

# Reduction of polycyclic hydrocarbons with potassium–graphite intercalate $KC_8$

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## Abstract

Aromatic polycyclic hydrocarbons were reduced by potassium–graphite intercalate  $KC_8$  to give  $4n\pi$  anti-aromatic systems. The reduction process was followed by nuclear magnetic resonance (NMR) and was compared to the reduction process with potassium metal. The latter allowed insight into the reaction mechanism of  $KC_8$ .

**Keywords:** Polycyclic hydrocarbons; Graphite intercalate; Potassium; Intercalation

## 1. Introduction

1954 Rüdorff and Schulze [1] described, using X-ray diffraction, the structure of the first-stage intercalation compound of potassium and graphite,  $KC_8$ : the graphite layers are planar and congruent to one another and the potassium atoms are localized above the centers of the hexagons in four possible successive locations noted  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , as described in Fig. 1. The intercalate of the first stage,  $KC_8$ , is bronze colored, which results from the penetration of the potassium atoms between the graphite layers. Hennig [2] in 1965 recognized that the color of the intercalate indicates the extent of charge transfer from the potassium atoms to the graphite.

The reaction mechanism accepted today for the reductions by  $KC_8$  was described by Ebert et al. [3,4a]. Their model for

the reaction of  $KC_8$  was deduced from the reaction of  $KC_8$  with water. According to this mechanism, two species of potassium,  $K^0$  and  $K^+$ , having a fast electron exchange in the EPR time scale, exist in the space between the graphite layers of the first-stage intercalate  $KC_8$ . Part of the potassium atoms, those closer to the edge of the intercalate, which are more readily available for reaction and which have a reduction potential close to that of metallic potassium, will react according to the known chemistry of free potassium. The reduction potential of  $KC_8$  will then decrease and the chemistry of the intercalate will change as a result. A different mechanism was suggested by Rashkov et al. [4b] for the reduction of aromatic compounds with  $KC_{24}$ . However, the more recent Ebert mechanism seems more plausible.

Potassium metal reduces polycyclic hydrocarbons and forms  $\pi$ -conjugated anions, very often  $4n\pi$  systems — showing paratropicity. The paratropic shift in nuclear magnetic resonance (NMR) of the peripheral protons and the skeleton carbons in polycyclic systems have become a criterion, sometimes the only one, to estimate the anti-aromatic character of certain species [5–7]. The relationship between the electronic structure of polycyclic dianions and their NMR spectra was a subject of research in the last decade [8,9]. Minsky et al. [10] demonstrated the linear dependence existing between the paratropic shift, i.e., the extent of the anti-aromatic character and the energy gap, between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the dianions. The narrower the energy gap, the greater becomes the paratropic shift and the extent of the anti-aromaticity.

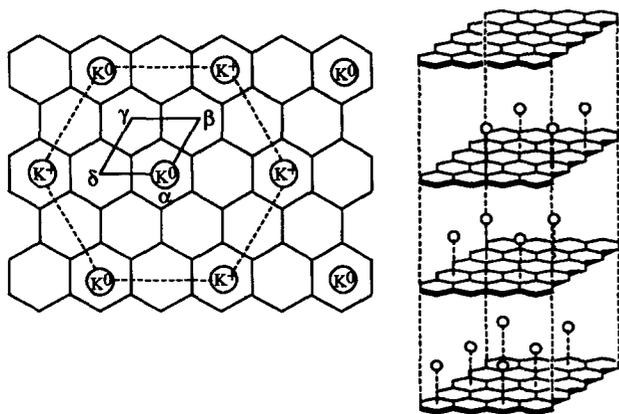


Fig. 1. Structure of the  $KC_8$  intercalate.



Scheme 1. The ion-pair equilibrium.

In the proton NMR spectra of dianions, the lineshape is yet another aspect to be considered. The extent of line broadening, in some cases up to the complete disappearance of the spectra, is linked to the concentration of paramagnetic species in the solution [11]. Thus, line broadening is also dependent on the HOMO–LUMO energy gap. Minsky et al. [10] have shown the influence of the HOMO–LUMO energy gap in polybenzenoid dianion systems with  $4n\pi$  electrons. On the basis of their findings, the polycyclic dianions were divided into three groups according to their gap  $\Delta E$  derived from  $(\omega\beta)$  HMO calculations. In the first group are the dianions with  $\Delta E > 0.4\beta$ ; the second group is composed of the dianions with  $0.2\beta < \Delta E < 0.4\beta$ ; and the third group of the dianions with  $\Delta E < 0.2\beta$ . For the first group,  $^1\text{H}$  NMR was obtained whatever the conditions, i.e., temperature, solvent and the counter-ion. For the third group, no  $^1\text{H}$  NMR spectra were obtained under any conditions. The second group of dianions exhibited a dependence of its NMR spectra on the conditions, i.e., the lineshapes in the proton spectra were dependent on the counter-cation, solvent and temperature. Based on these findings, it was assumed that an equilibrium exists between the triplet and the singlet states in the dianions, dependent on the HOMO–LUMO energy gap [10]. With  $\Delta E > 0.4\beta$ , the equilibrium is shifted towards the singlet state, but when  $\Delta E > 0.2\beta$ , the triplet electronic state is predominant. In the second group of dianions ( $0.2\beta < \Delta E < 0.4\beta$ ), the equilibrium depends on the conditions, which influence the ion pair equilibrium in the solution [12–15]. However, the ion solvation equilibrium is a continuum of states between two extremes, one of which is a free and the other a contact ion pair (Scheme 1). Thus, the extent of  $\Delta E$  is dependent on the ion pair equilibrium:

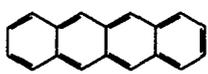
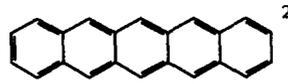
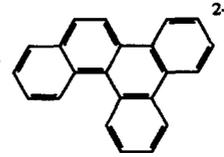
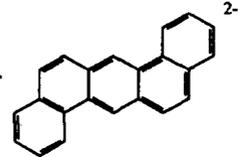
Until now, NMR spectra were obtained for polycyclic systems reduced by sodium or lithium, but, with potassium as a reducing agent, only very few systems gave well-resolved NMR spectra. Thus, in view of the special structure, the electronic properties and recent studies [16,17] on the synthetic applications of the first-stage intercalate,  $\text{KC}_8$  seemed to be the reagent of choice for the reduction of conjugated polycyclic  $\pi$  systems in order to obtain better understanding of the phenomena, as described by Minsky et al. [10].

## 2. Results and discussion

The polycyclic conjugated  $\pi$  systems for this research were chosen to be representative of a wide range of compounds. The benzenoid systems also had to be large enough to exclude penetration into the intercalate [17,18]. The conditions for

all the reduction reactions with  $\text{KC}_8$  were identical and the whole reaction was carried out in the NMR tube. The samples were prepared by transferring a suspension of  $\text{KC}_8$  in *n*-pentane, evaporating the solvent and adding the hydrocarbon to be reduced, in deuterated tetrahydrofuran ( $\text{THF-}d_8$ ). The polycyclic systems that were reduced and produced a well-resolved  $^1\text{H}$  NMR spectrum are: naphthalene (1), pentacene (2), benzo[*g*]chrysene (3), 12,14-di-*tert*-butylbenzo[*g*]chrysene (4), 1,2,5,6-di-benzanthracene (5) (Table 1).

Table 1  
NMR parameters of the reduction products of the polycyclic systems<sup>a</sup>

Charged system	$\text{KC}_8$ (K)	K (K)	Center of gravity (ppm)		Total paratropic shift (ppm)
			Neutral	Dianion	
$1^{2-}$ 	295	295	8.01	4.07	3.94
$2^{2-}$ 	295	295	8.08	4.95	3.13
$3^{2-}$ 		235	8.22	3.38	4.84
$4^{2-}$ 	295	295	8.01	4.76	3.25
$5^{2-}$ 	245	245	8.14	1.39	6.75

<sup>a</sup> Although we have obtained a well-resolved  $^1\text{H}$  NMR spectrum at 295 K for the reduction product  $4^{2-}/2\text{K}^+$ , either using  $\text{KC}_8$  or potassium,  $^1\text{H}$  NMR spectra were obtained for  $3^{2-}/2\text{K}^+$  only at 233 K and only with potassium as a reducing agent.

Table 2  
Dihedral angles of the bay in **3** and **4**<sup>a</sup>

System	$\Delta E$ (eV)	Dihedral angles of the bay carbons ( $^\circ$ )					
		C1–C1A–C1B–C14A			C1A–C1B–C14A–C14		
		MMX	MNDO	X-ray	MMX	MNDO	X-ray
<b>3</b>	7.55	24.73	19.68	19.19	25.37	16.43	19.38
<b>3</b> <sup>2-</sup>	4.84		10.56			23.60	
<b>4</b>	7.44	19.71	19.66	20.63	40.65	37.46	31.69
<b>4</b> <sup>2-</sup>	4.92		7.10			49.22	

<sup>a</sup> All semi-empirical calculations were carried out using the MNDO-PM3 method and a FORCE calculation was done to verify minimum energy. The PCMODEL used for the molecular calculations cannot handle delocalized charge, so no calculations on the dianions were done with this method.

Though  $\text{KC}_8$  was meant to be the reducing agent instead of potassium metal, we have also managed to reduce all the above hydrocarbons using potassium. This was feasible because of the high vacuum system employed in the preparation of the samples. Reduction was obtained with a potassium mirror, the solvent (THF-*d*<sub>8</sub>, dried on potassium–sodium alloy) was vacuum transferred, and the NMR tube was sealed in high vacuum. The results of the reduction with  $\text{KC}_8$  and potassium metal are summarized in Table 1. The fact that we managed to reduce the polycyclic systems using

both reagents helped us in understanding the mechanism of reduction by  $\text{KC}_8$ .

### 2.1. Naphthalene dianion ( $\text{I}^{2-}$ ) and pentacene dianion ( $\text{2}^{2-}$ )

Both these dianions have an energy gap  $\Delta E$  larger than  $0.4\beta$ ; thus a well-resolved  $^1\text{H}$  NMR spectrum was obtained at room temperature (295 K) with either  $\text{KC}_8$  or potassium as the reducing agent.

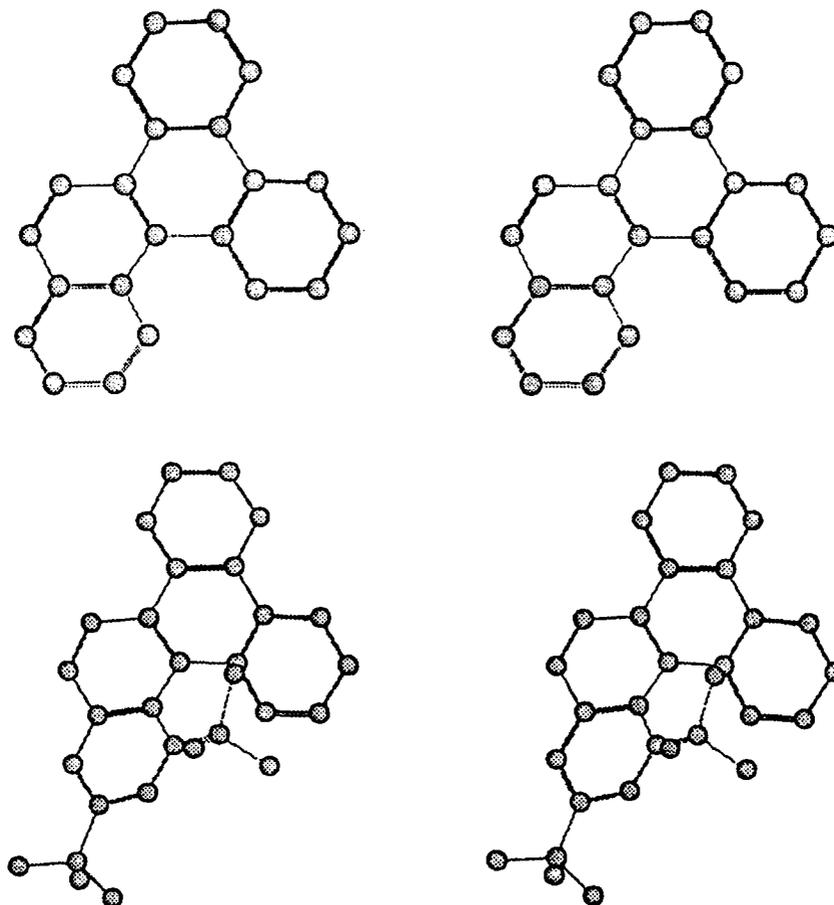


Fig. 2. Stereoscopic drawings of the helicene conformation of **3** and **4** as obtained from MNDO calculations.

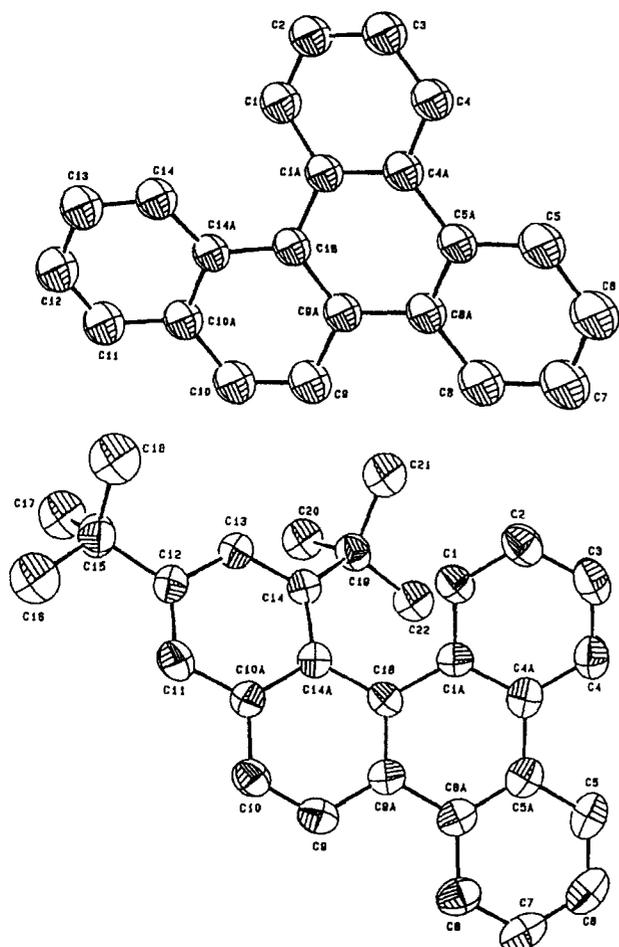


Fig. 3. Helicene conformation of **3** and **4** as obtained from X-ray diffraction results.

### 2.2. 1,2,5,6-Di-benzanthracene dianion ( $5^{2-}$ )

In this case the dianion HOMO–LUMO energy gap is  $0.251\beta$  (second group of dianions), and the lineshape of the proton NMR varies with the temperature. A well-resolved  $^1\text{H}$  NMR spectrum was obtained only at a low temperature (245 K), with  $\text{KC}_8$  or potassium.

### 2.3. Benzo[*g*]chrysene dianion ( $3^{2-}$ ) and 12,14-di-*tert*-butylbenzo[*g*]chrysene dianion ( $4^{2-}$ )

These two systems were of unique interest due to their twisted-helicene type of structure. The neutral compounds **3** and **4** were synthesized in two main steps: a Wittig reaction [19] followed by a photochemical ring closure [20]. From MMX [21] and MNDO [22] calculations, both **3** and **4** have a helicenic conformation (Table 2 and Fig. 2). Our calculations are confirmed by the X-ray diffraction results of the neutral compounds (Table 2 and Fig. 3). The influence of the spatial structure of rigid polybenzenoid charged systems was recently studied by Frim et al. [19] who determined the link between the extent of the twist angle of the bay carbons of charged helicenes and the extent of their anti-aromaticity.

For these helicenic compounds, we cannot rely on  $\omega\beta$  HMO calculations of  $\Delta E$  [19]: e.g., the  $\Delta E$  calculated for  $3^{2-}$  using  $\omega\beta$  HMO is  $0.165\beta$  [19] and we should have not obtained an NMR spectrum. This does not at all account for the experimental results shown in Table 1. A well-resolved proton NMR spectrum at room temperature for the reduction product  $4^{2-}/2\text{K}^+$  was obtained, using either  $\text{KC}_8$  or potassium; the  $^1\text{H}$  NMR spectrum was obtained for  $3^{2-}/2\text{K}^+$  only at low temperature (235 K) and only with potassium as a reducing agent.

On the basis of these results, we can account for the reaction mechanism of  $\text{KC}_8$ . As there is no difference whether  $\text{KC}_8$  or metallic potassium is used as reducing agent, or at what temperature the well-resolved proton NMR spectra are obtained, and as the solvent is identical in all the experiments, we can deduce that the counter-ion must be identical for all the dianions and that the counter-ion when using  $\text{KC}_8$  as a reducing agent is also  $\text{K}^+$ . Consequently, our results support the Ebert model [3,4a] as the general model for the reaction mechanism of  $\text{KC}_8$ .

## 3. Experimental

All the NMR analyses were performed on the Bruker WP-200 and AMX-400 pulsed FT spectrometers operating for  $^1\text{H}$  at 200.132 and 400.13 MHz, respectively. X-ray diffraction spectra were obtained on a Philips PW 1100/20 automatic diffractometer.

### 3.1. Materials

Potassium (Aldrich) was kept in paraffin oil and shortly before the reaction it was washed with petroleum ether (b.p. 60–80 °C). Commercially available THF- $d_8$  (Aldrich) was dried over potassium–sodium alloy under vacuum. The graphite (BDH, Synthetic) was kept in a closed vessel under argon. All hydrocarbons were available commercially (Aldrich) except benzo[*g*]chrysene (**3**) and 12,14-di-*tert*-butylbenzo[*g*]chrysene (**4**) which were prepared according to known procedures [19,20].

### 3.2. General procedure for reduction

The conditions in all the reduction reactions, using  $\text{KC}_8$ , were identical and the whole reaction was carried out in an NMR tube. The samples were prepared by transferring a suspension of  $\text{KC}_8$  in *n*-pentane to an NMR tube previously flame-dried. The solvent was then evaporated in vacuum. The hydrocarbon to be reacted, dissolved in deuterated tetrahydrofuran (THF- $d_8$ ), was then injected by a syringe and the tubes were then flame-sealed. All the reduction products, with  $\text{KC}_8$  or with potassium metal, were then quenched with oxygen and afforded the starting hydrocarbons.

The reduction of the hydrocarbons with potassium was carried out in the following manner. First, the solid hydro-

carbon was inserted into the NMR tube, then the tube was pumped and flame-dried. The potassium metal was distilled several times under vacuum before distillation into the tube. The deuterated THF was vacuum-transferred to the NMR tube which was then flame-sealed under vacuum. The reduction was followed by NMR spectroscopy.

### 3.3. Preparation of $KC_8$ -pentane suspension and the reduction of the hydrocarbon

The reagent ( $KC_8$ ) was previously prepared with the hydrocarbon according to the known procedure [17]. The reaction flask was then cooled to 0–5 °C with an ice–water bath and 5 ml of dried n-pentane were added. To an NMR tube, cooled to –78 °C with acetone–dry ice bath, with two 6 mm glass inlets fitted with septa and connected to a vacuum line, the  $KC_8$ -n-pentane suspension (1 ml) was injected. The n-pentane was then removed under vacuum and 10 mg of the hydrocarbon dissolved in 0.7 ml of dried THF- $d_8$  were injected into the NMR tube. The NMR tube was then flame-sealed under vacuum.

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