FINAL REPORT
THE EFFECTS OF MOLECULAR STRUCTURE ON THE ELECTRICAL CONDUCTIVITY OF POLYMERS

Grant NAG-3-956

by

Luke A. Burke
Department of Chemistry
Rutgers University
Camden, NJ 08102

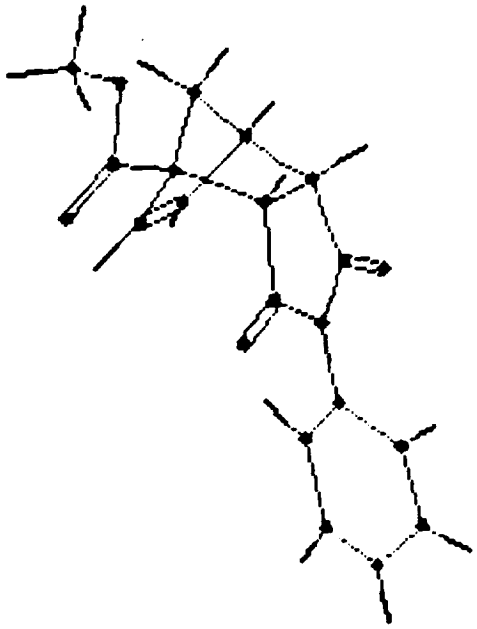
to

NASA Lewis Research Center
Cleveland, OH 44135

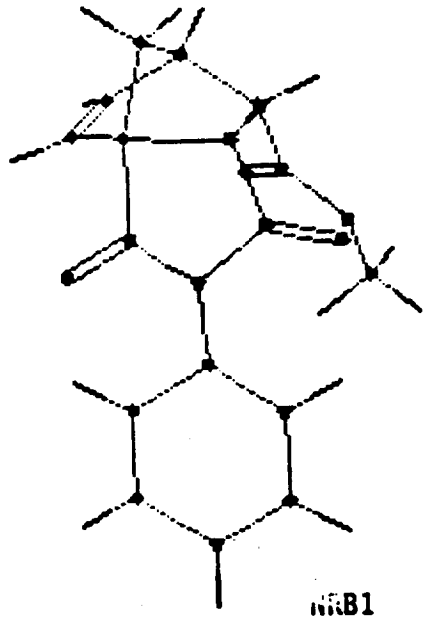
The role of Quantum Theoretical Methods is both predictive and supportive of experimental results in Chemistry. Present day methods are able to calculate vibrational spectra and stereochemical interactions for molecules of moderate size (up to 20 atoms). As for the predictive side, the electronic structure of molecules and polymers can be calculated in order to narrow down the field of many potential candidates, which would have the novel properties looked for. The following has been accomplished at the Rutgers Camden Chemistry Department as results of calculations on molecular and polymeric systems of interest to the Polymers Branch of the NASA Lewis Research Center, under Grant NAG3-956.

Results Supportive of Experimental Results

1) In preparing end caps for PMR-like materials, ethyl tricarboxynorbornene can possibly be imidized into either of two products, NRBS (a symmetrically formed imide) and NRB1 (an imide attached to the norbornene bridgehead.)



NRBS

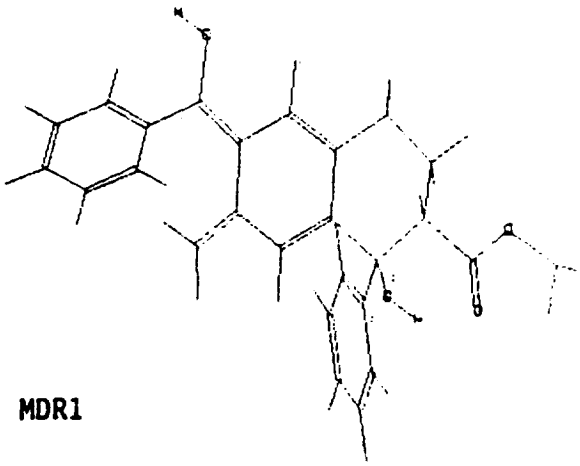


NRB1

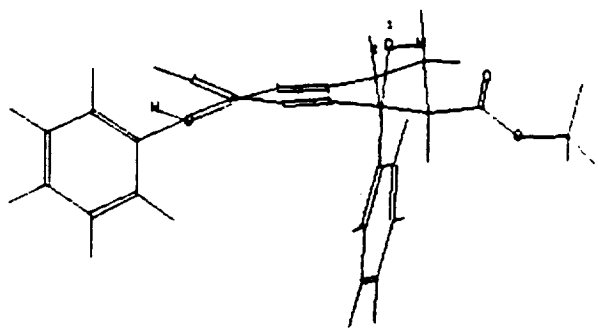
A typical approach to studying this question by theoretical methods would be first to optimize the geometries of these molecules using a Molecular Mechanics program. This gives a difference in energy of 17 kcal/mol in favor of NRBS; of this amount 12 kcal/mol is attributable to bond angle deformations in NRB1.

The next step is to optimize the geometries using a Quantum Mechanical Method such as the well-tested MNDO Method. Such a method can calculate enthalpies and entropies of formation as well as vibrational spectra. The internal energy, enthalpy, and free energy changes (298K) are calculated to be all 20.kcal/mol higher for NRB1. The fact that these three values are almost identical means that internal energy is the major contributor to the free energy difference between NRB1 and NRBS. Thus, the high bond energy strain in NRB1 seems to preclude it as a competing product in the imidization of ethyl tricarboxynorbornene. These results were published in Macromolecules 25, 3868-3873 (1992)

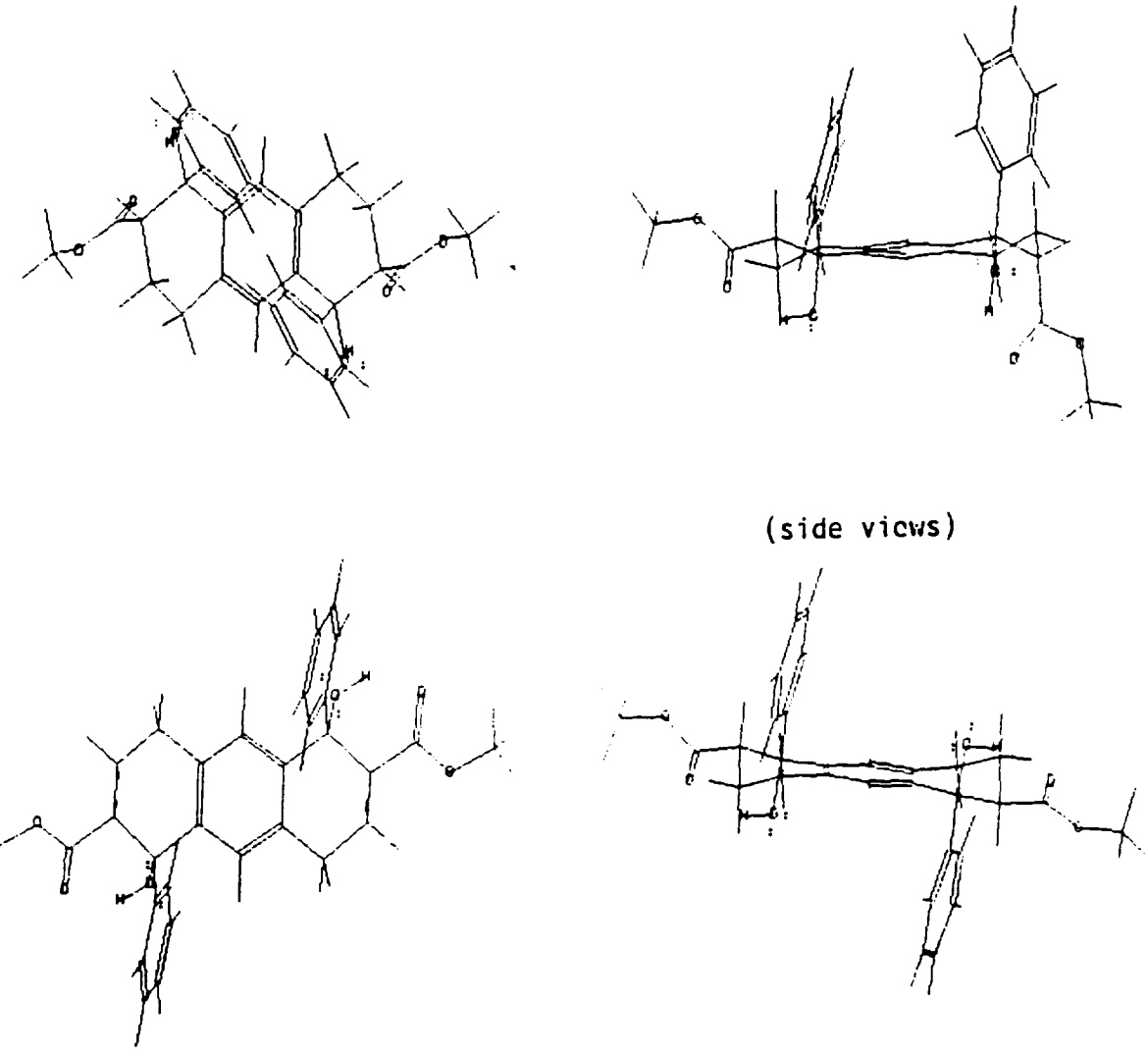
2) The Diels-Alder reaction can be an important consideration in some polymerization and depolymerization reactions. An example of how molecular modelling can aid in the interpretation of experimental results can be seen in the case of the addition of methyl acrylate (MA) to the compound MDR1. This latter compound



MDR1



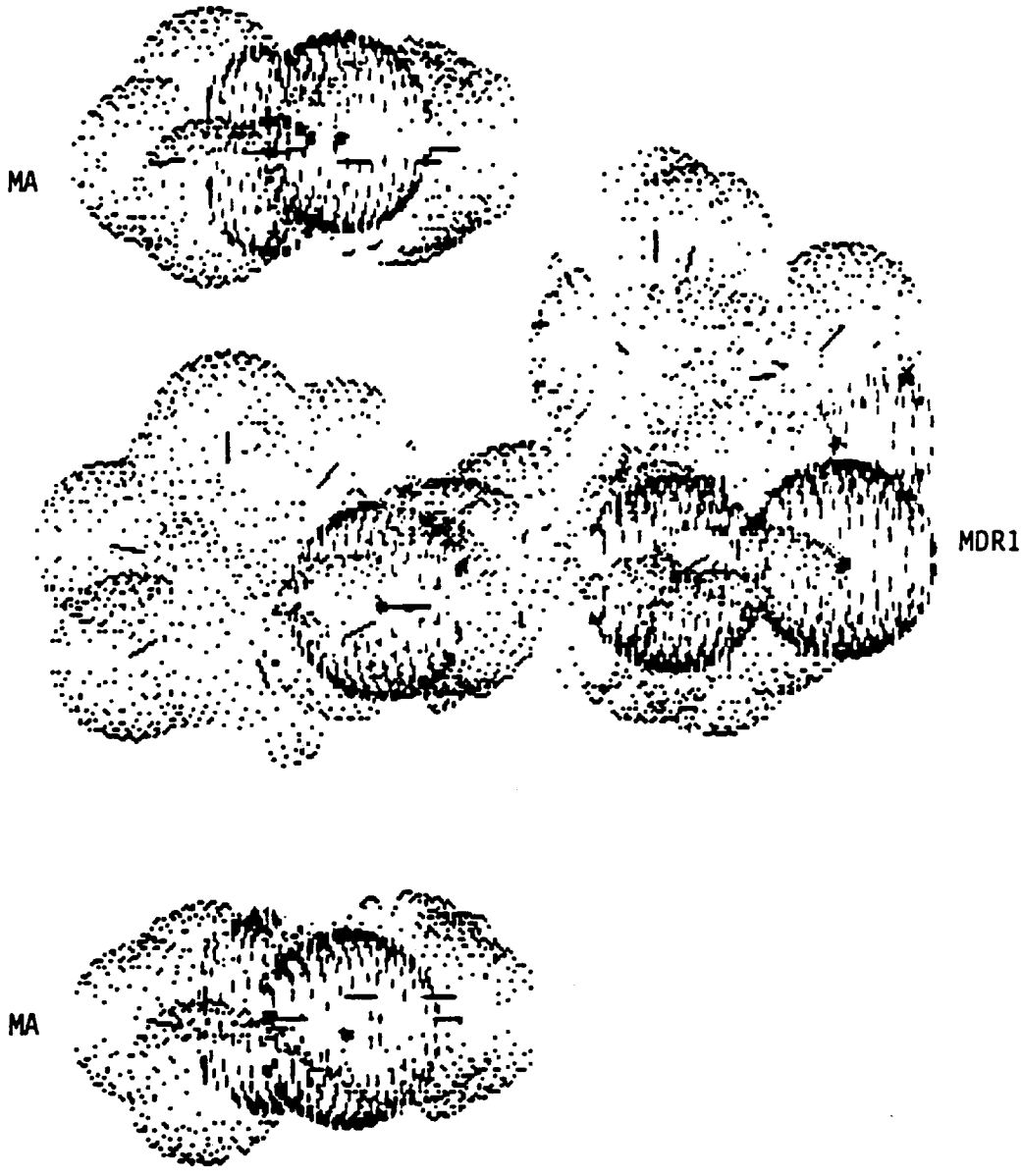
is an intermediate formed during a photo-chemical process. Two products are found experimentally. These products have very similar bond characteristics but were found to have melting points more than 50°C apart.



(side views)

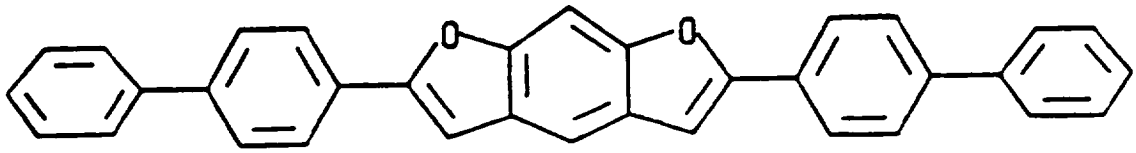
An explanation for this behavior can be seen from models of the products of addition of MA to either of the two sides of MDR1. Addition of MA on the side anti to the OH group causes the formation of an anti diol product, and addition to the syn side forms the syn diol.

Molecular modelling can visually indicate that the two sides of MDR1 are not equally available for attack by MA. The side which causes anti addition is more sterically hindered than the syn side and so syn diol product is predicted to be in excess of anti diol. Since the anti diol is expected to have more extensive intermolecular hydrogen bonding than the syn diol, the anti diol is predicted to have the higher melting point of the two products.

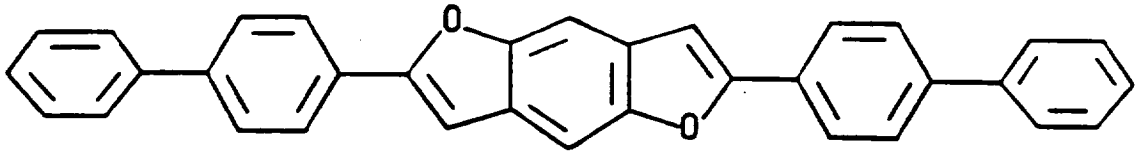


The Electronic Structure of Polymers

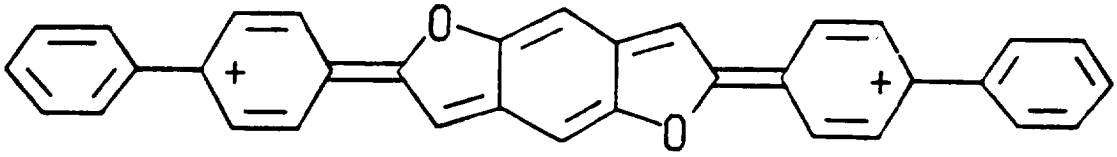
In the study of electrically conducting polymers, it has been found that the delocalization of charge throughout the pi system of a polymer can lead to high conductivity. Thus, when deciding between meta, meta difuranylbenzene (mdb) and para, para difuranylbenzene (pdb) as copolymers, it can be seen from simple resonance structures that dications are delocalized through the phynylene as well as the pdb copolymers, while the charges would be localized on the mdb or phenylene moeity when mdb is used.



mdb



pdb

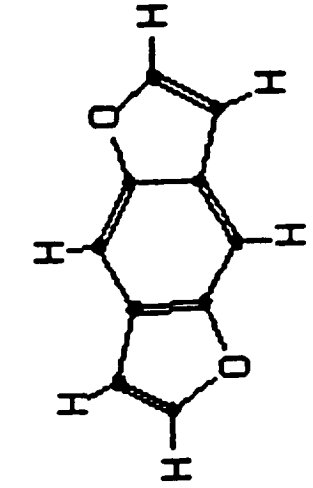


oxidized pdb

Quantum Theoretical Methods allow the quantification of this effect. Molecular Mechanics can be combined with the Valence Effective Hamiltonian (VEH) method to calculate band gaps of polymers and optical transitions of molecules. Table I summarizes the results found on phenyl substituted analogs of mdb and pdb as well as for benzofuram, I, where the experimental value of the optical transitions are known. Good agreement can be found between the VEH calculated value and experiment for I. It can also be seen that mdb and substituted mdb absorb at lower wavelengths than pdb and substituted pdb (II-III, IV-V, and VI-VII). Also, substitution at the 2 and 2′ positions causes absorption at higher wavelengths than at the 3 and d′ positions (IV-VI and V-VII).

As absorption at higher wavelengths is a sign of greater conjugation and delocalization through pi systems, calculations of the band structure for the polymers have been carried out on the 2,2′ rather than the 3,3′ connections on mdb and pdb.

The same trend of higher wavelength absorption (lower band gap) is found for the polymeric analogs of pdb (VIII-IX and X-XI). Use of the fluorene rather than the phenyl copolymer gives similar band gaps to the phenyl case. Fluorene is more acidic than most hydrocarbons and thus forms anions easily. The band gap for the fluorene anion is calculated to be nearly the same as in the neutral case -- when the geometry of the unit cell is identical in the two cases except for removal of the proton in the anion. This geometric constraint is not realistic, however. Delocalization of charge throughout pi systems causes a large distortion of the lattice which, as has been calculated for polyaniline,



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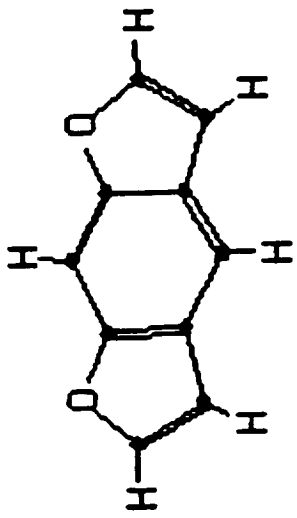

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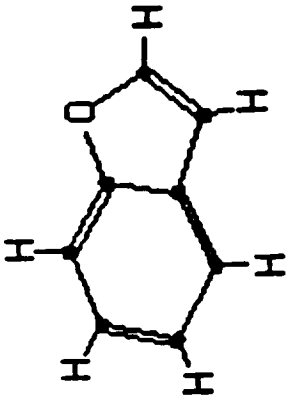
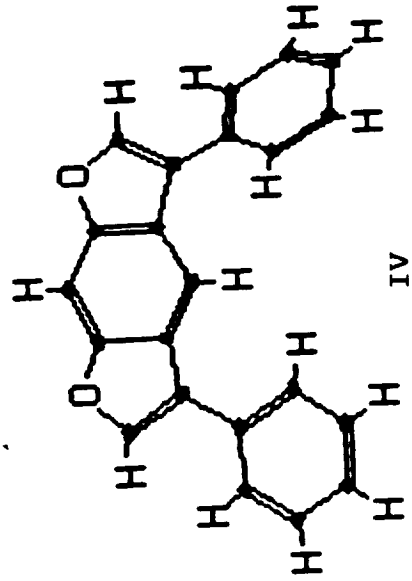


I



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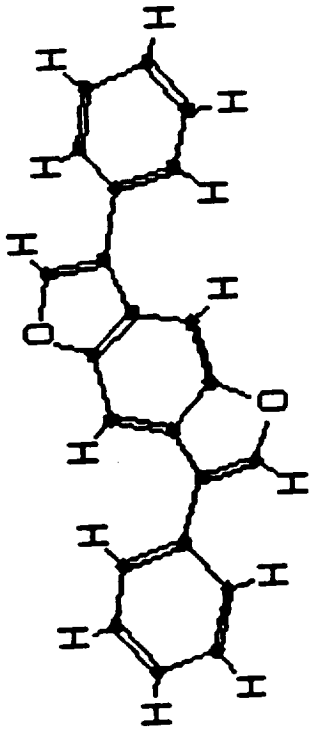

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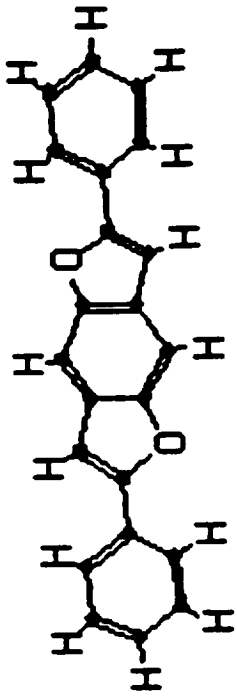

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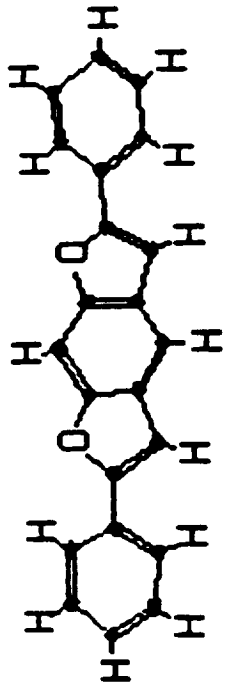
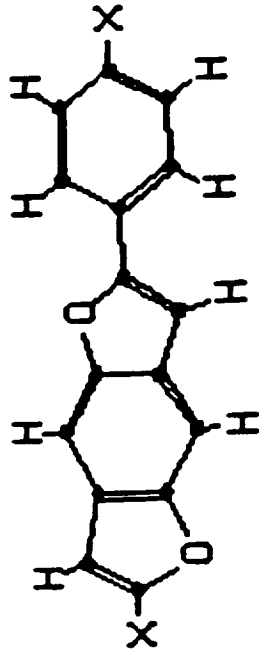


VI



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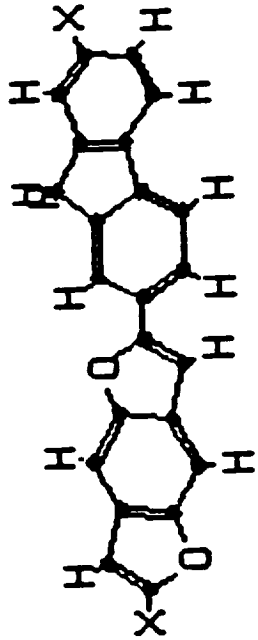

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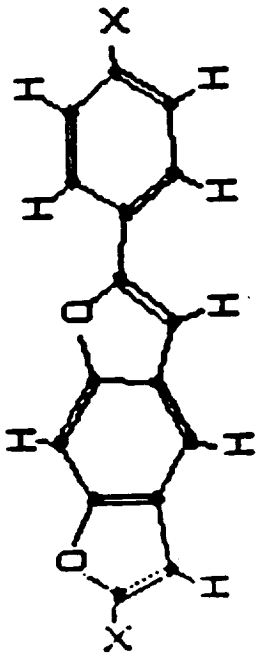
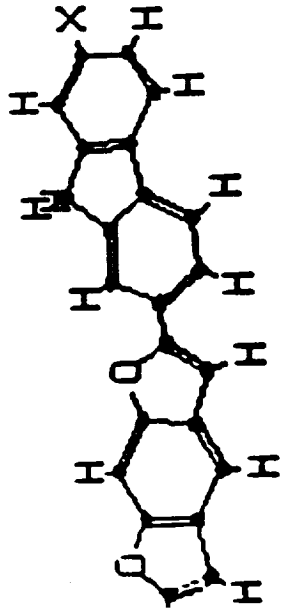


VIIIA



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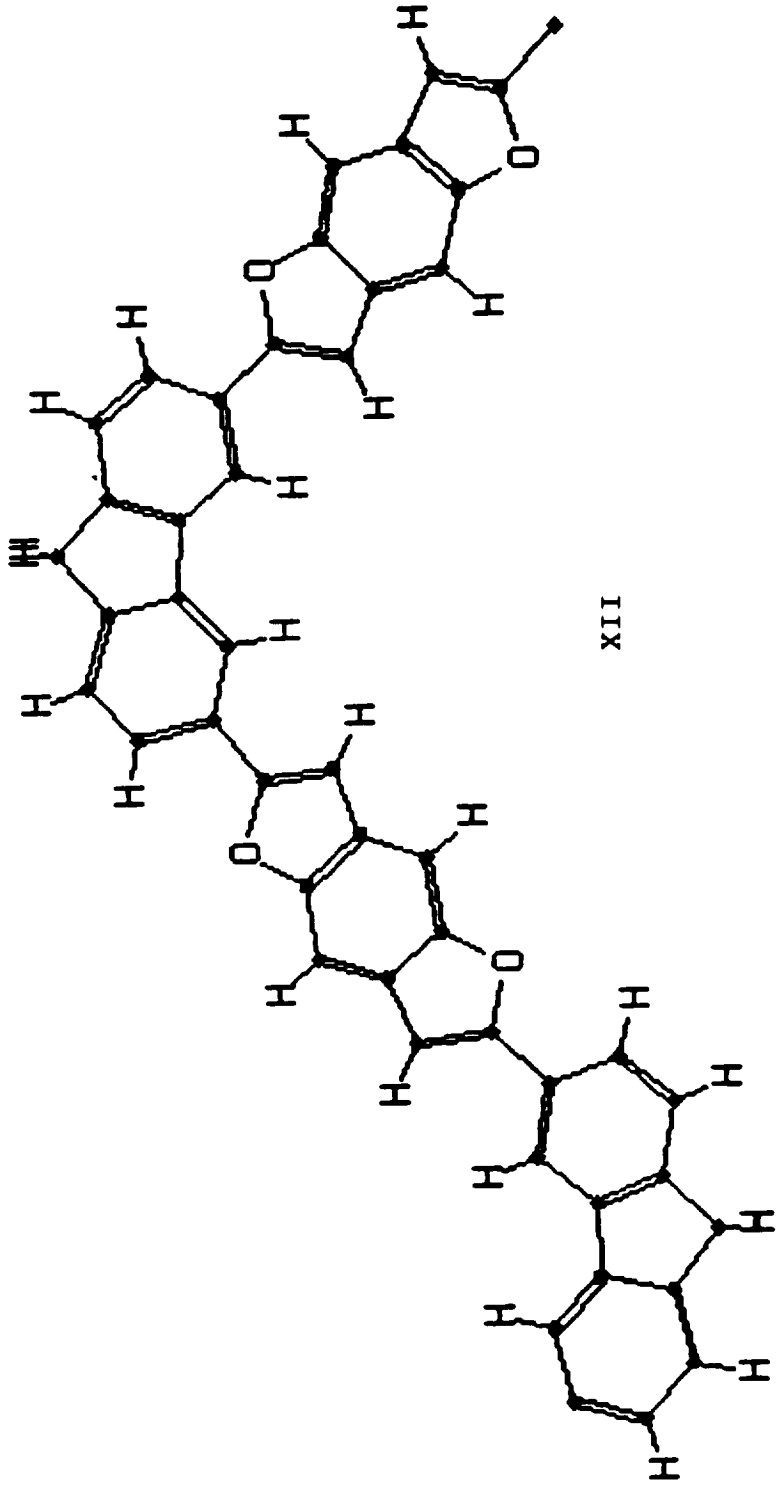

XII

Molecules	E_{Lu-Ho} au	nm
Benzofuran I	0.194	235
I (experimental)		245
meta difurano benzene (mdb) II	0.195	233
para difurano benzene (pdb) III	0.151	267
3,3′ diphenyl mdb IV	0.145	315
3,3′ diphenyl pdb V	0.136	335
2,2′ diphenyl mdb VI	0.138	330
2,2′ diphenyl pdb VII	0.118	385

Polymers	band gap au
poly para phenylene, 2,2′ mdb VIII	0.188 au
poly " 2,2′ pdb IX	0.093
poly 2,7 fluorenyl, 2,2′ mdb X	0.116
X anion	0.115
poly 2,7 " , 2.2′ pdb XI	0.097
XI anion	0.099
poly 3,6 fluorenyl, 2,2′ pdb XII	0.120
XII anion	0.103

TABLE I

polyheteroaromatics, and other conducting polymers, brings about a large reduction in band gap.