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1,3-Dipolar Cycloaddition Reactions of 2,4,6-Cycloheptatrien-1-imines with Benzonitrile Oxides Leading to 1,2,4-Oxadiazaspiro[4.6]undeca-2,6,8,10-tetraenes

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1,3-Dipolar cycloaddition reactions of *N*-aryl-2,4,6-cycloheptatrien-1-imines with *p*-substituted benzonitrile oxides afforded [2+3]-type cycloadducts in considerable yields. A study of the substituent effect on the reaction rate revealed that the reactions proceeded through nucleophilic reactions of imines to nitrile oxides. Thermal isomerizations and addition reactions of the adducts showed that the contribution of a valence isomerization between cycloheptatriene and norcaradiene lay to the side of the cycloheptatriene form. A comparison of the UV spectra between the adduct and its derivative, which was reduced by catalytic hydrogenation, implies that the spiroconjugation between cycloheptatriene and a five-membered heterocyclic moiety causes a shift of the equilibrium.

1,3-Diploar cycloaddition reactions are one of the most useful reactions for the syntheses of heterocyclic compounds, due to a high degree of site-, regio-, and stereoselectivity. Furthermore, these reactions have attracted the attention of chemists from the stand point of reaction mechanisms. Nitrile oxides are known to be among the active dipoles in 1,3-dipolar reactions, and have been extensively investigated from the viewpoints of synthetic utility and of elucidation of the reaction mechanism of 1,3-dipolar reactions.[1] In spite of many studies concerning the reaction of nitrile oxides, we are unaware of their reactions with troponoid compounds, except for the reaction with 2,4,6-cycloheptatrien-1-one.[2]

2,4,6-Cycloheptatrien-1-imines possess dipolar properties due to the contributions of 6π electrons aromatic structures as well as the case of 2,4,6-cycloheptatrien-1-one.[3] Despite their aromaticities, 2,4,6-cycloheptatrien-1-imines are fairly active in addition reactions, and are known to react only as 8π components.[4] Gandolfi and Toma reported that the reactions of 2,4,6-cycloheptatrien-1-imines with benzonitrile phenylimide afforded [8+4]-type adducts via [2+3]-type cycloadducts as the intermediates.[4a] However, they did not succeed in isolating the [2+3]-type adducts.

As a series of our investigations concerning cycloaddition reactions of troponoid compounds,[4c,5] we studied the reactions of *N*-aryl-2,4,6-cycloheptatrien-1-imines with *p*-substituted benzonitrile oxides to give [2+3]-type cycloadducts in good yields. Here, the results are reported.

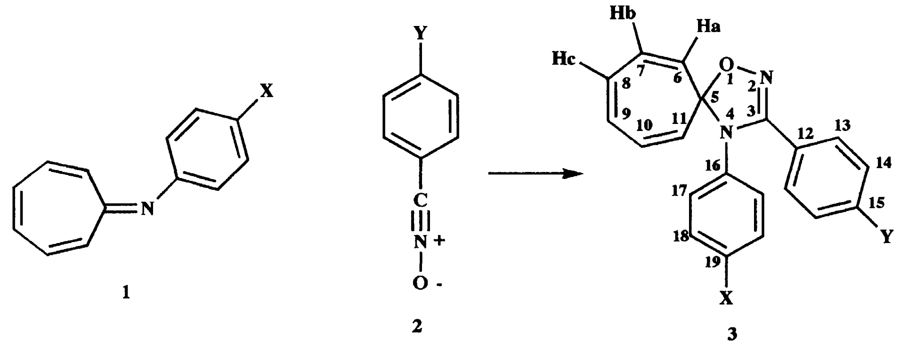
Results and Discussion

A mixture of *N*-*p*-methoxyphenyl-2,4,6-cycloheptatrien-1-imine (**1a**)[6] and two equimolar amounts of benzonitrile oxide (**2a**)[7] was stirred at room temperature for 30 min to give a [2+3]-type adduct (**3a**), 1,2,4-oxadiazaspiro[4.6]undeca-2,6,8,10-tetraene derivative, in 90% yield. Analogous reactions using **1b**—**d** and **2a**—**e** afforded the corresponding adducts (**3**) in considerable yields. The results are summarized in Table 1.

The structures of **3** were elucidated on the bases of their spectral properties. The mass spectra demonstrated that the products were 1 : 1 adducts of **1** and **2**. ^{1}H and ^{13}C NMR spectra showed the existence of 7,7-disubstituted 2,4,6-cycloheptatriene moieties and two aryl groups. The chemical shifts of the signal of C_5 (ca. 100 ppm) on oxadiazoline moieties of **3** are similar to

Table 1. Yields of the Adducts

2,4,6-Cycloheptatrien-1-imines	Nitrile oxides	Adducts yields (%)
1a	**2a**	**3a** (90)
1b	**2a**	**3b** (86)
1c	**2a**	**3c** (92)
1d	**2a**	**3d** (98)
1b	**2b**	**3e** (77)
1b	**2c**	**3f** (89)
1b	**2d**	**3g** (95)
1b	**2e**	**3h** (98)
1c	**2b**	**3i** (89)
1c	**2c**	**3j** (91)
1c	**2d**	**3k** (91)
1c	**2e**	**3l** (87)



a: X=OMe,
b: X=Me,
c: X=Cl,
d: X=Br

a: Y=H,
b: Y=OMe,
c: Y=Me,
d: Y=Cl,
e: Y=CN

a: X=OMe, Y=H,
b: X=Me, Y=H,
c: X=Cl, Y=H,
d: X=Br, Y=H,
e: X=Me, Y=OMe,
f: X=Me, Y=Me,
g: X=Me, Y=Cl,
h: X=Me, Y=CN,
i: X=Cl, Y=OMe,
j: X=Cl, Y=Me,
k: X=Cl, Y=Cl,
l: X=Cl, Y=CN

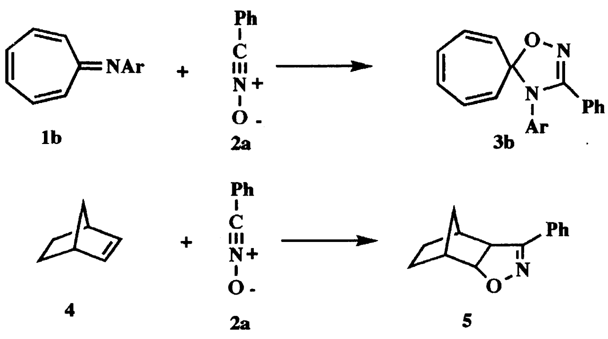
Scheme 1.

those of the analogous compounds.[8)] NOE experiments taught that the two aryl groups are located close to each other. Irradiation on the signals of the aryl groups of **3a** (H_{17} and H_{18}) caused a 20% enhancement of the signals of the phenyl protons, supporting the structure of **3** to be as shown in Scheme 1, which has the aryl and phenyl groups adjoining each other.

For the purpose of the clarifying the solvent effect in the reaction, competition reaction experiments were performed. Benzonitrile oxide (**2a**) was reacted with a 1 : 1 mixture of *N*-*p*-tolyl-2,4,6-cycloheptatrien-1-imine (**1b**) and nobornene (**4**) in various solvents of different polarity (Scheme 2). The relative rate ratios (k_{1b}/k_4) of the two reactions, i.e., the reaction of **2a** with **1b** and the reaction of **2a** with **4**, were calculated using the yields of each adduct (**3b** and **5**). The results are summaried in Table 2. The reaction of **2a** with **4** is known to be a concerted reaction;[1b)] therefore, the relative rate ratios (k_{1b}/k_4) reflect the degree of influence of the solvent polarity on the reaction rate of **1b** with **4**. The obtained ratios (k_{1b}/k_4) show that the solvent effect on the reaction rate of **1b** with **2a** is too small to support the existence of any ionic intermediates.[4a)] Thus, the reaction is considered to proceed through a concerted pathway.

Table 2. The Results of the Competition Reactions of Nitrile Oxides with Excess 2,4,6-Cycloheptatrien-1-imines and Norbornene in Solvents of Different Polarity

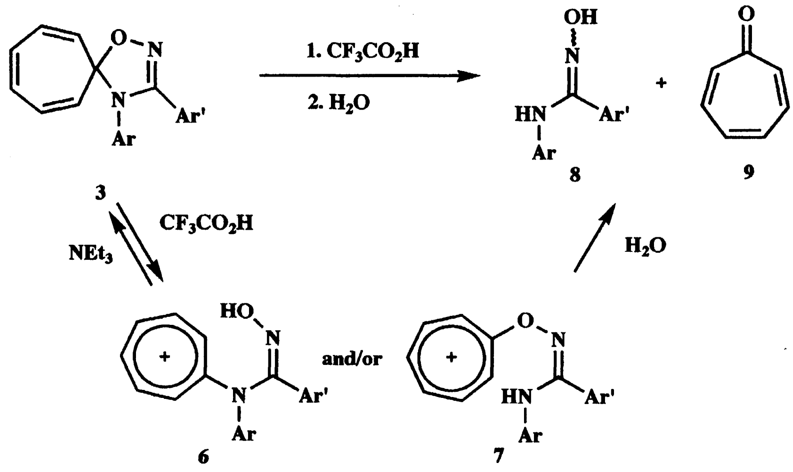
Solvent	E_T	k_{1b}/k_4
MeOH	55.5	1.89
EtOH	51.9	1.61
MeCN	46.0	1.56
AcOEt	38.1	0.66
PhH	34.5	0.51
CCl_4	32.5	0.57
n-hexane	30.9	0.45



Scheme 2.

In order to elucidate the substituent effect in this reaction, the relative rate ratios (k_X/k_H) on the reactions of **1** with *p*-substituted benzonitrile oxides (**2a**—**d**) were measured in a similar way to our previous method.[9)] The ratios of 1.00 : 0.46 : 0.54 : 1.35 for **2a** : **2b** : **2c** : **2d** using **1b** and 1.00 : 0.56 : 0.65 : 1.32 for those using **1c** were obtained (Fig. 1). There are fairly good linear relations between their logarithms ($\log k_X/k_H$) and Hammett's sigma values (σ_p).[10)] The magnitude of the ρ-values (+0.99 and +0.76) is small, suggesting that the reaction proceeded via a concerted manner and, that the positive ρ-values reflect the nucleophilic attact of **1** to **2**. Thus, the reaction is governed by the interaction between the HOMO of **1** and the LUMO of **2**.[9)]

The ^{1}H NMR spectrum of **3b** was measured in the presence of trifluoroacetic acid (Fig. 2). As the signals of the 2,4,6-cycloheptatriene moiety (at 5.95 ppm (H_a) and 6.40 ppm (H_b and H_c)) disappeared, the signals of tropylium ion species (**6b** and/or **7b**) appeared at 8.30—9.00 ppm. The treatment of **6b** and/or **7b** with triethylamine afforded the starting materials (**3b**) quantitatively (Scheme 3). On the other hand, the hydrolysis of the ions (**6b** and/or **7b**) using water gave an oxime derivative (**8b**) and 2,4,6-cycloheptatrien-1-one (**9**), in quantitative yields, respectively. A similar hydrolysis using **3d** afforded the corresponding oxime derivative



Scheme 3.

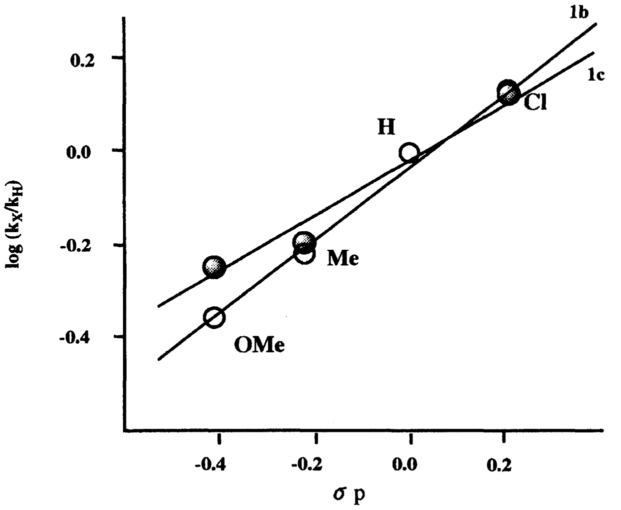


Fig. 1. Correlation of relative rate ratios of the reactions of benzonitrile oxides for *N*-*p*-tolyl-2,4,6-cycloheptatrien-1-imine (**1b**): ○ and *N*-*p*-chlorophenyl-2,4,6-cycloheptatrien-1-imine (**1c**): ● with Hammett's σ_p Values.

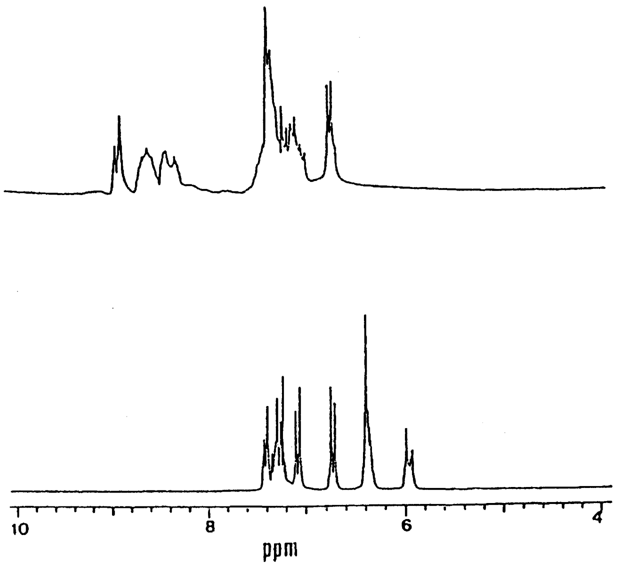


Fig. 2. Upper; ^{1}H NMR spectrum of **3b** in the presence of trifluoroacetic acid in $CDCl_3$. Lower; ^{1}H NMR spectrum of **3b** in $CDCl_3$.

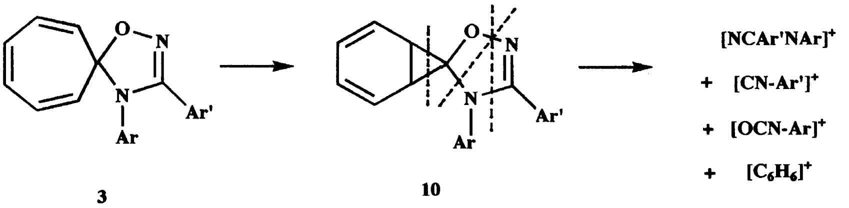
(**8d**) and **9** in quantitative yields, respectively.

The formation of the ionic species (**6** and/or **7**) was considered to proceed through the protonation on the nitrogen and/or oxygen atoms of **3**. A subsequent cleavage of the C–N and/or C–O bonds afforded the cations. Neutralization of the cations by triethylamine formed **3**; however, the addition of water caused a decomposition of the cation.

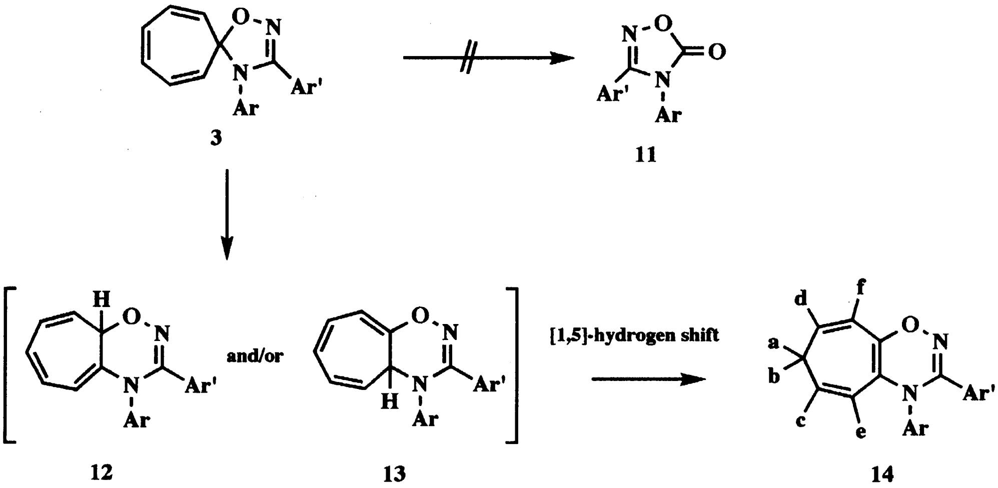
The structures of **3** were clarified to have a cycloheptatriene ring. On the contrary, similar spiro-compounds, such as spiro[4.6]undecapentaene derivatives, are known to exist as norcaradiene forms at room temperature and to give only norcaradiene-type cycloadducts in reactions with dienophiles.[11,12] Though no contribution of the norcaradiene form (**10**) could be detected in the ^{1}H NMR spectra of **3**, the mass spectra showed some interesting fragment peaks of $[NCAr'NAr]^+$, $[NCAr']^+$, $[OCNAr]^+$, and $[C_6H_6]^+$ (Scheme 4). It seems reasonable to consider that these fragment peaks generate through the norcaradiene form (**10**).

Previously, Gandolfi and Toma reported that the thermal decomposition of the adduct between cycloheptatrien-1-imine with benzonitrile phenylimide in the presence of air gave triazolinone derivatives through the norcaradiene form.[4a)] A similar thermal reaction using **3** under the same reaction condition (in toluene at 110 °C in the presence of air) did not afford any product, except for polymeric materials; however, the thermal reaction of **3c** at lower temperature (at 60 °C for 50 h) gave a thermal isomer (**14c**), 4,7-dihydrocyclohepta[*e*]-[1,2,4]oxadiazine derivatives, in 14% yield (Scheme 5). A similar thermal reaction of **3d** also afforded the corresponding product (**14d**) in 9% yield.

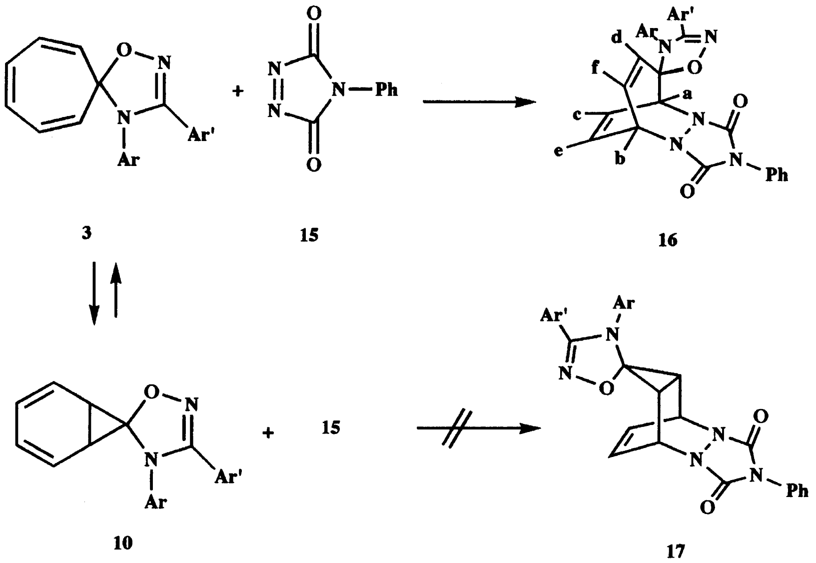
The structures of the products (**14**) were deduced



Scheme 4.



Scheme 5.



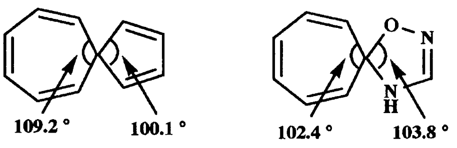
Scheme 6.

using their spectral properties, and were confirmed by their coincidence to those of the analogous 4,5-disubstituted cycloheptatriene derivatives.[4c)] The molecular ion peaks of the products (**14**) coincided with those of the starting materials (**3**). The ^{1}H and ^{13}C NMR spectra showed the existence of 4,5-disubstituted cycloheptatriene and two aryl groups. The chemical shifts of carbon atoms (C_3; 156 ppm, C_5; 141 ppm, C_6; 146 ppm) on the heterocyclic moieties in ^{13}C NMR spectra were very similar to those of the analogous compounds.[8)]

This thermal reaction is considered to proceed through a ring expansion of the five-membered ring to give the 1,7-disubstituted cycloheptatriene derivative (**12** and/or **13**). A subsequent [1,5]-hydrogen shift of the angular proton gave the final products (**14**).[13)]

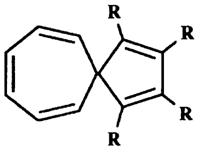
In order to clarify whether **3** possesses a contribution of its norcaradiene form or not, cycloaddition reactions of **3** with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**15**) were performed (Scheme 6).

A mixture of **3b** and **15** in dichloromethane was



18 19

Fig. 3. The external and internal angles of **18** and **19** calculated by PM3 Method.



20

a: R=Cl,
b: R=Ph

Fig. 4.

stirred at room temperature for 2 h to give the [4+2]-type cycloadduct (**16b**) in 58% yield. Similar reactions using **3c** and **3g** also gave the corresponding adducts (**16c** and **16g**) in 65 and 46% yields, respectively.

The structures of **16** were deduced as follows. The mass spectra demonstrated that the products were 1 : 1 adducts between **3** and **15**. The IR spectra showed absorptions of the carbonyl group at ca. 1710 cm^{-1}. The assignment of the protons in the ^{1}H NMR spectra was made using the double-resonance technique. The absence of characteristic signals for the cyclopropane ring at a very high field (ca. 0.5—3.0 ppm)[14] in the ^{1}H NMR spectra means that the structure of **17** is not suitable for that of the product. The ^{13}C NMR spectra showed the existence of oxadiazoline moieties (C_1, ca. 114 ppm, C_2; ca. 158 ppm).[8] The configurations of the oxadiazoline rings were determined by an NOE experiment. Irradiation on the signals of aryl protons caused a 9% enhancement in the signal of the proton H_c, supporting the structures of **16** to be as shown in the figure. This result suggests that the contribution of the norcaradiene form (**10**) in **3** is either quite small or does not exist.

Due to our desire to explain the inclination of the equilibrium of **3** on the side of the cycloheptatriene form, we carefully examined **3** according to the previously reported factors: e.g. 1) the external angle at the C_5 position,[15] 2) the stabilization of the antisymmetric component of the Walsh orbital pair between C_6 and C_{11} due to the introduction of the acceptor orbital of the electron withdrawing substituent at C_5 position,[16] and so on.[17,18] The external angle at the spiro atom position of the cycloheptatriene moiety of **3** was evaluated by a PM3 MO calculation using a model compound (**19**) and a reference compound (**18**) (Fig. 3), which was known to be in a norcaradiene form.[19] The calculations showed that the value for **19** (103.8°) is larger than that for **18** (100.1°). In other words, the internal angle is smaller in **19**. This result indicates that **19** should prefer the norcaradiene form compared with **18**. Thus, the angle failes to account for the fact.

The signals of the protons H_a on the cycloheptatriene moiety of **3** (H_a; 5.90—6.60 ppm) were observed at lower fields than those of the analogous compounds (**20a**; 5.18, **20b**; 5.00 ppm) (Fig. 4).[11] This result means that the heterocyclic moiety of **3** behaves as an electron-withdrawing group. The MO calculation on **19** also suggests that introducing the oxadiazoline ring causes electron drawing from the seven-membered ring to the oxadiazoline moiety (the total electron density on the seven membered ring moiety was +0.100). Therefore, the stabilization of the antisymmetric component of the Walsh orbital in a cycloheptatriene moiety is not appropriate for an explanation in this case.

From these considerations, neither of the previously reported explanations seems to be valid in this case.[15—18] One explanation for the sole contribution

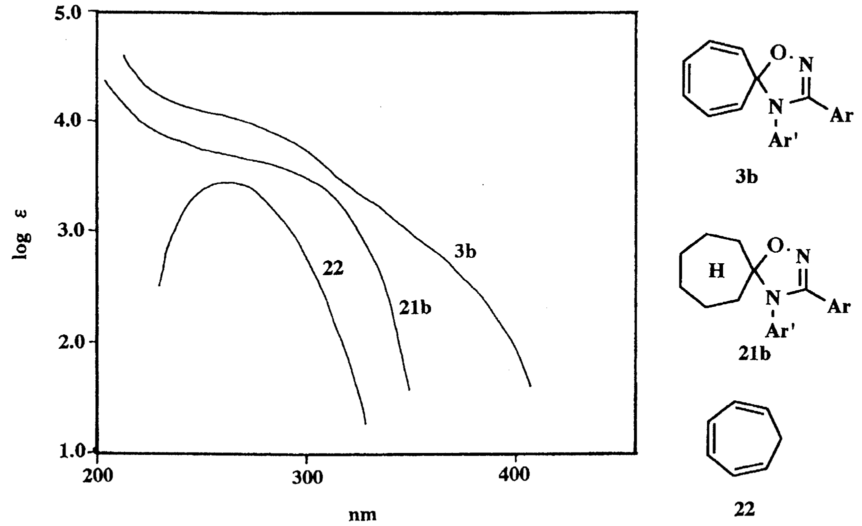


Fig. 5. UV spectra of **3b**, **21b**, and **22**.

of the cycloheptatriene form in **3** may be the stablization caused by the formation of the spiroconjugation between the five-membered heterocyclic ring and the cycloheptatriene moiety.[20)]

Comparing the UV spectra of (Fig. 5) **3b** and **21b**, which was derived from **3b** by catalytic hydrogenation, a bathochromic shift is found in **3b**. This result implies the existence of spiroconjugation between the five-membered heterocyclic part and the cycloheptatriene moiety.[20,21)]

Therefore, we propose another responsible factor to force the equilibrium to the side of cycloheptatriene form: spiroconjugation between cycloheptatriene and the five-membered heterocyclic moiety.

Experimental

The melting points were recorded on a Yanagimoto Micro Melting Point apparatus and were uncorrected. NMR spectra were measured with Hitachi R-90 or Varian XL-200 spectrometers. IR and UV spectra were measured with JASCO FT/IR-5300 and Hitachi 220A spectrophotometers, respectively. Mass spectra were taken on a Hitachi M-2000S spectrometer. Wakogel C-200 and Wakogel B-5 F were used for column and thin-layer chromatography, respectively.

General Procedure of the Addition Reactions of *N*-Aryl-2,4,6-cycloheptatrien-1-imines (1) with Nitrile Oxides (2). To a solution of **1** (0.5 mmol) and triethylamine (1.0 mmol) in dichloromethane (1.0 ml) was slowly added a solution of the corresponding benzohydroximoyl chloride (1.0 mmol) in dichloromethane (2.0 ml) at room temperature. After the addition was completed, the mixture was further stirred for 30 min and then poured into water, extracted with dichloromethane, and dried over anhydrous sodium sulfate. Removal of the solvent and chromatographic purification gave **3**.

3a: Pale yellow crystals, mp 118—119 °C (from toluene). High-resolution MS Found: *m/z* 330.1343. Calcd for $C_{21}H_{18}N_2O_2$: M, 330.1367. MS *m/z* (rel intensity) 330 (M^+; 19), 224 (10), 149 (100), 103 (95), 78 (68). UV (MeOH) 226 (sh. log ε, 4.24), 257 (sh. 3.91), 278 (sh. 3.77), 310 nm (sh. 3.30). IR (KBr) 1605, 1555, 1505, 1440, 1395, 1300, 1255, 1160, 1090, 770, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.71 (3H, s, Me), 6.04 (2H, m, H_a), 6.42 (4H, m, H_b and H_c), 6.65—6.95 (4H, m, aryl protons), 7.20—7.60 (5H, m, phenyl protons). ^{13}C NMR ($CDCl_3$) δ=55.3 (OMe), 99.6 (C_5), 114.0 (C_{18}), 125.8 (C_{12}), 127.3 (C_6, C_{11}, and C_{17}), 128.2 (C_7 and C_{10}), 128.4 (C_{13} or C_{14}), 129.0 (C_{14} or C_{13}), 129.7 (C_8 and C_9), 130.1 (C_{15}), 130.9 (C_{16}), 153.9 (C_3), 157.8 (C_{19}). Found: C, 76.08; H, 5.63; N, 8.49%. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.35; H, 5.49; N, 8.48%.

3b: Pale yellow crystals, mp 116—117 °C (from benzene). High-resolution MS Found: *m/z* 314.1410. Calcd for $C_{21}H_{18}N_2O$: M, 314.1417. MS *m/z* (rel intensity) 314 (M^+; 8), 208 (40), 133 (100), 103 (85), 78 (100). UV (MeOH) 252 (sh. log ε, 4.05), 282 (sh. 3.79), 297 (sh. 3.62), 313 nm (3.31). IR (KBr) 1595, 1560, 1510, 1445, 1390, 1300, 1260, 1130, 1060, 760, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.26 (3H, s, Me), 6.04 (2H, m, H_a), 6.42 (4H, m, H_b and H_c), 6.70—7.05 (4H, m, aryl protons), 7.15—7.65 (5H, m, phenyl protons). ^{13}C NMR ($CDCl_3$) δ=20.9 (Me), 99.6 (C_5), 125.8 (C_{12}), 126.9 (C_6 and C_{11}), 127.4 (C_{17}), 127.5 (C_7 and C_{10}), 128.3 (C_{13} or C_{14}), 128.4 (C_{14} or C_{13}), 129.1 (C_{19}), 129.4 (C_{18}), 129.8 (C_8 and C_9), 130.1 (C_{15}), 135.6 (C_{16}), 153.7 (C_3). Found: C, 80.16; H, 5.78; N, 8.86%. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91%.

3c: Pale yellow crystals, mp 104—105 °C (from benzene). High-resolution MS Found: *m/z* 334.0893. Calcd for $C_{20}H_{15}N_2OCl$: M, 334.0872. MS *m/z* (rel intensity) 336 (M^+; 5), 334 (M^+; 14), 230 (30), 228 (84), 155 (33), 153 (100), 103 (93), 78 (100). UV (MeOH): 252 (log ε, 3.96), 282 (sh. 3.84), 299 (sh. 3.60), 312 nm (3.27). IR (KBr) 1595, 1560, 1490, 1445, 1390, 1310, 1180, 1090, 765, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=6.02 (2H, m, H_a), 6.45 (4H, m, H_b and H_c), 6.74—7.22 (4H, m, aryl protons), 7.25—7.70 (5H, m, phenyl protons). ^{13}C NMR ($CDCl_3$) δ=100.2 (C_5), 125.4 (C_{12}), 127.1 (C_6 and C_{11}), 127.7 (C_7 and C_{10}), 128.0 (C_{17}), 128.1 (C_{13} or C_{14}), 128.6 (C_{14} or C_{13}), 128.8 (C_{18}), 129.9 (C_8 and C_9), 130.5 (C_{15}), 131.3 (C_{19}), 136.9 (C_{16}), 153.3 (C_3). Found: C, 71.89; H, 4.70; N, 8.23%. Calcd for $C_{20}H_{15}N_2OCl$: C, 71.75; H, 4.52; N, 8.37%.

3d: Pale yellow crystals, mp 120—121 °C (from toluene). High-resolution MS Found: *m/z* 378.0354. Calcd for $C_{20}H_{15}N_2OBr$: M, 378.0367. MS *m/z* (rel intensity) 380 (M^+; 13), 378 (M^+; 14), 274 (56), 199 (68), 197 (73), 103 (100), 78 (95). UV (MeOH) 258 (log ε, 4.03), 283 (3.93), 312 nm (3.48). IR (KBr) 1595, 1555, 1485, 1445, 1405, 1295, 1155, 1070, 770, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=6.06 (2H, m, H_a), 6.50 (4H, m, H_b and H_c), 6.68—7.70 (9H, m, aromatic protons). ^{13}C NMR ($CDCl_3$) δ=100.2 (C_5), 119.1 (C_{19}), 125.4 (C_{12}), 127.1 (C_6 and C_{11}), 127.7 (C_7 and C_{10}), 128.2 (C_{13} or C_{14}), 128.6 (C_{14} or C_{13}), 129.9 (C_8 and C_9), 130.5 (C_{15}), 131.8 (C_{18}), 137.4 (C_{16}), 153.2 (C_3). Found: C, 63.55; H, 4.24; N, 7.31%. Calcd for $C_{20}H_{15}N_2OBr$: C, 63.34; H, 3.99; N, 7.39%.

3e: Pale yellow crystals, mp 136—137 °C (from benzene). High-resolution MS Found: *m/z* 334.1522. Calcd for $C_{22}H_{20}N_2O_2$: M, 344.1522. MS *m/z* (rel intensity) 344 (M^+; 12), 329 (100), 238 (13), 133 (48), 107 (38), 78 (25). IR (KBr) 2940, 2847, 1609, 1591, 1557, 1514, 1426, 1391, 1256, 1175, 1090, 831, 816 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.20 (3H, s, Me), 3.70 (3H, s, OMe), 5.92 (2H, m, H_a), 6.30 (4H, m, H_b and H_c), 6.50—7.50 (8H, m, aromatic protons). ^{13}C NMR ($CDCl_3$) δ=20.9 (Me), 55.2 (OMe), 99.3 (C_5), 113.8 (C_{14}), 117.9 (C_{12}), 127.0 (C_6 and C_{11}), 127.3 (C_{17}), 127.6 (C_7 and C_{10}), 129.3 (C_{18}), 129.8 (C_8, C_9, and C_{13}), 130.0 (C_{19}), 135.7 (C_{16}), 153.5 (C_3), 161.0 (C_{15}). Found: C, 76.60; H, 5.87; N, 8.08%. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13%.

3f: Pale yellow crystals, mp 142—143 °C (from benzene). High-resolution MS Found: *m/z* 328.1583. Calcd for $C_{22}H_{20}N_2O$: M, 328.1575. MS *m/z* (rel intensity) 328 (M^+; 4), 222 (26), 133 (95), 117 (100), 78 (100). IR (KBr) 2924, 2855, 1597, 1514, 1458, 1420, 1391, 1298, 1183, 1142, 1082, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.27 (3H, s, Me), 2.32 (3H, s, Me), 6.04 (2H, m, H_a), 6.42 (4H, m, H_b and H_c), 6.72—7.44 (8H, m, aromatic protons). ^{13}C NMR ($CDCl_3$) δ=20.9 (Me), 21.4, (Me), 99.4 (C_5), 122.8 (C_{12}), 126.9 (C_6 and C_{11}), 127.3 (C_{17}), 127.6 (C_7 and C_{10}), 128.1 (C_{13} or C_{14}), 129.1 (C_{14} or C_{13}), 129.3 (C_{18}), 129.7 (C_8 and C_9), 135.5 (C_{16} or C_{19}), 135.7 (C_{19} or C_{16}), 140.3 (C_{15}), 153.7 (C_3). Found: C, 80.66; H, 6.19; N, 8.47%. Calcd for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53%.

3g: Pale yellow crystals, mp 97—98 °C (from benzene). High-resolution MS Found: *m/z* 350.0978. Calcd for $C_{21}H_{17}N_2OCl$: M, 350.0998. MS *m/z* (rel intensity) 348 (M^+; 25), 242 (100), 133 (100), 102 (36), 78 (100). IR (KBr) 2924, 2855, 1593, 1512, 1495, 1496, 1453, 1404, 1385, 1306, 1142, 1088, 824 cm^{-1}. ^1HNMR ($CDCl_3$) δ=2.20 (3H, s, Me), 5.90 (2H, m, H_a), 6.40 (4H, m, H_b and H_c), 6.60—7.50 (8H, m, aromatic protons). ^{13}CNMR ($CDCl_3$) δ=21.0 (Me), 99.9 (C_5), 124.4 (C_{12} or, C_8 and C_9), 127.1 (C_6 and C_{11}), 127.3 (C_{17}), 127.5 (C_7 and C_{10}), 128.7 (C_{13} or C_{14}), 129.5 (C_{14} or C_{13}, and C_{18}), 129.8 (C_8 and C_9), 130.0 (C_{19}), 135.3 (C_{16}), 136.1 (C_{15} or C_{12}), 152.9 (C_3). Found: C, 72.58; H, 5.05; N, 8.03%. Calcd for $C_{21}H_{17}N_2OCl$: C, 72.31; H, 4.91; N, 8.03%.

3h: Pale yellow crystals, mp 116—118 °C (from ethyl acetate). High-resolution MS Found: *m/z* 339.1372. Calcd for $C_{22}H_{17}N_3O$: M, 339.1370. MS *m/z* (rel intensity) 339 (M^+; 5), 233 (8), 133 (100), 128 (100), 78 (100). IR (KBr) 2926, 2857, 2234, 1589, 1545, 1514, 1453, 1418, 1393, 1302, 1144, 1092, 835 cm^{-1}. ^1HNMR ($CDCl_3$) δ=2.29 (3H, s, Me), 6.01 (2H, m, H_a), 6.47 (4H, m, H_b and H_c), 6.64—7.66 (8H, m, aromatic protons). ^{13}CNMR ($CDCl_3$) δ=21.0 (Me), 100.6 (C_5), 126.8 (C_6 and C_{11}), 127.1 (C_{17}), 127.7 (C_7 and C_{10}), 128.6 (C_{14} or C_{15}), 129.8 (C_8 and C_9), 129.9 (C_{18}), 132.1 (C_{15} or C_{14}), 152.2 (C_3). Found: C, 77.68; H, 5.11; N, 12.18%. Calcd for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38%.

3i: Pale yellow crystals, mp 117—118 °C (from ethyl acetate). High-resolution MS Found: *m/z* 363.0890. Calcd for $C_{21}H_{16}N_2O_2Cl$: M, 363.0898. MS *m/z* (rel intensity) 364 (M^+; 3), 258 (6), 133 (100), 118 (43), 78 (100). IR (KBr) 2963, 2928, 2855, 1593, 1516, 1493, 1453, 1424, 1385, 1315, 1258, 1179, 1086, 829, 818 cm^{-1}. ^1HNMR ($CDCl_3$) δ=3.75 (3H, s, OMe), 5.92 (2H, m, H_a), 6.35 (4H, m, H_b and H_c), 6.60—7.50 (8H, m, aromatic protons). ^{13}CNMR ($CDCl_3$) δ=55.3 (OMe), 99.9 (C_5), 114.0 (C_{14}), 117.4 (C_{12}), 127.2 (C_6 and C_{11}), 127.6 (C_7 and C_{10}), 128.0 (C_{17}), 128.8 (C_{18}), 129.7 (C_{13}), 129.8 (C_8 and C_9), 131.2 (C_{19}), 137.0 (C_{16}), 153.0 (C_3), 161.2 (C_{15}). Found: C, 69.30; H, 4.77; N, 7.70%. Calcd for $C_{21}H_{17}N_2O_2Cl$: C, 69.14; H, 4.70; N, 7.68%.

3j: Colorless oil. High-resolution MS Found: *m/z* 348.1003. Calcd for $C_{21}H_{17}N_2OCl$: M, 348.1028. MS *m/z* (rel intensity) 348 (M^+; 13), 242 (90), 155 (100), 153 (60), 118 (95), 117 (80), 78 (100). IR (KBr) 2924, 2855, 1593, 1516, 1493, 1418, 1385, 1092, 820 cm^{-1}. ^1HNMR ($CDCl_3$) δ=2.33 (3H, s, Me), 6.01 (2H, m, H_a), 6.44 (4H, m, H_b and H_c), 6.69—7.59 (8H, m, aromatic protons). ^{13}CNMR ($CDCl_3$) δ=21.4 (Me), 127.2 (C_6 and C_{11}), 127.6 (C_7 and C_{10}), 127.9 (C_{13} or C_{14}), 128.1 (C_{17}), 128.8 (C_{18}), 129.3 (C_{14} or C_{13}), 129.8 (C_8 and C_9), 131.2 (C_{19}), 135.6 (C_{16}), 152.3 (C_3).

3k: Colorless oil. High-resolution MS Found: *m/z* 368.0457. Calcd for $C_{20}H_{14}N_2OCl_2$: M, 368.0481. MS *m/z* (rel intensity) 368 (M^+; 50), 153 (11), 102 (71), 78 (100). IR (KBr) 2924, 2859, 1593, 1493, 1402, 1383, 1312, 1144, 1092, 1015, 827 cm^{-1}. ^1HNMR ($CDCl_3$) δ=5.90 (2H, m, H_a), 6.40 (4H, m, H_b and H_c), 6.60—7.50 (8H, m, aromatic protons). ^{13}CNMR ($CDCl_3$) δ=100.5 (C_5), 123.9 (C_{12} or C_{15}), 126.8 (C_6 and C_{11}), 127.8 (C_7 and C_{10}), 128.1 (C_{17}), 128.9 (C_{13} or C_{14}), 129.0 (C_{18}), 129.4 (C_{14} or C_{13}), 129.9 (C_8 and C_9), 131.7 (C_{19}), 136.5 (C_{15} or C_{12}), 136.6 (C_{16}), 152.4 (C_3).

3l: Colorless oil. High-resolution MS Found: *m/z* 358.0746. Calcd for $C_{21}H_{13}N_3OCl$: M, 358.0746. MS *m/z* (rel intensity) 358 (M^+; 4), 239 (25), 128 (100), 102 (7), 78 (100). IR (KBr) 2924, 2853, 2230, 1590, 1508, 1493, 1418, 1387, 1090, 833 cm^{-1}. ^1HNMR ($CDCl_3$) δ=5.99 (2H, m, H_a), 6.45 (4H, m, H_b and H_c), 6.71—7.75 (8H, m, aromatic protons). ^{13}CNMR ($CDCl_3$) δ=101.2 (C_5), 126.4 (C_6 and C_{11}), 128.0 (C_7 and C_{10}), 128.2 (C_{17}), 128.5 (C_{14} or C_{15}), 129.2 (C_{18}), 130.0 (C_8 and C_9), 132.3 (C_{15} or C_{14}), 152.1 (C_3).

General Procedure of the Competition Reactions of 2a with 1b and 4. To a solution of **1b** (0.9 mmol), **4** (0.9 mmol), and triethylamine (0.9 mmol) in a solvent (12 ml) was slowly added a solution of benzohydroximoyl chloride (0.3 mmol) in a solvent (5 ml) at room temperature; the mixture was then stirred for 30 min. After the usual work up, the mixture was separated with thin-layer chromatography on silica gel using hexane : ethyl acetate 4 : 1 as a developing solvent to give **3b** (R_f=0.47) and **5** (R_f=0.60).

General Procedure of the Competition Reactions of 1b or 1c with 2a and *p*-Substituted Benzonitrile Oxides (2b—2d). To a solution of **1** (0.5 mmol) and triethylamine (3.0 mmol) in dichloromethane (3.0 mmol) was slowly added a solution of benzohydroximoyl chloride (1.5 mmol) and *p*-substituted benzohydroximoyl chloride (1.5 mmol) in dichloromethane (10 ml); the mixture was then stirred at room temperature for 30 min. After the usual workup, the mixture was separated with column chromatography on silica gel to give **3a** and the corresponding adduct (**3b—d**).

Hydrolysis of 3. To a solution of **3** (0.7 mmol) in dichloromethane (5 ml) was added trifluoroacetic acid (150 mg, 1.3 mmol) and a few drops of water. The mixture was stirred at room temperature for 1 h, poured into water, and separated into organic and water layers. Removal of dichloromethane in the organic layer gave a colorless oil, which was separated by column chromatography on silica gel to give **8** quantitatively. The water layer was neutralized by triethylamine and extracted with chloroform; the organic layer was then dried over anhydrous sodium sulfate. Removal of chloroform gave a colorless oil of 2,4,6-cycloheptatrien-1-one (**9**) (60 mg, 80% yield).

8b: Colorless crystals, mp 196—198 °C (from ethyl acetate). High-resolution MS Found: *m/z* 226.1132. Calcd for $C_{14}H_{14}N_2O$: M, 226.1105. MS *m/z* (rel intensity) 266 (87), 209 (100), 278 (73), 107 (75), 106 (76). IR (KBr) 3405, 1647, 1588, 1495, 1385, 943, 820 cm^{-1}. ^1HNMR ($CDCl_3$) δ=2.20 (3H, s, Me), 6.40—7.50 (9H, m, aromatic protons). Found: C, 74.05; H, 6.30; N, 12.15%. Calcd for $C_{14}H_{14}N_2O$: 74.31; H, 6.24; N, 12.38%.

8d: Colorless crystals, mp 163—164 °C (from benzene). High-resolution MS Found: *m/z* 290.0086. Calcd for $C_{13}H_{11}N_2OBr$: M, 290.0054. MS *m/z* (rel intensity) 292 (M^+; 11), 290 (M^+; 13), 276 (11), 194 (16), 149 (100). IR (KBr) 3397, 1630, 1600, 1520, 1275, 966, 814 cm^{-1}. ^1HNMR ($CDCl_3$) δ=6.50—7.60 (9H, m, aromatic protons). Found: C, 53.60; H, 3.88; N, 9.49%. Calcd for $C_{13}H_{11}N_2OBr$: C, 53.63; H, 3.80; N, 9.62%.

Thermal Isomerizations of 3. A solution of **3** (0.66 mmol) in benzene (5 ml) was heated at 60 °C for 50 h. Removal of benzene gave a brown oil, which was separated by thin-layer chromatography on silica gel to give **14**.

14c: Colorless oil. High-resolution MS Found: *m/z* 334.0855. Calcd for $C_{20}H_{15}N_2OCl$: M, 334.0871. MS *m/z* (rel intensity) 334 (M^+; 8), 304 (33), 283 (20), 214 (50), 180 (100). IR (oil) 1603, 1495, 1466, 1397, 1379, 1275 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.55 (t, 2H, H_a and H_b), 5.30—5.55 (2H, m, H_c and H_d), 6.15 (1H, d, H_e), 6.87 (1H, d, H_f), 7.10—7.50 (9H, m, aromatic protons). Coupling constants in Hz; $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.5$, $J_{ce}=9.7$, $J_{df}=9.7$. ^{13}C NMR ($CDCl_3$) δ=27.2, 117.0, 118.2, 118.9, 124.2, 127.4, 128.3, 128.6, 128.7, 129.0, 129.3, 129.9, 134.8, 135.4, 141.4, 146.7, 157.5.

14d: Colorless oil. High-resolution MS Found: *m/z* 378.0351. Calcd for $C_{20}H_{15}N_2OBr$: M, 378.0367. MS *m/z* (rel intensity) 378 (M^+; 10), 314 (100). IR (oil) 1624, 1489, 1397, 1381, 1275 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.57 (2H, t, H_a and H_b), 5.25—5.55 (2H, m, H_c and H_d), 6.15 (1H, d, H_e), 6.86 (1H, d, H_f), 7.00—7.65 (9H, m, aromatic protons). Coupling constants in Hz; $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.7$, $J_{ce}=9.8$, $J_{df}=9.8$. ^{13}C NMR ($CDCl_3$) δ=27.3, 117.0, 118.3, 118.9, 124.2, 128.4, 128.7, 129.3, 129.5, 132.9, 133.2, 135.9, 141.5, 146.7, 156.3.

General Procedure of the Addition Reactions of 3 with 15. A mixture of **3** (0.4 mmol) and **15** (0.4 mmol) in dichloromethane (2.0 ml) was stirred for 5 h and separated by thin-layer chromatography on silica gel to give **16**.

16b: Colorless crystals, mp 210—212 °C (decomp) (from dichloromethane–ethyl acetate). High-resolution MS Found: *m/z* 490.1883. Calcd for $C_{29}H_{24}N_5O_3$: M, 490.1879. MS *m/z* (rel intensity) 490 (M^+; 40), 313 (83), 194 (30), 154 (100). IR (KBr) 1711, 1593, 1562, 1512, 1406, 1360, 1263, 1128, 1072 cm^{-1}. UV (MeOH) 260 nm (sh. log ε, 3.92). ^{1}H NMR ($CDCl_3$) δ=2.23 (3H, s, Me), 2.95 (1H, ddm, H_a), 5.10 (1H, dd, H_b), 6.02 (1H, dd, H_c), 6.17 (1H, d, H_d), 6.51 (1H, ddd, H_e), 6.76 (1H, dd, H_f), 6.97—7.72 (14H, m, aromatic protons). Coupling constants in Hz; $J_{ac}=3.4$, $J_{ae}=1.8$, $J_{be}=6.9$, $J_{bf}=6.9$, $J_{ce}=11.3$, $J_{df}=9.5$. ^{13}C NMR ($CDCl_3$) δ=49.5, 74.2, 114.0, 125.7, 128.0, 128.5, 128.6, 129.2, 129.3, 129.4, 129.6, 129.9, 130.0, 130.1, 130.5, 134.1, 135.2, 136.5, 151.5, 152.9, 158.0. Found: C, 70.88; H, 4.79; N, 14.15%. Calcd for $C_{29}H_{23}N_5O_3$: C, 71.16; H, 4.74; N, 14.31%.

16c: Colorless crystals, mp 227—228 °C (decomp) (from dichloromethane–ethyl acetate). High-resolution MS Found: *m/z* 510.1305. Calcd for $C_{28}H_{21}N_5O_3Cl$: M, 510.1333. MS *m/z* (rel intensity) 510 (M^+; 5), 307 (16), 214 (3), 154 (100). IR (KBr) 1713, 1595, 1561, 1493, 1406, 1360, 1263, 1128, 1072 cm^{-1}. UV (MeOH) 258 nm (sh. log ε, 4.00). ^{1}H NMR ($CDCl_3$) δ=4.93 (1H, ddm, H_a), 5.12 (1H, dd, H_b), 6.03 (1H, dd, H_c), 6.10 (1H, d, H_d), 6.52 (1H, ddd, H_e), 6.80 (1H, dd, H_f), 7.07—7.82 (14H, m, aromatic protons). Coupling constants in Hz; $J_{ac}=3.0$, $J_{ae}=1.9$, $J_{be}=6.9$, $J_{bf}=6.9$, $J_{ce}=11.2$, $J_{df}=9.5$. ^{13}C NMR ($CDCl_3$) δ=49.6, 74.1, 114.0, 125.7, 128.2, 128.3, 128.7, 131.1, 134.5, 137.6, 151.7, 152.9, 157.6. Found: C, 65.85; H, 3.88; N, 13.55%. Calcd for $C_{28}H_{20}N_5O_3Cl$: C, 65.95; H, 3.95; N, 13.73%.

16g: Colorless crystals, mp 208—210 °C (decomp) (from dichloromethane–ethyl acetate). High-resolution MS Found: *m/z* 524.1513. Calcd for $C_{29}H_{23}N_5O_3Cl$: M, 524.1489. MS *m/z* (rel intensity) 524 (M^+; 18), 347 (35), 307 (18), 154 (100). IR (KBr) 1713, 1593, 1559, 1503, 1402, 1362, 1262, 1127, 1086 cm^{-1}. UV (MeOH) 253 nm (log ε, 4.18). ^{1}H NMR ($CDCl_3$) δ=2.25 (3H, s, Me), 4.90 (1H, ddm, H_a), 5.10 (1H, dd, H_b), 6.00 (1H, dd, H_c), 6.13 (1H, d, H_d), 6.50 (1H, ddd, H_e), 6.75 (1H, dd, H_f), 6.89—7.65 (13H, m, aromatic protons). Coupling constants in Hz; $J_{ac}=3.0$, $J_{ae}=2.0$, $J_{be}=7.0$, $J_{bf}=7.0$, $J_{ce}=11.0$, $J_{df}=10.0$. ^{13}C NMR ($CDCl_3$) δ=21.0, 49.4, 74.3, 114.0, 125.7, 128.3, 128.4, 128.6, 129.1, 129.2, 129.3, 130.1, 130.2, 130.6, 130.9, 134.3, 135.6, 136.0, 137.9, 151.6, 152.8, 157.3. Found: C, 66.55; H, 4.32; N, 13.34%. Calcd for $C_{29}H_{22}N_5O_3Cl$: C, 66.48; H, 4.23; N, 13.37%.

Synthesis of 21b. A solution of **3b** (2.29 g, 7.3 mmol) and 5% Pd/C (0.90 g) in benzene (20 ml) was stirred ar room temperature under hydrogen at 1 atom for 24 h. Removal of Pd/C by filtration and of the solvent by evaporation gave colorless oil, which was separated with column chromatography on silica gel using hexane : ethyl acetate, 19 : 1 as an eluent to give colorless oily **21b** (1.33 g, 42% yield).

21b: Colorless oil. High-resolution MS Found: *m/z* 320.1903. Calcd for $C_{21}H_{24}N_2O$: M, 320.1887. MS *m/z* (rel intensity) 320 (M^+; 65), 263 (100), 209 (75). ^{1}H NMR ($CDCl_3$) δ=1.30—2.20 (12H, m, cycloheptane moiety), 2.25 (3H, s, Me), 6.75—7.40 (9H, m, aromatic protons). ^{13}C NMR ($CDCl_3$) δ=20.9, 21.8, 29.0, 39.1, 104.6, 126.4, 127.8, 128.1, 128.2, 129.7, 129.8, 136.1, 136.3, 155.7.

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21) In order to clarify the electronic contribution between these two ring moieties, ^{13}C- and ^{15}N NMR spectra of **3b** and **21b** were measured Fig. 6. However no significant difference was observed in the chemical shifts of the signals of these atoms. ^{15}N NMR spectral measurements of **3b** and **21b** were carried out by the following procedure. ^{15}N Enriched nitromethane (δ=380.23 ppm) was used as an external standard. The sample solution contained **3b** or **21b** (5.6 mmol) and chromium(III) acetate (0.34 mmol) as a relaxation agent in deuteriochloroform (2.2 ml). Puls width, puls interval, and data acquisition times were 20 μs, 5.0 s, and 0.522 s, respectively. The accumulation of 9000 times was made to obtain the spectra.

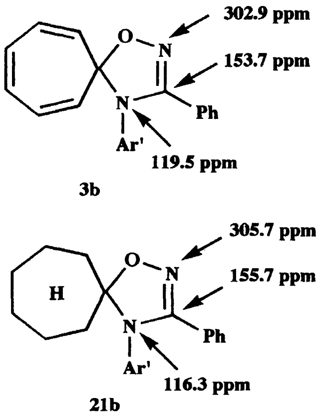

Fig. 6. ^{13}C- and ^{15}N NMR spectral chemical shifts of the heterocyclic moieties of **3b** and **21b**.