

[2.2](1,4)Benzo[*g*]chrysenoparacyclophane Dianion: A Novel, Paratropic, Double-Layered Carbanion

By Ron Frim, Mordecai Rabinovitz,* Henning Hopf,* and Joachim Hucker

Dedicated to Professor Heinz A. Staab on the occasion of his 60th birthday

An outstanding characteristic of the [2_n]paracyclophanes is the through-space interaction of the two fully conjugated π-electron systems of the separate layers. As demonstrated by the electronic properties of these compounds,^[1] the two layers afford one overall π-electron system.^[2] Very little is known, however, about this interaction in charged paracyclophanes. Diatropic anionic [2.2]paracyclophanes have previously been studied,^[3-7] but no paratropic [2.2]paracyclophane systems have been reported.

We wish to report the first [2.2]paracyclophane in which a 4nπ paratropic dianion interacts with a virtually neutral benzene moiety. In this case the benzene ring acts as an "observer," which is located in a well-defined position and can be used to probe the spatial interactions due to both charge and anisotropy effects.

The system of choice is [2.2](1,4)benzo[*g*]chrysenoparacyclophane dianion **1**²⁻, obtained by metal reduction of [2.2](1,4)benzo[*g*]chrysenoparacyclophane **1** (Scheme 1). To synthesize this hydrocarbon,^[8,9] the phosphonate **2** (R = CH₂PO(OEt)₂), prepared from 4-bromomethyl[2.2]paracyclophane **2** (R = CH₂Br) by the Arbuzov reaction, was coupled with commercially available 9-formylphenanthrene in a Wittig-Horner reaction. The resulting *trans* olefin, formed in 40% yield, was subsequently photocyclized by irradiation (Hanau TQ 150 lamp) in a toluene solution in the presence of iodine, providing the benzochrysenophane **1**^[9] (18%, colorless plates, m.p. = 267–269°, dec.). By an analogous route, the chrysenophane **3**^[9] was prepared (34%, colorless needles, m.p. = 149–152°C) with a Wittig reaction between 4-formyl[2.2]paracyclophane **2**

(R = CHO) and the ylid prepared from 1-naphthylmethylphosphonium bromide serving as the initial step.

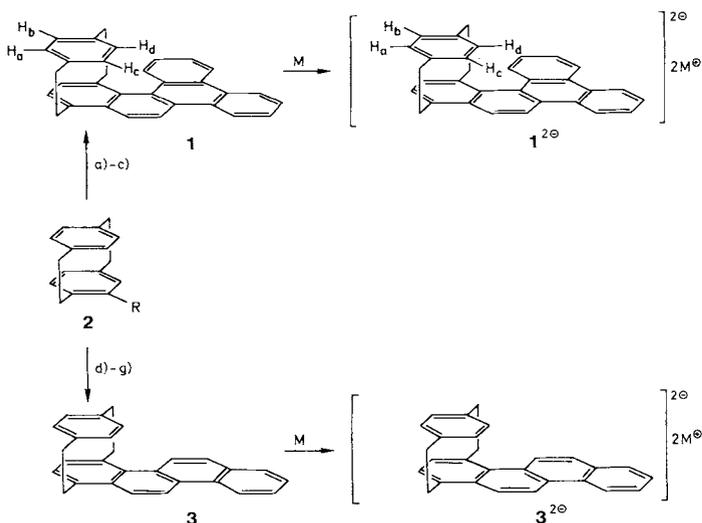
Reaction of **1** with lithium or sodium metal in [D₈]tetrahydrofuran ([D₈]THF) at –78°C afforded deep green solutions, which exhibit well-resolved ¹H- and ¹³C-NMR spectra (Table 1). The ¹H-NMR signals appear in the range of δ = 10.31–0.91 for the sodium salt and 9.81–1.14 for the lithium salt. The bridge protons of **1**²⁻/2Li⁺ give rise to broad signals at δ = 1.14 (2H), 1.65 (2H), 2.82 (2H), and 3.15 (2H). The dianionic nature of **1**²⁻/2Li⁺ and **1**²⁻/2Na⁺ is deduced from the general similarity of their spectra to those of other dianionic polycycles which were studied previously.^[10] Quenching of **1**²⁻/2Li⁺ and **1**²⁻/2Na⁺ with oxygen gave **1** in quantitative yield, proving that no skeletal changes had occurred.

The most revealing part of the spectra of **1**²⁻ (both lithium and sodium salts) consists of four doublets (one proton each), which are attributed to the atoms H_a, H_b, H_c,

Table 1. ¹H- and ¹³C-NMR data for **1** and **1**²⁻ [a].

Compd	¹ H-NMR	¹³ C-NMR
1 [b]	8.95–8.85 (2H, m, p. [c]), 8.79 (2H, d, <i>J</i> = 9.0, p.), 8.64 (1H, dd, <i>J</i> ₁ = 8.2, <i>J</i> ₂ = 1.14, p.), 8.07 (1H, d, <i>J</i> = 8.97, p.), 7.88–7.77 (2H, m, p.), 7.76–7.54 (2H, m, p.), 7.66 (1H, d, <i>J</i> = 7.36, p.), 6.95 (1H, d, <i>J</i> = 7.31, p.), 6.70 (H _m , dd, <i>J</i> ₁ = 7.9, <i>J</i> ₂ = 1.9, bz. [c]), 6.57 (H _b , dd, <i>J</i> ₁ = 7.9, <i>J</i> ₂ = 1.8, bz.), 5.92 (H _c , dd, <i>J</i> ₁ = 7.78, <i>J</i> ₂ = 1.8, bz.), 5.08 (H _a , dd, <i>J</i> ₁ = 7.8, <i>J</i> ₂ = 1.8, bz.), 4.05–3.97 (1H, m, bridge), 3.63–3.09 (5H, m, bridge), 2.72–2.57 (1H, m, bridge), 2.42–2.31 (1H, m, bridge)	139.7, 139.6, 138.8, 137.0, 136.7, 133.8, 132.9, 132.0, 131.3, 131.2, 131.0, 130.7, 130.4, 129.6, 129.2, 128.5, 128.1, 127.8, 127.7, 127.3, 126.8, 126.3, 124.8, 124.4, 124.2, 124.1, 120.2 (arom. C), 39.0, 35.6, 35.5, 34.3 (bridge C)
1 ²⁻ /2Na ⁺ [d]	10.31 (H _d , d, <i>J</i> = 6.96, bz.), 8.68 (H _c , d, <i>J</i> = 6.96, bz.), 7.96 (H _b , d, <i>J</i> = 6.22, bz.), 6.46 (H _m , d, <i>J</i> = 6.2, bz.), 4.90 (1H, t, <i>J</i> = 6.5, p.), 4.76 (1H, t, <i>J</i> = 6.68, p.), 4.08 (2H, unresolved d, <i>J</i> = 6.7, p.), 3.93 (1H, d, <i>J</i> = 7.2, p.), 3.82 (1H, d, <i>J</i> = 7.3, p.), 3.31 (3H, unresolved d, <i>J</i> = 6.9, p.), 2.32–2.22 (3H, m, bridge and p.), 1.98 (1H, unresolved t, p.), 1.48 (1H, unresolved m, bridge), 1.27 (1H, d, <i>J</i> = 6.1, p.), 0.91 (3H, unresolved m, bridge) and protons under THF at 3.67	175.9, 152.7, 148.7, 146.2, 146.0, 143.6, 140.4, 135.2, 134.2, 134.1, 131.8, 131.0, 130.7, 129.4, 127.4, 125.0, 124.3, 124.0, 120.2, 117.4, 117.1, 116.5, 115.2, 114.6, 104.3, 103.5, 100.8 (arom. C), 37.3, 35.5, 33.2, 33.0 (bridge C)
1 ²⁻ /2Li ⁺ [d]	9.81 (H _d , d, <i>J</i> = 6.8, bz.), 8.40 (H _c , d, <i>J</i> = 6.9, bz.), 7.54 (H _b , d, <i>J</i> = 6.5, bz.), 6.49 (H _m , d, <i>J</i> = 7.1, bz.), 5.27 (1H, t, <i>J</i> = 6.5, p.), 5.16 (1H, t, <i>J</i> = 6.7, p.), 4.64 (1H, t, <i>J</i> = 7.2, p.), 4.59 (1H, d, <i>J</i> = 7.3, p.), 4.46 (2H, unresolved d, p.), 4.01 (1H, d, <i>J</i> = 6.6, p.), 3.67 (2H, under solvent signals, p.), 3.15 (1H, unresolved m, bridge), 2.29 (1H, d, <i>J</i> = 8.0, p.), 2.82 (1H, unresolved d, bridge), 2.16 (1H, unresolved t, p.), 1.65 (1H, unresolved m, bridge), 1.53 (1H, d, <i>J</i> = 6.2, p.), 1.30 (1H, unresolved m), 1.14 (2H, unresolved m, bridge)	175.5, 151.3, 146.8, 144.8, 144.5, 142.9, 140.6, 133.8, 132.2, 131.6, 130.6, 129.9, 126.6, 125.2, 124.7, 124.1, 123.6, 120.7, 117.4, 116.9, 115.8, 113.7, 104.6, 102.0, 95.0, 70.7 (arom. C), 37.1, 35.5, 33.5, 33.1 (bridge C)

[a] Chemical shifts (δ values) are given relative to TMS (int. standard); coupling constants in Hz. The chemical shifts were calibrated by the THF line at δ = 3.67 ppm. The ¹³C-NMR spectra are {¹H}-broadband decoupled and were measured in [D₈]THF. [b] At room temperature. [c] p = protons of the polycyclic layer; bz. = protons of the benzene ring. [d] At 195°K.



Scheme 1. a) *n*BuLi, THF; b) 9-formylphenanthrene; c) *hv*, I₂, toluene; d) NaH, THF; e) α-naphthyl-CH₂PPh₃Br; f) **2** (R = CHO), THF; g) *hv*, I₂, toluene.

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and H_d of the benzene ring, as deduced from double resonance experiments (Table 1). A conspicuous feature of these spectra is the appearance of extremely low-field bands assigned to H_c and H_d. These signals are registered at $\delta = 10.31$ and 8.68 for $1^{2\ominus}/2Na^{\oplus}$, a very low field indeed for a neutral benzene moiety. Similar reduction experiments carried out on **3** resulted in only very broad ¹H-NMR signals in the same region as for $1^{2\ominus}$, and no well-resolved spectrum could be obtained. Quenching of $3^{2\ominus}$ with O₂ afforded the neutral hydrocarbon **3** in good yield. Prolonged reaction of **1** and **3** with the alkali metals led to cleavage of the cyclophane bridge, as shown by quenching experiments. A similar cleavage was previously observed by Müllen et al. in the case of the nonparatropic anthracenophane dianion.^[4]

When a double-deck anion such as $1^{2\ominus}$ is formed, the following spectral phenomena are expected: (a) a high-field shift of the protons of the charged polycyclic moiety due to the negative charge and even more so to the formation of a paratropic $4n\pi$ species;^[11, 12] (b) a shift of the signals of the neutral benzene ring due to the through-space interaction between the two conjugated layers.

As expected, the protons of the charged polycyclic layer of $1^{2\ominus}$ show pronounced high-field shifts. The peculiar and unusually pronounced low-field shift of the uncharged benzene ring layer is caused by the through-space interaction between the two π -electron systems and is attributed to the anisotropy of the $4n\pi$ doubly charged polycyclic moiety of $1^{2\ominus}$. The extremely low-field signals of one proton of the benzene moiety ($\delta = 10.31$ for $1^{2\ominus}/2Na^{\oplus}$) show that this interaction is very significant. In the neutral hydrocarbon **1** the benzene protons H_c and H_d are shifted to higher field (Table 1). H_d is presumably shifted more than H_c,^[2a] while H_a and H_b appear in the "normal" aromatic region of the ¹H-NMR spectrum. In dianion $1^{2\ominus}$, owing to its different electronic structure and anisotropy, the same arguments should be reversed. The protons H_c and H_d are more influenced by the paratropicity of the charged $4n\pi$ layer, and the H_d signal is most strongly shifted.

The ¹³C-NMR spectrum for the aromatic carbons of $1^{2\ominus}/2Li^{\oplus}$ and $1^{2\ominus}/2Na^{\oplus}$ are in the range of $\delta = 70$ – 175 versus a range of $\delta = 120$ – 140 for **1** (Table 1). The center of gravity of the ¹³C-NMR spectra of $1^{2\ominus}/2Li^{\oplus}$ and $1^{2\ominus}/2Na^{\oplus}$ did not change significantly. This may arise from the opposing effects of the charge and the anisotropy already mentioned. The failure in observing [2.2](1,4)chrysenoparacyclophane dianion $3^{2\ominus}$ arises not only from the cleavage of the bridge but also is due to the nature of the dianion.^[13] It has been previously demonstrated that the appearance and line shape of polycyclic $4n\pi$ conjugated dianions is a function of several parameters.^[12] Similarly, chryseno dianion affords a much less resolved ¹H-NMR spectrum than benzo[g]chryseno dianion.^[10]

From the above it can be concluded that in the first paratropic three-dimensional $4n\pi$ system, $1^{2\ominus}$, a new aspect of the through-space interaction involves a charged polycyclic layer and a neutral benzene layer, reminiscent of the paracyclophane donor-acceptor systems studied by Staab et al.^[14]

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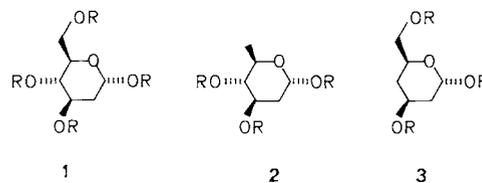
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Synthesis of 2-Deoxy Sugars**

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2-Deoxy sugars, particularly the compounds **1**–**3** (R = H, Ac), which are required for the formation of compactin,^[1] olivomycin,^[2] and milbemycin,^[3] are important



targets of natural product synthesis. However, the syntheses of 2-deoxy sugars reported to date have been laborious; they could be prepared, for example, from glycosyl halides by reductive elimination to give the glycals followed by solvomercuration and subsequent demercuration.^[4] We have now developed a new method by which glycosyl halides can be converted directly into the 2-deoxy sugars. The procedure is based on the rapid and irreversible migration of the acyloxy group in the β -acyloxyalkyl radical **4** to give the acyloxyalkyl radical **5**.^[5]

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