[Chem. Pharm. Bull.
28(4)1207—1213(1980)]

Tautomerism of 4-Amino- and 4-Arylamino-1,2-naphthoquinones

Hiroshige Yano, Miyuki Yamasaki, Yukiko Shimomura (née Sakai),
Masatake Iwasaki, Mutsuko Ohta, Yohko Furuno,[1a)]
Keiki Kouno, Yukio Ono, and Yo Ueda[1b)]

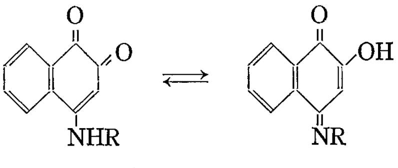
Daiichi College of Pharmaceutical Sciences[1a)] *and Faculty of Pharmaceutical Sciences, Kyushu University*[1b)]

(Received October 13, 1979)

The ^{13}C chemical shifts of 4-amino- and 4-arylamino-1,2-naphthoquinones measured in DMSO-d_6, pyridine-d_5 and a D_2O solution of NaOD indicated that the predominant tautomer in neutral solvents is the 1,2-dioxo-4-amino-naphthalene (Ia) form, while that in weak basic solvents is the 1-oxo-2-hydroxy-4-imino-naphthalene (Ib) form and that in an aqueous solution of NaOH is the anion of the Ib form. The electronic spectrum of 4-anilino-1,2-naphthoquinone measured in a mixture of EtOH and 0.05 M H_2SO_4 (1: 4 by volume) indicated that its tautomeric form in an aqueous strong acid solution is the Ia form and that the compound is hydrolyzed quickly to produce 2-hydroxy-1,4-naphthoquinone. The magnitudes of substituent effects observed in the electronic spectra of 4-(4′-substituted)-anilino-1,2-naphthoquinones measured in EtOH were found to be smaller than those measured in pyridine. This difference was considered to provide confirmation that the predominant tautomer in neutral solvents is the Ia form. The theoretical π—π^* transition energies of 4-arylamino-1,2-naphthoquinones were calculated for both the Ia and the Ib forms by means of Pariser-Parr-Pople type molecular orbital calculations.

Keywords——2-methoxy-N-phenyl-1,4-naphthoquinone; 4-(N-methyl)anilino-1,2-naphthoquinone; 4-amino-1,2-naphthoquinone; 4-arylamino-1,2-naphthoquinone; proton tautomerism; electronic spectra; ^{13}C NMR spectra; molecular orbital calculation of π—π^* transition energy; substituent effect; 2-hydroxy-1,4-naphthoquinone

4-Arylamino-1,2-naphthoquinones, which are the colored reaction products of aromatic primary amines with the salt of 1,2-naphthoquinone-4-sulfonic acid, are potentially useful as antimalarials, antibacterials, anticancer drugs and antioxidants. A tautomerism, Ia$\rightleftarrows$Ib, exists in 4-amino- and 4-arylamino-1,2-naphthoquinones, but conficting reports have appeared on this point. Namely, Fieser *et al.*[2)] concluded that Ia (R=H) is the more stable tautomer at pH below 10.4, whereas Ib (R=H) is the more stable tautomer at pH above 11.5, based on their experimental results obtained by the potentiometric method. In contrast, Harmon *et al.*[3)] stated in their report that Ia (R=H and C_6H_4X) is the more stable tautomer at pH 4—13 and that the tautomer Ib (R=H and C_6H_4X) is stable only in the pH region of 0—0.8, based on experimental results obtained by the electronic spectral method. Therefore, we reexamined the tautomerism of 4-amino- and 4-arylamino-1,2-naphthoquinones in order to obtain conclusive evidence. This paper describes the results of our investigation.



R=C_6H_4X or Y
(X and Y are substituents)
Chart 1

[1)] Location: *a) 22-1, Tamagawa-cho, Minami-ku, Fukuoka, 815, Japan*; *b) Maedashi 3-1-1, Higashi-ku, Fukuoka, 812, Japan.*

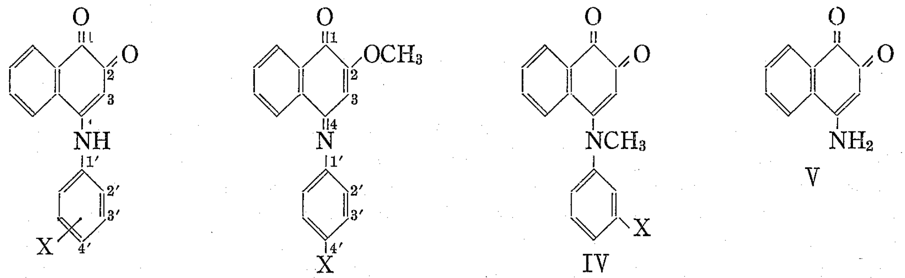
[2)] L. Fieser and M. Fieser, *J. Am. Chem. Soc.*, **56**, 1565 (1934).

[3)] R.E. Harmon, L.M. Phipps, J.A. Howell, and S.K. Gupta, *Tetrahedron*, **25**, 5807 (1969).

Results and Discussion

Tautomeric Forms in Neutral Solvents, Pyridine and Aqueous NaOH Solution

The compounds employed in this work were 4-anilino-1,2-naphthoquinone derivatives (II), 2-methoxy-N-phenyl-1,4-naphthoquinone-imine derivatives (III), 4-(N-methyl)anilino-1,2-naphthoquinone derivatives (IV) and 4-amino-1,2-naphthoquinone (V). Among them, many compounds of group II are scarcely soluble in CHCl$_3$, MeOH, benzene, dioxane and CH$_3$CN, so the neutral solvent employable in the mesurement of ^{13}C nuclear magnetic resonance (NMR) spectra was limited to DMSO-d_6.



II III IV

IIa: X=H
IIb: X at the 3′ position
IIc: X at the 4′ position

Chart 2

The ^{13}C NMR spectra of IIa, IIb (X=OH), IIc (X=OH), III (X=H and Cl), IV (X=H and CH$_2$) and V were measured in DMSO-d_6. Furthermore, the ^{13}C NMR spectra of pyridine solutions of IIb (X=OH) and IIc (X=NO$_2$), and of a solution of IIc (X=OH) in a D$_2$O solution of NaOD were measured. 1,4-Naphthoquinone and its 2-hydroxy and 2-methoxy derivatives were also subjected to the mesurement of ^{13}C NMR spectra in order to obtain reference spectra. All of the spectral data are listed in Table I.

Table I. ^{13}C Chemical Shifts of 4-Amino- and 4-Arylamino-1,2-naphthoquinones and of Related Compounds

Compound	X	Solvent$^{a)}$	^{13}C Chemical shift, δ (ppm)				
			C (1)	C (2)	C (3)	C (4)	C (1′)
1,4-Naphthoquinone		D	184.2	138.3			
2-OH-1,4-naphthoquinone		D	184.1	159.1	110.8	180.8	
2-OH-1,4-naphthoquinone		P	185.1	161.7	111.7	182.5	
2-OCH$_3$-1,4-naphthoquinone		D	183.9	160.0	109.5	178.9	
IIa		D	176.1$^{b)}$	180.5$^{b)}$	100.5	154.3	147.6
IIb	OH	D	175.0$^{b)}$	180.6$^{b)}$	100.3	157.7$^{b)}$	154.1$^{b)}$
IIc	OH	D	174.9$^{b)}$	180.9$^{b)}$	99.7	155.9$^{b)}$	154.6$^{b)}$
III	H	D	178.8	155.6	101.4	153.8	149.4
III	Cl	D	178.6	155.8	101.2	154.4	148.3
IV	H	D	177.2$^{b)}$	179.7$^{b)}$	110.7	158.3	147.5
IV	CH$_3$	D	177.1$^{b)}$	179.8$^{b)}$	110.6	158.3	147.5
V		D	174.1$^{b)}$	181.6$^{b)}$	100.7	157.6	
IIb	OH	P	181.9	159.5	104.4	155.9	149.8
IIc	NO$_2$	P	181.7	158.4	104.2	157.1	144.0
IIc	OH	B	189.4	167.8	106.3$^{b)}$	160.2$^{b)}$	138.7$^{b)}$

a) D: DMSO-d_6, P: pyridine-d_5, B: NaOD in D$_2$O.
b) Tentative assignment.

Since an adjacent hydroxyl group is known to deshield the carbonyl carbon,[4] the ^{13}C chemical shifts of 2-hydroxy-1,4-naphthoquinone observed in both DMSO-d_6 and pyridine-d_5 were assigned as shown in Table I. The ^{13}C chemical shifts of the $C_{(1)}$, $C_{(2)}$, $C_{(3)}$ and $C_{(4)}$ atoms of 2-methoxy-1,4-naphthoquinone were found to be similar to those of the corresponding carbon atoms of the 2-hydroxy derivative.

The ^{13}C chemical shifts at 174.1 and 181.6 ppm of V were assigned tentatively to the $C_{(1)}$ and $C_{(2)}$ atoms, respectively, according to the tentative assignment in 1,2-naphthoquinone.[5] Even though the assignment is tentative, the presence of two highly deshielded carbon atoms in V indicates clearly that the Ia form (R=H) is the predominant tautomer in DMSO.

Little comment seems necessary on the ^{13}C chemical shifts of the carbonyl carbon atoms of III (X=H and Cl) and IV (X=H and CH_3). In each of the spectra of IIa, IIb (X=OH) and IIc (X=OH) measured in DMSO-d_6, a pair of ^{13}C chemical shifts assignable to two carbonyl carbons, 176.1 and 180.5 ppm for IIa, 175.0 and 180.6 ppm for IIb (X=OH), and 174.9 and 180.9 ppm for IIc (X=OH), were observed. The spectra of IIb (X=OH) and IIc (X=NO_2) measured in pyridine-d_5, each showed only one ^{13}C chemical shift assignable to the carbonyl carbon atom, at 181.9 ppm for IIb (X=OH) and 181.7 ppm for IIc (X=NO_2). In the spectrum of IIc (X=H) measured in NaOD solution only one ^{13}C chemical shift assignable to the carbonyl carbon, 189.4 ppm, was observed. The chemical shift of the olefinic carbon atom at the $C_{(2)}$ position, 167.8 ppm, together with the chemical shift of the carbonyl carbon atom mentioned above, indicates that IIc (X=H) dissolves in NaOD solution to form an anion of the tautomer Ib.

The measurements of ^{13}C NMR spectra mentioned above clearly indicate that the Ia form of 4-amino- and 4-arylamino-1,2-napthoquinones is the predominant tautomer in solvents having neutral properties, and that the Ib form is the predominant tautomer in solvents having basicity stronger than or equal to that of pyridine.

Tautomeric Form in Acidic Solvents

A solution of IIa in EtOH was diluted with four volumes of aqueous 0.05 M H_2SO_4, and the electronic spectrum of the resulting solution was measured at 2, 8, 30 and 60 min after the addition of the H_2SO_4 solution.

The spectra measured at elapsed times of 2 and 8 min did not show any noticeable difference from the spectrum measured in EtOH–H_2O (1: 4 by volume), and lacked a doublet of absorption maxima centered at around 250 nm which was described by Harmon *et al.* as their only evidence for the presence of the Ib form in an aqueous strong acid solution. The spectrum measured at 30 min showed indications of the appearance of the doublet mentioned above. The existence of this doublet was clear in the spectrum measured at 60 min. The spectrum of IIa was also measured in EtOH–0.5 M H_2SO_4 (1: 4 by volume). The spectral change was found to be faster than that of the above case. However, the doublet could not be observed in the spectra measured at 30 sec, 2 min or 5 min after the preparation of the solution. In order to investigate the reason for this spectral change, the substance (s) present in an aqueous strong acid solution of IIa was examined by chemical methods. Namely, a part of a solution of IIa in EtOH–0.05 M H_2SO_4 (1: 4 by volume) was neutralized with dilute aqueous NaOH after 3 min, and another part of the same solution was neutralized at 60 min. TLC of the $CHCl_3$ extracts of these two neutralized solutions indicated that IIa was present in both extracts and that 2-hydroxy-1,4-naphthoquinone was present in the extract of the reaction mixture neutralized at an elapsed time of 60 min. The above findings clearly indicate that the predominant tautomeric form is IIa in both neutral solvents and strong acidic solvents

---

[4] J.B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York and London, 1972, p. 287.

[5] St. Berger and A. Rieker, "The Chemistry of the Quinoid Compounds," Part 1, ed. by S. Patai, John Wiley and Sons Ltd., New York, 1974, p. 184.

NII-Electronic Library Service

having a pH of about 0, and that the delayed appearance of the doublet can be attributed to the delayed production of the hydrolysis product, 2-hydroxy-1,4-naphthoquinone.

In the case of V, the electronic spectrum of its solution in EtOH–0.05 M H_2SO_4 (1: 4 by volume) measured at 2 min after the preparation of the solution was already quite different from the spectrum of its solution in EtOH–H_2O (1: 4 by volume). The spectrum had a doublet of absorption maxima centered at around 250 nm. In the spectra measured at 8, 30 and 60 min the doublet became increasingly distinct. The amount of the hydrolysis product, 2-hydroxy-1,4-naphthoquinone, in the acidic solution was found to increase gradually in parallel with the intensification of the doublet. The results of spectral and chemical investigations indicate that the hydrolysis reaction of V occurs almost immediately after dissolution in an aqueous strong acid solution.

III (X=H) and IV (X=H) were also found to be hydrolyzed to 2-hydroxy-1,4-naphthoquinone rapidly at room temperature on dissolution in EtOH–0.05 M H_2SO_4 (1: 4 by volume).

Table II shows the spectral data for IIa, IIb, IIc, III, IV and V measured in EtOH and also the data for IIa and IIc measured in pyridine. The spectra of IIa, IIb and IIc measured in EtOH showed that an electron-donating substituent causes a bathochromic shift of the absorption maximum of the longest wavelength absorption band. A linear correlation (cor-

TABLE II. Absorption Maxima of 4-Amino- and 4-Arylamino-1,2-naphthoquinones

	Compounds X	Solvent	λ_{max}, nm (log ε)
IIa		EtOH	243 (4.36), 283 (4.13), 340^{sh} (3.74), 460 (3.69)
IIb	NO_2	EtOH	222 (4.14), 245 (4.15), 288 (4.04), 338 (3.68), 435 (3.37)
IIb	$COCH_3$	EtOH	225 (4.28), 286 (4.03), 333^{sh} (3.70), 452 (3.51)
IIb	Cl	EtOH	242 (4.34), 285 (4.19), 335 (3.82), 448 (3.66)
IIb	CH_3	EtOH	238 (4.35), 278 (4.22), 330^{sh} (3.72), 450 (3.66)
IIb	OC_2H_5	EtOH	242 (4.41), 280 (4.23), 335^{sh} (3.78), 460 (3.72)
IIb	OCH_3	EtOH	240 (4.40), 280 (4.23), 335^{sh} (3.77), 457 (3.70)
IIb	OH	EtOH	243 (4.36), 283 (4.21), 340^{sh}, 466 (3.70)
IIc	NO_2	EtOH	240^{sh}, 285^{sh}, 304 (4.22), 343 (4.10), 400, 441 (3.80)
IIc	CN	EtOH	250 (4.24), 290 (4.15), 337 (3.76), 440 (3.53)
IIc	$COCH_3$	EtOH	246 (4.30), 257^{sh} (4.27), 294^{sh} (4.33), 299 (4.34), 334^{sh} (3.99), 448 (3.68)
IIc	Cl	EtOH	243 (4.40), 285 (4.18), 330^{sh} (3.81), 458 (3.70)
IIc	CH_3	EtOH	244 (4.40), 282 (4.14), 340^{sh} (3.75), 467 (3.71)
IIc	OC_2H_5	EtOH	245 (4.38), 280 (4.17), 348 (3.60), 480 (3.67)
IIc	OCH_3	EtOH	244 (4.50), 280 (4.23), 479 (3.77)
IIc	OH	EtOH	245 (4.43), 280 (4.21), 347 (4.14), 484 (3.77)
IIc	$N(CH_3)_2$	EtOH	263 (4.56), 290^{sh} (4.20), 524 (3.77)
III	NO_2	EtOH	248 (4.12), 256 (4.10), 304 (4.31), 406^{sh} (3.72)
III	CN	EtOH	250 (4.39), 255^{sh} (4.37), 289^{sh} (4.41), 296 (4.42), 341 (3.92), 410 (3.59)
III	$COCH_3$	EtOH	250^{sh}, 257 (4.24), 299 (4.49), 340^{sh} (3.99), 426 (3.62)
III	Cl	EtOH	233 (4.31), 255^{sh} (4.09), 293 (4.31), 340 (3.85), 436 (3.58)
III	H	EtOH	246^{sh} (4.08), 252^{sh} (4.06), 288 (4.28), 336 (3.84), 433 (3.51)
III	OCH_3	EtOH	239 (4.31), 255^{sh} (3.98), 289 (4.24), 334^{sh} (3.84), 474 (3.75)
III	$N(CH_3)_2$	EtOH	249 (4.33), 292 (4.28), 327^{sh} (4.05), 570 (3.99)
IV	H	EtOH	246 (4.36), 274^{sh} (4.08), 321 (3.77), 370 (3.61), 466 (3.82)
IV	CH_3	EtOH	247 (4.37), 277 (4.08), 322 (3.78), 468 (3.86)
V		EtOH	235 (4.20), 273 (4.31), 280^{sh}, 330^{sh}, 456 (3.56)
IIa		pyridine[a)]	446
IIc	CN	pyridine[a)]	420
IIc	$COCH_3$	pyridine[a)]	434
IIc	Cl	pyridine[a)]	445
IIc	OCH_3	pyridine[a)]	478
IIc	$N(CH_3)_2$	pyridine[a)]	567

a) Spectra in the visible region were determined.

relation coefficient $r=-0.925$) was found between the wavelengths of absorption maxima and Hammett's σ constants of the substituents. The spectra of IIa and IIc measured in pyridine showed even more marked substituent effects on the longest wavelength absorption maxima. In the case of the spectra of compounds III the substituent effect was as strong as that found in the case of the spectra of IIa and IIc measured in pyridine.

The difference in the magnitude of substituent effects observed in the spectra of IIa and IIc measured in EtOH and in the spectra of the same compounds measured in pyridine provides further confirmation that the Ia form of II is the predominant tautomer in EtOH (a neutral solvent). The reasoning is as follows. The proedminant tautomer of II in pyridine was proved to be the Ib form in the preceding part of this paper. In the Ib form, the two aromatic rings may conjugate effectively *via* the sp^2 hybridized nitrogen atom, resulting in rather strong substituent effects. In contrast, in the Ia form effective conjugation of the two aromatic rings may not be possible because of the presence of the sp^3 hybridized nitrogen atom. The theoretical transition energies of the group of compounds IIc for both the Ia and Ib forms and those of the group of compounds III, calculated using the Pariser-Parr-Pople type molecular orbital method, are shown in Table III. The results support our conclusions derived from the measurement of electronic spectra.

Table III. Calculated Transition Energies of the Lowest π-π^* Absorption Band

	Compound X	Tautomeric form	Calcd. transition energy (nm, f)
Ⅱa		Ia	460 (0.188)
Ⅱc	CN	Ia	449 (0.250)
Ⅱc	$COCH_3$	Ia	452 (0.221)
Ⅱc	Cl	Ia	468 (0.188)
Ⅱc	OCH_3	Ia	471 (0.188)
Ⅱc	$N(CH_3)_2$	Ia	503 (0.182)
IV	H	Ia	466 (0.176)
IV	CH_3	Ia	466 (0.178)
Ⅱa		Ib	446 (0.260)
Ⅱc	CN	Ib	434 (0.204)
Ⅱc	$COCH_3$	Ib	434 (0.293)
Ⅱc	Cl	Ib	466 (0.226)
Ⅱc	OCH_3	Ib	476 (0.211)
Ⅱc	$N(CH_3)_2$	Ib	556 (0.150)
Ⅲ	CN		424 (0.123)
Ⅲ	$COCH_3$		423 (0.334)
Ⅲ	Cl		453 (0.248)
Ⅲ	H		433 (0.291)
Ⅲ	OCH_3		463 (0.230)
Ⅲ	$N(CH_3)_2$		543 (0.158)

Conclusion

The Ia form of 4-amino- and 4-arylamino-1,2-naphthoquinones is the predominant tautomer in neutral solvents. This form is also the predominant tautomeric form in aqueous acid solutions, even if the pH of the solvent is nearly 0. Both groups of compounds are hydrolyzed to form 2-hydroxy-1,4-naphthoquinone very quickly in an aqueous strong acid solution at room temperature.

The Ib form is the predominant tautomer in basic solvents, including pyridine.

Experimental

All melting points were determined on a Yanaco MP-500 apparatus and are uncorrected. ^{13}C NMR spectra were taken on a JEOL FX-100 spectrometer using TMS (or DSS) as an internal standard, and chemical shifts (δ) are given in ppm relative to the internal standard. UV spectra were taken on a Union SM-401 spectrometer.

General Procedure for the Preparation of 4-Arylamino-1,2-naphthoquinones (II and IV)——A solution of 0.01 mol of arylamine in 20 ml of EtOH was added with stirring to a solution of 0.01 mol of potassium 1,2-naphthoquinone-4-sulfonate in 280 ml of H_2O, and the reaction mixture was stirred for 30 min at room temperature. The precipitated reaction product was separated by filtration, washed with H_2O and recrystallized twice from MeOH.

General Procedure for the Preparation of 2-Methoxy-N-phenyl-1,4-naphthoquinone-imines (III)——A suspension of 0.1 g of 4-arylamino-1,2-naphthoquinone in 3 ml of dimethylsulfate was treated with 7 ml of aqueous 30% NaOH solution. The reaction mixture was warmed gradually with stirring in a water bath until the water bath temperature reached 60° and was stirred for a further 60 min. The mixture was then heated in a boiling water bath for 30 min. After cooling, the reaction product was extracted with EtOAc. The EtOAc layer was washed with H_2O, dried over anhyd. Na_2SO_4 and evaporated to dryness. The residue was purified by a column chromatography on alumina, if necessary, and was recrystallized twice from EtOH.

The appearances, melting points and the results of elemental analyses of new compounds were as follows.

IIb (X=$COCH_3$): Yellowish-red needles, mp 264°, *Anal.* Calcd for $C_{18}H_{13}NO_3$: C, 74.21; H, 4.50; N, 4.81. Found: C, 74.25; H, 4.22; N, 4.58.

IIb (X=OC_2H_5): Yellowish-red needles, mp 229—231°, *Anal.* Calcd for $C_{18}H_{15}NO_3$: C, 73.70; H, 5.15; N, 4.78. Found: C, 73.71; H, 4.99; N, 4.69.

IIb (X=OH): Deep red needles, mp 287°, *Anal.* Calcd for $C_{16}H_{17}NO_3$: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.19; H, 4.24; N, 5.12.

IIc (X=CN): Yellowish-red needles, mp 285°, *Anal.* Calcd for $C_{17}H_{10}N_2O_2$: C, 74.44; H, 3.68; N, 10.21. Found: C, 74.31; H, 3.74; N, 10.10.

IIc (X=$N(CH_3)_2$): Black needles, mp 257°, *Anal.* Calcd for $C_{18}H_{16}N_2O_2$: C, 73.96; H, 5.52; N, 9.58. Found: C, 73.69; H, 5.29; N, 9.39.

III (X=NO_2): Orange prisms, mp 253.5°, *Anal.* Calcd for $C_{17}H_{12}N_2O_4$: C, 66.23; H, 3.92; N, 9.09. Found: C, 66.13; H, 4.04; N, 9.03.

III (X=CN): Yellow-orange needles, mp 197—217°, *Anal.* Calcd for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72. Found: C, 74.78; H, 4.31; N, 9.69.

III (X=$COCH_3$): Yellow-orange needles, mp 200°, *Anal.* Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.54; H, 5.07; N, 4.57.

III (X=Cl): Yellow-orange needles, mp 164.5°, *Anal.* Calcd for $C_{17}H_{12}ClNO_2$: C, 68.58; H, 4.06; N, 4.70. Found: C, 68.53; H, 4.10; N, 4.60.

III (X=CCH_3): Yellowish-red needles, mp 175°, *Anal.* Calcd for $C_{18}H_{15}NO_3$: C, 73.70; H, 5.15; N, 4.78. Found: C, 73.69; H, 5.19; N, 4.69.

III (X=$N(CH_3)_2$): Black needles, mp 194°, *Anal.* Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.43; H, 5.96; N, 9.09.

IV (X=CH_3). Red prisms, mp 118.5°, *Anal.* Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.08; H, 5.59; N, 4.97.

General Procedure for the Detection and Identification of the Hydrolysis Product——1) By TLC. TLC was performed on Merck silica gel 60 F_{254} TLC plates using a mixture of MeOH and $CHCl_3$ (1:10) as a developing solvent.

A solution of *ca.* 1 mg of the compound to be tested in 20 ml of MeOH was diluted with 80 ml of 0.05 M H_2SO_4, and the reaction mixture was kept for a definite time at room temperature. An aliquot of 20 ml of the reaction mixture was neutralized with dilute NaOH solution, and then made weakly acidic with dilute acetic acid solution. The reaction products were extracted with $CHCl_3$, and the $CHCl_3$ layer was washed with H_2O, dried over anhyd. Na_2SO_4 and evaporated to dryness. The residue was dissolved in MeOH and spotted on a TLC plate.

2) By IR. A solution of 0.1 g of the testing compound in 100 ml of MeOH was diluted with 400 ml of 0.05 M H_2SO_4. The reaction mixture was treated as in the case of identification by TLC. The reaction products were separated by column chromatography on silica gel, and the components of the reaction mixture were identified from their IR spectra.

Molecular Orbital Calculations——The P-P-P type molecular orbital calculation is known to be applicable to a molecule of nonplanar structure.[6] The parameters κ defined by the equation, $\beta_{rs}=-\kappa S_{rs}(I_r+I_s)$, were determined as 0.3396, 0.2982 and 0.3094 so that the results fit the observed energies of the lowest π—π^* bands of three structural types, the Ia form of IIc and the Ib form of IIc and III, respectively. In the CI

---

[6] Y. Ioki, H. Kawana, and K. Nishimoto, *Bull. Chem. Soc. Jpn.*, **51**, 963 (1978).

NII-Electronic Library Service

calculation, 36 singly excited configurations were included. In the case of the Ia form, the valence angle $\angle C_{(4)}NC_{(1')}$, the face angle between the plane of naphthoquinone and the plane of $C_{(4)}$, N and $C_{(1')}$, and the face angle between the latter plane and the plane of N, $C_{(1')}$ and $C_{(2')}$ were assumed to be 133.6°, 39.3° and 21.7°, respectively, based on the X-ray crystallographic data for 4,4′-dichloro-biphenylamine.[7] In the case of the Ib form, the face angle between the plane of $C_{(4)}$, N and $C_{(1')}$ and the plane of N, $C_{(1')}$ and $C_{(2')}$ was assumed to be 64°, based on the X-ray crystallographic data for 4-methoxy-indophenol N-oxide.[8] The geometries of the naphthoquinone moieties of the Ia and Ib forms were taken from the data for 1,2-naphthoquinone and 2-hydroxy-1,4-naphthoquinone given by Kuboyama *et al.*[9] The geometries of the phenyl rings of the Ia and Ib forms were standard reported values.[10]

Acknowledgement The authors are grateful to Mr. Y. Tanaka for the measurement of NMR spectra and to Mr. M. Shidō, Mr. M. Abe and Mr. T. Miyazaki for the elemental analyses.

---

7) K. Plieth and G. Ruban, *Z. Kristallogr.*, **16**, 161 (1961).

8) C. Romers and B. Hesper, *Acta Crystallogr.*, **20**, 162 (1966).

9) A. Kuboyama and H. Arano, *Bull. Chem. Soc. Jpn.*, **49**, 1401 (1976); A. Kuboyama, S. Matsuzaki, H. Takagi, and H. Arano, *ibid.*, **47**, 1604 (1974).

10) J.A. Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N.Y., 1970.

NII-Electronic Library Service