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Neighboring Effect by Heteroaromatic Rings: Formation of Skeletally Rearranged Adducts by Cycloaddition Reaction of Norbornadiene-Fused Pyridazines and Pyrazines with 4-Phenyl-1,2,4-triazole-3,5(4*H*)-dione

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Abstract: Norbornadiene-fused pyridazines and pyrazines reacted with 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione to give skeletally rearranged adducts in moderate yields. A similar reaction with fused pyridazine *N*-oxides or a fused pyrazine *N*-oxide resulted in the regioselective formation of the rearranged adduct. The formations of the skeletally rearranged adducts would be ascribed to the intervention of bridged heteroarenium ion intermediates formed by the neighboring group participation of heteroaromatic rings.

Introduction

Neighboring group participation has been found to play an important role to control the reactivity and selectivity of organic reactions.[1,2] However, the neighboring effect by heteroaromatic rings is less understood in contrast to the detailed studies on the benzene ring systems.[3–6] In the course of our recent studies to explore the possibility of the neighboring group participation by heteroaromatic rings,[7–10] we have found that even electron-deficient six-membered rings have an ability to participate in the stabilization of remote cationic centers. For instance, the acid-induced ring-opening reaction of the epoxide **1** has been found exclusively to provide the bis(trifluoroacetoxy) derivatives **2** in regio- and stereoselective manners.[8] The pyridazine *N*-oxide ring was found to contribute not only to the selectivities but also to the reactivity, because the reaction of an epoxide of the diphenylpyridazine **7** without *N*-oxide group under the same conditions resulted in the recovery of the starting material.[8] Unfortunately, the bromination reaction of the norbornadiene-fused pyridazine **6** or **10** gave only a mixture of complex

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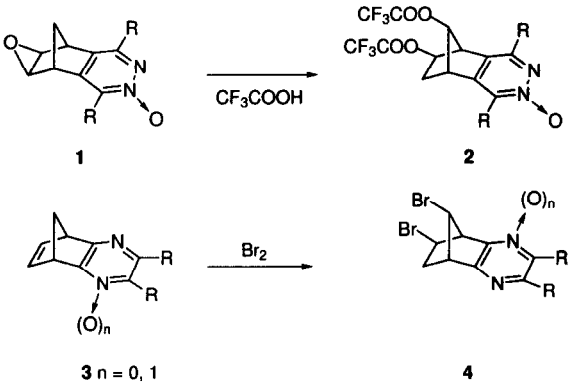
products.[11] On the other hand, the bromination reaction of the norbornadiene-fused pyrazines **3** has been found to give skeletally rearranged adducts **4** along with *cis* and *trans* adducts in a variety of ratios depending on the substituents.[7]

As an extension of these results, we undertook a study dealing with the cycloaddition reaction of norbornadiene-fused pyridazines and pyrazines with 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (**5**). 4-Substituted 1,2,4-triazole-3,5(4*H*)-diones have been known to afford the skeletally rearranged adducts on treatments with benzonorbornadiene[12,13] as well as strained bicyclic alkenes.[13–19] The formations of [2 + 2] adducts by the reactions of triazolediones with some bicyclic[17,20] and other alkenes[21,22,23–26] have been also reported. Thus, we consider it is worthwhile to investigate the possibility and the selectivity for providing a rearranged adduct and/or a [2 + 2] adduct by the reactions of norbornadiene-fused pyridazines and pyrazines with **5**. One of the advantages for the use of the triazoledione **5** would be to suppress the complexity of reaction products, because it is impossible to form a *trans* adduct as observed for the bromination of the fused pyrazines **3**. Herein we report the results and their mechanistic interpretations.



1 **2**

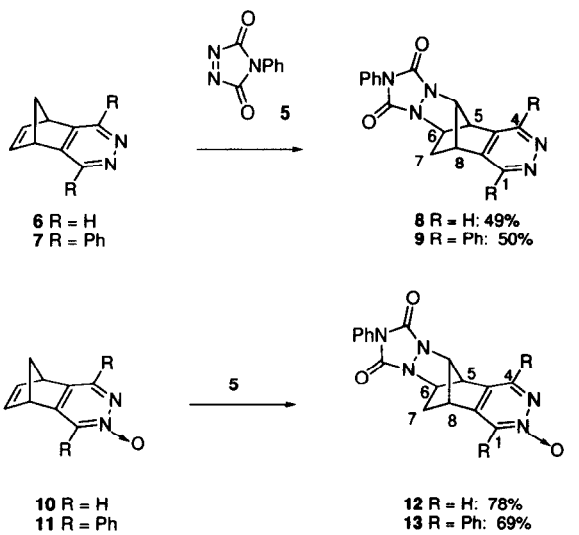
3 n = 0, 1 **4**

Scheme 1

Results and Discussion

The reaction of the norbornadiene-fused pyridazine **6** with the triazoledione **5** did not proceed at room temperature while that of benzonorbornadiene has been reported to finish in 14 h at room temperature or in 30 min under refluxing in chloroform.[12,13] When the fused pyridazine **6** was heated with a large excess amount of **5** for 5 days under refluxing in acetonitrile, the skeletally rearranged adduct **8** was obtained in 49% yield. We could not detect the formations of any other adducts. The structure of **8** was determined on the basis of the observation of

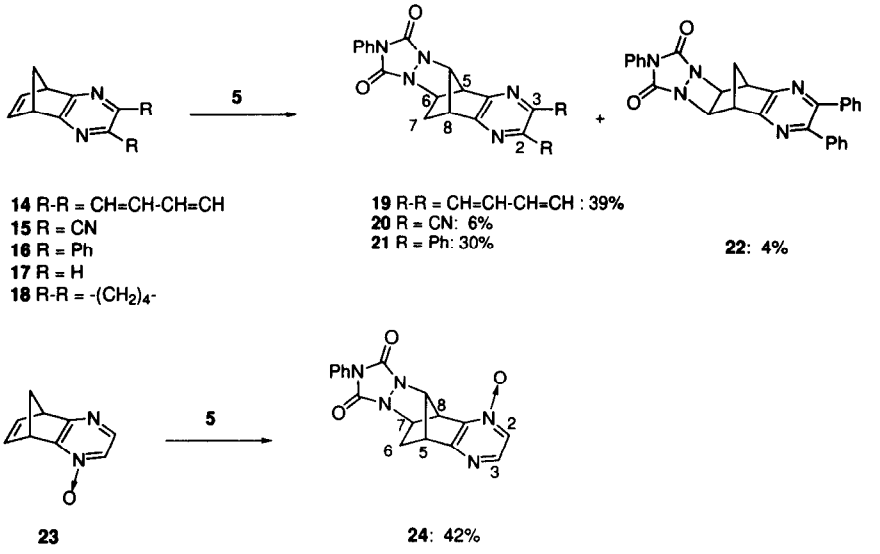
a geminal spin coupling (J=13 Hz) at 7-H protons. The value of the coupling constant, which is larger than that usually observed for the methylene-bridge protons of norbornene systems,[27] indicates the formation of a skeletally rearranged product. The protons at 6-H, 7-H_{exo}, and 7-H_{endo} of the rearranged adducts such as **2** has been usually described to represent the AA'B splitting pattern. However, we could not observe the spin coupling between 6-H and 7-H_{exo} for the adduct **8**. The optimized structure of **8** calculated by PM3-MNDO method revealed that the dihedral angle between these protons is almost orthogonal (88°), which is consistent with the absence of the vicinal spin coupling. The reaction of the diphenylpyridazine **7** with the triazoledione **5** similarly gave the rearranged adduct **9** in 50% yield. Upon treatment with **5**, the norbornadiene-fused pyridazine *N*-oxides **10** and **11** provided the rearranged adducts **12** and **13** respectively in a regioselective manner. Regiochemistry of these adducts **12** and **13** was clearly deduced from the observation of the NOE between 4-H and 5-H protons for **12**, and the NOE between 5-H and *ortho* protons of 4-phenyl group for **13**; the *ortho* protons of 4-phenyl group on the pyridazine *N*-oxide ring has been elucidated to appear at the lower field in contrast to those of 1-phenyl group.[8]



Scheme 2

The reactions of the norbornadiene-fused pyrazines with **5** have given rather different results. Although the methanophenazine **14** reacted with the triazoledione **5** to give the rearranged adduct **19** in 39% yield, the dicyanopyrazine **15** provided only a 6% yield of **20**. We

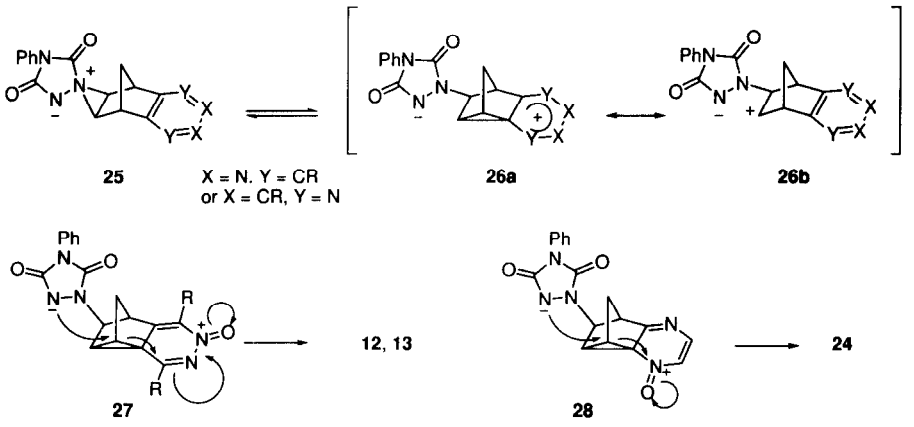
could not obtain any other characterizable products. The diphenylpyrazine **16** afforded the rearranged adduct **21** (30%) accompanied by the formation of the [2 + 2] adduct **22** (4%). The ^{1}H and ^{13}C NMR spectral data of **22** supported the presence of C_s symmetry, and the lack of the vicinal spin coupling between 5-H and 6-H suggested the *exo-cis* configuration of **22**. Unfortunately, the pyrazine **17** and the cyclohexene-fused pyrazine **18** gave a mixture of complex products. The pyrazine *N*-oxide **23** reacted with **5** to result in the regioselective formation of **24**. Regiochemistry of **24** was elucidated from the measurement of its ^{1}H NMR spectrum with successive addition of $Eu(fod)_3$; the signal at 8-H proton is shifted downfield to the largest extent along with the second largest downfield shift of 2-H proton on the pyrazine ring.[28]



Scheme 3

A plausible mechanism for the present reactions is illustrated in Scheme 4. The reaction of norbornadiene-fused pyridazines and pyrazines with the triazoledione **5** would initially form the aziridinium imide intermediate **25**.[25,26] The carbon–nitrogen bond cleavage of the aziridinium ring by the neighboring group participation of the pyridazine or pyrazine ring would provide a resonance hybrid of **26a** and **26b**. The subsequent Wagner–Meerwein type skeletal rearrangement would result in the formation of rearranged adducts. Generally, a pyrazine ring has been known to be more electron-deficient than a pyridazine ring according to their pK_a

values.[29] The electron-deficiency of pyrazine rings would retard the neighboring effect of the pyrazine ring toward the remote cationic center to cause the complexity of the reactions. The formation of the [2 + 2] adduct **22** would be attributable to a less contribution of the bridged structure **26a** in the resonance hybrid of the cationic intermediate. Regioselective formation of the skeletally rearranged adducts for the reactions of the pyridazine and pyrazine *N*-oxides **10**, **11**, and **23** is well explained by the respective formation of the bridged heteroarenium ions **27** and **28** due to the electron-donating property of the *N*-oxide group.



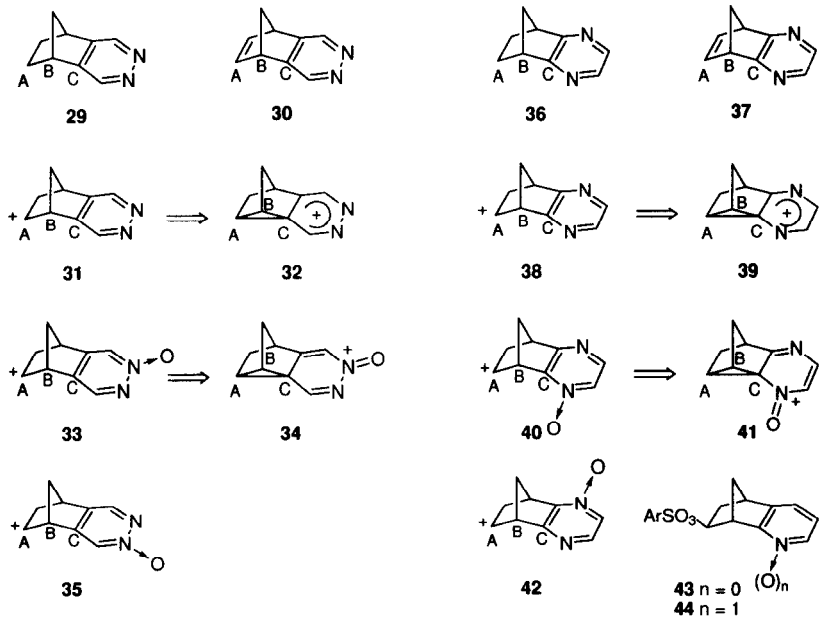
Scheme 4

In order to obtain a knowledge about cationic species, *ab initio* (6-31G*) calculations were performed on the norbornene derivatives **29**–**31**, **33**, and **35**, as well as **36**–**38**, **40**, and **42**. Calculations on the pyridazine- and pyrazine-fused norbornenyl cations **31** and **38** provided the bridged structures **32** and **39** as the optimized ones, respectively. The total energy and the selected atomic distances are shown in Table 1. The atomic distances of A–C and B–C are 0.168 nm for **32** and 0.165 nm for **39**, the values of which are much shorter than the corresponding atomic distances of A–C (0.244 – 0.246 nm) obtained for **29**, **30**, **36**, and **37**. The results suggest that even electron-deficient pyridazine and pyrazine rings have an ability to participate in the stabilization of remote cationic centers to some extent.

The norbornenyl cation of the pyridazine *N*-oxide **33**, where the cationic center is located at the homo *para* position of the *N*-oxide group, resulted to give the bridged structure **34**. The atomic distances of A–C and B–C are both 0.157 nm, which is comparably shorter than that of **32**. In contrast, the regioisomeric *N*-oxide **35**, where the cationic center is located at homo *meta* position, did not afford the corresponding bridged structure. The comparison of total

energies between **34** and **35** revealed that the bridged ion **34** is more stable by 27.9 kcal/mol. The pyrazine *N*-oxide **40** similarly afforded the bridged structure **41**, which is also more stable by 17.4 kcal/mol than the non-bridged regioisomer **42**. The significant difference of the total energies between the bridged and non-bridged ions would cause the observed regioselectivity of Wagner-Meerwein rearrangement for the cycloaddition reactions of the norbornadiene-fused pyridazine and pyrazine *N*-oxides.

Previously, Tanida *et al.* studied on the solvolyses of the pyridine derivatives **43** and **44**. In these cases, the rate enhancement by introduction of the *N*-oxide group could not be observed and the neighboring group participation of the pyridine *N*-oxide group toward the homo *ortho* position was concluded to be negative.[3–5] However, our findings on the regioselective formation of **24** by the reaction of **23** with **5** clearly suggest the presence of neighboring effect by a pyrazine *N*-oxide ring toward the homo *ortho* position.



Scheme 5

In conclusion, we have demonstrated that the triazoledione **5** reacted with the noroborna-diene-fused pyridazines and pyrazines to give the skeletally rearranged adducts, which would be ascribed to the intermediacy of the bridged heteroarenium ions despite electron-deficient six-membered heteroaromatic, and the subsequent Wagner-Meerwein type rearrangement. Although we can not completely exclude the possibility of 1,2-aryl migration without the inter-

Table 1. Total Energy (hartrees) and Selected Atomic Distances (nm) of Pyridazine- and Pyrazine-Fused Norbornenyl Cations and Related Compounds Calculated by Ab Initio (6-31G*) Method.

Compd	total energy	A–B	B–C	A–C	Compd	total energy	A–B	B–C	A–C
29	−455.482713	.155	.151	.246	**36**	−455.519680	.155	.151	.246
30	−454.276191	.154	.153	.245	**37**	−454.314229	.154	.152	.244
32	−454.599969	.141	.168	.168	**39**	−454.648761	.142	.165	.165
34	−529.419653	.145	.157	.157	**41**	−529.438964	.145	.157	.157
35	−529.375200	.146	.156	.214	**42**	−529.411311	.145	.157	.211

vention of bridged heteroarenium ions, the regioselectivity observed for the reactions with the pyridazine and pyrazine *N*-oxides as well as the results of *ab initio* calculations would suggest the intermediacy of bridged heteroarenium ions.

Experimental

General. All the melting points were determined with a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra were obtained with a JEOL Diamond 20 spectrometer. NMR spectra were recorded either with JEOL JNM-LA300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) or JEOL JNM-LA400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectrometer. Assignments of the ^{1}H and ^{13}C signals are based on DEPT, H-H COSY, and C-H COSY measurements. Mass spectra were measured with a Shimadzu GCMS-QP1000EX spectrometer operating in the electron impact mode (70eV). High resolution mass spectra (HR-MS) were taken with a JEOL DX-300 spectrometer. Elemental analyses were performed with a Perkin–Elmer Model 240 apparatus. MPLC separations were carried out by a YAMAZEN YFLC-600-10V system with a YAMAZEN Ultra Pack^{TM} Column (Si-40B, silica gel). Solvents were dried and purified by standard methods. Norbornadiene-fused pyridazines **6**, **7**, **10**, and **11**, and norbornadiene-fused pyrazines **14**, **15**, **17**, and **23** were prepared by the procedures as previously described.[8,9] The triazoledione **5** was synthesized according to the literature.[30]

5,8-Dihydro-5,8-methano-1,4-diphenylphthalazine 2-Oxide (11): A solution of the norbornadiene-fused diphenylpyridazine **7** (154 mg, 0.5 mmol) and MCPBA (80%, 94 mg, 0.4 mmol) in dichloromethane (10 cm^3) was stirred at room temperature for 24 h. The organic

phase was washed with aqueous sodium hydrogen sulfide and aqueous sodium carbonate, and dried over Na_2SO_4. After removal of the solvent, the residue was separated by MPLC (ethyl acetate–dichloromethane 3/20) to give **11** (91 mg, 57% based on the pyridazine **7**): Colorless needles (from ethanol); decomp 230 °C; IR (KBr) 3005, 1560, 1352, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=2.32 (2H, m, 9-H), 3.91 (1H, m, 8-H), 4.31 (1H, m, 5-H), 6.90 (1H, dd, J=5 and 3 Hz, 7-H), 7.04 (1H, dd, J=5 and 3 Hz, 6-H), 7.51 (6H, m), 7.60 (2H, m, *ortho* protons of 1-phenyl), 7.77 (2H, m, *ortho* protons of 4-phenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=49.0 (C-5), 49.9 (C-8), 68.2 (C-9), 128.5 (CH, Ph), 128.7 (CH, Ph), 129.7 (CH, Ph), 129.8 (CH, Ph), 130.2, 134.6, 138.9 (C-4a), 139.8 (C-1), 141.6 (C-7), 143.0 (C-6), 150.1 (C-4), 159.9 (C-8a), 2C missing; Observed NOE by NOESY: 5-H and *ortho* protons of 4-phenyl; MS m/z (rel intensity) 312 (100; M^+), 296 (26; **7**). Found: C, 80.70; H, 5.23; N, 9.08%. Calcd for $C_{21}H_{16}N_2O_3$: C, 80.75; H, 5.16; N, 8.97%.

Reaction of 5,8-Dihydro-5,8-methanophthalazine (6) and the Triazoledione 5. A solution of the norbornadiene-fused pyridazine **6** (75 mg, 0.5 mmol) and the triazoledione **5** (87 mg, 0.5 mmol) in anhydrous acetonitrile (10 cm^3) was refluxed for 5 days. During that period, the triazoledione **5** (87 mg, 0.5 mmol) was added every 12 h. Insoluble material was removed by suction and the filtrate was concentrated. The residue was separated by TLC (alumina, ethyl acetate) to give 2,4,6,12,13-pentaaza-4-phenylpentacyclo[7.7.0.0^{2,6}.0^{7,16}.0^{10,15}]hexadeca-10,12,14-triene-3,5-dione (**8**) (82 mg, 49%): Colorless needles (from acetonitrile); mp 241–242 °C; IR (KBr) 1786, 1709, 1495, 1132 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, 45 °C) δ=1.44 (1H, ddd, J=13, 5, 1.5 Hz, 7-H$_{endo}$), 2.38 (1H, dd, J=13 and 5.5 Hz, 7H$_{exo}$), 3.70 (1H, br s, 5-H), 3.83 (1H, dm, J=5.5 Hz, 8-H), 4.71 (1H, dd, J=5 and 1.5 Hz, 6-H), 4.85 (1H, dm, J=1.5 Hz, 9-H), 7.38–7.51 (5H, m, Ph), 9.20 (1H, d, J=1 Hz, 1-H), 9.23 (1H, d, J=1 Hz, 4-H); ^{13}C NMR ($CDCl_3$, 100 MHz, 45 °C) δ=33.7 (C-7), 44.1 (C-8), 50.4 (C-5), 57.5 (C-6), 79.9 (C-9), 125.3, 128.7, 129.4, 131.3, 136.5, 144.2 (C-1), 145.4, 147.2 (C-4), 156.2 (CO), 156.7 (CO); Observed NOE by NOESY: 1-H and 8-H, 4-H and 5-H; MS m/z (rel intensity) 319 (68; M^+), 171 (24; M – PhNCO – CO), 144 (11; **6**), 130 (100; phthalazine). Found: C, 63.72; H, 4.22; N, 21.70%. Calcd for $C_{17}H_{13}N_5O_2$: C, 63.94; H, 4.10; N, 21.93%.

Reaction of 5,8-Dihydro-5,8-methano-1,4-diphenylphthalazine (7) and the Triazoledione 5. A solution of **7** (150 mg, 0.5 mmol) and the triazoledione **5** (87 mg, 0.5 mmol) in anhydrous acetonitrile (10 cm^3) was refluxed for 5 days. During that period, the triazoledione **5** (87 mg, 0.5 mmol) was added every 12 h. Insoluble material was removed by suction and the filtrate was concentrated. The residue was separated by column chro-

matography (silica gel, ethyl acetate–dichloromethane 2/3) to give 2,4,6,12,13-pentaaza-4,11,14-triphenylpentacyclo[7.7.0.$0^{2,6}$.$0^{7,16}$.$0^{10,15}$]hexadeca-10,12,14-triene-3,5-dione (**9**) (119 mg, 50%): Colorless needles (from benzene); mp >300 °C; IR (KBr) 1778, 1720, 1492 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.80 (1H, ddd, J=13, 5, 1.5 Hz, 7-H_{endo}), 2.52 (1H, dd, J=13 and 5.5 Hz, 7H_{exo}), 3.88 (1H, br s, 5-H), 4.13 (1H, dm, J=5.5 Hz, 8-H), 4.79 (1H, d, J=1.5 Hz, 9-H), 4.96 (1H, dd, J=5 and 1.5 Hz, 6-H), 7.36–7.61 (11H, m, Ph), 7.86 (4H, m); ^{13}C NMR ($CDCl_3$, 400 MHz) δ=33.6 (C-7), 44.4 (C-8), 52.0 (C-5), 57.8 (C-6), 78.4 (C-9), 125.2, 128.3, 128.5, 128.6, 129.0, 129.2, 129.3, 129.8, 130.0, 131.1, 134.6, 135.2, 135.4, 143.8, 152.2, 152.3, 155.9 (CO), 156.1 (CO); MS m/z (rel intensity) 471 (7; M^+), 294 (24; **7** − 2H). Found: C, 74.16; H, 4.44; N, 14.70%. Calcd for $C_{29}H_{21}N_5O_2$: C, 73.87; H, 4.49; N, 14.85%.

Reaction of 5,8-Dihydro-5,8-methanophthalazine 2-Oxide (10) and the Triazoledione 5. A solution of **10** (83 mg, 0.5 mmol) and **5** (87 mg, 0.5 mmol) was refluxed for 5 days. During that period, **5** (87 mg, 0.5 mmol) was added every 12 h. Insoluble material was removed by suction and the filtrate was concentrated. Methanol was added to the residue, and the resulting solid was collected by suction to give 2,4,6,12,13-pentaaza-4-phenylpentacyclo[7.7.0.$0^{2,6}$.$0^{7,16}$.$0^{10,15}$]hexadeca-10,12,14-triene-3,5-dione 12-oxide (**12**) (135 mg, 78%): White powder (from acetone); decomp 215 °C; IR (KBr) 1785, 1708,1423, 1394 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ=1.52 (1H, dd, J=13, 4.5 Hz, 7-H_{endo}), 2.17 (1H, dd, J=13 and 5.5 Hz, 7H_{exo}), 3.79 (1H, dm, J=5.5 Hz, 8-H), 4.11 (1H, br s, 5-H), 4.74 (1H, dd, J=4.5 and 1.5 Hz, 6-H), 4.85 (1H, br s, 9-H), 7.50 (5H, m, Ph), 8.36 (1H, s, 1-H) 8.50 (1H, s, 4-H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ=32.9 (C-7), 43.9 (C-8), 49.2 (C-5), 57.7 (C-6), 77.1 (C-9), 126.4, 126.5 (C-1), 128.1, 128.6, 129.0, 131.3 (C-4), 145.0, 154.3, 155.7 (CO), 156.2 (CO); Observed NOE by NOESY: 1-H and 8-H, 4-H and 5-H; MS m/z (rel intensity) 335 (54; M^+), 319 (13; M − O), 216 (29; M − PhNCO), 160 (22; **10**), 146 (100; phthalazine *N*-oxide). Found: C, 61.06; H, 3.88; N, 20.97%. Calcd for $C_{17}H_{13}N_5O_3$: C, 60.89; H, 3.91; N, 20.89%.

Reaction of 5,8-Dihydro-5,8-methano-1,4-diphenylphthalazine 2-Oxide (11) and the Triazoledione 5. A solution of **11** (73 mg, 0.2 mmol) and the triazoledione **5** (43 mg, 0.25 mmol) in anhydrous acetonitrile (20 cm^3) was refluxed for 5 days. During that period, the triazoledione **5** (43 mg, 0.25 mmol) was added every 24 h. Insoluble material was removed by suction and the filtrate was concentrated. Chloroform was added to the residue, and the resulting solid was collected by suction to give 2,4,6,12,13-pentaaza-4,11,14-triphenylpentacyclo[7.7.0.$0^{2,6}$.$0^{7,16}$.$0^{10,15}$]hexadeca-10,12,14-triene-3,5-dione 12-oxide (**13**) (79 mg, 69%): Colorless needles (from ethyl acetate); mp >300 °C; IR (KBr) 1779, 1724, 1402, 1371

cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ=1.85 (1H, dd, J=13, 4.5 Hz, 7-H_{endo}), 2.21 (1H, dd, J=13 and 5.5 Hz, 7-H_{exo}), 3.55 (1H, d, J=5.5 Hz, 8-H), 4.30 (1H, br s, 5-H), 5.05 (1H, br s, 9-H), 5.15 (1H, dd, J=4.5 and 1.5 Hz, 6-H), 7.40–7.67 (13H, m), 7.83 (2H, m, *ortho* protons of 4-phenyl); ^{13}C NMR (DMSO-d_6, 100 MHz) δ=33.0 (C-7), 44.9 (C-8), 51.2 (C-5), 57.7 (C-6), 76.1 (C-9), 124.2, 126.5, 126.8, 128.4, 128.5, 128.8, 129.0, 129.6, 129.8, 130.2, 131.4, 133.6, 136.8, 145.5, 153.2, 153.7, 155.1 (CO), 155.6 (CO); Observed NOE by NOESY: 5-H and *ortho* protons of 4-phenyl; MS m/z (rel intensity) 487 (42; M^+), 311 (52; **11** − H), 295 (54; **7** − H), 294 (100; **7** − 2H). Found: C, 71.63; H, 4.62; N, 14.40%. Calcd for $C_{29}H_{21}N_5O_3$: C, 71.45; H, 4.34; N, 14.37%.

5,8-Dihydro-3,4-diphenyl-5,8-methanoquinoxaline (16). A solution of bicyclo-[2.2.1]hept-5-ene-2,3-dione[31] (1.221 g, 10 mmol), 1,2-diphenylethylenediamine (2.505 g, 12 mmol), and *p*-toluenesulfonic acid (0.209 g, 1.1 mmol) in benzene (100 cm^3) was refluxed for 5 h while the resulting water was removed by a Dean-Stark apparatus. The organic layer was washed with aqueous sodium hydrogen carbonate and brine, and dried over Na_2SO_4. The crude 2,3,5,8-tetrahydro-5,8-methano-2,3-diphenylphenazine (a mixture of *trans* and *cis* isomers) was treated with nickel peroxide (11.4 g, 126 mmol) in refluxing benzene (300 cm^3) for 10 days. Insoluble materials were removed by filtration through celite and the filtrate was concentrated. The residue was crystallized from hexane to give **16** (1.148 g, 39% from the norbornenedione): Colorless needles (from hexane–ethyl acetate 5/1); mp 124–125 °C; IR (KBr) 3006, 1363, 1328 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ=2.64 (1H, br d, J=8 Hz, 9-H_s), 2.73 (1H, br d, J=8 Hz, 9-H_a), 4.00 (2H, m, 5-H and 8-H), 6.96 (2H, dm, J=2 Hz, 6-H and 7-H), 7.25–7.39 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=49.9 (C-5 and C-8), 66.9 (C-9), 127.9, 128.2, 129.9, 139.5, 142.9 (C-6 and C-7), 145.5 (C-2 and C-3), 166.0 (C-4a and C-8a); MS m/z (rel intensity) 296 (100; M^+), 193 (14; M − PhCN). Found: C, 85.27; H, 5.32; N, 9.33%. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45%.

1,2,3,4,6,9-Hexahydro-6,9-methanophenazine (18). A solution of bicyclo[2.2.1]hept-5-ene-2,3-dione (1.221 g, 10 mmol), 1,2-diaminocyclohexane (1.370 g, 12 mmol), and *p*-toluenesulfonic acid (0.192 g, 1 mmol) in benzene (75 cm^3) was refluxed for 4 h while the resulting water was removed by a Dean-Stark apparatus. The organic layer was washed with aqueous sodium hydrogen carbonate and brine, and dried over Na_2SO_4. The crude 1,2,3,4,4a,6,9,10a-octahydro-6,9-methanophenazine (a mixture of *trans* and *cis* isomers) was treated with activated MnO_2 (5.287 g, 61 mmol) in refluxing bromobenzene (100 cm^3) for 4 days. Insoluble materials were removed by filtration through celite, and the filtrate was concentrated. The reside was sepa-

rated by column chromatography (silica gel, hexane–ethyl acetate 1/1) to give **18** (154 mg, 8% from the norbornenedione): Light tan solid; mp 90 °C (unable to recrystallize due to the high solubility to organic solvents); IR (KBr) 2935, 1577, 1369, 1330, 1303, 1119 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.79 (4H, br s, 2-H and 3-H), 2.42 (1H, d, J=8 Hz, 11-H_s), 2.56 (1H, d, J=8 Hz, 11-H_a), 2.76 (4H, br s, 1-H and 4-H), 3.75 (2H, t, J=2 Hz, 6-H and 9-H), 6.80 (2H, s, 7-H and 8-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=22.8 (C-2 and C-3), 31.6 (C-1 and C-4), 49.7 (C-6 and C-9), 67.1 (C-11), 142.9 (C-7 and C-8), 144.3 (C-4a and C-10a), 165.1 (C-5a and C-9a); MS m/z (rel intensity) 198 (100; M^+), 90 (16; M − $C_4H_4N_2$). Picrate: yellow prisms (from methanol); mp 136–137 °C. Found: C, 53.47; H, 4.07; N, 16.61%. Calcd for $C_{19}H_{17}N_5O_7$: C, 53.40; H, 4.01; N, 16.39%.

Reaction of 1,4-Dihydro-1,4-methanophenazine (14) and the Triazoledione 5. A solution of **14** (97 mg, 0.5 mmol) and the triazoledione **5** (87 mg, 0.5 mmol) in acetonitrile (10 cm^3) was refluxed for 3 days. During that period, **5** (87 mg, 0.5 mmol) was added every 24 h. Insoluble materials were removed by filtration and the filtrate was concentrated. The residue was separated by TLC (silica gel, ethyl acetate) to give 4,6,8,13,20-pentaaza-6-phenylhexacyclo[10.8.0.0^{2,9}.0^{3,11}.0^{4,8}.0^{14,19}]icosa-1(20),12,14(19),15,17-pentaene-5,7-dione (**19**) (72 mg, 39%): White solid (from hexane–ethyl acetate 4/1); mp 290 °C; IR (KBr) 1784, 1712, 1502, 1410 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.76 (1H, ddd, J=14, 5, and 1 Hz, 3-H_{endo}), 2.55 (1H, dd, J=14 and 6 Hz, 3-H_{exo}), 3.89 (1H, s, 1-H), 4.02 (1H, dt, J=6 and 2 Hz, 4-H), 4.90 (1H, dd, J=5 and 2 Hz, 2-H), 5.02 (1H, br d, J=1 Hz, 11-H), 7.43 (1H, m), 7.52 (4H, m), 7.77 (2H, m), 8.05 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=33.3 (C-3), 46.5 (C-1), 53.5 (C-4), 58.8 (C-2), 74.7 (C-11), 125.4, 128.7, 129.2, 129.4, 129.6, 130.0, 131.2, 142.1, 142.3, 153.1, 156.2 (CO), 157.0 (CO), 160.0, 1C missing; MS m/z (rel intensity) 369 (100; M^+), 250 (41; M − PhNCO), 119 (33; PhNCO). Found: C, 68.10; H, 4.26; N, 18.78%. Calcd for $C_{21}H_{15}N_5O_2$: C; 68.28; H, 4.09; N, 18.96%.

Reaction of 2,3-Dicyano-5,8-dihydro-5,8-methanoquinoxaline (15) and the Triazoledione 5. A solution of **15** (291 mg, 1.5 mmol) and the triazoledione **5** (263 mg, 1.5 mmol) in acetonitrile (10 cm^3) was refluxed for 12 days. During that period, **5** (263 mg, 1.5 mmol) was added every 24 h. Insoluble materials were removed by filtration and the filtrate was concentrated. The residue was separated by TLC (silica gel, hexane–ethyl acetate 1/1) to give 2,4,6,11,14-pentaaza-12,13-dicyano-4-phenylpentacyclo[7.7.0.0^{2,6}.0^{7,16}.0^{10,15}]hexadeca-10,12,14-triene-3,5-dione (**20**) (33 mg, 6%): White solid; decomp 145 °C; IR (KBr) 2229, 1784, 1720, 1493, 1410 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ=1.70 (1H, dd, J=13 and 5, 7-H_{endo}), 2.38

(1H, dd, J=13 and 6 Hz, 7-H_{exo}), 4.03 (1H, dt, J=6 and 2 Hz, 8-H), 4.47 (1H, m, 5-H), 4.92 (1H, dd, J=5 and 2 Hz, 6-H), 5.23 (1H, m, 9-H), 7.46 (1H, m), 7.53 (4H, m); ^{13}C NMR (DMSO-d_6, 100 MHz) δ=31.6 (C-7), 45.8 (C-5), 52.6 (C-8), 57.5 (C-6), 76.6 (C-9), 114.3 (CN), 114.4 (CN), 126.6, 128.6, 128.9, 130.9, 131.0, 131.2, 155.7, 156.5 (CO), 158.7 (CO), 164.7; MS m/z (rel intensity) 369 (9; M^+), 119 (33; PhNCO). HR-MS found: 369.1001. Calcd for $C_{19}H_{11}N_7O_2$: 369.0976.

Reaction of 5,8-Dihydro-5,8-methano-2,3-diphenylquinoxaline (16) and the Triazoledione 5. A solution of **16** (296 mg, 1 mmol) and the triazoledione **5** (175 mg, 1 mmol) in acetonitrile (10 cm^3) was refluxed for 4 days. During that period, **5** (175 mg, 1 mmol) was added every 24 h. Insoluble materials were removed by filtration and the filtrate was concentrated. Ethyl acetate was added to the residue and the resulting solid was collected by suction to give the rearranged adduct 2,4,6,11,14-pentaaza-4,12,13-triphenylpentacyclo[7.7.0.0^{2,6}.0^{7,16}.0^{10,15}]hexadeca-10,12,14-triene-3,5-dione (**21**) (131 mg, 28%). The filtrate was concentrated and the residue was separated by TLC (silica gel, hexane–ethyl acetate 2/1) to give **21** (10 mg, 2%; 30% in total) and 3,5,7,11,14-pentaaza-5-phenylpentacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{10,15}]hexadeca-10,12,14-triene-4,6-dione (**22**) (59 mg, 13%).

For **21**: White powder (from benzene); mp 272–274 °C; IR (KBr) 3059, 1788, 1716, 1496, 1404, 1369 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=1.78 (1H, ddd, J=13, 5, and 0.5 Hz, 7-H_{endo}), 2.49 (1H, dd, J=13 and 5 Hz, 7-H_{exo}), 3.89 (1H, br s, 5-H), 4.01 (1H, dm, J=5 Hz, 8-H), 4.87 (1H, dd, J=5 and 2 Hz, 6-H), 5.00 (1H, dm, J=0.5 Hz, 9-H), 7.30–7.40 (11H, m), 7.51 (4H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=33.4 (C-7), 46.4 (C-8), 53.2 (C-5), 58.3 (C-6), 76.0 (C-9), 125.4, 128.3, 128.4, 128.6, 128.7, 129.3, 129.6, 129.7, 132.1, 138.4, 138.5, 150.1 (C-4a and C-8a), 151.5 (C-2 or C-3), 151.7 (C-3 or C-2), 156.1 (CO), 156.8 (CO), 157.9 (C-8a or C-4a), 1C missing; MS m/z (rel intensity) 471 (39; M^+), 352 (100; M − PhNCO), 295 (72; **16** − H), 119 (23; PhNCO). Found: C, 74.06; H, 4.46; N, 14.62%. Calcd for $C_{29}H_{21}N_5O_2$: C, 73.87; H, 4.49; N, 14.85%.

For **22**: Colorless needles (from methanol); mp 162–163 °C; IR (KBr) 3051, 1786, 1728, 1500, 1396, 1360, 1144 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ=2.64 (1H, d, J=11 Hz, 9-H_s), 3.14 (1H, d, J=11 Hz, 9-H_a), 4.08 (2H, s, 5-H and 8-H), 4.86 (2H, s, 6-H and 7-H), 7.28–7.42 (10H, m), 7.51 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=40.5 (C-9), 46.9 (C-5 and C-8), 69.4 (C-6 and C-7), 125.2, 128.4, 128.7, 128.8, 129.4, 129.7, 131.3, 138.5, 151.3 (C-2 and C-3), 155.9 (CO), 161.7 (C-4a and C-8a); MS m/z (rel intensity) 471 (23; M^+), 352 (100; M − PhNCO), 295 (64; **16** − H), 119 (12; PhNCO). Found: C, 73.96; H, 4.77; N, 14.60%. Calcd for $C_{29}H_{21}N_5O_2$: C,

73.87; H, 4.49; N, 14.85%.

Reaction of 5,8-Dihydro-5,8-methanoquinoxaline 1-Oxide (23) and the Triazoledione 5. A solution of **23** (70 mg, 0.4 mmol) and the triazoledione **5** (303 mg, 1.7 mmol) in acetonitrile (10 cm^3) was refluxed for 34 h. The solution was concentrated and the residue was separated by column chromatography (silica gel, ethyl acetate–ethanol 97/3) to give 2,4,6,11,14-pentaaza-4-phenylpentacyclo[7.7.0.$0^{2,6}$.$0^{7,16}$.$0^{10,15}$] hexadeca-10,12,14-triene-3,5-dione 14-oxide (**24**) (55 mg, 41%): Light tan solid (from acetonitrile); decomp 253 °C; IR (KBr) 1776, 1720, 1585, 1431, 1396 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ=1.67 (1H, dd, J=14 and 4 Hz, 6-H_{endo}), 2.47 (1H, dd, J=14 and 5 Hz, 6-H_{exo}), 3.91 (1H, dt, J=5 and 2 Hz, 5-H), 4.15 (1H, br s, 8-H), 4.90 (1H, m, 7-H), 4.94 (1H, br s, 9-H), 7.42 (1H, m), 7.49 (4H, m), 7.91 (1H, d, J=4 Hz, 3-H), 8.20 (1H, d, J=4 Hz, 2-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=33.6 (C-6), 47.3 (C-5), 47.5 (C-8), 57.6 (C-7), 76.7 (C-9), 125.6, 128.9, 129.5, 131.1, 133.5 (C-3), 139.1 (C-4a), 145.9 (C-2), 156.1 (CO), 157.0 (CO), 165.2 (C-8a); MS m/z (rel intensity) 335 (100; M^+), 318 (19; M − OH), 119 (65; PhNCO). Found: C, 60.97; H, 3.70; N, 20.91%. Calcd for $C_{17}H_{13}N_5O_3$: C, 60.89; H, 3.91; N, 20.89%.

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