Quinone Diazides and Enaminones as a Source of New Azo Compounds with Potential Nonlinear Optical Properties

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Introduction

Quinone diazides are compounds that have intermediate reactivity between diazonium salts and aliphatic diazo ketones.[1] They can react by either loss or retention of molecular nitrogen, depending on reaction conditions. An example of the first case involves the formation of dihydrobenzofurans by a regiospecific route in reactions of *o*-quinone diazides with vinyl ethers under thermal conditions.[2] On the other hand, retention of nitrogen in azo-coupling reactions are often observed.[3] This type of reaction is widely used in industry for the synthesis of hydroxyazo dyes.[4]

Our group has been interested in the reactivity of α-diazocarbonyl compounds and enaminones. Thus, diazodiphenylethanone reacts with enaminones via its copper(II)-stabilized carbene to form pyrroles[5] or via diphenylketene under noncatalytic thermal conditions to form nucleophilic addition products.[6] 3-Diazo-1,3-dihydro-2*H*-indol-2-one derivatives react with enaminones to form triazoles.[7] Our continuing interest in the chemistry of enaminones and diazo carbonyls has led us to extend our reactivity studies to include the reactions of *o*-quinone diazides **1** with enaminones **2**. Since quinone diazides, especially nitro-substituted ones, are very sensitive to light we decided to try a one-pot procedure in order to avoid contact of the reacting mixture with light.

Results and Discussion

The quinone diazides **1** are generated in the reaction media by nitrosation of the proper *o*-aminophenol to form the diazonium salt **4** which is then neutralized to form **1**. The quinone diazides formed are reacted with enaminones **2** to produce the novel azo-enaminones **3** as determined by spectroscopic means.

It is essential for the obtention of the azo-enaminones **3** to work with quinone diazides. Tests involving the azo coupling between some corresponding diazonium salts and enaminones led to deaminated azo compounds **5**, as shown in Table 1. It is important to mention that methyl alcohol is used as the organic solvent in the reactions involving diazonium salts **4** in order to solubilize the reactants. No solvolysis product with methanol was detected, and when the azo-enaminones **3** are treated with acid no deaminated azo compounds are formed. Since these enaminones do not decompose in the reaction media and thermal analysis of the diazonium salts **4** indicates the presence of water of crystallization, we propose that the azo compounds **5** are formed by hydrolysis of the azo-coupling adduct initially formed, as shown in Scheme 1. When diazoniun salts **4** are previously neutralized to form quinone diazides **1** this hydrolysis does not take place.

AM1 geometry optimization indicate a tendency for two intramolecular hydrogen bonds with the azo group. X-ray crystallographic data for **3d**[8] indicate good agreement between X-ray and AM1 calculated geometries. Based on these data, all azo compounds described here are assumed to have the two hydrogen bonds linked to the azo group, as shown in Table 1.

Table 2 shows the AM1 optimized azo-conjugated skeleton to be almost planar, as expected for a system

Scheme 1. One-Pot Synthesis of Azo Compounds 3 and 5

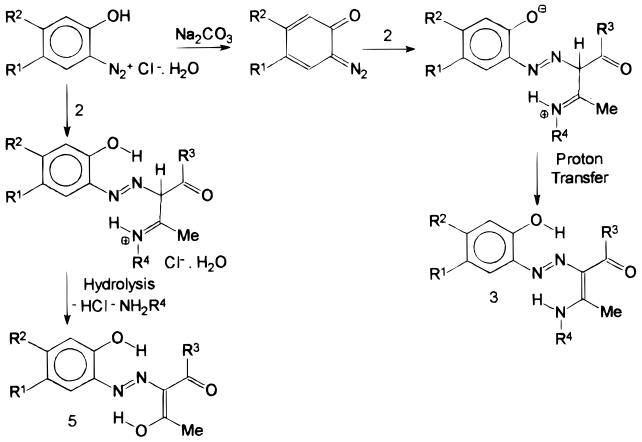
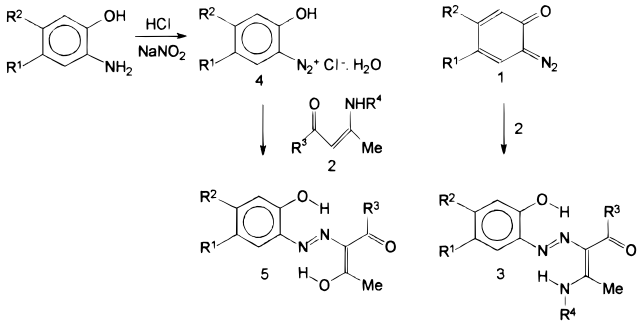


Table 1. Reaction Products of Quinone Diazides 1 and Diazonium Salts 4 with Enaminones 2



1 or **4**	**2**	**3** (% yield)	**5** (% yield)
1a (R^1 = Me, R^2 = H)	**2a** (R^3 = OEt, R^4 = Me)	**3a** (25)	
1b (R^1 = NO_2, R^2 = H)	**2a**	**3b** (74)	
1b	**2e** (R^3 = Me, R^4 = t-Bu)	**3c** (70)	
1c (R^1 = Cl, R^2 = NO_2)	**2b** (R^3 = OEt, R^4 = H)	**3d** (66)	
1c	**2a**	**3e** (67)	
1c	**2d** (R^3 = R^4 = Me)	**3f** (59)	
1c	**2c** (R^3 = OEt, R^4 = t-Bu)	**3g** (81)	
1c	**2e**	**3h** (70)	
1d (R^1 = H, R^2 = NO_2)	**2a**	**3i** (61)	
1d	**2e**	**3j** (58)	
4a (R^1 = R^2 = H)	**2a**		**5a** (40)
4b (R^1 = Cl, R^2 = NO_2)	**2a**		**5b** (71)
4b	**2d**		**5c** (66)

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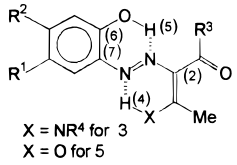
Table 2. AM1 Geometry Optimization Data. Selected Dihedral Angles (deg) for 3 and 5



compd	H(4)−X−C(3)−C(2)	H(5)−O−C(6)−C(7)	R^1-phenyl	R^2-phenyl
3a	3.42	1.65	0.15	0.01
3b	3.81	0.39	0.40	0.12
3c		2.28	0.36	0.11
3d	2.46	1.41	1.15	51.24
3e	2.54	0.90	1.28	53.96
3f	1.90	1.31	1.47	54.91
3g	3.59	0.37	2.47	52.31
3h	0.11	1.33	2.39	54.51
3i	3.92	0.01	0.20	0.05
3j	1.85	3.11	0.05	0.01
5b	0.53	1.62	1.33	54.56
5c	1.09	2.50	1.76	56.26

containing internal hydrogen bondings H(5)−azo and H(4)−azo. The AM1 method is known to describe hydrogen bonds reasonably well,[9] and specifically in the case of enaminones[10] this method showed good results for geometry optimizations.

The planarity of the azo skeleton leads to extensive conjugation throughout the molecule, and when the phenyl ring is attached to electron-withdrawing groups, like chlorine or nitro, a push-pull conjugation is observed.

As can be seen in Table 1, our procedure works especially well for the obtention of azo-enaminone compounds **3** with electron-withdrawing groups attached to the phenyl ring.

Organic compounds containing push-pull conjugation can present large optical second-order molecular polarizabilities and have important applications in second-order nonlinear optical (NLO) devices. Delocalization and intramolecular charge transfer effect of π-electrons in these molecules can cause large and fast nonlinear responses.[11]

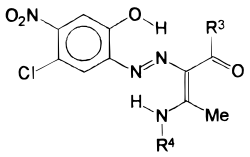
Extensive calculations using semiempirical models have been reported for many varieties of molecular architectures, and many of these calculations have not only determined numerical values for nonlinear response, but have also dealt with interpretation of the molecular geometry and the electronic structure of such organic conjugated molecules.[12,13]

We decided to evaluate the molecular polarizability of these azo compounds theoretically because we do not have conditions for measuring the molecular hyperpolarizabilities of the compounds experimentally. The AM1/finite-field method was chosen as our first approach since it is reasonably fast and has been used successfully

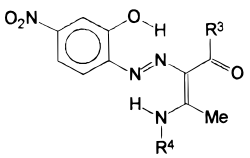
Table 3. AM1/Finite-Field Calculated Results for 3 and 5

compd	μ/D	$\langle\alpha\rangle$/Å^3	$\beta_{vec}/10^{30}$ esu
3a	4.67	27.16	6.07
3b	5.80	28.47	10.59
3c	4.58	30.28	18.74
3d	9.27	30.25	28.71
3e	8.37	28.34	16.64
3f	7.30	27.69	26.28
3g	10.04	34.20	25.77
3h	9.00	32.25	22.83
3i	9.19	29.15	24.20
3j	9.24	31.31	41.82
5b	6.11	27.13	13.21
5c	5.04	25.12	15.90

Table 4. Calculated Nitro Dihedral Angles (deg) and Hyperpolarizability Coefficients (esu) for Similar Push-Pull Azo-Enaminones 3



3e, 3h



3i, 3j

compd	nitro−phenyl angle	$\beta_{vec}/10^{30}$
3e (R^3 = OEt, R^4 = Me)	53.82	16.64
3i (R^3 = OEt, R^4 = Me)	0.05	24.20
3h (R^3 = Me, R^4 = t-Bu)	54.50	22.83
3j (R^3 = Me, R^4 = t-Bu)	0.17	41.82

for determining trends of molecular hyperpolarizabilities.[14] Since we are mainly interested in potential applications of our novel azo compounds in nonlinear optics and in establishing trends of hyperpolarizabilities for a series of related molecules, we believe that our approach remains meaningful.

Table 3 shows the finite-field calculated results for the azo compounds **3** and **5** where it can be seen that the push-pull conjugation is essential for a significant value of the molecular coefficient of hyperpolarizability, β_{vec}. Compound **3a** has no electron-withdrawing groups attached to the phenyl group and has the smallest value of β. Intermediate values are found for **3b**, **3c**, and **3e**, and for the compounds **5** which have a poor donating group (OH). Finally we have a series of six compounds which seem promising for second harmonic generation. They have significant values for β_{vec} and are almost planar.

On comparing the calculated β values for chloro/nitro and *p*-nitro azo-enaminones it can be seen that the *p*-nitro compounds have larger values for β. Table 4 shows a relationship between calculated β and the planarity of the conjugated skeleton.

One can suppose at first sight that this is a distortion of the AM1 geometry optimization, but again the preliminary X-ray crystallographic data[8] indicate a 28° dihedral angle between the nitro group and the phenyl ring for **3d** while the AM1 calculated dihedral angle is 51°. AM1 seems to overestimate the spatial interaction between two ortho electron-withdrawing groups on the phenyl ring. In either case the calculated finite-field β coefficient reflects this tendency.

In conclusion, our procedure allows one to obtain novel azo compounds in good yields, especially azo-enaminones

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containing push-pull conjugation. In addition, we propose the potential usefulness of the push-pull azoenaminones **3** in nonlinear optics, as second harmonic generators, based on theoretical finite-field static calculations.

Experimental Section

Melting points are uncorrected. The electron impact mass spectra were obtained at 70 eV. All IR spectra were measured as KBr pellets, and proton chemical shifts were measured relative to internal tetramethylsilane.

The enaminones **2** were prepared according to reported methods.[5−7]

General Procedure for Reactions of Quinone Diazides 1 with Enaminones 2. To a stirred solution of the proper aminophenol (2 mmol) and 1.2 mL of 6 N HCl in 2.5 mL of water at 0 °C was added, dropwise, $NaNO_2$ (2.5 mmol) in 3 mL of water. The excess nitrous acid was destroyed with about 5 mg of urea, and the solution was neutralized by addition of solid Na_2CO_3. The organic solvent (CH_2Cl_2, 20 mL) was then added, with vigorous stirring, and finally the desired enaminone (2 mmol) was added. The biphasic reaction mixture was kept in the absence of light for 7 days without stirring at room temperature and afforded the azo-coupling products **3**. All the products obtained were purified by recrystallization.

Ethyl 2-[[(*E*)-5′-Methyl-2′-hydroxyphenyl]diazo]-3(*E*)-(methylamino)-2-butenoate (3a). The crude material was submitted to column chromatography (silica gel) using mixtures of hexane and CH_2Cl_2 as eluents. Compound **3a** eluted with hexane/CH_2Cl_2 (1:1) and crystallized as yellow needles, mp 132 °C: IR 3242, 1660, 1528, 1510, 1529, 1463, 1390, 1359 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (t, 3H, J = 7.1 Hz), 2.29 (s, 3H), 2.54 (s, 3H), 3.1 (d, 3H, J = 5.1 Hz), 4.2 (q, 2H, J = 7.1 Hz), 6.7 (m, 3H), 12.2 (s, 1H); MS *m*/*z* (relative intensity) 277(98), 204(100), 157(18), 122(53), 107(8), 98(12), 83(78). Anal. Calcd for $C_{14}H_{19}N_3O_3$: C, 60.64; H, 6.91; N, 15.15. Found: C, 60.32; H, 6.91; N, 14.85.

Ethyl 2-[[(*E*)-5′-Nitro-2′-hydroxyphenyl]diazo]-3(*E*)-(methylamino)-2-butenoate (3b). The reaction mixture afforded crystalline product **3b** (red needles), mp 195 °C: IR 3442, 3077, 2980, 2932, 1703, 1654, 1604, 1583, 1480, 1442, 1399, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4 (t, 3H, J = 7 Hz), 2.6 (s, 3H), 3.3 (d, 3H, J = 5 Hz), 4.3 (q, 2H, J = 7 Hz), 7.0 (d, 1H, J = 9 Hz), 8.0 (dd, 1H, J = 2.8 and 9 Hz), 8.3 (d, 1H, J = 2.8 Hz), 13.4 (s, 1H), 13.9 (s, 1H); MS *m*/*z* (relative intensity) 308(81), 235(99), 170(9), 157(6), 114(17), 98(14), 83(100). Anal. Calcd for $C_{13}H_{16}N_4O_5$: C, 50.65; H, 5.23; N, 18.17. Found: C, 51.06; H, 5.05; N, 18.42.

3-[[(*E*)-5′-Nitro-2′-hydroxyphenyl]diazo]-4(*E*)-(*tert*-butylamino)-3-penten-2-one (3c). The reaction mixture afforded crystalline product **3c** (red needles), mp 201−203 °C: IR 3450, 2976, 1655, 1616, 1516, 1480 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (s, 9H), 2.45 (s, 3H), 2.73 (s, 3H), 7.0 (d, 1H, J = 9 Hz), 8.0 (dd, 1H, J = 2.8 and 9 Hz), 8.2 (s, 1H), 13.1 (s, 1H), 13.2 (s, 1H); MS *m*/*z* (relative intensity) 320(7), 277(30), 221(90), 175(20), 167(30), 98(25), 69(40), 57(100). Anal. Calcd for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.06; H, 6.04; N, 17.41.

Ethyl 2-[[(*E*)-5′-Chloro-2′-hydroxy-4′-nitrophenyl]diazo]-3(*E*)-amino-2-butenoate (3d). The reaction mixture afforded crystalline product **3d** (red needles), mp 183−186 °C: IR 3313, 1662, 1520, 1466, 1327 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3H, J = 7.2 Hz), 2.67 (s, 3H), 4.32 (q, 2H, J = 7.2 Hz), 6.6 (s, 1H), 7.53 (s, 1H), 7.61 (s, 1H), 12.3(s, 1H), 13.0 (s, 1H); MS *m*/*z* (relative intensity) 329(22), 328(11), 327(78), 256(27), 255(13), 254(100), 156(11), 100(18), 83(19), 69(37), 56(3). Anal. Calcd for $C_{12}H_{13}N_4O_5Cl$: C, 43.85; H, 3.99; N, 16.83. Found: C, 43.48; H, 3.54; N, 16.67.

Ethyl 2-[[(*E*)-5′-Chloro-2′-hydroxy-4′-nitrophenyl]diazo]-3(*E*)-(methylamino)-2-butenoate (3e). The reaction mixture afforded crystalline product **3e** (orange needles), mp 144 °C: IR 3994, 2981, 1688, 1610, 1526, 1473, 1400 cm^{-1}; ^1H NMR (CCl_4-TFA) δ 1.6 (t, 3H, J = 6 Hz), 3.1 (s, 3H), 3.7 (d, 3H, J = 6 Hz), 4.7 (q, 2H, J = 6 Hz), 7.6 (s, 2H); MS *m*/*z* (relative intensity) 344(8), 342(23), 270(16), 268(47), 223(2), 188(4), 170(7), 157(6), 143(4), 114(12), 98(11), 83(94) 56(100). Anal. Calcd for $C_{13}H_{15}N_4O_5Cl$: C, 41.73; H, 3.12; N, 15.02. Found: C, 41.76; H, 3.20; N, 15.16.

3-[(*E*)-5′-Chloro-2′-hydroxy-4′-nitrophenyl]diazo]-4(*E*)-(methylamino)-3-penten-2-one (3f). The reaction mixture afforded crystalline product **3f** (orange solid), mp 210 °C: IR 3485, 3388, 3104, 2938, 2725, 1634, 1576, 1524, 1432, 1356 cm^{-1}; ^1H NMR (CCl_4−TFA) δ 2.6 (s, 3H), 2.8 (s, 3H), 3.6 (s, 3H), 7.6 (m, 2H); MS *m*/*z* (relative intensity) 314(11), 312(30), 271(34), 269(100), 83(82), 56(70). Anal. Calcd for $C_{12}H_{13}N_4O_4Cl$: C, 46.09; H, 4.19; N, 17.92. Found: C, 45.62; H, 3.99; N, 17.43.

Ethyl 2-[[(*E*)-5′-Chloro-2′-hydroxy-4′-nitrophenyl]diazo]-3(*E*)-(*tert*-butylamino)-2-butenoate (3g). The reaction mixture afforded crystalline product **3g** (red needles), mp 172 °C: IR 3068, 1671, 1594, 1520, 1411, 1367 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4 (t, 3H, J = 7.1 Hz), 1.6 (s, 9H), 2.8 (s, 3H), 4.3 (q, 2H, J = 7.1 Hz), 7.3 (s, 1H), 7.5 (s, 1H), 13.0 (s, 1H), 14.1 (s, 1H); MS *m*/*z* (relative intensity) 386(13), 384(35), 312(11), 310(20), 257(31), 255(50), 156(12), 100(19), 83(15), 69(46), 56(100). Anal. Calcd for $C_{16}H_{21}N_4O_5Cl$: C, 49.94; H, 5.51; N, 14.94. Found: C, 50.43; H, 5.51; N, 14.89.

3-[[(*E*)-5′-Chloro-2′-hydroxy-4′-nitrophenyl]diazo]-4(*E*)-(*tert*-butylamino)-3-penten-2-one (3h). The reaction mixture afforded crystalline product **3h** (orange solid), mp 172−173 °C: IR 3433, 2984, 1637, 1584, 1528, 1371 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (s, 9H), 2.44 (s, 3H), 2.73 (s, 3H), 7.26 (s, 1H), 7.52 (s, 1H), 12.3 (s, 1H), 14.4 (s, 1H); MS *m*/*z* (relative intensity) 356(5), 354(14), 313(15), 311(41), 256(35), 254(100), 58(49), 57(56). Anal. Calcd for $C_{15}H_{19}N_4O_4Cl$: C, 50.78; H, 5.40; N, 15.79. Found: C, 50.97; H, 5.61; N, 15.94.

Ethyl 2-[[(*E*)-2′-Hydroxy-4′-nitrophenyl]diazo]-3(*E*)-(methylamino)-2-butenoate (3i). The reaction mixture afforded crystalline product **3i** (orange needles), mp 196 °C: IR 3684, 3448, 1695, 1602, 1522, 1472, 1398, 1381 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (t, 3H, J = 7.1 Hz), 2.68 (s, 3H), 3.23 (d, 3H, J = 4.9 Hz), 4.30 (q, 2H, J = 7.1 Hz), 7.43 (d, 1H, J = 8.7 Hz), 7.74 (dd, 1H, J = 2.4 and 8.7 Hz), 7.78 (d, 1H, J = 2.4 Hz), 13.1 (s, 1H), 13.8 (s, 1H); MS *m*/*z* (relative intensity) 308(42), 235(100), 179(4), 167(3), 153(8), 114(12), 98(10), 83(82), 56(68). Anal. Calcd for $C_{13}H_{16}N_4O_5$: C, 50.65; H, 5.23; N, 18.17. Found: C, 50.90; H, 4.90; N, 17.90.

3-[[(*E*)-2′-Hydroxy-4′-nitrophenyl]diazo]-4(*E*)-(*tert*-butylamino)-3-penten-2-one (3j). The reaction mixture afforded crystalline product **3j** (orange solid), mp 204−205 °C: IR 3444, 2974, 1667, 1622, 1598, 1519, 1478, 1361 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.6 (s, 9H), 2.4 (s, 3H), 2.9*, 7.65 (d, 1H, J = 8.7 Hz), 7.73 (dd, 1H, J = 2.4 and 8.7 Hz), 7.80 (d, 1H, J = 2.4 Hz); MS *m*/*z* (relative intensity) 320(7), 277(30), 221(60), 204(10), 154(60), 124(10), 108(10), 83(36), 58(100). Anal. Calcd for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.41; H, 6.41; N, 16.98.

General Procedure for Reactions of Diazonium Salts 4 with Enaminones 2. To a stirred solution of the proper aminophenol (2 mmol) and 1.2 mL of 6 N HCl in 2.5 mL of water at 0 °C was added, dropwise, $NaNO_2$ (2.5 mmol) in 3 mL of water. The excess nitrous acid was destroyed with about 5 mg of urea. The organic solvent (MeOH, 20 mL) was then added with vigorous stirring, and finally the desired enaminone (2 mmol) was added. The reaction mixture was kept in the absence of light for seven days without stirring at room temperature and afforded the azo-coupling deaminated products **5**. All the products obtained were purified by recrystallization.

Ethyl 2-[[(*E*)-2′-Hydroxybenzenediazo]-3(*E*)-hydroxy-2-butenoate (5a). The crude material was submitted to column chromatography (silica gel) using mixtures of hexane, CH_2Cl_2, and methanol as eluents. Compound **5a** eluted with methanol/CH_2Cl_2 (1:100) and crystallizes as yellow needles, mp 132−135 °C: IR 3426, 2976, 2738, 2677, 1689, 1614, 1576, 1532, 1477, 1400, 1377 cm^{-1}; ^1H NMR (CCl_4−TFA) δ 1.4 (t, 3H, J = 7 Hz), 2.4 (s, 3H), 4.2 (q, 2H, J = 7 Hz), 6.8 (m, 4H); MS *m*/*z* (relative intensity) 251(10), 250(80), 177(4), 176(28), 135(6), 134(83), 109(24), 108(100). Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.54; H, 5.64; N, 11.19. Found: C, 57.46; H, 5.65; N, 11.65.

Ethyl 2-[[(*E*)-5′-Chloro-2′-hydroxy-4′-nitrophenyl]diazo]-3(*E*)-hydroxy-2-butenoate (5b). The reaction mixture afforded crystalline product **5b** (yellow needles), mp 243 °C: IR 3122, 2989, 2933, 2756, 1671, 1595, 1520, 1411, 1362 cm^{-1}; ^1H NMR ($CDCl_3$−TFA) δ 1.45 (t, 3H, J = 7 Hz), 2.6 (s, 3H), 4.4 (q, 2H, J = 7 Hz), 7.4 (s, 1H), 7.6 (s, 1H) 7.7 (s, 1H); MS *m*/*z* (relative intensity) 332(29), 330(72), 286(34), 284(100), 258(8), 256(30), 241(9), 239(27), 213(18), 211(53), 188(27), 186(78), 141(15),

112(12), 78(11). Anal. Calcd for $C_{12}H_{12}N_3O_6Cl$: C, 43.72; H, 3.67; N, 12.75. Found: C, 43.75; H, 3.39; N, 12.53.

3-[[(*E*)-5′-Chloro-2′-hydroxy-4′-nitrophenyl]diazo]-4(*E*)-hydroxy-3-penten-2-one (5c). The reaction mixture afforded crystalline product **5c** (yellow needles), mp 245 °C: IR 3446, 3071, 1642, 1531, 1509, 1486, 1412, 1366 cm^{-1}; ^1H NMR (acetone-d_6) δ 2.50 (s, 3H), 2.55 (s, 3H), 7.68 (s, 1H), 7.84 (s, 1H), 14.2 (s, <1H); MS *m*/*z* (relative intensity) 302(15), 300(52), 258(22), 256(74), 189(18), 187(44), 78(26), 43(100). Anal. Calcd for $C_{11}H_{10}N_3O_5Cl$: C, 44.09; H, 3.63; N, 14.02. Found: C, 44.16; H, 3.16; N, 13.58.

Computational Details. All the calculations reported here have been carried out using the MOPAC6 semiempirical package (version 6.0)[9] at the Hartree-Fock level. Geometry optimizations were carried out using analytic gradient minimization method[16] (BFGS, precise option) and the molecular polarizabilities using the finite-field formalism.[17]

In the finite-field method the α and β components of the molecular polarizability can be calculated analytically via electric field derivatives of the total energy. The following expansion form was used:[18]

$$E = E^0 - \mu_i^0 F_i - {}^1/_2\alpha_{ij}F_iF_j - {}^1/_6\beta_{ijk}F_iF_jF_k - \ldots \quad (1)$$

where E^0 is the unperturbed energy, F_i is the component of the electric field in the i direction, μ^0 is the permanent dipole moment of the molecule, and α and β are the static first- and second-order molecular polarizability tensors, respectively.

The dipole moments are expressed in debyes (D), the average polarizabilities $\langle\alpha\rangle$ in cubic angstroms ($Å^3$),

$$\langle\alpha\rangle = {}^1/_3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

The β hyperpolarizabilities are expressed in electrostatic units (esu) in terms of:

$$\beta_{vec} = (\beta_x^2 + \beta_y^2 + \beta_z^2) \quad (3)$$

where

$$\beta_i = \beta_{iii} + {}^1/_3\sum_{i\neq j}(\beta_{ijj} + 2\beta_{jji}) \quad (4)$$

and i,j = x,y,z.

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