Photo Valence Isomerization of 8,9-Bis(*N*-cyclohexylcarbamoyloxymethyl)-[6]paracyclophane[1)]

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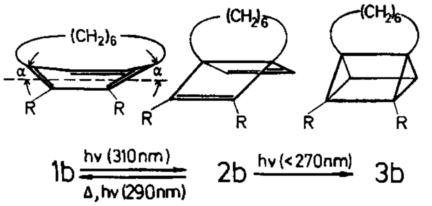
Irradiation in the wavelength range of $\lambda = 270-320$ nm of 8,9-bis(*N*-cyclohexylcarbamoyloxymethyl)-[6]paracyclophane (**1b**) in dilute fluid solutions produces the 1,4-Dewar isomer **2b** in a quantum yield of 2.8% while the quantum yield of the rearomatization is 19% in heptane at room temperature. A photostationary equilibrium may be attained which depends strongly on the wavelength of irradiation. At $\lambda = 290$ nm 76% of the [6]paracyclophane isomer **1b** is obtained whereas at $\lambda = 310$ nm 83% of the Dewar isomer **2b** is formed in ethanol. The thermal back reaction **2b** → **1b** follows the Arrhenius law ($E_a = 95.9 \pm 4.0$ kJ/mol, lg $A = 10.6 \pm 0.4$ in heptane). By irradiating **1b** with $\lambda < 270$ nm the prismane isomer **3b** is formed via the Dewar isomer **2b**.

The aromatic system of anthracene may be deformed from planarity by introducing steric strain by large substituents in position 9. This deformation has a great influence on the photochemical properties of these molecules. For example, irradiation of 9-*tert*-butylanthracene results in the formation of its 9,10-Dewar isomer, while e.g. 9-trimethylsilylanthracene and 9-methylanthracene are photochemically stable at infinite dilution[2)]. An alternative way of deforming a benzene ring is by bridging its two opposite positions with an *n*-membered methylene chain. Synthesis, structure and chemical reactivity of these [*n*]paracyclophanes constitute a very active field of research[3)].

The angles of deformation α (Scheme 1) are known to increase with decreasing length of the chain. Thus, for [*n*]-paracyclophanes with long methylene chains ($n \geq 7$) the aromatic isomer is thermodynamically more stable than the Dewar isomer, while for a short chain the equilibrium is assumed to be shifted to the Dewar isomer[4)]. Furthermore, the mutual interconversion of [*n*]paracyclophanes and their Dewar isomers on irradiation is a general reaction for short methylene chains (n = 4, 5, 6)[5-11)]. In some of these cases the corresponding prismanes are formed under suitable conditions. For n = 7, however, no photochemical formation of the Dewar isomer has been found[11)]. The borderline case of [6]paracyclophane with a deformation angle of ca. 20°[5-7,12-14)] appears to be the most interesting one.

Scheme 1



1,2,3	R
a	CH_2OH
b	$CH_2OCONHC_6H_{11}$
c	$CH_2OCONHC_6H_5$
d	$COOC_2H_5$
e	CH_2OAc

In a detailed study of **1d**, Dreeskamp et al. have determined its photochemical properties[15)]. This compound, however, suffers from the disadvantage that the ethoxycarbonyl groups are attached to the aromatic system and influence the absorption spectra. The ideal molecule for studying the photochemical properties of the aromatic ring with no influence of the substituents would be [6]paracyclophane itself[16)] or a derivative with alkyl substituents. Unfortunately, these compounds are not available so far in desirable amounts. Hence the disubstituted [6]paracyclophane **1b** with methylene substituents connected directly to the aromatic system and its Dewar isomer **2b** have been chosen as suitable model substances.

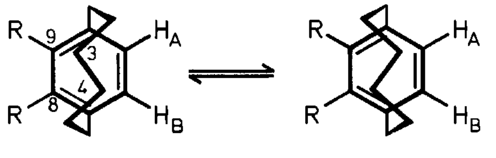
Results

Synthesis of [6]Paracyclophanes 1b and 1c and Their Dewar Isomers 2b and 2c

All new compounds are synthesized from [6]paracyclophane-8,9-dimethanol (**1a**)[5,17)]. The Dewar isomer **2a** is obtained in 78% yield by irradiation of **1a** in ether with Pyrex-filtered UV light of a mercury lamp[5,17)]. **1a** as well as **2a** are rather sensitive compounds; therefore, a conversion into more stable crystalline derivatives is highly desirable. This can be achieved by conversion into the urethanes **1b**, **1c**, **2b**, and **2c** with the corresponding isocyanates in the presence of catalytic amounts of triethylamine[17]. The structures of all new urethanes have been established by their spectroscopic and analytical data (see Experimental).

The title compound **1b** shows a temperature-dependent ^{1}H-NMR spectrum which is characteristic of [6]paracyclophanes[5-9,17,18]. The AB system of the aromatic protons (δ = 7.15 and 7.26, ^3J = 8.3 Hz at $-75\,^\circ$C in CD_2Cl_2) shows coalescence at 280 K. The calculated free enthalpy of activation ΔG^{+}(280 K) = 57.4 kJ/mol for the intramolecular flipping **1bA** $\rightleftharpoons$ **1bB** of the hexano bridge corresponds within the errors with the value [ΔG^{+}(277 K) = 58.3 kJ/mol] for the diethyl ester **1d**[5,18] (Scheme 2). This demonstrates that different substituents at C-8 and C-9 have little or even no influence on the barrier of this intramolecular dynamic process.

Scheme 2



1bA 1bB

Bickelhaupt and van Straten[6] have reported ΔG^{+} (293 K) = 58.2 ($\pm$1.3) kJ/mol for [6]paracyclophane itself. In the UV and ^{1}H-NMR spectra of **1c** considerable overlap of the absorptions of the phenyl groups and the cyclophane part is observed; therefore, the following experiments have been carried out only with the bis(*N*-cyclohexyl) derivatives **1b** and **2b**. Fortunately, these compounds with four methylene groups attached directly to the strained ring systems are of sufficient chemical stability for our studies.

Reactions Leading to the Dewar Isomer

The UV spectrum of **1b** shows three absorption bands corresponding to the three bands of benzene, but shifted to longer wavelengths (Figure 1). This agrees with the rule[3] that in [*n*]paracyclophanes the characteristic absorption bands are retained but shifted to longer wavelengths with decreasing *n*. The absorption of the Dewar isomer **2b** occurs as expected at still shorter wavelengths. Irradiation of **1b** in the wavelength range of λ = 270–320 nm results in a photostationary equilibrium (Figure 2). The photoproduct is identified as the Dewar isomer **2b** by the NMR spectra in comparison with data reported in the literature[5,17]. The quantum yields of the photochemical reactions **1b** ⟶ **2b** and **2b** ⟶ **1b** are obtained from the initial slopes of the curves in Figure 2. They are measured relative to the well-known quantum yield of the *trans-cis* isomerization of azobenzene (ϕ = 0.14)[19] both at λ = 270 and 310 nm. Within experimental precision they have been found to be independent of the irradiation wavelength. The quantum yield of formation of the Dewar isomer **1b** ⟶ **2b** is 0.028, in contrast to the rearomatization **2b** ⟶ **1b**, which occurs with the much larger quantum yield of 0.19 in heptane at room temperature; in ethanol the analogous quantum yields are 0.03 and 0.14, respectively.

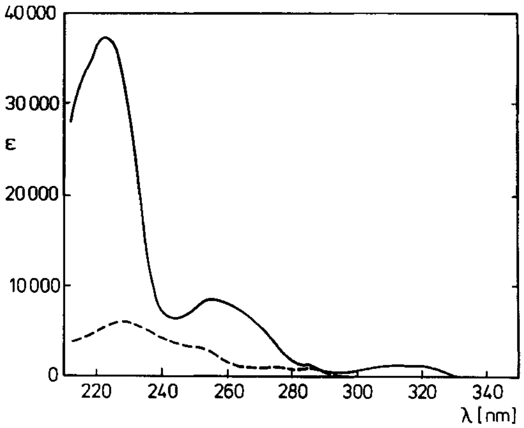


Figure 1. UV absorption spectrum of **1b** (straight line) and its Dewar isomer **2b** (dotted line) in ethanol

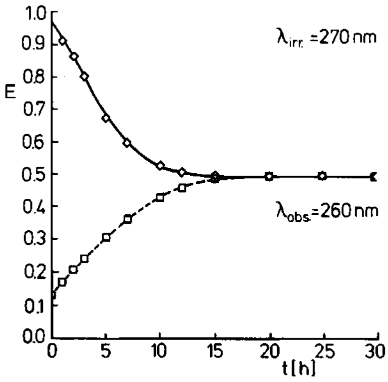


Figure 2. Changes of the extinction (at λ = 260 nm) in the UV spectra during the irradiation at λ = 270 nm of **1b** (straight line) and its Dewar isomer **2b** (dotted line) in ethanol

Assuming that the quantum yields are independent of the wavelength in the region considered the photostationary equilibrium constant *K* may be calculated with the known extinction coefficients of the pure compounds **1b** and **2b** given in Figure 1 and the quantum yields given above.

$$K = \frac{c_{\text{phane}}}{c_{\text{Dewar}}} = \frac{\varepsilon_{\text{Dewar}}}{\varepsilon_{\text{phane}}} \cdot \frac{\phi_{\text{Dewar} \to \text{phane}}}{\phi_{\text{phane} \to \text{Dewar}}} \qquad (1)$$

c: concentration; ε: extinction coefficient; ϕ: quantum yield.

In Figure 3 the value of *K* thus calculated is given as a function of irradiation wavelength together with the photostationary constants *K* determined at λ = 310, 290, and 270 nm. By just changing the irradiation wavelength the concentration of **1b** in the photostationary state is shifted from 17% at λ = 310 nm to 76% at λ = 290 nm. The good agreement between the experimental and calculated data for *K* are taken as an additional proof that the determination of the ratios of quantum yields and extinction coefficients are essentially correct and no side reactions occur to any significant extent.

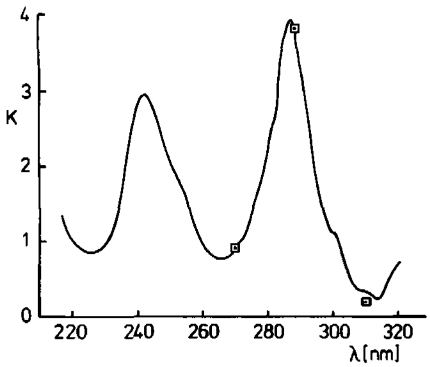


Figure 3. Photostationary equilibrium constant K as a function of the irradiation wavelength calculated according to equation (1) with ethanol as solvent; ⊡ experimental data

The rearomatization reaction **2b** → **1b** also occurs thermally. The kinetics of this reaction has been studied by UV and ^{1}H-NMR spectroscopy. The change of UV absorption at one wavelength $\Delta E(\lambda_1)$ is proportional to the changes at other wavelengths $\Delta E(\lambda_2)$ ... $\Delta E(\lambda_i)$, indicating a first-order reaction affording only one product[20]. This is also confirmed by ^{1}H-NMR spectroscopy. From the temperature dependence of the rate of the reaction the experimental activation energy is obtained and found to be nearly independent of the solvents used (see Table 1).

Table 1. Arrhenius parameters of the rearomatization reaction **2b** → **1b** in different solvents

E_a [kJ/mol]	lg A	solvent
100.2 ± 5.2	11.4 ± 0.6	ethanol
95.9 ± 4.0	10.6 ± 0.4	*n*-heptane
96.8 ± 3.1	10.7 ± 0.8	DMSO

Attempts to measure the enthalpy of this reaction by calorimetry by analogy with previous work[15] have failed due to a decomposition of either **1b** or **2b** at elevated temperatures.

Reactions Affording the Prismane Isomer

A photochemical conversion of the Dewar isomer **2b** into a further product is observed by irradiation of dilute solutions of **1b** or **2b** with light of $\lambda < 270$ nm. The ^{1}H-NMR spectrum of this compound shows a sharp singlet at $\delta = 2.2$ and an unresolved multiplet centered at $\delta = 4.1$. By analogy with previous work on **1d**[15] we assign to this compound the prismane structure **3b**. A detailed analysis of the concentrations of the three valence isomers **1b**, **2b**, and **3b** with increasing irradiation time is performed by ^{1}H-NMR spectroscopy. The irradiation wavelength is $\lambda = 250$ nm, and the temperature is reduced to retard thermal back reactions. From these studies it is concluded that the prismane isomer **3b** is produced photochemically via the Dewar isomer **2b** as an intermediate.

At higher temperatures the prismane isomer **3b** decomposes with a halflife of 1 h at 90°C. Different products are obtained with **1b** as the main product. Another product is supposed to be an aromatic compound with the methylene chain attached to the *ortho* positions of the benzene ring as in the case of the prismane isomer of 8,9-bis(ethoxycarbonyl)-[6]paracyclophane[5]. Also by analogy with this compound the product ratio depends on the treatment of the surface of the Pyrex glass used. If it is cleaned with a solution of ammonia in order to eliminate all traces of acid, a maximum of 50% of [6]paracyclophane derivative **1b** can be obtained.

Discussion

The properties of a photochemical and a thermal valence isomerization between **1b** and its Dewar isomer **2b** determined in this work are in line with those previously investigated in the cases of 9-*tert*-butylanthracene[2] and 8,9-bis(ethoxycarbonyl)-[6]paracyclophane (**1d**)[15]. In all three examples a small quantum yield for the formation of the Dewar isomer is observed while the quantum yield of the reverse reaction is much higher (see Table 2). Furthermore, the activation energy of the thermal rearomatization reaction is remarkably constant around $E_a \approx 95 \pm 5$ kJ/mol. This value of E_a also agrees with the activation energy of the aromatization reaction in those cases where the Dewar isomer has been synthesized by chemical means[21–23] and found to be in the range of $E_a \approx 100 \pm 10$ kJ/mol. The only exception is hexamethyl Dewar benzene where $E_a = 155.7$ kJ/mol[24]. The existence of these regularities lends further support to a hypothesis advanced earlier[2,15]: The potential energy surfaces are very similar for these valence isomerizations. An angle α defining the deviation of the six-membered ring from planarity serves as the reaction coordinate. Both in the Dewar isomer and in the transition state of the rearomatization reaction this deviation from planarity is large. It is caused by the valence structure, and no significant steric strain exists. For the aromatic ring on the other hand the deviation from planarity is caused by steric interaction of the substituent, i.e. the hexamethylene chain or *tert*-butyl group in the cases discussed here. If this interaction is large, the angle α is also large and the energy of the aromatic molecule is raised relative to its Dewar isomer. Hence, the reaction enthalpy of the aromatization reaction is relatively low in these cases[2,15]. However, since the absorption spectra are not markedly changed by this interaction the energy of the aromatic molecule after light absorption is also high; hence, the activation barrier to a photochemical valence isomerization to the Dewar isomer is lowered (see Figure 4 of ref.[2]). It appears that in the [n]-paracyclophanes with $n = 6$ this barrier is sufficiently low to allow a photoisomerization while for $n \geq 7$ it is too high, and no analogous photoreactions have yet been observed in these cases.

When in 1962 van Tamelen and Pappas synthesized the first member of the "Dewar benzene class" by a photochemical route[25] they used 1,2,4-tri-*tert*-butylbenzene as starting material. Apparently, they were guided by the idea, that bulky substituents "should stabilize by virtue of steric factors, the non-aromatic member"[25]. From all evidence pro-

Table 2. Quantum yields of the photochemical valence isomerization of disubstituted [6]paracyclophanes and their Dewar isomers

Compound	$\phi_{\text{Dewar} \rightarrow \text{phane}}$	$\phi_{\text{phane} \rightarrow \text{Dewar}}$	solvent
1b	0.19	0.028	*n*-heptane
	0.14	0.030	ethanol
1d[15]	0.12	0.024	*n*-heptane
1e[15]	0.16	0.019	*n*-heptane
	$\phi_{\text{Dewar} \rightarrow \text{anthr.}}$	$\phi_{\text{anthr.} \rightarrow \text{Dewar}}$	
9-*tert*-butyl-anthracene[2]	0.4	0.016	*n*-heptane

duced since then a somewhat different view of the function of steric strain seems to emerge: Bulky substituents as in the case of 9-*tert*-butylanthracene or short methylene chains as in the case of [6]paracyclophanes do not significantly affect the thermal back reaction of the Dewar isomer to the aromatic form. The activation energies for these thermal reactions are always large in accordance with the Woodward-Hoffmann rules[26] and – with the exception of the extreme case of hexamethylbenzene[24] – nearly constant[27]. For the photochemical formation of the Dewar isomer, however, a sufficient deformation of the aromatic ring is necessary. This deformation produced by steric strain will lower the potential energy barrier on the excited-state surface to the reaction furnishing the Dewar isomer. Hence, this reaction will compete with other deactivation processes of the electronically excited aromatic isomer only if the deformation of the aromatic system is sufficiently large.

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Experimental

Melting points: Büchi (Dr. Tottoli). – IR: Perkin-Elmer 283 B. – ^{1}H NMR: Varian EM 390, Bruker AM 300 and 400. – ^{13}C NMR: Bruker AM 300. – MS: Finnigan MAT 8230; for further details see ref.[17].

All syntheses were carried out under N_2 with dry solvents. For spectroscopic and kinetic studies the following spectrometers and solvents were used: UV: UV-240 Shimadzu Corp., Kyoto (Japan); ^{1}H NMR: Bruker MW 250 with an integrated computer ASPECT 2000. Solvents: Ethanol and *n*-heptane (Merck UVASOL), [D$_6$]DMSO, [D$_8$]toluene (Aldrich).

The irradiations were performed with a 200-W mercury-xenon lamp (901 B00111, Philips) and a monochromator (M4QIII, Zeiss, Oberkochen/Württ., F.R.G.). Before irradiation, the solutions of the [6]paracyclophane **1b** and its Dewar isomer **2b** were purged with nitrogen so that any reaction with oxygen was avoided. Concentrations used were ca. 10^{-4} M for UV spectroscopy, 10^{-2} M for NMR spectroscopy, and 10^{-1} M for calorimetry.

1. *8,9-Bis-(N-cyclohexylcarbamoyloxymethyl)-[6]paracyclophane* (**1b**): To a solution of 100 mg (0.45 mmol) of **1a**[5] in 20 ml of ether was added 117 mg (0.94 mmol) of cyclohexyl isocyanate in 2.9 ml of ether. After the addition of one drop of triethylamine, the mixture was stirred at room temperature for 3 h. The solvent was evaporated and the residue recrystallized from ether/pentane to give 148 mg (70%) of **1b**, m.p. 175°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3330 cm^{-1} (NH), 2930 and 2850 (CH), 1690 (C=O), 1530 (amide II), 1225 (COC). – ^{1}H NMR (CDCl$_3$, +20°C): δ = −0.8 to −0.3 (br. m, 2H, 2*H*CH), 0.4–3.0 (br. m, 30H, 15 CH$_2$), 3.5 (m, 2H, 2 CH), 3.8 (s, 2H, 2 NH), 4.9 (m, 4H, 2 OCH$_2$), 7.25 (s, 2H, 2 =CH); [CD$_2$Cl$_2$, reference CHDCl$_2$ (δ = 5.308), −75°C]: δ = −0.65 (m, 1H, *H*CH), −0.3 (m, 1H, *H*CH), 0.65 and 0.85 (2 m, 2H, CH$_2$), 1.25 (m, 14H, 7 CH$_2$), 1.7 (m, 6H, 3 CH$_2$), 2.1 (m, 4H, 2 CH$_2$), 2.5 (m, 2H, CH$_2$), 2.85 (m, 2H, CH$_2$), 3.25 (m, 2H, 2 CH), 4.8 (m, 4H, 2 OCH$_2$), 5.7 and 5.8 (2 s, 2H, 2 NH), 7.15 and 7.26 (AB, J = 8.3 Hz, 2H, 11-H/12-H; the AB system shows coalescence at +7°C. – ^{13}C NMR (CD$_2$Cl$_2$, −75°C): δ = 20.12 (t, 2 CH$_2$), 24.50 (t, 4 CH$_2$), 24.62 (t, 4 CH$_2$), 27.06 (t, 2 CH$_2$), 34.35 (t, 2 CH$_2$), 34.87 (t, 2 CH$_2$), 49.73 (d, 2 CH), 58.23 (t, 2 OCH$_2$), 132.91 (d, C-11/C-12), 137.28 (s, C-8/C-9), 142.01 (s, C-7/C-10), 155.63 (s, 2 NCOO); the ^{13}C-NMR spectra of all urethanes showed additional small signals for the urethane part probably due to the (*E*)/(*Z*) isomerism of the amide bond. – MS (70 eV): *m/z* (%) = 470 (2) [M$^+$], 202 (100).

$C_{28}H_{42}N_2O_4$ (470.7)	Calcd.	C 71.46 H 8.99
	Found	C 71.29 H 8.98

2. *8,9-Bis(N-Phenylcarbamoyloxymethyl)-[6]paracyclophane* (**1c**): **1c** was prepared by analogy with **1b** from 80 mg (0.36 mmol) of **1a** in 20 ml of ether, 89 mg (0.75 mmol) of phenyl isocyanate in 2 ml of ether, and one drop of triethylamine. The solvent was evaporated and the remaining colorless oil recrystallized from tetrahydrofuran/ether/pentane to give 129 mg (78%) of **1c**, m.p. 184°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3330 cm^{-1} (NH), 2920 and 2870 (CH), 1720 (C=O), 1530 (amide II), 1220 (COC). – UV (CH$_3$CN): λ_{max} (lg ε) = 256 nm (3.58). – ^{1}H NMR ([D$_5$]pyridine, +20°C): δ = 0.8–2.2 (br. m, 12H, 6 CH$_2$), 5.1 (s, 4H, 2 OCH$_2$), 7.05 (m, 2H, phenyl H), 7.25 (s, 2H, 11-H/12-H), 7.3 (m, 4H, phenyl H), 7.85 (m, 4H, phenyl H), 9.3 (s, 2H, 2 NH); ([D$_5$]pyridine, −35°C): δ = −1.4 to +1.0 (br. m, 8H, 4 CH$_2$), 1.2–2.7 (m, 4H, 2 CH$_2$), 5.45 (s, 4H, 2 OCH$_2$), 6.5–6.7 (m, 4H, phenyl H), 6.8–6.95 (m, 4H, phenyl H), 7.4–7.5 (m, 2H, 11-H/12-H), 7.5–7.6 (m, 2H, phenyl H), 11–11.1 (br. s, 2H, 2 NH). – ^{13}C NMR ([D$_5$]pyridine): δ = 20.22 (br. t, 2 CH$_2$), 25.98 (br. t, 2 CH$_2$), 33.97 (br. t, 2 CH$_2$), 61.16 (t, 2 OCH$_2$), 118.99 (d, 4 phenyl C), 122.21 (d, 2 phenyl C), 128.97 (d, 4 phenyl C), 133.87 (s, C-8/C-9), 134.12 (d, 2 =CH), 144.8 (s, C-10/C-7), 148.2 (s, 2 phenyl C), 154.17 (s, 2 NCOO); All signals were of weak intensity, because **1c** is only sparingly soluble. – MS (70 eV): *m/z* (%) = 458 (5) [M$^+$], 202 (90), 119 (100).

$C_{28}H_{30}N_2O_4$ (458.6)	Calcd.	C 73.35 H 6.59
	Found	C 72.83 H 6.60

3. *Tricyclo[6.2.2.0^{1,8}]dodeca-9,11-dien-9,10-dimethanol* (**2a**): A solution of 220 mg (1.0 mmol) of [6]paracyclophane-8,9-dimethanol (**1a**)[5] in 80 ml of ether was irradiated with a high-pressure mercury lamp (Pyrex, Philips HPK 125 W) at 11°C for 11.5 h. The solvent was evaporated and the residue chromatographed with ether on silica gel (Merck, 0.063–0.2 mm) to give 172 mg (78%) of **2a** as a colorless oil. – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (br., OH), 2910 and 2850 (C–H). – ^{1}H NMR (CDCl$_3$): δ = 0.70–1.75 (m, 8H, 4 CH$_2$), 1.82–1.95 (m, 4H, 2 CH$_2$), 4.03 and 4.3 (AA'MM' system, 4H, 2 OCH$_2$), 4.65 (s, 2H, 2 OH), 6.55 (s, 2H, 2 =CH). – ^{13}C NMR (CDCl$_3$): δ = 25.32 (t, 2 CH$_2$), 25.81 (t, 2 CH$_2$), 26.37 (t, 2 CH$_2$), 59.69 (t, 2 OCH$_2$), 61.73 (s, C-1/C-8), 145.01 (d, 2 =CH), 147.40 (s, C-9/C-10). – MS (70 eV): *m/z* (%) = 220 (1) [M$^+$], 202 (2) [M$^+$ – H$_2$O], 91 (100).

4. *9,10-Bis(N-cyclohexylcarbamoyloxymethyl)tricyclo-[6.2.2.0^{1,8}]dodeca-9,11-diene* (**2b**): **2b** was prepared by analogy with **1b** from 100 mg (0.45 mmol) of **2a** in 20 ml of ether, 117 mg (0.94

mmol) of cyclohexyl isocyanate in 2.9 ml of ether, and one drop of triethylamine. The solvent was evaporated and the residue recrystallized from ether/pentane to give 157 mg (74%) **2b**, m.p. 167–170°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3320 cm^{-1} (NH), 2930 and 2850 (CH), 1685 (C=O), 1625 (C=C), 1535 (amide II), 1230 (COC). – ^{1}H NMR ($CDCl_3$, +20°C): δ = 1.18 (m, 6H, 3 CH_2), 1.35 (m, 4H, 2 CH_2), 1.55 (m, 10H, 5 CH_2), 1.7 (m, 4H, 2 CH_2), 1.95 (m, 8H, 4 CH_2), 3.45 (br. m, 2H, 2 CH), 4.6 and 4.7 (2 AB, *J* = 11 Hz, 4H, 2 OCH_2), 6.5 (s, 2H, =CH), 2 NH proton signals could not be localized at +20°C; (CD_2Cl_2, −60°C): δ = 1.0 (m, 6H, 3 CH_2), 1.25 (m, 4H, 2 CH_2), 1.45 (m, 10H, 5 CH_2), 1.7 (m, 4H, 2 CH_2), 1.85 (m, 8H, 4 CH_2), 3.25 (br. m, 2H, 2 CH), 4.49 and 4.6 (2 AB, *J* = 11 Hz, 4H, 2 OCH_2), 6.45 (s, 2H, =CH), 7.0–8.9 (very br. s, 2H, 2 NH). – ^{13}C NMR ($CDCl_3$): δ = 24.84 (t, 2 CH_2), 24.99 (t, 4 CH_2), 26.42 (t, 2 CH_2), 33.49 (t, 4 CH_2), 34.02 (t, 4 CH_2), 49.95 (d, 2 CH), 60.17 (t, 2 OCH_2), 62.69 (s, C-1/C-8), 144.11 (d, C-11/C-12), 145.36 (s, C-9/C-10), 155.51 (s, 2 NCOO). – MS (70 eV): *m/z* (%) = 470 (1) [M^+], 202 (100).

$C_{28}H_{42}N_2O_4$ (470.7) Calcd. C 71.46 H 8.99
Found C 71.45 H 8.98

5. *9,10-Bis(N-phenylcarbamoyloxymethyl)tricyclo[6.2.2.0^{1,8}]dodeca-9,11-diene* (**2c**): **2c** was prepared by analogy with **1b** from 62 mg (0.29 mmol) of **2a** in 10 ml of ether, 71 mg (0.60 mmol) of phenyl isocyanate in 1.6 ml of ether, and one drop of triethylamine. **2c** crystallized after the evaporation of the solvent. It was recrystallized from tetrahydrofuran/ether to give 95 mg (72%) of **2c**, m.p. 201–205°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (NH), 2930 and 2880 (CH), 1700 (C=O), 1648 (C=C), 1530 (amide II), 1230 (COC). – ^{1}H NMR ([D_5]pyridine): δ = 1.3–1.6 (m, 8H, 4 CH_2), 1.95 (m, 4H, 2 CH_2), 4.95 and 5.05 (both AB, *J* = 11 Hz, 4H, 2 OCH_2), 6.45 (s, 2H, 2 =CH), 7.0–7.1 (m, 2H, phenyl H), 7.3–7.4 (m, 4H, phenyl H), 7.8–7.95 (m, 4H, phenyl H), 9.3 (br. s, 2H, 2 NH). – ^{13}C NMR ([D_5]pyridine): δ = 25.27 (t, 2 CH_2), 25.42 (t, 2 CH_2), 26.35 (t, 2 CH_2), 59.75 (s, C-1/C-8), 62.76 (t, 2 OCH_2), 119.03 (d, 4 phenyl C), 122.23 (d, 2 phenyl C), 128.93 (d, 4 phenyl C), 140.51 (s, C-9/C-10), 144.78 (d, 2 =CH), 147.35 (s, 2 phenyl C), 153.45 (s, 2 NCOO). – MS (70 eV): *m/z* (%) = 458 (3) [M^+], 202 (100).

$C_{28}H_{30}N_2O_4$ (458.6) Calcd. C 73.35 H 6.59
Found C 73.26 H 6.43

CAS Registry Numbers

1a: 101410-39-3 / **1b**: 133947-57-6 / **1c**: 133947-58-7 / **2a**: 133947-59-8 / **2b**: 133947-60-1 / **2c**: 133947-61-2 / **3b**: 133947-62-3 / cyclohexyl isocyanate: 3173-53-3 / phenyl isocyanate: 103-71-9

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[1] Dedicated to Professor *Horst Prinzbach* on the occasion of his 60th birthday.

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[27] *Note added in proof* (June 15, 1991): Recently, H. Sakurai, K. Ebata, C. Kabuto, A. Sekiguchi, *J. Am. Chem. Soc.* **112** (1990) 1799, reported E_a = 88.8 kJ/mol for the thermal aromatization of hexakis(trimethylsilyl) Dewar benzene.

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