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Harrell L. Sellers, Lothar Schäfer*

Department of Chemistry, University of Arkansas
Fayetteville, Arkansas 72701

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Carbon-13 Nuclear Magnetic Resonance of *cis*- and *trans*-Polyacetylenes^{1a}

Sir:

Polyacetylene, (CH)_x, is the simplest conjugated organic covalent polymer in which the electrons from the unsaturated π system are expected to be delocalized along the polymer chains. However, because of the combined effects of bond alternation² and Coulomb correlation,³ there is an energy gap in the excitation spectrum leading to semiconducting behavior.⁴⁻⁷

Studies by Shirakawa et al.⁴⁻⁷ show that both the *cis* (A) and the *trans* (B) isomers can be synthesized in the form of silvery, flexible, crystalline films. Recent investigations show that both isomers may be doped with small quantities of electron-attracting species such as iodine, AsF₅,⁸⁻¹⁰ etc., or with electron

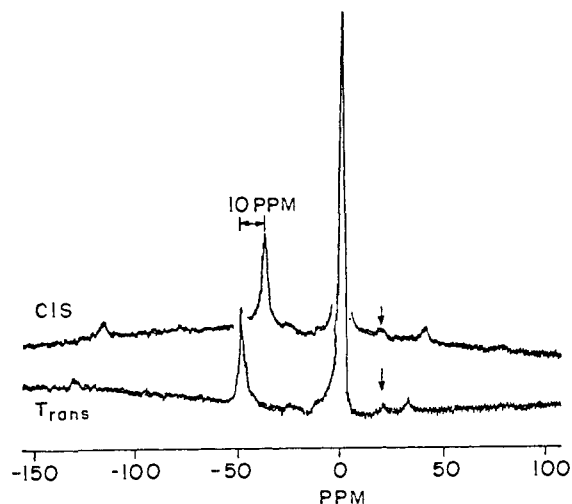
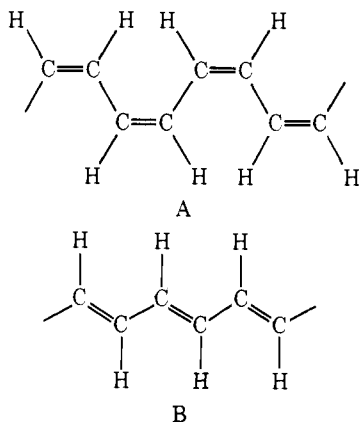


Figure 1. Natural abundance ¹³C spectra of *cis*- and *trans*-polyacetylenes, obtained in an external field of 39 T. Total averaging time was ~1 h to each ~0.5-g sample. Weak lines not mentioned in the text are spinning sidebands. To convert the Delrin-based shift scale to parts per million downfield from Me₄Si, subtract 90 ppm and change the sign.

donors such as sodium¹⁰ to give a series of semiconductors whose conductivity increases with dopant concentration. In the range of 1-3 mol % dopant concentration, the doped films undergo a semiconductor-metal transition to yield flexible films of "organic metals".^{9,10} The conductivity of some of these films are remarkably high, up to 10¹² times greater than the parent polymer. Thus polycrystalline films of [CH(AsF₅)_{0.14}]_x have a room temperature conductivity of 1.0 × 10³ Ω⁻¹ cm⁻¹. This is better than the best single crystals of TTF-TCNQ and related organic conductors.

Elemental analyses of both isomers correspond exactly to the empirical formula (CH)_x.⁶⁻⁸ Identification of the isomers has been made by vibrational spectroscopic studies of thin films.⁴ These data do not, however, show if some cross-linking had occurred by means of sp³-hybridized carbon during polymerization. The empirical formula would be unchanged even if some of the -CH= sp²-hybridized carbon atoms were in fact in the -CH< sp³-hybridized form. Bromination of the polymer to give (CHBr)_x resulted in only ~75% of the expected bromine uptake assuming that all carbons were sp² hybridized and that bromine added completely to all double bonds. The fact that the (CH)_x is insoluble in all solvents tested to date makes it impossible to carry out the bromination under homogeneous conditions which would tend to promote complete bromination. It was therefore not possible to determine whether or not the *cis* or *trans* isomers were "structurally pure". This was a particularly important matter since any interruption of the π system in the polymer by the presence of sp³-hybridized carbon atoms might be expected to affect significantly the electrical properties of the doped or undoped (CH)_x. In order to interpret the physical studies on these materials, it is of fundamental importance to have definitive information on the extent of cross-linking and the concentration of sp³-hybridized carbon.

Among experimental methods which might be applied in such studies, NMR offers a special advantage since chemical shifts are highly diagnostic of chemical structure, and should lend themselves to detection of chemical and stereochemical impurities which represent defects in the idealized *cis*- or *trans*-polyene chains.

Conventional NMR techniques are incapable of resolving shifts of the expected size except in liquids, whereas the properties which make (CH)_x interesting are characteristic of the ordered solid state. Accordingly we have used *cis*- and *trans*-(CH)_x to illustrate the usefulness of "modern" methods

for obtaining high resolution NMR spectra of rigid solids. Specifically we have used the proton-enhancement method¹¹ to detect natural-abundance ¹³C in these systems without dipolar broadening by the protons. We have combined this technique with rapid magic-angle sample rotation¹² to remove powder broadening arising from anisotropies in the chemical shifts.

Nominally pure *cis*- and *trans*-(CH)_x were prepared as described previously^{6,7} and packed into the hollow stems of Delrin rotors of the Beams variety,^{12,13} which were rotated at ~3.3 kHz. The resulting spectra are shown in Figure 1.

The dominant feature in each (apart from the strong ¹³C resonance of the Delrin rotor) is a single line arising from the polyene carbons. The *cis* and *trans* shifts differ by 10 ppm; the *trans* polymer has no detectible *cis* impurity and vice-versa. Each spectrum shows a weaker line (~5%) at higher field, which can probably be ascribed to sp³-hybridized carbon defects such as would occur in chain terminations, cross-links, or hydrogenated double bonds. This puts an upper limit on the amount of sp³-hybridized carbon which can be present. Note that only one such line is evident. The *cis* and *trans* isomers are, therefore, essentially structurally pure in the as-synthesized films.

The *trans* backbone shift (+139 ppm from Me₄Si) is similar to that of the central carbons of butadiene (+137.2 ppm) and of *trans*-hexatriene (+137.4 ppm); the backbone shift of the *cis* polymer (+129 ppm) is close to that of benzene (128 ppm). That is, the shifts are of purely chemical origin and reflect no metallic character. This is consistent with the fact that the pure polymers are semiconductors ($\sigma_{cis-(CH)_x} = 1.7 \times 10^{-9}$, $\sigma_{trans-(CH)_x} = 4.4 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$) at room temperature,¹⁰ whereas metallic electrical and optical properties only appear with dopants such as iodine or AsF₅, etc., after the dopant concentration exceeds ~1–3%.^{9,10} The shifts which we observe here will be useful as reference points for comparison with the NMR spectra of doped polyacetylenes.

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M. M. Maricq, J. S. Waugh

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

A. G. MacDiarmid,^{1b} H. Shirakawa, A. J. Heeger^{1c}

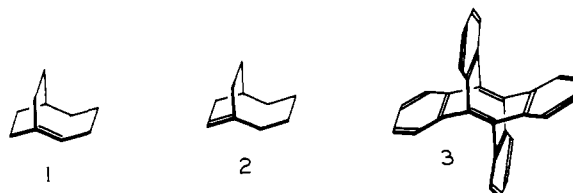
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Received April 28, 1978

Bicyclo[4.2.2]deca-1,5-diene, a Bridgehead Diene

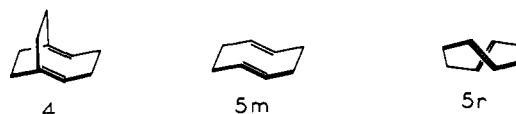
Sir:

For many years bridgehead alkenes were regarded as too unstable to exist,¹ but these substances now are recognized as respectable organic compounds.² A relationship between bridgehead alkenes and *trans*-cycloalkenes has been established:³ bicyclic bridgehead alkenes which have the bridgehead double bond endocyclic and *trans* in rings of at least eight members are generally isolable, whereas those compounds which are bridged *trans*-cycloheptenes or smaller never have been isolated though they can be generated and detected. There are now numerous examples of bridgehead alkenes in various ring systems.² In the bicyclo[4.2.2]decane ring system the two parent bridge head alkenes, **1** and **2**, have been synthesized.⁴



There are far fewer examples of bridgehead dienes. The most notable example is 9,9',10,10'-tetrahydrodianthracene (**3**);⁵ other examples of bridgehead dienes are paracyclophanes,⁶ metacyclophanes,⁶ and [1,5]⁷ and [1,6]⁸ bridged annulenes.

We now report on the synthesis and chemistry of bicyclo[4.2.2]deca-1,5-diene (**4**). Bridgehead diene **4** is an ethano-bridged derivative of *trans,trans*-cycloocta-1,5-diene (**5**) in its meso conformation **5m**. Diene **5**, thought to have the



racemic conformation **5r**,⁹ is isolable at low temperatures but decomposes to a polymer at room temperature.^{9a} Accordingly, bridgehead diene **4** can be expected to possess limited stability at ambient temperatures.

The synthesis of **4** is shown in Scheme I. Reaction of the bishydrazone of cyclohexane-1,4-dione (**6**)¹⁰ with iodine and triethylamine¹¹ produced a mixture¹² of 1,4-diiodocyclohexa-1,3-diene (**7**), mp 94–96 °C, 1,4-diiodocyclohexa-1,4-diene (**8**), mp 118–119 °C, 1,4,4-triiodocyclohexene (**9**), mp 82–83 °C, and 1,1,4,4-tetraiodocyclohexane (**10**), mp 152 °C dec. Treatment of the mixture of reaction products with 1,5-diazabicyclo[4.3.0]non-5-ene converted **9** and **10** selectively into **7**, giving an overall 41% yield of **7**.

Diiodocyclohexadienes **7** and **8** are easily separable by vapor phase chromatography, but in practice it is more efficient to use the mixture directly in the following cycloaddition reaction. The mixture of **7** and **8** was heated together with cyclobutene at 100 °C for 30 days to give 85% (based on **7**) of a 20:1 mixture of adducts **11**, mp 101.5–102 °C, and **12**. At higher temperatures cyclobutene opens to 1,3-butadiene which dimerizes and oligomerizes.

Reduction of the double bonds in **11** and **12** with diimide gave 1,4-diiodobicyclo[4.2.2.0^{2,5}]decane (**13**), mp 192–193 °C, in 84% yield (*m/e* 388; ¹H NMR δ 2.0–3.2; ¹³C NMR, five resonances at 21.6, 39.8, 43.6, 45.4 and 51.3 ppm from Me₄Si).

Reaction of **13** with *tert*-butyllithium in dimethyl ether at –78 °C gave bridgehead diene **4**. Significantly, very little or none of the isomeric diene **14** was produced under these conditions. Treatment of the reaction mixture with ozone at –78