Charge-Transfer Complexes of Indenophanes with \( \pi \)-Acceptors

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The charge-transfer (CT) spectra of the \( \pi \)-complexes formed by a number of \( \pi \)-acceptors with several indenophanes as well as indene as a model compound have been measured in methylene chloride at 20°C. Association constants and transition energies of these complexes as well as ionization potentials of the \( \pi \)-donors have been determined. The data obtained indicate the existence of transannular electronic interactions in the indenophane nucleus. Furthermore, the pseudo-para and meta[2.2]indenophane isomers (3 and 4) show a large difference in their \( \pi \)-base strength. A good linear relationship has been observed between the association constants and \( \lambda_{\text{max}} \) of the long wavelength CT bands for the \( \pi \)-complexes of these \( \pi \)-donors with both tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ). All CT complexes studied have a 1:1 stoichiometry.

(Keys: Charge-transfer spectra; \( \pi \)-Complexes; Indenophanes)

Charge-transfer-Komplexe aus Indenophanen und \( \pi \)-Akzeptoren

Die Charge-transfer-Spektren (CT-Spektren) von \( \pi \)-Komplexen aus Indenophanen bzw. der Modellverbindung Inden und verschiedenen \( \pi \)-Akzeptoren wurden in Methylenchlorid bei 20°C bestimmt. Die Assoziationskonstanten und Übergangsentnergien dieser Komplexe sowie die Ionisationspotentiale der \( \pi \)-Donatoren wurden ermittelt. Die Daten sprechen für das Vorliegen transannularer elektronischer Wechselwirkungen im Indenophan-System. Die isomeren pseudo-para- und -meta[2.2]indenophane 3 und 4 unterscheiden sich in ihrer \( \pi \)-Basizität deutlich. Es besteht eine gute lineare Korrelation zwischen den Assoziationskonstanten und \( \lambda_{\text{max}} \) der langwelligen CT-Banden der verschiedenen \( \pi \)-Donatoren mit Tetracyanoethylen (TCNE) und 2,3-Dichlor-5,6-dicyano-p-benzoquinon (DDQ). Alle untersuchten CT-Komplexe besitzen 1:1-Stöchiometrie.
Introduction

The $\pi$-donor properties of indene (1) are established from its ability to form complexes with hexacarbonyl chromium, 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone. It has been reported that in the (indene) Cr(CO)$_3$ complex the benzene ring is complexed with Cr(CO)$_3$ and not the five-membered ring. Also, this complex is less stable relative to tricarbonyl chromium complexes of [2.2]paracyclophanes.

A number of novel indenophanes (2-4, Fig. 1) have been prepared recently. The objective of the present study was to compare the importance of transannular electronic interactions on the $\pi$-basicity of this interesting class of compounds with those of indene, as a model compound, and 4,5,12,13-tetramethyl[2.2]paracyclophane (5, Fig. 2), as a highly basic $\pi$-donor. In addition, we wished to apply the tool of CT complexation to differentiate between the $\pi$-base character of the two isomeric forms 3 and 4. The relative base strength of the $\pi$-donors 1-4 were

\[ \text{TCNE} \quad \text{TCNQ} \quad \text{CNIND} \]

\[ R^1 = R^2 = \text{Cl}; \ CHL \]
\[ R^1 = R^2 = \text{Br}; \ BRL \]
\[ R^1 = \text{Cl}, R^2 = \text{CN}; \ DDQ \]

Fig. 1