1,3-Dipolar Cycloaddition Reactions
of 1,4-Benzoquinones with Nitrilimines

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The cycloaddition reactions of some aryl conjugated *p*-benzoquinones with nitrilimines were studied. Depending upon the reaction conditions mono- and/or bis- adducts were isolated only from carbon-carbon double bond. The structure determination was unequivocally established by an X-ray analysis carried out on a bis-adduct. The observed regio-, as well as site-selectivity, was qualitatively correlated with frontier molecular orbitals of the reacting species.

Introduction.

It is well known that 1,3-dipolar cycloaddition reactions of 1,4-quinones provide a convenient one step synthesis of condensed heterocyclic quinones [1]. There are many examples of reaction between 1,4-benzoquinones with 1,3-dipoles. Cycloadditions with nitrile oxides give cycloadducts only from the carbon-carbon double bonds [2]. However several substituted 1,4-benzoquinones give occasionally cycloadducts either from carbon-carbon double bond or from the carbon oxygen double bond [3-6]. An account on site- and regio-selectivity of these reactions [7] correlates experimental data with calculated energy levels and coefficients of FMO's of the reacting species. Cycloadditions with other 1,3 dipoles are also known. Of interest are reactions with diazomethane and of mesoionic oxazolium oxides, leading to indazole and isoindole quinones respectively [1,8]. The purpose of this work is to study the cycloaddition reactions of *p*-benzoquinones with nitrilimines.

Results and Discussion.

Nitrilimines **2**, generated *in situ*, by the action of triethylamine on the corresponding aryl hydrazonoyl chlorides **1**, were allowed to react with 2-aryl-1,4-benzoquinones **3** at room temperature for about 2 days resulting mono- **5** and/or bis-cyclo adducts **6**, according to the following reaction scheme (Scheme 1).

The primary formed mono-adducts **4** could not be isolated since they are readily aromatized by oxidation to the final pyrazole derivatives **5** or **6**. The oxidation process was evidenced by the fact that in all cases studied, 2-aryl-1,4-hydroquinones were isolated. The molar ratio of the reactants used determines the relative amounts of cycloadducts formed. When equimolar amounts of reactants were used both mono- and bis-adducts were formed and bis adducts were obtained in higher yields, obviously because a part of quinone was consumed in the oxidation process of primary adduct **4**. Excess of nitrilimine gave only bis-adducts, as in the case of bis-adducts **6a,f**, while in

Scheme 1
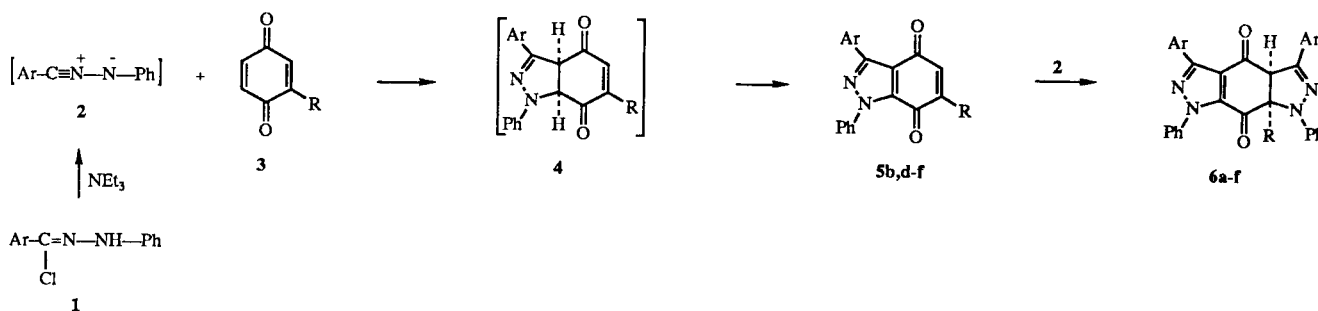
Compounds 1 and 2   Ar: **a**, C$_6$H$_5$; **b**, 4-CH$_3$-C$_6$H$_4$; **c**, 4-Cl-C$_6$H$_4$
Compounds 3   R: **a**, C$_6$H$_4$; **b**, 4-CH$_3$-C$_6$H$_4$; **c**, 4-CH$_3$O-C$_6$H$_4$
Compounds 5 and 6   Ar/R: **a**, C$_6$H$_5$/C$_6$H$_5$; **b**, 4-CH$_3$-C$_6$H$_4$/C$_6$H$_5$;
                     c, 4-Cl-C$_6$H$_4$/C$_6$H$_5$; **b**, C$_6$H$_4$/4-CH$_3$-C$_6$H$_4$
                     e, 4-Cl-C$_6$H$_4$/4-CH$_3$-C$_6$H$_4$; **f**, C$_6$H$_5$/ 4-CH$_3$O-C$_6$H$_4$

one case where excess of 2-[4-methylphenyl]-*p*-benzoquin-one **3b** was used, the mono-adduct **5d** was isolated in higher yield than the corresponding bis-adduct **6e**.

The ir spectra of mono-adducts **5** have the carbonyl absorption at about 1650-1660 cm^{-1} and the carbon nitrogen double bond at about 1590-1600 cm^{-1}. For bis-adducts **6** the carbonyl absorption is at about 1680-1710 cm^{-1} and the carbon nitrogen double bond at about 1590 cm^{-1}. The ^{1}H nmr spectra of mono-adducts **5** have peaks for the olefinic proton at δ 6.82-6.90 (s) while the corresponding pyrazoline proton of bis- adducts **6** resonates at δ 4.64-4.70 (s). These chemical shifts of pyrazoline protons are analogous to those observed for the 4-H shifts of some closely related pyrazoline derivatives [9-11] and this could be of some importance for the assignment of certain regio chemistry to the isolated products. In the mass spectra both mono- and bis-adducts give peaks for the molecular ion, which is almost in all cases of mono-adducts the base peak. The retro 1,3-dipolar cycloaddition, pattern characteristic for many cycloaddition products [12,13], is not observed in mono-adducts **5**. This fragmentation is normally observed in all bis-adducts **6**, affording the corresponding nitrilimine and mono-adduct fragments.

All reactions studied showed a remarkable site- and regio-selectivity. Thus, mono-adducts from the carbon-oxygen double bond or from the aryl conjugated double bond were not detected. The unsubstituted carbon-carbon double bond is more reactive, probably because of the readily aromatization of the intermediate formed pyrazoline **4** and also of steric reasons. So it is reasonable to assume that bis adducts **6** were formed by addition of the second nitrilimine molecule to the already formed mono-adduct **5** and consequently the regio chemistry of the first addition is the same for both adducts. This was supported by an independed experiment, where mono ad-duct **5c** reacted with an additional amount of diphenyl-nitrilimine and afforded almost quantitatively the bis-adduct **6c**.

There are two possible regio-isomers for mono-adducts to the unsubstituted carbon-carbon double bond and four for bis-adducts. From the available data it was not possible to assign certain structures for both, so an X-ray crystallographic analysis has been performed on the bis adduct **6a**. The established molecular structure and the labeling sequence is presented in the ORTEP drawing of Figure 1, which also illustrates the conformational
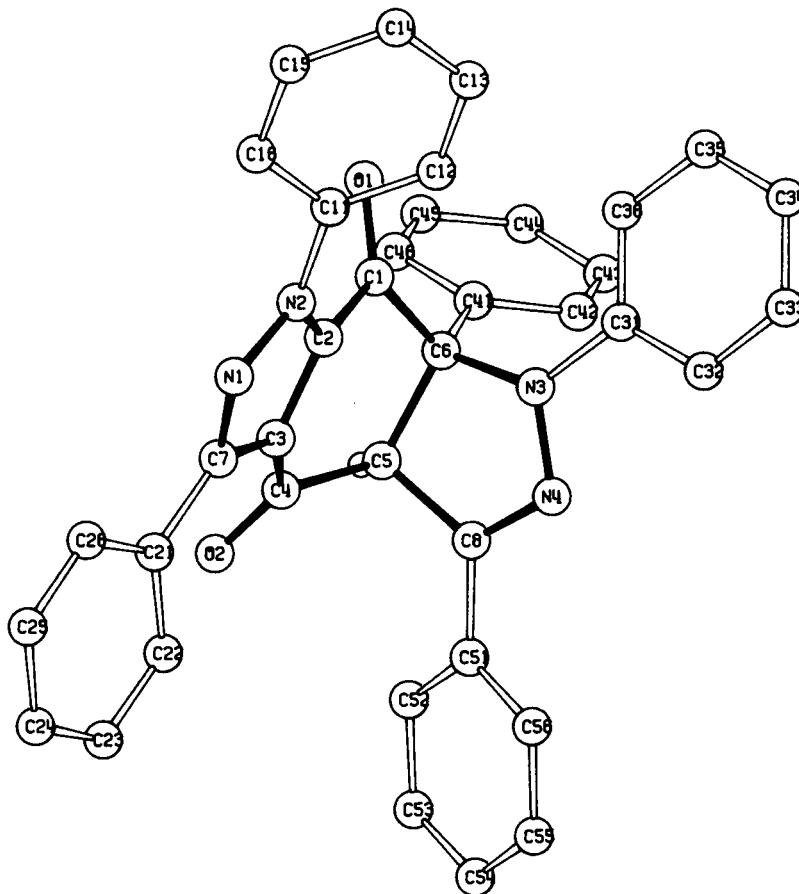

Figure 1. ORTEP drawing of compound **6a**.

Table 1

Summary of Crystal and Intensity Collection Data

Formula	$C_{38}H_{26}N_4O_2$
fw	570.65
a,b,d (Å)	14.959(2), 18.813(4), 11.366(2)
β (deg)	112.99(1)
V (Å^3)	2944.4(8)
Z	4
D$_{calcd}$ (Mg m-3)	1.287
D$_{measd}$ (Mg m^{-3})	1.28
Space group	P2$_1$/c
Radiation	Mo Kα (0.71069) Zr-filtered
μ (cm^{-1})	0.45
Scan speed (deg/min)	variable between 2.2 and 16.0
Scan range (deg)	1.7 plus α$_1$-α$_2$
Bkgd counting (s)	0.5 of scan time
2Θ limit (deg)	49.0
Data collected/unique	5822/4986
Data used	4162 with Fo>2.5σ^2(Fo)
Fint	0.009
Weighting scheme	1/w=o^2(Fo)+0.0007Fo^2
F(000)	1192
Nr [1]	501
|Δ/σ| max	0.120
(Δρ)$_{max}$(eÅ $^{-3}$)	0.156
(Δρ)$_{min}$(eÅ $^{-3}$)	-0.135
S [2]	1.98
R [3] (obsd/all data)	0.0426/0.0518
Rw [4] (obsd/all data)	0.0538/0.0549

[1] Nr = Number of refined parameters. [2] S = $[\Sigma w(\Delta F)^2/(N-P)]^{1/2}$ P = Nb of Parameters, N = Nb of observed reflections. [3] R = Σ |ΔF|/Σ |Fo|. [4] Rw = $[\Sigma w(\Delta F)^2/\Sigma w$ |Fo|$^2]^{1/2}$.

geometry of the molecule. A summary of crystal and intensity data are given in Table 1 while positional parameters as well as selected bond distances and angles are listed in Tables 2 and 3 respectively. From these data it is concluded that all interatomic distances are as expected with the exception of C5-C6 (1.563 Å) and C6-N3 (1.486 Å) which are considerably longer than other analogous cases [14]. The assignment of structure **5** for the mono-adducts was based on the already mentioned assumption that pyrazole ring should have the same regio-form in both mono- and bis-adducts.

The observed regio- and site-selectivity may be explained in terms of the frontier orbital interaction of the reacting species [15,16]. Houk *et al.* have systematically examine the influence of substituents upon the shapes of FMO's of benzoquinones and napthoquinones [17] and summarised the most probable positions of attack either by nucleophiles or by the anionic terminus of dienes and 1,3-dipoles. Thus for conjugating substituents at C2 of 1,4-benzoquinone ring the most reactive positions are in the order C6 > C5 > C3. This indicates that the first

Table 2

Positional Parameters (x10^4) of the Non-H Atoms; E.s.d.'s in Parentheses

Atom	X	Y	Z
O(1)	3042.6(8)	-71.0(6)	2975(1)
O(2)	591.8(8)	-566.5(6)	-1433(1)
N(1)	3022(1)	-1952.9(7)	846(1)
N(2)	3349(1)	-1401.4(7)	1678(1)
N(3)	3419.4(9)	580.1(7)	508(1)
N(4)	3119(1)	649.2(7)	-792(1)
C(1)	2853(1)	-116.3(8)	1844(1)
C(2)	2840(1)	-799.8(8)	1190(1)
C(3)	2139(1)	-970.1(8)	2(1)
C(4)	1409(1)	-437.1(8)	-673(1)
C(5)	1745(1)	335.7(9)	-389(1)
C(6)	2593(1)	516.8(8)	911(1)
C(7)	2274(1)	-1710.5(9)	-161(1)
C(8)	2197(1)	538.9(8)	-1329(1)
C(11)	4188(1)	-1505.8(9)	2828(2)
C(12)	4903(1)	-994(1)	3225(2)
C(13)	5718(2)	-1101(2)	4328(2)
C(14)	5818(2)	-1727(1)	5002(2)
C(15)	5098(2)	-2234(1)	4595(2)
C(16)	4276(2)	-2125(1)	3507(2)
C(21)	1783(1)	-2205.0(9)	-1228(2)
C(22)	1243(2)	-1970(1)	-2452(2)
C(23)	810(2)	-2452(1)	-3438(2)
C(24)	925(2)	-3165(1)	-3213(2)
C(25)	1477(2)	-3407(1)	-2007(2)
C(26)	1898(2)	-2929(1)	-1022(2)
C(31)	4392(1)	754.7(8)	1281(1)
C(32)	5068(1)	796.4(9)	726(2)
C(33)	6029(1)	940(1)	1489(2)
C(34)	6327(2)	1044(1)	2777(2)
C(35)	5660(1)	1008(1)	3326(2)
C(36)	4690(1)	866(1)	2587(2)
C(41)	2350(1)	1250.9(8)	1429(1)
C(42)	2721(2)	1851(1)	1252(2)
C(43)	2434(2)	2473(1)	1635(3)
C(44)	1770(2)	2459(1)	2198(2)
C(45)	1386(2)	1827(1)	2356(2)
C(46)	1674(1)	1202(1)	1978(2)
C(51)	1681(1)	595.2(8)	-2719(1)
C(52)	694(1)	746(1)	-3261(2)
C(53)	233(2)	838(1)	-4371(2)
C(54)	738(2)	768(1)	-5342(2)
C(55)	1713(2)	609(1)	-4814(2)
C(56)	2188(2)	526(1)	-3507(2)

cycloaddition takes place on the unsubstituted double bond and the anionic terminus of 1,3-dipole interacts with the C6 of quinone ring, in agreement with the observed regio-form of pyrazole ring. As regards the regio-selectivity of the second addition to the aryl conjugated alkene moiety, it is assumed that the unsubstituted carbon atom should have the larger coefficient on both HOMO and LUMO [15]. It is expected that the attached carbonyls presumably have the same effects on both carbon atoms coefficients. Thus, considering a linear arrangement of

Table 3

Selected Interatomic Distances and Internal Angles of Compound **6a**

a. Bond Distances (Å)

C1-C2	1.481(2)	C5-C4	1.531(2)	N1-N2	1.359(2)
C1-C6	1.540(2)	O2-C4	1.215(2)	C11-N2	1.429(2)
O1-C1	1.207(2)	C5-C6	1.563(2)	C7-N1	1.330(2)
C3-C2	1.385(2)	C8-C5	1.520(3)	C21-C7	1.477(2)
N2-C2	1.356(2)	H5-C2	0.967(18)	N4-C8	1.288(2)
C4-C3	1.460(2)	N3-C6	1.482(2)	C51-C8	1.466(2)
C7-C3	1.430(2)	C41-C6	1.520(3)	N4-N3	1.372(2)
				C31-N3	1.413(2)

b. Angles (°)

C6-C1-C2	112.1(1)	C8-C5-C4	100.9(1)
C3-C2-C1	123.1(1)	C5-C6-C1	112.1(1)
N2-C2-C3	107.2(1)	N3-C6-C5	101.1(1)
C4-C3-C2	118.6(1)	N1-N2-C2	111.1(1)
C7-C3-C2	105.1(1)	C7-N1-N2	106.8(1)
C5-C4-C3	115.2(1)	N1-C7-C3	109.6(1)
C6-C5-C4	119.0(1)	N4-C8-C5	113.3(1)
		N4-N3-C6	112.1(1)

nitrilimine molecule where the larger coefficient at HOMO is located on the anionic nitrogen atom and at LUMO on the carbon atom [15], both interactions lead to the observed regio-form of pyrazoline ring.

It should be noted that unsubstituted 1,4-benzoquinone (R = H) was also used as dipolarophile, but without definite results. The reaction of benzoquinone with diphenylnitrilimine was examined using excess (1:2) either of the quinone or of the 1,3-dipole. When nitrilimine was used in excess a bis adduct of the possible structure **7a** or **7b** has been isolated in low yield (Scheme 2). On the other hand when benzoquinone was used in excess the mono-adduct **8** was formed in low yield, which was fully characterized by its spectral data (ir ¹H nmr, ms) and elemental analysis. However in both cases the main reaction product was a yellow microcrystalline product, insoluble to common solvents, whose structure has not been characterized yet. The available data (ir, ms, elemental analysis) suggests a bis adduct structure, but the problem of its structure remains open for further considerations.

Scheme 2

7a   7b   8
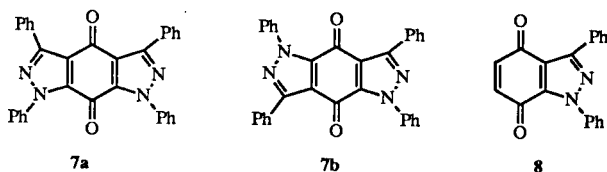
EXPERIMENTAL

All melting points are uncorrected and they were obtained with a Kofler, hot stage apparatus. The ir spectra (Nujol muls) were obtained with a Perkin Elmer Model 297 spectrophotometer. The nmr spectra, reported in δ units, were obtained in deuteriochloroform solutions, with a Brucker AW 80 spectrometer, with tetramethylsilane as internal standard. The mass spectra were measured with a Hittacki-Perkin-Elmer, Model RMU-6L spectrometer, with an ionization energy of 70 eV. Elemental analyses were performed with a Perkin-Elmer analyzer model 240-B.

Aryl benzoquinones **3** were prepared from 1,4-benzoquinone and diazotized appropriate substituted aromatic amines, in the presence of sodium acetate [18] or sodium bicarbonate [19]. Diaryl nitrilimines **2** were liberated *in situ* from the corresponding *N*-phenylarylhydrazonoyl chlorides **1**, with triethylamine [20]. All reactions were carried out in benzene solution at room temperature for about 3 days. Insoluble triethylamine hydrochloride was removed and cycloadducts were isolated from the residue with silica gel column chromatography. Quantities of the reacting species, eluants and all other data are detailed in the following experimental part. Yields are based on the amount of the quinone used.

This reaction was carried out using 0.92 g (5 mmoles) of the quinone **3a** 2.3 g (10 mmoles) of diphenylhydrazonoyl chloride **1a** and 2.0 g (20 mmoles) of triethylamine. The residue was chromatographed using chloroform as the eluant. A red band containing the bis-adduct **6a** was eluted first followed by minor non identified by-products and finally the hydroquinone band was eluted with a mixture of chloroform containing a little amount of methanol. Compound **6a** had mp 190-193° (red crystals from dichloromethane-hexane) yield 30%; ir: 1710, 1680 (C=O), 1595 (C=N) cm⁻¹; ¹H nmr: δ 4.7 (s, 1H), 6.65-6.90 (m, 2H), 6.90-7.70 (m, 19H), 7.9-8.1 (m, 4H); ms: m/z (%) 570 (M⁺, 41), 543 (5), 542 (9), 527 (21), 526 (46), 376 (100), 348 (13), 347 (22), 194 (21), 166 (32), 165 (30), 143 (40), 116 (20), 115 (45), 105 (100), 91 (20), 77 (100).

Anal. Calcd. for $C_{38}H_{26}N_4O_2$ (MW, 570.62): C, 79.98; H, 4.56; N, 9.82. Found: C, 80.14; H, 4.63; N, 10.01.

2-Phenyl-1,4-hydroquinone had mp 97-99° (0.45 g of white crystals from dichloromethane-hexane), lit [21] mp 96-98°.

Reaction of 2-Phenyl-1,4-benzoquinone **3a** with *N*-Phenyl-(4-methylphenyl)nitrilimine **2b**.

This reaction was carried out using 0.46 g (2.5 mmoles) of benzoquinone **3a**, 0.62 g (2.5 mmoles) of hydrazonoyl chloride **1b** and 0.6 (4.4 mmoles) of triethylamine. The residue was chromatographed on a silica gel column with chloroform as the eluant. A red band containing mainly the bis-adduct **6b** was eluted first followed by an orange band containing the mono-adduct **5b**, which was further purified by tlc preparative using pre-coated silica gel plates and chloroform as the eluant. The corresponding 2-phenyl-1,4-hydroquinone was finally eluted by addition of a little amount of methanol to the eluant.

Compound **6b**.

This compound had mp 240-242° (red crystals from dichloromethane-hexane), yield 20%; ir: 1700, 1680 (C=O), 1590 (C=N) cm⁻¹; ¹H nmr: δ 2.37 (s, 3H), 2.39 (s, 3H), 4.70 (s, 1H), 6.70-6.95 (m, 2H), 7.0-7.6 (m, 17H), 7.65-8.0 (m, 4H); ms: m/z (%) 598 (M⁺, 1) 570 (1), 555 (5), 554 (1), 390 (100), 375 (15), 362 (10), 361 (15), 208 (11), 180 (25), 165 (100), 143 (10), 117 (5), 103 (5), 102 (5), 102 (5), 91 (5), 77 (15).

Anal. Calcd. for $C_{40}H_{30}N_4O_2$ (MW, 598.67): C, 80.24; H, 5.05; N, 9.36. Found: C, 79.93; H, 5.03; N, 9.41.

Compound **5b**.

This compound had mp 215-217° (orange crystals from dichloromethane-hexane), yield 5%; ir: 1660 (C=O), 1600 (C=N) cm^{-1}; ^{1}H nmr: δ 2.3 (s, 3H), 6.85 (s, 1H), 7.0-7.9 (m, 12H), 8.1 (d, 2H, J = 7 Hz); ms: m/z (%) 390 (M$^+$, 100), 374 (6), 362 (50), 285 (5), 271 (5), 243 (3), 216 (8), 143 (30), 102 (10), 91 (10), 77 (40).

Anal. Calcd. for $C_{26}H_{18}N_2O_2$ (MW, 390.42): C, 79.98; H, 4.65; N, 7.18. Found: C, 79.83; H, 4.57; N, 7.27.

Reaction of 2-Phenyl-1,4-benzoquinone **3a** with *N*-Phenyl-(4-chlorophenyl)nitrilimine **2c**.

This reaction was carried out using equimolar amounts of quinone (0.46 g, 2.5 mmoles) and hydrazonoyl chloride **1c** (0.67 g, 2.5 mmoles), in the presence of triethylamine (0.8 g, 7.9 mmoles). The residue was chromatographed on silica gel column using chloroform as the eluant to give a red band containing mainly the bis-adduct **6c** followed by a band containing mono-adduct **5c** and a little amount of bis-adduct **6c** and finally the 2-phenyl-1,4-hydroquinone band.

Bis-adduct **6c** had mp 250-252° (red crystals from dichloromethane-hexane), yield 20%; ir: 1705, 1680 (C=O), 1590 (C=N) cm^{-1}; ^{1}H nmr: δ 4.64 (s, 1H), 6.64-6.86 (m, 2H), 6.9-7.75 (m, 17H), 7.85-8.0 (m, 4H); ms: m/z (%) 638 (M$^+$, 5), 610 (2), 594 (5), 410 (100), 381 (20), 375 (15), 244 (17), 228 (46), 165 (100), 143 (80), 139 (14), 137 (25), 103 (36), 91 (17), 77 (95).

Anal. Calcd. for $C_{38}H_{24}N_4O_2Cl_2$ (MW, 639.51): C, 71.36: H, 3.78; N, 8.76. Found: C, 71.52; H, 3.82; N, 8.71.

The second band containing the mono-adduct **5c** was chromatographed again on silica gel column using dichloromethane as the eluant to give pure mono-adduct **5c**, mp 235-238° (yellow crystals from dichloromethane-hexane), yield 5%; ir: 1660 (C=O), 1590 (C=N) cm^{-1}; ^{1}H nmr: δ 6.82 (s, 1H), 7.2-7.8 (m, 12H), 7.9-8.2 (m, 2H); ms: m/z (%) 410 (M$^+$, 100), 382 (90), 375 (15), 244 (3), 216 (5), 143 (25), 137 (4), 105 (5), 103 (5), 102 (7), 77 (25).

Anal. Calcd. for $C_{25}H_{15}N_2O_2Cl$ (MW, 410.85): C, 73.08; H, 3.68; N, 6.82. Found: C, 72.86; H, 3.68; N, 6.42.

Reaction of 2-(4-methylphenyl)-1,4-benzoquinone **3b** with Diphenylnitrilimine **2a**.

This reaction was carried out using excess of the quinone **3b** (0.99 g, 5 mmoles) the hydrazonoyl chloride **1a** (0.58 g, 2.5 mmoles) and triethylamine (0.5 g, 5 mmoles). The insoluble triethylamine hydrochloride was removed and the filtrate was partly evaporated. A part of mono-adduct **5d** (0.2 g) was cystallized out and the residue was chromatographed on silica gel column using benzene as the eluant. A red band containing the bis-adduct was eluted first followed by a band containing both mono- and bis-adducts **5d** and **6d**, a band containing the mono-adduct **5d**, a band of unreacted benzoquinone (0.14 g) and finally the hydroquinone band, which was eluted by the addition of a little amount of methanol to the eluant.

Mono-adduct **5d**, had mp 223-225° (orange crystals from dichloromethane-hexane) overall yield 25%; ir: 1650 (C=O), 1590, 1600 (C=C, C=N) cm^{-1}; ^{1}H nmr δ 2.3 (s, 3H), 6.9 (s, 1H), 7.1-7.9 (m, 12 H), 8.05-8.35 (m, 2H); ms: m/z (%) 390 (M$^+$, 100), 375 (20), 362 (30), 346 (1), 143 (26), 115 (14), 103 (2), 77 (28).

Anal. Calcd. for $C_{26}H_{18}N_2O_2$ (MW, 390.42): C, 79.98; H, 4.65; N, 7.17. Found: C, 79.76; H, 4.61; N, 6.98.

Bis-adduct **6d** had mp 217-219° (red crystals from dichloromethane-hexane), yield 4%; ir: 1690 (C=O), 1590 (C=N); ^{1}H nmr

δ 2.3 (s, 3H), 4.65 (s, 1H), 6.7-6.9 (m, 2H), 6.9-7.6 (m, 20H), 7.7-8.1 (m, 4H); ms: m/z (%) 584 (M$^+$, 10), 556 (1), 540 (10), 390 (40), 362 (1), 194 (80), 165 (100), 143 (30), 115 (25), 103 (25), 77 (30).

Anal. Calcd. for $C_{39}H_{28}N_4O_2$ (MW, 584.64): C, 80.11; H, 4.83; N, 9.58. Found: C, 80.23; H, 4.91; N, 9.49.

The 2-(4-methylphenyl)-1,4-hydroquinone (0.30 g) had mp 120-122° (dichloromethane-hexane), lit [18] 123°.

Reaction of Mono-adduct **5d** with Diphenylnitrilimine **2a**.

Mono-adduct **5d** (0.08 g, 0.2 mmole) and the hydrazonoyl chloride **1a** (0.1 g, 0.3 mmole) were allowed to react with triethylamine (0.1 g, 0.1 mole) in benzene solution and at room temperature. The orange colour of the solution gradually turned to red and after about 12 hours the reaction was completed affording almost quantitatively the bis-adduct **6d**.

Reaction of 2-(4-Methylphenyl)-1,4-benzoquinone **3b** with *N*-phenyl(4-chlorophenyl)nitrilimine **3c**.

This reaction was carried out using equimolar amounts of the quinone **3b** (0.495 g, 2.5 mmoles) the hydrazonoyl chloride **1c** (0.67 g, 2.5 mmoles) and triethylamine (0.4 g, 4 mmoles). The residue was chromatographed on silica using a 10% ethyl acetate-hexane mixture as the eluant. A little amount of unreacted chloride was eluted first followed by a band containing both mono- and bis-adducts **5e** and **6e**. The slow moving hydroquinone band was eluted by adding a little amount of methanol. The band of mono- and bis-adducts, was chromatographed again on silica using benzene as the eluant to give bis-adduct **6e** and a mixture of mono- and bis-adduct, which were finally separated by tlc preparative, on pre-coated silica gel plates, using benzene as the eluant.

Bis-adduct **5e** had mp 233-234° (red crystals from dichloromethane-hexane), yield 15%; ir: 1710, 1680 (C=O), 1600 (C=N) cm^{-1}; ^{1}H nmr: δ 2.35 (s, 3H), 4.6 (s, 1H), 6.7 (d, 2H, J = 7 Hz), 7.0-7.5 (m, 16H), 7.9-8.05 (m, 4H); ms: m/z (%) 652 (M$^+$, 4), 624 (1), 608 (3), 607 (4), 424 (100), 396 (9), 395 (10), 389 (8), 374 (15), 228 (38), 200 (30), 165 (100), 143 (55), 137 (13), 115 (16), 111 (6), 77 (50).

Anal. Calcd. for $C_{39}H_{26}N_4O_2Cl_2$ (MW, 653.54): C, 71.66; H, 4.01; N, 8.57. Found: C, 71.86; H, 4.17; N, 8.58.

Mono-adduct **5e** had mp 250-252° (orange crystals from benzene), yield 5%; ir: 1660 (C=O), 1590, 1600 (C=C, C=N) cm^{-1}; ^{1}H nmr: δ 2.4 (s, 3H), 6.9 (s, 1H), 7.2-7.75 (m, 11H), 8.15 (d, 2H, J = 7 Hz); ms: m/z (%), 424 (M$^+$, 70), 409 (17), 396 (30), 231 (10), 143 (54), 137 (45), 116 (30), 115 (65), 111 (20), 103 (20), 91 (15), 77 (100).

Anal. Calcd. for $C_{26}H_{17}N_2O_2Cl$ (MW, 424,88): C, 73.49; H, 4.0; N, 6.60. Found: C, 73.20; H, 4.01; N, 6.28.

Reaction of 2-(4-Methoxyphenyl)-1,4-benzoquinone **3c** with Diphenylnitrilimine **2a**.

This reaction was carried out using 0.535 g, (2.5 mmoles) of the quinone **3c**, 1.15 g (5 mmoles) of the chloride **1a** and 0.61 g (6 mmoles) of triethylamine. The residue was chromatographed on silica using chloroform as the eluant to give some unreactive chloride (0.4 g) followed by a red band containing the bis-adduct **6f**, some non-identified minor by-products and finally the hydroquinone band.

Bis-adduct **6f** had mp 234-235°C (red crystals from dichloromethane-hexane), yield 27%; ir: 1690 (C=O), 1590, 1600

(C = C, C = N); cm⁻¹; ¹H nmr: δ 3.85 (s, 3H), 4.7 (s, 1H), 6.65-7.6 (m, 20H), 7.7-8.2 (m, 4H); ms: m/z) (%), 600 (M⁺, 2), 572 (1), 556 (2), 406 (55), 379 (7), 378 (6), 376 (5), 194 (80), 166 (58), 165 (46), 143 (63), 139 (50), 132 (11), 126 (10), 115 (22), 103 (44), 77 (100).

Anal. Calcd. for $C_{39}H_{28}N_4O_3$ (MW, 600.6): C, 77.98; H, 4.70; N, 9.33. Found: C, 77.99; H, 4.88; N, 9.40.

The 2-(4-methoxyphenyl)-1,4-hydroquinone (0.2 g) had mp 109-111° (dichloromethane-hexane), lit [18] 111-112°.

Reaction of 1,4-Benzoquinone with Diphenylnitrilimine **2a**.

This reaction was carried out using 0.27 g (2.5 mmoles) of 1,4-benzoquinone, 1.15 g (5 mmoles) of the diphenyl hydrazonoyl chloride **1a** and 0.73 g (7.2 mmoles) of triethylamine in benzene solution. Almost immediately after the addition of triethylamine a yellow precipitate began to separate. After two days at room temperature the solid was washed several times with water to remove the triethylamine hydrochloride, dried to open air and had mp >320°. Almost insoluble to all common solvents, (chloroform, ethanol, ether, benzene), yield 35%; ir: 1670, 1655 (C = O), 1590 (C = N) cm⁻¹; ms: m/z (%) 492 (M⁺, 100), 464 (16), 416 (5), 361 (2), 300 (8), 293 (11), 218 (6), 195 (4), 194 (2), 165 (8), 143 (10), 141 (28), 115 (12), 105 (24), 104 (16), 103 (40). 77 (75).

Anal. Calcd. for $C_{32}H_{20}N_4O_2$ (MW, 492.51): C, 78.03; H, 4.09; N, 11.38. Found: C, 77.91; H, 4.25; N, 11.16.

The residue was chromatographed on silica gel column eluting with chloroform. A little amount of unreacted chloride (0.05 g) was eluted first, followed by a band containing the bis-adduct **7** and finally the hydroquinone band (0.1 g). The crude bis-adduct **7** was diluted in dichloromethane, then filtered to remove traces of insoluble material, and crystallised by the addition of hexane to give 0.1 g (8%) of analytical pure **7a**, mp 255-257° (orange crystals); ir: 1660 (C = O), 1590 (C = N) cm⁻¹; ¹H nmr δ 6.48-7.58 (m, 18H), 8.03-8.27 (m, 2H); ms: m/z (%) 492 (M⁺, 2), 194 (30), 165 (20), 141 (10), 111 (20), 105 (45), 103 (30), 91 (30), 77 (100).

Anal. Calcd. for $C_{32}H_{20}N_4O_2$ (MW, 492.51): C, 78.03; H, 4.09; N, 11.38. Found: C, 78.04; H, 4.41; N, 11.62.

This reaction was repeated using excess of benzoquinone (0.54 g, 5 mmoles), the hydrazonoyl chloride (0.58 g, 2.5 mmoles) and triethylamine (0.3 g, 3 mmoles). After 3 days at room temperature the insoluble adduct (0.3 g, 25%) was removed and the residue was chromatographed on silica gel column using a 50% chloroform-hexane mixture as the eluant. A little amount (0.04 g) of unreacted chloride was eluted first followed by a red band containing the mono-adduct **8**. Traces of insoluble material was removed and the residue was diluted in a dichloromethane-hexane mixture to give 0.1 g (8%) of analytical pure **8**, mp 192-194°; ir: 1655 (C = O), 1595 (C = N) cm⁻¹; ¹H nmr: δ 6.66 and 6.80 (two d, AB system, J = 10 Hz), 7.39-7.69 (m, 7H), 8.08-8.29 (m, 2H); ms: m/z (%) 300 (M⁺, 100), 299 (40), 272 (28), 243 (2), 223 (2), 218 (2), 195 (3), 169 (8), 143 (17), 141 (10), 140 (12), 115 (6), 113 (5), 103 (12), 77 (100).

Anal. Calcd. for $C_{19}H_{12}N_2O_2$ (MW, 300.31): C, 75.99; H, 4.03; N, 9.33. Found: C, 75.97; H, 4.12; N, 9.38.

X-ray Structure Determination.

Complete crystal data and parameters for data collection are reported in Table I. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 15 automatically centered reflections in the range $17° > 2\theta > 25°$ on a Syntex P2₁ diffractometer wth Zr-filtered MoKα radiation. The intencities of three standards monitored after every 67 reflections were stable with a scatter of less than 3% from their respective means. L_p but no absorption corrections were applied. The structure was solved by direct methods and refined with SHELX76 [22] by full-matrix least squares on which $\Sigma w\Delta^2$ was minimized. H position located from a difference Fourier map. Non-H atoms anisotropic, H atoms isotropic. One reflection showing poor agreement was given zero weight during final refinement cycles. The final atomic parameters of the non-H atoms are given in Table II.

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