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CONDUCTIVITY OF IODINE DOPED OLIGOMERIC HETEROCYCLIC AZOMETHINES

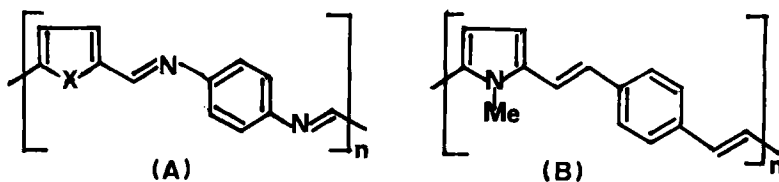
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Abstract A number of azomethines derived from aromatic diami-
 nes and pyrrole or thiophene aldehydes have been prepared and
 subsequently doped with iodine: these CT complexes show very
 low conductivities comparable with those of iodine doped pyr-
 role and N,N'-dipyrrylmethane

INTRODUCTION

Exploitation of the analogy of the C=C and C=N bond has led us
 to describe N,N'-dicyano-1,4-benzoquinonediimines as bis-aza analo-
 gues of TCNQ.¹ We have pursued this idea for designing aza-analo-
 gues (A) of poly-N-methylpyrrolyl-p-phenylene vinylene (B): in
 fact the tetramer obtained by MacDiarmid et al.² is susceptible
 of iodine doping to give a material endowed with high electric con-

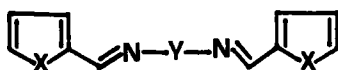


ductivity ($\sigma_{RT} = 1 \text{ Scm}^{-1}$)

SYNTHESIS OF SUBSTRATES

While the formation of the vinylene double bond in B required
 a high energy content bis-carbanion as an intermediate, formation

of azomethine bridge connecting the benzenoid and the heterocyclic ring in (A) could be simply formed by condensation of a diamine and a dialdehyde. To investigate the effect of the length of the chain and then offer a more complete landscape of the behaviour of iodine doped materials, we first studied the condensation of aromatic diamines with monoaldehydes. Thus, *p*-phenylenediamine and pyrrole-2-aldehyde, *N*-methylpyrrole-2-aldehyde, and thiophene-2-aldehyde condensed to give azomethines 1-3 respectively. Analogous reactions of the same aldehydes with 1,5-diaminonaphtalene afforded compounds 4-6 respectively. Condensation procedures are reported in Table I. Reaction of pyrrole-2,5-dialdehyde³ and *p*-phenylenediamine in DMF-toluene at 120° afforded an insoluble orange-red material, the elemental analysis of which is in accord with



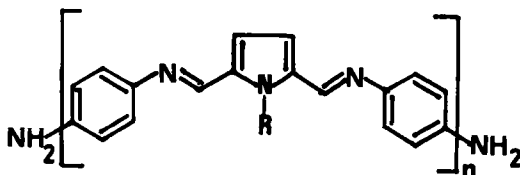
- 1: X=NH Y=1,4-C₆H₄^a
 2: X=NMe Y=1,4-C₆H₄
 3: X=S Y=1,4-C₆H₄

- 4: X=NH Y=1,5-C₁₀H₆^b
 5: X=NMe Y=1,5-C₁₀H₆
 6: X=S Y=1,5-C₁₀H₆

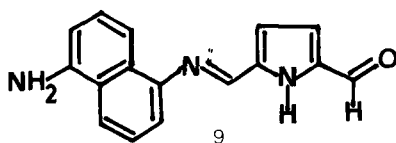
(a) *p*-phenylene

(b) 1,5-naphtylen

structure 7. Instead, the reaction of *p*-phenylenediamine with *N*-methylpyrrole-2,5-dialdehyde in boiling toluene afforded the monome-



- 7: R=H n=3
 8: R=Me n=1



ric doubly condensed product 8. The reaction of 1,5-diaminonaphthalene with pyrrole-2,5-dialdehyde in DMF at 120° slowly separated an insoluble product, the analysis of which is in accord with the monocondensation product 9.

Compounds 1-9 could be doped in bulk with iodine vapours at room temperature to give in most cases black powders, generally insoluble in common organic solvents. In few cases (e.g. starting from pyrrole-2-aldehyde and 1,5-diaminonaphthalene, N-methylpyrrole-2-aldehyde and 1,5-diaminonaphthalene) the azomethine afforded upon doping gummy black materials. The elemental analytical data of the complexes suggested for each case the substrate: dopant ratios, concisely reported in Table I as empirical formulas.

CONDUCTIVITIES

Room temperature conductivities of iodine doped azomethines 1-9 are reported in Table I. Conductivities were measured on compressed pellets (6000 Kg/cm²). It appears that the length of the conjugated system is almost ineffective in determining the relative conductivities of the doped monomeric compounds and of the oligomeric materials. For this reason we have also doped with iodine both pyrrole and N,N'-dipyrrylmethane and have obtained the corresponding CT complexes: the iodine content of these materials was deduced from their elemental analysis. Both complexes showed conductivities at room temperature strictly analogous to those of the previously considered azomethines. Iodine doped materials sho-

wed broad temperature independent esr signals. While the C=N double bond can substitute favourably a C=C double bond in electron accepting systems, results of this investigation clearly show that this analogy does not apply in the case of donor systems.

TABLE I. Conductivities of Iodine doped azomethines

Compound	Method ^a	C.T.C. Formula	$\sigma \times 10^9 (\Omega^{-1} \text{cm}^{-1})$
1	A	$[\text{C}_{16}\text{H}_{14}\text{N}_4]\text{I}_{3.1}$	0.63
2	B	$[\text{C}_{18}\text{H}_{18}\text{N}_4]\text{I}_{4.8}$	45
3	B	$[\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}_2]\text{I}_{1.8}$	unsuitable pellet
4	C	gummy material	--
5	C	gummy material	--
6	B	$[\text{C}_{20}\text{H}_{14}\text{N}_2\text{S}_2]\text{I}_{2.9}$	69
7	D	$[\text{C}_{42}\text{H}_{35}\text{N}_{11}]\text{I}_{5.8}$	9.4
8	E	$[\text{C}_{19}\text{H}_{19}\text{N}_5]\text{I}_3$	unsuitable pellet
9	F	$[\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}]\text{I}_{1.8}$	6.5

- a. (A) in CH_2Cl_2 and Na_2SO_4 . (B) in CH_2Cl_2 with molecular sieves (4Å). (C) in PhCH_3 with molecular sieves. (D) in PhCH_3 and DMF (1:1), aldehyde/diamine=4/5. (E) in PhCH_3 , aldehyde/diamine=1/2. (F) in DMF solution, aldehyde/diamine=2/3.

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