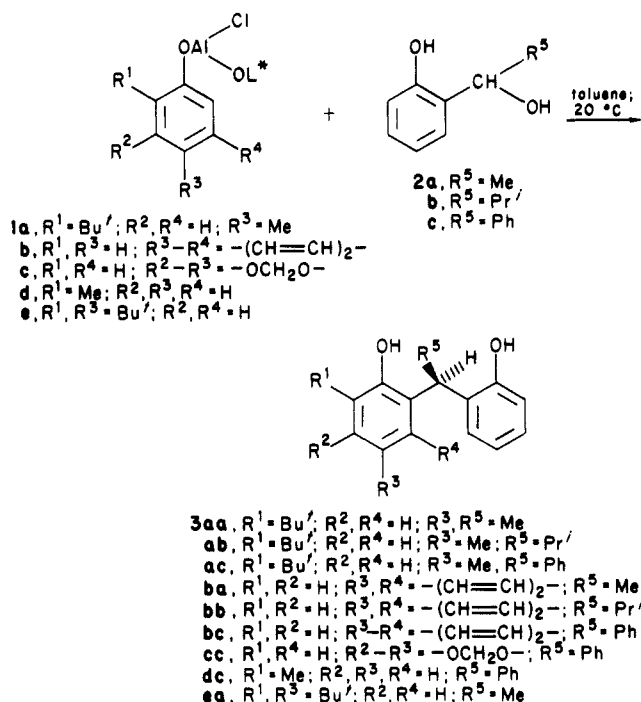


Table I
Asymmetric Synthesis of Binuclear Oligomers 3^a

entry	reactants	product	time, days	% yield ^b	$[\alpha]^{20}_D$, ^c deg	ee, ^d %
1	1a + 2a	3aa	2	76	-7.2	28
2	1a + 2b	3ab	5	57	+2.1	12
3	1a + 2c	3ac	2	60	-14.4	41
4	1b + 2a	3ba	5	39	-6.0	28
5	1b + 2b	3bb	5	45	+3.2	18
6	1b + 2c	3bc	5	49	-8.8	36
7	1c + 2c	3cc	1	85	-6.0	33
8	1d + 2c	3dc	2	74	-4.1	29
9	1e + 2a	3ea	2	88	-8.7	37

^a All these reactions were carried out in 0.1 M toluene solution at $20 \pm 0.5^\circ\text{C}$. ^b Isolated yield of >98% pure material. All compounds gave appropriate analytical and spectral data. ^c c 0.5 (ethanol). ^d Determined by 270 MHz ^1H NMR in CDCl_3 using $\text{Eu}(\text{hfc})_3$ chiral shift reagent.

Scheme I^a

^a L* = (-)-menthyl.

to 1 M did not improve the degree of induction and cooling from +20 to -20 $^\circ\text{C}$ resulted in slightly reduced stereoselection.

In summary, we believe that this work, featuring a unique enantiocontrolled alkylation of phenols, may provide useful insight and applicability in the area of asymmetric synthesis of optically active ortho-substituted novolac-type oligomers. Extension of this reaction to the synthesis of higher oligomers is under way, and we are increasing our efforts to obtain higher enantiodifferentiating efficiencies than those reported herein.

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- $[\alpha]^{20}_D$ -49° (c 10, ethanol), available from Farmitalia-Carlo Erba, Italy.
- 1 M solution in hexane, available from Aldrich Chemical Co.

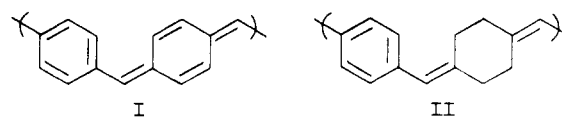
Communications to the Editor

Synthesis of a New Conjugated Hydrocarbon Polymer

The search for electrically conducting organic polymers has expanded enormously since the preparation of polyacetylene film¹ and the subsequent discovery² that its electrical conductivity, on doping with various oxidants, can be varied over a range of 11 orders of magnitude to a maximum value of $560 \Omega^{-1} \text{cm}^{-1}$. The few intervening years have seen the synthesis of other conducting organic polymers such as poly(phenylacetylene),³ poly(methylacetylene),⁴ poly(2,5-thiophenediyl),⁵ poly(propargyl halides),⁶ poly((trifluoromethyl)acetylene),⁷ polypyrrole,⁸ poly(phenylene sulfide),⁹ poly(*p*-phenylene),¹⁰ and poly(phenylenevinylene).¹¹

We now report the synthesis of poly(1,4-xylylidene-2',5'-cyclohexadien-1',4'-ylidene) (I) by the Wittig reaction.

We had previously reported the synthesis of the model compound, 1,4-cyclohexadienylbis(benzylidene) by the same route.¹²



Polymer I represents a new class of conjugated polymers in which benzenoid rings alternate with quinonoid rings. We believe that this molecular system should be characterized by a high degree of electron delocalization because it can be described in terms of two equivalent resonance forms each of which contains relatively high-energy quinonoid rings:

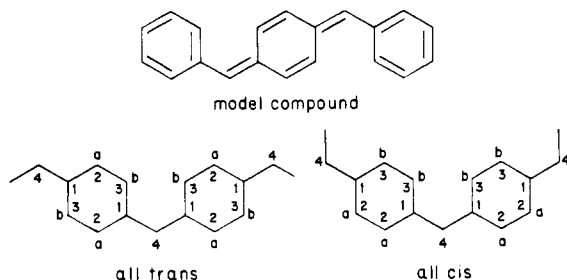


We have prepared I by the Wittig reaction on equivalent amounts of phenyllithium, 1,4-cyclohexanedione, and *p*-xylylenebis(triphenylphosphonium chloride) in *N,N*-dimethylformamide (DMF) for 5 days at a final temperature of 145 °C. The solid product (20% conversion) was filtered and washed with alcohol to give a lemon green, flaky solid, mp 265–267 °C. This product is slightly soluble in CS₂. It was purified by washing with methanol and extracting with CS₂ in a Soxhlet apparatus. The IR spectrum of this material showed peaks at 3050, 3080, 1600, 1515, 1450, 810, 745, and 685 cm⁻¹ (KBr pellet). The ¹³C NMR spectrum (CS₂) showed only four resonances: δ 126.561, 126.886, 127.591, 128.67 (Me₄Si); similarly, the ¹H NMR spectrum showed only two resonances: δ 6.99 (s, 1 H), 7.39 (m, 4 H). The UV spectrum (CS₂) showed λ_{max} 378.4 nm, log ε 3.896. Elemental analysis (calcd for C₁₄H₁₄ (II): C, 92.25; H, 7.72; found: C, 93.17; H, 6.71) suggests that dehydrogenation of the expected Wittig product II occurred to yield I (anal. calcd for C₁₄H₁₀ (I): C, 94.34; H, 5.66). We suggest that dehydrogenation of II to I was effected by triphenylphosphine oxide. This reaction should give triphenylphosphine and water; however, no triphenylphosphine could be isolated.

The elemental analysis totals 99.88% C and H; thus 0.12% of the product consists of other elements, probably carbonyl oxygen and triphenylphosphonium end groups. Assuming that the polymer contains either or both of these end groups, the 0.12% discrepancy in the C,H analysis suggests a $\overline{DP} > 70$. The end groups, especially triphenylphosphonium chloride, could also account for the difference between observed and calculated C,H analyses.

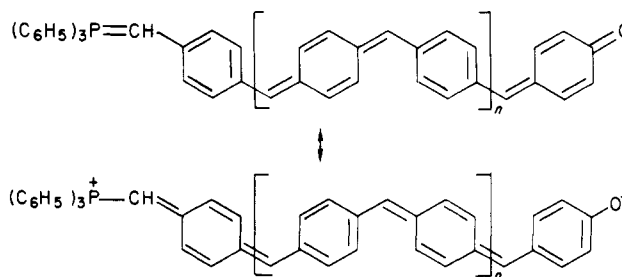
We believe I has a narrow melting point range (265–267 °C) because it has a narrow molecular weight distribution due to its precipitation from the reaction mixture as it reaches a molecular weight that renders it insoluble.

Compared to the ¹H NMR resonances of the model compound¹² shown below, the corresponding resonances of I suggest equivalence of the rings. Moreover, the all-trans form would exhibit greater splitting in the aromatic region than the all-cis form. The existence of four resonances in the ¹³C NMR spectrum of I is also consistent with ring equivalence. In the formulas below letters refer to the different ring protons and numbers refer to the different carbons. Obviously ¹³C NMR cannot distinguish between cis and trans isomerism.



The UV absorption λ_{max} of I at 378.4 nm is also consistent with a system of delocalized electrons when compared with λ_{max} of 295, 305, and 320 nm for the model compound.¹²

The equivalence of rings in I is consistent with the high \overline{DP} suggested by elemental analysis. With long chains the effect of end groups in favoring one resonance form over the other is minimal especially with polar end groups:



The electrical conductivity of a crystal of I, measured with the four-probe apparatus described by Wnek,¹³ was less than 10⁻⁷ Ω⁻¹ cm⁻¹. Doping with I₂ vapor raised the conductivity to 6 × 10⁻⁵ Ω⁻¹ cm⁻¹.

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Highly Stable Unilayer Vesicles Formed by Cationic Cholesterol-Containing Polymers

Recently, the effort to construct synthetic vesicle systems which can be employed as mimetic biological systems has become intense. This is founded on the obvious expectation that successful endeavor in vesicle science could lead to various practical applications.¹

Formation of biomembrane-like bilayer vesicles from a totally synthetic didodecyldimethylammonium bromide was first reported by Kunitake et al.² However, synthetic