(m, 2 H), 2.26–2.19 (m, 2 H), 1.88–1.85 (m, 1 H), 1.86 (d, J = 9 Hz, 1 H), 1.18 (s, 3 H), 0.43 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 193.19, 103.09, 87.07, 76.66, 70.63, 66.29, 65.49, 41.74, 41.22, 35.43, 27.57, 26.70, 21.32; $[\alpha]^{23}_D$ −420.3° (c 0.25, CCl_4); MS, m/z (M^+) calcd 308.0863, obsd 308.0865.

Dehydrative Coupling of 33. A deoxygenated solution of **33** (20 mg, 0.065 mmol), p-toluenesulfonyl chloride (6.2 mg, 0.032 mmol), and triethylamine (4 drops) in dry benzene (20 mL) was stirred at room temperature under nitrogen for 44 h. Water was added and the product was extracted into ethyl acetate (3 × 30 mL). The combined organic extracts were dried, filtered, and concentrated. The yellow solid was purified by chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether) to afford 19 mg (46%) of **34** as a yellow-orange solid, mp 160.5–162 °C (from hexanes): IR (CCl_4, cm^{-1}) 3100, 2980, 2930, 2865, 1740, 1465, 1445, 1370, 1240, 1105, 1045, 1000, 938, 845; ^{1}H NMR (300 MHz, C_6D_6) δ 4.33 (s, 2 H), 4.32 (s, 2 H), 4.09 (s, 2 H), 4.06 (s, 2 H), 4.02 (s, 10 H), 2.66 (dd, J = 3, 16 Hz, 2 H), 2.62–2.57 (m, 2 H), 2.34–2.28 (m, 4 H), 1.99–1.95 (m, 2 H), 1.24 (s, 6 H), 0.87 (t, J = 7 Hz, 2 H), 0.55 (s, 6 H); $[\alpha]^{23}_D$ −351.1° (c 0.24, CCl_4); MS, m/z (M^+) calcd 602.1934, obsd 602.1895.

(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,3a,7a-η)-5,5-dimethyl-2-formyl-4,5,6,7-tetrahydro-4,6-methano-2*H*-inden-1-yl]ruthenium (36 and 37). A solution of **4** (102 mg, 0.472 mmol) and **35** (184 mg, 0.424 mmol) in 1,2-dichloroethane (40 mL) was heated to reflux under a blanket of nitrogen for 24 h. After being cooled to room temperature, 2 N sodium hydroxide (15 mL) and ethanol (15 mL) were added and the mixture was stirred for 90 min, diluted with water (100 mL), extracted into dichloromethane (2 × 100 mL), dried, filtered, and concentrated. Purification by chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) provided a 7:93 mixture of **36** and **37** as a dark brown, viscous oil, 139 mg (93%). The key signals used for integration were the methyl signals (in C_6D_6) due to **36** (δ 1.14, 1.05) and **37** (δ 1.20, 0.62).

(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,3a,7a-η)-5,5-dimethyl-4,5,6,7-tetrahydro-2-(hydroxymethyl)-4,6-methano-2*H*-inden-1-yl]ruthenium (38 and 39). A solution of the **36**/**37** mixture (85.4 mg, 0.242 mmol) in 95% ethanol (25 mL) was treated with sodium borohydride (15 mg, 0.386 mmol) and stirred at room temperature under nitrogen for 45 min. Water (50 mL) was added and the product was extracted into ether (3 × 50 mL). The combined ethereal extracts were dried, filtered, and concentrated to leave a pale yellow solid. The alcohols were separated by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether).

For **38**: 4.8 mg (6%); dark tan solid, mp 90–92 °C; IR (CCl_4, cm^{-1}) 3525, 3460, 3100, 2980, 2930, 2865, 2080, 1880, 1730, 1475, 1460, 1440, 1390, 1370, 1355, 1295, 1235, 1095, 1040, 995, 935, 915, 845, 630, 600; ^{1}H NMR (300 MHz, C_6D_6) δ 4.46 (s, 1 H), 4.38 (s, 5 H), 4.31 (s, 1 H), 4.02 (s, 2 H), 2.54 (dd, J = 2, 16 Hz, 1 H), 2.47–2.42 (m, 2 H), 2.36 (dd, J = 4, 16 Hz, 1 H), 2.30 (t, J = 5 Hz, 1 H), 1.93–1.912 (m, 1 H), 1.25 (s, 3 H), 1.19 (s, 3 H), 0.99 (d, J = 9 Hz, 1 H); $[\alpha]^{23}_D$ +130.5° (c 0.19, CCl_4).

For **39**: 62 mg (72%); off-white powder. The analytical sample was obtained by sublimation [95 °C, 0.5 Torr]: mp 123–124 °C; IR (CCl_4, cm^{-1}) 3620, 3500, 3080, 2965, 2920, 2880, 1460, 1410, 1380, 1360, 1258, 1098, 10250, 995; ^{1}H NMR (300 MHz, C_6D_6) δ 4.54 (s, 1 H), 4.47 (s, 1 H), 4.38 (s, 5 H), 3.99 (d, J = 5 Hz, 2 H), 2.55 (dd, J = 3, 16 Hz, 1 H), 2.48 (d, J = 9 Hz, 1 H), 2.40 (dd, J = 3, 16 Hz, 1 H), 2.23 (t, J = 5 Hz, 1 H), 1.97–1.92 (m, 1 H), 1.81 (d, J = 9 Hz, 1 H), 1.25 (s, 3 H), 1.00 (t, J = 5 Hz, 1 H), 0.70 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 103.30, 93.17, 86.32, 71.71, 69.43, 67.67, 59.30, 42.53, 41.28, 37.61, 27.75, 27.12, 21.90; $[\alpha]^{23}_D$ −186.6° (c 1.1, CCl_4); MS, m/z (M^+) calcd 356.0708, obsd 356.0738.

Anal. Calcd for $C_{18}H_{22}ORu$: C, 60.83; H, 6.24. Found: C, 60.85; H, 6.32.

Acknowledgment. We thank the National Institutes of Health for support of this research program through Grant CA-122115.

Physico-Chemical Studies of Doubly and Triply Unsaturated *syn*- and *anti*-Sesquinorbornanes. Photoelectron Spectroscopy, Molecular Orbital Calculations, and Deuterium-Induced ^{13}C NMR Shifts

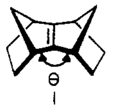
Hermann Künzer,[1a,2] Edwin Litterst,[1b] Rolf Gleiter,*[1b] and Leo A. Paquette*[1a]

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, and the Organisch-Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg 1, West Germany

Received February 18, 1987

The photoelectron spectra of the *syn*- and *anti*-sesquinorbornadienes and -trienes **3**–**6** have been measured and compared to those recorded for the parent olefins **1** and **2**. These data have been analyzed with the aid of STO-3G and extended Hückel molecular orbital calculations. Deuterium-induced NMR shifts of ^{13}C resonance frequencies have been measured for the C-2 deuterium-labeled substrates **9**, **10**, and **13**. Various components of these three studies have provided diagnostic information concerning the bending about the central π bond that materializes in the syn series, although it has not been possible to gauge with any accuracy the magnitude of the deformation angle θ.

syn-Sesquinorbornene (**1**) has attracted the attention of many chemists due to its molecular structure and its reactivity. Several X-ray studies on **1** and its derivatives[3-5] reveal that the central double bond deviates by 12–22° from planarity. In contrast, most[3,4] though not all[6-8] *anti*-sesquinorbornenes (e.g., **2**) possess an essentially planar double bond. The bending observed in **1** has been rationalized in terms of (a) a diminished destabilizing in-



1

2

---

[1] (a) The Ohio State University. (b) Organisch-Chemisches Institut der Universitat Heidelberg.

[2] Postdoctoral fellowship awardee of the Deutsche Forschungsgemeinschaft, 1985–1986.

[3] Watson, W. H.; Galloy, J.; Barlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

[4] (a) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3148. (b) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *Ibid.* **1983**, *105*, 3136. (c) Paquette, L. A.; Künzer, H.; Green, K. E.; DeLucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *Ibid.* **1986**, *108*, 3453.

[5] Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818.

[6] Ermer, O.; Bödecker, C.-D. *Helv. Chim. Acta* **1983**, *66*, 943.

[7] Gajhede, M.; Jørgensen, F. S.; Kopecky, K. R.; Watson, W. H.; Kashyap, R. P. *J. Org. Chem.* **1985**, *50*, 4395.

[8] Paquette, L. A.; Green, K. E.; Hsu, L.-Y. *J. Org. Chem.* **1984**, *49*, 3650.

0022-3263/87/1952-4740$01.50/0

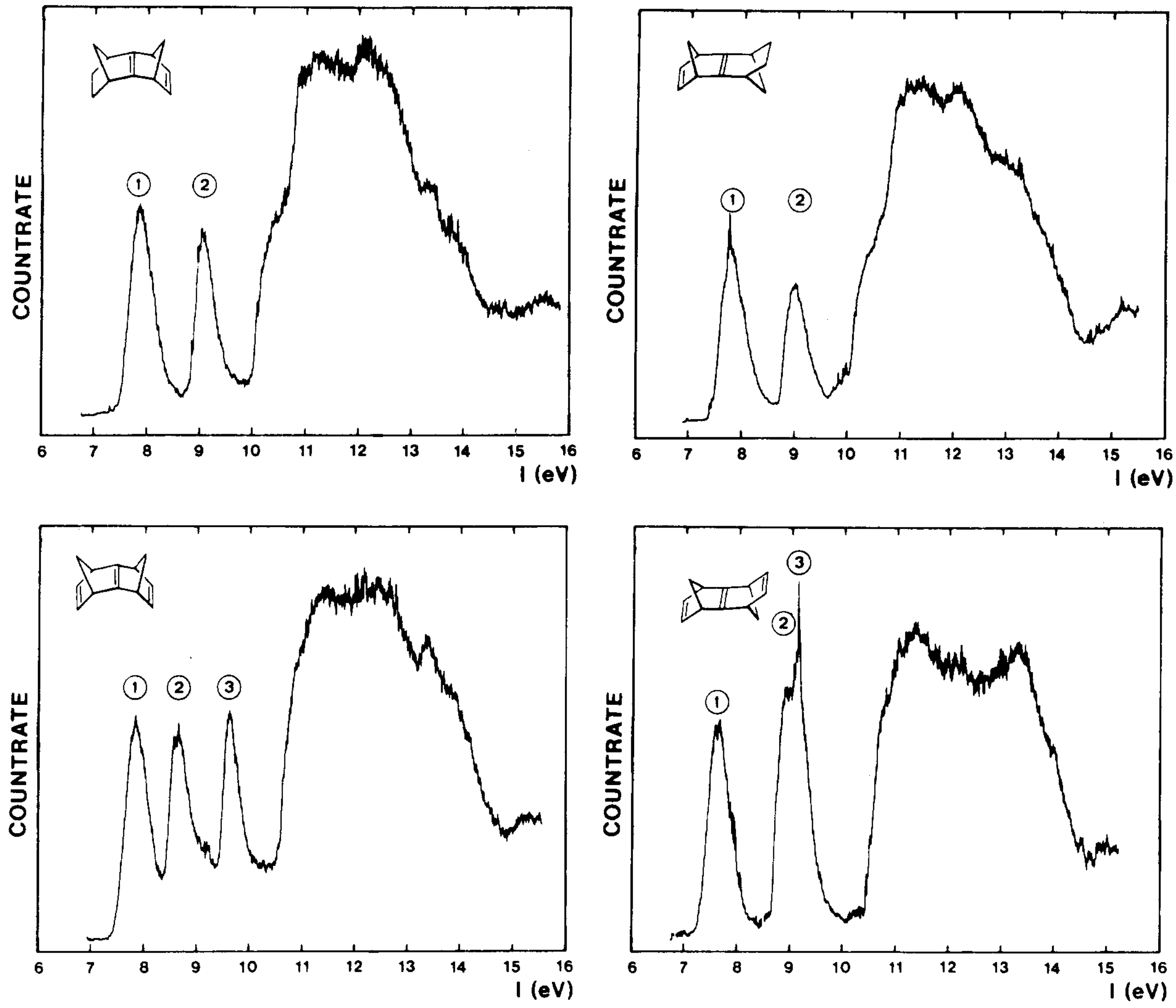


Figure 1. Photoelectron spectra of **3–6**.

teraction between the π-MO and a lower energy σ orbital localized mainly within the five-membered rings[9] and (b) the relief of unfavorable torsional interactions.[10,11]

The finding that the first ionization energy of **1** (8.12 eV) is higher than that of **2** (7.90 eV)[12] can be advanced in favor of the electronic effects just mentioned. As a direct consequence of the bending in **1**, the rotation of the pπ lobes results in less effective overlap with those σ orbitals that are localized principally in the bridges (see below). This effect likely gains no importance in relation to the planar double bond in **2**.


bent


planar

In an attempt to develop further our understanding of the electronic structures of **1** and **2** as well as their congeners **3–6**, photoelectron (PE) spectroscopic investigations have been carried out in conjunction with molecular orbital calculations. Attempts to quantify $^2H/^1H$ isotope effects on ^{13}C chemical shifts in **4**, **6**, and the quadricyclane **7** are also detailed.


3


4


5


6


7

Photoelectron Spectroscopic Studies. The PE spectra of **3–6** are illustrated in Figure 1. Those recorded for **3** and **5** are quite similar in the sense that there are two bands at approximately 8 and 9 eV which are well separated from strongly overlapping bands at higher energy. In contrast, the PE spectra of **4** and **6** are markedly different. In that of syn triene **4**, three well-separated, nearly equally spaced bands are seen below 10 eV, while in the spectrum of anti triene **6**, the bands at approximately 9 eV overlap strongly.

For the interpretation of these spectra, reliance is placed on the validity of Koopmans' theorem ($-\epsilon_j = I_{v,j}$),[13] which permits correlation of the measured vertical ionization energies ($I_{v,j}$) with the calculated orbital energies ($-\epsilon_j$). Our

---

(9) (a) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, *927*. (b) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *39*, 3345.

(10) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980.

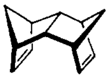
(11) For additional theoretical commentary concerning these molecules, consult: (a) Jørgensen, F. S. *Tetrahedron Lett.* **1983**, *5289*. (b) Johnson, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1135.

(12) (a) Brown, R. S.; Buschek, J. M.; Kopecky, K. R.; Miller, A. J. *J. Org. Chem.* **1983**, *48*, 3692. (b) Gleiter, R.; Paquette, L. A.; unpublished results.

(13) Koopmans, T. *Physica* **1934**, *1*, 104.

empirical interpretation begins with the PE spectra of **1** and **2**. In each instance, the first band is attributed to an ionization event from the π-MO. Introduction of a second double bond as in **3** and **5** affects the first ionization energy only slightly. This is as it should be if the ionization energies of the respective central double bonds (7.90 and 8.12 eV) are compared with that of a peripheral double bond. For the latter value, the datum recorded for norbornene (8.97 eV)[14] is used as reference. This comparison discloses that the corresponding basis orbital energy gap between the two π-moieties is on the order of 1 eV. Arguments having their origin in perturbation theory[15] require that the resulting interaction between these levels be small. For reasons of geometry, the split in **3** and **5** should be close to that seen in norbornadiene. Comparison of the split between the first two bands in **3** (1.22 eV) and **5** (0.90 eV) with that demonstrated for norbornadiene (0.86 eV)[15] supports this conclusion.

The difference between the orbital energies of central and peripheral double bonds gives rise to the expectation in **4** and **6** that their outermost double bonds should interact effectively only with each other. Geometrical considerations suggest that spatial interaction between the peripheral double bonds should also be possible uniquely in **4**. In actuality, it is precisely these differences that surface in the PE spectra of **4** and **6**. In both cases, the first band is seen to be essentially unaffected when comparison is made directly to **3** and **5**, respectively. The second and third bands are, however, noticeably split in **4**, the resonance integral amounting to $\beta = {}^1/_2(I_{v,2} - I_{v,3}) = 0.5$ eV. This value is satisfyingly close to that observed for **8** ($\beta = 0.45$ eV).[16]



8

Molecular Orbital Calculations. In order to lend added credence to the preceding interpretation, minimal basis (STO-3G)[17] ab initio calculations have been carried out. The geometrical parameters adopted were those derived from an earlier MINDO/3 calculation.[9] The predicted C–C bond lengths were between 1.53 and 1.54 Å for the single bonds and 1.35 Å for the double bonds in all six compounds. For **1** and **4**, the dihedral angle θ between the molecular planes was varied while leaving all other parameters unchanged. Values of 169° (for **1** and **3**) and 171° (for **4**) were obtained. The resultant θ for **1** is in close agreement with that found for this monoolefin (170°) when all parameters were optimized by means of a minimal basis set. The angles predicted by the extended Hückel method were 167° for **1** and **3** and 169° for **4**. Both methods agree insofar as they predict a slightly smaller dihedral angle for **4** than for **1** and **3**. As concerns **5** and **6**, both methods converged to a θ value of 180°.

When Allinger's MM2 force field[18] was applied to these molecules, a somewhat different ordering of θ was arrived at: **1** = 162°, **3** = 155°, and **4** = 153°. According to this method, therefore, the dihedral angle decreases regularly as a function of the increasing number of double bonds. Our observation that the split between bands 2 and 3 in the PE spectrum of **4** amounts to the split observed for **8** could be interpreted in favor of a more acute bending in **4** than in **1**. For **8**, the dihedral angle has been calculated (MM2) to be 127.7°.

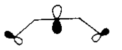
Table I. Comparison between Vertical Ionization Energies ($I_{v,j}$) and Calculated Orbital Energies ($-\epsilon_j$) of 1–6 (All Values Are in eV)

compd	$I_{v,j}$	assignment	$-\epsilon_j$(STO-3G)	$-\epsilon_c^{\text{corr}\,a}$
1	8.12	$11a_1$ (π)	6.71	8.05
3	7.87	$20a'$ (π)	6.48	7.77
	9.09	$19a'$ (π)	7.70	9.24
4	7.84	$11a_1$ (π)	6.31	7.57
	8.66	$9b_2$ (π)	7.24	8.69
	9.63	$10a_1$ (π)	7.95	9.54
2	7.90	$10b_u$ (π)	6.56	7.87
5	7.80	$20a'$ (π)	6.39	7.67
	9.0	$19a'$ (π)	7.42	8.90
6	7.65	$10b_u$ (π)	6.23	7.48
	9.0	$9b_u$ (π)	7.27	8.72
	9.2	$10a_g$ (π)	7.62	9.14

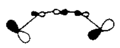
[a] $-\epsilon_j^{\text{corr}} = \epsilon_j(\text{STO-3G}) + 0.2\epsilon_j(\text{STO-3G})$.

The calculated ionization energies (STO-3G) for **1**–**6** are listed in Table I. These calculations are based on the MINDO/3 geometries for **1**–**6** mentioned above. When recourse was made to the MM2 geometries, the values for the π-MOs did not change. In the last column of Table I are compiled the ionization energies to which the empirical correction $I_{v,j} = -(\epsilon_j + 0.2\epsilon_j)$ has been applied. This formula is very close to that suggested by Brundle, Robin, and Basch.[19] The agreement with experiment is considered to be good, especially the close parallelism between the energy differences involving the first three MOs of **4** and **6** and those of the recorded ionization events.

For the wave functions, it is predicted that $11a_1$, the HOMO of **4**, is mainly localized at the central carbons while $9b_2$ and $10a_1$ show larger coefficients at the peripheral double bonds (see below). An analysis of the calculated wave functions shows that a high lying σ orbital of b_2 symmetry influences $9b_2$ only slightly, while $11a_1$ and $10a_1$ are unaffected by π/σ interaction.



$11a_1$



$9b_2$

$10a_1$

Deuterium Isotope Effects. The study of deuterium isotope effects on the chemical shifts of carbon atoms in specifically labeled compounds has shown strong signs of developing into a useful tool for structural studies.[20] It has recently been demonstrated that the degree of hybridization of carbon atoms directly attached to a deuteron is linearly correlated to the magnitude of the α-isotope effect in the series ethane-d_1, ethylene-d_1, and acetylene-d_1.[21] More recently, impressive correlations were reported for γ- and δ-isotope effects in norbornene-like molecules.[22]

It was therefore of interest to examine if the hybridization changes associated with the differences in internal

---

(14) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745.

(15) (a) Heilbronner, E.; Bock, H. *Das HMO Modell und seine Anwendung*; Verlag Chemie: Weinheim, 1968. (b) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975.

(16) Prinzbach, H.; Sedelmeier, G.; Martin, H.-D. *Angew. Chem.* **1977**, *89*, 111.

(17) Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769.

(18) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

(19) Brundle, C. R.; Robin, M. B.; Basch, H. *J. Chem. Phys.* **1970**, *53*, 2196.

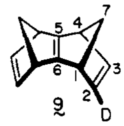
(20) (a) Forsyth, D. A. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Ed.; Elsevier: Amsterdam, 19884; Vol. 6. (b) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 106.

(21) Wesener, J. R.; Moskau, D.; Günther, H. *Tetrahedron Lett.* **1985**, 1491; *J. Am. Chem. Soc.* **1985**, *107*, 7307.

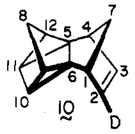
(22) Künzer, H.; Cottrell, C. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 8089.

π-bond deformation within 4 and 6 might be similarly responsive to remote isotopic substitution. From the outset, we were well aware that the chemical shifts of the central olefinic carbon atoms in this pair of trienes did not reflect their planarity status.[4c] Notwithstanding, this study constitutes the first application of deuterium isotope effects on chemical shifts to the evaluation of bending in olefinic double bonds.

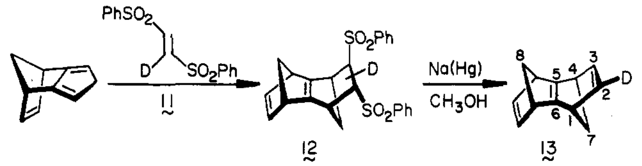
The deuteriated systems **9** and **10** were prepared as described elsewhere.[23] The synthesis of **13** paralleled methodology developed for the unlabeled compound[4c,24] and is detailed in the Experimental Section. Since **9** and **13** are sensitive to oxygen, these hydrocarbons were dissolved in degassed CD_2Cl_2 immediately following their preparation, transferred to NMR tubes with strict exclusion of air, and sealed under vacuum following three freeze–thaw cycles. The level of deuterium incorporation for **9** and **13** was 86% and 89%, respectively, as determined by ^1H NMR spectroscopy. Simultaneously, a second set of samples containing **9** and **13** was prepared starting from the corresponding monodeuteriated disulfones to which approximately 20% of the unlabeled counterpart had been added. These isotopically diluted triene samples served for the unequivocal determination of the sign of the isotopic splittings of the carbon signals. For quadricyclane derivative **10**, no comparable precautions had to be taken because this substance is not oxygen-sensitive. The ratio of deuteriated to undeuteriated material was simply adjusted by the addition of an aliquot of d_0 material.



9



10



The ^{13}C NMR spectra of these samples were recorded at 303 K and 125.749 MHz under conditions of ^1H-WALTZ-16 decoupling.[25] Resonances due to C-5, C-6, and C-7 were also recorded individually in order to insure a digital resolution of up to 0.031 Hz/point. Lorentz to Gaussian line shape transformations were utilized to enhance spectral resolution.[26]

The determination of isotope effects on ^{13}C chemical shifts is based on the specific assignments given in Table II. The isotope effects on individual carbon resonances ($\Delta\delta_{C_i}$) are compiled in Table III. The distinction between positions C-5/C-6 in **9**, **10**, and **13** and C-7/C-8 in **13** has its origins in the normal sequencing $^1J_{(C,D)} > {}^3J_{(C,D)} > {}^2J_{(C,D)} > {}^4J_{(C,D)}$,[20,27] the consequence of which is appreciable line broadening at C-6 and C-7 compared to C-5 and C-8.

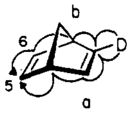
Table II. ^{13}C **Chemical Shift Assignments to 4, 6, and 7 (125 MHz,** CD_2Cl_2 **Solution)**[a]

compd	C	shift, ppm
4	C-5,6	172.55
	C-2,3	140.68
	C-7	69.45
	C-1,4	50.43
6	C-5,6	173.59
	C-2,3	144.27
	C-7	77.89
	C-1,4	50.87
7	C-2,3	135.87
	C-7	49.17
	C-1,4	42.33
	C-8	38.36
	C-5,6	36.43
	C-9,12	27.08
	C-10,11	15.47

[a] See formulas **9**, **10**, and **13** for numbering schemes.

As was demonstrated earlier in structurally simpler norbornenyl systems,[22] all carbon atoms of the labeled half in **9**, **10**, and **13** exhibit isotope effects of appreciable magnitude. Positive γ-isotope effects are observed at C-4, while those at C-6/C-7 exhibit a negative sign. The δ-isotope effects at C-5 are also negative, whereas the strikingly large ϵ-effect at C-8 in **13** happens to be positive. The isotope effects operative at C-5/C-6, i.e., at the central π bond, are clearly related to the particular hybridization at these positions, as is evident from a comparison of the $\Delta\delta_{C_i}$ values for these carbon atoms in **9**, **10**, and **13** (Table III). The $\Delta\delta_{C_i}$'s observed for **9** and **13** are slightly more negative than those encountered in norbornadiene-*2-d*.[22] This difference, however, is not per se convincingly indicative of enhanced pyramidalization in **9** relative to **13**, chiefly because the trends at C-5 and C-6 go in opposite directions.

Relevantly, isotope effects at distant carbon atoms may be recognized to originate by propagation via the bonding network of the carbon skeleton as illustrated in **14**. In cyclic systems such as this, there exist two short δ-routes to C-5. Of course, comparable transmission pathways are present in **9** and **13**. To a crude first approximation, route a is similar for **9** and **13**, whereas route b should differ for these two compounds if the central double bond were planar in **13** and folded in **9**.



14

Polarization along the central double bond may be defined by $\Delta\Delta\delta = |\Delta\delta_{C\text{-}5}| - |\Delta\delta_{C\text{-}6}|$. The parametrization generates values of 5.2 ppb for **9** and 8.6 ppb for **13**. Interestingly, the $\Delta\Delta\delta$ for *anti*-sesquinorbornatriene is close to that of norbornadiene itself (8.8 ppb). Although a correlation may be hinted at here, there is at present an insufficient number of reference compounds available to confirm the relationship. On the negative side, the $\Delta\Delta\delta$ value for quadricyclane **10** (4.7 ppb) falls close to that for **9**, thereby potentially discounting this trend as an indicator of pyramidalization.

The extreme low-field shift for C-7 in norbornadiene is believed to result from a depletion of electron density in those σ bonds interconnecting C-7 to the bridgehead carbon atoms in favor of the π-LUMO's of the flanking olefinic bonds.[28] If the lobes within the LUMO of **9** do

---

[23] (a) Paquette, L. A.; Künzer, H. *J. Am. Chem. Soc.* **1986**, *108*, 7431. (b) Paquette, L. A.; Künzer, H.; Kesselmayer, M., manuscript in preparation.

[24] DeLucchi, O.; Licini, G.; Pasquato, L. *J. Chem. Soc., Chem. Commun.* **1985**, 418.

[25] Shaka, A. J.; Keeler, J.; Frenkiel, T.; Freeman, R. *J. Magn. Reson.* **1983**, *52*, 335.

[26] Ferrige, A. G.; Lindon, J. C. *J. Magn. Reson.* **1978**, *31*, 337.

[27] Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1984; p 451.

[28] Bicker, R.; Kessler, H.; Zimmerman, G. *Chem. Ber.* **1978**, *111*, 3200.

[29] De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596.

Table III. $^2H/^1H$ Isotope Effects ($\Delta\delta_{Ci}$) on ^{13}C Chemical Shifts (ppb)[a,b]

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
9	106.8	288.5	132.8	15.1	−18.1	−12.9	−29.9	
10	105.6	226.1	141.9	14.9	−14.5	−9.8	−13.6	
13	107.9	272.0	136.0	20.8	−20.5	−11.9	−44.5	20.6

[a] Isotope effects are defined as $\Delta\delta_{Ci} = \delta_{Ci}^{RH} - \delta_{Ci}^{RD}$; positive values are therefore shifts to higher field. [b] Experimental error limits are ±0.5 ppb.

indeed rotate outwardly as a consequence of central π-bond deformation, less efficient overlap should result. This is, in fact, evident in the relative shielding of C-7 within **9** and the relatively small isotope effect at this position. Optimal overlap is preserved, however, in the flat central portion of **13**. The expectations are an obvious deshielding of C-7 and a more substantive isotope effect at C-7/C-8.

Conclusions. The PE spectra of **4** and **6** owe their striking dissimilarity predominantly to the strong through-space interaction of the peripheral double bonds in the syn isomer. Since the resonance integral for **4** compares very closely to that of **8**, the implication that the syn triene is appreciably folded at its central double bond would appear justified. In the anti isomer, this interaction is virtually and perhaps totally absent.

Both STO-3G and extended Hückel calculations point to folded conformations for all three unsaturated *syn*-sesquinorbornanes and predict the existence of a somewhat smaller band in **4** than in **1** and **3**. In contrast, the θ value for all three anti derivatives converged at 180 °C. When recourse was made to MM2 procedures, the dihedral angles within **1**, **3**, and **4** were seen instead to decrease regularly as a function of the number of unsaturated centers. This reversal in ordering probably materializes because of the excessive weighting given by MM2 to nonbonded H–H interactions. In this specific instance, we see that θ correlates with the incremental removal of intramolecular steric crowding between the two syn-oriented ethano bridges.

Finally, the appreciable folding in *syn*-sesquinorbornatriene is quite apparent in the relative shielding of C-7 in its 2-*d* derivative (**9**). When the central double bond is planar, as it presumably is in the monodeuteriated anti triene **13**, optimal σ-π overlap returns and is reflected in an obvious deshielding of C-7. Otherwise, $^2H/^1H$ correlations on ^{13}C chemical shifts have not proven necessarily confirmatory of enhanced pyramidalization in **9**. This is quite possibly a reflection of the fact that isotope effects are fundamentally vibrational in origin, such that electronic potential energy surfaces are not affected (Born–Oppenheimer approximation). Since the chief contribution to $\Delta\delta$ arises from the anharmonic segment of the expression for chemical shielding,[30] the state of hybridization at C-5 and C-6 may not be linearly responsive to the charge redistribution that accompanies the difference in zero-point vibrational energy for a shorter C–D bond.

Experimental Section

Complete details for the preparation of **3**–**6** can be found in ref 4c. Quadricyclanes **7** and **10** were prepared according to ref 23b, as was triene **9**. The PE spectra of **3**–**6** were recorded on a Perkin-Elmer PS18 instrument at room temperature by using multiscanning techniques made possible by electronic data acquisition with a Hewlett-Packard HP 1000 computer. The spectra have been calibrated with Ar and Xe. A resolution of 25 eV on the $^2p_{3/2}$ Ar line was obtained.

(*E*)-1,2-Bis(phenylsulfonyl)ethylene-*1-d* (11). A solution of 6.2 g of the monodeuterio *Z* isomer[23] in 50 mL of dichloromethane containing 50 mg of iodine was photoisomerized with a 450-W Hanovia lamp according to precedent.[29] The crude product was recrystallized from acetonitrile to give 4.8 g (77%) of **11**, mp 221 °C.

Cycloaddition of 11 to Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene. Reaction of 1.3 g (10 mmol) of the triene with 3.09 g (10 mmol) of **11** in 40 mL of chloroform as previously detailed furnished 3.16 g (71%) of **12**, mp 164 °C.

Reductive Elimination of 12. A 329 mg (0.75 mmol) sample of **12** was desulfonylated as described earlier[4c] to give 47 mg (40%) of crystalline **13**. The triene was introduced into an NMR tube as follows. Methylene-d_2 chloride (1 g) contained in a Schlenk tube was degassed by means of five freeze–thaw cycles and placed under an atmosphere of argon. This solvent was next transferred by canula to a second Schlenk flask containing the triene by applying a positive argon pressure. A jointed NMR tube had previously been stoppered with a rubber septum containing a 5-mL septum-capped syringe housing a small plug of glass wool. This part of the system was flushed with argon and the triene solution was transferred under positive argon pressure (with filtration) into the NMR tube, which was subsequently subjected to three freeze–thaw cycles and sealed.

Acknowledgment. We are grateful to the National Institutes of Health (Grant CA-12115) and the Fonds der Chemischen Industrie for financial support. The assistance provided by Dr. Charles E. Cottrell in recording the 500-MHz ^1H and 125-MHz ^{13}C NMR spectra was invaluable to the conduct of this research.

---

(30) Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4983.