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Tautomerism (Hydroxyazo versus Ketohydrazone Form) of [2.2.2]Cyclophane-1,2-dione Monoarylhydrazones: an ^{1}H-NMR Study

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ABSTRACT

Hydroxyazo–ketohydrazone tautomerism of arylhydrazones of para–para–para-, para–meta–para-, *and* para–ortho–para-*[2.2.2]cyclophane-1,2-dione* ***1a***, ***1b*** *and* ***1c*** *was studied by means of* ^{1}*H-NMR spectroscopy. Except for the phenylhydrazones* ***4ba*** *and* ***4ca*** *of* ***1b*** *and* ***1c***, *which exist as the ketohydrazone* ***4-H***, *the azo tautomer* ***4-A*** *is predominant in solution, and is more favored in chloroform and benzene than in acetonitrile. A good correlation was found between the strain of the cyclophane ring and the δ-value of OH proton in* ***4-H***.

1 INTRODUCTION

Hydroxyazo–ketohydrazone tautomerism of the monohydrazone of *vic*-dicarbonyl and 1,2-dicarbonyl-substituted olefinic systems (Scheme 1) is well known.[1] The tautomerism of these systems incorporated in a naphthalene skeleton which is one of the important fundamental structures of commercial dyestuffs, has been extensively studied. Hydroxyazo–ketohydrazone equilibrations are known to be sensitive to structural changes and the substituent in the hydrazine as well as to chemical media (solvent effect).

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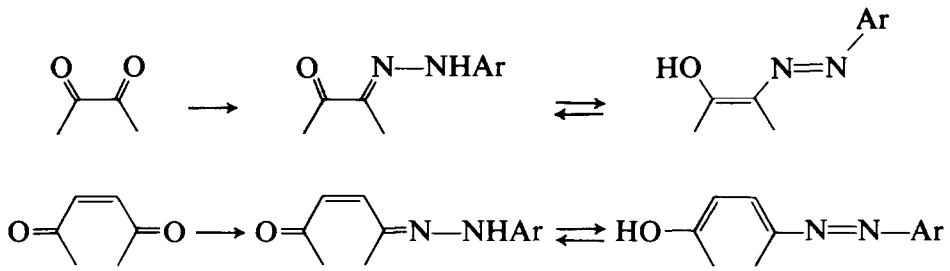


Scheme 1

We have been interested in the chemical properties of functional groups in the cyclophane skeleton because, reflecting their unique chemical environments, they are expected to show unusual chemical behavior. Recently we prepared [2.2.2]cyclophanes,[2] **1a**, **1b** and **1c**, each having a 1,2-dicarbonyl moiety in their bridges, by the reaction of [2.2.2]cyclophanes containing a 1,2,5-thiadiazole ring with Grignard reagents. In this present paper, we report the effect of the cyclophane-ring structure on the hydroxyazo–ketohydrazone tautomerism of the arylhydrazones of [2.2.2]cyclophane-1,2-diones (**1**).

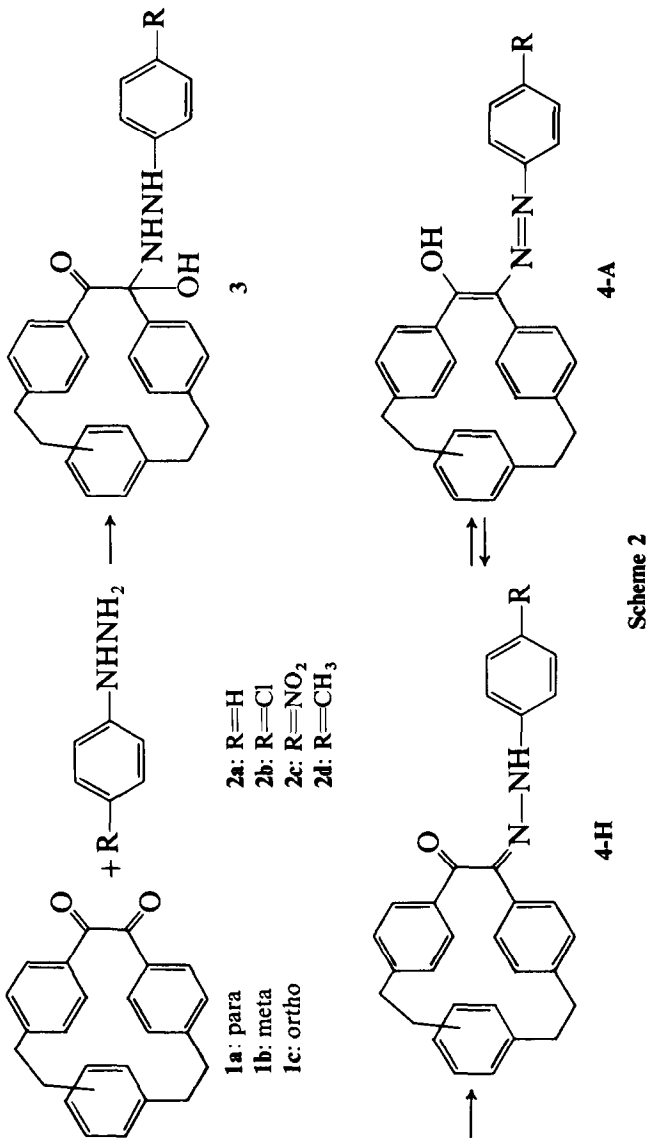
2 RESULTS AND DISCUSSION

2.1 Preparation of 4

The reaction of *para*-[2^3]cyclophane **1a** with phenylhydrazine (**2a**) gave an unstable yellow solid **3aa**, which, from its spectral data and elemental analysis, was identified as the 1:1-adduct of **1a** and **2a**. Compound **3aa** was readily dehydrated in refluxing ethanol, giving **4aa-A** in the hydroxyazo form. The reaction of **2a**–HCl gave similar results. On the other hand, the *meta*- and *ortho* analogues, **1b** and **1c**, gave the corresponding **4ba** and **4ca** in ketohydrazone form **4ba-H** and **4ca-H**, respectively, in the reaction with **2a** and **2a** as its hydrochloride **2a**–HCl (see Scheme 2).

The hydrazones **4ba-H** and **4ca-H** tautomerized into the hydroxyazo tautomers **4ba-A** and **4ca-A**, respectively, when dissolved in deuteriochloroform. The azo form of **4ba** afforded the ketohydrazone **4ba-H** on recrystallization from ethyl acetate.

Reaction of **1a** with *p*-nitrophenylhydrazine (**2c**) gave the azo form **4ac-A** via the unstable **3ac**. In contrast, reaction with *p*-chlorophenylhydrazinium chloride (**2b**–HCl) and *p*-methylphenylhydrazinium chloride (**2d**–HCl) in ethanol afforded the dehydrated products **4ab-A** and **4ad-A**. Reactions of **1b** or **1c** with **2b**–HCl, **2c** and **2d**–HCl afforded **4bb-A**, **4bc-A** and **4bd-A**, and


1a: para
1b: meta
1c: ortho
+ R
NHNH2
2a: R=H
2b: R=Cl
2c: R=NO2
2d: R=CH3
NHNH
OH
3
N=N
4-A
N—NH
4-H

Scheme 2

TABLE 1
Physical Properties of **4**

Compound	*Recrystallization solvent*	*Appearance*
4aa-A	Hexane	Yellow needles
4ab-A	Hexane	Yellow prisms
4ac-A	Cyclohexane	Yellow plates
4ad-A	Hexane	Reddish brown prisms
4ba-H	Ethyl acetate	Yellow needles
4ba-A	Deuteriochloroform	Yellow solid
4bb-A	Cyclohexane	Orange prisms
4bc-A	Carbon tetrachloride	Yellow prisms
4bd-A	Hexane	Reddish brown prisms
4ca-H	Benzene	Yellow needles
4cc-A	Carbon tetrachloride	Yellow needles
4cd-A	Cyclohexane	Orange prisms

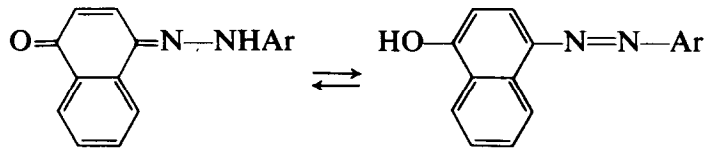
those of **1c** with **2c** and **2d**–HCl gave **4cc-A** and **4cd-A**, respectively. The recrystallization solvents and appearance of compounds **4** are summarized in Table 1.

2.2 Tautomerism

The ratios of the azo and hydrazone forms of **4** were determined by ^{1}H-NMR spectroscopy and are summarized in Table 2.

TABLE 2
Relative Ratios of Hydroxyazo Form and Ketohydrazone Form of **4** and δ-Values of OH and NH Protons

		Ratio A/H			*δ OH/NH*		
Compound	*R*	*In CD_3CN*	*In $CDCl_3$*	*In C_6D_6*	*In CD_3CN*	*In $CDCl_3$*	*In C_6D_6*
4aa	H	80/20	100/0	95/5	12·16/8·80	12·66	13·02/8·14
4ab	Cl	95/5	100/0	100/0	11·96/8·86	12·56	12·72
4ac	NO_2	70/30	100/0	100/0	11·32/9·24	12·03	12·00
4ad	CH_3	70/30	90/10	95/5	12·38/8·74	12·83/8·34	13·28/8·16
4ba	H		5/95			13·27/8·46	
4bb	Cl		100/0	100/0		13·19	13·29
4bc	NO_2		95/5	100/0		12·82/8·68	12·76
4bd	CH_3	65/35	95/5	100/0	13·10/8·92	13·42/8·44	13·82
4ca	H		0/100			8·37	
4cc	NO_2		80/20			13·07/8·60	
4cd	CH_3		100/0			13·50	



Scheme 3

It has been reported that, in 4-arylazo-1-naphthols,[3] the equilibrium between the azo and hydrazone tautomer (Scheme 3) depends on the solvent polarity and the azo form is predominant in solvents of high dielectric constant.

The solvent effect on the azo–hydrazone equilibrium of **4** is the reverse of that with 1-arylazo-4-naphthols, the azo form being more favored in chloroform compared with acetonitrile. The azo–hydrazone tautomeric equilibrium also depends upon substituent effects. The effect of a substituent in the *para* position of the arylhydrazine on the equilibrium of **4** is unusual in that both electron-withdrawing and electron-donating substituents favor the azo forms rather than hydrazone.

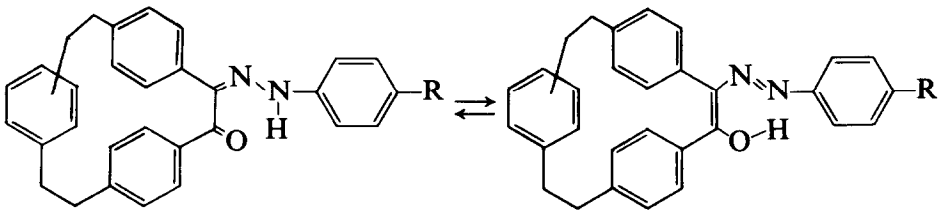
Interestingly, the effect of the cyclophane-ring structure is clearly shown in the equilibrium in phenylhydrazones **4aa**, **4ba** and **4ca**. Compounds **4aa–4ad**, in which all of the three benzene rings are connected in a *para* fashion, predominantly adopt the azo form **4-A** in the solid phase and in deuteriochloroform and trideuterioacetonitrile solution, whilst the *meta* and *ortho* isomers, **4b** and **4c**, exist in the hydrazone form **4-H**. This is in accord with the decreasing order of cyclophane-ring strain from **4aa–4ad** to **4ba–4bd** and **4ca–4cd**. The hydrazone form is favoured in the less strained cyclophanes. Such a marked influence of the cyclophane ring was not observed in arylhydrazones **4** bearing a *para* substituent.

2.3 ^{1}H-NMR spectra of 4

δ-Values of the hydroxy and amido proton of **4** in hexadeuteriobenzene, deuteriochloroform, and trideuterioacetonitrile are shown in Table 2.

Introduction of a nitro group and a chlorine atom lowered the electron density on the NH nitrogen atom of the hydrazone **4-H**. Thus, NH signals of **4-H** bearing the electron-withdrawing group was observed at lower field relative to the unsubstituted and *p*-methyl-substituted **4-H**. In the azo tautomer **4-A**, the hydrogen bonding between the OH group and the azo nitrogen atom may be weakened (Scheme 4), as an electron-withdrawing group decreases the electron density on the nitrogen atom. The OH-protons of **4ab-A** and **4ac-A** appeared at higher field than those of **4aa-A** and **4ad-A**, as expected.

Finally, it should be noted that OH signals are sensitive to the ring strain



4-H **4-A**

Scheme 4

of cyclophanes **4**. The signal of *para–para–para*-cyclophanes **4aa-A–4ad-A** appeared at 0·6–0·8 ppm higher field than the corresponding ones of *para–meta–para* cyclophanes **4ba-A–4bd-A**, which showed the signals at about 0·1–0·3 ppm higher field than *para–ortho–para* cyclophanes **4ba-A–4bd-A**. This seems to be in agreement with the decreasing order of the cyclophane-ring strain in **4-A**.

3 EXPERIMENTAL

3.1 General

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nippon Bunko A-102 spectrophotometer (KBr). ^{1}H-NMR (internal Me_4Si) spectra were taken on a Nippon Denshi JEOL FT-100 NMR spectrometer in $CDCl_3$. Mass spectra were recorded on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct-inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300). Preparative thin-layer chromatography was conducted on concentrating-zone precoated plate (20 cm × 20 cm, Kiesel gel $60F_{254}S$).

3.2 Phenylhydrazone of 1a (4aa)

A mixture of **1a** (80 mg, 0·24 mmol) and **2a** (28 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 1·5 h and the precipitated yellow prisms **3aa** (98 mg) were collected by filtration, m.p. 127–131°C (decomp.). IR, *v*: 3450, 3300, 3250, 3050, 2930, 2870, 1670, 1600, 1510, 1440, 1260, 1220, 1180, 1050, 930, 750, 690 cm^{-1}. MS: *m/e* 340 ($M^+ - NH_2NHPh$). Analysis: calcd for $C_{30}H_{28}O_2N_2$: C, 80·3; H, 6·3; N, 6·25. Found: C, 80·2; H, 6·3; N, 6·4%.

Compound **3aa** was refluxed in ethanol (5 ml) for 2 h and the solvent was evaporated *in vacuo*. The residue was washed with a small amount of ethanol

giving **4aa**, which, on recrystallization from hexane, afforded **4aa-A** (54 mg, 54%) as yellow needles, m.p. 163–168°C (decomp.). IR ν, 3050, 2930, 2850, 1600, 1590, 1510, 1460, 1440, 1230, 1180, 1170, 1030, 1010. 970, 820, 750, 690 cm^{-1}. ^{1}H-NMR δ, 2·96 (4H, s), 3·02 (4H, s), 6·56–7·36 (17H, m), 12·66 (1H, br s). MS: *m/e* 430 (M^+). Analysis: Calcd for $C_{30}H_{26}ON_2$: C, 83·7; H, 6·1; N, 6·5. Found: C, 83·3; H, 6·1; N, 6·7%.

3.3 Phenylhydrazone of 1b (4ba)

A mixture of **1b** (80 mg, 0·24 mmol) and **2a** (28 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 0·5 h and the precipitated unstable **3ba** (89 mg) was collected by filtration. Compound **3ba** was then refluxed in ethanol (5 mL) for 2 h and the precipitate filtered. Recrystallization from ethyl acetate gave **4ba-H** (65 mg, 64%) as yellow needles, m.p. 218–222°C (decomp.). IR ν, 3230, 3030, 2950, 2870, 1650, 1610, 1530, 1510, 1490, 1240, 1190, 1160, 1080, 1060, 1020, 920, 760 cm^{-1}. ^{1}H-NMR δ, 2·60–3·12 (8H, m), 6·16 (1H, br s), 6·66 (2H, d, J = 8·5 Hz), 7·01 (2H, d, J = 8·5 Hz), 6·80–7·38 (12H, m), 8·46 (1H, br s). MS: *m/e* 430 (M^+). Analysis: Calcd for $C_{30}H_{26}ON_2$: C, 83·7; H, 6·1; N, 6·5. Found: C, 83·5; H, 6·15; N, 6·7.

3.4 Phenylhydrazone of 1c (4ca)

A mixture of **1c** (60 mg, 0·18 mmol) and **2a** (21 mg, 0·19 mmol) in ethanol (5 ml) was stirred at room temperature for 1 h and the precipitated yellow unstable **3ca** (71 mg) was collected by filtration. **3ca** was then refluxed in ethanol (5 ml) for 2 h and the precipitate filtered and recrystallized from benzene, affording **4ca-H** (47 mg, 62%) as yellow needles; m.p. 283–287°C (decomp.). IR ν 3240, 3030, 2950, 1650, 1610, 1540, 1500, 1490, 1230, 1170, 1080, 1060, 1020, 920, 830, 760, 750, 740 cm^{-1}. ^{1}H-NMR δ 2·64–3·16 (8H, s), 6·63 (2H, d, J = 8·5 Hz), 6·76 (2H, s), 6·77 (2H, s), 6·80 (2H, d, J = 8·5 Hz), 6·88–7·60 (9H, m), 8·37 (1H, br s). MS: *m/e* 430 (M^+). Analysis: Calcd for $C_{30}H_{26}ON_2$: C, 83·7; H, 6·1; N, 6·5. Found: C, 83·9; H, 6·1; N, 6·5%.

3·5 *p*-Chlorophenylhydrazone of 1a (4ab)

A mixture of **1a** (80 mg, 0·24 mmol) and **2b**–HCl (46 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 15 h and the precipitated **4ab** was filtered. The filtrate was evaporated *in vacuo* and the residue was extracted with CH_2Cl_2 (5 ml). The extract was subjected to PLC using ethyl acetate–carbon tetrachloride (1:10) as an eluant, giving additional **4ab**. Recrystallization from hexane afforded **4ab-A** (78 mg, 71%) as yellow prisms; m.p. 179–187°C (decomp.). IR ν 3030, 2930, 2860, 1610, 1600, 1520,

1500, 1230, 1180, 1170, 1030, 1010, 970, 830 cm^{-1}. ^{1}H-NMR δ 2·99 (4H, s), 3·04 (4H, s), 6·75 (2H, d, J = 8·5 Hz), 6·81 (2H, s), 6·83 (2H, s), 6·85 (4H, s), 6·96 (2H, d, J = 8·5 Hz), 7·23 (4H, s), 12·56 (1H, br, s). MS: *m/e* 466 (M^+), 464 (M^+). Analysis: Calcd for $C_{30}H_{25}ON_2Cl$: C, 77·5; H, 5·4; N, 6·0. Found: C, 77·8; H, 5·55; N, 5·9%.

3.6 *p*-Chlorophenylhydrazone of 1b (4bb)

A mixture of **1b** (80 mg, 0·24 mmol) and **2b**–HCl (46 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 13 h and treated as described in the preparation of **4ab**, giving **4bb** which, on recrystallization from cyclohexane, gave **4bb-H** (83 mg, 76%) as orange prisms; m.p. 231–233°C. IR ν 3030, 2930, 2860, 1610, 1600, 1520, 1500, 1220, 1180, 1170, 1030, 1010, 970, 830 cm^{-1}. ^{1}H-NMR δ, 2·60–3·12 (8H, m), 6·33 (1H, br s), 6·72 (2H, d, J = 8·5 Hz), 6·83 (2H, s), 6·84 (2H, s), 6·93 (2H, d, J = 8·5 Hz), 7·00–7·34 (7H, m), 13·19 (1H, br s). MS: *m/e* 466 (M^+), 464 (M^+). Analysis: Calcd for $C_{30}H_{25}ON_2Cl$: C, 77·5; H, 5·4; N, 6·0. Found: C, 78·0; H, 5·65; N, 6·1%.

3.7 *p*-Nitrophenylhydrazone of 1a (4ac)

A mixture of **1a** (80 mg, 0·24 mmol) and **2c** (40 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 2 h and the precipitated yellow powder **3ac** (95 mg) was collected by filtration. Compound **3ac** was then refluxed in ethanol (5 ml) for 15 h. The solvent was evaporated *in vacuo* and the residue was chromatographed using benzene as an eluant. Crude **4ac** was recrystallized from cyclohexane, giving **4ac-A** (50 mg, 45%) as yellow plates; m.p. 201–205°C (decomp.). IR ν 3300, 3050, 2950, 2870, 1600, 1530, 1510, 1330, 1250, 1170, 1110, 1010, 970 cm^{-1}. ^{1}H-NMR δ 2·98 (4H, s), 3·04 (4H, s), 6·76 (2H, d, J = 8·5 Hz), 6·78 (2H, s), 6·80 (2H, s), 6·87 (4H, s), 6·98 (2H, d, J = 8·5 Hz), 7·28 (2H, d, J = 9 Hz), 8·17 (2H, d, J = 9 Hz), 12·03 (1H, br s). MS: *m/e* 475 (M^+). Analysis: Calcd for $C_{30}H_{25}O_3N_3$: C, 75·8; H, 5·3; N, 8·8. Found: C, 75·7; H, 5·4; N, 8·9%.

3.8 *p*-Nitrophenylhydrazone of 1b (4bc)

A mixture of **1b** (80 mg, 0·24 mmol) and **2c** (40 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 2 h and the precipitated yellow powder **3bc** (102 mg) was collected by filtration. Compound **3bc** was refluxed in ethanol (5 ml) for 4 h and the precipitated **4bc** was filtered. The filtrate was evaporated *in vacuo* and the residue was washed with hot ethanol (1 ml), giving additional **4bc**. Recrystallization from carbon tetrachloride afforded

4bc-A (94 mg, 84%) as yellow prisms; m.p. 233–234°C (decomp.). IR ν 3040, 2950, 2870, 1600, 1530, 1510, 1330, 1010 cm^{-1}. ^{1}H-NMR δ 2·60–3·16 (8H, m), 6·32 (1H, br s), 6·76 (2H, d, J = 8·5 Hz), 6·88 (4H, s), 6·98 (2H, d, J = 8·5 Hz), 7·02–7·22 (3H, m), 7·37 (2H, d, J = 9 Hz), 8·24 (2H, d, J = 9 Hz), 12·82 (1H, br s). MS: *m/e* 475 (M^+). Analysis: Calcd for $C_{30}H_{25}O_3N_3$: C, 75·8; H, 5·3; N, 8·8%. Found: C, 75·5; H, 5·3; N, 8·95%.

3.9 *p*-Nitrophenylhydrazone of 1c (4cc)

A mixture of **1c** (80 mg, 0·24 mmol) and **2c** (40 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 2·5 h and the precipitated **3cc** (88 mg) was collected by filtration. Compound **3cc** was refluxed in ethanol (5 ml) for 4 h and the precipitated **4cc** was filtered and purified by PLC using methylene chloride as an eluant and subsequently by recrystallization from carbon tetrachloride: **4cc-A** (78 mg, 70%) as yellow needles; m.p. 233–234°C (decomp.). IR ν 3030, 2930, 2880, 1600, 1530, 1510, 1330, 1240, 1160, 1110, 1000 cm^{-1}. ^{1}H-NMR δ 2·66–3·20 (8H, m), 6·56–6·92 (8H, m), 7·08–7·58 (6H, m), 8·12–8·32 (2H, m), 8·60 and 13·07 (total 1H, br s). MS: *m/e* 475 (M^+). Analysis: Calcd for $C_{30}H_{25}O_3N_3$: C, 75·8; H, 5·3; N, 8·8. Found: C, 75·6; H, 5·3; N, 9·0%.

The filtrate was evaporated *in vacuo* and the residue was washed with methylene chloride (0·5 ml) and then recrystallized from chloroform, giving the bishydrazone **5** as reddish orange needles (5 mg); m.p. 286–290°C (decomp.). IR ν 3320, 3020, 2930, 1600, 1500, 1330, 1260, 1110, 840, 750 cm^{-1}; ^{1}H-NMR δ 2·64–3·16 (8H, m), 6·54–6·88 (8H, m), 6·96–7·56 (8H, m), 8·12–8·24 (6H, m). MS: *m/e* 610 (M^+). Analysis: Calcd for $C_{36}H_{30}O_4N_6$: C, 70·8; H, 4·95; N, 13·8. Found: C, 70·8; H, 5·0; N, 13·6%.

3.10 *p*-Methylphenylhydrazone of 1a (4ad)

A mixture of **1a** (80 mg, 0·24 mmol) and **2d**–HCl (41 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 2 h and the precipitated **4a** was collected by filtration. The filtrate was evaporated *in vacuo* and the residue extracted with methylene chloride (5 ml). The extract was evaporated *in vacuo* and the residue was chromatographed with hexane–ethyl acetate (8:1) as eluant, giving additional **4ad**. Recrystallization from hexane afforded **4ad-A** (76 mg, 72%) as reddish brown prisms; m.p. 150–152°C (decomp.). IR ν 3030, 2930, 2860, 1610, 1510, 1440, 1410, 1220, 1170, 1030, 1010, 970, 820 cm^{-1}. ^{1}H-NMR δ 2·30 (3H, s), 2·97 (4H, s), 3·02 (4H, s), 6·72 (2H, d, J = 8·5 Hz), 6·79 (2H, s), 6·81 (2H, s), 6·82 (2H, s), 6·92 (2H, d, J = 8·5 Hz), 7·00–7·20 (4H, m), 12·83 (1H, br s). MS: *m/e* 444 (M^+). Analysis: Calcd for $C_{31}H_{28}ON_2$: C, 83·75; H, 6·35; N, 6·3. Found: C, 83·5; H, 6·4; N, 6·3%.

3.11 *p*-Methylphenylhydrazone of 1b (4bd)

A mixture of **1b** (80 mg, 0·24 mmol) and **2d**–HCl (41 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 2·5 h and the precipitated **4bd** was collected by filtration. The filtrate was evaporated *in vacuo* and the residue extracted with methylene chloride (5 ml). The extract was evaporated *in vacuo* and the residue was chromatographed, using benzene as eluant, giving additional **4bd**. Recrystallization from hexane gave **4bd-A** (82 mg, 79%) as reddish brown prisms; m.p. 229–232°C (decomp.). IR ν 3030, 2930, 2870, 1520, 1220, 1180, 1040, 1020, 970 cm^{-1}. ^{1}H-NMR δ 2·33 (3H, s), 2·68–3·16 (8H, m), 6·35 (1H, br s), 6·72 (2H, d, J = 8·5 Hz), 6·83 (2H, s), 6·86 (2H, s), 6·93 (2H, d, J = 8·5 Hz), 7·00–7·36 (7H, m), 13·42 (1H, br s). MS: *m/e* 444 (M^+). Analysis: Calcd for $C_{31}H_{28}ON_2$: C, 83·75; H, 6·35; N, 6·3. Found: C, 83·8; H, 6·4; N, 6·3%.

3.12 *p*-Methylphenylhydrazone of 1c (4cd)

A mixture of **1c** (80 mg, 0·24 mmol) and **2d**–HCl (41 mg, 0·26 mmol) in ethanol (5 ml) was stirred at room temperature for 3 h and the precipitated **4cd** was collected by filtration. The filtrate was evaporated *in vacuo* and the residue was extracted with methylene chloride (5 ml). The extract was evaporated *in vacuo*, giving additional **4cd**. Recrystallization from cyclohexane afforded **4cd-A** (89 mg, 85%) as orange prisms; m.p. 213–218°C (decomp.). IR ν 3040, 2940, 2880, 1610, 1520, 1220, 1180, 1030, 1010, 970 cm^{-1}. ^{1}H-NMR δ 2·33 (3H, s), 2·64–3·16 (8H, m), 6·64 (2H, d, J = 8·5 Hz), 6·68 (2H, s), 6·70 (2H, s), 6·74 (2H, d, J = 8·5 Hz), 7·02–7·58 (4H, m), 7·14 (2H, d, J = 9 Hz), 7·28 (2H, d, J = 9 Hz), 13·50 (1H, br s). MS: *m/e* 444 (M^+). Analysis: Calcd for $C_{31}H_{28}ON_2$: C, 83·75; H, 6·35; N, 6·3. Found: C, 83·9; H, 6·4; N, 6·2%.

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