

double bonds in 1,3-pentadiene is indicative of the geometry and electronic distribution of the excited state.³³

Of the proposed excited states, biradical excited states of the allylmethylene or cyclopropylmethylene types^{14,23} would be expected to show preferential rotation about the methyl-substituted double bond in 1,3-pentadiene due to methyl stabilization of the radical center. A cross-bonded-type excited state would show no difference in the rotation rates for the two double bonds.³⁵⁻³⁷ However, the factor of at least 25 in the isomerization efficiencies of the unsubstituted double bond over the methyl-substituted double bond can be attributed to the involvement of excited states with zwitterionic character.

Of the two thermodynamically favored zwitterionic excited states only the minimum represented by Z_{1A} will lead to the observed facile isomerization of the 1,2-double bond. The relaxation process leading from the maximum at the spectroscopic state to the minima on the excited state potential surface should be quite sensitive to the relative energies of these minima. The pathway favored should be toward the lowest energy minimum since this will have the highest density of states at the energy of the spectroscopic state. In addition, presumably the slope of the potential surface near the spectroscopic state should be greater toward the lowest energy minimum. Differences in the moments of inertia of the ends of the dienes may have some influence but results on conjugated systems show favored rotation of the group with the larger moment of inertia.⁸ Also, immediate relief of strain in the spectroscopic state or distortion of the ground state which might produce a spectroscopic state on a sloping potential energy surface could lead to isomerization to minima other than that of lowest energy. Neither of these mechanisms should be operative in this case, which suggests that the Z_{1A} state is indeed the lowest energy vibrationally relaxed excited state. Thus our results, in agreement with most calculations,^{18,19} but in disagreement with Dauben's early findings, suggest that Z_{1A} , an allyl cation-methylene anion zwitterionic species is the lowest energy excited state for this 1,3-diene system.

We cannot identify the species which leads to 3,4-double bond isomerization after longer irradiation times. An excited biradical, which has been calculated to be a low-lying excited state, could be responsible.¹⁸ Also, populating either Z_{1B} - or Z_{2B} -type excited states would lead to 3,4-double bond isomerization. It should be pointed out that the methyl group should stabilize Z_2 much more than Z_1 which could make Z_{1A} and Z_{2B} very close in energy. This extreme sensitivity of the ordering of the lowest lying excited states could explain Dauben's observation of an allyl anion-methylene cation as the lowest energy excited state on what was in his case a 1,3,4-trialkyl-substituted diene system. Thermal equilibration of these various types of zwitterionic states, as suggested by Salem,¹⁹ cannot be the general case since this would lead to rotation about both double bonds upon absorption of a single photon which is not observed.^{27,38}

This work suggests that a polarized, i.e., zwitterionic type, excited state is the vibrationally relaxed excited state produced upon photolysis in a 1,3-diene system. We can infer for 1,3-pentadiene and almost certainly for 1,3-butadiene itself that an

allyl cation-methylene anion best describes the electronic distribution in this state. Substituent effects on the electronic charge distribution in this state appear to be very subtle and we are now investigating these substituent effects and the effect of temperature for the excited states of both the *s-cis* and the *s-trans* rotamers for a variety of acyclic 1,3-dienes.

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Registry No. 1-*cis*-Deuterio-*trans*-1,3-pentadiene, 79957-93-0.

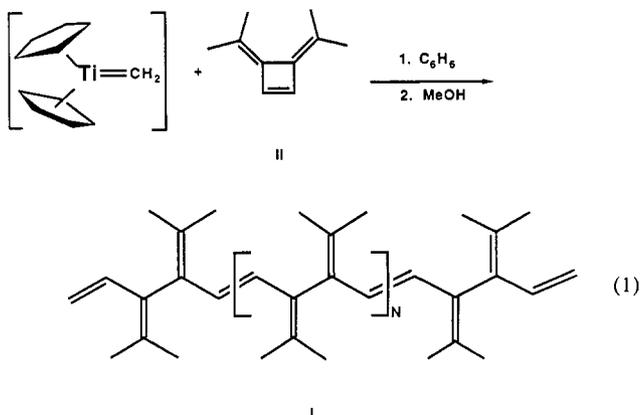
Synthesis and Properties of a Novel Cross-Conjugated Conductive Polymer Precursor: Poly(3,4-diisopropylidencyclobutene)

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Conductive polymers have recently become an active area of research due to interest in their mechanisms of conduction and potential applications.¹ Despite numerous reports in the literature,¹ only a few structural types of conductive polymers have been synthesized and characterized. The general approach to efficient organic conductors has centered on highly conjugated systems that are extensively delocalized. We now report a different approach involving a novel precursor polymer (I) with cross-conjugated olefins in its backbone. The polymer is not extensively delocalized in its undoped state; however, it yields materials with moderate conductivity and paramagnetism with oxidative doping. Despite the lack of delocalization, I is easily oxidized and allows high carrier concentrations. This material can be easily processed as a result of its solubility in common organic solvents.

Poly(3,4-diisopropylidencyclobutene) (I), an air-sensitive, clear film or white powder, was synthesized by ring-opening olefin metathesis polymerization² of 3,4-diisopropylidencyclobutene (II) using titanocene methylidene sources³ as catalysts (eq 1). Studies



in our laboratory on the polymerization of norbornene³ and other strained cyclic olefins⁴ have revealed that this catalyst can con-

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(33) Since significant quantum yield changes for photoreactions have been reported upon deuterium substitution of a carbon-carbon double bond,³⁴ a 1% solution of a mixture d_1 and d_0 *trans*-pentadiene in diethyl- d_{10} ether was photolyzed. The deuterium isotope NMR shift allowed all six isomers of the pentadienes to be observed at 400 MHz. Photolysis of this mixture showed no detectable difference (within 5%) in the rate of isomerization to the *cis*-pentadiene and in the final photostationary state for both the d_1 and d_0 compounds.

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(3) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733-742.

stitute a living polymerization system and thereby afford polymers of controllable molecular weight with little cross-linking. Using this catalyst, we have been able to synthesize I with a range of molecular weights^{5a} as well as block copolymers of I and norbornene.^{5b}

Polymer I is soluble in a variety of organic solvents, so it can be cast into flexible amorphous films, spin coated on substrates, or precipitated as fibers.⁶ The π -system of the undoped polymer is segregated into triene segments as shown by a single UV-vis peak at 278 nm and an extinction coefficient of $20\,000\text{ M}^{-1}\text{ cm}^{-1}$ per triene unit.^{7,8} The segregation of the polymer's π -system is the result of steric interactions that force a nonplanar polymer backbone.⁹ A polymer conformation that avoids steric interactions and results in triene isolation is accomplished by a torsion about the single bonds between the cross-conjugated olefins.⁹ Films of the undoped polymer are insulators. Upon oxidative doping these films become shiny black and metallic in appearance.¹⁰ When heavily doped¹¹ with iodine, these materials exhibit conductivities from 10^{-3} to 10^{-4} S/cm ,¹² depending on the fabrication technique.¹³ Comparable conductivities have been reported for other conductive polymer systems.¹ The heavily oxidized material is brittle; however, heavily doped block copolymers of I and polynorbornene (polynorbornene is an excellent elastomer) maintain good mechanical properties (i.e., flexibility and stretchability). The copolymers exhibit lower conductivities as a result of the insulating regions of polynorbornene. A heavily doped block copolymer sample with approximately 1:1 of I and polynorbornene gave a conductivity of 10^{-4} S/cm (film).

The ease of oxidation of I is surprising in light of the trieneic nature of the electronic states. The nature of the charged states is yet to be determined; however, the ease of oxidation suggests that stabilized carbocations are formed. Therefore, it is likely that the polymer adapts a more planar structure to delocalize and hence stabilize the charge. Heavily doped samples of I appear to be reasonably air stable, exhibiting moderate conductivities of 10^{-4} to 10^{-5} S/cm (pressed pellet) after 6–8 months of air exposure. Thermoelectric power measurements¹⁴ on films of I saturated with iodine reveal that the charge carriers are positively charged.

Solid-state CP-MAS ^{13}C NMR spectra¹⁵ of I (Figure 1) show two inequivalent methyl groups at 19 and 22 ppm and three

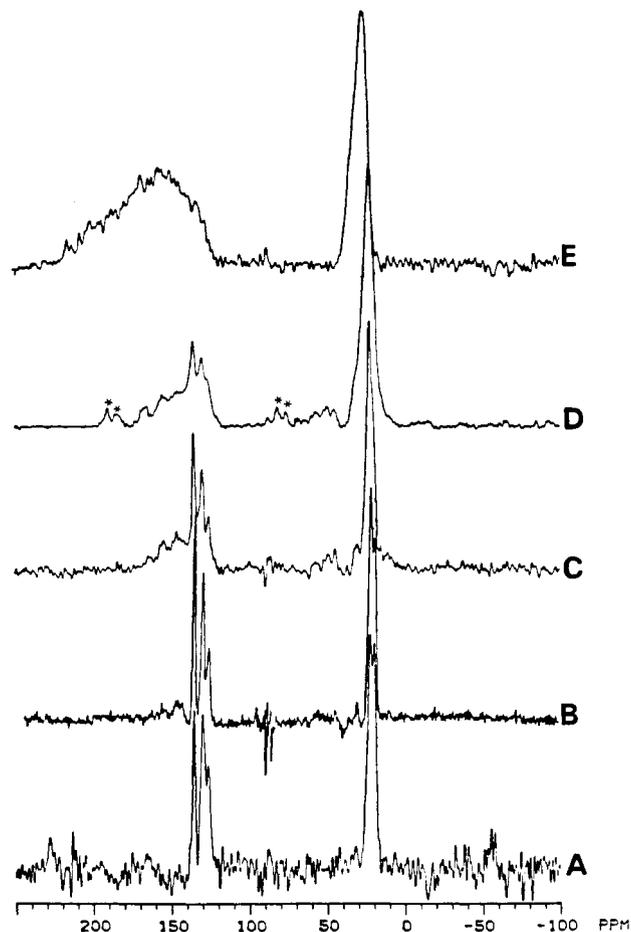


Figure 1. Solid-state CP-MAS ^{13}C NMR spectra of I doped with iodine. Percentages of iodine by weight: (A) 0%; (B) 13%; (C) 35%; (D) 45%; (E) = 60%. *s indicate spinning side bands.

olefinic carbon signals at 125, 129, and 135 ppm.¹⁶ Upon exposure to iodine, broad resonances that correspond to delocalized carbocations appear.¹⁷ At low (13%) and intermediate doping levels (35%), two distinct peaks at 146 and 156 ppm are observed (Figure 1). At very high dopant levels (60%) the polymer's spectrum indicates the presence of an increased concentration of paramagnetic species, and only broad signals that are shifted downfield can be observed.

In an effort to address the nature of the carrier species, I and the oxidized materials were studied by ESR spectroscopy. ESR spectra of undoped and lightly doped (<13% iodine) films of I exhibit a single isotropic Gaussian signal with a g factor of 2.0027 and a peak to peak line width (H_{pp}) of 18 G. The spin density of the undoped polymer is about 10^{-5} spin/monomer unit.¹⁸ At low and intermediate dopant levels, the spin density is independent of dopant concentration and is approximately equal to that of the undoped polymer. When heavily doped with iodine, the polymer exhibits an increase in paramagnetism; the major component of which is temperature independent in nature. An increase in paramagnetism has been associated with a transition to a metallic state in other systems.^{19,20} Samples saturated with iodine have about 10^{-3} spin/monomer unit and exhibit a nearly isotropic ESR signal with a narrowed Lorentzian line shape ($g = 2.0028$, H_{pp}

(4) Grubbs, R. H.; et al., unpublished results.

(5) (a) I has been synthesized with average molecular weights (relative to polystyrene standards) of 12 000–51 000 and dispersities as low as 2.1 (determined by gel permeation chromatography). (b) A detailed description of the synthesis of these block copolymers is forthcoming.

(6) No X-ray diffraction was observed for powders or films. Fibers were produced by elongation and precipitation of concentrated solutions of the polymer in methanol.

(7) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*; Wiley: New York, 1981.

(8) The extinction coefficient was determined by using chloroform as a solvent. Solution UV-vis spectra were the same as those of thin films. Thicker films had maxima that were red shifted by 10–20 nm.

(9) Space-filling models suggest the presence of large steric interactions that should restrict the polymer π -system from planarity. Models also suggest a torsion about the single bond between the cross-conjugated olefins.

(10) Thin films (ca. 0.1 μm or less) are brown; however, thicker films (10 μm or more) and pressed pellets of doped powders are shiny black.

(11) Films and powders of I were doped by exposure to iodine vapor at room temperature in vacuum. Excess dopant was removed in vacuo (ca. 1 h). Samples were saturated at approximately 60–65% by weight iodine. The iodine concentration of saturated samples would decrease to 50–55% with prolonged evacuation (i.e., days). Reduction of doped samples with potassium naphthalide and extraction with solvent resulted in removal of the iodine and afforded clear, slightly yellowed films with the same UV-vis maxima as the films before doping.

(12) Conductivities were made with the DC four-point probe method: Seeger, K. *Semiconductor Physics* Springer-Verlag: New York, 1973.

(13) Thick films (30–70 μm) gave conductivities of 10^{-3} S/cm when saturated with iodine, and these films often cracked. Pressed pellets gave conductivities on the same order. Higher reported values were irreproducible.

(14) Measurement was made with a hot probe in air. Wieder, H. H. *Laboratory Notes on Electrical and Galvanomagnetic Measurements*; Elsevier Scientific: Amsterdam, 1979.

(15) Solid-state NMR spectra were obtained on a home-built spectrometer operating at a carbon frequency of 50.36 MHz with spinning rates of 3–5 kHz. Data manipulation was performed on a Nicolet computer using left-shifts and nonlinear base-line fits to eliminate the rolling base line. Chemical shifts were referenced to an external standard of adamantane.

(16) The chemical shifts are the same as obtained in solution, and the peak at 125 ppm was determined to be the proton-bearing olefinic carbon.

(17) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon 13 Nuclear Magnetic Resonance Spectroscopy*; Wiley-Interscience: 1980.

(18) Spin densities were determined by double integration against a 2,2-diphenyl-1-picrylhydrazyl hydrate standard.

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(20) Moraes, F.; Chen, J.; Chung, T. C.; Heeger, A. J. *Synth. Met.* **1985**, *11*, 271–292. Moraes, F.; Davidov, D.; Kobayashi, M.; Chung, T. C.; Chen, J.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1985**, *10*, 169–179.

= 8 G). A popular theory of how conduction occurs in conductive polymers formulates the carrier species for a polymer such as I in terms of polarons (radical cations) and bipolarons (spinless dications).^{19,21} These species are charged-localized lattice deformations with electronic states in the band gap. Our ESR studies suggest that bipolarons and/or singly charged cations are initially formed, and at high dopant levels polarons and/or neutral radicals are also present.

Our results demonstrate a new route to a conducting composition by oxidative treatment of a novel cross-conjugated polymer. Others have also obtained conducting compositions by oxidation of precursor polymers lacking extensive delocalization.²² We are currently investigating the extent of the modification of I with doping and the properties of derivatives of I.

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Registry No. I (homopolymer), 104584-99-8; (I)(norbornene) (copolymer), 105502-58-7; I₂, 7553-56-2.

Supplementary Material Available: UV-vis spectra, ESR spectra, ESR line-shape analysis, and temperature dependence of the total magnetic susceptibility (4 pages). Ordering information is given on any current masthead page.

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 (b) Chien, J. C. W.; Babu, G. N.; Hirsch, J. A. *Nature (London)* **1985**, *314*, 723-724. (c) Shacklette, L. W.; Elsenbaumer, R. L.; Chance, R. R.; Eckhardt, H.; Frommer, J. E.; and Baughman, R. H. *J. Chem. Phys.* **1981**, *75*, 1919-1927.

A Novel Transformation of a Carbonyl to a CF₂ Group

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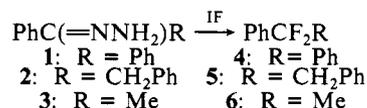
The construction of the CF₂ moiety is of importance to organic chemistry from several aspects, including some of considerable biological interest.¹ This has led to the development of a few general, but somewhat limited, methods for its construction. Thus the incorporation of the CF₂ unit into a target molecule can be accomplished by using ethylbromodifluoro acetate² or CF₂ containing Freons.³ Another method, limited to the construction of a benzylic CF₂ group, was developed by reacting some diazo derivatives, or compounds which generate this moiety in situ, with fluorine.⁴ Recently we have demonstrated a new transformation of an acetylenic bond into derivatives containing the CF₂ group.⁵

(1) See, for example: *Biomedical Aspects of Fluorine Chemistry*; Filler, R.; Kobayashi, Y., Eds.; Elsevier Biomedical: Amsterdam, 1982. Fried, J.; Halinan, E. A.; Szewdo, M. J., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3871 and references therein. Middleton, W. J.; Bingham, E. M. *J. Org. Chem.* **1980**, *45*, 2883. Cross, B. E.; Erasmunson, A.; Filippone, P. *J. Chem. Soc., Perkin Trans. I* **1981**, 1293. Weigert, F. *J. Org. Chem.* **1980**, *45*, 3476.
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 (5) Rozen, S.; Brand, M. *J. Org. Chem.* **1986**, *51*, 222.

The most widely used method, however, is the general transformation of a carbonyl group into the CF₂ moiety by using SF₄⁶ or its most important derivative (diethylamino)sulfur trifluoride (DAST) developed mainly by Middleton.⁷ This method although quite popular, has its own limitations, including harsh reaction conditions, toxicity, and some stability problems. Similar fluorides such as MoF₆ have also been used.⁶

We present here a new method for the CO → CF₂ conversion using easily available reagents and starting materials. Recently, as a part of our goal to introduce elemental fluorine to organic chemistry methodology,⁸ we have synthesized in situ iodine monofluoride, IF, and demonstrated some of its unique chemistry.⁹ One of the most noticeable features of this reagent is the nucleophilic power of its fluoride which is not heavily solvated as in most other sources. This fact, combined with Barton's reaction of unsubstituted hydrazones with elemental iodine,¹⁰ encouraged us to react IF with various hydrazone derivatives under very mild reaction conditions, yielding eventually the desired CF₂ group.

Thus the hydrazones of benzophenone (**1**), deoxybenzoin (**2**), and acetophenone (**3**) when treated with an excess of IF produced, correspondingly, diphenyl difluoromethane (**4**) in 65% yield, 1,1-difluoro-1,2-diphenylethane (**5**) in 75% yield, and (1,1-difluoroethyl)benzene (**6**) in 45% yield.¹¹



While F₂ reacts with hydrazones derived from some aryl ketones to produce the CF₂ group, only tars result in other cases.^{4b} However, the much milder IF was found to react satisfactorily with every hydrazone that we have tried. Thus, for example, hydrazones derived from the cyclic 4-*tert*-butylcyclohexanone (**7**), the steroidal 3-cholestanone (**8**), and the straight-chain 2-decanone (**9**) were all converted in yields of about 70% to the corresponding difluoroalkanes (**10-12**).

In both iodination¹⁰ and fluorination⁴ of hydrazones with the respective elements, it was necessary to work with an unsubstituted hydrazone. The reaction involves the elimination of HX (X = I or F), an essential step toward the formation of the diazo moiety, which then extrudes N₂, supplying the main driving force of the reaction. In order to find out if this is also the mechanism with IF and since unsubstituted hydrazones are not very stable, we started experiments with substituted ones. Thus *N*-methyl- and *N,N*-dimethylhydrazones of 2-decanone (**13** and **14**) were prepared and reacted with IF. In the case of **13** the yield of **12** was similar to that of the unsubstituted **9**, although a higher final temperature (raising to 25 °C) and a longer reaction time of up to an hour were needed. Even a longer reaction time of 4 h was required with the *N,N*-dimethylhydrazone **14** and then only a 50% yield of the difluoro product **12** was obtained. The substituted *N*-alkylhydrazones, however, are also not always very stable so we

(6) See, for example: Boswell, G. A.; Ripka, W. C.; Schribner, R. M.; Tullock, C. W. *Org. React.* **1974**, *21*, 1. Mathey, F.; Bensoam, J. *Tetrahedron* **1971**, *27*, 3965.

(7) Middleton, W. J. *J. Org. Chem.* **1975**, *40*, 574.

(8) See, for example: (a) Gal, C.; Rozen, S. *Tetrahedron Lett.* **1984**, *25*, 449. Rozen, S.; Lerman, O.; Kol, M.; Hebel, D. *J. Org. Chem.* **1985**, *50*, 4753. Rozen, S.; Brand, M. *Synthesis* **1985**, 665.

(9) Rozen, S.; Brand, M. *J. Org. Chem.* **1985**, *50*, 3342. See also ref 5.

(10) Barton, D. H. R.; O'Brien, R. E.; Sternhell, S. *J. Chem. Soc.* **1962**, 470.

(11) A typical reaction was performed by pouring a solution of the appropriate hydrazone, usually about 2 g in 20-30 mL of chloroform into a 3-4-fold molar excess of IF suspended in CFCl₃ at -78 °C. The latter was prepared from I₂ and F₂ according to ref 5 and 9. In some cases (see text) the temperature was then gradually allowed to raise to 25 °C. The reaction was monitored by GC on 5% SE-30 column. Apart from **12**, all the gem-difluoro products are described in the literature and their physical and spectral properties are identical with those published. The spectral properties as well as the microanalysis of **12** are also in excellent agreement with the proposed structure. In some cases the low boiling point of the products presents some difficulties in the isolation process. The products are usually accompanied by 10-15% of the corresponding α-iododifluoro compounds of type -CHICF₂-. Present experiments are aimed at reducing these minor quantities of iodo derivatives to the difluoro compounds themselves.