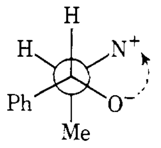
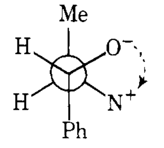
of the chiral catalyst with otherwise achiral dimethylsulfonium methylide. The ylide attack thus occurs preferentially on one of the enantiotopic faces of benzaldehyde.[11-13]


V


VI

In order to confirm this proposal the solvent effect has been investigated. In a water-miscible solvent such as tetrahydrofuran or acetonitrile, the oxirane formation in the presence of Ia proceeded in 66 or 48% chemical yield with negligible asymmetric induction (9.1 or 0% enantiomeric excess, respectively). This is understood in terms that these solvents favor the protonation of dipole V converting it to an ammonium hydroxide of no enantioselectivity similarly as III and IV. In benzene, therefore, the catalysis did proceed with a high degree of induction (65% chemical yield, $[\alpha]^{24}\mathrm{D}$ +4.60 (c 8.92), 58% enantiomeric excess).[14]

Finally the change of the molar ratio of the catalyst to benzaldehyde gave remarkable response in the induction in the benzaldehyde-Ib reaction system (mole ratio, chemical yield (%), $[\alpha]^{31}\mathrm{D}$ (c), enantiomeric excess (%)): $\frac{1}{100}$, 61, +2.32° (2.16), 35;[6b] $\frac{1}{5}$, 45, +6.43° (1.64), 97.[6b] This finding shows that nearly complete asymmetric induction can be attained in the presence of as much as 0.2 equiv of the catalyst used. In the duplicated experiment 89% enantiomeric excess[6b] (51% chemical yield) was obtained.

References and Notes

(1) (a) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971; (b) J. W. Scott and D. Valentine, Jr., *Science*, **184**, 943 (1974); (c) T. D. Inch, *Synthesis*, 466 (1970); (d) I. Ojima, *Yuki Gosei Kagaku Kyokai Shi*, **32**, 687 (1974).

(2) (a) E. H. Cordes and R. B. Dunlap, *Acc. Chem. Res.*, **2**, 329 (1969); (b) J. Dockx, *Synthesis*, 441 (1973); (c) E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **13**, 170 (1974); (d) J.-P. Behr and J.-M. Lehn, *J. Am. Chem. Soc.*, **95**, 6108 (1973).

(3) I. Tabushi and Y. Kuroda, *Tetrahedron Lett.*, 3613 (1974).

(4) The ammonium salt was prepared by quaternization of commercially available ephedrine (100% optically pure) with methyl bromide. The precipitated salt was washed with n-hexane and dried: mp 215°, $[\alpha]^{31}\mathrm{D}$ −22.5° (c 2.18, water).

(5) A. Merz and G. Märkl, *Angew. Chem.*, **85**, 867 (1973).

(6) The optical rotation of 2-phenyloxirane is dependent upon the concentration; the optical rotation of the same sample was found to be $[\alpha]^{25}\mathrm{D}$ +3.78° (c 3.40). The recorded maximum value is (a) $[\alpha]\mathrm{D}$ +7.94 (c 9.78, acetone) (C. R. Johnson and C. W. Schroeck, *J. Am. Chem. Soc.*, **95**, 7418 (1973)) (b) $[\alpha]\mathrm{D}$ +6.64 (c 4.9, acetone) (C. R. Johnson and C. W. Schroeck, *ibid.*, **93**, 5303 (1971)). Therefore the optical yield in this report was estimated on the basis of either the value (a) or (b) depending on the value of c.

(7) Each salt was prepared by the quaternization of N-methylephedrine[8] with alkyl bromide: Ib, mp 182–185° dec, $[\alpha]^{31}\mathrm{D}$ −13.9° (c 2.42, water); Ic mp 189–190° dec, $[\alpha]^{31}\mathrm{D}$ −12.2° (c 3.27, water); Id, no apparent melting point, $[\alpha]^{31}\mathrm{D}$ −8.3° (c 2.19, water).

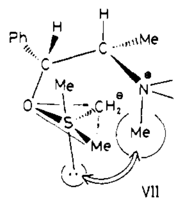
(8) K. Nakajima, *Nippon Kagaku Zasshi*, **81**, 1476 (1960).

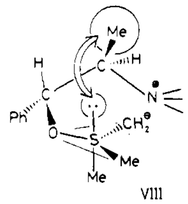
(9) (±)-ψ-Ephedrine was resolved upon treatment with tartaric acid to yield (−)-ψ-ephedrine $[\alpha]^{33}\mathrm{D}$ −43.7° (c 1.14, EtOH). Methylation of (−)-ψ-ephedrine was carried out according to the reported procedure,[8] giving (−)-N-methyl-ψ-ephedrine $[\alpha]^{33}\mathrm{D}$ −39.8° (c 1.22, EtOH). The tertiary amine was mixed with methyl bromide or ethyl bromide, and the resulting salts were collected, washed with n-hexane, and dried: IIa, mp 182–186° dec, $[\alpha]^{31}\mathrm{D}$ −34.8 (c 1.89, water); IIb, mp 160–164° dec, $[\alpha]^{31}\mathrm{D}$ −38.7° (c 0.59, water).

(10) III, no apparent melting point, $[\alpha]^{20}\mathrm{D}$ −1.99 (c 2.51, water); IV, mp 210°, $[\alpha]^{20}\mathrm{D}$ −88° (c 0.40, water).

(11) The rate enhancement effect of the β-hydroxyethyl unit in the quaternary ammonium salt has been observed in ester hydrolysis: (a) G. Meyer, *C.R. Acad. Sci., Ser. C*, **276**, 1599 (1973); (b) C. Lapinte and P. Viout, *Tetrahedron Lett.*, 4221 (1972); (c) *ibid.*, 1113 (1973); (d) V. Gani, C. Lapinte, and P. Viout, *ibid.*, 4435 (1973); (e) C. A. Bunton, L. Robinson, and M. F. Stam, *ibid.*, 121 (1971); see also (f) Y. Ohgo, Y. Natori, S. Takeuchi, and J. Yoshimura, *Chem. Lett.*, 1327 (1974).

(12) A possible explanation of the oxirane chirality is based on the intermediates VII and VIII containing pentavalent, trigonal bipyramidal sulfur resulting from I and II, respectively. The hypothesis is also supported by the fact that methylphenylsulfonium methylide derived from dimethylphenylsulfonium tetrafluoroborate under this condition gave a lower asymmetric induction: 87% yield, $[\alpha]^{22}\mathrm{D}$ +1.95° (c 5.64), 25% enantiomeric excess. In this case the chiral dipole V supposedly interacted with the chiral ylide disfavorably.


VII


VIII

Less severe non-bonded interaction in the preferred conformer of skew boat type.

(13) Under similar condition acetophenone afforded 2-methyl-2-phenyloxirane (76% yield, 15% conversion) of $[\alpha]^{18}\mathrm{D}$ −10.8° (c 0.98, acetone). The enantiomeric excess value was not estimated as the optical rotation of the pure sample had been unknown.

(14) n-Hexane as a solvent proved futile.

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Electron Spin Resonance Spectra and Structures of 9-Benzonorbornenyl and 9-Benzonorbornadienyl Radicals

Sir:

The radicals in the title and related compounds are of interest with respect to their structure,[1,2] stereoselectivity in radical-transfer reactions,[1b,3] and possible bishomoallylic and bishomobenzylic interactions. Recently Underwood and Friedman[4] reported the structure of 9-azabenzonorbornene and 9-azabenzonorbornadiene complexed to nickel acetylacetonate with the conclusion that the NH bond lies anti to the aromatic ring in both the substrates.[5] In the present investigation, interestingly the ESR data showed that the C_9–H_9 bond lies syn to the aromatic ring in 9-benzonorbornenyl (I) and 9-benzonorbornadienyl (II) radicals, which prompted us to make a preliminary report on these radicals.

The ESR spectrum of Figure 1 was observed during photolysis[6] of a cyclopropane solution of a mixture of 9-*anti*-bromobenzonorbornadiene,[7] triethylsilane, and di-*tert*-butyl peroxide[8] at −116°. The spectrum was analyzed as a doublet of 8.27 G split into two sets of 1:2:1 triplets of 1.68 and 0.28 G, respectively, split further into 1:4:6:4:1 quintets of 0.14 G.[9] Cristol and Noreen[3a] reported that the reduction of 9-*anti*-bromobenzonorbornadiene with tri-*n*-butyltin deuteride at 60° (azobisisobutyronitrile initiation) resulted in *syn*- and *anti*-9-deuteriobenzonorbornadiene without rearrangement of the skeleton. Thus the spectrum in Figure 1 was assigned to II. Figure 2 shows the ESR spectrum of I at −120° generated similarly from 9-*anti*-bromobenzonorbornene.[7] This spectrum consists of a doublet (12.7_8 G) of three sets of 1:2:1 triplets (1.93, 1.33, and 0.29 G).[9]

The largest doublets of I (12.7_8 G) and II (8.27 G) are due to α-protons (H_9). These radicals (I and II) together with the radicals III and IV are listed below in decreasing order of their α-proton hyperfine splitting constants (hfsc). Dobbs, Gilbert, and Norman[10] found a monotonic relationship between $J(^{13}CH)$ of R_2CH_2 and $a(H_\alpha)$ of $R_2\dot{C}H$. Values of $J(^{13}CH)$ between C_7 and H_7 of norbornane and norbornene and those between C_9 and H_9 of benzonorbornene and benzonorbornadiene were observed to be 132, 133, 133, and 135 Hz, respectively. These values, together with the $J(^{13}CH)$-$a(H_\alpha)$ relationship, predict that the α-proton

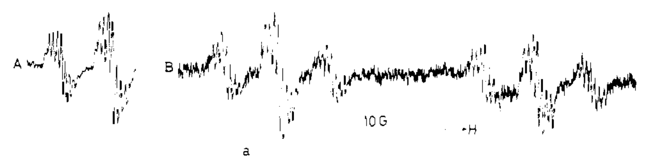


Figure 1. (B) Spectrum of the 9-benzonorbornadienyl radical in cyclopropane solution at −116°; (A) the underlined part (a) of B observed with higher resolution, higher gain, and longer response time setting.

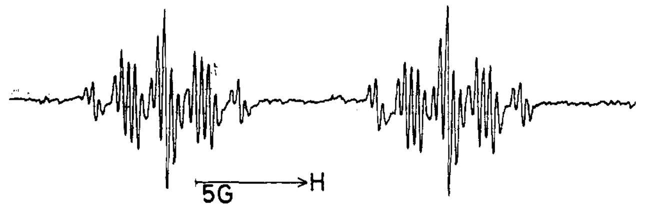
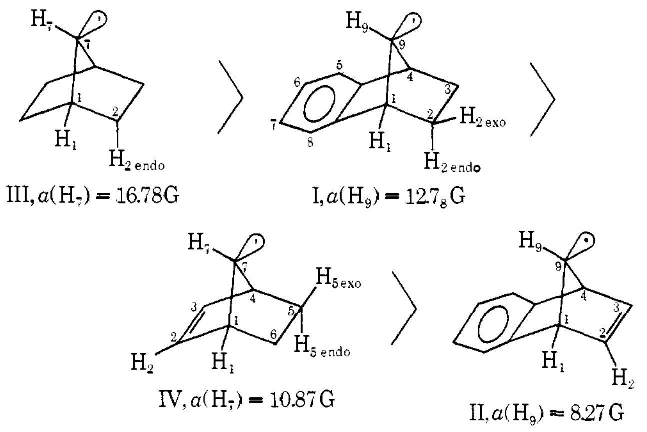


Figure 2. Spectrum of 9-benzonorbornenyl radical in cyclopropane solution at −120°

hfsc's of I-IV are negative.[11] With this sign assignment, a radical with a smaller (absolute) value of $a(H_\alpha)$ is expected to have a more pyramidal carbon atom at the radical center. It should be pointed out that this ordering follows the decrease of the $C_\beta C_\alpha C_{\beta'}$ ($C_1C_7C_4$ of III and IV and $C_1C_9C_4$ of I and II) bond-angle,[12]



III, $a(H_7) = 16.78$G

I, $a(H_9) = 12.7_8$G

IV, $a(H_7) = 10.87$G

II, $a(H_9) = 8.27$G

Increasing the pyramidality of the trivalent carbon atom of any one of the four radicals will result in a decrease of the dihedral angle between the odd electron orbital axis on C_α and the C_1-H_1 (and C_1-H_4) bond. Thus a negative monotonic relationship is expected between $a(H_\alpha)$ and $a(H_1)$. Figure 3 shows the plots of $a(H_\alpha)$ and hfsc's which may be assigned to the bridgehead protons. On the basis of the above discussion and the plots in Figure 3, the triplets of 1.68, 1.54, and 1.33 G are assigned to the bridgehead proton of II, IV,[13] and I, respectively.

The smallest two hfsc's for II (0.28 G two protons, 0.14 G four protons) presumably belong to two pairs of phenylene and a pair of vinylene protons, although the assignments are not clear for the moment. In any case, the vinylene proton hfsc of II (0.14 or 0.28 G) is far smaller than that of IV (1.20 G), the C_7-H_7 bond of which lies syn to the vinylene group at its most stable configuration.[1b] Thus the C_9-H_9 bond of II is concluded to tilt in anti direction to the vinylene group.

The largest triplet of I (1.93 G) is assigned to H_{2endo} and H_{3endo}. This value is quite similar to H_{5endo} hfsc of IV (2.06 G).[1b] Thus, it is concluded that the C_9-H_9 bond in I prefers to lie anti to the saturated bridging group (i.e. syn to the phenylene group) as in the case of IV.[1b] On the other hand, we may expect $a(H_{2endo})$ of I to be 3-8 G, on the basis of a comparison between the observed values of $a(H_{5endo})$ of III (3.53 G)[1b] and IV (2.06 G),[1b] when the C_9-H_9 bond of I prefers to lie anti to the phenylene ring. We prefer the assignment of the smallest triplet of 0.29 G of I to a pair of phenylene protons, because of the consistency with hfsc's of I, II, and IV.

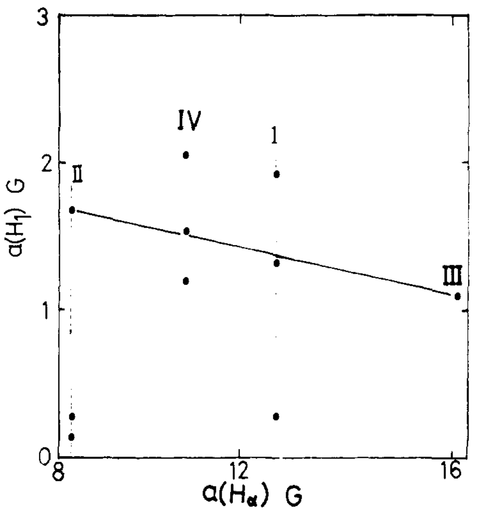
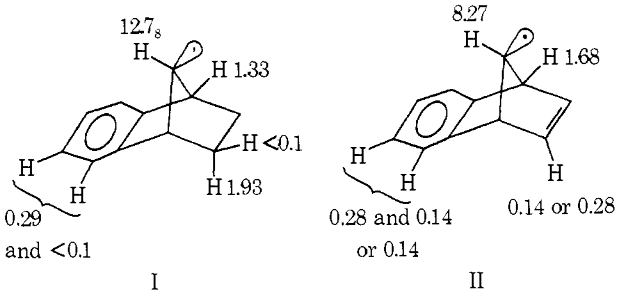


Figure 3. Relationship between α-proton hfsc's ($a(H_\alpha)$) for I, II, III, and IV and observed hfsc's which may be assigned to bridgehead protons (H_1).

These results for radicals I, II, and IV imply that the bishomobenzylic interaction in II is larger than the bishomoallylic interaction. The assignments of the hfsc's for I and II are summarized below.



I

II

Acknowledgment. The authors thank Drs. H. Tanida and T. Tsushima for their helpful suggestions on preparation of the bromides, Dr. P. J. Krusic, Professors K. Fukui and I. Morishima, and Mr. K. Yoshikawa for discussions, and Professor Y. Deguchi for giving them a chance to use the JEOL JEC-6 computer for simulation. They are also indebted to Mr. T. Inubushi for the measurements of ^{13}C PFT NMR spectra.

References and Notes

(1) (a) P. Bakuzis, J. K. Kochi, and P. J. Krusic, *J. Am. Chem. Soc.*, **92**, 1434 (1970); (b) J. K. Kochi, P. Bakuzis, and P. J. Krusic, *ibid.*, **95**, 1516 (1973).

(2) I. Morishima, K. Yoshikawa, K. Bekki, M. Kohno, and K. Arita, *J. Am. Chem. Soc.*, **95**, 5815 (1973).

(3) (a) S. I. Cristol and A. L. Noreen, *J. Am. Chem. Soc.*, **91**, 3969 (1969); (b) G. A. Russell and G. W. Holland, *ibid.*, **91**, 3968 (1969).

(4) G. R. Underwood and H. S. Friedman, *J. Am. Chem. Soc.*, **96**, 4989 (1974).

(5) This conclusion is doubtful. See I. Morishima, K. Yoshikawa, and K. Bekki, to be submitted to *J. Am. Chem. Soc.*

(6) Photolysis ESR experiments were done with a JEOL PE-1X spectrometer and Philips SP-500 mercury lamp.

(7) Prepared according to the method of Wilt and Chenier: J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562 (1970).

(8) Cf. A. Hudson and R. A. Jackson, *Chem. Comm.* 1327 (1969).

(9) The spectrum was successfully simulated with these parameters. Copies of the calculated spectra were provided to the referees.

(10) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. A*, 124 (1971); Cf. also H. Fisher, Z. Naturforsch., *Teil A*, **20**, 428 (1965).

(11) (a) The negative sign of $a(H_7)$ of IV conflicts with the work of Kochi, Bakuzis, and Krusic,[1b] in which $a(H_7)$ of IV was suggested to be positive to explain its unusual temperature dependence. However, the temperature dependence of $a(H_7)$ of IV (with negative sign) may be explained (1) by assuming a broad anharmonic single-minimum potential for the out-of-plane vibration of the C_7H_7 bond or (2)[11b] by assuming an asymmetrical broad double-minimum potential with a low barrier to the inversion of the C_7–H_7 bond; (b) suggested by P. J. Krusic.

(12) Cf. T. Kawamura, T. Koyama, and T. Yonezawa, *J. Am. Chem. Soc.*, **95**, 3220 (1973), and also ref 10.

(13) This interchanges the assignment suggested by Kochi, Bakuzis, and Krusic[1b] of the vinylene and bridgehead protons of IV. We suggest the assignments of $a(H_2)$ = 1.20 and $a(H_1)$ = 1.54 G for IV.

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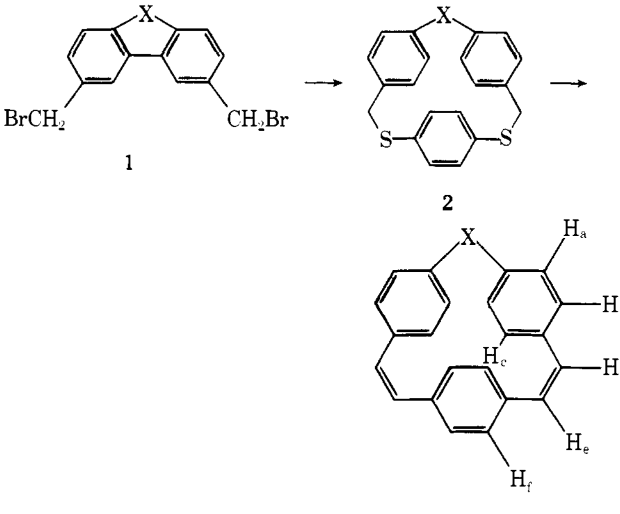
Bridged [18]Annulenes. Dependency of the Ring Current Contribution to Chemical Shift on the Contour of the Annulene Perimeter[1]

Sir:

The discovery that $4n + 2$ annulenes are diatropic, whereas $4n$ annulenes are paratropic has had a profound impact on the assessment of aromatic character.[2] Commonly, qualitative conclusions about the aromaticity of a newly synthesized molecule are made simply on the basis of the observed proton chemical shifts. In a significant development in this regard, Haddon has proposed that analyses of ring current contributions to proton chemical shifts can provide a quantitative measure of aromaticity.[3] In the use of proton chemical shift data, it is important, therefore, to understand as well as possible all of the factors affecting ring current contributions to proton chemical shifts. In this communication we provide experimental evidence that, aside from planarity, the contour of the loop of the annulene perimeter plays an important role in determining the magnitude of the ring current contribution.

Recently, we reported a photochemical procedure for preparing bridged [18]annulenes.[4] This method has proved to be general and has provided a number of new bridged [18]annulenes, of which the properties of three—**5**, **6**, and **7**—are important to the present discussion. The stilbene derivatives necessary for the photochemical preparations of **5**, **6**, and **7** were synthesized as follows. The coupling of 3,3′-bis(bromomethyl)biphenyl (**1a**)[5] with 1,4-bis(mercaptomethyl)benzene proceeded in 52% yield to give the dithiacyclophane **2a**, mp 215–216°.[6] Subjection of **2a** to a Stevens rearrangement followed by a Hofmann elimination readily gave **3a**: ^1H NMR ($CDCl_3$), a multiplet at τ 2.6–3.0 (6 H, Ar*H*), a singlet at 2.72 (4 H, H_f), doublets at 2.90 and 3.37 (4 H, H_d and H_e, $J_{d,e}$ = 12 Hz), and a singlet at 3.26 (2 H, H_c).[7]

For the synthesis of **1b**, treatment of 5,5′-bis(carbomethoxy)-2,2′-dimethylbiphenyl[8] with *N*-bromosuccinimide in boiling carbon tetrachloride for 5 hr gave 5,5′-bis(carbomethoxy)-2,2′-bis(bromomethyl)biphenyl, mp 131–133°, in 30% yield. The reduction of this diester with diisobutylaluminum hydride in benzene followed directly by addition of phenyllithium to the reduction mixture gave 3,6-bis(hydroxymethyl)-9,10-dihydrophenanthrene, mp 95–97°, in 65% yield. Reaction of 3,6-bis(hydroxymethyl)-9,10-dihydrophenanthrene with phosphorus tribromide in ether then led to **1b**, mp 224–226°, in 97% yield. Coupling of **1b** with 1,4-bis(mercaptomethyl)benzene gave **2b** in 86% yield.[6] Again, subjection of **2b** to a Stevens rearrangement followed by a Hofmann elimination led to **3b**: ^1H NMR ($CDCl_3$), multiplet at τ 3.11 (4 H, $H_{a,b}$), singlet at 3.21 (2H, H_c), doublet at 3.03 (2H, H_d, $J_{d,e}$ = 11.5 Hz), doublet at 3.47 (2 H, H_e, $J_{d,e}$ = 11.5 Hz), singlet at 2.81 (4 H, H_f), and a singlet at 7.20 (4 H, $ArCH_2$-).[7]



1

2

3

a, X = -H, -H
b, X = $-CH_2CH_2-$

The synthesis of **4** (^1H NMR ($CDCl_3$), a singlet at τ 3.14 (6 H, -C*H*=C*H*-) and a singlet at 3.26 (12 H, Ar*H*)) was carried out as described by Cram and Dewhirst,[9] who also irradiated **4** in 1959 in an attempt to make **7**.

The irradiations of **3a**, **3b**, and **4** were conducted in each case in carefully degassed perdeuteriotetrahydrofuran solutions held at −80° using a low pressure mercury lamp (2537 Å). After a short period of irradiation, the solutions became colored (orange to red) and new signals appeared in their ^1H NMR spectrums, which grew in intensity on prolonged irradiation. In the case of **3a**, the new ^1H NMR signals are in accord with the formation of the tetrahydrobenzo[*g,h,i*]perylene derivative **5**. The assignment of the signals for the individual protons are as follows: a doublet at τ 0.90 (2 H, H_a, $J_{a,b}$ = 9 Hz), a doublet of doublets at 2.53 (2 H, H_b, $J_{a,b}$ = 9 Hz; $J_{b,c}$ = 7 Hz), a doublet at 2.14 (2 H, H_c, $J_{b,c}$ = 7 Hz), a multiplet at 2.06 (4 H, H_d and H_e), a singlet at 2.32 (2 H, H_f), a multiplet at 12.58 (2 H, H_g), and a multiplet at 12.86 (2 H, H_h). In the case of the irradiation of **3b**, the photoproduct has the analogous structure **6** with the proton chemical shift assignments being a doublet at τ 2.79 (2 H, H_b, $J_{b,c}$ = 7 Hz), a doublet at 2.25 (2 H, H_c, $J_{b,c}$ = 7 Hz), a broad singlet at 2.14 (4 H, H_d and H_e), a singlet at 2.42 (2 H, H_f), a multiplet at 7.26 (4 H, H_a), a multiplet at 12.53 (2 H, H_g), and a multiplet at 12.88 (2 H, H_h). Thus **5** and **6** have very similar ^1H NMR spectra. Since both conjugated systems have the same benzo[*g,h,i*]perylene-shaped perimeter, this is as expected. As compared to their precursor dienes (**3a** and **3b**), both **5** and **6** show a shift of the signals for the external protons to lower field and a sharp shift of the signals for the internal protons to high field. This is in accord with the formation of the $4n + 2$ bridged [18]annulenes.[10]

In the case of the irradiation of **4**, examination of molecular models suggests that the photoproduct should have the stereochemistry (C_2 symmetry) shown by **7**. The ^1H NMR spectrum of **7** is in accord with this with the assignments being made as follows: the external protons provide an AB quartet at τ 0.60 (4 H, $J_{a,b}$ = 8 Hz) and a singlet at 0.52 (8 H), whereas the internal protons exhibit an AA′BB′CC′ multiplet centered at τ 16.44 (2 H), a doublet of doublets at