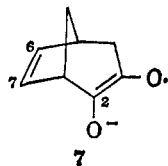


Figure 2. First derivative e.s.r. spectrum of semidione **5** prepared by reaction of a trace of oxygen with bicyclo[3.2.2]nonan-3-one (0.05 *M*) in dimethyl sulfoxide containing potassium *t*-butoxide (0.10 *M*) at 25°.

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

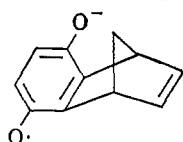
One of the problems in obtaining a unique assignment of splitting constants is illustrated by the fact that replacement of three of the hydrogen atoms in **2** by methyl groups to give **3** reduces the number of hydrogen atoms for which hyperfine splitting can be detected not by three but by four. The 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,<sup>2</sup> 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.<sup>4</sup>

(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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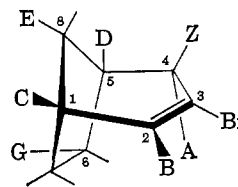
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### Multiple Long-Range Couplings between Protons in the Bicyclo[3.2.1]octene-2 Skeleton<sup>1,2</sup>

Sir:

We have reported recently<sup>3</sup> that *exo* 4-substituted derivatives<sup>4</sup> 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 model<sup>5</sup> 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 III<sup>6</sup> and its 5-methyl derivative<sup>7</sup> (IV) by the double irradiation technique<sup>8</sup> revealed that all the aforementioned expectations were realized.<sup>9</sup> The geminal,<sup>10</sup> 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)).

**Table I.** Coupling Constants (in c.p.s.) of the Vinyl and Allylic Protons of Bicyclo[3.2.1]octene-2 Derivatives

	$J_{AZ}^{(10)}$	$J_{BC}$	$J_{AD}$	$J_{ZD}$	$ J_{AE} $	$ J_{ZG} $	$ J_{BE} $	$ J_{BZ} $	$ J_{BA} $
III	-17.0	+7.0	+2.0	+4.7	0.6	2.4	0.6	2.0	1.0
IV	-17.0	+7.0			0.6	2.2	0.6	2.0	1.4
V		+7.0			0.6		0.5		1.2

and the bridgehead proton ( $J_{AD}$  and  $J_{ZD}$ ) accord well with those found in *exo*- and *endo*-allylic substituted derivatives of I.<sup>3,11</sup> This agreement is particularly reassuring since the stereochemistry of allylic protons in these structures cannot be predicted by the Karplus equation.<sup>7,12</sup>

It is interesting to note that the two pairs of W-disposed protons (ZG and AE) have apparently similar geometries, yet their coupling constants are appreciably different.

Similarly, the C-4-Z and C-4-A bonds appear to possess the same angular relationship to the plane described by C-2-C-3-C-4, but nonetheless the vinyl-allylic coupling constants  $|J_{BZ}|$  and  $|J_{BA}|$  are quite different in III and somewhat different in the 5-methyl compound IV. These inequalities suggest that III may be distorted so that the C-4-Z bond is more axial than the C-4-A bond with respect to the plane described by C-2-C-3-C-4. It is worth remembering that vinyl-allylic coupling constants are composed of two components,  $J^o$  and  $J^r$ , which are opposite in sign, and consequently are quite sensitive to any alteration in the geometric relationship of the coupled protons.<sup>13</sup>

As we have already mentioned,<sup>3</sup> *exo* substitution at C-4 by bromine or hydroxyl (I and II) caused the coupling between B and A to vanish. This result may stem from an enhancement of the above-mentioned distortion on insertion of a polar substituent *exo* at C-4.<sup>13,14</sup> It is interesting to observe that *exo*-4-deuterio-5-methylbicyclo[3.2.1]octene-2 (V)<sup>15</sup> retains vinyl-allylic coupling (see Table I).

Nevertheless, although we believe that intramolecular flexion exerts a determinative influence on vinyl-allylic coupling in the bicyclo[3.2.1]octene-2 skeleton, substituent effects should not be discounted. These matters are presently under active study, and our results and interpretations will be reported later.

Finally, we wish to draw attention to the striking parallel between the present long-range couplings of the vinyl proton and the long-range interactions experienced in the electron paramagnetic resonance spectra of radical anions which possess a bicyclo[3.2.1]octene-2 skeleton.<sup>16</sup> Apparently, both kinds of coupling involve participation of the olefinic bond in inter-

(11) *exo*-1-Methyl-2,3-benzbicyclo[3.2.1]octanol-4 and its *endo* isomer had allylic coupling constants ( $J$ ) of 2.8 and 5.0 c.p.s., respectively: W. Herz and G. Caple, *J. Am. Chem. Soc.*, **84**, 3517 (1962).

(12) M. Karplus, *ibid.*, **85**, 2870 (1963).

(13) Calculation predicts that the C-4-Z bond makes an angle of 67° to the plane described by C-2-C-3-C-4, whereas the corresponding angle for the C-4-A bond should be 55° (see E. W. Garbisch, *ibid.*, **86**, 5561 (1964)).

(14) A reasonable explanation is as follows. Repulsion between the dipoles associated with the C-4-Z (*e.g.*, when Z is Br) and C-3-Br bonds will cause the C-4-A bond to rotate into the null coupling sector which lies between 40 and 30° to the C-2-C-3-C-4 plane.

(15) C. W. Jefford, J. Gunsher, S. Mahajan, and B. Waegell, *Tetrahedron Letters*, No. **28**, 2333 (1965).

(16) G. A. Russell, K. Y. Chang, and C. W. Jefford, *J. Am. Chem. Soc.*, **87**, 4383 (1965).

action mechanisms which have common stereochemical features.<sup>17</sup>

**Acknowledgments.** We thank the National Science Foundation and the donors to the Petroleum Research Fund, administered by the American Chemical Society, for the provision of research funds.

(17) However, coupling between the vinyl proton and an ethane bridge proton (which might be inferred from e.p.r. data) is not observed in the n.m.r. spectra of I-V.

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### The Form of d Orbitals in Carbon-Sulfur $\pi$ Bonds<sup>1</sup>

Sir:

Recently a substituent interference experiment on the intensity of the  $^1L_b$  bands in substituted benzenes was proposed for ascertaining participation of d orbitals in a conjugation scheme.<sup>2</sup> Application of this experiment to phenylsilanes<sup>2</sup> and to the lower halogens<sup>3</sup> demonstrated that the Si 3d and the Cl, Br, I *nd* (or  $(n+1)p$ ) orbitals are in fact populated.<sup>4</sup> In divalent sulfur compounds there are two views: (1) that the sulfur 3p and 3d orbitals<sup>4</sup> are both utilized in S-C  $\pi$  bonding,<sup>5,6</sup> and (2) that use of 3d<sup>4</sup> is unimportant and that the bond involves only inclusion of sulfur 3p electrons in an olefinic or aryl  $\pi$  shell.<sup>7</sup> It is possible to decide between (1) and (2) by a substituent interference experiment.

In thiophenol the inflection band at 2800 Å. (Table I) can be assigned with little doubt as the benzene analog  $^1L_b \leftarrow ^1A$  transition.<sup>8</sup> If the sulfur 3d orbitals are utilized in  $\pi$  bonding to the ring, the intensity of the  $L_b$  band in *p*-methylthiophenol will have a destructive interference term resulting in the intensity being decreased from that of thiophenol itself. On the other hand, any 3p $\pi$ (S)-2p $\pi$ (C) bonding will lead to a constructive term causing the intensity to increase. The distinct decrease in the molar extinction coefficient of *p*-methylthiophenol ( $\epsilon \sim 300$ ) from that for thiophenol ( $\epsilon \sim 700$ ) establishes that the S d orbitals do importantly

(1) Supported in part by the Air Force Office of Scientific Research, Grant AF-AFOSR 742-65, and by the National Science Foundation.

(2) L. Goodman, A. Konstam, and L. H. Sommer, *J. Am. Chem. Soc.*, **87**, 1012 (1965).

(3) L. Goodman and L. J. Frolen, *J. Chem. Phys.*, **30**, 1361 (1959).

(4) The interference experiment does not distinguish between population of *nd* and  $(n+1)p$  orbitals. A weak argument against utilization of  $(n+1)p$  orbitals in halogens is given by J. R. Hoyland and L. Goodman, *J. Phys. Chem.*, **64**, 1816 (1960). This argument does not necessarily apply to SiH<sub>4</sub>, however. We are in accord with a referee's suggestion that the main results of these papers do not distinguish between the 3d or 4p as the acceptor orbitals of sulfur. However, 3d seems to us to be more probable.

(5) D. P. Craig and C. Zauli, *Gazz. chim. ital.*, **90**, 1700 (1960).

(6) See, *e.g.*, R. J. Gillespie, *Can. J. Chem.*, **33**, 818 (1960).

(7) See, *e.g.*, (a) G. Bergson, *Arkiv Kemi*, **16**, 315 (1960); **18**, 409, (1961); **19**, 181, 265 (1962); (b) A. Mangini and R. Passerini, *J. Chem. Soc.*, 4954 (1956).

(8) W. W. Robertson and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5250 (1950). The more intense band at 2400 Å. is very probably a charge-transfer band S(3p $\pi$ )  $\rightarrow$  ring ( $\pi^*$ ). The decrease in intensity in the series C<sub>6</sub>H<sub>5</sub>(Et)S, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>(Et)S, and C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>(Et)S observed by E. A. Fehnal and M. Carmack, *ibid.*, **71**, 84 (1949), confirms this assignment.