

Cyclophanes, XXVII<sup>1)</sup>

## [2.2]Indenophane Mono- and Dianions: Preparation and Nuclear Magnetic Resonance Spectra

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The preparation and chemical and physical properties of negatively charged polycyclic cyclophanes are reported. The through-space electronic interactions and the through-space anisotropy effects were deduced from proton and carbon nuclear magnetic resonance data. The systems studied belong to two main groups: a)  $4n\pi$ -polycyclic dianions which are paratropic, e.g. [2.2]benzo[*g*]chrysenophane dianion ( $12^{2-}$ ), and b)  $(4n+2)\pi$ -polycyclic mono- and dianions, which are diatropic. In the dianions both layers are charged, e.g. *syn*-[2.2]indenocyclophane ( $13^{2-}$ ) and its *anti* isomer ( $14^{2-}$ ). The monoanions studied are [2.2]benzoindenocyclophane ( $15^{1-}$ ), 4,5,17,18-tetramethyl[2.2]benzoindenocyclophane ( $16^{1-}$ ), and 12-methyl[2.2]benzoindenocyclophane ( $17^{1-}$ ). The spectroscopic properties of the layered anions were compared with those of 1,4-dimethylindenyl anion ( $11^{1-}$ ) and with literature data of neutral cyclophanes, viz. 1–11. A differentiation between the anisotropy and charge-transfer effects has been made and it enables the estimation of the net through-space interaction.

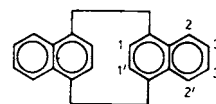
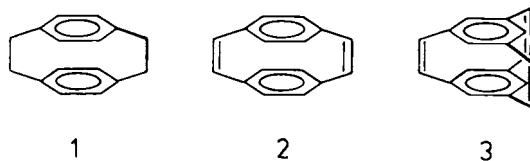
Cyclophanes are molecules of long lasting interest among synthetic and theoretical chemists<sup>2)</sup>. The wide interest in the [2<sub>n</sub>]cyclophanes emerged from the phenomenon of through-space interaction of the conjugated  $\pi$  systems found in these layered compounds. There are two major characteristics of such interactions: a) when placed in an applied magnetic field, there are through-space magnetic interactions, and b) optical spectroscopy reveals a through-space electronic interaction which involves a mixing between the two  $\pi$  arrays, thus forming one overall  $\pi$  system<sup>2,3)</sup>. A combined study of both the magnetic properties and electronic through-space interactions of the cyclophanes can be achieved by NMR spectroscopy. Ionic cyclophanes offer the advantage of enhancing both the donor-acceptor properties and the mutual magnetic interactions of the interacting halves of the molecule.

NMR parameters of the [2.2]paracyclophanes have been explored since the early days of cyclophane chemistry<sup>4)</sup>. As [2.2]paracyclophanes are not expected to show conformational mobility, neutral model compounds to which the NMR parameters can be compared

### Cyclophane, XXVII<sup>1)</sup>. — [2.2]Indenophan-Mono- und Dianionen: Darstellung und kernmagnetische Resonanz-Spektren

Die Darstellung, chemischen und physikalischen Eigenschaften negativ geladener polycyclischer Cyclophane werden beschrieben. Through-space-elektronische Wechselwirkungen und through-space-Anisotropieeffekte werden aus den Protonen- und Kohlenstoffkernresonanzspektren abgeleitet. Die untersuchten Systeme gehören zu zwei Hauptgruppen: a) paratropische  $4n\pi$ -polycyclische Dianionen, z. B. [2.2]Benzo[*g*]chrysenocyclophan-Dianion ( $12^{2-}$ ) und b)  $(4n+2)\pi$ -polycyclische Mono- und Dianionen, die diatrop sind. In den Dianionen sind beide Decks geladen: z. B. *syn*-[2.2]Indenocyclophan-Dianion ( $13^{2-}$ ) und sein *anti*-Isomer ( $14^{2-}$ ). Bei den untersuchten Monoanionen handelt es sich um die des [2.2]-Benzoindenocyclophan ( $15^{1-}$ ), 4,5,17,18-Tetramethyl[2.2]benzoindenocyclophan ( $16^{1-}$ ) und des 12-Methyl[2.2]benzoindenocyclophan ( $17^{1-}$ ). Die spektroskopischen Eigenschaften der lagigen Anionen werden mit denjenigen von 1,4-Dimethylindenyl-Anion ( $11^{1-}$ ) und mit Literaturwerten der neutralen Cyclophane 1–11 verglichen. Es wird eine Trennung von Anisotropie- und charge-transfer-Effekten durchgeführt, die es erlaubt, die Netto-through-space-Wechselwirkung abzuschätzen.

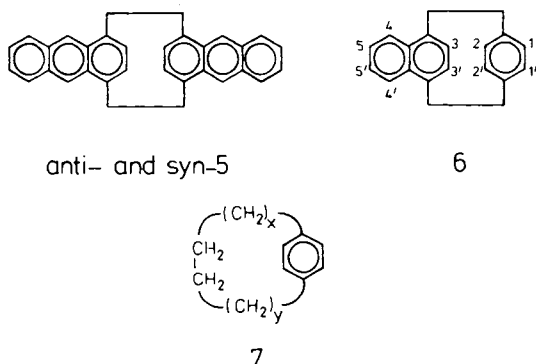
are easily attainable. Furthermore, since a large number of X-ray studies have been carried out on these systems, their spatial structure in the solid state has also been elucidated<sup>5)</sup>. An understanding of the geometry of a given system in conjunction with the ring current model and its relationship to magnetic anisotropy effects on the various nuclei can rationalize very well the observed NMR chemical shifts<sup>4)</sup>. It should, however, be noted that each nucleus experiences an induced magnetic anisotropy, which is composed of



anti- and syn-4

the effect resulting from its own conjugated system as well as from the through-space anisotropy. The comparison of the chemical shifts of [2.2]paracyclophane (**1**) with [2.2]paracyclophandiene (**2**) and the triene **3** shows that the main effect is the through-space anisotropy and not a through-bond conjugation<sup>4,6)</sup>.

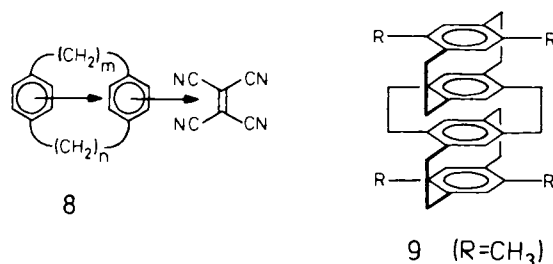
The latter could be ruled out due to the geometry of the system. Certain polycyclic paracyclophanes can exist as *syn* and *anti* pairs of isomers, and this allows the mutual anisotropy of similar or identical layers in differing spatial arrangements to be studied. A well-pronounced effect can be seen in molecules such as [2.2](1,4)-naphthalenophane<sup>6)</sup> (**4**) or [2.2](1,4)anthracenophane<sup>7)</sup> (**5**). Those systems containing only one polycyclic layer also exhibit significant chemical shift changes as compared to the parent system **1**. For example, in [2.2](1,4)parabenzonaphthalenophane<sup>6a)</sup> (**6**) two benzene protons 1-H and 1'-H show a chemical shift similar to that observed in **1** ( $\delta = 6.33$ ), while the other pair of protons shows a chemical shift of 5.5. This observation is in line with the expected magnitude of the magnetic anisotropy induced upon one pair of protons by the  $\pi$ -electron cloud of the naphthalene layer. In the *syn* and *anti* pair of isomers of [2.2](1,4)naphthalenophane (**4**) this effect is even more pronounced. At room temperature their mobility is restricted and they show different spectra due to the prevalence of different spatial magnetic anisotropies in each of the isomers. While *anti*-**4** shows a pair of protons (1-H, 1'-H) which are shifted to a particularly high field ( $\delta = 5.77$ ) compared to those of **1**, the *syn* isomer does not show a high-field effect (1-H, 1'-H, 6.72, Table 1). The significant difference in the chemical shifts between 1-H and 1'-H of the two isomers stems from the drastic change of the magnetic environment. Similarly, the [2.2](1,4)anthracenophane (**5**), which also has two geometric isomers, exhibits a two-proton band at 6.71 for the *syn* isomer, whereas the same protons of the *anti* compound are registered at  $\delta = 5.47$ . These two examples may suffice to illustrate a phenomenon common to these systems.



The other major interaction characteristic of the cyclophanes, viz. the electronic through-space interaction, was studied by UV/VIS spectroscopy. As early as 1951, Cram had suggested that both the bending of the benzene component and the proximity of the two  $\pi$ -delocalized systems are responsible for the unusual spectroscopic data<sup>1,8)</sup>. Modification of the chain length of the cyclophane bridges affects the UV spectra of the hydrocarbons. Cram compared [2.2]- with [4.4]paracyclophane<sup>9)</sup> and demonstrated that the latter shows the typical UV absorptions of a substituted benzene ring. However, studies on [*n*]paracyclophanes **7**<sup>8-11)</sup> have shown that the spectral changes do not originate from the bending of the aromatic rings, but rather that the mixing of the two  $\pi$  systems is the main factor in determining the optical spectroscopy of these systems<sup>12)</sup>.

Another approach to the study of the charge transfer between the two layers of a cyclophane would be the inspec-

tion of an excess or a deficiency of electrons in one of the components and its effect on the other. In an extreme case one layer can act as a donor and the other one as an acceptor. A  $\pi$ - $\pi$  complex **8** is formed when a [*m.n*]paracyclophane ( $\pi$  base) is allowed to react with an external acceptor like tetracyanoethylene (TCNE,  $\pi$  acid). The strength of the  $\pi$  base decreases in the order [*m.n*] = [3.3] > [4.3] > [2.2] > [4.4] > [6.6]  $\approx$  (*p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>)<sub>2</sub>. Except for **1**, the observed order correlates very well with the distance between the two benzene rings, i.e. a smaller interlayer distance results in an increased  $\pi$  basicity. This is an outcome of the participation of the  $\pi$  electrons of the noncomplexed benzene ring in the bonding of structure **8**<sup>13)</sup>.



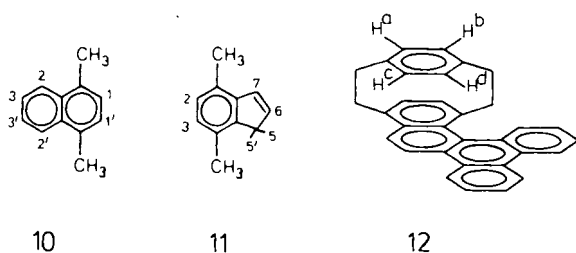
A complementary experiment has shown that electron-withdrawing substituents on the non-complexed benzene rings decrease the  $\pi$  basicity of the entire system and cause corresponding color changes in the complex<sup>13)</sup>. It has been concluded that there are three factors which influence the through-space delocalization of the two aromatic rings: a) the interlayer distance, b) the degree of planarity of the layers, and c) the degree of hyperconjugation between the aromatic rings and the methylene bridge which, in turn, depends on the degree of distortion of the methylene bridges with respect to the rings. Multilayered systems enable the study of additional decks. The  $\pi$  complexes of multilayered cyclophanes such as **9** show a good correlation between the location of the charge-transfer band and the dissociation constant of the complex. Due to the charge transfer between the various layers in **9**, the system has a higher basicity than that of e.g. **1**, and the  $\pi$  complex is consequently stronger<sup>14,15)</sup>. This phenomenon holds true for up to five stacked rings. From six-layered molecules on, the properties no longer change<sup>14b)</sup>. Further proof for a three-dimensional delocalization in cyclophanes stems from electron reduction experiments on these systems. ESR studies show that when  $m = n = 2$  or 3, the additional electron, which produces a radical anion, is delocalized over the entire cyclophane<sup>2f,16)</sup>. When  $m = n > 4$ , the extra electron is delocalized over only one ring, as is the case in linear structures, e.g. C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>.

As already mentioned, negatively charged decks can also operate as electron donors. The information that these systems deliver may eventually enable the extra effects which originate from the presence of a charged delocalized layer or layers to be estimated.

The differentiation between the various effects, i.e. magnetic anisotropy and three-dimensional delocalization (or charge transfer), can be achieved by one physical method, namely NMR spectroscopy.

This requires a comparison between the properties of charged layered compounds and the appropriate model structures. These should possess very similar geometry and

an identical number of  $\pi$  electrons in the cyclophane layers, the main difference being the charge. One can compare a naphthalene layer with an indenyl anion layer since both possess  $10\pi$  electrons. A comparison should also be made with 1,4-dimethylnaphthalene (**10**) and the 1,4-dimethylindene anion (**11**, Table 1). Anionic species can be prepared by either a proton abstraction<sup>17)</sup> or by a two-electron reduction process<sup>18)</sup>. Cyclopentadienyl and indenyl anions are good examples for the first method of preparation, and the cyclooctatetraene dianion exemplifies the metal reduction process of  $\pi$ -conjugated neutral systems. The magnetic anisotropy criterion is used very frequently as an experimental criterion for  $[4n+2]\pi$ -Hückeloid systems. Another group of conjugated systems is the  $4n\pi$ -conjugated molecules for which the term antiaromatic was coined by Breslow<sup>19)</sup>.



<sup>1</sup>H- and <sup>13</sup>C-NMR spectra studied and compared with those of appropriate model compounds.

The <sup>1</sup>H data are summarized in Table 1, the carbon spectra are reported in Table 2.

The assignments were assisted by 2D techniques, and details are reported in the Experimental Section. The anions were prepared in [D<sub>8</sub>]THF by the addition of an excess of methyllithium in the NMR tube as also described below. The anions are stable species which can be kept in a capped tube for weeks at room temperature. Their stability is comparable to that of the 1,4-dimethylindenyl anion (**11**<sup>1-</sup>) which was prepared (Experimental Section) and employed as a reference system. The anions were quenched with D<sub>2</sub>O and water. In the latter experiment most of the starting material was recovered. The deuterated products were analyzed by mass spectrometry: the M + 1 or M + 2 peaks were always observed and they are, of course, indicative of the mono- and dianions, respectively. Furthermore, the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of these materials were recorded to show where the deuterium is located. The anion of the chrysenophane **12** was prepared as reported previously<sup>25)</sup>.

Compared to the neutral molecules discussed above, an additional parameter is involved in anionic cyclophanes, namely the mutual interaction of charged moieties<sup>26)</sup>. We concentrated our studies on charged phanes with  $[4n+2]\pi$  decks for the following reasons: a) these ions are stable, b) the complications which may arise from line broadening and shifts due to the presence of paramagnetic species in electron transfer processes are avoided, and, most importantly, c) these systems involve a "built-in" electron donor deck. Whereas the studies on the neutral paracyclophanes are quite systematic, no comprehensive investigations on anionic species of this type have so far been performed<sup>27)</sup>. In the present NMR study, a whole family of  $[4n+2]\pi$  mono- and dianionic paracyclophanes has been studied.

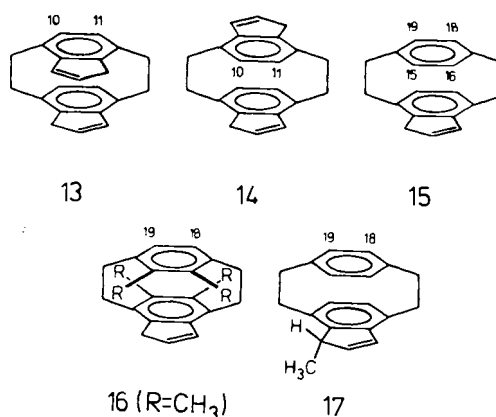
These are systems which show destabilization relative to model  $[4n+2]$  or even  $[4n+1]$  systems, and they are expected to cause a high-field shift of their protons (the so-called paratropic shift). It therefore seems that the NMR criterion for the diatropic  $[4n+2]\pi$ -electron systems or for the paratropic ones, is very useful. Such systems and their magnetic properties have been reviewed by Haddon<sup>20)</sup>. However, NMR spectroscopy also affords information on the degree of charging due to the shielding or deshielding resulting from the charge<sup>21)</sup>. The correlation between the charge and the proton and carbon chemical shifts in  $[4n+2]\pi$  systems have been well-established<sup>22,23)</sup>.

The spectroscopic properties of the  $4n\pi$  series depend on the degree of paratropicity or, more precisely, on their HOMO-LUMO gap<sup>24)</sup>. In this case, paratropicity and diatropicity refer only to protons in the perimeter of the molecule. When looking for through-space interactions, it should be noted that their effect depends on the respective positions of the studied nuclei. Systems with  $[4n+2]\pi$ -electrons induce magnetic fields in other parts of the molecules which, depending upon the geometric location of the nuclei in question with respect to the  $\pi$  system, can either add to (diatropicity) or operate against (paratropicity) the external field. Those nuclei located outside the ring show diatropicity while those inside or just above the ring exhibit paratropicity.

Charged cyclophanes are now described and the mutual interaction of the charge, diatropicity and paratropicity of protons and carbon atoms enables a differentiation between induced magnetic and electronic effects. For this very reason, the  $[4n+2]\pi$  indenyl anion was chosen and compared with isoelectronic neutral system, naphthalene.

## Results and Discussion

From the indenyl cyclophanes **13**–**17** the five anions **13**<sup>2-</sup>, **14**<sup>2-</sup>, **15**<sup>1-</sup>, **16**<sup>1-</sup>, and **17**<sup>1-</sup> were prepared, and the



The excess charge in these species will influence their electronic structure and consequently their <sup>1</sup>H- and <sup>13</sup>C-NMR parameters. Comparison of the charged and neutral systems may therefore shed light on the special properties of the charged cyclophanes. Four factors should be considered in this comparison: a) the effect of the mutual anisotropy between the two aromatic components, b) the effect of the geometry on the behavior of the *syn* and *anti* isomers,

Table 1. <sup>1</sup>H-NMR spectroscopic parameters of [2.2]paracyclophanes and anions

System a)	<sup>1</sup> H patterns b,c), aromatic protons	<sup>1</sup> H patterns b), aliphatic protons
anti-4 d)	5.77 (t, 4H, 1-H), 7.74 (m, 4H, 2-H), 7.41 (m, 4H, 3-H).	3.75 (m, 4H, br.), 3.00 (m, 4H, br.).
syn-4 d)	6.72 (s, 4H, 1-H), 7.49 (s, 4H, 2-H), 6.85 (s, 4H, 3-H).	3.58 (m, 8H, br.).
6 d)	7.56 (m, 2H, 4,4'-H), 7.30 (m, 2H, 5,5'-H) 6.62 (s, 2H, 3,3'-H), 6.33 (s, 2H, 1,1'-H), 5.50 (s, 2H, 2,2'-H).	3.70 (m, 2H, br.), 3.19 (2H, br.), 3.03 (s, 4H, br.).
10 d)	7.97 (AA'BB', 2H, 6,7-H), 7.42 (AA'BB', 2H, 5,8-H), 7.13 (s, 2H, 2,3-H).	not reported.
11 e)	7.07 (dt, 1H, J <sub>1</sub> =5.59, J <sub>2</sub> =1.9Hz, 7-H), 7.01 (d, 1H, J=7.64 Hz, 2-H or 3-H), 6.92 (d, 1H, J=7.64Hz, 2-H or 3-H), 6.60 (dt, 1H, J <sub>1</sub> =5.56, J <sub>2</sub> =1.9Hz, 6-H).	3.34 (s, 2H, 5,5'-H), 2.46 (s, 3H, CH <sub>3</sub> ), 2.38 (s, 3H, CH <sub>3</sub> ).
11 <sup>1-</sup> e)	6.55 (t, 1H, J=3.3Hz, 6-H), 6.33 (s, 2H, 2,3-H), 6.02 (d, 2H, J=3.3Hz, 5,7-H).	2.50 (s, 6H, CH <sub>3</sub> ).
13	6.75 (dt, 2H, J <sub>1</sub> =5.5, J <sub>2</sub> =1.82Hz, 7-H or 6-H), 6.59-6.46 (m, 4H, 10,11 <sup>2</sup> -H), 6.13 (dt, 2H, J <sub>1</sub> =5.6, J <sub>2</sub> =2.0Hz, 6-H or 7-H).	3.48-2.88 (unresolved m, 12H, br. + 5,5'-H).
13 <sup>2-</sup> e)	6.04 (s, 4H, 10,11-H), 5.83 (t, 2H, J=3.3Hz, 6-H), 5.50 (d, 4H, J=3.3Hz, 5,7-H).	3.77-3.70; 3.17-3.10 (symmetric unre- solved m, 8H, br.).
14 e)	6.90 (dt, 2H, J <sub>1</sub> =5.55, J <sub>2</sub> =1.9Hz, 6-H), 6.54 (dt, 2H, J <sub>1</sub> =5.5; J <sub>2</sub> =2.0Hz, 7-H).	3.41-2.78 (m, 8H, br.), 3.13 (d, 4H, J=1.85Hz, 5,5'-H).
14 <sup>2-</sup> e)	6.32 (t, 2H, J=3.3Hz, 6,20-H), 5.77 (d, 4H, J=3.3Hz, 5,7,19,21-H), 5.20 (s, 4H, 10,11,15,-16-H).	3.33-3.15 (m, 4H, br.), 2.90-2.78 (m, 8H, br., center 3.05).
15 e)	6.87 (dt, 1H, J <sub>1</sub> =5.5, J <sub>2</sub> =1.9Hz, 6-H or 7-H), 6.53 (dt, 1H, J <sub>1</sub> =5.5, J <sub>2</sub> =1.9Hz, 7-H or 6-H), 6.56-6.43 (m, 4H, 10,11 <sup>2</sup> -H + solv.), 6.53: 18,19-H), 6.30 (d, 2H, J=1.45Hz, 15,16-H).	3.47-2.85 (m, 10H, br. + 5,5'-H).
15 <sup>1-</sup> e)	6.40 (t, 1H, J=3.26Hz, 6-H), 6.29 (s, 2H, 18,19-H), 5.94 (s, 2H, 10,11-H), 5.84 (s, 2H, 15,16-H).	2.92-2.70 (m, 8H, br.).
16 e)	6.98 (dt, 1H, J <sub>1</sub> =5.5, J <sub>2</sub> =2.0Hz, 7-H or 6-H), 6.53 (s, 2H, 18,19-H), <sup>2</sup> 6.27 (dt, 1H, J <sub>1</sub> =5.5, J <sub>2</sub> =2.0Hz, 6-H or 7-H).	3.56-2.77 (m, 10H, br.), 3.29 (t, J=20Hz, 5,5'-H), 2.03 (s, 3H, 22-CH <sub>3</sub> or 23-CH <sub>3</sub> ), 1.95 (s, 3H, 20-CH <sub>3</sub> ), 1.88 (s, 3H, 21-CH <sub>3</sub> ).
16 <sup>1-</sup> e)	6.30 (s, 2H, 18,19-H), 6.15 (t, 1H, J=3.3 6-H), 5.77 (d, 2H, J=3.3Hz, 5,7-H).	3.6-3.3, 2.81-2.70 (m, br.), 2.07 (s, 6H, 22-CH <sub>3</sub> , 23-CH <sub>3</sub> ), 1.89 (s, 6H, 20-CH <sub>3</sub> , 21-CH <sub>3</sub> ).
17 e)	6.61 (dd, 1H, J <sub>1</sub> =5.2, J <sub>2</sub> =1.9Hz, 7-H), 6.53 (s, 2H, 18,19-H), 6.45 (d, 1H, J=7.6Hz, 10-H or 11-H), 6.37 (2d, 2H, J=7.6 and 5.6Hz, 10-H or 11-H, 6-H), 6.29 (d, 2H, J=6.67Hz, 15-16-H).	1.17 (d, 3H, J=7.6Hz, CH <sub>3</sub> ), 3.30-2.86 (m, 8H, br.).
17 <sup>1-</sup> e)	6.27 (center of two overlapping d, 2H, J=1.5Hz, 18,19-H), 6.12 (d, 1H, J=3.3Hz, 10-H or 11-H), 5.95 (dd, 1H, J <sub>1</sub> =7.5, J <sub>2</sub> =1.14Hz, 6-H), 5.87 (d, 2H, J=1.5Hz, 15,16-H), 5.68 (d, 1H, J=3.2 Hz, 10H or 11-H), 5.52 (dd, 1H, J <sub>1</sub> =7.4, J <sub>2</sub> =1.04Hz, 7-H).	
18 f)	6.32 (s, 4H, six-membered ring), 6.12 (s, 4H, six-membered ring), 5.63 (s, 4H, six-membered ring), 3.75 (t, 2H, J=2.3 Hz, five-membered ring), 3.67 (d, 4H, J=2.3Hz, five-membered ring).	2.82-2.52 (m, 16H, br.).
19 d)	6.53 (s, 2H, 2,2'-H), 6.38 (s, 2H, 1,1'-H), 6.20 (s, 2H, 3,3'-H).	3.23 (t, 1H, -), 3.02 (s, -), 2.90 (s, -), 2.85 (s, -), 2.80 (s, -), 2.72 (s, -), 2.42 (m, 4H, -), 1.66 (m, 4H).
20 d)	6.25 (s, 4H, 1, 1', 1'', 1'''-H).	2.87 (s, 8H, br.), 2.40 (m, 8H, 2-H), 1.63 (m, 8H, 3-H).

a) For numbering of the protons see the formula schemes. — b) Chemical shifts are given in  $\delta$  values with reference to (CH<sub>3</sub>)<sub>4</sub>Si. — c) Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br. = bridge protons, — = assignments not reported. — d) Chemical shifts, multiplicity, and relative signal areas (where reported) were taken from ref.<sup>4)</sup>. — e) Chemical shifts were recorded in [D<sub>8</sub>]THF at room temperature and calibrated by the THF line at  $\delta$  = 3.67. — f) Spectra recorded in CDCl<sub>3</sub> at room temperature.

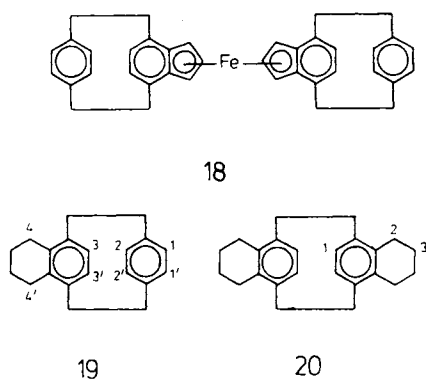
Table 2.  $^{13}\text{C}$ -NMR data of [2.2]paracyclophanes and [2.2]paracyclophane dianions<sup>a)</sup>

	Aromatic carbons					Aliphatic carbons		
<b>11</b>	143.58	142.49	133.08	130.85	130.16	38.35	18.05	17.90
	127.81	127.71	126.11					
<b>11<sup>1-</sup></b>	128.47	124.93	114.89	113.47	90.65	19.57		
<b>13</b>	146.80	144.55	134.39	132.59	132.52	39.25	32.12	30.96
	132.19	127.06	125.84					
<b>13<sup>2-</sup></b>	129.91	129.54	124.9	95.20	91.76	34.43		
<b>14</b>	146.32	144.11	134.26	132.60	132.04	39.13	31.97	30.91
	131.89	126.76	125.58					
<b>14<sup>2-</sup></b>	130.77	127.92	118.88	111.48	92.24	33.21		
<b>15</b>	147.17	144.60	139.09	138.87	135.17	39.08	35.01	
	133.35	133.16	132.98	132.67	132.58	34.30	32.67	
	132.58	130.82	128.21	125.68		32.62		
<b>15<sup>1-</sup></b>	136.40	131.17	130.57	129.56	121.44	35.03	34.06	
	120.76	113.02	95.60					
<b>16</b>	144.05	142.60		137.37	136.45			
	135.98	135.42	134.13	133.55	131.31			
	130.08	126.42	126.12					
<b>16<sup>1-</sup></b>	136.79	135.47	130.33	127.12	124.53	31.97	29.60	
	123.89	110.86	93.08			17.49	15.97	

<sup>a)</sup> For numbering see formula schemes. — Chemical shifts are given in  $\delta$  values referenced to  $\text{Me}_4\text{Si}$ . — The spectra were  $\{^1\text{H}\}$ -broad-band-decoupled and measured in  $[\text{D}_8]\text{THF}$ .

respectively, c) the through-space electron delocalization between the various components, and d) the size of the  $\pi$  system. These factors, which are intimately linked to one another, allow differentiation between condensed planar and three-dimensional anions. The geometry should influence both the anisotropy and the electronic structure. It has previously been shown that the [2.2]paracyclophanes are relatively rigid systems and therefore the geometry-dependent mutual  $\pi$  interactions are meaningful<sup>4)</sup>. This geometry constraint enables the correlation between the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR chemical shifts and the structure of the anions. The assignments were based on 1D- and 2D-NMR techniques. From the data in Table 1 it can be seen that the anisotropy effects are similar in the neutral and in the charged systems. For comparison, we chose systems in which one deck is composed of either a single ring component or a condensed two ring component and the other deck has a condensed bicyclic system<sup>6)</sup>. As a probe for the anisotropy effect, we chose protons 15-H and 16-H of the benzene ring layer in systems **15**/

**15<sup>1-</sup>**. These two protons are sensitive "observers" sitting in a well-defined position relative to the layer in which the modification of the anisotropy takes place. The other two protons, i.e. 18-H and 19-H of the benzene ring layer, are more remote from this region. One should therefore expect that these protons should not be influenced significantly by the system's structure. The signals of 15-H and 16-H of [2.2](1,4)benzoidenoparacyclophane (**15**) appear at  $\delta = 6.30$ , while those of 18-H and 19-H are registered at 6.35. The same proton signals of the charged system **15<sup>1-</sup>** appear at  $\delta = 5.84$  and 6.29, respectively (Table 1). A neutral pair of compounds which shows the influence of an anisotropic effect is the [2.2](1,4)benzotetralinocyclophane<sup>6)</sup> (**19**) and [2.2](1,4)naphthalenophane<sup>6)</sup> (**4**). From this pair of compounds the anisotropy sustained by a bicyclic system (aromatic and alicyclic) is deduced. The naphthalene moiety of **4** is a  $10\pi$  system as is the delocalized anion **15<sup>1-</sup>**. The signals of 1-H, 1'-H, 2-H, and 2'-H of the alicyclic system **19** appear at  $\delta = 6.38$  and 6.53, respectively (Table 1).



These two pairs of compounds allow a differentiation between anisotropy and the charge transfer (vide infra) between the two decks. The signals of 15-H and 16-H show a significant high-field shift in  $15^{1-}$  (5.84) as compared with the parent neutral system **15** (6.30). Similarly, the corresponding protons of [2.2](1,4)benzonaphthalenophane (**6**) also show a high-field shift (5.50) as compared to [2.2](1,4)parabenzotetralinophane (**19**,  $\delta = 6.53$ ), while the signals of 1-H and 1'-H show almost no high-field shift difference between the two systems, viz.  $\delta = 6.38$  and 6.33. Upon charging of **15**, 18-H and 19-H undergo a slight high-field shift (0.24 ppm, vide infra). The influence of the geometry can thus be deduced by comparing the two stereoisomers  $13^{2-}$  and  $14^{2-}$ . In these systems only two protons on the benzo moiety are available. The *syn* isomer is not expected to exhibit any significant influence of the through-space anisotropy due to the geometry of the molecule. For the same reasons, the *anti* isomer should display a significant through-space high-field shift. Indeed, upon formation of an anion of the *syn* compound,  $13^{2-}$ , the high-field shift of the 10-H and 11-H signals is ca. 0.5 ppm originating from the shielding effect of the negative charge. The same effect is observed upon formation of an anion starting from 1,4-dimethylindene (**11**, Table 1). Protons 10-H and 11-H of the *anti* anion  $14^{2-}$  show signals at 5.19 which are high-field shifted by 1.0 ppm as compared to neutral **14**. This difference of 0.5 ppm between the *syn* and the *anti* isomers originates from a through-space anisotropy effect. One arrives at a similar result by comparing [2.2](1,4)tetralinophane (**20**) with [2.2]naphthalenophane (**4**) on the one hand and between the *syn* and *anti* isomers of **4** on the other hand. Indeed, upon comparing to the fully aromatic **4**, a high-field shift of 0.5 ppm is observed for protons 1-H and 1'-H. The comparison between *syn* and *anti* **4** shows the same trend. Protons 1-H and 1'-H of the two isomers differ in their chemical shifts by 1.0 ppm (Table 1). In general, those protons which do not sense an additional anisotropic effect show a similar chemical shift to the protons of [2.2]paracyclophane (**1**) itself. This is observed for 1-H and 1'-H of the *syn* isomer of **4**. In the 4,5,17,18-tetramethyl derivative of [2.2]benzoindenophane (**16**), the methyl groups on the benzene part provide a probe for the influence of the through-space anisotropy. These groups do not participate in the conjugated aromatic systems and hence are free from charge-transfer effects. As expected, the protons of these methyl groups experience a

greater high-field shift than those of the methyl groups on the indene part. Another approach which enables differentiation between magnetic anisotropy and other effects is to examine  $4n\pi$  paratropic ions. In such systems a low-field shift is expected for the neutral layer in contrast to the high-field shift observed in the  $[4n+2]\pi$  series. Such a system was prepared by an electron transfer process. The neutral hydrocarbon [2.2](1,4)benzo[*g*]chrysenobenzoparacyclophane<sup>25a)</sup> (**12**) was treated with alkali metals to afford the respective dianion, viz.  $12^{2-}$ . Indeed, this  $4n\pi$  dianion exerted a strong anisotropic effect on the benzene layer. The protons of this neutral layer are shifted to an extremely low field for a neutral  $[4n+2]\pi$  system, i.e.  $H_d$  at  $\delta = 10.31$  and  $H_c$  at 8.68 (Table 3). It should be noted that in layered compounds, contrary to perimeter systems, the carbon shifts are also affected by anisotropy effects. Therefore, a second independent set of data can be determined which helps to differentiate between anisotropy and electron transfer phenomena (Table 3).

Table 3.  $^1\text{H-NMR}$  data of  $12^{2-}/2\text{Na}^{+a)}$

10.31 (d, 1H, $J = 6.96$ Hz, $H_d$ , bz.),	8.68 (d, 1H, $J = 6.96$ Hz, $H_c$ , bz.),
7.96 (d, 1H, $J = 6.22$ Hz, $H_b$ , bz.),	6.46 (d, 1H, $J = 6.2$ Hz, $H_a$ , bz.),
4.90 (t, 1H, $J = 6.5$ Hz, p.),	4.76 (t, 1H, $J = 6.68$ Hz, p.),
4.08 (unresolved d, 2H, $J = 6.7$ Hz, p.),	3.93 (d, 1H, $J = 7.2$ Hz, p.),
3.82 (d, 1H, $J = 7.3$ Hz, p.),	3.31 (unresolved d, 3H, $J = 6.9$ Hz, p.),
2.32–2.22 (m, 3H, H br. + p.),	1.98 (unresolved t, 1H, p.),
1.48 (unresolved m, 1.27 (d, 1H, $J = 6.1$ Hz, p.),	0.91 (unresolved m, 3H, H br.),

<sup>a)</sup> Chemical shifts are given in  $\delta$  values referenced to  $\text{Me}_4\text{Si}$ . – Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, bz. = benzene ring protons, p. = polycyclic layer protons, br. = bridge protons. – At 195 K in  $[\text{D}_8]\text{THF}$ .

The ability to differentiate between anisotropy and charge transfer in the anions by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR techniques (Table 1–3) gives us an estimate of the net interaction between the two  $\pi$  systems, as can be seen from Table 1. The chemical shifts of the protons of the benzene deck (1-H and 1'-H of **6** and **19**) do not show meaningful deviations (ca. 0.05 ppm). It therefore follows that those protons which are not located above the other layer are insensitive to anisotropy effects. They can therefore serve as probes for the through-space charge transfer. In anionic systems these protons can serve the same purpose. The effect of the excess charge on the through-space interaction can be examined if the number of electrons ( $10\pi$ ) and hence the anisotropic effect is kept constant. When the proton shifts of 18-H and 19-H of the neutral  $6\pi$  deck of **15** are compared with those of the charged  $6\pi$ – $10\pi$  system  $15^{1-}$ , a shift of 0.2 ppm is observed (Table 1). Following the previously discussed effects, it is clear that this shift is a true effect which should be attributed to the more efficient charge transfer in the  $6\pi$ – $10\pi$  charged systems. This is rationalized in terms of a better donor property of the charged layer while in the neutral systems the decks have similar donor-acceptor properties. This observation was confirmed by similar phenomena noticed in other doubly layered systems, e.g. **16** and **17**. The proton shifts of 18-H and 19-H of the neutral com-

pounds **16** and **17** appear at  $\delta = 6.53$ . The relevant protons of the anions **16**<sup>1-</sup> and **17**<sup>1-</sup> show a high-field shift of ca. 0.2 ppm (6.26 and 6.30, respectively) and thus support our conclusion. The methyl derivatives (**16**, **17**) and the respective anions show the same behavior as the unsubstituted hydrocarbon **15**. We therefore conclude that the geometry of the system does not affect the chemical shift of 18-H and 19-H. An illuminating example is the closely related [2.2]-ferrocenophane **18**. Due to its special through-space charge transfer characteristics, most of the charge is confined to the ferrocene subunit. However, protons 18-H and 19-H of the benzene deck which are located away from the through-space anisotropy region, show a chemical shift of 6.32. This is the shift found in **15**<sup>1-</sup>, an observation complementary to the previous ones where we could show that any additional high-field shift stems from a through-space charge transfer. We could therefore demonstrate in **18** a "flow of charge" across the entire dimeric structure.

In conclusion, then, the two main effects which can be deduced from the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of the above cyclophanes and their anions are the through-space anisotropy and the charge transfer. The latter effect, despite being smaller in magnitude, is meaningful and should be taken into account.

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## Experimental

IR (KBr): Perkin-Elmer 157 G and Perkin-Elmer 1420. — UV (Ethanol): Beckman UV 5230. — MS: MS 9 and MS 30 (AEI Manchester) and CH-7 (Atlas MAT). — Routine NMR: <sup>1</sup>H: EM-360 (Varian), HFX-90 (Bruker); <sup>13</sup>C: XL-100 (25.2 MHz, Varian), all in CDCl<sub>3</sub>/int. TMS; NMR spectra of the anions: see below. — M.p. were taken on a Kofler hotstage and are uncorrected.

Methylolithium (1.55 M in dimethyl ether) and [D<sub>8</sub>]THF (95%) were purchased from Aldrich. The preparation of *syn*-<sup>28,29</sup>(**13**), *anti*-[2.2]indenophane<sup>28,29</sup> (**14**), [2.2]benzoindenophane<sup>30</sup> (**15**), 4,5,17,18-tetramethyl[2.2]benzoindenophane<sup>28</sup> (**16**), and  $\alpha$ -methyl[2.2]benzoindenophane<sup>28</sup> (**17**) has already been described. All hydrocarbons were sublimed under high vacuum prior to anionization. — *1,4-Dimethylindene* (**11**) was also obtained by a published procedure; however, since the experimental details in the literature<sup>31–33</sup> are cursory and spectroscopic data are almost completely lacking, our preparation of this basic hydrocarbon is repeated here: a) *1,4-Dimethylindan-1-one*<sup>31,32</sup>: A solution of 26.6 g (0.21 mol) of  $\beta$ -chloropropionyl chloride and 21.2 g (0.20 mol) of *p*-xylene in 40 ml of CS<sub>2</sub> was added over 1 h to 64.0 g (0.48 mol) of anhydrous AlCl<sub>3</sub> covered with 100 ml of CS<sub>2</sub> in a 1-l three-necked round-bottomed flask fitted with a dropping funnel, condenser, and a mechanical stirrer. After a further 3 h of stirring, the CS<sub>2</sub> was removed under reduced pressure. To the resulting oily remainder was added 250 ml of concd. H<sub>2</sub>SO<sub>4</sub>, and the mixture was heated at 100°C for 40 min. After being cooled to room temp., the mixture was poured onto 1 kg of crushed ice. The product mixture was extracted with methylene dichloride (3 × 500 ml), and the combined organic layers were washed with saturated NaHCO<sub>3</sub> solution (2 × 250 ml) and water, and dried with MgSO<sub>4</sub>. Removal of the solvent afforded a

sticky, yellow solid which was chromatographed (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, R<sub>f</sub> = 0.34) to give 15.0 g (47%) of a pale yellow solid, a portion of which was purified by sublimation (45°C, 0.1 Torr), affording a colorless, crystalline solid; m.p. 76.5–77°C (ref.<sup>32</sup> 76–77°C). — IR:  $\tilde{\nu} = 3015$  cm<sup>-1</sup> (w), 2860 (w), 1705 (s), 1583 (m), 990 (w), 898 (w), 839 (m), 610 (m). — <sup>1</sup>H NMR:  $\delta = 7.20$  (d, *J* = 7.5 Hz, 1H, 5-H), 6.98 (d, *J* = 7.5 Hz, 1H, 6-H), 2.91 (t, *J* = 5.9 Hz, 2H, 3-H), 2.63 (m, 2H, 2-H), 2.58 (s, 3H, 11-H), 2.28 (s, 3H, 10-H). — <sup>13</sup>C NMR:  $\delta = 207.8, 154.5, 135.8, 134.2, 132.6, 129.1, 36.6, 24.2, 17.7, 15.2$ . — UV:  $\lambda_{\max}$  (lg  $\epsilon$ ) = 215 nm (4.328), 252 (4.097), 303 (3.431). — MS (70 eV): *m/z* (%) = 161 (12), 160 (100) [M<sup>+</sup>], 159 (13), 145 (12), 132 (39), 131 (22), 118 (24), 117 (82). — b) *1,4-Dimethylindan-1-ol*<sup>33</sup>: The above indanone (6.11 g, 38.1 mmol) and LiAlH<sub>4</sub> (4.34 g, 0.114 mol) were stirred for 4 h in boiling THF under N<sub>2</sub>. The reaction mixture was cooled to 0°C and water (2.1 ml, 0.117 mol) was added dropwise over 5 min. The mixture was filtered and the solids were washed several times with dry THF. The filtrate was dried with MgSO<sub>4</sub> and evaporated under reduced pressure leaving 5.65 g (34.8 mmol, 91%) of the alcohol as a colorless solid, a portion of which was sublimed (40°C, 0.1 Torr) for characterization: m.p. 67–68°C (ref.<sup>33</sup> 68°C). — IR:  $\tilde{\nu} = 3310$  cm<sup>-1</sup> (br, s), 2965 (m), 2930 (m), 1500 (s), 1455 (m), 1068 (s), 1050 (s), 895 (m), 810 (s). — <sup>1</sup>H NMR:  $\delta = 6.97, 6.91$  (AB-q, *J* = 7.6 Hz, 2H, 5-H, 6-H), 5.23 (dd, *J*<sub>1</sub> = 6.7, *J*<sub>2</sub> = 1.9 Hz, 1H, 1-H), 2.98, 2.71 (m, 2H, 3-H), 2.36, 2.21 (2 × s, 2 × 3 H, 10-H, 11-H), 2.31, 2.01 (m, 2H, 2-H). — <sup>13</sup>C NMR:  $\delta = 142.7, 142.5, 132.2, 131.4, 129.4, 128.2, 75.6, 34.7, 28.8, 18.5, 17.9$ . — UV:  $\lambda_{\max}$  (lg  $\epsilon$ ) = 207 nm (4.033), 214 (3.991), 253 (3.114), 276 (2.681). — MS (70 eV): *m/z* (%) = 162 (55) [M<sup>+</sup>], 161 (34), 107 (100), 145 (22), 144 (41), 129 (28), 128 (13), 115 (13). — c) *1,4-Dimethylindene*<sup>33</sup> (**11**): To a stirred solution of the indanol (5.65 g, 34.8 mmol) in 200 ml of boiling benzene under N<sub>2</sub> was added 50 mg (0.26 mmol) of *p*-toluenesulfonic acid. Stirring was continued for 15 min, and the solution was poured into a separatory funnel containing 100 ml of 1 M NaOH solution. The layers were separated and the organic phase was washed with another portion of 1 M NaOH solution, water, and dried with MgSO<sub>4</sub>. After removal of the solvent and chromatography (SiO<sub>2</sub>, CCl<sub>4</sub>, R<sub>f</sub> = 0.51) of the remaining yellow oil, a colorless oil was obtained (3.70 g, 25.7 mmol, 74%). — IR (film):  $\tilde{\nu} = 3170$  cm<sup>-1</sup> (m), 3140 (m), 2965 (m), 2940 (s), 2920 (s), 1495 (s), 1380 (s), 950 (m), 808 (s), 750 (s), 695 (s). — <sup>1</sup>H NMR:  $\delta = 6.96$  (d, *J* = 7.5 Hz, 1H, 5-H), 6.95 (dt, *J*<sub>1</sub> = 5.6, *J*<sub>2</sub> = 2.0 Hz, 1H, 1-H), 6.88 (d, *J* = 7.6 Hz, 1H, 6-H), 6.50 (dt, *J*<sub>1</sub> = 5.6, *J*<sub>2</sub> = 2.0 Hz, 1H, 2-H), 3.21 (t, *J* = 1.9 Hz, 2H, 3-H), 2.39 (s, 3H, 11-H), 2.28 (s, 3H, 10-H). — <sup>13</sup>C NMR:  $\delta = 143.2, 142.1, 133.1, 130.5, 130.1, 127.7, 127.6, 125.8, 38.2, 18.4, 18.2$ . — MS (70 eV): *m/z* (%) = 144 (74) [M<sup>+</sup>], 143 (16), 130 (12), 129 (100), 128 (41), 127 (51), 115 (12).

*Preparations of Anions. — General Procedure:* Methylolithium (0.5 ml, 1.55 M in ether, 0.78 mmol) was introduced into an evacuated (10<sup>-3</sup> Torr) extended NMR tube capped with a septum, and the ether was completely removed (white crystals). The tube was evacuated for an additional 0.5 h, and 10 to 20 mg (ca. 0.08 mmol) of the cyclophane hydrocarbon, dissolved in 0.6 ml of [D<sub>8</sub>]THF, was added at -78°C. After several minutes, the reaction mixture was allowed to reach room temp., and cooled again only whenever the evolution of gas was too violent. During the charging process of the system, color changes were noted. While the solution of the neutral system is pale yellow, the charged compounds showed an orange color which is observed as soon as the bubbling ceases and the reaction mixture becomes clear.

*Metal Reduction of 12:* Sodium wire was introduced to the upper part of an extended NMR tube containing a solution (ca. 0.01 mmol) of **12** in [D<sub>8</sub>]THF. The solution was frozen and degassed, and the tube sealed under vacuum. The solution was brought into

contact with the metal by turning it upside down. The solution with the first appearing color (red) shows no  $^1\text{H-NMR}$  lines corresponding to a radical monoanion. The second (green) color is that of the dianion.

*NMR spectra of the anions* were obtained on a Bruker SY-200 pulsed FT spectrometer operating at 200.132 and 50.323 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  NMR, respectively, equipped with a pulse programmer and an Aspect-2000 computer (32 K). Field/frequency regulations were maintained by  $^2\text{H}$  locking.

*Quenching of the Anions:* All  $[4n + 2]\pi$  anions were quenched by adding water with a syringe into the solution at  $-78^\circ\text{C}$ . When the reaction mixture had reached room temp., again the  $^1\text{H-NMR}$  spectrum was recorded: in each case the only product observed was the starting material. — The same quenching procedure was carried out with  $\text{D}_2\text{O}$ . In these experiments the respective deuterated compound was again the only detectable product, as shown by  $^1\text{H}$ - and  $^{13}\text{C-NMR}$  spectroscopy. Mass spectrometric analysis shows the  $M + 1$  peak as the main peak for the monoanions, and the  $M + 2$  peak for the bisanions. For the quenching of  $12^{2-}$ , oxygen was bubbled into the anion solution by a syringe at  $-78^\circ\text{C}$  at a slow rate. The deep color disappeared, and the  $^1\text{H-NMR}$  spectrum was recorded: the only product was the neutral substrate **12**.

#### CAS Registry Numbers

**11:** 6974-97-6 /  $11^{1-}$ : 117897-65-1 / **12:** 106975-74-0 /  $12^{1-}$ : 117897-66-2 /  $12^{2-}$ : 117917-39-2 / **13:** 103665-30-1 /  $13^{2-}$ : 117897-61-7 / **14:** 100164-04-3 /  $14^{2-}$ : 117957-29-6 / **15:** 86409-82-7 /  $15^{1-}$ : 117897-62-8 / **16:** 117957-28-5 /  $16^{1-}$ : 117897-63-9 / **17:** 103583-42-2 /  $17^{1-}$ : 117897-64-0 / *p*-xylene: 106-42-3 /  $\beta$ -chloropropionyl chloride: 625-36-5 / 1,4-dimethylindan-1-one: 5037-60-5 / 1,4-dimethylindan-1-ol: 70839-99-5

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