14.3, 14.7, and 15.0, respectively).[24a] These large differences cannot be explained by purely electronic considerations; however, consideration of steric effects allows for an easily understood explanation. The energy necessary for the conversion of planar **3** to a nonplanar conformation ($\alpha = 20°$) with a quasiaxial C–H bond is small (1.66 kcal/mol for model compound **8a**). In contrast, as Table IX shows, the energy necessary to convert the nonplanar, nonacidic, σ-complexes (with an equatorial C–H bond) into the conformation necessary for proton dissociation (the inverted conformation with a quasiaxial C–H bond) is considerable. Which means that there is a very low population of conformers with the "acidic" inverted conformation compared to those with the stable "nonacidic" conformation, or at the macroscopic level, the equilibrium situation is described by a high pK_a value. For the same reason, proton dissociation from the dimeric σ-complex (Scheme VII), **11**, is extremely difficult[25] (for the structure of **11**, see ref 8a).

Example 2: In the phloroglucinophane σ-complexes (Scheme VIII), the bridged structure fixes the alkyl substituent in the axial position and the H atom in the equatorial position. Although thermodynamically favorable, direct deprotonation of the equatorial protons in **12** is so strongly hindered kinetically that nucleophilic attach under formation of hemiacetals, **13**, occurs exclusively. The hemiacetals react further to give aromatic compounds **14**.[26]

Example 3: According to the stated rules, the nitration of various methylbenzenes (Scheme IX), for example, **15**, with nitrylacetate results in formation of σ-complex **16** with the sterically more demanding and electropositive CH_3 ligand in the quasiaxial position. Because of the poor leaving tendency of the CH_3^+ group, rearomatization to give **17** does not occur, and instead nucleophilic attack results in formation of **18**.[27]

In conclusion this study has combined experimental and theoretical methods to provide a better understanding of the interactions of steric and electronic effects that govern the properties of σ-complexes (cyclohexadienylium ions), important intermediates in the electrophilic substitution reactions for aromatic compounds. Considerations of the concepts elucidated combined with molecular modeling techniques at the semiempirical level should prove to be of considerable predictive value for designing chemical reactions and predicting the properties of the products.

Acknowledgment. We thank P. Kollat and A. Meier for technical assistance in the course of the experimental work.

Registry No. 2a, 26812-57-7; **2b**, 87176-46-3; **2c**, 83927-54-2; **2d**, 87176-51-0; **2e**, 87176-50-9; **2f**, 105970-37-4; **2g**, 105970-38-5; **2h**, 77023-09-7; **2i**, 105970-39-6; **2j**, 105970-40-9; **2k**, 71-43-2; **2l**, 108-88-3; **2m**, 105970-41-0; **2n**, 55563-53-6; **2o**, 105970-42-1; **2p**, 105970-43-2; **2q**, 105970-44-3; **2r**, 105970-45-4; **2s**, 65963-62-4; **2t**, 105970-46-5; **2u**, 105970-47-6; **2v**, 105970-48-7; **3a**, 105991-10-4; **3b**, 105970-49-8; **4a**, 105970-51-2; **5**, 20758-47-8; **8a**, 105970-52-3; **8b**, 105970-53-4; **8c**, 105970-54-5; **8d**, 105970-55-6; **8e**, 105970-56-7; **8f**, 105970-57-8; **8g**, 105970-58-9; **8h**, 105970-59-0; **8i**, 105970-60-3; **8j**, 105970-61-4; **8k**, 105970-62-5; **9a**, 27175-04-8; **9b**, 27084-06-6.

Supplementary Material Available: Anisotropic temperature factors for non-hydrogen atoms and fractional atomic coordinates and isotropic temperature factors for H atoms for **3a**, **3b**, **4a**, and **5** (19 pages); observed and calculated structure factor tables for **3a**, **3b**, **4a**, and **5** (206 pages). Ordering information is given on any current masthead page.

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Communications to the Editor

Polarization in the Excited State of 1,3-Pentadiene: Experimental Evidence for an Allyl Cation–Methylene Anion Species

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Zwitterionic excited states have been postulated as intermediates in a variety of photochemical reactions, including those comprising the visual process.[1-7] The "sudden polarization" phenomenon described by Salem,[1] which intimately involves zwitterionic excited states, was based on the work of Dauben[4] involving the photochemistry of 1,3-dienes. There has, however, been very little other experimental evidence for the involvement of zwitterionic intermediates in the photochemistry of this seminal system.[8,9] We wish to report here regioselective photochemistry of an unsymmetrical 1,3-diene which enables us to infer the excited-state charge distribution of the predicted allylmethylene species.

The first suggestion that geometrical relaxation in the excited state of a 1,3-diene caused a highly polar twisted allylmethylene species was made by Dauben in 1970.[4] Because high stereospecificity was observed in the photocyclization of *trans*-3-ethylidenecyclooctene,[13] a zwitterionic excited state consisting of an allyl anion and a methylene cation was proposed. In light of this, Dauben also proposed an excited state of this type for the

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(9) Products from the photolysis of 1,3-dienes in methanol have suggested the trapping of polar intermediates.[10,11] More careful studies show that the direct irradiation of 1,3-butadiene in methanol gave no light-induced addition of solvent, but upon addition of an acid, the previously reported products were obtained.[12]

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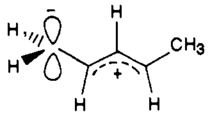
0002-7863/87/1509-0892$01.50/0 © 1987 American Chemical Society

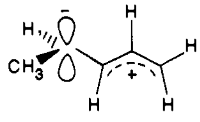
parent compound, 1,3-butadiene.[14] A similar zwitterionic intermediate was also assumed in the photocyclization of a hexatriene to bicyclo[3.1.0]hexene.[15]

Some time ago theoretical investigations of the excited states of ethylene suggested that the lowest twisted singlet state should be highly polarized.[16,17] More recent calculations support similar zwitterionic character in the lowest excited states of butadiene.[18,19] In contrast to Dauben's suggestion, both calculations found the lowest excited state minimum to be an allyl cation–methylene anion species, Z_1, with the next lowest state, Z_2, some 10–15 kcal/mol higher in energy, having the charge distribution proposed by Dauben.[4] Dual geometry optimizations showed a barrier of 6.6 kcal/mol between the two minima.[19] We felt the best way to investigate the nature of a zwitterionic allylmethylene-type excited state was to examine the regiochemistry of π-bond rotation in a simple unsymmetrical 1,3-diene containing an appropriate donor and stereochemical label.[20]

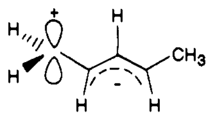
Introduction of a terminal methyl group on a butadiene molecule engenders four possible orthogonal allylmethylene zwitterionic forms. Of the four, the two which allow the methyl group to stabilize the cation, Z_{1A} and Z_{2B}, will be lower in energy; Z_{1A} should lead to facile rotation of the terminal methylene, whereas Z_{2B} should lead to facile rotation of the methyl-substituted double bond. In fact, Bruckmann and Salem[19] calculated the energies of these four species with a minimal basis set and found Z_{2B} only 0.1 kcal/mol higher in energy than Z_{1A}. A higher level calculation[18] gave a larger separation for Z_1 and Z_2 in the parent compound and suggests that the original calculation gave too low an energy for the Z_2-type zwitterions. Since these two zwitterions, Z_{1A} and Z_{2B}, would give different regioselectivity of double-bond isomerization, we synthesized *cis*-1-deuterio-*trans*-1,3-pentadiene.[21]



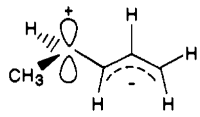
Z_{1A}



Z_{1B}



Z_{2A}



Z_{2B}

Direct excitation of *cis*- and *trans*-1,3-pentadiene in solution gives relatively inefficient cis–trans isomerization, $\Phi_{c\to t} = 0.09$ and $\Phi_{t\to c} = 0.11$, as well as even less efficient formation of 3-methylcyclobutene and 1,3-dimethylcyclopropene.[23-26] In fact the low quantum yield of isomerization, as compared to 2,4-hexadiene, led Saltiel to suggest that a 1-deuterio-1,3-pentadiene might give information concerning a proposed biradical excited state.[27] We report here that direct excitation of 1-*cis*-deuterio-*trans*-1,3-pentadiene in solution leads to highly regioselective rotation about the d_1-substituted methylene double bond.

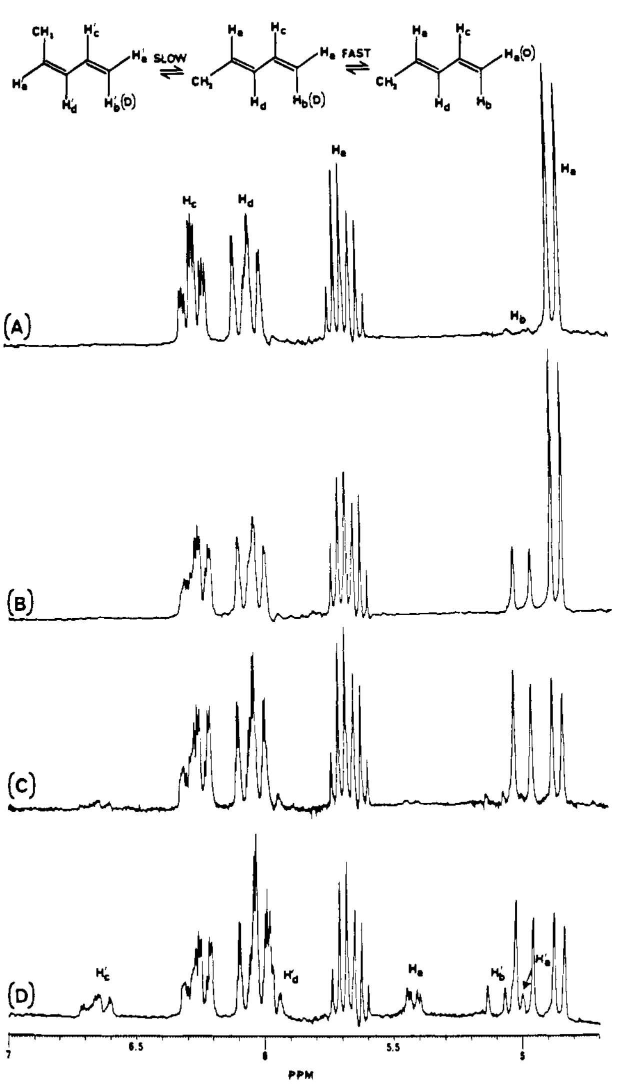


Figure 1. ^{1}H NMR (4.5–7.0 ppm, 250 MHz) of (A) *cis*-1-deuterio-*trans*-1,3-pentadiene (B) after a 2-min photolysis, (C) after a 30-min photolysis, and (D) after an 8-h photolysis.

Figure 1 shows a series of ^{1}H NMR spectra of a sample of *cis*-1-deuterio-*trans*-1,3-pentadiene irradiated for various lengths of time.[28] As seen in Figure 1B, when 25% isomerization about the deuterium-substituted double bond has occurred, there is no observable rotation about the methyl-substituted double bond. NMR spectra with high signal-to-noise ratios show that there must be less than 1% of the *cis*-1,3-pentadiene photoproduct produced at this time.[29] We believe this huge dichotomy of rotation of the

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[20] Other studies involving extended π-systems have examined regioselective isomerization.[8]

[21] 1-Deuterio-*trans*-3-penten-1-yne, produced from the protio alkyne via methyllithium and a D_2O quench, was reduced stereospecifically through monohydroboration[22] to afford the target pentadiene with greater than 98% stereoselectivity.

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[29] The large difference in isomerization efficiencies may seem unusual because a quantum yield for rotation about the methyl-substituted double bond of 1,3-pentadiene has been reported to be 0.1.[23] However, this study used 254-nm light[23] which undoubtedly photolyzed the s-cis conformer of the diene. Our present investigation used broad-band irradiation so the s-trans conformer is the primary light-absorbing species.[30] The different efficiencies of photochemical isomerization observed for each study can be attributed to the different photochemistry of the two conformers. Indeed we believe that the wavelength-dependent quantum yields observed for the pentadiene system[25] are also due to the photochemistry of the two conformers. The UV of s-cis and s-trans pentadiene,[31] which is very similar to that of the rotomers of isoprene,[32] does show a very difference in the absorptivity of the two conformers at 254 and 229 nm, the wavelengths used in the above study,[25] which are more than adequate to explain the changes in the quantum yields observed.

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.

Acknowledgment. We are very grateful to Professor Jack Saltiel for his extremely helpful suggestions, comments, and criticisms of this work and we thank the Biomedical Research Support Grant Program, National Institutes of Health (RR07085), for support for this project.

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

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

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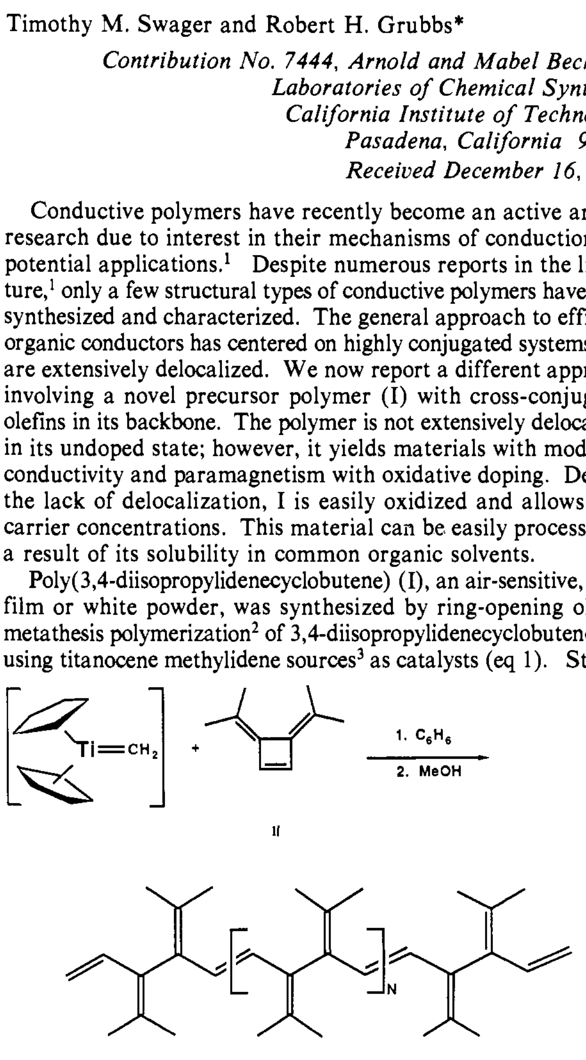
Conductive polymers have recently become an active area of research due to interest in their mechanisms of conduction and potential applications.[1] Despite numerous reports in the literature,[1] only a few structural types of conductive polymers have been synthesized and characterized. The general approach 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-diisopropylidenecyclobutene) (I), an air-sensitive, clear film or white powder, was synthesized by ring-opening olefin-metathesis polymerization[2] of 3,4-diisopropylidenecyclobutene (II) using titanocene methylidene sources[3] as catalysts (eq 1). Studies in our laboratory on the polymerization of norbornene[3] and other strained cyclic olefins[4] have revealed that this catalyst can con-



II

I

(1)

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