of Health, for support of this work under Research Grant No. CY-3753, to Dr. Victor Mark and Dr. John R. Van Wazer, Monsanto Chemical Company, for the P^{31} nmr spectra, and to the referee for his comments concerning the consideration of the equilibrium between structures Ia and Ib and the possibilities of the intra- *vs.* the intermolecular interpretation of the rearrangement of Ia to Ib.

Bridged Polycyclic Compounds. XXXII. The Proton Magnetic Resonance Spectra of Some Dibenzobicyclo[2.2.2]octadienes[1]

STANLEY J. CRISTOL, THOMAS W. RUSSELL, JERRY R. MOHRIG, AND DONALD E. PLORDE

Department of Chemistry, University of Colorado, Boulder, Colorado 80304

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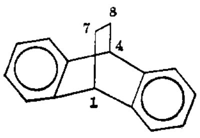
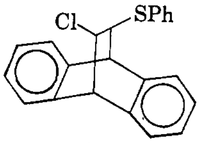
Proton magnetic resonance spectra for a number of 7- and 8-substituted dibenzobicyclo[2.2.2]octadienes have been measured. Correlations of these data lead to generalizations which permit stereochemical assignments for substituents in this system and permit differentiation of compounds in this system from those in the isomeric dibenzobicyclo[3.2.1]octadiene system.

In the course of elucidating the stereochemical consequences of some carbonium ion reactions in derivatives of dibenzobicyclo[2.2.2]octadiene (I)[2] and dibenzobicyclo[3.2.1]octadiene[2] and of some addition reactions to dibenzobicyclo[2.2.2]octatriene[3] and 7-chlorodibenzobicyclo[2.2.2]octatriene,[3] a large number of mono- and disubstituted dibenzobicyclo[2.2.2]-octadienes with known stereochemistry became available. Examination of the proton magnetic resonance spectra of these compounds led to useful correlations by which compounds in this system can be assigned stereochemical configurations and can also be distinguished from isomeric compounds in the dibenzobicyclo[3.2.1]-octadiene series.[4]



I



II

The structures and configurations of many of the compounds listed in Table I have been proved in this laboratory by chemical[2,3] and dipole moment[5] studies as previously reported. The remaining compounds will be described in detail in later papers.

The spectra discussed herein were obtained using a Varian Associates A-60 n.m.r. spectrometer operating at ambient temperature. Most spectra were taken in carbon tetrachloride solution, except that in a few cases that are noted, chloroform, deuteriochloroform, acetone, or benzene was used as the solvent for solubility reasons and, in some cases, to affect chemical shifts of protons to allow a more precise analysis of the spectrum. In general, saturated or supersaturated solutions of the compounds were used. The spectra were scanned over a range τ 1.7–10.0 using tetramethylsilane (τ 10) as an internal standard.

Since the chemical shifts of the protons were usually different enough to give separate peaks for each proton, it was possible to assign spectral frequencies to each of the four aliphatic protons in most of the 7,8-disubstituted dibenzobicyclo[2.2.2]octadienes and to each of the five aliphatic protons in most of the 7-substituted dibenzobicyclo[2.2.2]octadienes.

The basis for the spectral assignments for the disubstituted compounds may be illustrated by the proton assignments in the p.m.r. spectrum of *trans*-7-chloro-8-phenylthiodibenzobicyclo[2.2.2]octadiene (II). The spectrum of this compound has five absorption peaks, four of which correspond to the four different aliphatic hydrogens bound to carbon and the last of which corresponds to aromatic hydrogens. The absorptions at τ 5.68, 5.87, 6.06, and 6.57 show equal relative areas, while the complex absorption pattern around τ 2.85[6] integrates to 13 times each of the other absorptions.

The two lower-field aliphatic absorptions of II are doublets and the two higher-field absorptions are a triplet and a quartet. This indicates that the absorptions at τ 5.66 and 5.87 are due to the two benzhydrylic bridgehead hydrogens attached to C-1 and C-4. From the correlation of all of the p.m.r. spectra of the dibenzobicyclo[2.2.2]octadiene compounds listed in Table I, the data are consistent with this assignment. Similarly, the aliphatic hydrogens in diphenylmethane are at τ 6.08.[7]

From the data in Table I on the monosubstituted compounds (**14** and **17**), it is seen that the absorption of a benzhydrylic bridgehead hydrogen vicinal to a sulfur atom is at a higher field than is the absorption of a similar hydrogen vicinal to a chlorine atom. It is on this basis that the absorption at τ 5.66 is assigned to the hydrogen on C-1 (adjacent to chlorine) and the

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(1) Paper XXXI: S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Am. Chem. Soc.*, **87**, 4007 (1965).

(2) (a) S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6155 (1960); (b) S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **85**, 2675 (1963); (c) S. J. Cristol, Abstracts of the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, 1963, p. 12; (d) S. J. Cristol and D. D. Tanner, *J. Am. Chem. Soc.*, **86**, 3122 (1964); (e) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965); (f) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965).

(3) (a) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957); (b) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).

(4) For a discussion of the proton magnetic resonance spectra of compounds in the dibenzobicyclo[3.2.1]octadiene series, see S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *ibid.*, **30**, 1956 (1965); A. R. Katritzky and B. Wallis, *Chem. Ind.* (London), 2025 (1964).

(5) D. D. Tanner and T. S. Gilman, *J. Am. Chem. Soc.*, **85**, 2892 (1963).

(6) In all of the spectra, the large complex multiplet around τ 2.5–3.5 was used only for the determination of relative peak areas. The splitting patterns and changes in chemical shifts of these hydrogens were not studied.

(7) G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance Shielding Values (Spectral Positions) for Hydrogen in Organic Structures," Central Research Department, Minnesota Mining and Manufacturing Co., Inc., St. Paul, Minn., March 28, 1958.

TABLE I

PROTON ASSIGNMENTS IN THE DIBENZOBICYCLO[2.2.2]OCTADIENE SYSTEM[a]

		Chemical shifts, τ						
No.	Compound	1-H	4-H	7-H	*trans* 8-H	*cis* 8-H	Other	*J*, c.p.s.
1	*trans*-7-Chloro-8-phenylthio-I	5.66 (2)	5.87 (2)	6.06 (3)		6.57 (4)		$J_{1,7} = 3.0$ $J_{4,8} = 2.5$ $J_{7,8} = 3.0$
2	*cis*-7-Chloro-8-phenylthio-I[b]	5.58 (2)	5.76 (2)	5.45 (4)	6.21 (4)			$J_{1,7} = J_{4,8} = 2.0$ $J_{7,8} = 9.0$
3	*trans*-7-Chloro-8-methylthio-I	5.68 (2)	5.79 (2)	6.00 (3)		7.03 (4)	7.92 (methyl)	$J_{1,7} = 2.7$ $J_{4,8} = 2.4$ $J_{7,8} = 3.6$
4	*cis*-7-Chloro-8-methylthio-I	5.65 (2)	5.70 (2)	5.60 (4)	6.85 (4)		7.97 (methyl)	$J_{1,7} = J_{4,8} = 2.3$ $J_{7,8} = 8.2$
5	*cis*-7-Chloro-8-tolylthio-I[c]	5.40 (2)	5.68 (2)	5.21 (4)	6.09 (4)		(methyl)[d]	$J_{1,7} = 3.0$ $J_{4,8} = 2.0$ $J_{7,8} = 8.6$
6	*trans*-7-Chloro-8-acetoxy-I	5.69 (2)	5.55 (2)	6.10 (3)		5.06 (3)	8.11 (acetate methyl)	$J_{1,7} = J_{4,8} = 2.5$ $J_{7,8} = 2.5$
7	*cis*-7-Chloro-8-acetoxy-I	5.50–5.70			4.89 (4)		8.10 (acetate methyl)	$J_{4,8} = 2.5$ $J_{7,8} = 8.0$
8	*trans*-7-Iodo-8-acetoxy-I	5.60 (2)		6.14 (3)		4.80 (3)	8.09 (acetate methyl)	$J_{1,7} = J_{4,8} = 3.0$ $J_{7,8} = 3.0$
9	7-Keto-I	5.31 (1)	5.59 (3)		7.85 (2)			$J_{4,8} = 2.6$ $J_{8,8} = 0$
10	*cis*-7-*p*-Toluenesulfonyloxy-8-deuterio-I	5.51 (2)	5.84 (2)	5.11 (4)	7.89 (4)		7.63 (methyl)	$J_{1,7} = 3.3$ $J_{4,8} = 2.8$ $J_{7,8} = 8.7$
11	*cis*-7-Acetoxy-8-deuterio-I[e]	5.50 (2)	5.79 (2)	4.98 (4)	7.73 (4)		8.18 (acetate methyl)	$J_{1,7} = 2.5$ $J_{4,8} = 3.0$ $J_{7,8} = 9.0$
12	7-Amino-I	6.10 (2)	5.92 (3)	6.89 (3, 3)	7.86 (2, 3, 2)	9.03 (4, 4)	9.32 (amine)	$J_{1,7} = J_{4,8} = 2.5$ *trans* $J_{7,8} = 3.0$ *cis* $J_{7,8} = 9.5$ *gem* $J_{8,8} = 12.3$
13	7-Hydroxy-I	5.92 (2)	5.85 (3)	6.06 (3, 3)	7.81 (2, 4, 2)	8.82 (3, 3)	8.71 (hydroxyl)	$J_{1,7} = J_{4,8} = 3.0$ *trans* $J_{7,8} = 3.0$ *cis* $J_{7,8} = 8.5$ *gem* $J_{8,8} = 12.8$
14	7-Chloro-I	5.60 (2)	5.82 (3)	5.86 (3, 3)	7.60 (2, 2, 2)	8.25 (4, 4)		$J_{1,7} = J_{4,8} = 2.5$ *trans* $J_{7,8} = 2.5$ *cis* $J_{7,8} = 8.0$ *gem* $J_{8,8} = 14.0$
15	7-Acetoxy-I	5.60 (2)	5.87 (3)	5.10 (3, 3)	7.75 (2, 4, 2)	8.59 (4, 4)	8.24 (acetate methyl)	$J_{1,7} = J_{4,8} = 2.6$ *trans* $J_{7,8} = 3.3$ *cis* $J_{7,8} = 8.8$ *gem* $J_{8,8} = 13.0$
16	7-*p*-Toluenesulfonyloxy-I	5.51 (2)	5.87 (3)	5.12 (3, 3)	7.92 (2, 2, 2)	8.50 (4, 4)	7.63 (methyl)	$J_{1,7} = 3.0$ $J_{4,8} = 2.5$ *trans* $J_{7,8} = 3.5$ *cis* $J_{7,8} = 9.0$ *gem* $J_{8,8} = 13.8$
17	7-Phenylthio-I	5.72 (2)	5.80 (3)	6.48 (4, 4)	7.72 (2, 3, 2)	8.56 (4, 4)		$J_{1,7} = 2.8$ $J_{4,8} = 2.6$ *trans* $J_{7,8} = 4.6$ *cis* $J_{7,8} = 9.2$ *gem* $J_{8,8} = 12.6$
18	*trans*-7-Phenylthio-8-deuterio-I	5.75 (2)	5.81 (2)	6.48 (4)		8.55 (4)		$J_{1,7} = J_{4,8} = 2.6$ *trans* $J_{7,8} = 4.6$
19	*trans*-7,8-Dichloro-I[f,g]	5.73 (3)		5.92 (4)				
20	*cis*-7,8-Dichloro-I[f,h,i]	5.86 (4)		6.03 (4)				
21	*trans*-7,8-Dihydroxy-I[e,f]	5.73 (2)		6.30 (3)			4.49 (hydroxyl)	
22	*cis*-7,8-Diacetoxy-I[f]	5.60 (3)		4.96 (3)			8.15 (acetate methyl)	
23	7,8-Epoxy-I[f]	5.56 (4)		6.55 (4)				
24	7,8-(Dichloromethano)-I[f]	5.48 (3)		7.90 (3)				
25	7,8-(Chloromethano)-I[f]	5.15 (4)		8.20 (4)			8.02 (α-Cl)	
26	Hydrocarbon I[j,k]	5.71 (5)		8.32 (3)				
27	7,8-Dehydro-I[f,l]	5.03 (4)		3.15 (3)				
28	7-Chloro-7,8-dehydro-I[m]	5.11 (1)	5.08 (2)					$J_{4,8} = 6.0$

[a] I is an abbreviation for dibenzobicyclo[2.2.2]octadiene. τ values are for the center of the resonance pattern and, when no exception is indicated, are measured in carbon tetrachloride solution. Integral numbers in parentheses after the chemical shift value indicate the complexity of the resonance pattern, for example, (3, 3) indicates that two triplets comprise the pattern (or two sets of overlapping doublets, as the case may be). Values between columns indicate no discernible chemical shift difference between the hydrogens. *trans* 8-H refers to the hydrogen of C-8 that is *trans* to the substituent on C-7. Its coupling will be with the hydrogen on C-7. This hydrogen will be *cis* to the hydrogen on carbon-8. Similarly, the coupling of the *cis* 8-H will be with the hydrogen *trans* on C-7. Both will also couple with the adjacent bridgehead hydrogen. In order to reduce confusion, we have chosen to number the substituents according to formula I. [b] $BrCCl_3$ solvent. [c] Acetone solvent. [d] This peak was obscured by the resonance of the acetone solvent. [e] Chloroform solvent. [f] An example of the A_2B_2 (or A_2X_2) case discussed briefly herein. [g] τ values determined from carbon tetrachloride solution; multiplicity values determined from acetone solution. This compound has one singlet peak at τ 5.91 in benzene solution. [h] This compound gives rise to an unresolved absorption at τ 5.51 in chloroform solution. The assignment for the protons at C-1, C-4, and C-7, C-8 may be reversed. The compound was not soluble enough to run in carbon tetrachloride. [i] Benzene solvent. [j] An A_2X_4 case. We are currently unaware of any theoretical method for the calculation of coupling constants for this case from the observed spectrum. [k] These values are identical with those determined by K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964). [l] These values are similar to those reported by C. F. Wilcox and F. D. Roberts, Jr., *J. Org. Chem.*, **30**, 1959 (1965). [m] The absorption of the 8-hydrogen occurs with the aromatic absorptions and cannot be definitely located.

absorption at τ 5.87 to the hydrogen on C-4 (adjacent to sulfur). For example, when the phenylthio group in II (**1**, Table I) is changed for a methylthio group (**3**, Table I), the doublet at τ 5.66 changes to only τ 5.68 while the doublet at τ 5.87 moves to τ 5.79. Similarly, when the phenylthio group is changed for an acetoxy group (compound **6**), the doublet at τ 5.66 moves to τ 5.69 while the doublet at τ 5.87 disappears and a new doublet at τ 5.55 appears.

The two absorption patterns remaining must be, from their multiplicity, the hydrogens on C-7 and C-8. Again, by a comparison of the data in Table I on the monosubstituted compounds **14** and **17**, it is seen that the absorption due to hydrogen α to sulfur is at about τ 0.5 higher field than a hydrogen α to a chlorine. Also, when the phenylthio group (compound **1**) is changed for a methylthio group (compound **3**), the only large difference in the positions of the absorption peaks is the shift of a quartet from τ 6.57 to 7.03. Similarly, when the phenylthio group is changed for an acetoxy group (compound **6**), the only large difference observable is the shift of a resonance pattern from τ 6.57 to 5.06.

This leads to the assignment of the τ 6.06 resonance to the hydrogen on C-7 α to the chlorine and of the τ 6.57 resonance to the hydrogen on C-8 α to the sulfur.

This assignment of the bridge hydrogens is consistent with the findings of Tiers[7] that hydrogens α to sulfur absorb at a higher field than hydrogens α to chlorine; for example, the α-hydrogens in dipropyl thioether absorb at τ 7.61 and in ethyl mercaptan at τ 7.56, whereas the α-hydrogens absorb at τ 6.55 in propyl chloride and at τ 6.43 in ethyl chloride.

A deuterioboration of dibenzobicyclo[2.2.2]octatriene, through which a *cis*-deuterated *p*-toluenesulfonate ester (**10**) and a *cis*-deuterated acetate (**11**) were subsequently prepared, led to an unambiguous assignment of the geminal hydrogens in monosubstituted compounds in this system. Previously, the assignment, although correct, was based on the coupling constants discussed below. A comparison of the spectra of the two *p*-toluenesulfonates (**10** and **16**) indicates that the highest-field multiplet in compound **16** (at τ 8.50) is due to the *cis* 8-H and the next highest-field multiplet at τ 7.92 is due to the *trans* 8-H. Similar results were obtained from the acetate **15** and the *cis*-deuterioacetate **11**. It is of interest to note that, in all monosubstituted cases (compounds **10**–**18**), the hydrogen *cis* to an electron-attracting substituent absorbs at a higher field than does an epimeric hydrogen *trans* to the substituent. This may also be true for disubstituted compounds (compounds **1**–**8**), although this is uncertain because of uncertainties in assignments for compounds **19** and **20**.

The results obtained for the spin–spin coupling constants for the aliphatic hydrogens in this system are tabulated in Table I and are summarized in Table II. Only geminal and vicinal couplings are considered. Although high-resolution spectra showed some small secondary couplings, undoubtedly due to long-range interactions, no attempt was made to identify the sources of these couplings.

TABLE II

AVERAGE VALUES FOR COUPLING CONSTANTS FOR 7- AND 8-SUBSTITUTED DIBENZOBICYCLO[2.2.2]OCTADIENES

Compound type	No. of examples	Spin–spin coupling constant, J, c.p.s.[a]
cis-7,8-Disubstituted and 7-monosubstituted (*cis*-7,8-protons)	12	$J_{7,8}$ = 8.8 ± 0.8
trans-7,8-Disubstituted and 7-monosubstituted (*trans* 7,8-protons)	11	$J_{7,8}$ = 3.5 ± 1.1
7-Monosubstituted (geminal 8-protons)	6	$J_{8,8}$ = 13.1 ± 0.9
All (bridgehead–bridge protons)	18	$J_{1,7}$ = $J_{4,8}$ = 2.6 ± 0.7

[a] Coupling constants are *ranges*.

An example of the interpretation of the coupling constants is found in the spectrum of 7-dibenzobicyclo[2.2.2]octadienyl *p*-toluenesulfonate (**16**, Table I) and the analogous *cis*-8-deuterated species (**10**). In both spectra, the absorption at τ 5.51, assigned to the 1-hydrogen vicinal to the sulfonyloxy group, is a doublet with a splitting of 3 c.p.s. The doublets are partially split again, but this secondary splitting is small and not completely resolved. The absorption at τ 5.87, assigned to the 4-H, is a triplet in the undeuterated sulfonate ester and a doublet in the deuterated sulfonate ester, indicating a correct assignment of the bridgehead hydrogen absorptions. The bridgehead–bridge proton coupling constant here is about 2.6 c.p.s.

The absorption at τ 5.12 in the undeuterated *p*-toluenesulfonate has been assigned to the 7-H, α to the sulfonyloxy substituent. It appears as a pair of triplets with a major coupling of 9 c.p.s., and with two smaller couplings of about 3 c.p.s. each. The corresponding *cis*-deuterated sulfonate ester absorption at τ 5.11 appears as a pair of doublets with a major coupling constant of 8.7 c.p.s. and a minor coupling of *ca.* 3 c.p.s.

The two high-field patterns, which are assigned to the two hydrogens at C-8, appear as complex multiplets in the undeuterated sulfonate ester. The 9-c.p.s. *cis* coupling, as well as a 2.5-c.p.s. coupling with the adjacent bridgehead hydrogen, is observable in the τ 7.9 absorption. The multiplet at τ 8.5, missing in the spectrum of the deuterated isomer, contains couplings of 2.5 and 3.5 c.p.s. with the adjacent bridgehead hydrogen and the *trans*-7-hydrogen, respectively. A large coupling of almost 14 c.p.s. is the major coupling in both the τ 7.9 and 8.5 absorptions. This large coupling, varying from 12 to 14 c.p.s. in compounds **12–17**, is attributed to a geminal coupling of the two 8-hydrogens, as it is a minimum of 3 c.p.s. larger than the largest *cis* coupling observed in this system. Further evidence for this assignment is that the large coupling is only observed in the monosubstituted compounds (**12–17**), whereas the 8.0–9.5-c.p.s. coupling is observed in all of the *cis*-disubstituted compounds (**2**, **4**, **5**, **7**, **10**, and **11**).

The A_2B_2, or A_2X_2, case referred to in Table I, and for which no coupling constants were given, yields spectra which do not indicate the stereochemistry of the substituents by a simple inspection. Grant, Hirst, and Gutowsky[8] have presented the results of quantum mechanical calculations which allow a relatively simple calculation of the actual coupling constants from the observed spectrum.

The coupling constants of the *trans*-7,8-dichloride (**19**, Table I) were calculated by this method and yielded the following results: $J_{1,7} = J_{4,8} = 2.8$ c.p.s., $J_{7,8} = 2.8$ c.p.s., $J_{1,8} = J_{4,7} = 0.5$ c.p.s., and $J_{1,4} = 0.0$ c.p.s. The calculation was made from a spectrum taken as a saturated solution in acetone, about 1–1.5 *M*.

As the method depends on the accurate identification of each of the six lines comprising one-half of the A_2B_2 spectrum, or each of the ten lines comprising one-half of the A_2X_2 spectrum, a high concentration of the compounds is necessary to distinguish the low-intensity transitions from the background noise. Such concentrations were not attained for the other A_2B_2 cases (compounds **20–25** and **27**) in any of the solvents tested.

The stereochemical configuration of a 7- and 8-disubstituted dibenzobicyclo[2.2.2]octadiene can readily be determined by an examination of its p.m.r. spectrum save for one exception: the compound must be substituted by two nonequivalent groups in order to eliminate the consequences of the A_2B_2 spectral case. For example, there is no apparent difference between the spectra of the *cis*- and the *trans*-7,8-dichlorides except for a difference in the chemical shifts of the two resonances. If adequate concentrations of the compounds can be attained, then even for these special cases, one may determine the stereochemistry of the groups.

In the spectra of 7,8-disubstituted derivatives of I, in which the two substituents are nonequivalent, the absorption pattern assigned to the 7-hydrogen is a triplet, or occasionally a poorly resolved quartet, in *trans*-disubstituted compounds. These protons have coupling constants of 2–4 c.p.s. with the adjacent bridgehead hydrogen and the *trans*-8-hydrogen. If, however, the absorption peak assigned to the 7-hydrogen is a distinct pair of doublets with a major coupling of 8–9.5 c.p.s., and a secondary coupling of 2–3 c.p.s., then the compound is *cis* disubstituted.

This relationship between stereochemical configuration and p.m.r. spectral pattern in this series of related compounds has been without exception in this laboratory. It is fortunate that, in this system, only one member of an epimeric pair is necessary in order to establish stereochemical configuration.

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[8] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963), and pertinent references therein.