Synthesis of a New Polyconjugated System: Polycyclophane

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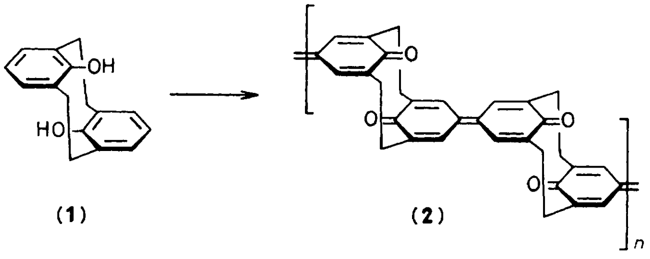
A new polyconjugated system in which the electron delocalization occurs through repeated metacyclophane and diphenoquinone moieties was obtained by an oxidative carbon–carbon coupling of 8,16-dihydroxy-[2.2]metacyclophane.

The concept of a polyconjugated system (PCS) has been one of the most important requirements for the realization of polymers with unusual properties, such as high thermal stability, rigidity, catalytic activity, or electrical conductivity.[1] Until very recently most of the PCS's have been based on electron delocalization through transverse overlaps of π-electron orbitals, as has been demonstrated with polyacetylene.[2] On the other hand metallic or superconductive charge-transfer complexes like tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) or tetramethyltetraselenafulvalene-perchlorate (TMTSF-ClO_4) have longitudinal overlap of the π-electron wave functions along a stacking axis of molecules.[3] In this sense cofacially-stacked polyphthalocyanines[4] seem to be the only polymer-counterparts of such molecular charge-transfer complexes.

In this communication we report on the design and synthesis of a new PCS which mimics the charge-transfer complexes having electron delocalization facilitated by longitudinal overlap of the π-electron orbitals. Cyclophane compounds were adopted as a basic constituent because they have a strong longitudinal π-electron interaction between the two benzene rings separated by a very short interplanar distance (*e.g.*, 3.1 Å for [2.2]paracyclophane[5]) and because they can have an intramolecular mixed-valence interaction[6,7] which is a necessary condition for metallic conductivity in molecular conductors. To test the polycyclophane synthesis we used 8,16-dihydroxy-[2.2]metacyclophane [DHMCP, (**1**)] as a starting monomer which was supposed to polymerize *via* a diphenoquinone-type linkage. This polymerization procedure is analogous to the oxidative carbon–carbon coupling of 2,6-disubstituted phenols which has been used by Hay *et al.* for the preparation of various monomeric and polymeric diphenoquinones.[8,9]

Compound (**1**) was prepared using a procedure described by Tashiro *et al.*[7] Colourlesss prisms of (**1**) were crystallized from hexane : benzene (1 : 1) in total yields of *ca.* 4%; i.r. and ^{1}H n.m.r. spectra were used to confirm the molecular structure. The polymerization was carried out in a chloroform solution of (**1**) in the presence of an excess of $FeCl_3$ catalyst. Bright orange–red powders were quantitatively precipitated after stirring of the solution (*ca.* 1 h, 0—5 °C). The product did not dissolve in solvents and did not melt without decomposition, indicating the formation of high molecular wieght compounds. Thus the polymerization proceeded very readily, but, if the reaction was carried out under reflux, the precipitated product assumed a brown–black tint and its i.r. absorption spectrum suggested that cleavage at the methylene bridges of the



(**1**) (**2**)

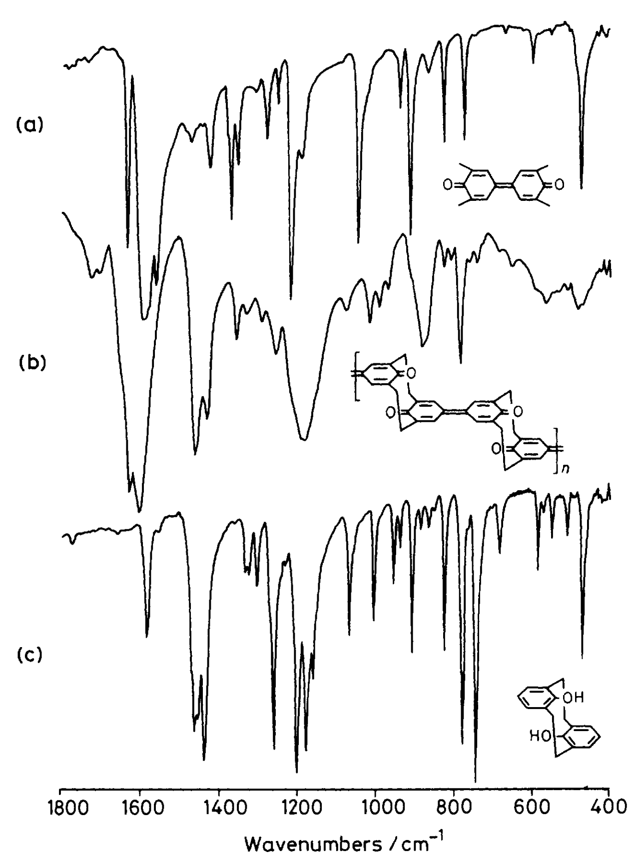


Figure 1. I.r. absorption spectra of 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (a), poly(metacyclophane) (b), and 8,16-dihydroxy-[2.2]metacyclophane (c).

cyclophane skeleton had occurred. A lutidine–CuCl catalyst which has been used for the polymerization of poly(phenylene oxide)[10] was also examined but it did not give any polymerized products.

The elemental analysis data were C = 79.3 and H = 6.0% by weight which agreed well with calculated values (C = 81.3 and H = 5.1%) for structure (**2**). The i.r. absorption spectrum of the product [Figure 1(b)] was characterized by a strong and exceptionally low C=O stretching band[11] at about 1600 cm^{-1}, which offers evidence for the existence of a diphenoquinone skeleton structure [Figure 1(a)]. In addition, from comparison of the spectrum of (**2**) with that of (**1**), the former retains C–H (methylene bridge) stretching bands at about 2900 cm^{-1} but lacks out-of-plane bending bands (700—800 cm^{-1}) of three protons adjacent to the aromatic ring. All these data consistently confirm that (**1**) was polymerized *via* C–C coupling to form the desired poly(metacyclophane) with diphenoquinone linkage [PMCP, (**2**)].

Thermogravimetric analysis in a nitrogen atmosphere showed that (**2**) is an excellent high-temperature polymer with a decomposition temperature of 420 °C and char yields of about 40% at 1000 °C. The electronic absorption spectrum of (**2**) was remarkably similar to that of 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone but red-shifted by about 70 nm; the π–π^* absorption peaked at 470 nm with an absorption edge at 700 nm (1.8 eV). The electrical conductivity of a pressed pellet of the pristine polymer was about 10^{-9} S cm^{-1} at room temperature. The absorption edge and the electrical conductivity are almost the same order of magnitude as those of *cis*-polyacetylene,[12] which suggests that (**2**) has the same degree of electron delocalization as the latter. Preliminary studies on the chemical doping of (**2**) were carried out with H_2SO_4 vapour and an enhancement of the room-temperature conductivity by about five orders of magnitude was observed. The conductivity is thought to be limited by the small amount of the dopant moiety in the polymer owing to the relatively high crystallinity of (**2**).

In conclusion, an oxidative C–C coupling of (**1**) under mild conditions yielded a new polyconjugated system which has repeated metacyclophane and diphenoquinone moieties as its skeleton.

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