Planar Chiral Systems, I

Optical Resolution of [2.2]Paracyclophanes by High-Performance Liquid Chromatography on Tris(3,5-dimethylphenylcarbamates) of Cellulose and Amylose

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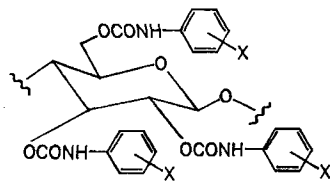
Received September 21, 1989

Key Words: Resolution, optical / Stationary phases, chiral / Amylose carbamates / Cellulose carbamates / [2.2]Paracyclophanes, functionalized

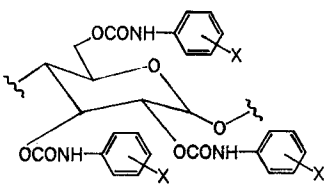
Optical resolution of 22 [2.2]paracyclophane derivatives was examined by high-performance liquid chromatography (HPLC) using tris(3,5-dimethylphenylcarbamates) of cellulose and amylose as chiral stationary phases. Most compounds were completely separated into enantiomers at least on one of the stationary phases. The preparation of the new cyclophane derivatives **10, 11, 12, 14, 16,** and **19** as well as a new procedure for the synthesis of 4-fluoro-[2.2]paracyclophane (**3**) are described.

Although one of the reasons for the continuing interest[1] in the preparation of novel cyclophane systems rests on the stereochemical properties of these bridged aromatics[2-4], their utilization as chiral reagents is conspicuously lacking[5]. This is surprising, since – compared to many classical optically active reagents – especially the substituted [2.2]paracyclophanes offer the advantage of not only possessing no racemizable α-hydrogen atom but also show a very high configurational stability: it takes temperatures well above 200°C and long reaction times before an optically active [2.2]paracyclophane looses its activity[6].

Against this background we examined the optical resolution of 22 chiral [2.2]paracyclophanes (**1**–**22**) by HPLC using cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC) and amylose tris(3,5-dimethylphenylcarbamate) (ADMPC) as chiral stationary phases (CSPs). CDMPC and ADMPC have been used for optical resolution of various racemic compounds[7-9].

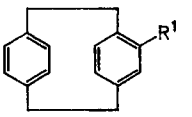


X = 3,5-Me_2
CDMPC

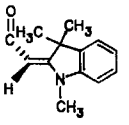


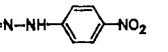
X = 3,5-Me_2
ADMPC

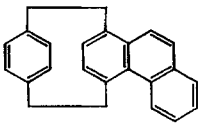
Most of the cyclophanes originate from our ongoing work in this area and have been prepared previously. The amide **10**, the Fischer base derivative **11**, the *p*-nitrophenylhydrazone **12** as well as the methylamino derivative **14**, the nitroso compound **16**, and the phenanthrenophane **19** are described here for the first time (see Experimental); we furthermore present a new route to 4-fluoro-[2.2]paracyclophane (**3**).



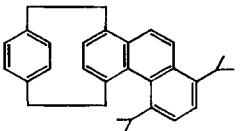
	R^1
1	CH_3
2	$CH=CH_2$
3	F
4	Cl
5	Br
6	CO_2H

	R^1
7	$CO_2C_2H_5$
8	CH_2OH
9	$COCH_3$
10	$CON(C_2H_5)_2$
11	

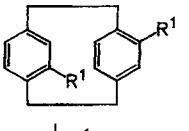
	R^1
12	
13	NH_2
14	$NHCH_3$
15	$N(CH_3)_2$
16	NCH_3NO
17	NO_2



18



19



	R^1
20	CH_2OH
21	CHO
22	CN

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The preparation of CDMPC and ADMPC packings has been reported previously[8,9]. The packings were then filled into a stainless-steel tube (25 × 0.46 cm) by a slurry method.

Chromatographic analyses were performed with a JASCO TRI-ROTAR-II, equipped with UV (UVIDEC 100-V) and polarimetric (DIP-181-C) detectors using a hexane/2-propanol mixture as an eluent at 25°C. Dead time (t_0) was estimated with tris(1,3,5-tri-*tert*-butyl)benzene[10].

All cyclophane derivatives examined were resolved at least on one of the columns. Figure 1 shows the chromatogram of the resolution of *N,N*-diethyl-[2.2]paracyclophane-4-carboxamide (**10**) on CDMPC. The amide was completely resolved giving elution times t_1 and t_2 for (−) and (+) isomers, respectively. Capacity factors, k_1' [$= (t_1 - t_0)/t_0$] and k_2' [$= (t_2 - t_0)/t_0$], which represent the strength of the interaction between the stationary phase and the enantiomers, were 0.56 and 1.26, respectively. The chiral recognition ability of the CSP may be evaluated from the separation factor α ($= k_2'/k_1'$), and the resolution of two peaks is expressed by the resolution factor R_s [$= 2(t_2 - t_1)/(W_1 + W_2)$]. In Figure 1, α is 2.25 and R_s is 5.08.

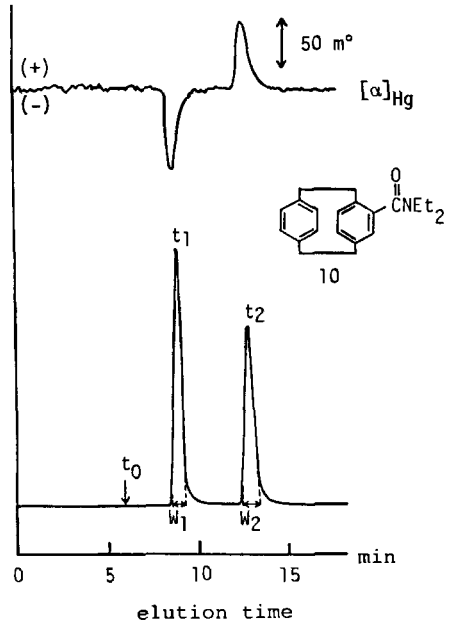

Figure 1. Optical resolution of *N,N*-diethyl-[2.2]paracyclophane-4-carboxamide (**10**) on CDMPC [eluent: hexane/2-propanol (90:10); flow rate 0.5 ml/min; 25 °C]; m° = 10⁻³ degree

Figure 2 shows the chromatograms of the resolution of **2**, **20**, and **21** on CDMPC, and the results of the optical resolution of all [2.2]paracyclophane derivatives on CDMPC and ADMPC are summarized in Table 1. The separation factors α of the various cyclophanes on the CDMPC and ADMPC columns are strongly dependent on the substituents of the racemates.

In most separations CDMPC showed higher optical resolving ability than ADMPC. However, paracyclophanes having halogen, dimethylamino or a nitro substituent, i.e. **3**, **4**, **5**, **15**, and **17**, were not well resolved on CDMPC. These compounds were, however, almost completely resolved on ADMPC using hexane as an eluent as shown in Figure 3. Some of the cyclophanes containing hetero atoms in the substituents were very efficiently resolved showing substantial α values; for example 9.39 for **7** and 2.28 for **12**.

It is also noteworthy that CDMPC can separate the aromatic hydrocarbons **1**, **2**, **18**, and **19**. Three pseudo*ortho*-substituted paracyclophanes (**20**–**22**), which are expected to be useful as novel chiral reagents, were also completely resolved. Altogether, these results indicate that the combination of CDMPC and ADMPC can cover the optical reso-

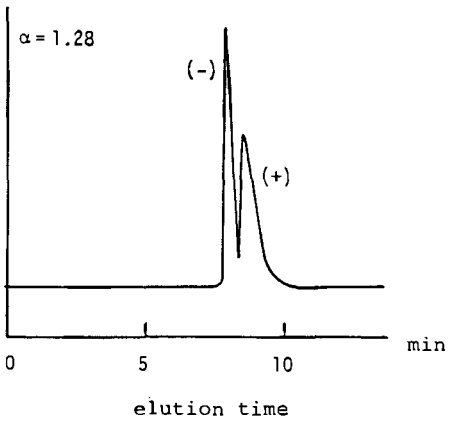

Figure 3. Optical resolution of 4-chloro-[2.2]paracyclophane (**4**) on ADMPC (eluent: hexane; flow rate 0.5 ml/min; 25°C)

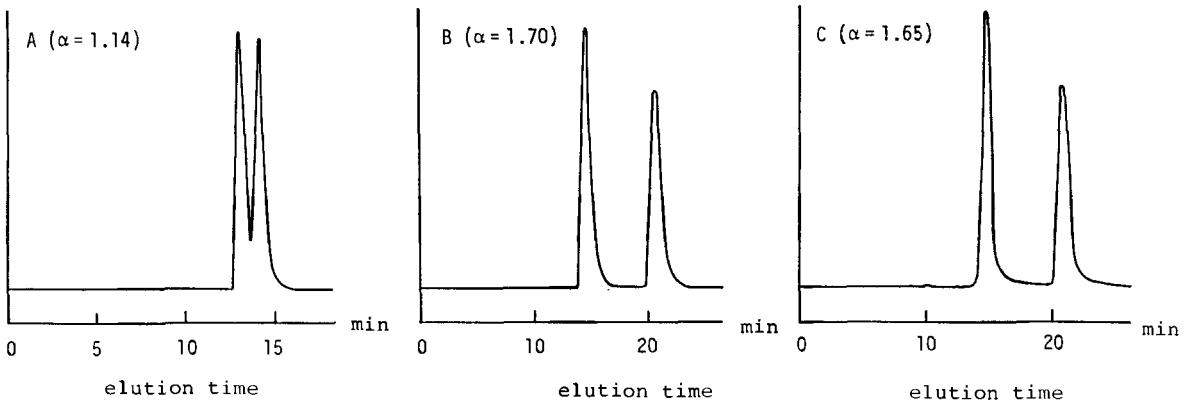

Figure 2. Optical resolution of 4-vinyl-[2.2]paracyclophane (**2**) (A), 4,12-bis(hydroxymethyl)-[2.2]paracyclophane (**20**) (B), and [2.2]paracyclophane-4,12-dicarbaldehyde (**21**) (C) on CDMPC [eluent: hexane/2-propanol (90:10); flow rate 0.5 ml/min; 25°C]

Table 1. Optical resolution of [2.2]paracyclophane derivatives **1**–**22** on CDMPC and ADMPC[a]

	CDMPC			ADMPC		
	k_1'	α	R_s	k_1'	α	R_s
1	0.93(−)	1.11	0.97	0.20(−)	ca. 1	
2	0.81(+)	1.14	1.24	0.23(−)	ca. 1	
3	0.80(−)	1.04		2.16(+)	1.09	0.83[b]
4	0.88(−)	ca. 1		0.44(−)	1.28	0.97[b]
5	0.90(−)	1.06		0.70(−)	1.58	1.76[b]
6	1.10(−)	1.28	1.75[c]			
7	2.30(−)	9.39	15.03[d]	0.81(+)	ca. 1	
8	3.19(+)	1.53	4.67	2.82(+)	1.12	1.02
9	1.11(+)	1.14	1.19	0.74(+)	ca. 1	
10	0.56(−)	2.25	5.08	0.40(−)	1.13	
11	1.17(−)	2.27	4.48	2.09(+)	1.10	0.79[e]
12	2.09(−)	2.28	6.28	5.86(+)	1.19	0.88[f]
13	4.77(+)	1.53	3.30	2.87(+)	1.10	0.83[g]
14	3.66(+)	1.25	2.38	0.55(+)	ca. 1	
15	0.60(−)	ca. 1		2.24(−)	1.13	0.96[b]
16	2.11(+)	1.58	4.87	1.45(−)	1.13	0.97
17	1.88(−)	1.07		1.46(−)	1.23	1.03[b]
18	1.23(−)	1.40	1.60	0.40(+)	ca. 1	
19	0.30(−)	1.83	2.30	0.10(+)	ca. 1	
20	1.48(+)	1.70	4.45	3.14(+)	1.24	1.99
21	1.78(−)	1.65	5.36	1.69(+)	1.13	0.83
22	1.67(−)	1.22	1.85	2.54(−)	1.20	1.84

[a] Eluent: hexane/2-propanol (90:10); 0.5 ml/min. – [b] Eluent: hexane. – [c] Eluent: hexane/2-propanol/trifluoroacetic acid (90:10:1). – [d] 1 ml/min. – [e] Data for the main isomer only (cf. Experimental). – [f] Eluent: hexane/2-propanol (80:20). – [g] Eluent: hexane/2-propanol/diethylamine (80:20:0.1).

lution of a broad range of compounds. The elution orders of enantiomers of paracyclophanes such as **2, 3, 7, 11, 12,** and **16** were opposite on CDMPC and ADMPC. This indicates that the chiral surrounding around adsorbing sites is quite different between CDMPC and ADMPC. It has been considered that the most important adsorbing sites for chiral recognition are the polar carbamate groups of the polysaccharide derivatives[9]. The carbamate groups can interact with the polar groups of racemic compounds through hydrogen bond or dipole-dipole interaction. The above results suggest that π-π interaction may also be responsible for chiral recognition.

Preparative separation of the paracyclophanes was also possible on CDMPC. For instance, 5 mg of **21** was resolved in one injection on the present analytical column.

We thank the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft* for the support of our work and *Prof. Dr. L. Ernst* (*NMR Laboratory of the Chemical Institutes of the University of Braunschweig*) for the NMR and *Dr. H. M. Schiebel* for the mass spectra.

Experimental

NMR: Varian EM-360 and T 60 and Bruker WM 400 (400.1 MHz, ^{1}H NMR); Bruker AM 300 (75 MHz) and WM 400 (100.6 MHz, ^{13}C NMR); all spectra in $CDCl_3$/internal standards TMS and $CDCl_3$ (δ_C = 77.05). – IR (KBr): Perkin-Elmer 1420. – UV: Beckman UV 5230. – MS: Finnigan 8430. – M.p.: Kofler hot-stage.

The following compounds were obtained according to literature procedures: 4-methyl- (**1**)[11], 4-vinyl- (**2**)[12], 4-chloro- (**4**)[13], 4-bromo- (**5**)[14], 4-carboxy- (**6**)[13], 4-ethoxycarbonyl- (**7**)[15], 4-hydroxymethyl- (**8**)[16], 4-acetyl- (**9**)[13], 4-amino- (**13**)[13], 4-dimethylamino- (**15**)[17], 4-nitro-[2.2]paracyclophane (**17**)[13], [2.2](1,4)phenanthrenoparacyclophane (**18**)[18], 4,12-bis(hydroxymethyl)- (**20**)[19], 4,12-diformyl- (**21**)[20], and 4,12-dicyano-[2.2]paracyclophane (**22**)[21].

Although *4-fluoro-[2.2]paracyclophane* (**3**) has been described in the literature[22] we find the following method of its preparation superior: To a stirred and cooled (−10°C) suspension of 1.72 g (11.5 mmol) of nitrosyl tetrafluoroborate in 20 ml of xylene (mixture of isomers) a solution of 2.23 g (10.0 mmol) of 4-amino-[2.2]paracyclophane (**13**)[13] in 150 ml of xylene is added at such a rate that the reaction temp. never exceeds −2°C. After warming to room temp. (N_2 evolution) the reaction mixture is gently heated and finally kept at reflux temp. for 30 min. The solvent is removed, the remaining dark brown residue is dissolved in dichloromethane, and the solution is heated at reflux with 30 ml of 2 M aqueous NaOH solution for 15 min. The organic phase is separated, washed with water, and dried with magnesium sulfate. Removal of the solvent provides 2.10 g of a tarry residue which is purified by successive chromatography on alumina (activity II–III; dichloromethane) and silica gel [benzene/cyclohexane (1:1)] yielding 1.11 g of a yellow solid. Recrystallization (ethanol) and digestion (pentane) furnishes 0.45 g (20%) of **3**, whose spectroscopic data are identical with those reported in ref.[22].

N,N-Diethyl-[2.2]paracyclophane-4-carboxamide (**10**): To a stirred solution of 1.00 g (4.8 mmol) of [2.2]paracyclophane in 60 ml of freshly distilled nitrobenzene 0.68 g (5 mmol) of diethylcarbamoyl chloride followed by 0.56 ml (5 mmol) of tin tetrachloride are added at room temp. employing syringe techniques. After 3 h at 110°C the red solution is cooled to room temp. and hydrolyzed. The aqueous phase is extracted carefully with dichloromethane, and the combined organic phases are dried with potassium carbonate. The solvent and excess nitrobenzene are removed in vacuo, and the remaining oil is purified by column chromatography on silica gel using dichloromethane as eluent. Besides 0.50 g of the starting material 0.33 g (22%) of **10** is isolated as colorless needles, m.p. 84°C (ethanol). – ^{1}H NMR (400 MHz): δ = 7.20 (dd, J_1 = 7.2, J_2 = 2.0 Hz, 1H), 6.62–6.36 (m, 6H), 3.62 (m, 1H), 3.42 (m, 1H), 3.27 to 3.06 (m, 4H), 3.03–2.80 (m, 6H), 1.24 (t, J = 7.1 Hz, 3H), 0.83 (t, J = 7.1 Hz, 3H). – ^{13}C NMR (100 MHz): δ = 170.80, 139.84, 139.34, 139.11, 136.98 (5 s), 134.84 (d), 133.86 (d), 133.75 (s), 133.06 (2 d), 132.36, 131.70, 130.03 (3 d), 42.42, 39.14, 35.42, 35.37, 35.33, 33.46 (6 t), 13.92 (q), 13.06 (q). – IR: $\tilde{\nu}$ = 2980 cm^{-1} (s), 2920 (s), 1640 (vs), 1470 (s), 1430 (s), 1280 (s), 1090 (s), 1070 (s), 900 (m), 820 (s). – UV (ethanol): λ_{max} (lgε) = 225 nm (4.29), 207 (4.35). – MS (70 eV): *m/z* (%) = 307 (66) [M$^+$], 278 (13), 236 (9), 202 (100), 175 (12), 132 (22), 104 (44).

$C_{21}H_{25}NO$ (307.43) Calcd. C 82.05 H 8.24 N 4.40
Found C 82.04 H 8.20 N 4.56

4-[2.2]Paracyclophanyl (1',3',3'-Trimethylindolin-2'-ylidenemethyl) Ketone [(*E*/*Z*) mixture] (**11**): 2.31 g (9.18 mmol) of [2.2]paracyclophane-4-carboxylic acid[13] (**6**) is converted into the corresponding acid chloride by treatment with 1.92 g (9.22 mmol) of phosphorous pentachloride. The raw intermediate (2.23 g, 90%) is dissolved in 50 ml of dichloromethane, and within 5 min a solution of 3 ml (3.06 g, 17.6 mmol) of 1,3,3-trimethyl-2-methyleneindolin (the so-called Fischer base) in 12 ml of dichloromethane is added at room temp. under N_2. After stirring for 2 h at room temp., water (20 ml) is added, the organic phase is separated, washed several times with water, and dried with magnesium sulfate. The solvent is removed in vacuo, and the remaining residue chromatographed on silica gel (dichloromethane) and recrystallized from acetone yielding 2.41 g (72%) of **11** as yellow plates, m.p. 178.5°C. – ^{1}H NMR [400 MHz, (*E*/*Z*) mixture]: δ = 7.30–6.47 (m), 5.56 (s), 5.48 (s), 3.98 to

3.91 (m), 3.86–3.79 (m), 3.67 (s), 3.17 (s), 3.17–2.58 (m), 1.92–1.91 (d), 1.41–1.40 (d). – ^{13}C NMR [100 MHz, signals of main isomer (83%) only]: δ = 189.71, 170.98, 143.64, 143.30, 140.21, 139.84, 139.46, 139.25, 138.85 (9 s), 135.61, 134.17, 132.59, 132.55, 132.39, 132.29, 131.72, 127.42, 121.96, 121.89, 107.32, 95.95 (12 d), 48.07 (s), 35.59, 35.55, 35.37, 35.24 (4 t), 29.63, 24.04, 23.28 (3 q). – IR: $\tilde{\nu}$ = 2950 cm^{-1} (m), 2925 (s), 2850 (m), 1630 (s), 1615 (m), 1540 (s), 1490 (m), 1300 (s), 1130 (s), 805 (vs), 745 (vs). – UV (ethanol): λ_{max} (lgε) = 381 nm (4.47), 301 (3.64, sh), 294 (3.67, sh), 268 (3.86, sh), 234 (4.23, sh), 216 (4.39, sh). – MS (70 eV): *m/z* (%) = 407 (92) [M$^+$], 303 (42), 158 (100), 104 (12).

$C_{29}H_{29}NO$ (407.56) Calcd. C 85.47 H 7.17 N 3.44
Found C 85.74 H 7.36 N 3.48

[2.2]Paracyclophane-4-carbaldehyde p-Nitrophenylhydrazone (**12**): 2 ml of conc. sulfuric acid is added to 0.35 g (2.29 mmol) of p-nitrophenylhydrazine, and the still warm solution is diluted with 3 ml of water. To this solution 0.50 g (2.12 mmol) of [2.2]paracyclophane-4-carbaldehyde[23] in 30 ml of ethanol is added, and the reaction mixture is briefly heated at reflux. After 16 h at room temp. shiny, orange-red crystals have precipitated, which are removed by filtration, washed with water and ethanol, and dried yielding 0.70 g (89%) of **12**, m.p. 210–211°C. – ^{1}H NMR (400 MHz): δ = 11.37 (s, 1H), 8.27 (d, *J* = 9.3 Hz, 2H), 8.17 (s, 1H), 7.27 (d, *J* = 9.3 Hz, 2H), 6.95 (d, *J* ⩾ 1.6 Hz, 1H), 6.69–6.51 (m, 11H), 3.82–3.74 (m, 1H), 3.31–2.95 (m, 7H). – ^{13}C NMR (100 MHz): δ = 150.23 (s), 141.66 (d), 139.39, 138.60, 138.35, 138.00, 137.70 (5 s), 134.88 (d), 133.87 (s), 132.66, 132.37, 131.24, 131.20, 129.96, 125.83, 110.62 (7 d), 34.28, 34.00, 33.81, 33.12 (4 t). – IR: $\tilde{\nu}$ = 3255 cm^{-1} (m), 2920 (w), 1600 (vs), 1320 (vs), 1275 (s), 835 (m). – UV (ethanol): λ_{max} (lgε) = 417 nm (4.56), 335 (3.77, sh), 301 (3.80), 237 (4.18, sh), 219 (4.40, sh). – MS (70 eV): *m/z* (%) = 371 (22) [M$^+$], 266 (23), 130 (100), 104 (26).

$C_{23}H_{21}N_3O_2$ (371.44) Calcd. C 74.37 H 5.70 N 11.31
Found C 74.04 H 5.67 N 11.17

4-Methylamino-[2.2]paracyclophane (**14**): [2.2]Paracyclophane-4-carboxylic acid[13] (**6**) (4.14 g, 16.4 mmol), dissolved in 50 ml of dry benzene, is converted into the corresponding isocyanate according to a literature procedure[13]. The solution is added to a cooled suspension (0°C) of 0.66 g (17.4 mmol) of lithium aluminium hydride in 25 ml of absolute ether, the reaction mixture is warmed to room temp. and finally heated at reflux for 2 h. Excess hydride is destroyed by the careful addition of water, and after heating the mixture for 30 min with 30% aqueous sodium hydroxide solution, the phases are separated. The aqueous layer is washed several times with toluene, and the combined organic layers are dried with magnesium sulfate. Removal of the solvent provides 3.80 g of a brown raw product which is recrystallized from methanol/water (9:1) yielding 3.51 g (90%) of **14**, as brown needles, m.p. 119–120°C. – ^{1}H NMR (400 MHz): δ = 6.87–6.06 (m, 6H), 5.29 (s, 1H), 3.10–2.87 (m, 8H), 2.72 (s, 3H), 2.70–2.61 (m, 1H). – ^{13}C NMR (100 MHz): δ = 147.48, 141.37, 138.85, 138.73 (4 s), 134.67, 133.27, 132.43, 130.80, 127.10 (5 d), 123.74 (s), 120.99 (d), 116.10 (d), 35.32, 35.26, 32.87, 32.51 (4 t), 30.05 (q). – IR: $\tilde{\nu}$ = 3325 cm^{-1} (w), 2920 (m), 1595 (vs), 1570 (s), 1510 (s), 1415 (s), 850 (m), 795 (m), 720 (s). – UV (ethanol): λ_{max} (lgε) = 326 nm (3.13), 282 (3.61). – MS (70 eV): *m/z* (%) = 237 (26) [M$^+$], 133 (100), 104 (22).

$C_{17}H_{19}N$ (237.35) Calcd. C 86.03 H 8.07 N 5.90
Found C 85.87 H 8.16 N 5.90

N-Methyl-N-nitroso-[2.2]paracyclophan-4-amine (**16**): 1.00 g (4.20 mmol) 4-methylamino-[2.2]paracyclophane (**14**) is dissolved in 10 ml of glacial acetic acid and treated with a solution of 0.30 g (4.35 mmol) of sodium nitrite in 5 ml of water at room temp. After stirring for 19 h, the precipitate is removed by filtration and recrystallized from methanol/water (1:1) yielding 1.01 g (89%) of **16** as green-brown microcrystals, m.p. 120°C. – ^{1}H NMR (400 MHz): δ = 6.64–6.49 (m, 7H), 3.39 (s, 3H), 3.38–2.88 (m, 8H). – ^{13}C NMR (100 MHz): δ = 141.79, 141.54, 139.26, 139.05 (4 s), 136.54, 133.59, 132.88, 132.87 (4 d), 132.58 (s), 132.48, 130.61, 125.90 (3 d), 36.24 (q), 35.32, 34.98, 34.96, 33.12 (4 t). – IR: $\tilde{\nu}$ = 2935 cm^{-1} (m), 1465 (m), 1435 (s), 1425 (vs), 1200 (s), 1075 (m). – UV (ethanol): λ_{max} (lgε) = 355 nm (2.62, sh), 2.83 (3.71), 224 (4.33). – MS (70 eV): *m/z* (%) = 266 (2) [M$^+$], 236 (100), 221 (20), 132 (78), 105 (80).

$C_{17}H_{18}N_2O$ (266.34) Calcd. C 76.66 H 6.81 N 10.53
Found C 76.76 H 6.92 N 10.53

6,9-Diisopropyl-[2.2](1,4)phenanthrenoparacyclophane (**19**): A solution of 0.66 g (1.70 mmol) of 4-(2,5-diisopropylstyryl)-[2.2]paracyclophane[18], 0.17 g (0.67 mmol) of iodine, and 0.4 ml of biacetyl in 240 ml of absolute toluene is placed into an all-quartz photoreactor equipped with a Hanau TQ 150 high-pressure mercury source. The reaction mixture is irradiated for 75 min while dry N_2 is passed through a low-lying frit. The excess iodine is reduced by sodium bisulfite treatment, the organic phase is separated, washed carefully with water, and dried with magnesium sulfate. The toluene is removed by rotatory evaporation, and the remaining yellow oil is subjected to preparative thick-layer chromatography (silica gel, CCl_4) providing a main fraction which is purified a second time using cyclohexane as the eluent yielding 0.31 g (0.79 mmol, 47%) of **19** as a colorless oil which soon solidifies. An analytically pure sample is obtained by recrystallization from ethanol as colorless plates, m.p. 115–118°C. – ^{1}H NMR (400 MHz): δ = 8.00 (d, *J* = 9.2 Hz, 1H), 7.53 (d, *J* = 9.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.99 (d, *J* = 7.8 Hz, 1H), 5.13 (d, *J* = 7.8 Hz, 1H), 4.22 (sept, *J* = 6.7 Hz, 1H), 3.82 (m, 1H), 3.81 (m, 1H), 3.52 (m, 1H), 3.35 (m, 1H), 3.22 (m, 1H), 3.04 (m, 1H), 2.99 (m, 1H), 2.74 (m, 1H), 2.59 (m, 1H), 1.60 (d, *J* = 6.8 Hz, 3H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.46 (d, *J* = 6.7 Hz, 3H), 0.47 (d, *J* = 6.6 Hz, 3H). – ^{13}C NMR (100 MHz): δ = 144.68, 141.39, 139.17, 138.51, 138.29, 135.06, 133.85, 130.41, 130.26, 129.00 (10 s), 132.89, 132.29, 130.84, 130.68, 128.43, 127.35, 123.25, 122.28, 122.23, 121.15 (10 d), 30.83, 28.60 (2 d), 36.01, 35.19, 34.76, 33.91 (4 t), 27.42, 24.30, 23.52, 21.32 (4 q). – IR: $\tilde{\nu}$ = 3040 cm^{-1} (w), 3010 (w), 2960 (m), 2920 (m), 1460 (m), 1380 (m), 1360 (m), 930 (m), 860 (m), 830 (s), 795 (s), 720 (m). – UV (acetonitrile): λ_{max} (lgε) = 333 nm (4.01), 318 (4.04), 284 (4.43), 218 (sh, 4.48), 207 (4.65). – MS (70 eV): *m/z* (%) = 392 (34) [M$^+$], 288 (100), 273 (93), 258 (20), 245 (57), 203 (49).

$C_{30}H_{32}$ (392.62) Calcd. C 91.77 H 8.23 Found C 91.76 H 8.13

CAS Registry Numbers

(±)-**1**: 123535-91-1 / (+)-**1**: 33483-69-1 / (−)-**1**: 24351-81-3 / (±)-**1** (R=H): 1633-22-3 / (±)-**1** (R=CHO): 36325-27-6 / (±)-**1** (R=NCO): 123439-18-9 / (±)-**1** [R = 2,5-(*i*Pr)$_2$C$_6$H$_3$CH=CH]: 123439-19-0 / (±)-**2**: 123439-05-4 / (+)-**2**: 123439-21-4 / (−)-**2**: 123439-34-9 / (±)-**3**: 123439-06-5 / (+)-**3**: 123439-22-5 / (−)-**3**: 123439-35-0 / (±)-**4**: 123493-07-6 / (+)-**4**: 123439-23-6 / (−)-**4**: 123439-36-1 / (±)-**5**: 78655-73-9 / (+)-**5**: 37503-80-3 / (−)-**5**: 37503-79-0 / (±)-**6**: 20586-49-6 / (+)-**6**: 19776-83-1 / (−)-**6**: 108340-94-9 / (±)-**7**: 123439-08-7 / (+)-**7**: 123439-24-7 / (−)-**7**: 123439-37-2 / (±)-**8**: 123535-92-2 / (+)-**8**: 24351-80-2 / (−)-**8**: 108235-40-1 / (±)-**9**: 123535-93-3 / (+)-**9**: 37503-93-8 / (−)-**9**: 36325-28-7 / (±)-**10**: 123439-09-8 / (+)-**10**: 123439-25-8 / (−)-**10**: 123439-38-3 / (±)-(*E*)-**11**: 123439-10-1 / (±)-(*Z*)-**11**: 123439-20-3 / (+)-(*E*)-**11**: 123439-26-9 / (+)-(*Z*)-**11**: 123439-46-3 / (−)-(*E*)-**11**: 123439-39-1 / (−)-(*Z*)-**11**: 123439-47-4 / (±)-**12**: 123439-11-2 / (+)-**12**: 123439-27-0 / (−)-**12**: 123439-40-7 / (±)-**13**: 123439-12-3 / (+)-**13**: 123439-

28-1 / (−)-**13**: 123439-41-8 / (±)-**14**: 123439-13-4 / (+)-**14**: 123439-29-2 / (−)-**14**: 123439-42-9 / (±)-**15**: 123439-14-5 / (+)-**15**: 123439-30-5 / (−)-**15**: 123463-17-2 / (±)-**16**: 123439-15-6 / (+)-**16**: 123439-31-6 / (−)-**16**: 123439-43-0 / (±)-**17**: 123535-94-4 / (+)-**17**: 123535-98-8 / (−)-**17**: 123537-28-0 / (±)-**18**: 123439-16-7 / (+)-**18**: 123439-32-7 / (−)-**18**: 123439-44-1 / (±)-**19**: 123439-17-8 / (+)-**19**: 123439-33-8 / (−)-**19**: 123439-45-2 / (±)-**20**: 123535-95-5 / (+)-**20**: 123535-99-9 / (−)-**20**: 123536-02-7 / (±)-**21**: 123535-96-6 / (+)-**21**: 123536-00-5 / (−)-**21**: 123536-03-8 / (±)-**22**: 123535-97-7 / (+)-**22**: 123536-01-6 / (−)-**22**: 123536-04-9 / CDMPC: 103938-44-9 / ADMPC: 112049-40-8 / Et_2NCOCl: 88-10-8 / $(Ac)_2$: 431-03-8 / *p*-$O_2NC_6H_4NHNH_2$: 100-16-3 / 1,3,3-trimethyl-2-methyleneindoline: 118-12-7

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