Tetrahedron Vol. 43, No. 16, pp. 3787 to 3795, 1987
Printed in Great Britain.

0040–4020/87 $3.00+.00

DITHIA-DIAZA[n.2]PARACYCLOPHANE-ENES

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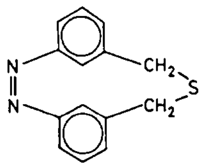
(*Received in Germany* 23 *March* 1987)

Abstract – The dithia-diaza[n.2]paracyclophane-enes 3a – 3h (n = 6 – 14) were synthesized starting from p-hydrazotoluene by using the rigid group prinziple and the high dilution technique. 3a – 3c exist only in the cis-azo configuration, while 3d and 3e are obtained as mixtures of the cis- and trans-isomers. 3f – 3h are formed as pure trans-azoarene derivatives. A thermal cis/trans-isomerisation is observed only for 3e, but 3d – 3f can be transformed into pure cis-azoarene derivatives by photoisomerization. The ^{1}H-NMR- and UV/VIS spectra of 3a – 3h are discussed. Both types of spectra show characteristic differences for the cis- and trans-isomers.

Recently, we have shown[1,2] that thia-diaza[3.2]cyclophane-enes 1 and 2 can be prepared from suitable hydrazoarene derivatives by using a combination of the rigid group principle[3] and the high dilution technique.[4] The unique structural feature of these cyclophanes is an azo-bridge between the two benzene rings, which is responsible for the interesting physical and spectroscopic properties[5] of these compounds. The rather rigid conformations of 1 and 2 force the azo group into a strained cis-configuration. However, by increasing the length of the second bridge the diazacyclophane can eventually adopt the more stable trans-configuration at the azo group, and it should be possible to observe a cis/trans-isomerization of these diaza[n.2]cyclophanes. In this paper we report the synthesis of some dithia-diaza[n.2]paracyclophane-enes 3 to test this idea.



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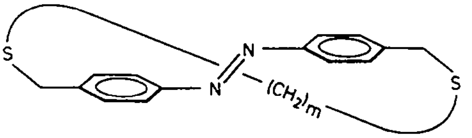
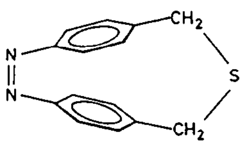


trans-3a-3h



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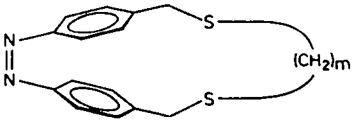
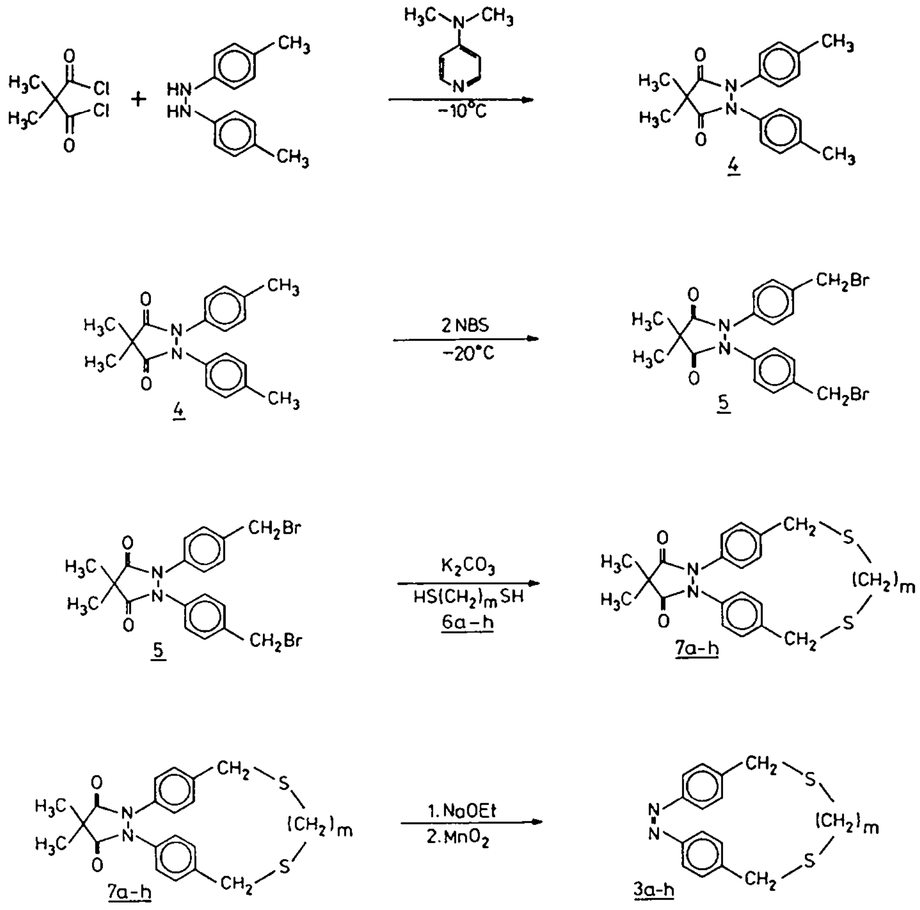


cis-3a-3h

SYNTHESIS

The synthesis of the series of dithia-diaza[n.2]paracyclophane-enes followed the route shown in Scheme 1 starting with 1,2-ditolyl-4,4-dimethylpyrazolidin-3,5-dione 4. It has been shown before[2]



Scheme 1 : Synthesis of dithia-diaza[n.2]paracyclophane-enes 3a - 3h

that the hydrazotoluene derivative 4 is much more suitable as a starting material for the synthesis of diazacyclophanes than the 2,3-ditolyl-phthalazin-1,4-dione used before[1] because of its better solubility and the much easier deprotection in the last step of the synthesis.

4 can be brominated with NBS to the dibromide 5 under carefully optimized experimental conditions. 5 contains the azoarene moiety with the reactive bromomethyl groups in a rigid cis-geometry which is essential for the construction of the second cyclophane bridge at least for the first members of the series. The cyclization of 5 was performed by the reaction with α,ω-dithiols 6a - 6h and base under high dilution conditions. The yields of the N-protected dithia-diaza[n.2]paracyclophanes 7a - 7h were considerably larger when dry K_2CO_3 was used as a base with benzene as solvent and 18-crown-6 as a phase transfer catalyst instead of the more usual dithiol method using NaOH or KOH and a benzene/ethanol mixture as solvent.[6] The yield of 7a - 7h after purification by column chromatography depends on the chain length of the cyclophane bridge formed and decreases slightly with decreasing m. The protecting dimethylmalonyl group of 7a - 7h is removed by alkaline hydrolysis, and the best results were obtained by using solid sodium ethanolate in dimethoxyethane and a N_2-atmosphere to avoid the formation of azoxy compounds. The hydrazocyclophanes thus formed are sensitive to oxidation and were oxidized by MnO_2 to the final dithia-diaza[n.2]-paracyclophane-enes 3a - 3h after extraction into ethyl acetate. 3a - 3h are purified by column chromatography. As will be discussed later, 3d - 3e are mixtures of the cis- and trans-isomers which can be separated by thin layer chromatography. The other dithia-diazacyclophanes are uniform compounds, however, 3a - 3e are obtained as orange crystals while 3e - 3h are more deeply coloured and are red. This is a first indication of different cis- and trans-configurations at the azo group throughout the series.

CONFIGURATIONS AND CONFORMATIONS OF 3a - 3h BY ^{1}H-NMR SPECTROSCOPY

The cyclophanes 3 show a clear dependence of the configuration at the azo group and of the conformations of the molecules on the chain length of the second "dithia"-bridge. The inspection of Dreiding models reveals that a planar trans-configuration at the azo group requires at least 9 CH$_2$-groups in the dithia-bridge between the two S-atoms. In this case the dithia-bridge forms an expanded chain across the trans-azobenzene moiety. Thus, only 3h ($m = 12$) and 3g ($m = 9$) should behave as normal derivatives of trans-azotoluene. The shortening of the CH$_2$-chain with $m = 8$ results in a twisted trans-azo group with a dihedral angle at the azo group smaller than 180°. This angle has to be below 90° if $m = 5$. Hence, 3a - 3c can exist only with a cis-configuration at the azo group. However, even 3a ($m = 2$) should be only slightly strained in spite of its short dithia-bridge and its rather rigid structure.

These expectations derived from Dreiding models are corroborated by the ^{1}H-NMR spectra of 3a - 3h. The relevant data obtained with CDCl$_3$ as a solvent are given in Table 1.

Table 1: ^{1}H-NMR data of dithia-diaza[n.2]paracyclophanes

			$H_{arom.}$(ppm)		$H_{aliph.}$(ppm)		
	m		4H(AA')	4H(BB')	4H(H_a)	4H(H_b)	other
3a	2	trans	-	-	-	-	-
		cis	7.00	6.44	3.54	2.00	-
3b	4	trans	-	-	-	-	-
		cis	7.11	6.62	3.59	1.95	1.40(4H)
3c	5	trans	-	-	-	-	-
		cis	7.17	6.72	3.63	2.17	1.25(6H)
3d	6	trans	7.88	7.38	3.78	1.87	0.20 - 0.03(8H)
		cis	7.21	6.82	3.63	2.16	1.44(4H);1.12(4H)
3e	7	trans	7.89	7.39	3.80	2.08	0.41(4H);0.06(2H);-0.07(4H)
		cis	7.20	6.87	3.61	2.17	1.50(4H);1.23(4H);1.04(2H)
3f	8	trans	7.89	7.42	3.78	2.14	0.40(8H);0.25(4H)
		cis	7.22	6.86	3.66	2.30	1.49(4H);1.27(8H)
3g	9	trans	7.90	7.34	3.77	2.17	0.56(10H);0.39(4H)
		cis	7.18	6.85	3.62	2.35	1.53(4H);1.28(10H)
3h	12	trans	7.88	7.46	3.74	2.36	1.20(8H);0.70(12H)
		cis	7.19	6.82	3.65	2.32	1.52(4H);1.27(16H)
p-azotoluene		trans	7.81	7.29	2.42 (CH$_3$)		
		cis	7.05	6.75	2.28 (CH$_3$)		

The para-substituted azobenzene moiety of 3 gives rise to signals in the ^{1}H-NMR spectra corresponding to an AA'BB'-system observed for trans-para-azotoluene[7] and proves a trans-azo configuration as the most stable form of 3h as expected. In this spectrum the singlet at 3.7 ppm is due to the protons at the benzylic positions of the dithia-bridge (H_a), and the signal at 2.36 ppm is assigned to the CH$_2$-groups of the CH$_2$-chain adjacent to the S-atom (H_b). The form of the signal is nearly the triplet expected for an A$_2$X$_2$-spin system. The protons of the remaining 10 CH$_2$-groups of 3h give rise to two multiplet signal groups at 0.9 - 1.5 and 0.6 - 0.8 ppm.

The ^{1}H-NMR spectrum of 3g ($m = 9$, Fig. 1c) contains the same signal groups for the aromatic protons at 7.3/7.9 ppm and for the benzylic H_a-protons at 3.8 ppm. Thus, the trans-azo configuration clearly is again the preferred form of 3g. Interestingly, a small high field shift to 2.2 ppm and a larger one at 0.4/0.6 ppm is observed for the H_b-protons and for the remaining protons of the CH$_2$-groups of the dithia-bridge, respectively. This corroborates the conclusion derived from the Dreiding models that trans-3g has an expanded CH$_2$-chain of the dithia-bridge which spans over the azobenzene moiety. In this conformation the CH_2-groups are positioned directly over the benzene rings. Hence the NMR signals of the corresponding protons are shifted to higher fields by the ring current of the azobenzene group. Similar effects are observed in the ^{1}H-NMR spectra of 3e (m = 7, Fig. 1b) and 3f (m = 8). Although the azobenzene moiety of these cyclophanes can exist only in a twisted trans-configuration (assuming otherwise normal bond lengths and bond angles in the molecule) the signals of the AA'BB'-system of the aromatic protons and of the benzylic H_a-protons appear still at the "normal" trans-position. However, the signals of the H_b-protons and especially of the protons of the other CH_2-groups of the dithia-bridge experience further shifts to higher fields. Probably, this indicates that the strain in the trans-dithia-diazacyclophanes trans-3e and trans-3f does not lead to a much twisted trans-azo group but results in a distortion of the bond angles along the CH_2-chain of the dithia-bridge. The extended CH_2-chain is forced to approach the benzene rings very close in the conformations thus adopted, and this explains the observed extreme high field position of the NMR signals of the corresponding protons. A strained conformation especially in the case of trans-3e is also indicated by the form of the signal of the H_b-protons which now corresponds to the XX'-part of an AA'XX'-spin system indicating the more rigid nature of the extended CH_2-chain.

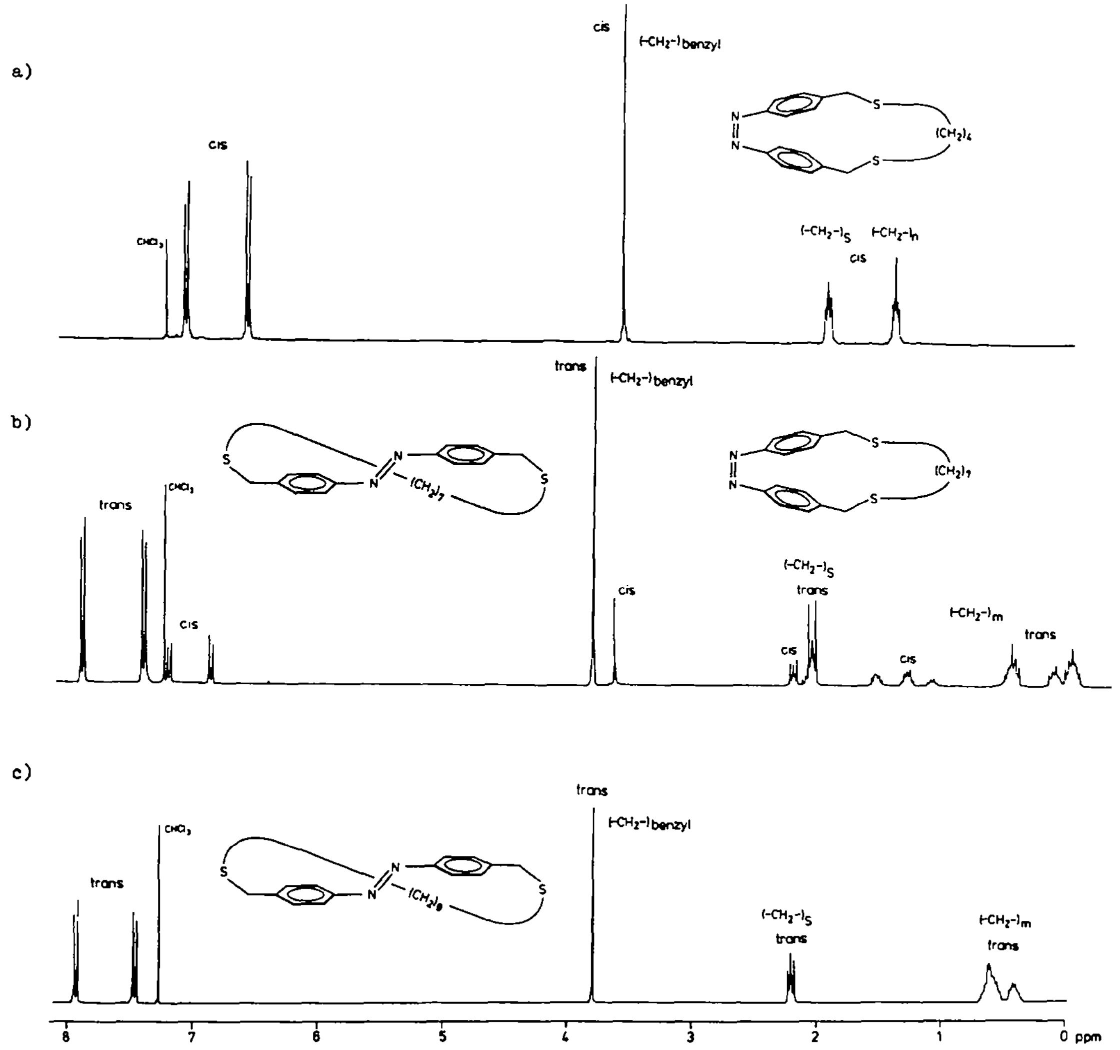


Figure 1 : ^{1}H-NMR spectra (300 MHz) of a) dithia-diaza[8.2]paracyclophane-ene 3b
b) dithia-diaza[11.2]paracyclophane-ene 3e, and c) dithia-diaza[13.2]paracyclophane-ene 3g

The dithia-diaza[n.2]paracyclophane-enes 3a - 3c can only adopt a cis-azo configuration. The ^{1}H-NMR spectra of these compounds (Table 1) contain again the signals of an AA'BB'-spin system typical of a parasubstituted azobenzene but now at 6.7/7.2 ppm in the case of 3b (Fig. 1a) and 3c. This shift of ca. 0.7 ppm to a higher field compared to the trans-derivatives can be explained by a "face-to-face"-orientation of the two benzene rings in cis-3b and cis-3c. Indeed, the AA'BB'-signal of the aromatic protons is further shifted to 6.44/7.0 ppm in the ^{1}H-NMR spectrum of cis-3a which prefers the face-to-face-conformation because of the short dithia-bridge. A small high field shift of ca. 0.2 ppm is experienced by the benzylic protons H_a which gives rise to a singlet now at 3.6 ppm. In contrast to these shifts to higher fields, the H_b protons of the CH_2-groups adjacent to the S-atoms give rise to signals at ppm values similar to those of the trans-dithia-diaza[n.2]paracyclophane-enes trans-3f - trans-3h, while the signals of the remaining protons of the dithia-bridges appear even at lower fields than those of the trans-compounds. Obviously, the CH_2-groups of the cis-dithia-bridge protrude sidewards out of the region of the cis-azo benzene moiety.

An inspection of the ^{1}H-NMR spectra of 3d (m = 6) and 3e (m = 7, Fig. 1b) reveals that both dithia-diaza[n.2]paracyclophanes are a mixture of cis- and trans-isomers. This is most easily seen by the signals of the aromatic protons (two AA'BB'-spin systems at 6.9/7.2 and 7.4/7.9 ppm, respectively) and of the benzylic H_a-protons (two singlets at 3.6 and 3.8 ppm, respectively). A cis/trans-ratio of 77/23 and 22/78 is derived from these signals for 3d and 3e, respectively. However, only in the case of 3e the cis- and trans-azo isomers are in thermal equilibrium with each other, because the cis/trans-ratio shows a clear dependence on the temperature. Neither the cis-isomers are formed by heating trans-3f - trans-3h in solution at temperatures below thermal degradation, nor the trans-isomers are generated by heating solutions of cis-3a - cis-3d. Thus, only 3e has a small activation energy for the thermal cis/trans-isomerization which is certainly a ground state effect due to considerable strain in the trans-azo configuration.[8]

However, a photoisomerization occurs quite easily, and all trans-3 can be converted nearly completely into the corresponding cis-3 by this technique.[9] The cis/trans-composition of the mixture of the photostationary state at different wave lengths is shown in Table 2.

Table 2 : cis/trans-Ratio of dithia-diaza[n.2]paracyclophanes 3 at the photostationary state at different wave lengths[a)]

	m	day light cis/trans	λ = 369 nm cis/trans	λ = 443 nm cis/trans
3a	2	100/0	decomposition	
3b	4	100/0	decomposition	
3c	5	100/0	decomposition	
3d	6	77/23	100/0	50/50
3e	7	22/78	100/0	22/78
3f	8	0/100	100/0	0/100
3g	9	0/100	90/10	0/100
3h	12	0/100	90/10	0/100
p-azotoluene		0/100	85/15	0/100

a) determined by ^{1}H-NMR

The data of the ^{1}H-NMR spectra of cis-3e - cis-3h thus obtained are included in Table 1. Similarly, it is possible to generate pure trans-3f - trans-3h by photoisomerization.[9] However, 3d and 3e give only mixtures of the cis- and trans-isomers as photostationary states and no trans-3a - trans-3c are formed by photoisomerization. Nevertheless it is of interest that the much strained trans-3d (m = 6) is formed by photoisomerization with a lifetime of several hours in the dark.[9]

UV/VIS SPECTRA OF 3a - 3h

The characteristic data from the UV/VIS spectra of the dithia-diaza[n.2]paracyclophane-enes 3a - 3h are shown in Table 3. The spectra of cis-3e - cis-3h have been obtained after a photoisomerization of the corresponding trans-isomers. The spectrum of 3d corresponds to a mixture of cis- and trans-isomers. The data for the UV/VIS spectra of cis- and trans-para-azotoluene are included in Table 3 for comparison. These latter data show that the (unstrained) trans-azotoluene chromophore is characterized by an intense absorption at λ_{max} = 332 nm which is attributed to a ($\pi \rightarrow \pi^*$)-transition of the azo group. This absorption band is shifted to λ_{max} = 302 nm for the cis-isomer. In contrast to this a bathochromic shift of λ_{max} = 235 nm (trans) to λ_{max} = 244 nm (cis) is observed for the absorption band due to transitions of the arene chromophores. However, the effect of the cis/trans-configuration on the long wave length band of the ($n \rightarrow \pi^*$)-transition at λ_{max} = 432 nm (trans) and λ_{max} = 434 nm (cis) is rather small.[10]

Table 3 : UV/VIS spectra of dithia-diaza[n.2]paracyclophane-enes 3 (ethanol)

	m	configurations	$n \rightarrow \pi^*$ λ_{max} (ε)	$\pi \rightarrow \pi^*$ λ_{max} (ε)	$\Phi \rightarrow \Phi^*$ λ_{max} (ε)
3a	2	trans	-	-	-
		cis	392 (1000)	320s (3700)	240 (12500)
3b	4	trans	-	-	-
		cis	414 (1100)	284s (4000)	241 (11000)
3d	6	trans cis	434 (1500)	360s (5300) 315-345(7000)	242 (13000)
3e	7	trans	435 (1100)	360 (8600)	242 (9400)
		cis	435 (1800)	303 (6500)	245 (12300)
3f	8	trans	436 (1200)	355 (14000)	236 (14200)
		cis	440 (1900)	300 (6700)	248 (13000)
3g	9	trans	433 (1200)	350 (17500)	236 (14500)
		cis	435 (1700)	303 (7500)	240 (12500)
3h	12	trans	430 (1100)	343 (17500)	235 (11000)
		cis	432 (2000)	305 (7900)	240 (13700)
p-azotoluene		trans	432 (830)	332 (18300)	235 (11300)
		cis	434 (1500)	302 (5900)	244 (9200)

The UV/VIS spectra of cis- and trans-3e - 3h, which are unstrained compounds in both configurations, are similar to those of cis- and trans-para-azotoluene (Fig. 2). Thus, the spectra of the trans-dithia-diaza[n.2]paracyclophane-enes are composed of three bands at λ_{max} = 433 ± 3 nm, 340 ± 5 nm, and 236 ± 2 nm, respectively, while the spectra of the cis-isomers contain bands at λ_{max} = 435 ± 5 nm, 303 ± 3 nm, and 244 ± 4 nm. Furthermore, the intensities of these bands parallel those of the linear model compounds, especially with respect to the rather low intensities at shorter wave lengths for the cis-isomers.

The cyclophanes 3a - 3d exist only or predominantly in the cis-configuration. Interestingly, a hypsochromic shift of the band due to the ($n \rightarrow \pi^*$)-transition is observed for the cis-dithia-diaza-[n.2]paracyclophane-enes with short dithia-bridges. Thus, this band appears at λ_{max} = 392 nm in the spectrum of cis-3a instead of its normal position at 434 nm. This hypsochromic shift indicates probably a twisted cis-azoarene conformation of 3a (and 3b) with a face-to-face-orientation of the benzene rings. In this case, the azo group and the aromatic chromophore are more or less orthogonal to each other.

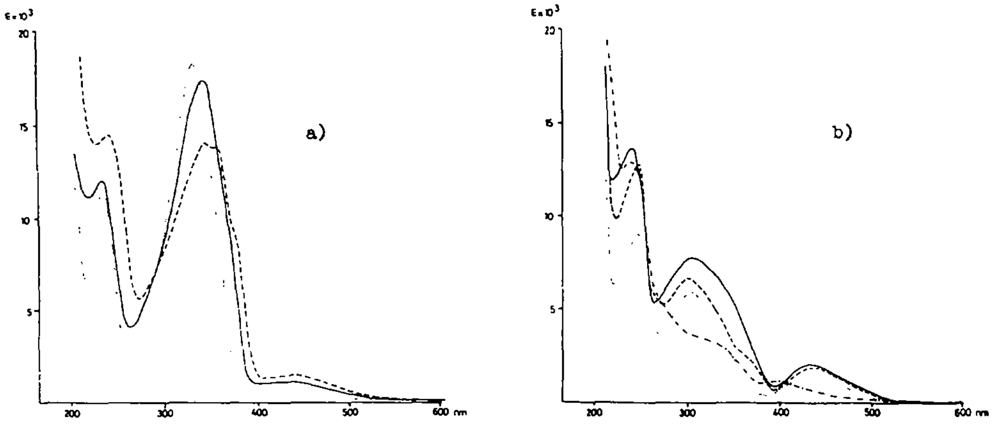


Figure 2 : UV/VIS spectra (ethanol) of
a) trans-dithia-diaza[n.2]paracyclophane-enes 3f(---), 3h(—), and trans-p-azotoluene(···);
b) cis-dithia-diaza[n.2]paracyclophane-enes 3a(·-·-), 3f(---), 3h(—), and cis-p-azotoluene(···)

EXPERIMENTAL

The melting points of the compounds were determined with an Electrothermal® melting point apparatus and are uncorrected. The ^{1}H-NMR spectra (300 MHz, $CDCl_3$) were obtained with a Bruker AM 300 NMR-spectrometer. The 70 eV mass spectra were measured with a MAT mass spectrometer 311A using a direct probe inlet system. The UV/VIS spectra were obtained with a Beckman spectrophotometer model 25 using ethanol as a solvent. The thin layer chromatography was performed with TLC (aluminium roll silica gel pre-coated, Merck, type 60F 254, 0,2 mm). The column chromatography was carried out with silica gel (type 60, 0,063 mm) as a stationary phase and petroleum ether/ethyl acetate, CH_2Cl_2 or toluene as eluents or with MPLC using pre-packed columns (Merck, LiChroprep Si 60, 40 - 63 µm).

1,2-Bis(p-tolyl)-4,4-dimethylpyrazolidin-3,5-dione (4)

4 was prepared by a method analogous to the condensation of 4,4'-diethoxycarbonylhydrazobenzene with alkylmalonyl dichlorides.[11] Dimethylmalonyl dichloride (21 ml, 0,1 mol) was dropped at -15°C into a mixture of 50 ml dry pyridine and 100 ml of dry $CHCl_3$. A small amount of N-dimethylaminopyridine was added, and 21 g (0,1 mol) p-hydrazotoluene in 250 ml of dry $CHCl_3$ was slowly dropped into the mixture at -15°C while stirring and flushing with dry N_2. The solution was stirred over night and brought to room temperature. The deep red reaction mixture was extracted with ice cold 2n HCl (500 ml in several portions) to remove the pyridine and was neutralized by washing with 5% $NaHCO_3$-solution. The pale yellow solution was washed with water, dried over Na_2SO_4, and the solvent was evaporated. The yellow residue was crystallized twice from diethyl ether. 4, white crystals, yield 17,2 g (56%), mp 148°C. R_f = 0,4 (petroleum ether/ethyl acetate 4/1); 0,3 (CH_2Cl_2). ^{1}H-NMR ($CDCl_3$) : 7,14 m (8H, arom.), 2,27 m (6H, CH_3-, tolyl), 1,48 s (6H, CH_3). MS: m/z 308 ($M^{+\cdot}$, 100%), 210 (13), 147 (34), 132 (88), 119 (39), 104 (16), 105 (16), 91 (15). Elemental analysis: cal.: C, 74,0%; H, 6,5%; N, 9,1%; exp.: C, 73,8%; H, 6,5%; N, 9,2%.

1,2-Bis(4-bromomethyl)phenyl)-4,4-dimethylpyrazolidin-3,5-dione (5)

10,7 g (0,06 mol) of NBS was added to a solution of 9,2 g (0,03 mol) 4 in 500 ml dry CH_2Cl_2. The mixture was cooled to -20°C, and the reaction was started by adding a drop of Br_2. The mixture was irradiated for 20 h with a 500 W photolamp at -20°C under vigorous stirring. The reaction was controlled by TLC and by ^{1}H-NMR spectroscopy, and the end of the reaction was recognized by a colour change to pale yellow. The solvent was evaporated, and the solid residue was extracted several times with 50 ml portions of CCl_4. The insoluble material was removed by filtration, and the clear solution was concentrated at reduced pressure. The product was crystallized by cooling to -4°C and was recrystallized from CCl_4 to give pure 5 (6,6 g, 47%) as white crystals, mp 171°C. R_f = 0,3 (CH_2Cl_2). ^{1}H-NMR ($CDCl_3$) : 7,33 s (8H, arom.), 4,42 s (4H, CH_2), 1,49 s (CH_3). MS: m/z 464/466/468 ($M^{+\cdot}$, 14/28/14), 385/387 (98/100), 307 (20), 153 (20), 147 (10), 146 (88), 131 (87), 90 (36), 89 (20). Elemental analysis: calc.: C, 48,9%; H, 3,86%; N, 6,01%; exp.: C, 48,3%; H, 3,98%; N, 6,09%.

N,N'-Dimethylmalonyl-dithia-diaza[n.2]paracyclophanes (7a - 7h)

General procedure for the cyclizations: in a one-component high dilution principle apparatus (DP-apparatus, F. Vögtle)[12] a solution of 1,86 g (4 mmol) of the dibromide 5 and 4 mmol of the relevant dithiol 6a - 6h in 200 ml benzene were dropped gradually over a period of 48 h to a well

Table 4 : N,N'-Dimethylmalonyl-dithia-diaza[n.2]paracyclophanes 7

compound		yield (%)	m.p. (°C)	mass spectrum (m/z;rel.int.)	exact mass determination
N,N'-Dimethylmalonyl-2,5-dithia-13,14-diaza-[6.2]paracyclophane	7a	41	213 EtOH	398(94,$M^{+\cdot}$),306(20),224(31), 175(23),164(56),146(35), 132(100), 90(24)	$C_{21}H_{22}N_2O_2S_2$ calc. 398,1123 exp. 398,1122
N,N'-Dimethylmalonyl-2,7-dithia-15,16-diaza-[8.2]paracyclophane	7b	54	179 EtOH	426(29,$M^{+\cdot}$),307(13),306(53), 291(18), 174(13), 146(41), 132(100), 90(14)	$C_{23}H_{26}N_2O_2S_2$ calc. 426,1436 exp. 426,1437
N,N'-Dimethylmalonyl-2,8-dithia-16,17-diaza-[9.2]paracyclophane	7c	45	215 EtOH	440(48,$M^{+\cdot}$),306(26),291(14) 174(10), 146(35), 132(100), 90(12)	$C_{24}H_{28}N_2O_2S_2$ calc. 440,1592 exp. 440,1590
N,N'-Dimethylmalonyl-2,9-dithia-17,18-diaza-[10.2]paracyclophane	7d	55	167 EtOH	454(78,$M^{+\cdot}$),306(16),291(16), 280(23), 174(11), 147(12), 146(43), 132(100), 90(15)	$C_{25}H_{30}N_2O_2S_2$ calc. 454,1749 exp. 454,1747
N,N'-Dimethylmalonyl-2,10-dithia-18,19-diaza-[11.2]paracyclophane	7e	43	160 EtOAc	468(100,$M^{+\cdot}$), 294(13), 146 (49), 132(97), 90(16)	$C_{26}H_{32}N_2O_2S_2$ calc. 468,1905 exp. 468,1903
N,N'-Dimethylmalonyl-2,11-dithia-19,20-diaza-[12.2]paracyclophane	7f	48	130 EtOAc	482(100,$M^{+\cdot}$), 308 (12), 175 (11), 147(11), 146(59), 132(86), 90(22)	$C_{27}H_{34}N_2O_2S_2$ calc. 482,2062 exp. 482,2063
N,N'-Dimethylmalonyl-2,12-dithia-20,21-diaza-[13.2]paracyclophane	7g	38	105 EtOAc	496(87,$M^{+\cdot}$),322(15),307(18) 175(14), 174(12), 160(19), 146(60), 132(100), 90(20)	$C_{28}H_{36}N_2O_2S_2$ calc. 496,2218 exp. 496,2218
N,N'-Dimethylmalonyl-2,15-dithia-23,24-diaza-[16.2]paracyclophane	7h	25	98 EtOAc	538(100,$M^{+\cdot}$), 364(14),307(18) 175(14), 174(12), 160(13) 146(50), 132(87), 90(13)	$C_{31}H_{42}N_2O_2S_2$ calc. 538,2688 exp. 538,2688

Table 5 : Dithia-diaza[n.2]paracyclophane-enes 3

compound		yield (%)	m.p. (°C)	mass spectrum (m/z,rel.int.)	exact mass determination
2,5-Dithia-13,14-diaza[6.2]-paracyclophane-13-ene	3a	15 yellow	210 EtOH	300(100,$M^{+\cdot}$),208(68),180(76), 179(31),178(20),166(68),165 (54),121(20),90(77),89(64)	$C_{16}H_{16}N_2S_2$ calc. 300,0755 exp. 300,0752
2,7-Dithia-15,16-diaza[8.2]-paracyclophane-15-ene	3b	17 orange	158 EtOH	328(8,$M^{+\cdot}$),208(100),180(21), 179(11),166(14),165(16), 90(33), 89(22)	$C_{18}H_{20}N_2S_2$ calc. 328,1068 exp. 328,1068
2,8-Dithia-16,17-diaza[9.2]-paracyclophane-16-ene	3c	20 orange	115	342(54,$M^{+\cdot}$),208(76),180(77), 179(25),178(23),166(40),165 (30),123(13),90(100),89(66)	$C_{19}H_{22}N_2S_2$ calc. 342,1225 exp. 342,1224
2,9-Dithia-17,18-diaza[10.2]-paracyclophane-17-ene	3d	35 orange	118 EtOH	356(76,$M^{+\cdot}$),208(50),180(100), 179(10),178(20),166(15),165 (15),123(11),90(56),89(27)	$C_{20}C_{24}N_2S_2$ calc. 356,1381 exp. 356,1379
2,10-Dithia-18,19-diaza[11.2]-paracyclophane-18-ene	3e	32 orange	227 CH_2Cl_2	370(81,$M^{+\cdot}$),208(50),207(11), 180(100),179(16),166(10), 165(14),91(14),90(52),89(27)	$C_{21}H_{26}N_2S_2$ calc. 370,1537 exp. 370,1536
2,11-Dithia-19,20-diaza[12.2]-paracyclophane-19-ene	3f	40 red	200 CH_2Cl_2	384(72,$M^{+\cdot}$),208(52),207(12), 180(100),165(12),123(12), 121(11),91(24),90(84),98(41)	$C_{22}H_{28}N_2S_2$ calc. 384,1694 exp. 384,1694
2,12-Dithia-20,21-diaza[13.2]-paracyclophane-20-ene	3g	44 red	200 CH_2Cl_2	398(94,$M^{+\cdot}$),208(71),207(17), 180(100),179(16),165(13), 123(12),91(21),90(83)	$C_{23}H_{30}N_2S_2$ calc. 398,1850 exp. 398,1849
2,15-Dithia-23,24-diaza[16.2]-paracyclophane-23-ene	3h	64 orange	193 CH_2Cl_2	440(100,$M^{+\cdot}$),209(53),208 (52),207(12),180(39),91 (14),90(33),89(14)	$C_{26}H_{36}N_2S_2$ calc. 440,2320 exp. 440,2319

stirred and rigorously boiling suspension of 9,2 K_2CO_3 and 300 mg 18-crown-6 in 2 l dry benzene under a stream of nitrogen. After complete addition of the reactants the mixture was boiled for additional 2 h. The insoluble products were removed by filtration, and the clear benzene solution was evaporated to dryness. The yellow residue was dissolved in CH_2Cl_2, washed several times with 5% NH_4Cl-solution and finally with water to remove the PT-catalyst and any salts. The polymeric materials were separated by column chromatography using petroleum ether/ethyl acetate 4/1 (7a - 7d) and CH_2Cl_2 (7e - 7h) as eluent, respectively. The further purification was performed by MPLC using CH_2Cl_2 as eluent and recrystallization from ethanol and ethyl acetate, respectively. 7a - 7h were obtained as white crystals, the yields and the physical data are listed in Table 4.

Dithia-diaza[n.2]paracyclophane-enes 3a - 3h

General procedure for the deprotection of 3a - 3h : 680 mg (10 mmol) of dry sodium ethanolate were added to a solution of 1 mmol of 3a - 3h in 100 ml dimethoxyethane. The mixture was stirred at room temperature under a stream of N_2 for 20 h. If the reaction is carried out without N_2 about 10% of the azoxy derivatives were formed which could be separated only with difficulty. During this period the colour of the solution turned from yellow to red-brown. The progress of the reaction was controlled by thin layer chromatography. At the end of the reaction most of the dimethoxyethane was evaporated at reduced pressure, and ice water was added to the residue. The aqueous layer was extracted several times with small portions of ethyl acetate. The combined organic solutions were washed with a saturated NaCl-solution and dried over Na_2SO_4. The solution contained mostly the reduced hydrazo derivatives of the dithia-diaza-cyclophane-enes, which were oxidized completely into 3a - 3h by heating the solution with MnO_2 to 70°C (3d - 3h) or simply by stirring the solution at the air at room temperature (3a - 3c). The raw-products 3a - 3h were filtered through silica gel and finally purified by MPLC with toluene as eluent. It was possible to isolate the pure cis-isomer of 3d by chromatography in the dark. Similarly, the pure trans-isomer of 3e was separated in the dark. The pure trans-3e - 3h were obtained by crystallization from ethanol and CH_2Cl_2, respectively. The yields and the physical data are given in Table 5.

Photoisomerization of 3d - 3h

The photoisomerization was performed by irradiation of a solution of 5 - 10 mg 3d - 3h in about 2 ml $CDCl_3$ within a NMR test tube using a photolamp NORMAG TQ 150/Z1. The strong emission of this lamp at $\lambda = 254$ nm was removed by filtering with Duran and an UV filter WG 305 and the relevant wave lengths were selected by using UV linefilters (Schott).
The cis → trans-isomerization of 3d was performed by irradiation at $\lambda = 443$ nm (T_{max} 41%, HW = 14 nm) for 4 h.
The trans → cis-isomerization of 3e - 3h was carried out by irradiation at $\lambda = 369$ nm (T_{max} 51%, HW = 7,9 nm) for 2 h. The ratio of the cis/trans-isomers was determined by ^{1}H-NMR.

Acknowledgement - The financial support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

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