for obtaining high resolution NMR spectra of rigid solids. Specifically we have used the proton-enhancement method[11] to detect natural-abundance ^{13}C in these systems without dipolar broadening by the protons. We have combined this technique with rapid magic-angle sample rotation[12] 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 ^{13}C 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 sp^3-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 sp^3-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 Me_4Si) 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 ($\sigma_{cis\text{-}(CH)_x} = 1.7 \times 10^{-9}$, $\sigma_{trans\text{-}(CH)_x} = 4.4 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$) at room temperature,[10] whereas metallic electrical and optical properties only appear with dopants such as iodine or AsF_5, 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.

References and Notes

(1) (a) Supported by the National Science Foundation and the Office of Naval Research. (b) Department of Chemistry. (c) Department of Physics.
(2) H. C. Longuet-Higgins and L. Salem, *Proc. R. Soc. London, Ser. A*, **251**, 172 (1959); G. Binsch and E. Heilbronnar, "Structural Chemistry and Molecular Biology", W. H. Freeman, San Francisco, 1968, p 815.
(3) E. H. Lieb and F. Y. Yu, *Phys. Rev. Lett.*, **20**, 1445 (1968). R. Peierls "Quantum Theory of Solids", Oxford University Press, Oxford, 1955, pp 108–112. J. Hubbard, *Proc. R. Soc. London, Ser. A*, **276**, 238 (1963); **277**, 237 (1964). A. A. Ovchinnikov, *Usp. Fiz. Nauk*, **108**, 81 (1973); *Sov. Phys.-Usp. (Engl. Trans.)*, **15**, 575 (1973).
(4) H. Shirakawa and S. Ikeda, *Polym. J.*, **2**, 231 (1971).
(5) H. Shirakawa, T. Ito, and S. Ikeda, *Polym. J.*, **4**, 460 (1973).
(6) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 11 (1974).
(7) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1943 (1975).
(8) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).
(9) C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).
(10) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. A. Park, and H. Shirakawa, *J. Am. Chem. Soc.*, **100**, 1013 (1978).
(11) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
(12) E. R. Andrew, A. Bradbury, and R. G. Eades, *Nature (London)*, **182**, 1659 (1958); J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc.*, **98**, 1031 (1976); M. M. Maricq and J. S. Waugh, *Chem. Phys. Lett.*, **47**, 327 (1977).
(13) J. W. Beams, *Rev. Sci. Instrum.*, **1**, 667 (1930).

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

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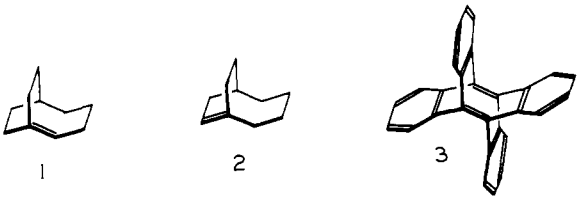
Bicyclo[4.2.2]deca-1,5-diene, a Bridgehead Diene

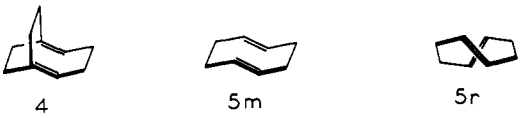
Sir:

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′-tetradehydrodianthracene (**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 triethylamine[11] produced a mixture[12] 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; ^{13}C NMR, five resonances at 21.6, 39.8, 43.6, 45.4 and 51.3 ppm from Me_4Si).

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

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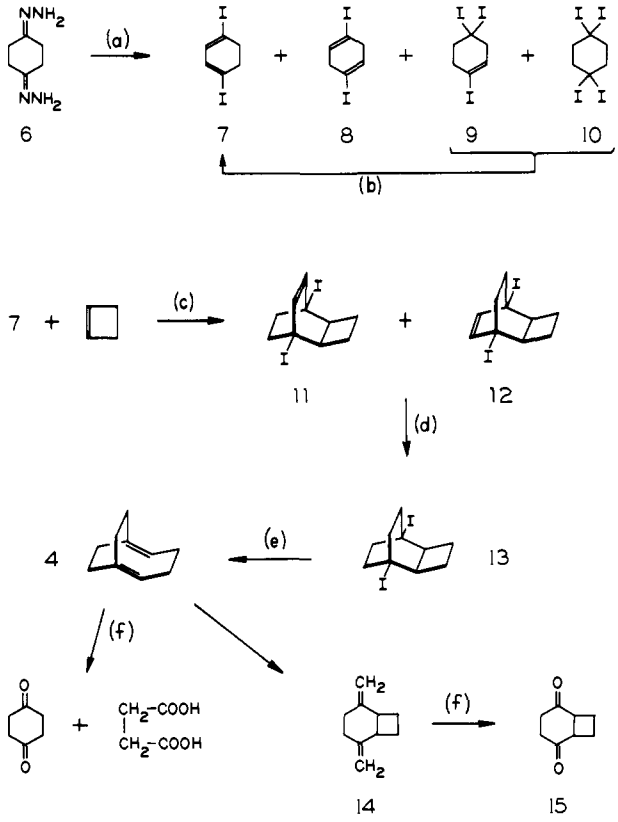
Scheme I



[a] (a) Iodine, triethylamine. (b) 1,5-Diazabicyclo[4.3.0]non-5-ene. (c) 100 °C, 30 days. (d) Diimide. (e) *tert*-Butyllithium, dimethyl ether, −78 °C. (f) Ozone.

°C gave cyclohexane-1,4-dione and succinic acid. No dione **15** was found. Diene **4** is thermally labile and very sensitive to oxygen and has not yet been isolated in a pure state. Attempts to purify **4** by gas chromatography caused isomerization to **14**: ^{1}H NMR δ 4.78 (4 H, br s), 3.06 (2 H, br s), 2.45–1.96 (8 H, complex). Ozonolysis of **14** gave dione **15**. The double bonds of **4** are held rigidly parallel and face to face facilitating the Cope rearrangement.

Partial purification of diene **4** after generation from **13** at −78 °C was accomplished by distillation at −25 °C. The vinyl protons of **4** resonate at δ 5.4 in the ^{1}H NMR spectrum. A Raman spectrum of a mixture of **4** and **14** shows bands at 1620 and 1637 cm^{-1}, which are assigned to the double-bond stretching frequencies of **4** and **14**, respectively. Warming the sample caused the band at 1620 cm^{-1} to decrease, while the band at 1637 cm^{-1} increased.

The rate of rearrangement of **4** into **14** has been measured by ^{1}H NMR spectroscopy by integrating the resonances for the vinyl hydrogens of **4** and **14** using benzene as an internal standard. The reaction rates are shown in Table I. The decrease in the resonance at δ 5.4 is accompanied by twofold increase in the resonance at δ 4.78 and, within the limits of the NMR method, the isomerization of **4** into **14** is quantitative.

In the deiodination of **13**, cleavage of either of the two ethano bridges of the bicyclo[2.2.2]octane ring system would lead directly to **14**. The exclusive formation of **4** by cleavage of the cyclobutano bridge of **13** is a remarkable example of kinetic product control in a reaction.

Table I. Reaction Rates for Isomerization of **4** into **14**

temp, °C	reaction rate, min^{-1}	$t_{1/2}$, min
25	2.2×10^{-3}	314
40	1.1×10^{-2}	64
E_a = 19.6 kcal/mol		

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References and Notes

(1) J. Bredt, *Justus Liebigs Ann. Chem.*, **437**, 1 (1924).
(2) For reviews see (a) G. L. Buchanan, *Chem. Soc. Rev.*, **3**, 41 (1974); (b) G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973); (c) J. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976).
(3) J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, **92**, 956 (1970).
(4) Anita O. Sy, Ph.D. Dissertation, University of Michigan, 1977.
(5) R. L. Viavattene, F. D. Greene, L. D. Cheung, R. Majeste, and L. M. Trefonas, *J. Am. Chem. Soc.*, **96**, 4342 (1974).
(6) (a) F. Vögtle and P. Neumann, *Top. Curr. Chem.* **48**, 67 (1974); (b) B. H. Smith, "Bridged Aromatic Compounds", Academic Press, New York, 1964; (c) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4**, 204 (1971).
(7) (a) S. Masamune, D. W. Brooks, K. Morio, and R. L. Sobszak, *J. Am. Chem. Soc.*, **98**, 8277 (1976); (b) L. T. Scott and W. R. Brunsvold, *ibid.*, **100**, 4320 (1978).
(8) E. Vogel and H. D. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 228 (1964).
(9) (a) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Am. Chem. Soc.*, **91**, 2608 (1969); (b) N. L. Allinger and J. T. Sprague, *ibid.*, **94**, 5734 (1972).
(10) N. A. Domnin and N. S. Glebovskaya, *J. Gen. Chem. USSR* (*Engl. Trans.*), **27**, 723 (1957).
(11) D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962).
(12) All new compounds described had infrared, NMR, and mass spectra in accord with assigned structures, and, except for compounds **4** and **10**, elemental analyses within 0.3% of calculated values were obtained.

John R. Wiseman,* Jeffrey J. Vanderbilt
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109
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Isolation and Structure of Amoorastatin[1]

Sir:

An aqueous extract of *Aphanamixis grandifolia* Bl. seeds was found during an initial study to contain the novel cell growth (murine P388 lymphocytic leukemia) inhibitory tetranortriterpene aphanastatin (**1**).[2] Further investigation (directed by bioasay) of the same extract, from this interesting Eastern Himalayan (India) plant, for antineoplastic constituents has now led to discovery of a new limonoid[3] designated amoorastatin[4] (**2a**) with even greater cell growth (P388)[5] inhibitory (ED_{50} = <0.001 μg/mL) properties. We report that interpretation of spectral data and confirmation by single-crystal X-ray analysis has made possible an unequivocal assignment of structure **2a** (C-28 *R* and *S*) to amoorastatin: mp 205 °C (sintering from 170 °C, crystals from chloroform–methanol); CD in dioxane, Δ^ϵ −4.01 (300 nm) and −3.64 (310 nm).

High resolution mass spectrometry allowed assignment of molecular formula $C_{28}H_{36}O_9$ (M^+, *m/e* 516.2362) and significant fragmentation ions were observed at *m/e* 498.2215 ($M^+ - 18$), 456.2175 ($M^+ - 60$), 438.2057 ($M^+ - 60, -18$) and a diagnostic fragment at 163.0754 ($C_{10}H_{11}O_2$). Acetylation (acetic anhydride–pyridine) of amoorastatin (**2a**) led to a peracetate derivative (**2b**) corresponding to empirical formula $C_{34}H_{42}O_{12}$ (M^+, *m/e* 642): mp 225–228 °C; $[\alpha]^{22}_D$ −97.4° (*c* 0.99, chloroform). Comparison of the 250-MHz ^{1}H NMR spectra obtained from aphanastatin (**1**)[2] with those of amoorastatin (**2a**) and the peracetate derivative **2b** (Table I) revealed a substantial amount of structural information. By this means it was ascertained that the aphanastatin A-ring substitution pattern was modified and the hydroxyl group at

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