronic properties. They are used in non linear optics (NLO),[1-3] in molecular electronic devices,[4-6] and in artificial photosynthetic models.[7-9]

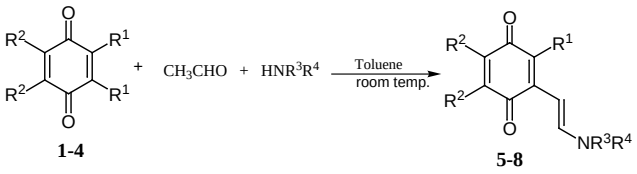
Several novel donor/acceptor naphthoquinone derivatives e.g. substituted benzo[b]phenoxazine-6,11-diones and their *N*-tosyl derivatives were recently prepared.[10] UV–Vis measurements and theoretical calculations proved the existence of an intramolecular electron transfer from the HOMO of the donor moiety to the LUMO of the acceptor (the quinonic fragment of the molecules).

In this paper, we describe the synthesis and properties of a different type of quinones which might show non-linear optical properties. These are the 3-dialkylaminovinyl derivatives of benzoquinone **5**−**7** and of naphthoquinone **8** and also the 3,6-bis(dialkylaminovinyl) derivatives of benzoquinone **9**. As can be seen from Scheme 1, the quinonic moieties were derived from chloranil, bromanil, DDQ, and 2,3-dichloronaphthoquinone.

The mono substituted enaminones **5**−**8** are combined donor-acceptor materials while the bis-substituted enaminones **9** are composed of two donors and one acceptor covalently bonded in the same molecule.The reaction proceeds via formation of an enamine,[11] which reacts with the haloquinone as describe in Scheme 2. Thus, using one equivalent of the enamine, the "blue quinones" **5**−**8** were formed in medium to high yields. The use of two equivalents of the enamine and tetrahalobenzoquinones resulted in formation of the red symmetrical bis-enaminones (**9b**, **9c**, **9e**).

Nonsymmetrical bis-enaminones, in which two different secondary amines are attached to the quinonic backbone (**9a**, **9d**) were prepared from the trihalobenzoquinones **2** and **3** as described in Scheme 3.

For spectroscopic data of compounds **5**–**9**, see Tables 1 and 2. The vinylic protons of the products appear in the ^{1}H NMR spectrum as two doublets, at δ = 5.54−5.93 and at δ = 8.25−8.89 (for the proton adjacent to the quinone).



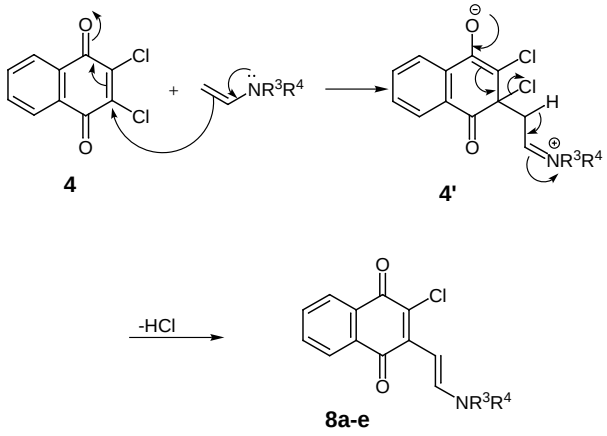
1-4 **5-8**

1,5 $R^1 = R^2 = Cl$ **2,6** $R^1 = R^2 = Br$

3,7 $R^1 = Cl$, $R^2 = CN$ **4,8** $R^1 = Cl$, R^2 =

5a	$R^3 = R^4 = C_2H_5$	**5b**	$R^3 = CH_3$, $R^4 = Bn$
5c	$R^3 = C_2H_5$, $R^4 = c\text{-}C_6H_{11}$	**5d**	$R^3 = R^4 = CH_3$
5e	$R^3 = R^4 = Bn$	**6a**	$R^3 = R^4 = Bn$
6b	$R^3 = CH_3$, $R^4 = Bn$	**6c**	$R^3 = R^4 = C_2H_5$
7a	$R^3 = R^4 = Bn$	**7b**	$R^3 = R^4 = C_2H_5$
8a	$R^3 = CH_3$, $R^4 = Bn$	**8b**	$R^3 = R^4 = C_2H_5$
8c	$R^3 = C_2H_5$, $R^4 = Ph$	**8d**	$R^3 = R^4 = Bn$
	8e $R^3 = C_2H_5$, $R^4 = c\text{-}C_6H_{11}$		

Scheme 1



4 **4'** **8a-e**

Scheme 2

The coupling constant are J = 12−13 Hz which proves that the compounds are in the *E* configuration.

The electronic absorption spectra of the blue mono enaminones compounds **5**−**8** show the expected naphtoquinonic bands in the UV region around 270−280 nm and at 320−340 nm. In addition, another band appeared in the visible region between 600−700 nm. This band is known

Table 1 Quinonic Enaminones **5–8**

Products	Yield[1] (%)	Mp (°C)	IR (KBr) ν cm^{-1}	^1H NMR ($CDCl_3$) δ (ppm), *J* (Hz)	MS (*m/z*)
5a	90	122–123	2960, 2890, 1583, 1497, 1439	8.25 (d, 1 H, *J* = 12.6), 5.64 (d, 1 H, *J* = 13.0), 3.48 (m, 4 H), 1.19 (t, 6 H)	310 $[M+3H]^+$, 292, 280
5b	95	132–134	2955, 2911, 2851, 1664, 1581, 1525	8.54 (d, 1 H, *J* = 12.6), 7.45 (m, 5 H), 5.61 (d, 1 H, 12.8), 4.72 (s, 2 H), 3.40 (s, 3 H)	357[$M+2H]^+$, 322, 265
5c[2,3]	90	102–103	2932, 2855, 1663, 1591, 1514	8.32 (d, 1 H, *J* = 12.8), 5.67 (d, 1 H, *J* = 12.5), 3.43–3.52 (m, 3 H), 1.15–1.85 (m, 13 H)	263 $[M+2H]^+$, 326, 282
5d	76	146–148	2961, 2820, 1659, 1588, 1521	8.32 (d, 1 H, *J* = 12.8), 5.58 (d, 1 H, *J* = 12.8), 3.23 (s, 6 H)	281 $[M+2H]^+$, 248, 230, 168
5e	93	122–124	2980, 2851, 1665, 1588, 1521	8.66 (d, 1 H, *J* = 13.0), 7.37 (s, 5 H), 7.24 (s, 5H), 5.88 (d, 1 H, *J* = 12.9), 4.50 (br s, 4 H)	434 $[M+3H]^+$, 364, 305, 230, 196
6a	76	130–132	2953, 2830, 1640, 1532, 1490	8.59 (d, 1 H, *J* = 13.0), 7.36 (br s, 10 H), 5.93 (d, 1 H, *J* = 12.8), 4.48 (br s, 4 H)	566 $[M+3H]^+$, 487, 409, 344, 196
6b	65	148–149	2965, 2889, 1600, 1497	8.49 (d, 1 H, *J* = 12.8), 7.40 (m, 5 H), 5.72 (d, 1 H, *J* = 12.9), 4.52 (s, 2 H), 2.91 (s, 3 H)	491 $[M+3H]^+$, 487, 367, 334
6c	67	140–142	2834, 2872, 1630, 1560	8.26 (d, 1 H, *J* = 12.8), 5.78 (d, 1 H, *J* = 12.6), 3.49 (q, 4 H), 1.25 (t, 6 H)	425 $[M+2H]^+$, 365, 342
7a	50	148–150	3165, 2198, 1563, 2970	8.89 (d, 1 H, *J* = 12.4), 7.34 (m, 10 H), 5.55 (d, 1 H), 4.62 (s, 2 H), 4.41 (s, 2 H)	417 $[M+3H]^+$, 330, 180
7b	44	132–134	3160, 2195, 2972, 1560	8.53 (d, 1 H, *J* = 12.7), 5.54 (d, 1 H, *J* = 12.7), 3.76 (q, 4 H), 1.18 (t, 6 H)	291 $[M+2H]^+$, 256, 204
8a	90	96–97	1674, 1599, 1569	8.70 (d, 1 H, *J* = 12.6), 8.15 (m,1 H), 7.99 (m, 1 H), 7.64 (m, 2 H), 7.34–7.39 (m, 5 H), 5.71 (d, 1 H, *J* = 12.9), 4.52 (s, 2 H), 2.88 (br s, 3 H)	340 $[M+3H]^+$, 318, 304
8b	86	86–88	1678, 1670, 1562, 1591	8.42 (d, 1 H, *J* = 12.9), 8.13 (m, 1 H), 7.95 (m, 1 H), 7.82 (m, 2 H), 5.61 (d, 1 H, *J* = 12.9), 3.46 (m, 4 H), 1.15 (t, 6 H)	292 $[M+3H]^+$, 256, 218, 159
8c	83	92–93	1690, 1600,1570, 1495	8.08 (m, 1 H), 7.95 (m, 1 H), 7.36 (d, 1 H, *J* = 12.2), 7.08 (m, 2 H), 6.55 (m, 5 H), 5.63 (br s, 1 H), 3.01 (q, 2 H),1.16 (t, 3 H)	338 $[M+H]^+$, 209, 192, 159
8d	82	154–156	1682, 1609, 1582, 1478	8.81 (d, 1 H, *J* = 13.0), 8.11 (m, 1 H), 7.99 (m, 1 H), 7.65 (m, 2 H), 7.39 (m, 5 H), 7.35 (m, 5 H), 5.92 (d, 1 H, *J* = 13.0), 4.49 (s, 4 H)	416 $[M+3H]^+$, 378, 324, 288, 225
8e	90	118–119	2942, 1682, 1600, 1502, 1555	8.57 (d, 1 H, *J* = 12.7), 8.12 (m, 1 H), 7.98 (m, 1 H), 7.67 (m, 2 H), 5.76 (d, 1 H, *J* = 13.0), 3.49 (m, 3 H), 1.89 (m, 4 H), 1.48 (m, 9 H)	344 $[M+H]^+$, 310, 262, 226, 192, 159

[1].Yields of isolated products based on the haloquinone were not optimized. Satisfactory microanalysis was obtained: C ± 0.31; H ± 0.19; N ± 0.28; Cl±36.

[2]. ^{13}C NMR ($CDCl_3$): δ (ppm) = 35, 61, 94, 128, 139, 140, 154, 177, 191. The other compounds also gave the correct ^{13}CNMR spectra.

[3]. λ_{max} (MeOH) = 208, 320, 694 nm. Similar absorptions were obtained for the other compounds.

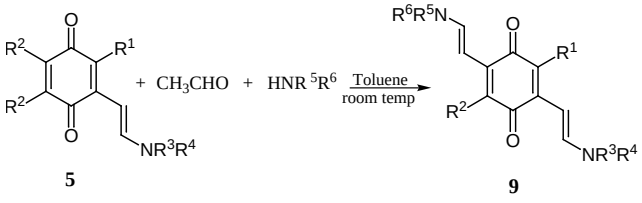
Table 2 Quinonic Bis-enaminones **(9)**

Products	Yield[3] (%)	Mp(°C)	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm), *J* (Hz)	MS (*m/z*)
9a	70	174−176	2960, 2895, 2816, 1583, 1497, 1439	8.68 (d, 2 H, *J* = 12.9), 7.34−7.29 (m, 5H), 5.55 (d, 2 H, *J* = 12.9), 4.41 (s, 2H), 2.83 (br s, 7H), 1.18 (br, s, 6H)	420 $[M+2H]^+$, 385, 351
9b	54	156−158	2952, 2850, 1665, 1592, 1522	8.73 (d, 2 H, *J* = 12.9), 7.22−7.28 (m, 20 H), 5.75 (d, 2 H, *J* = 13.0), 4.43 (s, 8 H)	618 $[M+H]^+$, 542, 430, 196
9c[1]	72	162−163	2952, 2886, 1528, 1501	8.44 (d, 2 H, *J* = 12.8), 5.43 (d, 2 H, *J* = 12.5), 3.39 (t, 4 H), 1.20 (t, 12 H, *J* = 5.8)	373 $[M+3H]^+$, 337, 302
9d[2]	65	156−158	3019, 2911, 1629, 1595, 1514	8.70 (d, 2 H, *J* = 12.6), 7.3 (m, 10 H), 5.60(br s, 2 H), 4.48 (s, 4 H), 2.88 (br s, 4 H)	468 $[M+2H]^+$, 430, 375
9e	90	192−194	2934, 2854, 1578, 1508, 1432	8.75 (d, 2 H, *J* = 12.8), 5.70 (d, 2 H, *J* = 12.8), 3.38 (q, 2 H), 3.1 (t, 1 H), 1.71 (m, 4 H), 1.43−1.54 (m, 12 H), 1.23 (t, 6 H)	480 $[M+2H]^+$, 444, 351

[1] ^{13}C –NMR ($CDCl_3$): δ (ppm) = 14, 43, 51, 67, 118, 141, 176. The other compounds alsogave the correct ^{13}CNMR spectra.
[2] λ_{max} (MeOH) = 208, 352, 552 nm. Similar absorptions were obtained for the other compounds.
[3] Satisfactory microanalysis was obtained: C ± 0.31; H ± 0.19; N ± 0.28; Cl±36.

to arise from HOMO to LUMO transition, which corresponds, in this case, to intramolecular electron transfer from the donor enamine moiety to the acceptor quinonic moiety of the molecule. Interestingly, the electronic absorption spectra of the red bis-enaminones **9** do not show the charge transfer absorption in the Vis region.

In the IR spectra, the two typical quinonic absorptions appear in the region of 1580−1690 cm^{-1}, and the conjugated vinylic moiety is observed between 2920−3030 cm^{-1}.



5 **9**

$R^1 = R^2 = Cl$

9a $R^3 = R^4 = C_2H_5$; $R^5 = CH_3$, R^6 = Bn
9b $R^3 = R^4 = R^5 = R^6$ = Bn
9c $R^3 = R^4 = R^5 = R^6 = C_2H_5$
9d $R^3 = R^5 = CH_3$, $R^4 = R^6$ = Bn
9e $R^3 = R^5 = C_2H_5$, $R^4 = R^6$ = *c* - C_6H_{11}

Scheme 3

IR spectra were recorded on a Nicolet 5ZDX FT−IR spectrometer. ^1H and ^{13}C NMR were run on a Bruker WP 200 SY spectrometer. Mass spectra (CI in CH_4) were obtained on a Finnigan 4020 quadropole spectrometer and UV−Vis spectra were measured using Hewlett Packard 8452A diode array spectrophotometer. All reagents were of commercial quality. Mps were determined using a Thomas−Hoovar capillary apparatus and are uncorrected.

General Procedure for the Preparation of 5−8

To a solution of tetrahalogenated 1,4-benzoquinone or 2,3-dichloronaphthoquinone (4.4 mmol) in toluene (60 mL) was added a mixture of acetaldehyde (4.4 mmol) and a secondary amine (8.8 mmol) in toluene (20 mL). The mixture was stirred at r.t. until the disappearance of the starting quinone (TLC). The blue colored solution was evaporated under reduced pressure and the resulting solid was purified by silica gel column chromatography using CH_2Cl_2 as the eluent. The products were recrystallized from *n*-hexane or petroleum ether (60−80 °C).

Symmetrical Bis-quinonic Enaminones (9b−9d)

A solution of *p*-chloranil (4.4 mmol) in toluene (70 mL) was added slowly to a cooled and stirred solution of acetaldehyde (8.8 mmol) and secondary amine (17.6 mmol). The stirring was continued for 2 h and then at r.t. for 2−5 h until TLC showed the disappearance of the chloranil and the mono substituted product.

The red purple solution was evaporated under reduced pressure and purified using neutral alumina column chromatography and CH_2Cl_2 as the eluent. The products were recrystallized from *n*-hexane.

Nonsymmetrical Bis-quinonic Enaminones (9a, 9e)

A solution of acetaldehyde (4.4 mmol) and secondary amine (8.8 mmol) in toluene (20 mL) was added dropwise to a cold solution of the monoquinonic enaminone **5** (4.4 mmol) in toluene (70 mL). The mixture was stirred for 2−7 h until the disappearance of the starting quinone **5** (TLC). The isolation and purification is as above for **9b**.

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