A Novel Isocyanate Reaction − The Formation and Structure of Unexpected Cycloadducts

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Phenyl isocyanate reacts with six-membered cyclic formamidines, e.g. with substituted 3,4-dihydroquinazolines **1**, at ambient temperature in an expected route to give the 1,3,5-triazines **4** by [2+2+2] cycloaddition. However, at elevated temperatures the unexpected cycloadducts **6**, **7** and **8** are formed from these substrates in a novel isocyanate reaction occurring both at the C–H bond of the formamidine moiety and at the C–H bond of the adjacent *N*-methylene group. Azomethine ylides **9** are generated as key intermediates in this new reaction. The kinetically controlled [3+2] cycloadduct **6** is formed by trapping **9** with isocyanate, whereas regioisomer **7** is the thermodynamically controlled cycloadduct. Dimerization to **8** is preferred by sterically less hindered azomethine ylides **9** under thermodynamic control. One X-ray structure analysis is given for each type of the cycloadducts obtained.

Introduction

For the reaction of isocyanates with simple *N*-methylene groups, e.g. with the CH_2 group of benzylamine,[1] the use of very strong bases appears to be mandatory. Thus, Katritzky et al.[1] obtained *N*-substituted amides of α-aminophenylacetic acid from benzylamine and isocyanates, using *tert*-butyllithium.

We have studied the reaction of 1,4,5,6-tetrahydropyrimidine and 1,6-dihydropyrimidine derivatives (in particular, a wide variety of substituted 3,4-dihydroquinazolines) with phenyl isocyanate at ambient and elevated temperatures, with the aim of finding a novel type of isocyanate reaction occurring at nonactivated C−H bonds of *N*-methylene groups without the assistance of very strong bases.[2] Surprisingly, such a reaction takes place both with 1-substituted 1,4,5,6-tetrahydropyrimidines and with 3-substituted 3,4-dihydroquinazolines **3**. The second reaction is more selective and is discussed below, using only a few selected examples **a**−**c** of substitution.

The reacting heterocycles **3** are cyclic formamidines with a six-membered ring. A priori, the reaction of formamidines with phenyl isocyanate, which has been studied extensively,[3] should be predictable enough: 1,3,5-Triazine derivatives are formed by a [2+2+2] cycloaddition reaction at low temperatures, while parabanic acid derivatives like **2** can be obtained at higher temperatures. The high-temperature reaction demands only a splitting of the C−H bond at the formamidine carbon atom, forming a carbene intermediate, which adds two isocyanate molecules in a [1+2+2] cycloaddition to give the parabanic acid structure. *N*-Methylene C−H bonds of formamidines have not previously been reported to be involved in an isocyanate reaction. Therefore, the main products from **3** and phenyl isocyanate were expected to be the [1,3,5]triazine derivatives **4** at low temperature, and the spiro compounds **5** at high temperature (Scheme 1). This would be comparable to the formation of spiro compounds **2**[3d] from 2-imidazolines **1** at elevated temperatures.

Results and Discussion

Under mild conditions, the [2+2+2] cycloadducts **4** were always obtained (for example **4c** in 48% yield at ambient temperature). However, we did not observe formation of structure **5** in our reaction mixtures.

At temperatures above 110 °C, three different cycloadduct structures **6**, **7** or **8**, depending on the reaction conditions and the substituent R′ in the 3-position of the 3,4-dihydroquinazolines **3**, were obtained as the main products in our reaction (Scheme 2). These polycyclic ring systems are unknown in the literature. Their structures indicate that this reaction involves not only the formyl hydrogen atom in the 2-position, but also one methylene hydrogen atom in the 4-position of **3**, always giving 1,3-diphenylurea and 1,3,5-triphenylbiuret as by-products containing the hydrogen atom from these positions.

Cycloadduct **6a** was obtained in 42% yield from 3-methyl-3,4-dihydroquinazoline (**3a**) after 5 h in boiling toluene containing an excess of phenyl isocyanate, whereas the polycyclic piperazine derivative **8a** resulted in 61% yield from **4a** and phenyl isocyanate after 6 h at the higher temperature of boiling *o*-dichlorobenzene. Compound **6a** was

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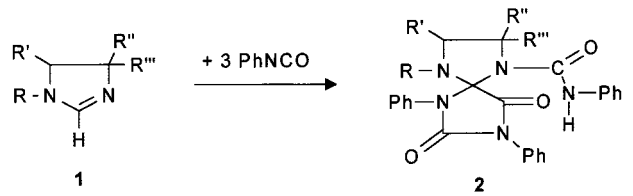
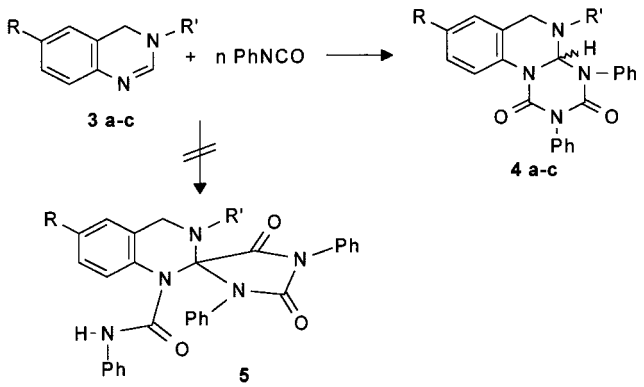
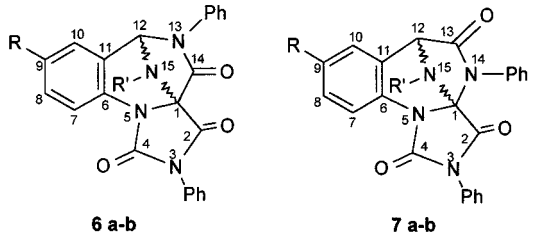
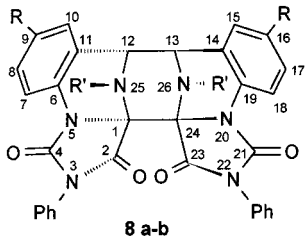




	R	R'
a	H	Me
b	Me	4-Me-C_6H_4
c	H	Bzl

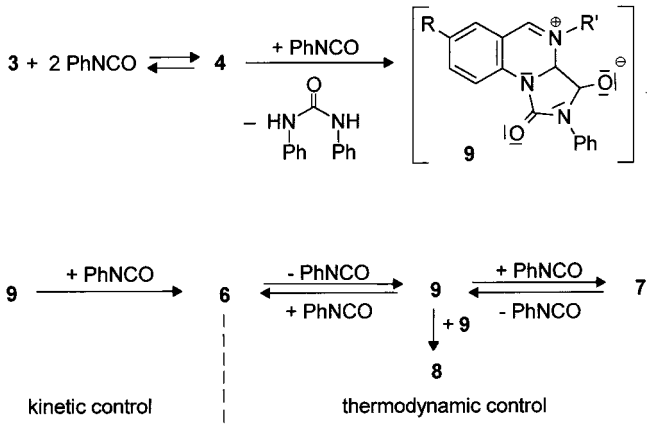
Scheme 1. Cycloaddition of phenyl isocyanate to 2-imidazolines[3d] and to 3,4-dihydroquinazolines





	R	R'
a	H	Me
b	Me	4-Me-C_6H_4

Scheme 2. Products of phenyl isocyanate cycloaddition at elevated temperatures



Scheme 3. Formation of cycloadducts **6**, **7** and **8**

formed with high selectivity, but separation and purification procedures decreased the isolated yield considerably. The formation of its regioisomer **7a** was never observed. Demonstrating the influence of the substituent R′ in the 3-position, **4b** gives **6b** in 76% yield after 4 h in boiling *o*-dichlorobenzene containing excess of phenyl isocyanate, whereas after 32 h the regioisomer **7b** becomes the main product. In spite of the considerable reaction time and the drastic reaction conditions, **8b** is formed only in trace amounts. Isolation of pure cycloadduct **7b**, free of traces of **6b**, is difficult and gives only 31% yield.

The structures of **4** and, especially, of the unexpected cycloadducts **6**, **7** and **8** provide a first clue as to the reaction mechanism (Scheme 3). The reaction starts with the rapid formation of triazine **4**, and continues with the conversion of **4** into the key intermediate **9** − an azomethine ylide − in the rate determining step. Finally, the heterocyclic azomethine ylide **9**, a reactive 1,3-dipole, is trapped by the dipolarophile phenyl isocyanate, giving the kinetically controlled [3+2] cycloadduct **6**. Thus, the essence of our novel reaction is the generation of a heterocyclic azomethine ylide from a cyclic formamidine resulting from an isocyanate. A probable but unproven mechanism of the triazine conversion into **9** has been discussed.[2] The thermal transformation of the quite unstable triazine ring of **4** into the azomethine ylide **9** with an imidazolidinedione moiety is likely to occur via a carbene as the key intermediate. However, no intermediate could be detected by NMR studies during this reaction. This important step of our novel reaction is the subject of further investigation.

The aryl-substituted regioisomers **6b** and **7b** are in a cycloaddition/cycloreversion equilibrium via **9b**. An increase in temperature or a prolongation of reaction time shifts this equilibrium towards the thermodynamically controlled cycloadduct **7b**.

As far as we know, this is the first example of the formation of two regioisomers by cycloaddition from azomethine ylides and an isocyanate. It has been pointed out[4] that the regioselectivity of the [3+2] cycloaddition of isocyanates to acceptor-substituted azomethine ylides is the result of linking the NCO carbon atom to the acceptor-substituted carbon atom of the azomethine ylide. In contrast, our substi-

tuted 1-oxo-2-phenyl-1,2-dihydroimidazo[1,5-*a*]quinazolin-4-ium-3-olate **9** has both acceptor and donor substituents at the ylide carbon atom C-3a and should be able to react under thermodynamic control as a capto-datively stabilized diradical[5] intermediate.

Azomethine ylides like **9a**, derived from 3,4-dihydroquinazolines with small alkyl substituents (e.g. methyl) in the 3-position have a strong tendency to stabilize themselves by dimerization. In such a way, the head-to-head dimer of **9a**, the piperazine derivative **8a**, is formed as a thermodynamically controlled product if the cycloaddition/cycloreversion equilibrium between **9a** and **6a** is shifted towards the ylide by an increase in temperature or an extension of reaction time.

The azomethine ylide dimer **8b** was prepared in 47% yield by heating melted **6b** to 290 °C and distilling off the phenyl isocyanate formed by the [5→3+2] cycloreversion reaction of **6b** at 1 kPa. We have exploited this [5→3+2] cycloreversion reaction as a general method with several compounds **6**,[2] using thermal decomposition of the 4-imidazolidinone ring to generate the corresponding azomethine ylides **9** and carrying out a great variety of 1,3-dipolar cycloadditions with them. In this manner, **6a** was converted into the cyclohexyl derivative **6d** by heating in excess cyclohexyl isocyanate, yielding 89% **6d**. The [3+2] cycloadduct of cyclohexyl isocyanate to **9a** was formed with the same regioselectivity as **6a**; hence the phenyl group in the 13-position of **6a** was replaced by a cyclohexyl substituent in **6d**. This conversion was necessary to obtain crystals of **6d** of a quality adequate for X-ray crystal structure analysis, it being impossible to obtain single crystals of **6a** directly.

The thermal decomposition of 4-imidazolidinones into isocyanates and azomethine ylides is similar to the well-established synthesis of azomethine ylides by thermal decarboxylation of 5-oxazolidinones.[6]

The different types of cycloadduct obtainable by this novel reaction can easily be distinguished by their characteristic ^{1}H- and ^{13}C-NMR spectra. However, X-ray diffraction studies were required in order to distinguish **6** from **7**, and head-to-head from head-to-tail dimer. Unfortunately, all cycloadducts were obtained as colorless microcrystalline or nearly amorphous powders and considerable efforts had to be made to obtain single crystals from at least one substance of each type of obtained cycloadduct. The problem was solved for compounds **4c**, **6d**, **7b** and **8a**, which crystallize as racemates.

In the crystal structure of the (4a*S*) enantiomer of **4c**, the tetrahydroquinazoline moiety forms a half-chair. In all cases, isocyanate cycloaddition creates stereogenic centers. The chiral carbon atom C-4a (C6 in Figure 1) is positioned under the molecular plane of the benzene ring and atoms C10 and N1 in Figure 1. Except for the chiral carbon atom, all atoms of the triazine ring are nearly planar, the regression surface of these five atoms being twisted by 43.4° around the C9−N1 bond axis against the plane of the benzene ring.

The molecular structures of the (1*S*,12*R*) enantiomer of **6d** and of the (1*S*,12*S*) enantiomer of **7b** (Figure 2) con-

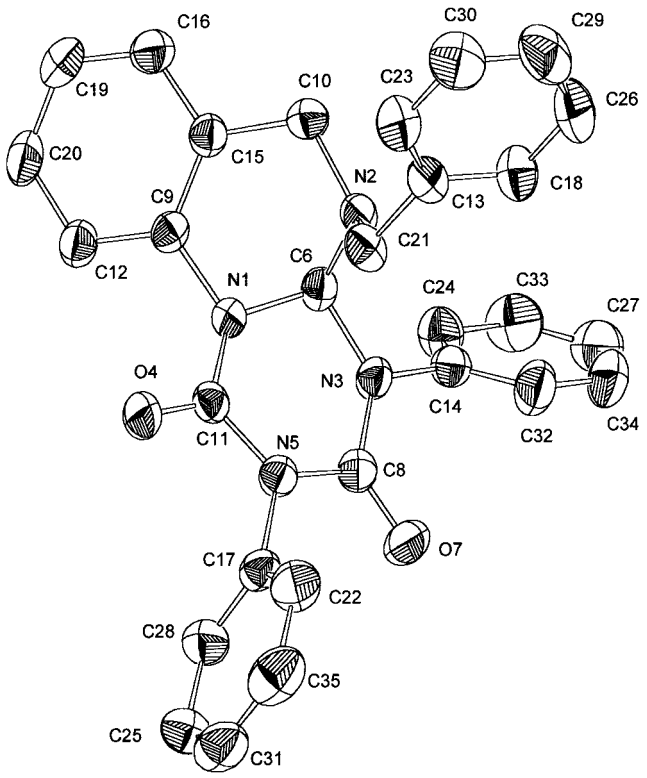


Figure 1. ORTEP plot (50% probability level, hydrogen atoms omitted for clarity) of the (4a*S*) enantiomer from the crystal structure of **4c**

firmed our general NMR assignment of the regioisomers **6** and **7**. The C−N bonds between atoms number 13 and 14 in the imidazolidinone rings of both cycloadducts have multiple-bond character, proven by a length of only 134.3 pm [N(1)−C(17) distance in Figure 2] in **6d** and of 137.5 pm [N(1)−C(24) distance in Figure 2] in **7b**. In addition to the short C−N distance observed, the C−C single bond between C-1 and C-14 [C(16) and C(17) in Figure 2] of length 154.8 pm is the longest bond of the molecule **6d**. Thus, the bonding structure of the imidazolidinone ring in type **6** cycloadducts may explain their tendency to undergo [5→3+2] cycloreversion to give the azomethine ylides **9** and isocyanates.

The preference for head-to-head dimerization of azomethine ylides **9** has been verified by the crystal structure of **8a**. Exclusive head-to-head dimerization leads to a chiral polycyclic piperazine derivative of chair conformation in the piperazine ring. The four chiral carbon atoms of the enantiomeric molecules **8a**, arranged in either (all-*R*) or (all-*S*) configuration, belong to the central piperazine moiety. The alternative head-to-tail arrangement of **9** to a piperazine chair would give an achiral dimer, a *meso* compound, which in most cases was not observed. The two piperazine ring C−C bonds formed by dimerization are the longest bonds of the molecule **8a**, and the bond between C-1 and C-24 (C1−C4 bond in Figure 3), with its length of 158.8 pm, belongs to the class of extraordinarily long carbon−carbon single bonds. Although the bonding structure of the piperazine ring appears to enable **8a** to undergo

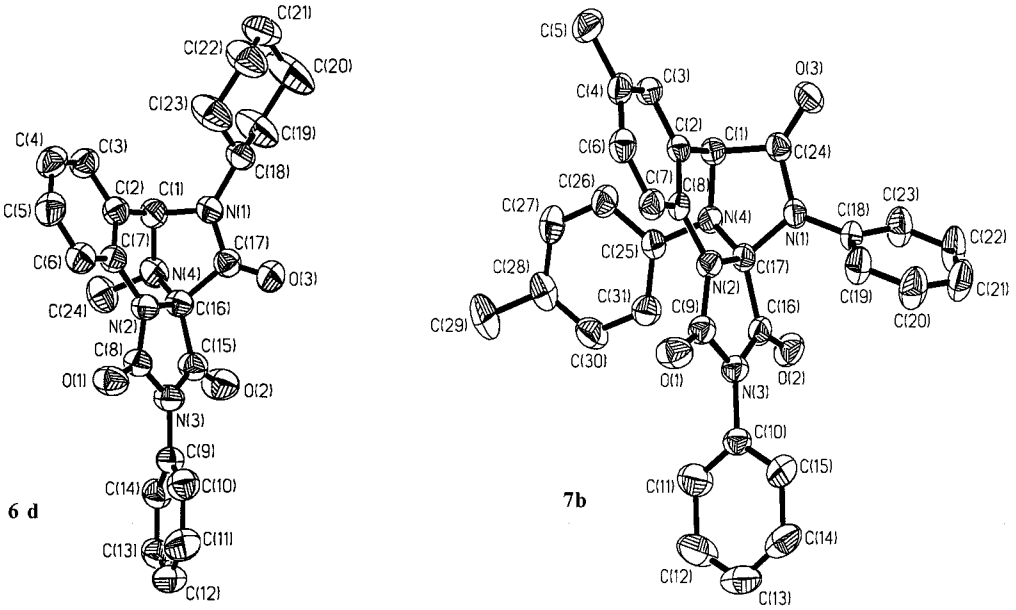


Figure 2. ORTEP plots (50% probability level, hydrogen atoms omitted for clarity) of the (1*S*,12*R*) enantiomer of the crystal structure of racemate **6d** and of the (1*S*, 12*S*) enantiomer from the crystal structure of racemate **7b**

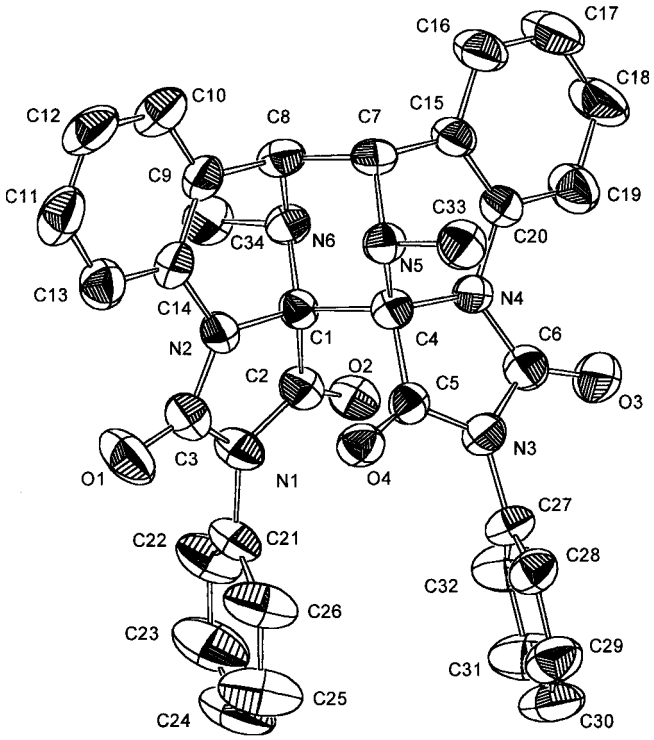


Figure 3. ORTEP plot (50% probability level, hydrogen atoms omitted for clarity) of the (1*S*,12*S*,13*S*,24*S*) enantiomer from the crystal structure of racemate **8a**

easy cycloreversion reaction, all head-to-head dimers **8** are surprisingly stable and cannot be used as sources of azomethine ylides **9**. Compound **8a** remains unchanged after boiling in 48% hydrobromic acid and reacts neither with boiling dimethyl acetylenedicarboxylate, nor with maleic anhydride in boiling *o*-dichlorobenzene. In contrast, piperazine derivatives formed by head-to-tail dimerization of N-hetarenium ylides[7] are known to be useful sources of such ylides. These give [3+2] cycloaddition products with reactive dipolarophiles and N-hetarenium bromides with hydrobromic acid. Decomposition of **8a** to give **9a** cation radicals is only observed in its mass spectrum, as an electron impact induced cycloreversion.

Conclusion

Our investigations have demonstrated that nonactivated endocyclic *N*-methylene C−H bonds can react with phenyl isocyanate in a one-pot procedure. This novel reaction allows the transformation of cyclic formamidines − e.g. 3-substituted 3,4-dihydroquinazolines − into heterocyclic azomethine ylides condensed with an imidazolidinedione ring. The reaction, depending on reaction conditions and the size of the formamidine *N*-substituent, has been used to synthesize regioisomeric cycloadducts of isocyanates with the generated azomethine ylides, or with the azomethine ylide dimers. The kinetically controlled [3+2] cycloadducts are useful sources of the heterocyclic azomethine ylides described, which are easily obtainable by thermal [5→3+2] cycloreversion of these cycloadducts.

Experimental Section

General: Solvents used in all reactions involving isocyanates were thoroughly dried according to common procedures and distilled. All reactions were carried out under argon or nitrogen. − Melting points were taken under a microscope (Boetius apparatus, type PHMK 05) and were corrected. − TLC: Precoated sheets, Alugram SIL G/UV$_{254}$ Macherey−Nagel; detection by UV extinction. − IR: Nicolet FT-IR 205. − ^{1}H- and ^{13}C-NMR spectra were recorded at room temp. in $CDCl_3$ unless otherwise indicated; in most cases with a Bruker ACD 200 spectrometer (^{1}H NMR 200.13 MHz, ^{13}C NMR 50.3 MHz always with broad-band decoupling and DEPT; GD in some cases), or with a Bruker WH 90 spectrometer (^{1}H

NMR 90 MHz, ^{13}C NMR 22.6 MHz), or a Bruker MSL 300 spectrometer (^{13}C NMR 75.5 MHz). Chemical shifts relative to internal TMS ($\delta = 0$) or to resonances of the solvent or solvent impurity $CHCl_3$ (^1H: $\delta = 7.25$, ^{13}C: $\delta = 77.0$). − MS: Finnigan MAT 95 mass spectrometer. − Elemental analyses: Carlo Erba Instruments EA 1108 Elemental Analyzer.

3,4-Dihydroquinazolines **3** were synthesized according to literature methods:

6-Methyl-3-(4-tolyl)-3,4-dihydroquinazoline (3b):[8] From a one-pot reaction of 4-toluidine, formaldehyde and formic acid in 27% yield. − ^1H NMR: $\delta = 7.48$ (s, 1 H, 2-H), 7.25−7.0 (m, 7 H, arom. H), 6.78 (s, 1 H, 5-H), 4.85 (s, 2 H, 4-H), 2.33 (s, 3 H, 6-CH_3), 2.29 (s, 3 H, 4′- CH_3). − ^{13}C NMR: $\delta = 146.3$ (C-2), 140.9 (C-1′), 138.7 (C-8a), 135.3 (C-6), 134.2 (C-4′), 130.1 (C-3′), 129.0 (C-5), 126.2 (C-7), 124.5 (C-8), 120.9 (C-4a), 118.1 (C-2′), 47.2 (C-4), 21.0 (6-CH_3), 20.7 (4′-CH_3).

3-Benzyl-3,4-dihydroquinazoline (3c):[9] From 2-nitrobenzaldehyde and benzylamine via *N*-(2-aminobenzyl)benzylamine. − ^1H NMR: $\delta = 7.39-6.90$ (m, 9 H, 2-H, arom. H), 6.74 (d, $^3J = 7.5$ Hz, 1 H 5-H), 4.36 (s, 2 H, 4-H), 4.26 (s, 2 H, CH_2). − ^{13}C NMR: $\delta = 150.1$ (C-2), 141.2 (C-8a), 134.9 (C-1′), 128.8 (C-3′), 128.2 (C-4′), 128.1 (C-7), 127.7 (C-2′), 125.6 (C-5), 124.7 (C-6), 124.4 (C-8), 120.1 (C-4a), 56.7 (CH_2), 46.2 (C-4).

3-Methyl-3,4-dihydroquinazoline (3a): This compound was prepared by an improved general method[10] for the syntheses of 3,4-dihydroquinazolines from 2-aminobenzylamines and triethyl orthoformate. Thus, *N*-(2-aminobenzyl)methylamine[11] (13.6 g, 0.1 mol) and triethyl orthoformate (50 mL, 0.3 mol) were heated slowly in a distillation apparatus with a 70-cm column in such a way that the head temp. was kept below 82 °C and only EtOH was distilled off. After 2 h, the bath temp. was increased to 170 °C and part of the triethyl orthoformate excess was distilled off. The remaining orthoformate was removed in vacuo. The distillation residue solidified after cooling and yielded 14 g (96%) of crude **3a**, m.p. 89−91 °C (ref.[12] 90−91 °C) and was used for the phenyl isocyanate reaction without further purification. − IR (KBr): $\tilde{\nu} = 2974.3$ cm^{-1}, 1623.3, 1601.2, 1574.8, 1489.8, 765.6 (γ-CH arom.). − ^1H NMR: $\delta = 7.18-6.79$ (m, 5 H, 2-H, 5-H, 6-H, 7-H, 8-H), 4.48 (s, 2 H, 4-H), 2.77 (s, 3 H, CH_3). − ^1H NMR: ($CDCl_3$ + [D_4]acetic acid): $\delta = 8.41$ (s, 1 H, 2-H), 7.21−6.90 (m, 4 H, 5-H, 6-H, 7-H, 8-H), 4.63 (s, 2 H, 4-H), 3.22 (s, 3 H, CH_3). − ^{13}C NMR: $\delta = 149.8$ (C-2), 140.9 (C-8a), 127.6 (C-7), 124.9 (C-5), 123.9 (C-6), 123.6 (C-8), 119.2 (C-4a), 48.1 (C-4), 39.0 (CH_3). − $C_9H_{10}N_2$ (146.2): calcd. C 73.94, H 6.89, N 19.16; found C 73.55, H 6.98, N 19.05.

General Procedure for the Synthesis of [2+2+2] Cycloadducts 4 from 3-Alkyl-3,4-dihydroquinazolines 3 (GP1): The 3,4-dihydroquinazoline **3** (0.01 mol) was added slowly in small portions to a stirred and chilled solution of phenyl isocyanate (0.04 mol) in Et_2O (25 mL) at 0 °C. Stirring was continued at room temp. and the crystallized **4** was separated by filtration when the mixture had nearly solidified or after 24 h. The crude product **4** was thoroughly washed with Et_2O and dried.

General Procedure for the Synthesis of [2+2+2] Cycloadducts 4 from 3-Aryl-3,4-dihydroquinazolines 3 (GP2): The 3,4-dihydroquinazoline **3** (0.01 mol) and phenyl isocyanate (11.9 g, 0.1 mol) were heated together at 80 °C. After 26 h, the mixture was cooled to room temp. and the crude product **4** was precipitated by addition of *n*-pentane (100 mL) and stirring. Then the liquid was removed by filtration or by decantation, and the crude cycloadduct was treated once more in the same way with *n*-pentane (100 mL). Finally, the crude product was stirred in MeOH (50 mL), filtered off with suction, washed with MeOH and dried.

Purification: In some cases, the crude [2+2+2] cycloadducts **4** obtained by GP1 or GP2 were contaminated with 1,3-diphenylurea and/or triphenyl isocyanurate. For the purpose of purification the crude product **4** was dissolved in CH_2Cl_2, using 20 mL of CH_2Cl_2/1 g of **4**, and the insoluble urea was filtered off. The filtrate was poured into double the volume of *n*-heptane and the solution was left to crystallize in an open beaker. The successively obtained crystalline fractions were analyzed: the first and second fractions contained mainly triphenyl isocyanurate, whereas the last fractions were pure **4**.

5-Methyl-2,4-diphenyl-4,4a,5,6-tetrahydro-1*H*-[1,3,5]triazino[1,2-*a*]quinazoline-1,3(2*H*)-dione (4a): According to GP1, **3a** and phenyl isocyanate yielded 3.2 g (83%) of **4a**, m.p. 137.5−139 °C (dec.). − IR (KBr): $\tilde{\nu} = 1720.2$ cm^{-1}, 1682.8, 1492.0, 1449.6 sh, 1433.4, 1426.5, 1418.8, 1376.6, 1258.2, 758.6, 695.3. − ^1H NMR: $\delta = 7.81$ (d, $^3J = 8$ Hz, 1 H, 10-H), 7.54−7.02 (m, 13 H, arom. H), 5.91 (s, 1 H, 4a-H), 4.40 (d, $^2J_{AB} = 18$ Hz, 1 H, 6-H, A-part of AB system), 3.88 (d, $^2J_{AB} = 18$ Hz, 1 H, 6-H, B-part of AB system), 2.63 (s, 3 H, CH_3). − ^{13}C NMR: $\delta = 150.3$ (C-1), 149.9 (C-3), 138.3 (C-10a), 135.7 (C-1′ 2-Ph), 135.0 (C-1′′ 4-Ph), 128.9 (2 C-3′ 2-Ph), 128.8 (2 C-3′′ 4-Ph), 128.6 (2 C-2′ 2-Ph), 128.0 (C-4′ 2-Ph), 127.7 (C-4′′ 4-Ph), 127.5 (2 C-2′′ 4-Ph), 126.4 (C-7), 126.2 (C-9), 125.5 (C-6a), 125.4 (C-8), 124.9 (C-10), 83.4 (C-4a), 54.0 (C-6), 32.9 (5-CH_3). − MS (EI, 12 eV); *m*/*z* (%): 384 (0.5) [M^+], 265 (2) [M^+ − PhNCO], 146 (50) [M^+ − 2 PhNCO], 145 (70) [quinazolinium cation], 119 (100) [$PhNCO^+$]. − MS (FD pos.); *m*/*z* (%): 384 (100) [M^+]. − $C_{23}H_{20}N_4O_2$ (384.4): calcd. C 71.86, H 5.24, N 14.57; found C 71.37, H 5.29, N 14.58.

8-Methyl-2,4-diphenyl-5-(4′-tolyl)-4,4a,5,6-tetrahydro-1*H*-[1,3,5]-triazino[1,2-*a*]quinazoline-1,3(2*H*)-dione (4b): Compound **3b** was converted in accordance with GP2, yielding 2.3 g (49%) of **4b**, m.p. 164−165 °C (dec.). − IR (KBr): $\tilde{\nu} = 1726.9$ cm^{-1}, 1687.2, 1499.8, 1433.8, 1428.6, 1257.6, 1219.9, 682.5. − ^1H NMR (90 MHz): $\delta = 8.0-7.05$ (m, 15 H, arom.-H), 6.68−6.50 (m, 2 H, arom.-H), 6.23 (s, 1 H, 4a-H), 4.94 (d, $^2J_{AB} = 18$ Hz, 1 H, 6-H, A-part of AB system), 4.52 (d, $^2J_{AB} = 18$ Hz, 1 H, 6-H, B-part of AB system), 2.42 (br. s, 6 H, 8-CH_3 and 4′-CH_3). − ^{13}C NMR: $\delta = 150.0$ (C-1), 149.6 (C-3), 142.1 (C-1′ 5-tolyl), 140.0 (C-10a), 136.2 (C-1′′ 2-Ph), 135.7 (C-1′′′ 4-Ph), 134.82 (C-4′ 5-tolyl), 134.8 (C-8), 130.3 (2 C-3′ 5-tolyl), 129.0 (2 C-3′′ 2-Ph), 128.9 (2 C-3′′′ 4-Ph), 128.4 (2 C-2′′ 2-Ph), 128.0 (C-4′′ 2-Ph), 127.6 (C-4′′′ 4-Ph), 127.0 (C-7), 126.9 (C-6a), 126.1 (2 C-2′′′ 4-Ph), 125.8 (C-9), 125.4 125.6 (C-10), 125.4 (2 C-2′ 5-tolyl), 82.8 (C-4a), 53.9 (C-6), 21.0 (4′-CH_3 5-tolyl) 20.8 (8-CH_3). − MS (EI, 12 eV); *m*/*z* (%): 474 (0.3) [M^+], 355 (0.5) [M^+ − PhNCO], 236 (60) [M^+ − 2 PhNCO], 235 (100) [quinazolinium cation], 119 (38) [$PhNCO^+$]. − $C_{30}H_{26}N_4O_2$ (474.6): calcd. C 75.93, H 5.52, N 11.81; found C 75.72, H 5.64, N 11.92.

5-Benzyl-2,4-diphenyl-4,4a,5,6-tetrahydro-1*H*-[1,3,5]triazino[1,2-*a*]-quinazoline-1,3(2*H*)-dione (4c): According to GP1, **3c** and phenyl isocyanate yielded 2.2 g (48%) of **4c**, m.p. 153−156 °C (dec.). Compound **4c** was recrystallized from MeOH by a controlled cooling-down process. Single crystals of **4c** for X-ray structure analysis were obtained by this procedure, m.p. 164−166 °C (dec.). − IR (KBr): $\tilde{\nu} = 1717.8$ cm^{-1}, 1686.6, 1491.8, 1435.8, 1382.3, 1262.7, 757.5, 694.0. − ^1H NMR: $\delta = 7.92$ (dd, $^3J = 7.5$ Hz, $^4J \approx 1$ Hz, 1 H, 10-H), 7.56−7.1 (m, 17 H, arom.-H), 6.96 (dd, $^3J = 7.5$ Hz, $^4J \approx 1$ Hz, 1 H, 7-H), 6.14 (s, 1 H, 4a-H), 4.32 (d, $^2J_{AB} = 12.9$ Hz, 1 H, CH_2, A-part of AB system 1), 4.05 (d, $^2J_{AB} = 17.6$ Hz, 1 H, 6-H, A-part of AB system 2), 3.85 (d, $^2J_{AB} = 17.6$ Hz, 1 H, 6-H, B-part of AB-

system 2), 3.68 (d, $^2J_{AB}$ = 12.9 Hz, 1 H, CH_2, B-part of AB system 1). − ^{13}C NMR: δ = 150.6 (C-1), 150.5 (C-3), 138.5 (C-10a), 136.6 (C-1′ 5-Bzl), 135.9 (C-1′′ 2-Ph), 135.5 (C-1′′′ 4-Ph), 129.3 (2 C-3′′ 2-Ph), 128.9 (2 C-3′ 5-Bzl and 2 C-3′′′ 4-Ph), 128.7 (2 C-2′′ 2-Ph), 128.6 (2 C-2′′′ 4-Ph), 128.4 (C-4′′ 2-Ph), 128.1 (C-4′′′ 4-Ph), 128.0 (2 C-2′ 5-Bzl), 127.6 (C-4′ 5-Bzl), 126.9 (C-7), 126.8 (C-9), 125.7 (C-8), 125.5 (C-6a), 124.9 (C-10), 83.9 (C-4a), 49.3 (C-6), 48.8 (CH_2 5-Bzl). − MS (EI, 70 eV); *m/z* (%): 460 (0.2) [M^+], 341 (2) [M^+ − PhNCO], 222 (98) [M^+ − 2 PhNCO], 221 (60) [quinazolinium cation], 119 (100) [$PhNCO^+$]. − $C_{29}H_{24}N_4O_2$ (460.5): calcd. C 75.63, H 5.25, N 12.17; found C 75.27, H 5.42, N 12.01.

General Procedure for the Synthesis of [3+2] Cycloadducts 6 from 3-Alkyl-3,4-dihydroquinazolines 3, or from Their [2+2+2] Cycloadducts 4 (GP3). − Starting from 3: A toluene solution containing **3** (0.4 mol·L^{-1}) and phenyl isocyanate (2.4 mol·L^{-1}) was refluxed for at least 5 h. Sometimes this method had the disadvantage that only catalytic trimerization of the isocyanate was observed as an irreproducible process. − **Starting from 4:** In order to avoid this effect, a toluene solution or suspension containing **4** (0.4 mol·L^{-1}) and phenyl isocyanate (1.6 mol·L^{-1}) was refluxed for at least 6 h. The reaction mixture was cooled to 40 °C and *n*-hexane was added in small portions with stirring until a solid product began to precipitate (too fast addition or addition of too large an amount of *n*-hexane caused an oily or tarry product to separate). After standing overnight for complete precipitation, crude **6** was filtered off with suction and washed with *n*-hexane. If the crude product had a sticky or tarry consistency it was poured into a small quantity of MeOH, warmed and stirred to dissolve impurities (e.g. 1,3,5-triphenylbiuret). After cooling the MeOH suspension and collecting and washing the solid with MeOH, a colorless microcrystalline powder **6** was obtained. If its yield was unsatisfactory, all the filtrates containing *n*-hexane were worked up as follows: A large amount of *n*-hexane was added to the combined filtrates, the *n*-hexane/toluene phase was decanted, and the tarry residue was extracted one more time with *n*-hexane. The residue was dissolved in warm MeOH, and the solution was left in a beaker to crystallize. The first and second successively obtained crystalline fractions consisted mainly of **6**, the last crystalline fractions being 1,3,5-triphenylbiuret. All crude product fractions were combined and analyzed together. If **6** contained 1,3-diphenylurea and/or triphenyl isocyanurate, it was purified successfully by the method described above for the purification of **4**.

15-Methyl-3,13-diphenyl-3,5,13,15-tetraazatetracyclo[10.2.1.0^{1,5}.0^{6,11}]pentadeca-6(11),7,9-triene-2,4,14-trione (6a): According to GP3 (6 h reflux), **4a** (38.4 g, 0.1 mol) and phenyl isocyanate yielded 23.12 g (57%) of **6a**, while according to GP3 (5 h reflux), **3a** (1.46 g, 0.01 mol) and phenyl isocyanate yielded 1.73 g (42%) of **6a**, m.p. 224−227 °C (acetone). − IR (KBr): ṽ = 1793.8 cm^{-1}, 1738.8, 1710.0, 1501.7 (sh), 1485.3, 1401.6 (sh), 1384.2, 1368.8, 1164.3, 753.9. − ^{1}H NMR: δ = 8.37 (d, ^3J = 8 Hz, 1 H, 7-H), 7.54−7.09 (m, 13 H, arom. H), 5.53 (s, 1 H, 12-H), 2.37 (s, 3 H, 15-CH_3). − ^{13}C NMR: δ = 163.7 (C-2), 162.4 (C-14), 150.7 (C-4), 135.4 (C-1′′ 13-Ph), 132.4 (C-6), 130.9 (s, C-8), 130.8 (C-1′ 3-Ph), 129.4 (2 C-3′′ 13-Ph), 129.3 (2 C-3′, 3-Ph), 129.0 (C-4′, 3-Ph), 127.5 (C-10), 126.5 (2 C-2′ 3-Ph), 126.3 (C-4′′ 13-Ph), 123.9 (C-9), 120.8 (2 C-2′′, 13-Ph), 119.3 (C-11), 118.1 (C-7), 80.9 (C-1), 77.7 (C-12), 31.6 (15-CH_3). − MS (EI, 12 eV); *m/z* (%): 410 (0.3) [M^+], 291 (100) [M^+ − PhNCO], 119 (68) [$PhNCO^+$], 28 (54) [CO^+]. − MS (FD pos.); *m/z* (%): 410 (100) [M^+], 382 (88) [M^+ − CO]. − $C_{24}H_{18}N_4O_3$ (410.4): calcd. C 70.23, H 4.42, N 13.65; found C 70.01, H 4.51, N 13.76.

15-Benzyl-3,13-diphenyl-3,5,13,15-tetraazatetracyclo[10.2.1.0^{1,5}.0^{6,11}]pentadeca-6(11),7,9-triene-2,4,14-trione (6c): According to GP3 (8.5 h reflux), **3c** (4.44 g, 0.02 mol) and phenyl isocyanate yielded 3.68 g (40%) of **4c** and 2.07 g (21%) of **6c**, m.p. 203−205 °C (acetone). − IR (KBr): ṽ = 1789.4 cm^{-1}, 1741.2, 1720.4, 1499.8, 1484.0, 1381.6, 1152.7, 751.81. − ^{1}H NMR: δ = 8.44 (d, ^3J = 8.2 Hz, 1 H, 7-H), 7.54−7.11 (m, 18 H, arom. H), 5.37 (s, 1 H, 12-H), 3.85 (d, $^2J_{AB}$ = 12.6 Hz, 1 H, CH_2, A-part of AB system), 3.46 (d, $^2J_{AB}$ = 12.6 Hz, 1 H, CH_2, B-part of AB system). − ^{13}C NMR: δ = 163.3 (C-2), 162.6 (C-14), 150.7 (C-4), 135.6 (C-1′′ 13-Ph), 133.6 (C-1′′′ 15-Bzl), 132.8 (C-6), 130.9 (C-8), 130.8 (C-1′ 3-Ph), 129.5 (2 C-3′′ 13-Ph), 129.3 (2 C-3′ 3-Ph), 129.1 (2 C-3′′′ 15-Bzl), 128.8 (C-4′ 3-Ph and 2 C-2′′′ 15-Bzl), 128.6 (C-4′′′ 15-Bzl), 127.5 (C-10), 126.4 (C-2′ 3-Ph), 126.2 (C-4′′, 13-Ph), 123.9 (C-9), 120.6 (C-2′′, 13-Ph), 119.4 (C-11), 118.2 (C-7), 80.5 (C-1), 75.5 (C-12), 49.5 (CH_2). − MS (EI, 12 eV); *m/z* (%): 486 (0.02) [M^+], 367 (100) [M^+ − PhNCO], 276 (61) [M^+ − PhNCO − $PhCH_2$·], 119 (3) [$PhNCO^+$], 91 (2) [$PhCH_2^+$]. − $C_{30}H_{22}N_4O_3$ (486.5): calcd. C 74.06, H 4.56, N 11.52; found C 74.39, H 4.86, N 11.72.

13-Cyclohexyl-15-methyl-3-phenyl-3,5,13,15-tetraazatetracyclo-[10.2.1.0^{1,5}.0^{6,11}]pentadeca-6(11),7,9-triene-2,4,14-trione (6d): A solution of **6a** (1.23 g, 0.003 mol) in cyclohexyl isocyanate (30 mL) was refluxed for 2 h and then 26 mL of isocyanate was distilled off under atmospheric pressure. The rest of the isocyanate was removed in vacuo at 1 hPa and a bath temp. below 90 °C. After cooling, the residue was washed with warm MeOH (15 mL) yielding 1.12 g (90%) of **6d**, m.p. 231−233 °C (acetone). − IR (KBr) ṽ = 1790.3 cm^{-1}, 1738.0, 1716.3, 1485.4, 1391.6, 1374.6, 1159.6, 759.1. − ^{1}H NMR: δ = 8.31 (d, ^3J = 8 Hz, 1 H, 7-H), 7.50−7.09 (m, 8 H, arom. H), 5.03 (s, 1 H, 12-H), 3.82 (m_c, 1 H, 1′′-H, cyclohexyl), 2.23 (s, 3 H, 15-CH_3), 1.88−1.06 (br. m, 10 H, cyclohexyl-H). − ^{13}C NMR: δ = 164.0 (C-2), 163.3 (C-14), 150.8 (C-4), 132.5 (C-6), 130.9 (C-1′ 3-Ph), 130.4 (C-8), 129.2 (2 C-3′ 3-Ph), 128.8 (C-4′ 3-Ph), 127.0 (C-10), 126.5 (2 C-2′ 3-Ph), 123.7 (C-9), 121.1 (C-11), 118.0 (C-7), 80.8 (C-1), 74.6 (C-12), 53.1 (C-1′′ 13-cyclohexyl), 31.64 (15-CH_3), 31.56 (C-2′′ 13-cyclohexyl), 30.8 (C-6′′ 13-cyclohexyl), 25.6 (C-3′′ 13-cyclohexyl), 25.5 (C-5′′ 13-cyclohexyl), 25.3 (C-4′′ 13-cyclohexyl). − MS (EI, 70 eV); *m/z* (%): 417 (0.2) [MH^+], 416 (0.4) [M^+], 292 (100) [MH^+ − $C_6H_{11}NCO$], 144 (50), 119 (15) [$PhNCO^+$], 91 (30), 60 (17), 43 (22). − $C_{24}H_{24}N_4O_3$ (416.5): cald. C 69.21, H 5.81, N 13.45; found C 69.58, H 5.90, N 13.60.

General Procedure for the Synthesis of [3+2] Cycloadducts 6 from 3-Aryl-3,4-dihydroquinazolines 3, or from Their [2+2+2] Cycloadducts 4 (GP4). − Starting from 3: A solution or suspension of **3** (0.8 mol·L^{-1}) in phenyl isocyanate was refluxed for at least 3 h. After cooling, the reaction mixture was poured with vigorous stirring into a ten-fold volume of *n*-hexane. The *n*-hexane/isocyanate phase was poured off, and the tarry residue was extracted with *n*-hexane. MeOH was added with stirring to the tarry residue until all tarry impurities dissolved, but the main part of **6** still remained undissolved. Then crude **6** was filtered off with suction and washed with MeOH. − **Starting from 4:** A solution or suspension of **4** (0.4 mol·L^{-1}) and phenyl isocyanate (1.6 mol·L^{-1}) in *o*-dichlorobenzene was refluxed for at least 4 h. Separation and purification of **6** were carried out as for GP3.

9-Methyl-3,13-diphenyl-15-(4′-tolyl)-3,5,13,15-tetraazatetracyclo-[10.2.1.0^{1,5}.0^{6,11}]pentadeca-6(11),7,9-triene-2,4,14-trione (6b): According to GP4 (3 h reflux), **3b** (2.36 g, 0.01 mol) and phenyl isocyanate yielded 2.99 g (60%) of **6b**, while according to GP4 (4 h reflux), **4b** (23.73 g, 0.05 mol) and phenyl isocyanate yielded 19.04 g (76.1%) of **6b**, m.p. 250−252 °C (acetone). − IR (KBr): ṽ = 1790.3

cm^{-1}, 1746.1, 1725.1, 1509.7 (sh), 1498.2, 1372.5, 1152.2, 752.3. − ^1H NMR: δ = 8.13 (d, ^3J = 8.2 Hz, 1 H, 7-H), 7.58−6.81 (m, 16 H, arom. H), 6.14 (s, 1 H, 12-H), 2.29 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3). − ^{13}C NMR: δ = 164.0 (C-2), 162.5 (C-14), 150.3 (C-4), 137.8 (C-1‴ 15-tolyl), 135.3 (C-1″ 13-Ph), 133.8 (C-4‴ 15-tolyl), 133.5 (C-9), 131.1 (C-8), 130.9 (C-1′ 3-Ph), 130.3 (2 C-3‴ 15-tolyl), 130.0 (C-6), 129.4 (2 C-3″ 13-Ph), 129.3 (2 C-3′, 3-Ph), 129.0 (C-4′ 3-Ph), 127.4 (C-10), 126.5 (2 C-2′ 3-Ph), 126.4 (2 C-4″ 13-Ph), 121.4 (C-11), 121.0 (2 C-2″ 13-Ph), 119.1 (2 C-2‴, 15-tolyl), 118.1 (C-7), 79.9 (C-1), 76.3 (C-12), 20.9 (CH_3), 20.6 (CH_3). − MS (EI, 12 eV); *m/z* (%): 500 (1.3) [M^+], 381 (100) [M^+ − PhNCO], 234 (74) [381 − PhNCO − CO], 219 (21) [234 − CH_3·], 207 (23) [234 − HCN], 119 (48) [$PhNCO^+$], 91 (40). − $C_{31}H_{24}N_4O_3$ (500.6): calcd. C 74.39, H 4.83, N 11.19; found C 74.21, H 4.80, N 11.09.

9-Methyl-3,14-diphenyl-15-(4′-tolyl)-3,5,14,15-tetraazatetracyclo-[10.2.1.0^{1,5}.0^{6,11}]pentadeca-6(11),7,9-triene-2,4,13-trione (7b): Compound **3b** (2.36 g, 0.01 mol) and phenyl isocyanate (7.14 g, 0.06 mol) in 25 mL of *o*-dichlorobenzene solution were refluxed for 32 h. The reaction mixture was worked up as for GP3 to yield 2.64 g (53%) of crude **7b** containing a small amount of regioisomer **6b**. TLC (1,2-dichloroethane): **7b**: R_f = 0.25; **6b**: R_f = 0.33. The crude product was refluxed in 80 mL of acetone and the insoluble residue was filtered off with suction from the hot solvent. No **6b** was detected by TLC analysis of the insoluble residue: 1.56 g (31%) of pure **7b** was obtained, m.p. 265−267 °C (toluene). − IR (KBr) $\tilde{\nu}$ = 1795.3 cm^{-1}, 1744.6, 1497.5, 1396.0, 1172.5 (sh), 1160.2, 747.3. − ^1H NMR: δ = 8.03 (d, ^3J = 8.3 Hz, 1 H, 7-H), 7.58−6.81 (m, 16 H, arom. H), 5.07 (s, 1 H, 12-H), 2.41 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3). − ^1H NMR ([D_6]acetone, 90 MHz): δ = 8.08 (d, ^3J = 8.3 Hz, 1 H, 7-H), 7.68−6.94 (m, 16 H, arom. H), 5.54 (s, 1 H, 12-H), 2.42 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3). − ^{13}C NMR (75.5 MHz): δ = 169.4 (C-13), 163.6 (C-2), 149.2 (C-4), 139.1 (C-1‴ 15-tolyl), 135.9 (C-1″ 14-Ph), 134.4 (C-4‴ 15-tolyl and C-9), 131.0 (C-8), 130.9 (C-1′ 3-Ph), 130.3 (2 C-3‴ 15-tolyl), 130.2 (C-6), 129.8 (2 C-3″ 14-Ph), 129.4 (2 C-3′, 3-Ph), 129.4 (C-4′ 3-Ph), 129.3 (C-10), 128.1 (C-4″ 14-Ph), 127.7 (2 C-2″ 14-Ph), 126.4 (2 C-2′ 3-Ph), 120.6 (2 C-2‴ 15-tolyl), 119.4 (C-11), 118.5 (C-7), 91.9 (C-1), 63.9 (C-12), 21.1 (CH_3), 20.6 (CH_3). − MS (EI, 12 eV); *m/z* (%): 500 (2) [M^+], 381 (100) [M^+ − PhNCO], 234 (100) [381 − PhNCO − CO], 219 (19) [234 − CH_3·], 207 (17) [234 − HCN], 119 (40) [$PhNCO^+$], 91 (38), 28 (62). − $C_{31}H_{24}N_4O_3$ (500.6): calcd. C 74.39, H 4.83, N 11.19; found C 74.12, H 4.78, N 11.11.

General Procedure for the Synthesis of Azomethine Ylide Dimers 8 from Cycloadducts 6 (GP5): Solutions (0.04 mol·L^{-1}) were prepared of 15-alkyl-substituted **6** in *o*-dichlorobenzene and of 15-aryl-substituted **6** in 1,2,4-trichlorobenzene. The corresponding dimers **8** were obtained by slow distillation of these solutions under atmospheric pressure. The distillation was stopped when 80% of the solvent (containing phenyl isocyanate from the cycloreversion reaction) had been distilled off. After cooling, insoluble solids were filtered off. The dimer **8** was precipitated from the filtrate by addition of *n*-hexane. It was separated, washed with *n*-hexane and then with MeOH. The obtained dimers were very pure in most cases.

25,26-Dimethyl-3,22-diphenyl-5,5,20,22,25,26-hexaazaheptacyclo-[22.0.1^{1,12}.1^{13,24}.0^{1,5}.0^{6,11}.0^{14,19}.0^{20,24}]hexacosa-6(11),7,9,14(19),15,17-hexaene-2,4,21,23-tetrone (8a): Compound **6a** (1.64 g, 4 mmol) was treated in accordance with GP5 to yield 0.83 g (72%)

Table 1. Crystallographic details for the X-ray analyses of **4c**, **6d**, **7b** and **8a**[14]

Compound	**4c**	**6d**	**7b**	**8a**
Empirical formula	$C_{29}H_{24}N_4O_2$	$C_{24}H_{24}N_4O_3$	$C_{31}H_{24}N_4O_3$	$C_{34}H_{26}N_6O_4$
Molecular mass	460.53	416.48	500.56	582.62
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Cell dimensions:				
a [pm]	1124.19(8)	1252.3(3)	972.6(2)	1349.2(2)
b [pm]	1106.63(10)	1370.1(4)	2010.8(3)	1427.4(1)
c [pm]	1890.29(15)	1256.0(3)	1285.3(2)	1604.1(2)
β [°]	95.561(6)	99.82(2)	100.71(2)	111.666(8)
$V \cdot 10^{-6}$ [pm^3]	2340.6(3)	2123.4(9)	2469.9(7)	2871.1(6)
d (calcd.) [$g \cdot cm^{-3}$]	1.307	1.303	1.3460	1.348
Z	4	4	4	4
Linear abs. μ [mm^{-1}]	0.084	0.088	0.089	0.091
Temp. [K]	293(2)	300(2)	300(2)	293(2)
Data collection				
Diffractometer	Enraf−Nonius CAD 4	Stoe IPDS	Stoe Stadi 4	Enraf−Nonius CAD 4
Radiation	Mo-K_α			
λ [Å]	0.71073			
Monochromator	graphite			
Crystal size [mm]	0.29 × 0.22 × 0.02	0.20 × 0.17 × 0.10	0.30 × 0.28 × 0.10	0.32 × 0.24 × 0.18
Data collection mode	ω-2θ scan	oscillation	ω-θ scan	ω-2θ scan
$2\theta_{max}$ [°]	54.00	53.92	56.04	46.00
Reciprocal lattice segment	$-13 \le h \le 13$	$-15 \le h \le 15$	$-12 \le h \le 12$	$0 \le h \le 15$
	$-6 \le k \le 13$	$-17 \le k \le 14$	$0 \le k \le 26$	$0 \le k \le 16$
	$-10 \le l \le 22$	$-13 \le l \le 15$	$-13 \le l \le 15$	$-18 \le l \le 17$
No. of refls. measd.	4324	11323	6146	4196
No. of refls. unique	4116	4450	5900	4002
Cut-off for obsd. data	$I > 2\sigma(I)$			
No. of unique obsd. data	2608	3463	3372	2026
R(*F*)	0.0488	0.0526	0.0466	0.0445
No. of parameters	316	280	419	400
Rw(F^2)	0.0967	0.134	0.130	0.094

of **8a**. The dimer was also obtained from **4a** (3.84 g, 0.01 mol) and phenyl isocyanate in accordance with GP4 (6 h reflux) to yield 1.79 g (61%) of **8a**, m.p. 329−336 °C. Colorless single crystals for X-ray structure analysis were obtained from an acetonitrile solution containing 10% H_2O, saturated with **8a** at 70 °C by controlled cooling to 50 °C over 40 h, m.p. 340−341 °C. − IR (KBr): $\tilde{\nu}$ = 1781.2 cm^{-1}, 1732.4, 1490.4, 1403.3, 1360.9, 1165.3, 752.1. − ^1H NMR: δ = 8.47 (d, ^3J = 8 Hz, 2 H, 7-H + 18-H), 7.54−7.09 (m, 16 H, arom. H), 3.83 (s, 2 H, 12-H + 13-H), 2.21 (s, 6 H, 25-CH_3 + 26-CH_3). − ^{13}C NMR: δ = 164.8 (C-2 + C-23), 150.7 (C-4 + C-21), 135.7 (C-6 + C-19), 130.6 (2 C-1′ 3-Ph + 22-Ph), 129.0 (4 C-3′ 3-Ph + 22-Ph), 128.9 (C-8 + C-17), 128.7 (2 C-4′ 3-Ph + 22-Ph), 126.5 (C-10 + C-15), 126.3 (C-2′ 3-Ph + 22-Ph), 123.8 (C-9 + C-16), 121.4 (C-11 + C-14), 117.9 (C-7 + C-18), 79.7 (C-1 + C-24), 66.8 (C-12 + C-13), 37.5 (25-CH_3 + 26-CH_3). − MS (EI, 70 eV); *m/z* (%): 583 (11) [MH^+], 292 (100) [M/2 + H^+], 144 (55) [M^+/2 − PhNCO − CO]. − $C_{34}H_{26}N_6O_4$ (582.6): cald. C 70.09, H 4.50, N 14.42; found C 69.92, H 4.52, N 14.52. − Using GP5, an insoluble solid (0.29 g, 25%) was isolated as a side-product. The m.p. was not determined (> 365 °C). The colorless powder of unknown structure was absolutely insoluble in all common solvents except for hot conc. sulfuric acid. This side-product was probably an isomer of **8a**, because its IR and mass spectra are similar to those of **8a** and its elemental analysis is identical to that of **8a**.

X-ray Structure Analyses of 4c, 6d, 7b and 8a: The structures were solved by direct phase determination using SHELXS-97.[13a] Refinements were carried out by a full-matrix least-squares method using SHELXL-97.[13b] Hydrogen atoms were found from difference electron density maps and refined without any constraints for **6d**, and using riding models with restrained isotropic *U* for all other compounds. See Table 1.

9,16-Dimethyl-3,22-diphenyl-25,26-bis(4′-tolyl)-5,5,20,22,25,26-hexaazaheptacyclo[22.0.1^{1,12}.1^{13,24}.0^{1,5}.0^{6,11}.0^{14,19}.0^{20,24}]hexacosa-6(11),7,9,14(19),15,17-hexaene-2,4,21,23-tetrone (8b): Compound **6b** (4 g, 8 mmol) was treated in accordance with GP5 to yield 1.36 g (45%) of **8b**. The dimer was also obtained from **6b** (3 g, 6 mmol) by dry distillation in a vacuum apparatus at 10 hPa and a bath temp. of 260−290 °C. Extraction of the distillation residue with boiling acetone yielded 1.07 g (47%) of **8b**, m.p. 358−362 °C (acetone). − IR (KBr): $\tilde{\nu}$ = 1784.6 cm^{-1}, 1500.0, 1401.4, 1176.2, 1156.5, 756.3. − ^1H NMR: δ = 8.42 (d, ^3J = 8.1 Hz, 2 H, 7-H + 18-H), 7.60−6.60 (m, 22 H, arom. H), 4.18 (s, 2 H, 12-H + 13-H), 2.38 (s, 6 H, 2 CH_3), 2.22 (s, 6 H, 2 CH_3). − ^{13}C NMR (75.5 MHz): δ = 163.0 (C-2 + C-23), 150.0 (C-4 + C-21), 142.3 (2 C-1′′ 25-tolyl + 26-tolyl), 135.3 (2 C-4′′ 25-tolyl + 26-tolyl), 133.4 (2 C-1′ 3-Ph + 22-Ph), 132.2 (C-9 + C-16), 129.9 (C-6 + C-19), 128.6 (4 C-3′′ 25-tolyl + 26-tolyl), 127.7 (4 C-3′ 3-Ph + 22-Ph and C-8 + C-17), 127.6 (2 C-4′ 3-Ph + 22-Ph), 125.7 (C-10 + C-15), 125.3 (4 C-2′ 3-Ph + 22-Ph), 124.5 (4 C-2′′ 25-tolyl + 26-tolyl), 123.2 (C-11 + C-14), 116.7 (C-7 + C-18), 78.0 (C-1 + C-24), 66.9 (C-12 + C-13), 19.1 (2 CH_3), 18.9 (2 CH_3). − MS (EI, 70 eV); *m/z* (%): 762 (4) [M^+], 381 (93) [M^+/2], 234 (100) [M^+/2 − PhNCO − CO]. − $C_{48}H_{38}N_6O_4$ (762.9): calcd. C 75.57, H 5.02, N 11.02; found C 75.69, H 4.76, N 10.85.

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[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136244 (**4c**), -135954 (**6d**), -135953 (**7b**) and -136243 (**8a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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