

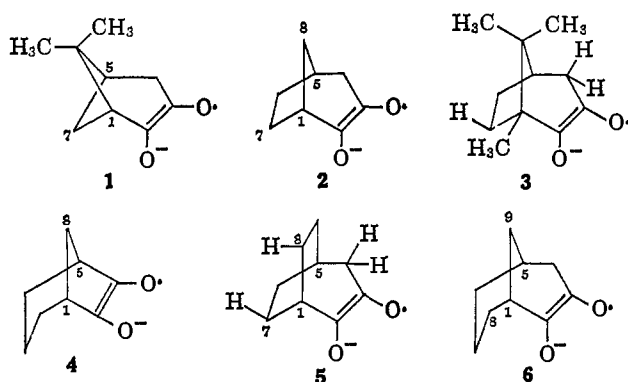
Acknowledgment. We wish to thank Professor H. Walborsky for a sample of bicyclo[2.2.2]octan-2-ol, Professor P. Yates for bicyclo[2.2.2]octane-2,3-dione, Dr. K. Morita for 1-methyl-4-methoxybicyclo[2.2.2]octan-2-one and its 5-methyl derivatives, Dr. O. Edwards for the atisine derivatives **5**, and Professor H. C. Brown for a sample of apocamphor.

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Long-Range Interactions in Semidiones in the Bicyclo[3.1.1]heptane, Bicyclo[3.2.1]octane, Bicyclo-[3.2.2]nonane, and Bicyclo[3.3.1]nonane Systems¹

Sir:

Semidiones **1-6** have been prepared by oxidation of the corresponding monoketones in dimethyl sulfoxide solution containing potassium *t*-butoxide.



Extensive long-range interactions are observed in all the radical anions. In view of our observations on the bicyclo[2.2.2]octane-2,3-semidione,² most of the major interactions can be assigned to carbon-hydrogen bonds α to the dicarbonyl system or β to the dicarbonyl system and in a zigzag arrangement with the carbonyl carbon p_z orbital.

Analysis of the hyperfine splitting in semidiones is simplified by the fact that in DMSO-*d*₆ the α -hydrogen atoms are replaced by deuterium atoms with a resultant change in the e.s.r. spectrum ($a^H/a^D \cong 7$). However, in bicyclic compounds such as **1**, **2**, or **4** such exchange at the bridgehead position is prohibited.

The hyperfine splittings observed for **1-6** are given in Table I together with an assignment of certain of the hyperfine splitting constants to specific hydrogen atoms.

The spectra observed for **3** (Figure 1) and **5** (Figure 2) are easily interpreted. For **5** two pairs of equivalent hydrogen atoms are indicated. The magnetic equivalence of a pair of hydrogen atoms at C-4 and a pair at C-7 and C-8 can be explained by dynamic interconversion between two asymmetric twist conforma-

(1) Application of E.s.r. Spectroscopy to Problems of Structure and Conformation. VI. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund.

(2) G. A. Russell and K. Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965).

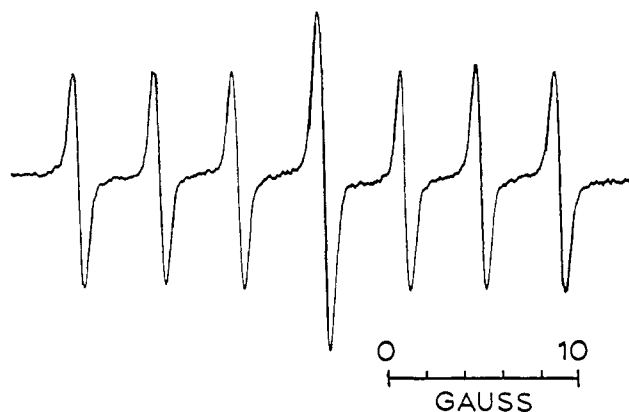


Figure 1. First derivative e.s.r. spectrum of semidione **3** prepared by reaction of a trace of oxygen with homocamphor (0.05 *M*) in dimethyl sulfoxide containing potassium *t*-butoxide (0.10 *M*) at 25°.

tions,³ but the lack of bridgehead splitting is surprising since time averaging cannot affect this nearly orthogonal dihedral angle.

Table I. Hyperfine Splitting Constants for Bicyclic Semidiones^a

Semi-dione	H.f.s.c., gauss	Assignment of H
1	9.46 (doublet) ^b	C-4
	9.04 (doublet) ^b	C-4
	3.88 (doublet)	<i>anti</i> -C-7
	0.42 (sextet)	C-1, <i>syn</i> -C-7, methyl
2	13.5 (doublet) ^b	C-4
	8.69 (doublet) ^b	C-4
	3.45 (doublet)	C-1 or <i>exo</i> -C-7 or <i>anti</i> -C-8
	2.13 (doublet)	C-1 or <i>exo</i> -C-7 or <i>anti</i> -C-8
	1.42 (doublet)	C-1 or <i>exo</i> -C-7 or <i>anti</i> -C-8
	0.28 (triplet)	<i>endo</i> -C-7 and <i>syn</i> -C-8
3	12.5 (doublet) ^b	C-4
	8.4 (doublet) ^b	C-4
	4.1 (doublet)	<i>exo</i> -C-7
	0.53 (sextet)	<i>syn</i> -C-8
4	5.51 (triplet)	<i>exo</i> -C-2,4
	4.03 (doublet)	<i>anti</i> -C-8
	0.53 (sextet)	C-1,4; <i>endo</i> -C-2,4; <i>syn</i> -C-8
5	10.5 (triplet) ^b	C-4
	2.2 (triplet)	<i>anti</i> -C-7,8
6	12.74 (doublet) ^b	C-4
	6.93 (doublet) ^b	C-4
	3.35 (doublet)	<i>exo</i> -C-8 or <i>anti</i> -C-9
	1.96 (doublet)	<i>exo</i> -C-8 or <i>anti</i> -C-9
	0.56 (doublet)	C-1

^a In DMSO at 25°. ^b Exchangeable in DMSO-*d*₆.

A considerable amount of work is required before unique hyperfine splitting constants can be rigorously assigned to all the hydrogen atoms involved. Our preliminary data are being presented at this time because the extension of this work to the assignment of structure of derivatives of **1-6**, of synthetic or natural origin, is obvious and in certain cases a unique struc-

(3) C. W. Jefford, J. Mahajan, B. Waegell, and K. Ramey, private communications.

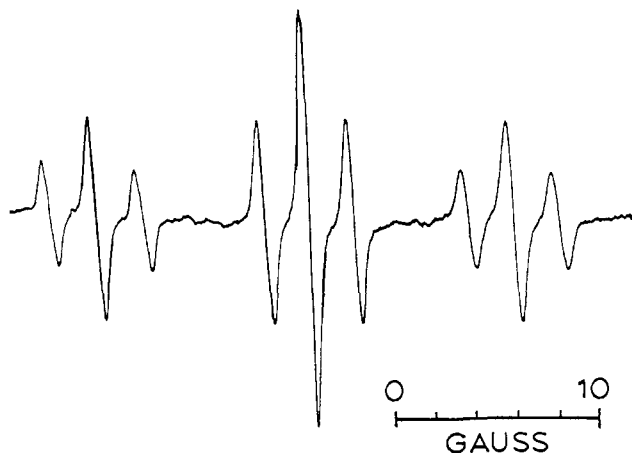
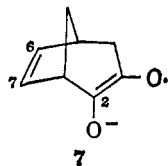


Figure 2. First derivative e.s.r. spectrum of semidione **5** prepared by reaction of a trace of oxygen with bicyclo[3.2.2]nonan-3-one (0.05 *M*) in dimethyl sulfoxide containing potassium *t*-butoxide (0.10 *M*) at 25°.

tural assignment can be made without a full assignment of all hyperfine splitting constants.

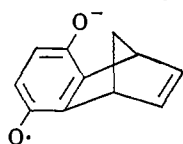
One of the problems in obtaining a unique assignment of splitting constants is illustrated by the fact that replacement of three of the hydrogen atoms in **2** by methyl groups to give **3** reduces the number of hydrogen atoms for which hyperfine splitting can be detected not by three but by four. The situation may be related to the methylated derivatives of bicyclo[2.2.1]heptane-2,3-semidione wherein hyperfine splitting has been observed for *endo*-hydrogens at C-5,6 in the presence but not in the absence of an *anti*-methyl group at C-7,² and emphasizes the effect of subtle changes in geometry upon long-range splitting.

Unsaturated derivatives of **2-6** apparently involve even more extensive long-range coupling. Thus, **7** prepared by oxidation of 3-ketobicyclo[3.2.1]octene-6 displays hyperfine splitting by all eight hydrogen atoms,



$a^H = 8.74, 7.70, 2.66, 1.20, 0.71, 0.49, 0.14,$ and 0.14 gauss. Apparently spin is transmitted to *p* orbitals of C-6,7 by virtue of the *W*-plan arrangement of the *p*_z orbitals on C-2 and C-7. Reduction of dibenzobicyclo[2.2.2]octadiene-2,3-dione with propiophenone in basic DMSO solution gives a high yield of the semidione which displays unusual stability since it is stable to oxygen for hours at 25°. The semidione shows interaction of the unpaired open with two sets of four equivalent hydrogen atoms, $a^H = 0.96, 0.31$ gauss. There is apparently a strong interaction between the *p*-orbitals on C-2,3 and the *p*-orbitals of the aromatic rings at C-5,6,7,8.⁴

(4) We had originally intended to examine such types of interaction in the bicyclo[2.2.1]heptene and bicyclo[2.2.2]octene systems. However, Professor L. M. Stock has informed us that he is investigating such interactions in the related semiquinones, *e.g.*



Acknowledgment. We are grateful to Professors G. Büchi and G. Quinkert for samples of homocamphor, to Professor H. Walborsky for a sample of bicyclo[3.2.1]octan-2-one, to Professor N. LeBel for a sample of 3-ketobicyclo[3.2.1]octene-6, and to Professor S. Cristol for a sample of dibenzobicyclo[2.2.2]octadiene-2,3-dione.

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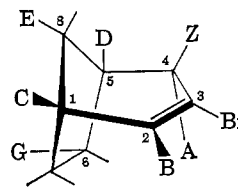
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Multiple Long-Range Couplings between Protons in the Bicyclo[3.2.1]octene-2 Skeleton^{1,2}

Sir:

We have reported recently³ that *exo* 4-substituted derivatives⁴ of 3-bromobicyclo[3.2.1]octene-2 (*e.g.*, I and II) exhibited only two long-range couplings between protons (A with E, and B with E). No vinyl-allylic coupling (B with A) was detected.

However, inspection of a Dreiding model⁵ of 3-bromobicyclo[3.2.1]octene-2 (III) indicates that three kinds of long-range coupling are predicted. These are *W*-plan (A with E, and Z with G), homoallylic (B with E), and vinyl-allylic (B with Z, and B with A). In other words, within the compass of the same mole-



I, Z = Br IV, D = methyl
II, Z = OH V, Z = deuterium, D = methyl
III

cule, five distinct remote couplings are expected.

We wish to report that examination of the parent compound III⁶ and its 5-methyl derivative⁷ (IV) by the double irradiation technique⁸ revealed that all the aforementioned expectations were realized.⁹ The geminal,¹⁰ vicinal, and remote coupling constants for the vinyl and allylic protons were unequivocally determined, and they are listed in Table I.

The magnitudes of the geminal and vicinal coupling constants are as expected. In fact, the values found for coupling between *endo*- and *exo*-allylic protons

(1) Part VII of a series: The Stereochemistry of the Bicyclo[3.2.1]octane System. For part VI see C. W. Jefford, J. Gunsher, and B. Waegell, *Tetrahedron Letters*, No. 38, 3405 (1965).

(2) Presented in part at the 8th European Congress on Molecular Spectroscopy, Copenhagen, Denmark, Aug. 15-20, 1965.

(3) C. W. Jefford, B. Waegell, and K. Ramey, *J. Am. Chem. Soc.*, **87**, 2191 (1965).

(4) *exo* designates the side of the molecule which bears the methylene bridge.

(5) W. Büchi, Glasapparatefabrik, Flawil, Switzerland.

(6) B. Waegell and C. W. Jefford, *Bull. soc. chim. France*, 844 (1964).

(7) C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Am. Chem. Soc.*, **87**, 2183 (1965).

(8) J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963).

(9) The details of our procedure have been described previously (see ref. 3).

(10) Assumed to be negative in sign (J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965)).