To the best of our knowledge, the novel octacyclic lactone **6** represents the first derivative in which all carbon atoms of two seven-membered rings are joined face-to-face, albeit through bridges of various sizes. We anticipate some potential applications of the present observation in the synthesis of caged polycyclic systems.

Experimental Section

For a general write up, see ref 7.

Heptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadecane-11,14-dicarboxaldehyde (4a,b). (Methoxymethyl)triphenylphosphonium chloride (1.5 g, 4.37 mmol) was suspended in 5 mL of dry ether under N_2, freshly sublimed sodium *tert*-amyloxide (360 mg, 3.32 mmol) in 2 mL of dry ether was introduced, and the mixture was stirred for 5 min. To the blood red ylide that formed was added the dione **1** (200 mg, 0.83 mmol) in 2 mL of tetrahydrofuran (THF), and the reaction mixture was stirred for 10 min at room temperature and quenched by the addition of 5 mL of water. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layer was washed with water and dried. Removal of solvent gave a crude material which was charged on a silica gel (20 g) column. Elution of the column with hexane removed the triphenylphosphine impurities. Further elution of the column with 5% ethyl acetate–hexane furnished a viscous liquid (120 mg), which was a mixture of dienol ethers **4a,b**. IR (neat): 2950, 1660, 1210, 1120 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 5.84 (2 H, s, C=C*H*OCH$_3$), 3.54 (6 H, s, OCH_3), 3.34 (2 H, m), 2.80–2.10 (10 H, series of m), 1.80–1.0 (4 H, m). ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 142.8, 117.9, 59.3, 51.4, 48.8, 43.8, 43.5, 43.3, 43.1, 39.5, 39.4, 38.1, 37.9.

To a solution of dienol ether mixture **4a,b** obtained above (120 mg) in 10 mL of ether cooled in an ice bath was added 1 mL of 35% $HClO_4$, and the reaction mixture was stirred for 3 h at 0–5 °C. It was then quenched with 2 mL of 10% $NaHCO_3$ and diluted with 5 mL of water. The ethereal layer was separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined ethereal layer was washed with water and dried. The residue obtained after the removal of solvent was charged on a silica gel (15 g) column. Elution with 10% ethyl acetate–hexane furnished the dialdehyde **5** (90 mg, 40% after two steps) as a mixture (3:5:12) of three isomers as revealed by the ^1H NMR spectrum. IR (neat): 2925, 2675, 1705, 730 cm^{-1}. ^1H NMR of mixture (100 MHz, $CDCl_3$): δ 9.76, 9.67, 9.40, 9.38 (all combined 1 H, singlets, C(O)*H*), 2.8 (4 H, br s), 2.65 (6 H, br s), 2.44 (4 H, br s), 1.65 (2 H, $^1/_2$ AB q, J_1 = 9 Hz), 1.23 (2 H, $^1/_2$ AB q, J = 9 Hz).

12,16-Dimethyl-14-oxaoctacyclo[8.7.1.1^{4,7}.$0^{2,9}$.$0^{3,8}$.$0^{5,16}$.$0^{6,12}$.$0^{11,17}$]nonadecan-13-one (6). Potassium hydride (~70 mg, 25% wt dispersion in oil, 0.43 mmol) was washed twice with dry hexane under N_2 to remove the mineral oil, and the residue was suspended in 2 mL of dry THF. A solution of the dialdehyde mixture **5** (50 mg, 0.186 mmol) in 1 mL of dry THF was added dropwise at −10 °C. After 2 min it was quenched with MeI (0.2 mL, freshly distilled over $CaCl_2$) and stirred further for 10 min. The reaction mixture was diluted with 5 mL of water and extracted with ethyl acetate (3 × 8 mL). The combined organic extract was washed with water and dried. Removal of solvent gave a crude material which was charged on a silica gel (5 g) column. Elution with 5% ethyl acetate–hexane furnished the lactone **6** (22 mg, 40%) which was recrystallized from dichloromethane–hexane. Mp: 240–243 °C dec. IR (KBr): 2125, 1720, 1200, 1090 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 3.92 (2 H, s, CH_2O), 2.64–2.4 (8 H, m), 2.28 (4 H, m), 1.43 (2 H, $^1/_2$ AB q, J = 10 Hz, CH_2), 1.32 (3 H, s, CH_3), 1.17 (2 H, $^1/_2$ AB q, J = 10 Hz, CH_2), 1.04 (3 H, s, CH_3). ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 178.1, 87.6, 46.8 (2 C), 46.1, 45.8 (2 C), 44.5 (2 C), 44.1 (2 C), 42.0 (2 C), 39.2 (2 C), 38.6 (2 C), 36.4, 23.2, 22.2. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.73; H, 8.18.

Acknowledgment. We thank UGC for a Special Assistance Programme in Organic Chemistry and for COSIST support in Organic Synthesis. S.P. thanks CSIR for a senior research fellowship.

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4-(Benzotriazol-1-yl)-6*H*-benzo[*c*]tetrazolo[1,5-*e*][1,2,5]triazepine, a New Heterocyclic Ring System Formed by a Novel Benzotriazole Ring Opening

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We recently[1] achieved reaction between two molecules of benzotriazole (**1**) and glyoxal (**2**) to obtain the glycol **3**, which with thionyl chloride gave the dichloroethane **4**. Compound **4** proved to be an intermediate for a number of interesting structures. With the sodium salt of ethanedithiol, it gave the 1,4-dithiin **7**, and with *o*-aminothiophenol, it gave the benzo-1,4-thiazine **8**. The chlorine atoms could also be displaced by simple sodium alkoxides or sodium thioalkoxides to give the corresponding diethers and dithioethers.

Following these successful reactions, we treated the dichloroethane **4** with sodium azide in the expectation of forming the disubstituted product, the 1,2-diazido derivative of **4**, similar to the reaction of 1-(chloromethyl)-benzotriazole with sodium azide.[2] Reaction occurred smoothly in dimethyl sulfoxide at room temperature, but the product did not show the expected molecular weight or elemental analysis. These values were consistent with 4,5-bis(benzotriazol-1-yl)-1,2,3-triazole (**5**). However, the aromatic region of the 300-MHz proton spectrum showed four one-proton doublets and four one-proton triplets, initially suggesting two nonequivalent 1-benzotriazole groups. Clearly neither had isomerized to a symmetrical 2-benzotriazole, a change recently observed in several other systems.[3] No change was seen in the spectrum up to 100 °C. The 75-MHz ^{13}C NMR spectrum had 14 signals between δ 112 and 148 and no others. The clear differences between these and those of other benzotriazoles led us to perform an X-ray crystallographic analysis, which proved the structure to be 4-(benzotriazol-1-yl)-6*H*-benzo[*c*]tetrazolo[1,5-*e*][1,2,5]triazepine (**6**). A suggested mechanism

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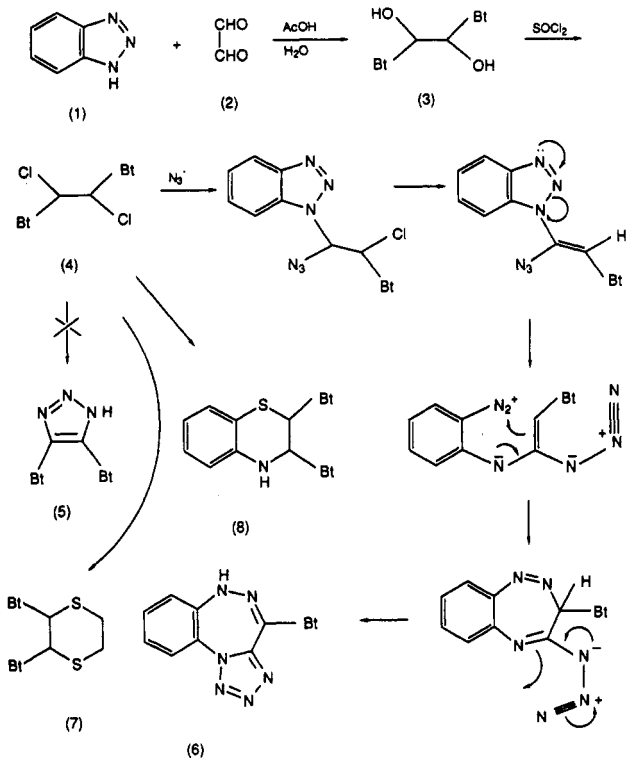
Scheme I[a]



[a] Bt = Benzotriazol-1-yl.

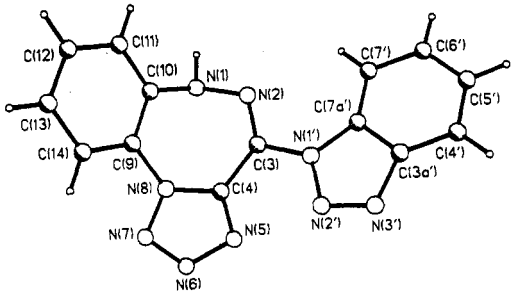


Figure 1. Perspective view and atom labeling of the crystal structure.

for its formation is given in Scheme I. No previous example of a tetrazolo[1,5-*e*][1,2,5]triazepine has been reported, nor have we found any analogous ring opening of a benzotriazole.

X-ray Crystal Structure. Figure 1 shows a perspective view and atom labeling of the crystal structure of the rearrangement product. Bond lengths and angles are given in Table I. Atom coordinates and thermal parameters are listed in Tables 2–4, which are deposited as supplementary material. The bond lengths and angles are similar to those found in related structures. As shown in Figure 2, the benzotetrazolotriazepine ring system is far from planar. In particular the seven-membered triazepine ring exists in a boat conformation with α and β angles of 33.6° and 60.3°, where these represent the angles between the N2–C3–C9–C10 mean plane and the mean planes through C3–C4–N8–C9 and N2–N1–C10, respectively. This conformation is similar to that of cycloheptatriene.[4] The tetrazole and benzene rings are both planar (maximum deviations 0.003 Å and 0.008 Å, respectively) and mutually inclined at an angle of 37.7°. The benzotriazole substituent is planar (maximum deviation 0.018 Å) and its mean plane

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Table I. Bond Lengths (Å) and Angles (deg)

N(1)–N(2)	1.422 (3)	N(1)–C(10)	1.426 (3)
N(2)–C(3)	1.278 (3)	C(3)–C(4)	1.476 (3)
C(3)–N(1′)	1.406 (3)	C(4)–N(5)	1.318 (2)
C(4)–N(8)	1.341 (3)	N(5)–N(6)	1.359 (3)
N(6)–N(7)	1.301 (2)	N(7)–N(8)	1.353 (2)
N(8)–C(9)	1.433 (2)	C(9)–C(10)	1.394 (3)
C(9)–C(14)	1.384 (3)	C(10)–C(11)	1.385 (3)
C(11)–C(12)	1.390 (3)	C(12)–C(13)	1.385 (3)
C(13)–C(14)	1.379 (3)	N(1′)–N(2′)	1.381 (3)
N(1′)–C(7a′)	1.376 (3)	N(2′)–N(3′)	1.291 (3)
N(3′)–C(3a′)	1.394 (3)	C(3a′)–C(4′)	1.398 (3)
C(3a′)–C(7a′)	1.391 (4)	C(4′)–C(5′)	1.371 (3)
C(5′)–C(6′)	1.408 (4)	C(6′)–C(7′)	1.380 (3)
C(7′)–C(7a′)	1.398 (3)		
N(2)–N(1)–C(10)	114.1 (2)	N(1)–N(2)–C(3)	115.4 (2)
N(2)–C(3)–C(4)	125.6 (2)	N(2)–C(3)–N(1′)	117.3 (2)
C(4)–C(3)–N(1′)	117.0 (2)	C(3)–C(4)–N(5)	128.0 (2)
C(3)–C(4)–N(8)	122.8 (2)	N(5)–C(4)–N(8)	109.1 (2)
C(4)–N(5)–N(6)	105.2 (2)	N(5)–N(6)–N(7)	111.6 (1)
N(6)–N(7)–N(8)	105.6 (2)	C(4)–N(8)–N(7)	108.5 (1)
C(4)–N(8)–C(9)	128.3 (2)	N(7)–N(8)–C(9)	123.2 (2)
N(8)–C(9)–C(10)	116.7 (2)	N(8)–C(9)–C(14)	120.6 (2)
C(10)–C(9)–C(14)	122.7 (2)	N(1)–C(10)–C(9)	119.6 (2)
N(1)–C(10)–C(11)	122.9 (2)	C(9)–C(10)–C(11)	117.5 (2)
C(10)–C(11)–C(12)	120.5 (2)	C(11)–C(12)–C(13)	120.8 (2)
C(12)–C(13)–C(14)	119.7 (2)	C(9)–C(14)–C(13)	118.9 (2)
C(3)–N(1′)–N(2′)	120.3 (2)	C(3)–N(1′)–C(7a′)	129.4 (2)
N(2′)–N(1′)–C(7a′)	110.1 (2)	N(1′)–N(2′)–N(3′)	108.1 (2)
N(2′)–N(3′)–C(3a′)	109.3 (2)	N(3′)–C(3a′)–C(4′)	130.1 (3)
N(3′)–C(3a′)–C(7a′)	108.3 (2)	C(4′)–C(3a′)–C(7a′)	121.6 (2)
C(3a′)–C(4′)–C(5′)	116.8 (3)	C(4′)–C(5′)–C(6′)	121.5 (2)
C(5′)–C(6′)–C(7′)	122.2 (2)	C(6′)–C(7′)–C(7a′)	116.1 (3)
N(1′)–C(7a′)–C(3a′)	104.1 (2)	N(1′)–C(7a′)–C(7′)	134.1 (3)
C(3a′)–C(7a′)–C(7′)	121.8 (2)		

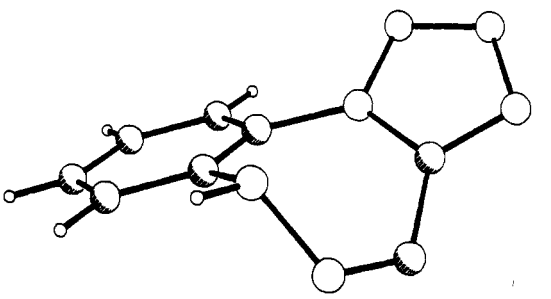

Figure 2. View showing the conformation of the triazepine ring.

inclined to the N2–C3–C4 plane at an angle of 17.0°. The molecules are linked in chains along the *a* axis by weak hydrogen bonds between the N1 hydrogen and N3′ of an adjacent molecule with an N···N separation of 3.111 Å.

Experimental Section

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra in DMSO-d_6 were recorded on a Varian VXR-300 spectrometer. 1,2-Bis(benzotriazol-1-yl)-1,2-dichloroethane was prepared as previously described.[1]

4-(Benzotriazol-1-yl)-6*H*-benzo[*c*]tetrazolo[1,5-*e*][1,2,5]triazepine. To DMSO (50 mL) were added 1,2-bis(benzotriazol-1-yl)-1,2-dichloroethane (**4**) (3.33 g, 10 mmol) and sodium azide (2.60 g, 20 mmol). After being stirred overnight at room temperature, the solution was poured into water (200 mL), and the resulting solid was collected by filtration and washed with water and cold ethanol. Recrystallization from ethanol gave yellow needles (1.91 g, 64%), mp 230–232 °C. ^{1}H NMR: δ 10.20 (s, 1 H, NH), 8.20 (d, 1 H), 8.02 (d, 1 H), 7.76 (d, 1 H), 7.68 (t, 1 H), 7.55 (t, 1 H), 7.40 (t, 1 H), 7.22 (t, 1 H), 7.07 (d, 1 H). ^{13}C NMR: δ 148.0, 144.7, 137.7, 132.3, 131.7, 128.9, 128.4, 126.0, 125.5, 125.1, 122.4, 120.8, 119.5, 112.1.

Anal. Calcd for $C_{14}H_9N_9$: C, 55.46; H, 2.97; N, 41.58. Found: C, 55.74; H, 3.00; N, 41.85.

Crystal Data, Solution, and Refinement. Intensity data were collected at −125 °C with a Nicolet R3m four-circle dif-

fractometer by using monochromatized Mo Kα (λ = 0.71069 Å) radiation and a yellow crystal measuring 0.25 × 0.25 × 0.11 mm. Cell parameters were determined by least-squares refinement, the setting angles of 25 accurately centered reflections ($2\theta > 20°$) being used. Throughout data collection the intensities of three standard reflections (005, 030, 400) were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects but no correction for absorption was deemed necessary. Reflections with $I > 3\sigma(I)$ were used for structure solution and refinement.

The structure was solved by direct methods and refined by blocked-cascade least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters. The benzene ring hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic equivalent of their carrier atoms. The position of the N1 hydrogen was determined from a difference map and successfully refined. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0.00144F_o^2]^{-1}$. A final difference map showed no features >0.27 e Å^{-3}. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL.[5] Final bond lengths and angles are given in Table I. Equations of mean planes are available from P.J.S.

Crystal data at −125 °C: $C_{14}H_9N_9$, M_r = 303.3, triclinic, space group $P\bar{1}$, a = 8.482 (2), b = 9.109 (4), and c = 10.268 (4) Å, α = 72.89 (3)°, β = 74.13 (3)°, γ = 60.27 (2)°, U = 650.6 (4) Å^3, F(000) = 312, Z = 2, D_c = 1.55 g cm^{-3}, μ(Mo Kα) = 0.98 cm^{-1}, ω scans, $2\theta_{max}$ = 52°, N = 2286, N_0 = 1591211 parameters, S = 1.00, R = 0.039, R_w = 0.041.

Supplementary Material Available: Atom coordinates and thermal parameters are listed in Tables 2-4 as supplementary material which includes tabulations of structure factors. Atom coordinates (Table 2) and thermal parameters (Table 3) for compound 6 (2 pages); observed and calculated structure factors for 6 (Table 4) (10 pages). Ordering information is given on any current masthead page.

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Identification of a Pair of Atropisomeric Porphyrins by ^{1}H NMR Investigations on Their Zinc Derivatives

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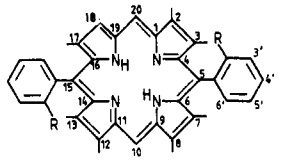
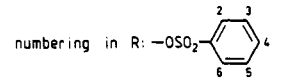
The phenomenon of atropisomerism in porphyrins with meso aryl substituents was described in 1969 for the first time by Gottwald and Ullman, who obtained four isomers in the synthesis of 5,10,15,20-tetrakis(2-hydroxyphenyl)-porphyrin.[1] Since then atropisomerism has been reported for tetra-meso[2] as well as di-meso[3] substituted aryl-porphyrins. The identification of the various atropisomers of the tetraarylporphyrins was based on a combination of arguments. In the first place the quantities of each isomer, present in the equilibrium mixture ($\alpha\alpha\alpha\alpha$:$\alpha\alpha\alpha\beta$:$\alpha\alpha\beta\beta$:$\alpha\beta\alpha\beta$ = 1:4:2:1) allow the $\alpha\alpha\alpha\beta$ and $\alpha\alpha\beta\beta$ isomers to be distinguished from the two others. Secondly, the $\alpha\alpha\alpha\alpha$ atropisomer is usually assumed to be the most polar isomer, with the lowest R_f value in adsorption chromatography. Finally, the ^{1}H NMR spectrum of the pure $\alpha\alpha\alpha\beta$ isomer shows three different sets of resonances for the meso arylprotons, unlike the other three isomers.[4] For the di-meso arylporphyrins, where only two atropisomers are to be expected in a statistical ratio of 1:1, identification was mainly based on the polarity (R_f value) and in a few cases verified by attaching a bridging alkyl chain which encompasses one face of the $\alpha\alpha$ isomer.[3]

During our synthetic work[5] we prepared a number of 5,15-diaryloctamethylporphyrins **1**. For the compounds **1a-f** the purified product contained two isomers, as was evident from the ^{1}H NMR spectrum which showed two sets of signals.



1

1a R = −OSO$_2$−C$_6$H$_4$−4F
1b R = −OSO$_2$−C$_6$H$_5$
1c R = −OSO$_2$−C$_6$H$_4$−4tBu
1d R = −OSO$_2$−C$_6$H$_4$−4OCH$_3$
1e R = −OSO$_2$−C$_6$H$_2$−2,4,6-triMe
1f R = −O(CH$_2$)$_2$−OSO$_2$−C$_6$H$_4$−4F



For **1a** the two isomers were separated. By refluxing for 30 h a xylene solution of the compound which was eluted as the first fraction from the silica gel column, a mixture of the isomers was reformed. On account of its higher R_f value we assigned the $\alpha\beta$ structure to this isomer. In the ^{1}H NMR spectrum in $CDCl_3$ solution the $\alpha\beta$ form showed a higher upfield shift Δδ for the sulfonylaryl protons than the $\alpha\alpha$ isomer.[6] This seemed reasonable as in the folded conformation, preferred by these porphyrins,[5] the phenyl groups of the $\alpha\beta$ form can occupy a position nearer to the centre of the porphyrin ring current than those of the $\alpha\alpha$ form. For the compounds **1b-f** we did not isolate the atropisomers but simply assumed the $\alpha\beta$ structure for the isomer with the higher upfield shifts Δδ (Table I; for

Table I. ^{1}H NMR Data for the Atropisomers of 1a-f

	chemical shift δ (upfield shift Δδ[a]) for the phenyl protons in R (ppm)			
	αα isomer		αβ isomer	
	H2,H6	H3,H5	H2,H6	H3,H5
1a	6.09 (1.81)	4.92 (2.31)	5.73 (2.17)	4.41 (2.82)
1b[b]	6.00 (1.83)	5.06 (2.30)	5.71 (2.12)	4.57 (2.79)
1c	5.95 (1.83)	5.42 (2.13)	5.81 (1.97)	5.16 (2.39)
1d	5.80 (1.99)	4.42 (2.58)	5.69 (2.10)	4.16 (2.84)
1e	-	4.94 (2.06)	-	4.06 (2.94)
1f	6.24 (1.68)	4.88 (2.38)	5.99 (1.93)	4.56 (2.70)

[a] Δδ for a proton is defined as (δ value in the aldehyde 2-R-C$_6$H$_4$CHO) − (δ value in the porphyrin). [b] For H4 δ (Δδ) αα isomer, 5.53 (2.01); δ (Δδ) αβ isomer, 4.92 (2.62).

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