Reaction of Amidine Phenylogous with *p*-Benzoquinones

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N-(4-Dimethylaminobenzylidene)anilines and N^1-(4-dimethylaminophenyl)-N^1,N^2-diphenylformamidine reacted with tetrachloro-, tetrabromo,- and tetrafluoro-*p*-benzoquinones via charge-transfer complexes formation giving 2-monoarylamino-3,5,6-trihalo-*p*-benzoquinones and 2,5-bis(arylamino)-3,6-dihalo-*p*-benzoquinones. The course of the reaction leading to the formation of the products has been interpreted.

Recently, we have shown that azomethines,[1] azomethine *N*-oxides[2] (nitrones), as well as heteroaromatic *N*-oxides[3] form charge-transfer complexes (CTC) with different electron-deficient π-systems as *p*-benzoquinones, tetracyanoethylene, and tetracyanoquinodimethane.

In the previous work[1] concerning the study of the CTC of aryl substituted azomethines with electron-poor *p*-benzoquinones, tetrachloro-*p*-benzoquinone (chloranil, CHL), tetrabromo-*p*-benzoquinone (bromanil, BRL), and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), we found that, the presence of dimethylamino group on the benzylidene ring increases the donor ability of the azomethine compound enough for immediate reaction with the *p*-benzoquinones. This behavior prompted us to study the chemical interaction between different *N*-(4-dimethylaminobenzylidene) anilines (**1a—i**) (Fig. 1), and the electron-deficient *p*-benzoquinones CHL, BRL and tetrafluoro-*p*-benzoquinone (fluoranil, FRL).

On addition of equimolar amounts of *p*-benzoquinones CHL, BRL, and FRL to azomethines (**1a—i**) in ethyl acetate, with admission of air at room temperature, a green color of the transient CTC was observed, which immediately changed to brown color and a solid product precipitated. When the reaction was followed spectrophotometrically, absorption maxima were observed in the range 620—728 nm, and were assigned to the CTC, since both the azomethines (**1a—i**) and the

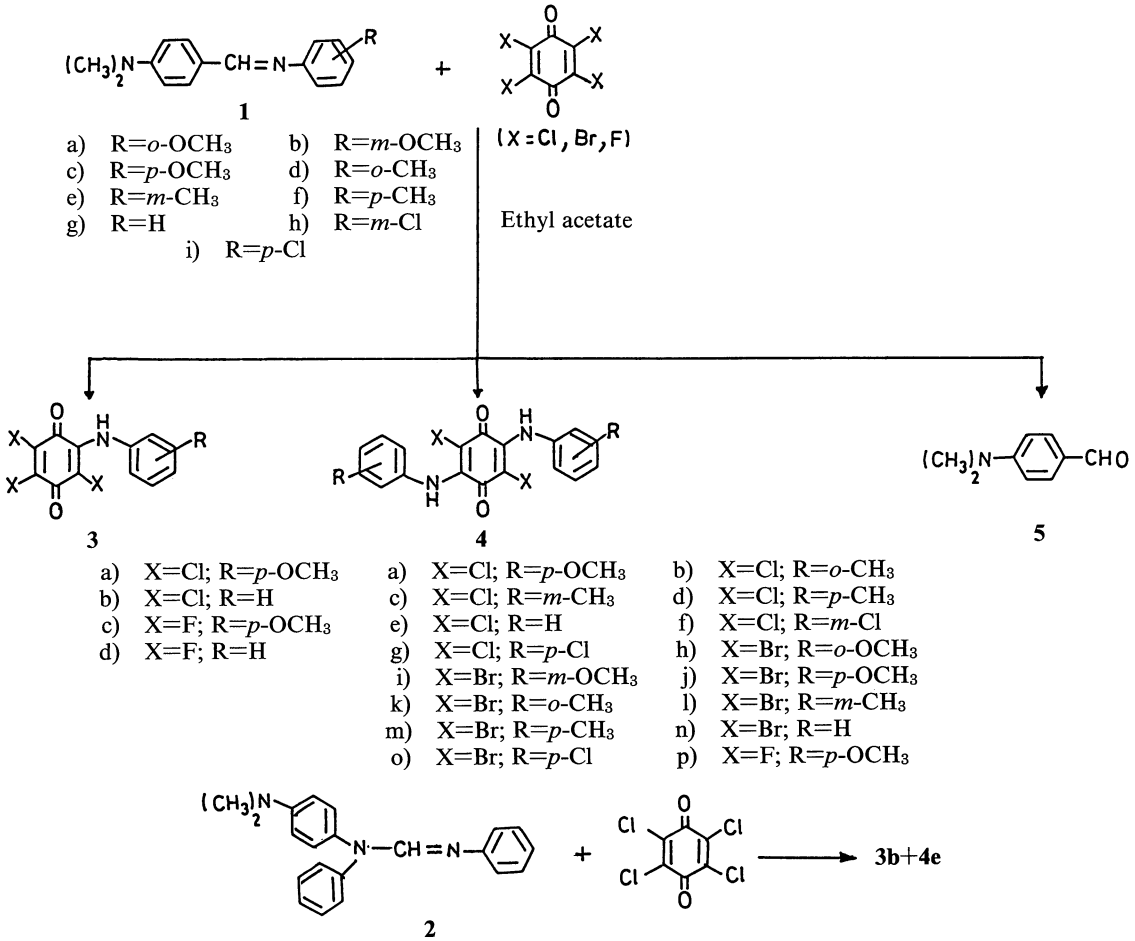

Fig. 1.

p-benzoquinones alone did not absorb in this region[4] (Table 1). The chromatographic separation of the reaction mixtures yielded the 2-arylamino-3,5,6-trihalo-*p*-benzoquinones (**3a**—**d**) as minor products (10—16%), the 2,5-bis(arylamino)-3,6-dihalo-*p*-benzoquinones (**4a**—**p**) (41—61%) as major products,[5] and 4-dimethylaminobenzaldehyde (**5**) (Fig. 1).

However, the reactions of other azomethines, which bear methoxy or methyl substituents instead of a dimethylamino group on the benzylidene ring led to the formation of relatively stable CTC and did not give the expected mono- and/or di-arylaminohalo-*p*-benzoquinone products. This result indicates that the presence of dimethylamino group on the benzylidene ring plays an important role in this reaction and is essential for the azomethine **1a**—**i** to be capable of undergoing this chemical reaction. On the other hand, the structures of the products **3a**—**d** and **4a**—**p** show that the active center of the azomethines **1a**—**i** is the nitrogen atom of the imino group. Thus, it may be assumed that the presence of the good electron-donating dimethylamino group in para position on the benzylidene ring, and consequently in conjugation with it, makes Schiff's bases (**1a**—**i**) to behave like amidines[6] (⩾N–CH=N–) or phenylogous amidines. This assumption could be rationalized through the formation of both the 2-arylamino- (**3b**) and the 2,5-bis-arylamino- (**4e**) derivatives (Fig. 1) from the reaction of the amidine **2** with chloranil under the same conditions.

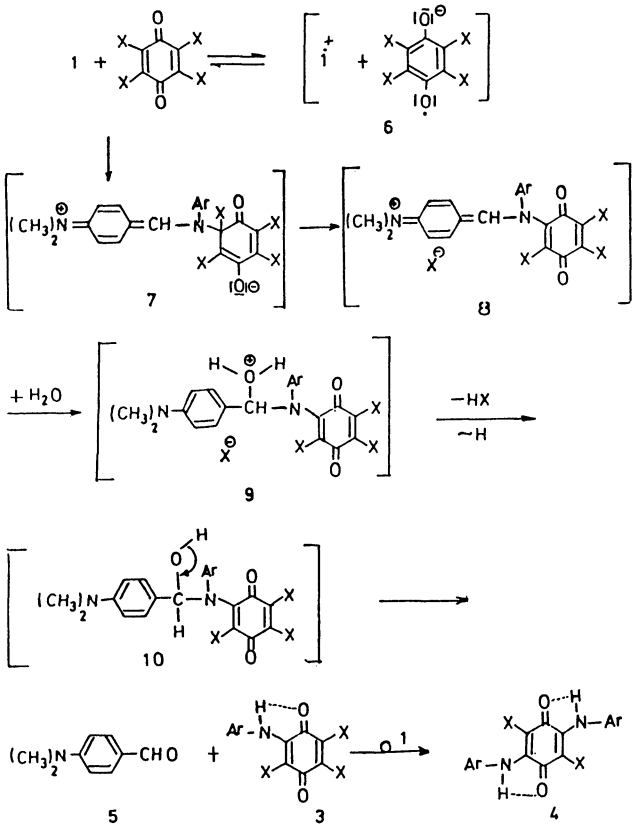

Fig. 2.

Table 1. Absorption (λ_{max}) of the Charge-Transfer Complexes of *p*-Benzoquinones with Various Donors in Dichloromethane at Room Temperature (25 °C)

Donor	Acceptor	λ_{max}/nm	Donor	Acceptor	λ_{max}/nm
1a	CHL	670	**1a**	BRL	710
1b	CHL	695	**1b**	BRL	714
1c	CHL	711	**1c**	BRL	728
1d	CHL	695	**1d**	BRL	717
1e	CHL	693	**1e**	BRL	710
1f	CHL	705	**1f**	BRL	721
1g	CHL	690	**1g**	BRL	707
1h	CHL	686	**1h**	BRL	700
1i	CHL	688	**1i**	BRL	705
1a	FLR	648(sh)	**1b**	FLR	632
1c	FLR	650	**1d**	FLR	641(sh)
1e	FLR	628	**1f**	FLR	640
1g	FLR	625	**1i**	FLR	620
2	CHL	586			

These findings can be interpreted according to Fig. 2. The mixing of the electron-deficient *p*-benzoquinones CHL, BRL, or FRL with each of the donors **1a**—**i** would lead initially to the formation of CTC **6**, which exists in equilibrium with the two reactants: Then the activation of the nitrogen atom of the imino group through the electron-pair of the dimethylamino group enables their nucleophilic attack on the *p*-benzoquinone forming **7**, which gives the salt **8**. The addition of H_2O molecule to the intermediate **8** followed by dehydrohalogenation, deprotonation on oxygen and protonation on the arylated nitrogen affords the 2-arylamino-*p*-benzoquinones (**3**) and 4-dimethylaminobenzaldehyde (**5**). Hydrolysis of the Schiff's base (which should generate the aldehyde and the free amine Ar–NH_2, which in turn would attack the quinone) prior to reaction with the quinone is considered unlikely, because there is no change in the Schiff's base under the similar conditions where a *p*-benzoquinone is absent. On the other hand, the salt **8** may be attacked by moisture faster than the free Schiff's base. The reaction of **3** with another molecule of amidine phenylogous **1** should lead to the formation of the major product **4** (Fig. 2). Proofs of the structures of the products were based firmly on elemental analysis, UV, IR, ^{1}H NMR, and the mass spectra, chemical reactions, or comparison with authentic samples (Tables 1—4).

Experimental

Melting points are uncorrected. UV-vis spectra were measured on a Perkin-Elmer Lambda 2 spectrophotometer using 1.0 cm stoppered silica cells. IR spectra were measured on a Shimadzu 408 spectrophotometer (KBr). The ^{1}H NMR spectra were recorded on Bruker Wp 80 (80 MHz), and the chemical shifts were expressed as δ (ppm) with TMS as the internal standard. The MS spectra were recorded on Finnigan MAT 8430 spectrometer at 70 eV. Elemental analyses were performed by microanalytical unit at Duisburg University, FRG, using Carlo ERBA strumentazione elemental analyzer Model 1106.

Table 2. Analytical and Physical Data of **3a—d** and **4a—p**

Compd	Yield %	Mp °C	Lit[a] mp	Color of crystal	Solvent of recryst	Molecular formula (M. Wt)	Analysis % found (calcd) C	H	N
3a	12	188—189		Blue	A	$C_{13}H_8Cl_3NO_3$ (332.569)	46.83 (46.95)	2.31 (2.42)	4.29 (4.20)
3b	16	>300	—	Blue	A	$C_{12}H_6Cl_3NO_2$ (302.526)	47.58 (47.63)	2.01 (1.99)	4.67 (4.63)
3c	14	140—142	—	Blue	A	$C_{13}H_8F_3NO_3$ (283.200)	55.51 (55.14)	2.87 (2.84)	4.87 (4.95)
3d	10	119—121	—	Brown		$C_{12}H_6F_2NO_2$ (253.146)	56.97 (56.93)	2.41 (2.39)	5.49 (5.53)
4a	44	295—296	298	Black	B	— —	— —	— —	— —
4b	48	275—277	—	Brown	B	$C_{20}H_{16}Cl_2N_2O_2$ (387.264)	61.94 (62.00)	4.21 (4.15)	7.19 (7.25)
4c	46	285d	—	Black	B	$C_{20}H_{16}Cl_2N_2O_2$ (387.264)	62.07 (62.00)	4.19 (4.15)	7.31 (7.25)
4d	53	306d	310d	Black	C	— —	— —	— —	— —
4e	51	314—316	315d	Brown	C	— —	— —	— —	— —
4f	41	305—306	—	Brown	B	$C_{18}H_{10}Cl_4N_2O_2$ (427.100)	50.41 (50.45)	2.39 (2.35)	6.49 (6.55)
4g	43	>330	350	Black	B	— —	— —	— —	— —
4h	54	240	—	Deep green	B	$C_{20}H_{16}Br_2N_2O_4$ (508.148)	46.99 (47.25)	3.14 (3.15)	5.48 (5.50)
4i	49	206—208	—	Brown	B	$C_{20}H_{16}Br_2N_2O_4$ (508.148)	47.23 (47.25)	3.12 (3.15)	5.52 (5.50)
4j	57	263d	267	Black	B	— —	— —	— —	— —
4k	51	220—221	—	Reddish brown	B	$C_{20}H_{16}Br_2N_2O_2$ (476.148)	50.28 (50.40)	3.31 (3.35)	5.93 (6.00)
4l	55	221—222	—	Brown	B	$C_{20}H_{16}Br_2N_2O_2$ (476.148)	50.41 (50.43)	3.42 (3.35)	5.84 (6.00)
4m	59	358d	360	Brown	—	— —	— —	— —	— —
4n	48	283—284	285	Brown	B	— —	— —	— —	— —
4o	41	318	320	Black	B	— —	— —	— —	— —
4p	61	272—273	—	Reddish brown	B	$C_{20}H_{16}F_2N_2O_4$ (386.360)	62.25 (62.18)	4.06 (4.17)	7.16 (7.25)

A=Cyclohexane
B=Acetone
C=Ethyl acetate
The percentage of yield of the aldehyde $(CH_3)_2N$-C_6H_4CHO is 20%.
a) Refs. 5 and 12.

Table 3. IR and ^1H NMR Spectra of the 2-Arylamino-3,5,6-trihalo-*p*-benzoquinone **3a—d** and 2,5-Bis(arylamino)-3,6-dihalo-*p*-benzoquinone **4a—p**

Compound	IR (KBr, cm^{-1})	^1H NMR[a] (δ, TMS)
3a	3250 (NH), 2900 (aliph. CH), 1690 (CO), 3010, 1605 (Ar-CH), 1585 (Ar-C=C).	
3b	3220 (NH), 1680 (CO), 1605 (Ar-CH), 1580 (Ar-C=C).	6.95—7.60 (m, 5H) Ar-H, 9.25 (br. s, 1H) NH.
3c	3360 (NH), 2885 (aliph. CH), 1680 (CO), 1620 (Ar-CH), 1500—1530 (Ar-C=C).	
3d	3310 (NH), 1695 (CO), 1610 (Ar-CH), 1525 (Ar-C=C).	6.80—7.60 (m, 5H) Ar-H, 9.20 (br. s, 1H) NH.
4a	3210 (NH), 2900 (aliph. CH), 1645 (CO), 1605 (Ar-CH), 1560—1580 (Ar-C=C).	
4b	3210 (NH), 1650 (CO), 3010, 1610 (Ar-CH), 1560-1570 (Ar-C=C).	2.20 (s, 6H) CH_3, 7.10—7.30 (m, 8H) Ar-H, 9.30 (br. s, 2H) NH.
4c	3210 (NH), 2900 (aliph. CH), 1645 (CO), 3010 (Ar-CH), 1560 (Ar-C=C).	2.31 (s, 6H) CH_3, 6.99—7.22 (m, 8H) Ar-H, 9.25 (br. s, 2H) NH.

Table 3. (Continued)

Compound	IR (KBr, cm^{-1})	^1H NMR[a] (δ, TMS)
4d	3250 (NH), 1645 (CO), 3010, 1610 (Ar–CH), 1560 (Ar–C=C).	2.28 (s, 6H) CH_3, 7.00—7.20 (m, 8H) Ar–H, 9.58 (br. s, 2H) NH.
4e	3240 (NH), 1645 (CO), 1600 (Ar–CH), 1575 (Ar–C=C).	7.14—7.40 (m, 10H) Ar–H, 9.78 (br. s, 2H) NH.
4f	3250 (NH), 1650 (CO), 1605 (Ar–CH), 1560 (Ar–C=C).	7.05—7.45 (m, 8H) Ar–H, 9.45 (br. s, 2H) NH.
4g	3250 (NH), 1645 (CO), 1610 (Ar–CH), 1560 (Ar–C=C).	7.00—7.10 (m, 8H) Ar–H, 9.25 (br. s, 2H) NH.
4h	3240 (NH), 1645 (CO), 1600 (Ar–CH), 1555 (Ar–C=C).	3.85 (s, 6H) OCH_3, 6.85—7.35 (m, 8H) Ar–H, 8.35 (br. s, 2H) NH.
4i	3250 (NH), 1645 (CO), 1610 (Ar–CH), 1570 (Ar–C=C).	3.78 (s, 6H) OCH_3, 6.70—7.35 (m, 8H) Ar–H, 9.40 (br. s, 2H) NH.
4j	3240 (NH), 1640 (CO), 1600 (Ar–CH), 1560 (Ar–C=C).	3.82 (s, 6H) OCH_3, 6.80—7.35 (m, 8H) Ar–H, 8.40 (br. s, 2H) NH.
4k	3210 (NH), 1655 (CO), 1610 (Ar–CH), 1585 (Ar–C=C).	2.30 (s, 6H) CH_3, 6.95—7.30 (m, 8H) Ar–H, 8.30 (br. s, 2H) NH.
4l	3240 (NH), 1645 (CO), 1600 (Ar–CH), 1560 (Ar–C=C).	2.35 (s, 6H) CH_3, 6.90—7.30 (m, 8H) Ar–H, 8.35 (br. s, 2H) NH.
4m	3250 (NH), 1645 (CO), 1610 (Ar–CH), 1565 (Ar–C=C).	2.35 (s, 6H) CH_3. 6.95—7.30 (m, 8H) Ar–H, 8.35 (br. s, 2H) NH.
4n	3250 (NH), 1645 (CO), 3010, 1600 (Ar–CH), 1565 (Ar–C=C).	7.10—7.40 (m, 10H) Ar–H, 8.50 (br. s, 2H) NH.
4o	3200 (NH), 1640 (CO), 1600 (Ar–CH), 1555 (Ar–C=C).	7.10—7.45 (m, 8H) Ar–H, 9.25 (br. s, 2H) NH.
4p	3250 (NH), 1665 (CO), 1610 (Ar–cH), 1585 (Ar–C=C).	3.77 (s, 6H) OCH_3, 6.80—7.20 (m, 8H) Ar–H, 8.75 (br. s, 2H) NH.

a) The solvent of ^1H NMR is DMSO-d_6 except **3b** and **3d** ($CDCl_3$).

Table 4. Mass Spectroscopy of 2-Arylamino-3,5,6-trihalo-*p*-benzoquinone **3a**—**d** and 2,5-Bis(arylamino)-3,6-dihalo-*p*-benzoquinone **4a**—**f**, **n**—**p**

Compound	MS m/z (rel intensity %)
3a	332½ (M^+, 100), 297 (73), 281 (17), 175 (50), 92 (26), 77 (30), 65 (50), 51 (22).
3b	302½ (M^+, 33), 267 (29), 175 (18), 77 (100), 51 (90).
3c	283 (M^+, 100), 268 (84), 248 (5), 212 (7), 192 (8), 92 (16), 77 (9), 65 (31).
3d	253 (M^+, 100), 206 (24), 108 (32), 77 (61), 51 (56).
4a	419 (M^+, 100), 403 (3), 383 (24), 367 (13), 348 (16), 347 (51), 331 (4), 174 (80), 123 (10), 77 (32), 65 (19).
4b	387 (M^+, 100), 351½ (64), 316 (39), 286 (13), 246 (12), 158 (41), 91 (64), 77 (24), 65 (52), 44 (18).
4c	387 (M^+, 58), 371 (8), 351½ (46), 315 (41), 91 (100), 77 (21), 65 (71).
4d	387 (M^+, 100), 371 (16), 351½ (47), 336 (12), 315 (49), 91 (100), 77 (25), 65 (70).
4e	359 (M^+, 90), 323 (77), 287 (38), 77 (100).
4f	427 (M^+, 10), 391½ (54), 356 (26), 320½ (4), 178 (100).
4n	448 (M^+, 46), 368 (24), 340 (18), 288 (22), 77 (100), 51 (40).
4o	516 (M^+, 37), 436 (17), 402 (14), 356 (7), 321 (16), 223 (34), 178 (100).
4p	386 (M^+, 100), 368 (10), 355 (69), 348 (41), 324 (7), 264 (5), 107 (4), 77 (10), 65 (9).

Preparative Layer Chromatography. Air dry 1.0 mm layers of silica gel Merck pf 254 on plates were employed for preparative TLC and bands were detected by indicator fluorescence quenching upon exposure to 254 mm UV-light.

Compounds: 2,3,5,6-Tetrachloro-*p*-benzoquinone (chloranil, CHL, Aldrich) and 2,3,5,6-tetrabromo-*p*-benzoquinone (bromanil, BRL, Merck) were recrystallized several times from benzene before use. 2,3,5,6-Tetrafluoro-*p*-benzoquinone (Fluoranil, FRL, Aldrich) was used without purification. Azomethines **1a**—**i** were prepared by the usual condensation reaction of 4-dimethylaminobenzaldehyde with substituted aromatic amines.[7,8] The amidine **2** was prepared according to the literature.[9] Ethyl acetate used as a solvent, was purified according to Vogel[10] and Organikum,[11] dried and distilled.

The Reaction of *p*-Benzoquinones, (BRL, CHL, FRL) with Azomethines 1a—i and Amidine[#] 2. General Procedure: To a solution of tetrahalo-*p*-benzoquinone (0.001 mol) in 20 ml dry ethyl acetate, the azomethine (0.001 mol) which was dissolved in 10 ml dry ethyl acetate was added dropwise with stirring at room temperature. The reaction mixture became deep green which turned immediately into brown color. The stirring was continued for 48 h with admission of air to complete the reaction.

The reaction mixture was filtered and the precipitate was washed several times with cold ethyl acetate until the mother liquor became clear. The filtrate was concentrated and the residue was chromatographed on thin-layer plates using toluene as eluent to give two zones; the first contained compound **3** which is characterized by a deep blue color, and the second the 4-dimethylaminobenzaldehyde.

The two zones were extracted with acetone and the products recrystallized from the suitable solvent to afford the pure compounds (see Table 2).

The precipitate was recrystallized from acetone to give a pure compounds of 2,5-bis(arylamino)-3,6-dihalo-*p*-benzoquinone **4**.

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[#] In the case of reaction with amidine **2**, the corresponding aldehyde could not be isolated in apure form.

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