Cyclophanes, XLVII[‡]

Novel Synthesis of Phenanthrenoparacyclophanes and Phenanthrenophanes and a Study of Their NMR Properties

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Keywords: Cyclophanes / Cycloadditions / Dehydrobenzene / NMR spectroscopy / Condensed aromatics

Reactions of 4-ethenyl[2.2]paracyclophane (**3**) and its derivatives or of 4-ethynyl[2.2]paracyclophane (**27**) with benzyne (**4**) afforded [2.2](1,4)phenanthrenoparacyclophanes **2**, **7**, and **9**. The diethenyl[2.2]paracyclophanes **16**, **19** and **22** reacted with **4** to give the stereoisomeric phenanthrenophanes **18**, **21** and **23**, respectively. The NMR spectra, in particular the ^{1}H chemical shifts, of the diethenylparacyclophanes, the [2.2]phenanthrenoparacyclophanes and the [2.2]phenanthrenophanes are discussed.

Introduction

[2.2]Paracyclophanes containing condensed polycyclic aromatic subunits are an interesting class of compounds from the point of view of their stereochemical and electronic properties. They also serve as precursors for the synthesis of novel compounds exhibiting interesting topologies.[2] The syntheses of phanes having one or more condensed polycyclic aromatic subunits generally involve multiple steps, often resulting in overall low yields of the desired product.[3−7] The simple photocyclization reaction of styryl[2.2]paracyclophane to form the parent phenanthrenoparacyclophane is an exception[8] (see below). Herein we report a simple and elegant method for the preparation of phenanthreno[2.2]paracyclophanes and the various stereoisomers of phenanthrenophanes based on the well-known cycloaddition reaction of benzyne with styrene and phenylacetylene to yield phenanthrene.[9] The present method allows the synthesis of phenanthreno[2.2]paracyclophanes that are substituted in positions 4 and 5 and the selective synthesis of the various stereoisomers of phenanthrenophanes from readily available ethenyl- and diethenyl[2.2]paracyclophane derivatives. We also present a systematic ^{1}H and ^{13}C NMR spectroscopic investigation of these molecules from the point of view of structural and stereochemical assignments of the various isomeric phenanthrenophanes.

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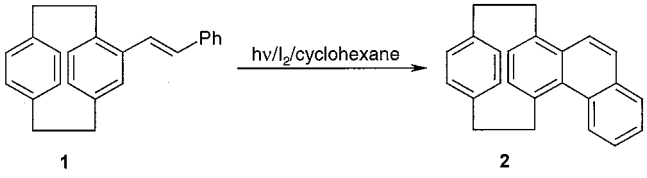
Results and Discussion

Reactions of Monoethenyl[2.2]paracyclophane Derivatives with Benzyne (4)

Some time ago, we described the preparation of [2.2](1,4)phenanthrenoparacyclophane (**2**)[8] by the photocyclization of 4-[(*E*)-2-phenyl-1-ethenyl][2.2]paracyclophane (**1**) (Scheme 1).



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Scheme 1. Photocyclization of styrylphanes to phenanthrenophanes

The same product should also be obtainable by the [4+2]cycloaddition of the readily available 4-ethenyl[2.2]paracyclophane (**3**)[10] with benzyne (**4**)[11,12] and, indeed, when this reaction is carried out in refluxing acetonitrile the expected [2.2](1,4)phenanthrenoparacyclophane (**2**) is produced as shown by comparison of its spectral data with those reported,[8] the yield amounting to a satisfactory 50%. The formation of **2** could occur by a primary cycloaddition process to give the intermediate adduct **5** followed by dehydrogenation (Scheme 2).

Analogously, an (*E*,*Z*) mixture of 4-(1-propenyl)[2.2]paracyclophane (**6**)[10,13] reacted with **4** and yielded 5-methyl-[2.2](1,4)phenanthrenoparacyclophane (**7**). Interestingly, the reaction of 4-(2-propenyl)[2.2]paracyclophane (**8**)[10,13] with **4** gave not only the expected 4-methyl[2.2](1,4)-phenanthrenoparacyclophane (**9**, 40%) but also the olefins **11** (31%) and **12** (20%) after separation and recrystalliza-

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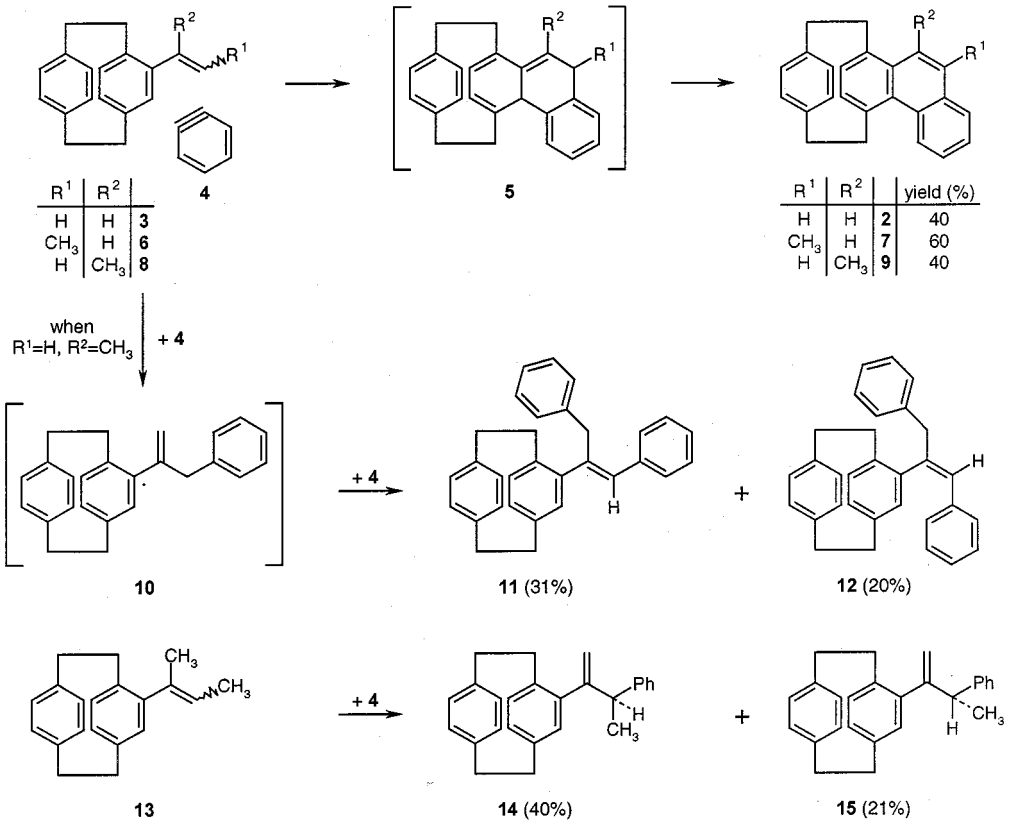


Scheme 2. Cycloaddition of dehydrobenzene (**4**) to different 4-vinyl[2.2]paracyclophanes

tion.[14] Cyclophanes **7** and **9** are probably formed from their respective olefinic precursors by the same mechanism by which **2** is produced from **3** (Scheme 2). The structures of these phenanthrene derivatives follow from a comparison of their NMR spectra with those of the parent compound **2**. The lack of the typical $J_{4,5}$ coupling of 9 Hz in the ^{1}H NMR spectra shows that both compounds carry the substituent on the central phenanthrene ring. While the ^{13}C chemical shift of the methyl group in **7** ($\delta = 20.3$) is comparable to that in 1-methylnaphthalene ($\delta = 19.2 \pm 0.1$),[15a] the methyl carbon atom in **9** ($\delta = 24.6$) is substantially deshielded due to the interaction with the *peri*-methylene group. Such *peri*-deshielding is known from 1,8-dimethylnaphthalene ($\delta = 25.8 \pm 0.2$).[15b] Likewise, the methylene carbon atom is deshielded itself: The ^{13}C NMR spectrum of **9** shows two methylene ^{13}C signals at $\delta \approx 39$ whereas there is only one deshielded CH_2 resonance signal for C-13 in the spectrum of **2**. Hence, **7** and **9** are the 5-methyl and 4-methyl derivatives of **2**, respectively.

The geometrical isomers **11** and **12** were distinguished by the chemical shifts of their benzylic carbon atoms and by ^{1}H{^{1}H} nuclear Overhauser effects. While the CH_2 carbon atom of the benzyl group at the (*E*)-configured double bond in **11** is shielded ($\delta = 39.2$) by the *cis*-interaction with the phenyl substituent, there is no such interaction in the (*Z*) isomer **12** and the corresponding ^{13}C shift is increased to $\delta = 44.2$, [cf. the methyl carbon atom shielding in (*Z*)-1-phenylpropene ($\delta = 14.6$)[15c] and its (*E*) isomer ($\delta = 18.4$)].[16] Saturation of the signal of 5-H, the proton *ortho* to the substituent in the cyclophane moiety, causes an enhancement of the β-proton resonance signal of the ethenyl group in **11** and of the *ortho*-proton signal of the phenyl group in **12**. There is also an NOE between the olefinic proton in **11** and the pseudo-*gem* and pseudo-*ortho* protons, which would not be expected for **12**. A plausible mechanism for the formation of **11** and **12** involves consecutive ene addition steps, via the primary product **10**, with two equivalents of **4** (Scheme 2).[14]

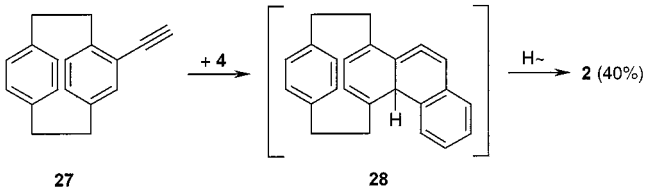
Surprisingly, treatment of 4-[(*E*,*Z*)-1-methyl-1-propenyl]-[2.2]paracyclophane (**13**)[10,13] with **4** did not give the expected 4,5-dimethyl derivative of **2**, but ene addition took place to give the two diastereomeric 4-[1-(1-phenylethyl)-ethenyl][2.2]paracyclophanes **14** (40%) and **15** (20%, Scheme 2). If formed at all, the [2+4]cycloadduct can only be of minor importance among the unidentified side-products. To the best of our knowledge, the analogous reaction of **4** with (1-methyl-1-propenyl)benzene or one of its derivatives has not been reported. The ^{13}C NMR chemical shifts of **14** and **15** are very similar. Only 4 out of 24 signal pairs show a difference larger than 0.5 ppm: Those for =C< (1.5 ppm), $=CH_2$ (1.4 ppm), Ph-C-2 (0.8 ppm), and CH_3 (0.9 ppm). The corresponding carbon nuclei are in the vicinity of the chiral center, one or two bonds away. This is a strong indication that the compounds are diastereomers and not constitutional isomers. Furthermore, the H,H-COSY spectra of *both* compounds show benzylic long-range coupling between 2-H of the phenyl group and the tertiary proton next to the CH_3 group. Hence **14** and **15**

are diastereomeric 4-[(1-phenylethyl)ethenyl][2.2]paracyclophanes.

Reactions of Diethenyl[2.2]paracyclophanes with 4

In addition to the reaction of **4** with monoethenyl derivatives of [2.2]paracyclophane we investigated its reaction with various *ar,ar′*-diethenyl derivatives. The pseudo-*para*-4,12-diethenyl[2.2]paracyclophane (**16**)[10,13,17] reacted with **4** to give 40% of *anti*-16-ethenyl[2.2](1,4)phenanthrenoparacyclophane (**17**) and 25% of pseudo-*para*-[2.2](1,4)phenanthrenophane (**18**). The yield of **18** is improved to 60% by increasing the amount of benzyne. The fact that **17** is indeed an intermediate en route to **18** was shown by an independent experiment in which the former was treated with additional **4** (Scheme 3) to yield the doubly annelated cyclophane.

pseudo-*meta*-4,13-Diethenyl[2.2]paracyclophane (**19**), prepared as described for **16** by a Wittig reaction of pseudo-*meta*-4,13-diformyl[2.2]paracyclophane[10,13] with methyltriphenylphosphonium bromide, was also treated with **4** and furnished 42% of *anti*-17-ethenyl[2.2](1,4)phenanthrenoparacyclophane (**20**) together with 27% of pseudo-*meta*-[2.2](1,4)(4,1)phenanthrenophane (**21**). Reaction of **19** with excess **4** gave **21** directly in 62% yield (Scheme 4). In the same manner, **20** reacted with **4** to give **21**.

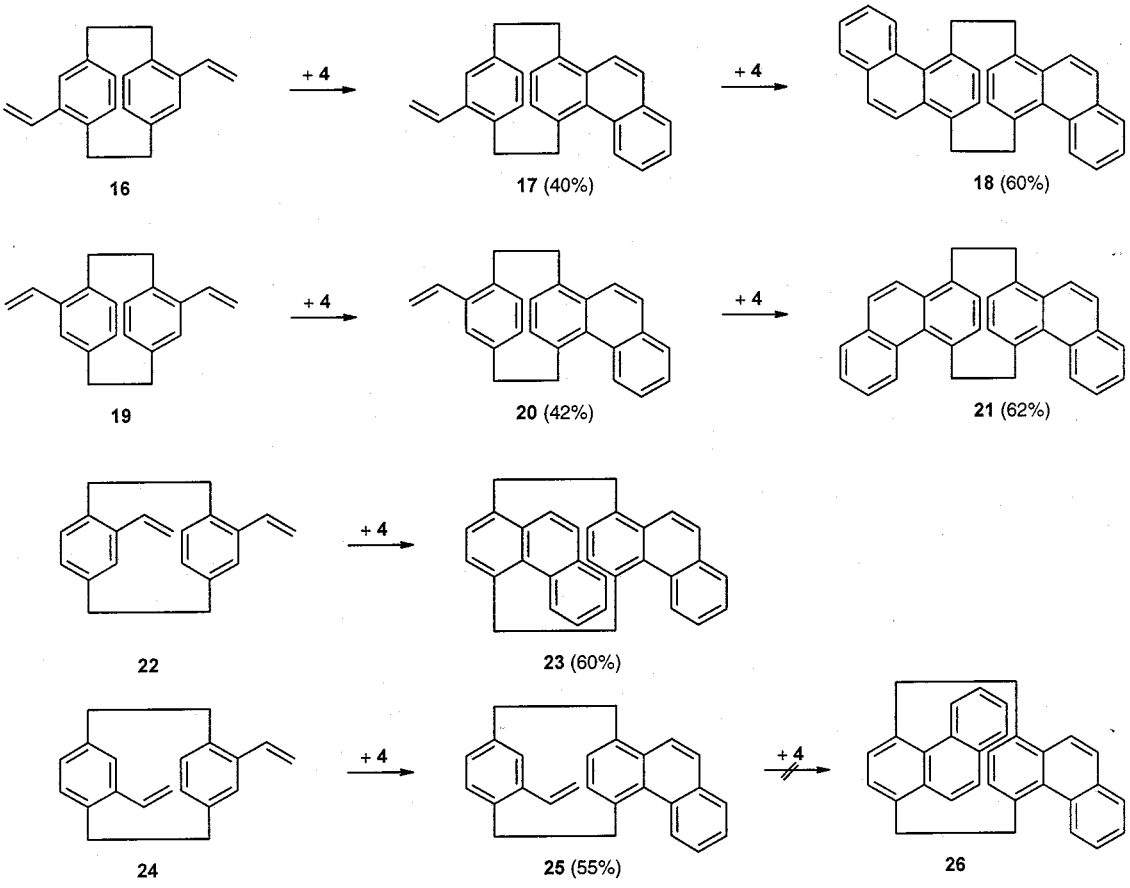


27 28

Scheme 4. Cycloaddition of dehydrobenzene (**4**) to 4-ethynyl[2.2]-paracyclophane (**27**)

The reaction of pseudo-*gem*-4,13-diethenyl[2.2]paracyclophane (**22**)[19] with **4** furnished pseudo-*gem*-[2.2](1,4)(4,1)phenanthrenophane (**23**) in 60% yield. For steric reasons and because of the favorable orientation of the two ethenyl groups, it had been assumed so far that under ''normal'' conditions (exposure to sunlight or heating), **22** would prefer to undergo an intramolecular [2+2]cycloaddition rather than any other reaction.[13,19] Owing to the very high reactivity of **4** this proved not to be true in the present case.

Unfortunately, the reaction of pseudo-*ortho*-4,12-diethenyl[2.2]paracyclophane (**24**)[19] with **4** gave only *syn*-16-ethenyl[2.2](1,4)phenanthrenoparacyclophane (**25**). Attempts to obtain the corresponding pseudo-*ortho*-



Scheme 3. Cycloaddition of dehydrobenzene (**4**) to various divinyl[2.2]paracyclophanes

[2.2](1,4)phenanthrenophane (**26**) either by treating **25** with **4** or by treating **24** with an excess of **4** failed. In conclusion, we have synthesized the pseudo-*gem* (**23**) and pseudo-*meta* (**21**) isomers of [2.2](1,4)(4,1)phenanthrenophane and the pseudo-*para* isomer (**18**) of [2.2](1,4)phenanthrenophane for the first time and have improved the synthesis of [2.2](1,4)phenanthrenoparacyclophane (**2**) by transforming styrene into phenanthrene subunits by means of [2+4]cycloadditions with **4**. 4-Ethynyl[2.2]paracyclophane (**27**) also reacted with benzyne (**4**) to afford **2** in 40% yield. In this case, the formation of **2** can also be rationalized by postulating a concerted mechanism that initially provides the isobenzene intermediate **28** which is aromatized to **2** by a hydrogen shift (Scheme 4).[20]

NMR Studies of the Ethenyl- and Phenanthrenophanes

(a) Diethenyl[2.2]paracyclophane Substrates 16, 19, 22 and 24

The diethenyl compounds used as starting materials have not been characterized previously by NMR spectroscopy, and hence complete assignments of their ^{1}H and ^{13}C NMR spectra were attempted. A comparison of the results for the four isomers (see Experimental Section) allows us to draw some qualitative conclusions as to the substituent effects of a single ethenyl group on the chemical shifts in [2.2]paracyclophane. The introduction of an ethenyl group at the 4-position causes deshielding of the *ortho* (ca. 0.1 ppm) and pseudo-*geminal* (ca. 0.2 ppm) protons and of the *syn* proton (ca. 0.4 ppm) at the *ortho*-methylene carbon atom C-2. It causes shielding of the *anti*-proton (ca. −0.3 ppm) in the same methylene group and also of the *syn*-proton (ca. −0.2 ppm) at C-1 and of the pseudo-*ortho* proton (−0.1 to −0.2 ppm). The major effects on the ^{13}C shifts are shielding of the *ortho* (−2 to −4 ppm), *para* (ca. −2 ppm), pseudo-*geminal* (ca. −2 ppm) and *ortho*-methylene (ca. −3 ppm) carbon atoms and deshielding of the *ipso*-carbon atom (ca. 5 ppm). The multiplet patterns in the ^{1}H NMR spectra of the methylene bridges reflect the molecular symmetries.[21] The pseudo-*ortho* compound **24** and the pseudo-*para* compound **16** have two equivalent bridges, each containing four chemically nonequivalent protons, hence they give one AKRX spectrum. In the pseudo-*meta* derivative **19** and in the pseudo-*geminal* analogue **22**, the bridges are in different environments but each bridge is symmetrical and has two sets of two chemically equivalent but magnetically nonequivalent protons. Compounds **19** and **22** therefore each give two different AA′XX′ spectra for the bridge hydrogen atoms.

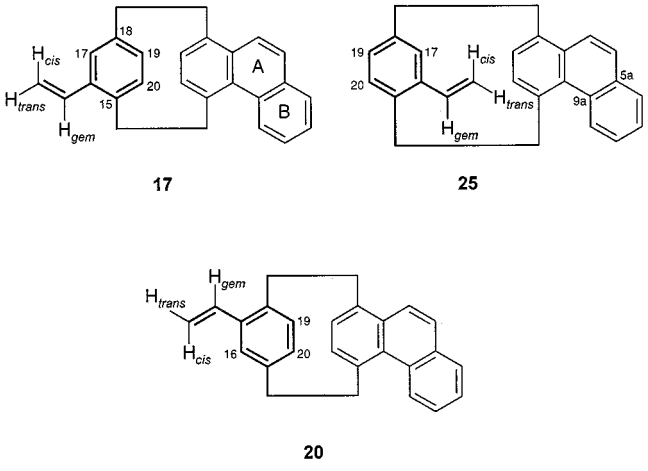
(b) Ethenyl[2.2](1,4)phenanthrenoparacyclophanes 17, 20 and 25

The structures of the isomeric ethenyl[2.2](1,4)phenanthrenoparacyclophanes **17**, **20** and **25** are confirmed by the chemical shifts of the vinyl protons and of the protons of the aromatic ring bearing the ethenyl group (see Table 1).

Table 1. ^{1}H chemical shifts of the ethenyl-substituted *para*-phenylene subunit in the ethenyl[2.2]phenanthrenoparacyclophanes **17**, **20** and **25**

	17	**20**	**25**	δ(**17**) − δ(**25**)
16-H	–	6.66	–	–
17-H	6.61	–	6.05	+0.56
19-H	5.85	5.81	6.59	−0.74
20-H	5.11	5.21	6.59	−1.48
H_{gem}	6.77	6.87	5.70	+1.07
H_{cis}	5.58	5.61	4.52	+1.06
H_{trans}	5.28	5.32	4.17	+1.11

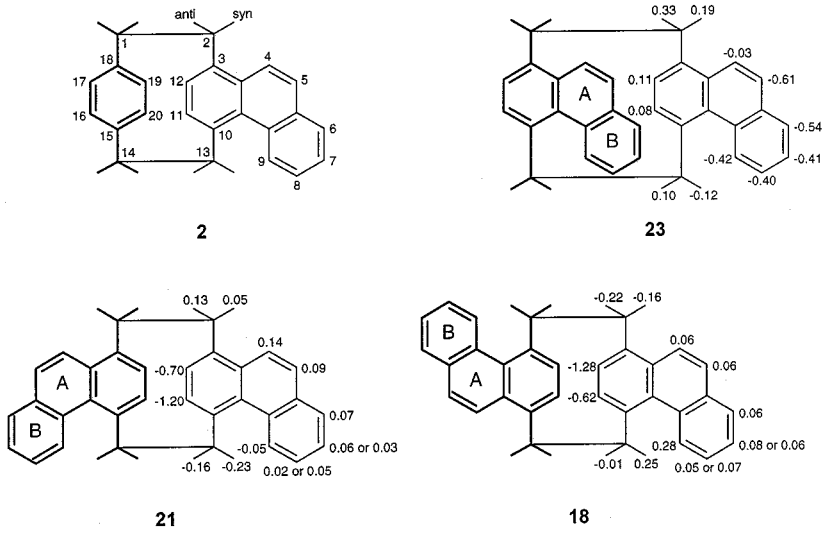
In compounds **17** and **20**, in which the phenanthrene system and the ethenyl group are *anti* to each other, protons 19-H and 20-H on the phenylene ring are strongly shielded by the ring current(s) of phenanthrene rings A and B (Scheme 5).



17 **25** **20**

Scheme 5. Orientation of the ethenyl protons with respect to phenanthrene rings A and B in **17**, **20**, and **25**

In the *syn* compound **25** the ethenyl group experiences heavy shielding. It is interesting to compare the chemical shifts of compounds **17** and **25**, which may be thought of as rotational isomers with respect to the C-15−C-18 axis. If one assumes that the influence of the ring currents of the central (A) and terminal (B) phenanthrene rings on the *anti* side of the ''upper'' phenylene ring is negligible, then the shift differences between constitutionally equivalent nuclei in **17** and **25** (rightmost column in Table 1) are a measure of the shielding caused by the combined ring currents of rings A and B. The difference between 19-H and 20-H is due to the extra shielding of 20-H by the outer ring B. The shielding effect of rings A and B on the three vinylic protons is almost identical, which may seem surprising at first. Yet a projection of the vinyl group onto the phenanthrene moiety in **25** (under the simplifying assumption of equal C−C bond lengths and 120° bond angles) shows that the olefinic double bond is superimposed on the C-5a−C-9a bond common to rings A and B, so that the three vinylic protons are in equivalent positions relative to the center of this bond. Thus, they should indeed experience approxim-



Scheme 6. ^{1}H chemical shift changes $\Delta\delta$ in **2** induced by formal addition of condensed aromatic rings A and B to give **23**, **21** and **18**; $\Delta\delta$ is defined, e.g., as δ(**23**) − δ(**2**)

ately the same combined shielding by the ring currents of A and B.

(c) [2.2]Phenanthrenophanes 18, 21 and 23

Similar to the diethenyl[2.2]paracyclophanes discussed above, the molecular symmetry of **18**, **21** and **23** is mirrored in the resonances of the bridge protons in the ^{1}H NMR spectra. The differences between the chemical shifts of the phenanthrenophanes **18**, **21**, and **23** on the one hand and of phenanthrenoparacyclophane **2** on the other are the shift changes induced in **2** by the three formal, geometrically different, additions of rings A and B (Scheme 6). Again, they demonstrate the ring-current effect of the naphthalenoid A−B unit.

In the pseudo-*geminal* phenanthrenophane **23**, relatively large effects (−0.40 to −0.61 ppm) are observed at the terminal and central rings of the lower phenanthrene deck. The effect at 4-H is, however, surprisingly small (−0.03 ppm). One may speculate that this could be due to an altering of the conformation along the C1−C2 bridge which might, by ensuing counteracting effects, cancel the expected shielding of 4-H. The differences in the vicinal H,H coupling constants between **2** and **23** do, indeed, indicate[8] conformational changes, although their exact nature is difficult to specify. In both *anti*-phenanthrenophanes **18** and **21**, the shift changes (relative to **2**) of the protons at the middle and outer phenanthrene ring are expectedly small, but they are substantial for 11-H and 12-H. Interestingly, the effect at 11-H in **21** is similar to that at 12-H in **18** and the effect at 12-H in **21** closely resembles that at 11-H in **18**. In both compounds, the proton closer to the terminal phenanthrene ring of the upper aromatic deck experiences the stronger ring current.

An interesting question with regard to the ^{1}H NMR spectra of the phenanthrenophanes is that of the additivity of the effects of twofold naphtho annelation. Comparison of the chemical shifts of [2.2](1,4)phenanthrenoparacyclophane (**2**) with those of [2.2]paracyclophane yields a set of shift increments which allow us to predict the ^{1}H chemical shifts of **18**, **21** and **23**, provided that these increments are additive. Table 2 contains the experimental ^{1}H shifts and those calculated from the increments $\Delta_i = \delta_i$(**2**) − δ_i([2.2]paracyclophane). It is evident that additivity is not observed perfectly. The average disagreement between experimental and predicted chemical shifts increases in the order **18** < **21** < **23**. This behavior can be rationalized by the expected strength of the mutual interaction between the two naphtho moieties added to [2.2]paracyclophane. This interaction is most unfavorable in the pseudo-*geminal* compound **23** where the naphtho systems are *syn* and eclipsed, less unfavorable in the pseudo-*meta* derivative **21** where they have an *anti* orientation and yet both point towards the same bridge and least unfavorable in the pseudo-*para* compound **18** where they are *anti* but pointing towards different bridges. Table 2 also shows that the deviations from additivity are most pronounced for the bridge protons which hints to conformational differences between the compounds compared.

Table 2. Comparison of experimental ^{1}H chemical shifts and those calculated from increments for the phenanthrenophanes **18**, **21** and **23** (see text for details)

	18			**21**			**23**		
	exp.	calcd.	diff.	exp.	calcd.	diff.	exp.	calcd.	diff.
δ_{2anti}	2.80	2.72	+0.08	3.15	2.93	+0.23	3.35	3.14	+0.21
δ_{2syn}	3.67	3.67	±0.00	3.88	3.94	−0.06	4.02	3.74	+0.28
δ_{11}	6.31	6.31	±0.00	5.73	5.69	+0.04	7.01	6.96	+0.05
δ_{12}	5.47	5.52	−0.05	6.05	6.13	−0.08	6.86	6.81	+0.05
δ_{13anti}	3.36	3.28	+0.08	3.21	3.07	+0.14	3.47	3.21	+0.26
δ_{13syn}	4.57	4.43	+0.14	4.09	4.16	−0.07	4.20	4.01	+0.19

Of the three isomeric phenanthrenophanes, only **23**, which has a pseudo-*geminal* orientation of its phenanthrene subunits, was available in sufficient amounts to permit a full assignment of the ^{13}C NMR spectrum by 2D methods. Inverse detection was not available. Comparison of the ^{13}C chemical shifts of **23** (see Experimental Section) with those

of phenanthrenoparacyclophane **2**[8] shows that formal addition of two aromatic rings to **2** causes a general shielding of all carbon nuclei (with the exception of C-5) of 0.5−2.0 ppm. As is usual in ^{13}C NMR spectroscopy,[22] one cannot decide whether this is due to steric and/or ring-current effects.

Experimental Section

Melting points are uncorrected. − MS: Finnigan MAT 8430 at 70 eV. − ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz): Bruker AM-400 with $CDCl_3$ as solvent, with tetramethylsilane (TMS) and $CDCl_3$ (δ = 77.05) as references for the ^1H and ^{13}C spectra, respectively. − NOE Difference Spectra: Saturation time 10 s, irradiation power level approximately 42 dB below 0.2 W (nominal). C,H-HETCOR:[23] Suppression of H,H couplings in the F_1 dimension,[24] relaxation delay 0.4 s, aromatic and aliphatic parts of the spectra recorded separately, polarization and refocussing delays both 3.125 ms for the aromatic region, 3.846 ms and 1.923 ms, respectively, for the CH_2 region. C,H-COLOC:[25] Relaxation delay 0.8 s, polarization and refocussing delays 30 and 37.5 ms, respectively. − Spectral analysis: Some non-first-order ^1H NMR spectra were analyzed iteratively with the program LCN387.[26] Rms errors between calculated and experimental line positions were normally well below 0.1 Hz and in a few cases (unresolved long-range couplings, occurrence of near-degenerate lines) 0.2−0.3 Hz. For some compounds, at the time of NMR analysis, there was not enough material at hand to obtain C,H-HETCOR and -COLOC spectra and inverse detection techniques were not available. In these cases, no assignments are given for the ^{13}C NMR spectra. − TLC: Silica gel PF_{254} plates (Merck), 20 cm × 48 cm, and on silica gel 7714 (Merck), respectively. Zones were detected by the quenching of indicator fluorescence upon exposure to 254 nm UV light. − FT-IR: Nicolet 320, as KBr pellets. − UV: Beckman UV 5230. − Elemental analyses: Microanalytical Laboratory of the Institute of Inorganic and Analytical Chemistry of the Technical University of Braunschweig. − Starting Materials: The starting materials were obtained as described before: **3**,[10,13] **6**,[10,13] **8**,[10,13] **16**,[13,19] **22**,[19] **24**,[19] **27**.[19]

pseudo-*meta*-4,13-Diethenyl[2.2]paracyclophane (19): To a suspension of methyltriphenylphosphonium bromide (13.0 g, 36.0 mmol) in 150 mL of anhydrous tetrahydrofuran, cooled to 0 °C, was added dropwise butyllithium in hexane (1.2 N, 32.4 g, 36.5 mmol). The mixture was stirred for 2 h at room temp., cooled to 0 °C again and a solution of pseudo-*meta*-4,13-diformyl[2.2]paracyclophane (2.5 g, 9.5 mmol) [27] in anhydrous tetrahydrofuran (20 mL) was added dropwise with stirring. Stirring was continued at room temp. for 18 h and then water (200 mL) was added. The organic layer was extracted with dichloromethane, washed several times with water and dried with anhydrous calcium chloride. The solvent was removed in vacuo and the residue purified by column chromatography using tetrachloromethane as the eluent. Compound **19** (2.2 g, 85%) was obtained as colorless crystals, m.p. 180 °C (from hexane). − IR (KBr): ν = 3100−3030 cm^{-1}, 2920−2850, 1590, 980, 770. − ^1H NMR: δ = 6.77 (dd, J = 17.5, 10.9 Hz, 2 H, vinyl-H_{gem}), 6.67 (d, J = 7.8 Hz, 2 H, 8-H), 6.61 (d, J = 1.8 Hz, 2 H, 5-H), 6.35 (dd, J = 7.8, 1.8 Hz, 2 H, 7-H), 5.55 (dd, J = 17.5, 1.3 Hz, 2 H, vinyl-H_{cis}), 5.27 (dd, J = 10.9, 1.3 Hz, 2 H, vinyl-H_{trans}), 3.38, 2.76 [AA′XX′, J_{gem} = −13.4, J_{trans} = 8.3 and 0, J_{cis} = 9.4 Hz, all ±0.4 Hz, 2 H each, 2-H_{syn} and 2-H_{anti} (rel. to the vinyl group), respectively], 3.09, 2.93 (AA′XX′, J_{gem} = −13.1, J_{trans} = 5.4 and 2.4, J_{cis} = 10.7 Hz, all ±0.1 Hz, 2 H each, 9-H_{anti} and 9-H_{syn}, respectively). − NOEs: saturating the 5-H signal caused positive NOEs for vinyl-H_{cis}, 9-H_{syn} and 7-H (= 16-H) and a negative NOE for vinyl-H_{trans}; saturation of the 8-H signal gave NOEs for 7-H and 2-H_{anti}. − ^{13}C NMR: δ = 139.59 (s, C-6), 138.17 (s, C-4), 137.74 (s, C-3), 134.97 (d, =CH), 131.11 (d, C-7), 130.79 (d, C-8), 129.59 (d, C-5), 114.14 (t, $=CH_2$), 35.00 (t, C-9), 32.83 (t, C-2). Assignments by C,H-HETCOR and -COLOC. − MS: m/z = 260 (80) [M^+], 244 (12), 131 (78), 130 (100), 128 (60), 127 (58), 115 (72), 104 (40), 50 (18), 43 (20). − $C_{20}H_{20}$ (260.4): calcd. C 92.26, H 7.74; found C 92.18, H 7.70.

pseudo-*para*-4,12-Diethenyl[2.2]paracyclophane (16): ^1H NMR: δ = 6.80 (dd, J = 17.5, 10.9 Hz, 2 H, vinyl-H_{gem}), 6.65 (br. d, J = 7.7 Hz, 2 H, 7-H), 6.54 (br. s, 2 H, 5-H), 6.31 (d, J = 7.7 Hz, 2 H, 8-H), 5.51 (br. d, J = 17.5 Hz, 2 H, vinyl-H_{cis}), 5.27 (br. d, J = 10.9 Hz, 2 H, vinyl-H_{trans}), 3.45 (ddd, J = −13.7, 10.3, 2.5 Hz, 2 H, 2-H_{syn}), 3.03 (ddd, J = −13.2, 10.7, 2.5 Hz, 2 H, 9-H_{syn}), 2.94 (ddd, J = −13.2, 10.3, 5.8 Hz, 2 H, 9-H_{anti}), 2.81 (ddd, J = −13.7, 10.7, 5.8 Hz, 2 H, 2-H_{anti}). − ^{13}C NMR: δ = 139.39 (s, C-6), 137.74 (s, C-4), 137.73 (s, C-3), 135.33 (d, =CH), 133.44 (d, C-8), 130.11 (d, C-5), 129.32 (d, C-7), 114.31 (t, $=CH_2$), 34.24 (t, C-9), 33.00 (t, C-2). Assignments by C,H-HETCOR and -COLOC.

pseudo-*gem*-4,13-Diethenyl[2.2]paracyclophane (22): ^1H NMR: δ = 6.82 (dd, J = 17.4, 10.9 Hz, 2 H, vinyl-H_{gem}), 6.59 (d, J = 1.6 Hz, 2 H, 5-H), 6.49 (d, J = 7.7 Hz, 2 H, 8-H), 6.46 (dd, J = 7.7, 1.6 Hz, 2 H, 7-H), 5.37 (dd, J = 17.4, 1.3 Hz, 2 H, vinyl-H_{cis}), 5.09 (dd, J = 10.9, 1.3 Hz, 2 H, vinyl-H_{trans}), 3.54, 2.97 (AA′XX′, $J_{gem} \approx -14$, $J_{trans} \approx 5$, both $J_{cis} \approx 10$ Hz, 2 H each, 2-H_{syn} and 2-H_{anti}, respectively), 3.05−3.04 (AA′BB′, 4 H, 9-H_{anti}, 9-H_{syn}). − ^{13}C NMR: δ = 139.39 (s, C-6), 138.12, 137.30 (both s, C-3, C-4), 135.55 (d, =CH), 134.64 (d, C-8), 132.47 (d, C-7), 129.84 (d, C-5), 114.68 (t, $=CH_2$), 35.09 (t, C-9), 32.53 (t, C-2). Assignments by C,H-HETCOR of the aromatic region.

pseudo-*ortho*-4,12-Diethenyl[2.2]paracyclophane (24): ^1H NMR: δ = 6.77 (br. s, 2 H, 5-H), 6.72 (dd, J = 17.5, 10.9 Hz, 2 H, vinyl-H_{gem}), 6.44 (s, 4 H, 7,8-H), 5.51 (br. d, J = 17.5 Hz, 2 H, vinyl-H_{cis}), 5.21 (br. d, J = 10.9 Hz, 2 H, vinyl-H_{trans}), 3.46 (dd, J = −13.6, 9.8 Hz, 2 H, 2-H_{syn}), 3.08 (dd, J = −13.1, 10.1 Hz, 2 H, 9-H_{anti}), 2.82 (ddd, J = −13.1, 9.8, 7.8 Hz, 2 H, 9-H_{syn}), 2.72 (ddd, J = −13.6, 10.1, 7.8 Hz, 2 H, 2-H_{anti}). − ^{13}C NMR: δ = 139.55 (s, C-6), 137.46, 137.19 (both s, C-3,4), 134.87, 134.44 (both d, =CH, C-8), 131.90 (d, C-7), 126.70 (d, C-5), 113.89 (t, $=CH_2$), 34.09, 33.82 (both t, C-2,9).

[2.2](1,4)Phenanthrenoparacylophane (2). − General Procedure: A solution of anthranilic acid (1.10 g, 8.00 mmol) in dry acetonitrile (20 mL) and a solution of isopentyl nitrite (1.02 g, 8.00 mmol) in dry acetonitrile (20 mL) were added simultaneously from two addition funnels over 6 h to a refluxing solution of **3** or **27** (1.0 mmol) in dry acetonitrile (50 mL). The reaction mixture was heated at reflux for 24 h. The solvent was evaporated under vacuum and the residue was purified by chromatography on plates using cyclohexane as the eluent. Compound **2** was obtained as an oil which solidified upon addition of *n*-hexane. Yield of **2**: (0.31 g, 50%) when **3** was the starting material and (0.25 g, 40%) when **27** was used as starting material; colorless crystals (ethanol); m.p. 169 °C. − IR (KBr): ν = 3064−3009 cm^{-1}, 2989−2854. − ^1H and ^{13}C NMR ($CDCl_3$) are in agreement with ref.[8] − MS: m/z =308 (43) [M^+], 205 (76), 203 (100), 191 (68), 104 (40), 84 (90).

5-Methyl[2.2](1,4)phenanthrenoparacylophane (7): Compound **7** was obtained by the same procedure as described for **2** using **6** (0.50 g, 2.00 mmol), anthranilic acid (1.10 g, 8.00 mmol) and isopentyl ni-

trite (1.02 g, 8.00 mmol). The product was purified chromatographically, eluent: cyclohexane; 0.35 g (50%) **7**, colorless crystals (ethanol). − M. p. 145−147 °C. − IR (KBr): ν = 3017−3020 cm^{-1}, 2950−2860, 1585. − ^1H NMR: δ = 8.53 (m, 1 H, 9-H), 8.05 (m, 1 H, 6-H), 7.58 (m, 1 H, 7-H), 7.55 (m, 1 H, 8-H), 7.48 (br. s, 1 H, 4-H), 6.90 (d, *J* = 7.4 Hz, 1 H, 11-H), 6.74 (d, *J* = 7.4 Hz, 1 H, 12-H), 6.55 (dd, *J* = 8.1, 1.7 Hz, 1 H, 17-H), 6.54 (dd, *J* = 8.1, 1.6 Hz, 1 H, 16-H), 5.85 (dd, *J* = 7.8, 1.7 Hz, 1 H, 19-H), 5.24 (dd, *J* = 7.8, 1.6 Hz, 1 H, 20-H), 4.30 (ddd, *J* = −14.5, 8.5, 4.8 Hz, 1 H, 13-H_{syn}), 3.84 (m, 1 H, 2-H_{syn}), 3.38 (ddd, *J* = −14.5, 8.8, 6.3 Hz, 1 H, 13-H_{anti}), 3.21 (m, 1 H, 1-H_{anti}), 3.02 (m, 1 H, 2-H_{anti}), 3.01 (m, 1 H, 1-H_{syn}), 2.91 (ddd, *J* = −13.4, 8.8, 4.8 Hz, 1 H, 14-H_{anti}), 2.81 (d, *J* = 1.0 Hz, 3 H, 5-CH_3), 2.76 (ddd, *J* = −13.4, 8.5, 6.3 Hz, 1 H, 14-H_{syn}). Assignment by homonuclear decoupling; *syn* and *anti* are relative to the outer phenanthrene rings; 19,20-H are *syn*, 16,17-H are *anti*. − ^{13}C NMR: δ = 138.72, 137.86, 136.06, 135.98, 133.69, 132.39, 131.90, 131.35, 130.92 (all quaternary C), 133.50, 132.01, 131.83, 131.50, 128.99, 128.51, 128.30, 125.67, 125.04, 124.16, 124.07 (all CH), 38.46, 34.79, 34.51, 33.48 (all CH_2), 20.26 (CH_3). − MS: *m/z* = 322 (36) [M^+], 218 (74), 217 (100), 203 (78), 202 (40), 104 (6). − $C_{25}H_{22}$ (322.4): calcd. C 93.12, H 6.88; found C 93.00, H 6.88.

Reaction of 4-(2-Propenyl)[2.2]paracyclophane (8) with 4: Compound **8** was made to react with **4** by applying the same procedure and using the same molar ratios of reactants as in the reaction of **6** with **4**. Chromatography with cyclohexane as the eluent provided three bands. − *First band (R_f = 0.35, cyclohexane):* 4-Methyl[2.2]-(1,4)phenanthrenoparacyclophane (**9**, 0.26 g, 40%), colorless crystals (benzene); m.p. 165 °C. − IR (KBr): ν = 3008−2956 cm^{-1}, 2950−2860, 1580. − ^1H NMR: δ = 8.43 (m, 1 H, 9-H), 7.78 (m, 1 H, 6-H), 7.53 (br. s, 1 H, 5-H), ca. 7.49 (m, 1 H, 7-H), ca. 7.47 (m, 1 H, 8-H), 6.92 (d, *J* = 7.6 Hz, 1 H, 11-H), 6.79 (d, *J* = 7.6 Hz, 1 H, 12-H), 6.61 (dd, *J* = 7.9, 1.8 Hz, 1 H, 17-H), 6.58 (dd, *J* = 7.9, 1.8 Hz, 1 H, 16-H), 5.74 (dd, *J* = 7.8, 1.8 Hz, 1 H, 19-H), 5.34 (dd, *J* = 7.8, 1.8 Hz, 1 H, 20-H), 4.31 (ddd, not 1st order, 1 H, 13-H_{syn}), 4.07 (dd, *J* = −14.2, 8.7 Hz, 1 H, 2-H_{syn}), 3.47 (m, 1 H, 13-H_{anti}), 3.24 (dd, *J* = −12.9, 9.2 Hz, 1 H, 1-H_{anti}), 3.00 (dt, *J* = −14.2, 9.5, 9.2 Hz, 1 H, 2-H_{anti}), 2.90 (m, 2 H, 14-H_{anti}, 14-H_{syn}), 2.85 (s, 3 H, 4-CH_3), 2.76 (dt, *J* = −12.9, 9.5, 8.7 Hz, 1 H, 1-H_{syn}). Assignments by H,H-COSY and homonuclear decoupling. NOEs: Saturation of the CH_3 resonance enhanced signals of 2-H_{syn}, 5-H (both strongly) and 19-H (weakly); saturation of the 9-H multiplet enhanced the 13-H_{syn} resonance and, more weakly, the 8-H signal. − ^{13}C NMR: δ = 139.01, 138.33, 137.51, 136.41, 134.55, 134.42, 132.56, 131.99, 129.64 (all quaternary C), 135.20, 133.88, 131.86, 130.56, 129.49, 129.29, 128.98, 128.64, 127.18, 125.72, 124.56 (all CH), 39.29, 39.22, 35.75, 34.85 (all CH_2), 24.61 (CH_3). − MS: *m/z* = 322 (8) [M^+], 306 (60), 220 (30), 219 (100), 203 (34), 202 (28), 128 (12), 104 (10). − $C_{25}H_{22}$ (322.4): calcd. C 93.12, H 6.88; found C 92.95, H 6.84. − *Second band (R_f = 0.30, cyclohexane):* 4-[(*E*)-1-Benzyl-2-phenylethenyl][2.2]paracyclophane (**11**, 0.25 g, 31%), colorless crystals (cyclohexane); m.p. 135 °C. − IR (KBr): ν = 3048−3003 cm^{-1}, 2954−2849, 1599, 970. − ^1H NMR: δ = 7.41 (m, 2 H, Ph-2-H), 7.35 (m, 2 H, Ph-3-H), 7.26 (m, 1 H, Ph-4-H), 7.13 (m, 2 H, Bzl-3-H), 7.05 (m, 1 H, Bzl-4-H), 7.02 (m, 2 H, Bzl-2-H), 6.93 (br. s, 1 H, =CH), 6.67 (dd, *J* = 7.9, 1.9 Hz, 1 H, 15-H), 6.63 (dd, *J* = 7.8, 2.0 Hz, 1 H, 12-H), 6.60 (dd, *J* = 7.8, 1.9 Hz, 1 H, 13-H), 6.49 (d, *J* = 1.9 Hz, 1 H, 5-H), 6.40 (d, *J* = 7.7 Hz, 1 H, 8-H), 6.38 (dd, *J* = 7.9, 2.0 Hz, 1 H, 16-H), 6.35 (dd, *J* = 7.7, 1.9 Hz, 1 H, 7-H), 4.42 (d, *J* = 15.5 Hz, 1 H of CH_2Ph), 3.80 (d, *J* = 15.5 Hz, 1 H of CH_2Ph), 3.35 (ddd, not 1st order, 1 H, 2-H_{syn}), 3.10 (m, 1 H, 1-H_{syn}), 3.07 (m, 1 H, 2-H_{anti}), ca. 3.05 (m, 2 H, 10-H), 3.03 (m, 1 H, 9-H_{anti}), 2.94 (m, 1 H, 1-H_{anti}), 2.92 (m, 1 H, 9-H_{syn}); assignments derived from H,H-COSY. NOEs: Saturation of the 5-H signal caused enhancements of the =CH signal and (to a minor extent) of the 9-H_{syn} resonance and of the CH_2 signal at δ = 3.80; saturation of the =CH signal caused NOEs of the resonances of Ph-2-H, 5-H, 15-H and 16-H. − ^{13}C NMR: δ = 143.72 (s, C-4), 141.49 (s, =C<), 139.85 (s, Bzl-C-1), 139.65 (s, C-14), 139.44 (s, C-11), 139.18 (s, C-6), 137.88 (s, Ph-C-1), 136.66 (s, C-3), 135.54 (d, C-8), 133.13 (d, C-13), 132.56 (d, C-7), 132.51 (d, =CH), 132.20 (d, 2 C, C-12,16), 131.38 (d, C-5), 129.84 (d, C-15), 128.72 (d, 2 C, Ph-C-2), 128.46 (d, 2 C, Ph-C-3), 128.34 (d, 2 C, Bzl-C-2), 128.27 (d, 2 C, Bzl-C-3), 126.93 (d, Ph-C-4), 125.80 (d, Bzl-C-4), 39.15 (t, CH_2Ph), 35.59 (t, C-1), 35.40 (t, C-10), 35.19 (t, C-9), 34.61 (t, C-2). Assignments were derived from C,H-HETCOR and -COLOC spectra; *syn* and *anti* refer to C-4. C-12,13 are *anti*, C-15,16 are *syn* to C-4. − MS: *m/z* =400 (32) [M^+], 309 (44), 295 (26), 205 (100), 165 (12), 104 (22), 91 (30), 83 (14), 71 (20), 57 (34). − $C_{31}H_{28}$ (400.5): calcd. C 92.95, H 7.05; found C 92.83, H, 7.04. − *Third band (R_f = 0.29, cyclohexane):* 4-[(*Z*)-1-Benzyl-2-phenylethenyl][2.2]paracyclophane (**12**, 0.16 g, 20%), colorless crystals (*n*-hexane); m.p. 135 °C. − IR (KBr): ν = 3045−3005 cm^{-1}, 2950−2840, 1598, 970. − ^1H NMR: δ = 7.48 (m, 2 H, Bzl-2-H), 7.41 (m, 2 H, Bzl-3-H), 7.30 (m, 1 H, Bzl-4-H), 6.97 (m, 3 H, Ph-3,4-H), 6.69 (m, 2 H, Ph-2-H), 6.62 (dd, *J* = 7.8, 1.8 Hz, 1 H, 12-H), 6.57 (dd, *J* = 7.8, 1.8 Hz, 1 H, 13-H), 6.50 (d, *J* = 1.8 Hz, 1 H, 5-H), 6.43 (dd, *J* = 7.9, 1.8 Hz, 1 H, 15-H), 6.35 (dd, *J* = 7.9, 1.8 Hz, 1 H, 16-H), 6.32 (dd, *J* = 7.8, 1.8 Hz, 1 H, 7-H), 6.188 (s, 1 H, =CH), 6.186 (d, *J* = 7.8, 1 H, 8-H), 4.09 (s, 2 H, CH_2Ph), bridge protons: 3.16−2.98 (m, 5 H), 2.91 (m, 1 H), 2.82 (ca. ddd, *J* ≈ 5, 10, 12−13 Hz, 1 H), 2.41 (ca. ddd, *J* ≈ 2−3, 10, 13 Hz, 1 H). Assignments from H,H-COSY. NOEs: Saturation of the 5-H signal caused enhancements of the 9-H_{syn}, CH_2Ph, 16-H, Bzl-2-H and Ph-2-H signals; *syn* and *anti* refer to C-4. C-12,13 are *anti*, C-15,16 are *syn* to C-4. − ^{13}C NMR: δ = 140.47, 140.11, 139.29, 139.11, 138.79 (2 C), 138.30, 138.06 (all quaternary C), 135.27, 133.18, 132.76, 132.51, 132.35, 131.67, 131.19, 129.64, 129.52 (2 C), 129.10 (2 C), 128.67 (2 C), 127.45 (2 C), 126.43, 126.10 (all CH), 44.15, 35.52, 35.44, 35.37, 33.56 (all CH_2). − MS: *m/z* = 401 (20)[M^+ + 1], 400 (48) [M^+], 309 (20), 295 (30), 205 (100), 165 (12), 141 (10), 121 (14), 105 (18), 91 (20), 71 (24), 69 (20). − $C_{31}H_{28}$ (400.5): calcd. C 92.95, H 7.05; found C 92.75, H 7.02.

Reaction of 4-[(*E*,*Z*)-1-Methyl-1-propenyl][2.2]paracyclophane (13) with 4

The 4-[(1-Phenylethyl)ethenyl][2.2]paracyclophane Diastereomers 14 and 15: Compound **4** was generated from anthranilic acid (2.20 g, 16.00 mmol) and isopentyl nitrite (2.03 g, 16.00 mmol) and added to 0.52 g (2.00 mmol) of **13** as described above. After removal of the acetonitrile, the residue was dissolved in acetone and subjected to thin-layer plate chromatography using pentane as the eluent and developing the plates three times. Two products were obtained. − *First band:* Compound **14** (0.27 g, 40%), colorless crystals (cyclohexane); m.p. 285 °C. − IR (KBr): ν = 3023−2987 cm^{-1}, 2960−2851, 1588. − ^1H NMR: δ = 7.38−7.29 (m, 4 H, Ph-2,3-H), 7.25 (m, 1 H, Ph-4-H), 6.65, 6.62, 6.59, 6.342 (all dd, *J* ≈ 7.8, 1.8 Hz, 1 H each, 12,13,15,16-H), 6.43 (d, *J* = 7.7 Hz, 1 H, 8-H), 6.41 (dd, *J* = 7.7, 1.8 Hz, 1 H, 7-H), 6.340 (d, *J* = 1.8 Hz, 1 H, 5-H), 5.31 (d, *J* = 1.7 Hz, 1 H of $=CH_2$), 4.86 (dd, *J* = 1.7, 1.3 Hz, 1 H of $=CH_2$), 3.71 (q, *J* = 7.2 Hz, C*H*CH_3), 1.14 (d, *J* = 7.2 Hz, CH_3), bridge protons: 3.33 (m, 1 H), 3.13−3.00 (m, 6 H), 2.98−2.89 (m, 2 H); assignments from H,H-COSY. NOEs: Saturation of the CH_3 signal enhanced signals of Ph-2-H (δ = 7.32), C*H*CH_3, =CH (δ = 4.86) and 5-H; it gave a negative NOE at

=CH (δ = 5.31); saturation of the C*H*CH_3 signal caused enhancements of the signals at δ = 3.33, 1.14, 7.32, 6.65, 6.340, 4.86 (order of decreasing enhancement). − ^{13}C NMR: δ = 156.41, 144.75, 142.46, 139.69, 139.43, 139.19, 136.39 (all quaternary C), 135.22, 133.07, 132.54, 132.31, 132.24, 131.83, 129.87, 128.30 (2 C), 128.12 (2 C), 126.25 (all CH), 114.52 (CH_2), 47.01 (CH), 35.51, 35.41, 35.16, 34.25 (all CH_2), 20.93 (CH_3). − MS: *m/z* = 338 (10) [M^+], 324 (56), 246 (28), 234 (100), 233 (60), 204 (22), 203 (28), 144 (26), 128 (12), 104 (42). − $C_{26}H_{26}$ (338.5): calcd. C 92.26, H 7.74; found C 92.21, H 7.75. − *Second band:* Compound **15** (0.14 g, 21%), colorless crystals (cyclohexane); m.p. 281−283 °C. − IR (KBr): ν = 3024−2987 cm^{-1}, 2960−2850, 1586. − ^{1}H NMR: δ = 7.07 (m, 2 H, Ph-3-H), 7.02−6.95 (m, 3 H, Ph-2,4-H), 6.60−6.53 (m, 3 H of 12,13,15,16-H), 6.29 (m, 1 H of 12,13,15,16-H), 6.32 (d, *J* = 7.7 Hz, 1 H, 8-H), 6.27 (dd, *J* = 7.7, 1.9 Hz, 1 H, 7-H), 6.20 (d, *J* = 1.9 Hz, 1 H, 5-H), 5.44 (t, *J* = 1.5 Hz, 1 H of =CH_2), 5.42 (d, *J* = 1.5 Hz, 1 H of =CH_2), 3.66 (q, *J* = 7.2 Hz, 1 H, C*H*CH_3), 3.11−2.79 (m, 8 H, CH_2CH_2), 1.48 (d, *J* = 7.2 Hz, 3 H, CH_3); assignments by H,H-COSY. NOEs: Saturation of the C*H*CH_3 signal caused an enhancement of the Ph-2-H signal; saturation of the CH_3 resonance signal gave NOEs of the Ph-2-H and =CH_2 signals. − ^{13}C NMR: δ = 154.89, 144.97, 142.72, 139.62, 139.41, 138.82, 136.42 (all quaternary C), 134.95, 133.05, 132.54, 132.34, 132.00, 131.73, 129.65, 127.99 (2 C), 127.32 (2 C), 125.81 (all CH), 113.14 (CH_2), 47.49 (CH), 35.48, 35.34, 35.11, 34.03 (all CH_2), 21.79 (CH_3). − MS: *m/z* = 338 (12) [M^+], 324 (60), 234 (100), 233 (52), 204 (24), 203 (38), 144 (32), 128 (14), 104 (40). − $C_{26}H_{26}$ (338.5): calcd. C 92.26, H 7.74; found C 92.18, H 7.70.

General Methods for the Syntheses of Phenanthrenophanes 18, 21 and 23

Method (a): A solution of **16** or **19** (0.52 g, 2.00 mmol) in anhydrous acetonitrile (20 mL) was heated at reflux, while solutions of anthranilic acid (2.47 g, 18.00 mmol) in dry acetonitrile (30 mL) and of isopentyl nitrite (2.29 g, 19.60 mmol) in dry acetonitrile (30 mL) were added concurrently over 6 h. After heating for a further 8 h, the solvent was evaporated in vacuo and the residue was subjected to plate chromatography using cyclohexane as the eluent. Two bands were separated and recrystallization of the products from *n*-hexane provided **17** (0.27 g, 40%) and **18** (0.20 g, 25%) when **16** was the starting material, and **20** (0.28 g, 42%) and **21** (0.22 g, 27%) in the case of **19**. With compounds **22** and **24** as the starting materials only **23** (0.49 g, 60%) and **25** (0.37 g, 55%), respectively were obtained as products.

Method (b): When the conditions of method (a) were applied to compounds **16**, **19**, **22** or **24** but with increased amounts (up to 36.0 mmol) of both anthranilic acid and isopentyl nitrite, the phenanthrenophanes **18** (0.49 g, 60%) and **21** (0.51 g, 62%) were obtained in better yields than in the above procedure, whereas compound **23** was obtained in the same yield as in the former method. Attempts to obtain **26** from **24** failed and only **25** was obtained in the same yield as before.

Method (c): When using method (a) with **17**, **20** or **25** (0.33 g, 1.00 mmol) and anthranilic acid (1.24 g, 9.00 mmol) and isopentyl nitrite (1.15 g, 9.80 mmol), both **18** and **21** (0.14 g, 34%) were obtained from **17** and **20**, respectively, whilst this method failed to transform **25** into **26**.

***anti*-16-Ethenyl[2.2](1,4)phenanthrenoparacyclophane (17):** R_f = 0.65, benzene; colorless crystals (benzene/cyclohexane); m.p. 172 °C. − IR (KBr): ν = 3054−3009 cm^{-1}, 2899−2850, 1599, 950, 750. − UV (CH_2Cl_2): λ_{max} (log ε) = 230 nm (3.47), 274 (3.61), 301 (4.01), 332 (5.00). − ^{1}H NMR: δ = 8.68 (m, 1 H, 9-H), 7.88 (m, 1 H, 6-H), 7.72, 7.67 (both d, *J* = 8.9 Hz, 1 H each, 4,5-H), 7.58−7.51 (m, 2 H, 7,8-H), 7.09, 6.71 (both d, *J* = 7.4 Hz, 1 H each, 11,12-H), 6.77 (dd, *J* = 17.4, 10.9 Hz, 1 H, vinyl-H_{gem}), 6.61 (br. d, *J* ≥ 1.4 Hz, 1 H, 17-H), 5.85 (dd, *J* = 7.7, 1.8 Hz, 1 H, 19-H), 5.58 (dd, *J* = 17.4, 1.2 Hz, 1 H, vinyl-H_{cis}), 5.28 (dd, *J* = 10.9, 1.2 Hz, 1 H, vinyl-H_{trans}), 5.11 (d, *J* = 7.7 Hz, 1 H, 20-H), 4.38 (m, 1 H, 13-H_{syn}), 3.86 (m, 1 H, 2-H_{syn}), remaining bridge protons: 3.30−2.95 (m, 5 H), 2.53 (m, 1 H). − ^{13}C NMR: δ = 138.00, 137.32, 137.17, 137.00, 135.81, 134.17, 132.88, 132.18, 131.19 (all quaternary C), 134.97, 131.86, 131.05, 129.23, 128.43, 128.37, 128.34, 127.31, 126.17, 125.84, 125.70, 124.45 (all CH), 114.04, 38.26, 33.93, 33.12, 32.28 (all CH_2). − MS: *m/z* = 334 (20) [M^+], 206 (18), 205 (34), 204 (58), 203 (100), 202 (32), 189 (26), 129 (8), 115 (6), 104 (40). − $C_{26}H_{22}$: (334.4); calcd. C 93.37, H 6.63; found C 93.38, H 6.62.

pseudo-*para*-[2.2](1,4)Phenanthrenophane (18): R_f = 0.60, benzene; colorless crystals (benzene); m.p. 250 °C. − IR (KBr): ν = 3045−3000 cm^{-1}, 2928−2853, 1605. − UV (CH_2Cl_2): λ_{max} (log ε) = 230 nm (3.47), 268 (3.53), 284 (3.74), 312 (4.11), 350 (5.28). − ^{1}H NMR: δ = 8.79 (m, 2 H, 9-H), 7.92 (m, 2 H, 6-H), 7.76 (d, *J* = 8.9 Hz, 2 H, 5-H), 7.69 (d, *J* = 8.9 Hz, 2 H, 4-H), ca. 7.60, ca. 7.58 (both m, 2 H each, 7,8-H), 6.31 (d, *J* = 7.4 Hz, 2 H, 11-H), 5.47 (d, *J* = 7.4 Hz, 2 H, 12-H), 4.57 (dd, J_{gem} = −14.5, J_{trans} = 0, J_{cis} ≈ 8.8 Hz, all ±0.3 Hz, 2 H, 13-H_{syn}), 3.67 (dd, J_{gem} = −13.6, J_{trans} = 0, J_{cis} = 8.9 Hz, all ±0.3 Hz, 2 H, 2-H_{syn}), 3.36 (dt, J_{gem} = −14.5, J_{trans} = 9.2, J_{cis} = 8.9 Hz, all ±0.3 Hz, 2 H, 13-H_{anti}), 2.80 (dt, J_{gem} = −13.6, J_{trans} = 9.2, J_{cis} = 8.8 Hz, all ±0.3 Hz, 2 H, 2-H_{anti}). Assignments by H,H-COSY. − ^{13}C NMR: δ = 136.13, 134.38, 133.62, 132.20, 131.37 (all quaternary C), 131.62, 128.45, 127.74, 126.96, 126.13, 125.88, 125.76, 124.10 (all CH), 38.50, 32.21 (both CH_2); signal for one quaternary C not observed. − MS: *m/z* = 408 (12) [M^+], 384 (8), 267 (28), 206 (30), 205 (80), 203 (100), 141 (14), 129 (10), 115 (14). − $C_{32}H_{24}$ (408.5): calcd. C 94.08, H 5.92; found C 93.93, H 5.91.

***anti*-17-Ethenyl[2.2](1,4)phenanthrenoparacyclophane (20):** R_f = 0.55, benzene; colorless crystals (benzene/cyclohexane); m.p. 182 °C. − IR (KBr): ν = 3050−2999 cm^{-1}, 2887−2872, 1590, 955, 754. − UV (CH_2Cl_2): λ_{max} (log ε) = 230 nm (3.47), 258 (3.89), 288 (3.78), 300 (4.01), 338 (5.01). − ^{1}H NMR: δ = 8.52 (m, 1 H, 9-H), 7.89 (m, 1 H, 6-H), 7.73 (d, *J* = 8.9 Hz, 1 H, 5-H), 7.64 (d, *J* = 8.9 Hz, 1 H, 4-H), 7.58−7.51 (m, 2 H, 7,8-H), 6.96, 6.86 (both d, *J* = 7.4 Hz, 1 H each, 11,12-H), 6.87 (dd, *J* = 17.4, 10.9 Hz, 1 H, vinyl-H_{gem}), 6.66 (d, *J* = 1.8 Hz, 1 H, 16-H), 5.81 (d, *J* = 7.7 Hz, 1 H, 19-H), 5.61 (dd, *J* = 17.4, 1.3 Hz, 1 H, vinyl-H_{cis}), 5.32 (dd, *J* = 10.9, 1.3 Hz, 1 H, vinyl-H_{trans}), 5.21 (dd, *J* = 7.7, 1.8 Hz, 1 H, 20-H), 4.33 (ddd, *J* = −14.5, 8.6, 5.1 Hz, 1 H, 13-H_{syn}), 3.76 (dd, *J* = −13.7, 9.5 Hz, 1 H, 2-H_{syn}), 3.50 (dd, *J* = −13.4, 9.5 Hz, 1 H, 1-H_{anti}), 3.41 (ddd, *J* = −14.5, 8.7, 6.1 Hz, 1 H, 13-H_{anti}), 3.05 (ddd, *J* = −13.7, 9.5, 8.6 Hz, 1 H, 2-H_{anti}), 2.90 (ddd, *J* = −13.3, 8.7, 5.1 Hz, 1 H, 14-H_{anti}), 2.87 (dt, *J* = −13.4, 9.5, 8.6 Hz, 1 H, 1-H_{syn}), 2.79 (ddd, *J* = −13.3, 8.6, 6.1 Hz, 1 H, 14-H_{syn}); assignment by H,H-COSY. − MS: *m/z* = 334 (40) [M^+], 206 (18), 205 (60), 204 (74), 203 (100), 202 (40), 189 (36), 167 (16), 149 (58), 129 (8), 115 (16), 104 (40). − $C_{26}H_{22}$ (334.4): calcd. C 93.37, H 6.63; found C 93.34, H 6.60.

pseudo-*meta*-[2.2](1,4)(4,1)Phenanthrenophane (21): R_f = 0.53, benzene; colorless crystals (benzene); m.p. 220 °C. − IR (KBr): ν = 3060−2989 cm^{-1}, 2928−2880, 1608. − UV (CH_2Cl_2): λ_{max} (log ε) = 230 nm (3.47), 268 (3.53), 274 (3.61), 284 (3.74), 316 (4.15), 354 (5.30). − ^{1}H NMR: δ = 8.46 (m, 2 H, 9-H), 7.93 (m, 2 H, 6-H), 7.786 (d, *J* ≈ 9 Hz, 2 H, 5-H), 7.774 (d, *J* ≈ 9 Hz, 2 H, 4-H), ca. 7.58, ca. 7.55 (both m, 2 H each, 7,8-H), 6.05 (d, *J* = 7.5 Hz,

2 H, 12-H), 5.73 (d, J = 7.5 Hz, 2 H, 11-H), 4.09 and 3.21 (AA′XX′, J_{gem} = −14.5, both $J_{trans} \approx$ 6.7, J_{cis} = 6.9 Hz, all ±0.2 Hz, 2 H each, 13-H_{syn}, 13-H_{anti}), 3.88 and 3.15 (AA′XX′, J_{gem} = −13.5, J_{trans} = 8.8 and 0.1 Hz, J_{cis} = 9.3 Hz, all ±0.4 Hz, 2 H each, 2-H_{syn}, 2-H_{anti}). Assignments by H,H-COSY and homonuclear decoupling. − ^{13}C NMR: δ = 135.67, 135.11, 133.36, 132.80, 132.22, 130.67 (all quaternary C), 130.34, 128.56, 128.26, 127.98, 126.08, 125.86, 125.47, 123.76 (all CH), 37.29, 32.58 (both CH_2). − MS: *m/z* = 408 (40) [M^+], 384 (12), 267 (32), 246 (14), 205 (54), 204 (100), 202 (44), 141 (18), 125 (20), 115 (14). − $C_{32}H_{24}$ (408.5): calcd. C 94.08, H 5.92; found C 93.93, H 5.91.

pseudo-*gem*-[2.2](1,4)(4,1)Phenanthrenophane (23): R_f = 0.73, benzene; colorless crystals (benzene); m.p. 218 °C. − IR (KBr): ν = 3065−3000 cm^{-1}, 2995−2890, 1610. − UV (CH_2Cl_2): λ_{max} (log ε) = 230 nm (3.47), 266 (3.50), 280 (3.70), 320 (4.12), 358 (5.33). − ^{1}H NMR: δ = 8.09 (m, 2 H, 9-H), 7.60 (d, J = 8.9 Hz, 2 H, 4-H), 7.32 (m, 2 H, 6-H), 7.13 (m, 2 H, 8-H), 7.11 (m, 2 H, 7-H), 7.09 (d, J = 8.9 Hz, 2 H, 5-H), 7.01 (d, J = 7.5 Hz, 2 H, 11-H), 6.86 (d, J = 7.5 Hz, 2 H, 12-H), 4.20 and 3.47 (AA′XX′, J_{gem} = −14.6, J_{trans} = 6.5, both $J_{cis} \approx$ 6.9 Hz, 2 H each, 13-H_{syn}, 13-H_{anti}), 4.02 and 3.35 (AA′XX′, J_{gem} = −13.6, J_{trans} = 4.1, J_{cis} = 10.9 and 10.0 Hz, 2 H each, 2-H_{syn}, 2-H_{anti}). Assignments by H,H-COSY and homonuclear decoupling. − ^{13}C NMR: δ = 135.86 (s, C-3), 135.75 (s, C-10), 133.31 (d, C-11), 132.12 (s, C-3a), 131.68 (s, C-5a), 131.31 (s, C-9b), 130.81 (d, C-12), 129.25 (s, C-9a), 127.27 (d, C-6), 126.84 (d, C-9), 126.66 (d, C-5), 125.17 (d, C-7), 124.46 (d, C-8), 123.17 (d, C-4), 38.14 (t, C-13), 31.97 (t, C-2). Assignments from C,H-HETCOR and -COLOC spectra. − MS: *m/z* = 408 (30) [M^+], 384 (22), 267 (38), 246 (18), 205 (28), 203 (100), 129 (46), 115 (14). − $C_{32}H_{24}$ (408.5): calcd. C 94.08, H 5.92; found C 93.88, H 5.92.

***syn*-16-Ethenyl[2.2](1,4)phenanthrenoparacyclophane (25):** R_f = 0.52, benzene; colorless crystals (benzene/cyclohexane); m.p. 162 °C. − IR (KBr): ν = 3052−3010 cm^{-1}, 2900−2852, 1595, 952, 749. − UV (CH_2Cl_2): λ_{max}(log ε) = 230 nm (3.47), 258 (3.89), 288 (3.78), 300 (4.01), 344 (5.05). − ^{1}H NMR: δ = 8.28 (m, 1 H, 9-H), 7.77 (m, 1 H, 6-H), 7.71, 7.67 (both d, J = 8.9 Hz, 1 H each, 4,5-H), 7.47, 7.46 (both m, 1 H each, 7,8-H), 6.95, 6.77 (both d, J = 7.4 Hz, 1 H each, 11,12-H), 6.59 (s, 2 H, 19,20-H), 6.05 (br. s, 1 H, 17-H), 5.70 (dd, J = 17.5, 10.9 Hz, 1 H, vinyl-H_{gem}), 4.52 (dd, J = 17.5, 1.1 Hz, 1 H, vinyl-H_{cis}), 4.22 (dt, J = −14.3, 8.5, 8.5 Hz, 1 H, 13-H_{syn}), 4.17 (dd, J = 10.9, 1.1 Hz, 1 H, vinyl-H_{trans}), remaining bridge protons: 3.87 (m, 1 H), 3.62 (ddd, J = −14.3, 8.5, 2.5 Hz, 1 H), 3.34 (ddd, J = −13.9, 8.5, 2.5, 1 H), 3.25 (m, 1 H), 3.08−2.96 (m, 2 H), 2.78 (dt, J = −13.9, 8.5, 8.5 Hz, 1 H); assignment by H,H-COSY. − ^{13}C NMR: δ = 138.62, 137.14, 136.83, 136.23, 135.98, 132.30 (all quaternary C), 134.05, 133.28, 132.78, 132.59, 130.27, 128.19, 127.72, 127.32, 126.02, 125.42, 124.96, 122.83 (all CH), 113.34, 34.94, 34.67, 34.45, 33.70 (all CH_2); signals for three quaternary C not observed due to insufficient signal/noise ratio. − MS: *m/z* = 334 (24) [M^+], 206 (12), 205 (36), 204 (60), 203 (100), 202 (30), 189 (28), 129 (8), 115 (12), 104 (60). − $C_{26}H_{22}$ (334.4): calcd. C 93.27, H 6.63; found C 93.38, H 6.62.

Acknowledgments

A. A. A. is indebted to the Ministry of Higher Education of Egypt (Mission Department) for providing the scholarship that enabled him to work under the supervision of Prof. H. Hopf for two years. He also thanks Prof. A. E. Mourad for his encouragement and help during this period. This work was partially supported by the Fonds der Chemischen Industrie, Frankfurt am Main. We are grateful to Mrs. Petra Holba-Schulz for NMR measurements.

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Received March 7, 2000
[O00110]