5686 *J. Org. Chem.* **1995**, *60*, 5686−5689

Electron Spin Resonance Studies of Substituent Effects. 5.[1,2] Combined Effects of Orbital Symmetry and Substituents on the Methylene Hyperfine Splitting in 1,2-Indansemidiones[†]

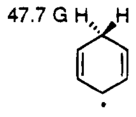
E. Thomas Strom

Mobil Exploration and Producing Technical Center,
Dallas, Texas 75381-9047

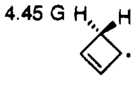
Received February 6, 1995

Introduction

Orbital symmetry can have a profound effect on methylene hyperfine splitting in free radicals where the methylene bridges two π atoms. The anomalously large methylene hyperfine splitting in cyclohexadienyl radical (**1**)[3] was explained by Whiffen[4] as resulting from the *like* sign of the molecular orbital coefficients in the semioccupied molecular orbital (SOMO) in the parent pentadienyl radical. Whiffen showed that the dependence of the methylene splitting for a methylene group bridging two π atoms is of the form $(c_1 + c_2)^2$, where c_1 and c_2 are Hückel coefficients in the SOMO, rather than the naively expected $c_1{}^2 + c_2{}^2$. The first expression gives far greater splitting constants than the second expression, provided the coefficients are of like sign. Whiffen also predicted an anomalously low methylene hyperfine splitting for cyclobutenyl radical (**2**) because the pertinent molecular orbital coefficients in the SOMO in the parent allyl radical are of *unlike* sign. When the ESR spectrum of cyclobutenyl radical was obtained later,[5] Whiffen's prediction was verified.

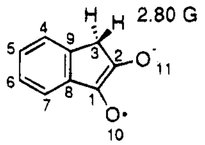


1

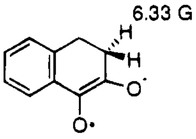


2

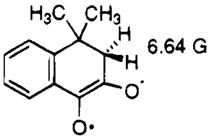
Orbital symmetry effects on methylene hyperfine splitting are more complex and interesting in radicals where there is no symmetry element. One such system is the anion radical of 1,2-indandione (1,2-indansemidione). This radical was first studied by Strom et al.[6] and Russell and co-workers.[7] Both groups noted that the methylene hyperfine splitting constants in the radical were surprisingly low and attributed this reduction to orbital symmetry effects. Methylene splitting constants from this earlier work for 1,2-indansemidione (**3**), from later work for 1,2-tetralinsemidione (**4**),[8] and for a derivative of the tetralin radical (**5**)[6] are shown below.



3



4



5

The ~2.8 G methylene splitting for radical **3** is only about 40% of the methylene splitting for the related radicals **4** and **5**. A simple molecular orbital calculation on **3** (see below), however, demonstrated that in the SOMO of this radical the coefficients for the β carbonyl carbon and the substituted *ortho*-carbon are of *opposite* sign, leading to a marked diminution of the methylene splitting.

Earlier we had found that *meta*- and *para*-substituted 1-phenyl-1,2-propanesemidiones[9,10] had methyl hyperfine splittings which gave a strong correlation with either Hammett σ constants or, where appropriate, with σ^- constants. We have studied these related substituted 1,2-indansemidiones to see how the orbital symmetry effects would mediate the substituent effect on the methylene hyperfine splitting.

Experimental Section

Materials. All but three of the compounds used were commercially available and used without further purification. 5-Chloro-1-indanone and 5-fluoro-1-indanone were obtained from Columbia Organic Chemicals. Dimethyl sulfoxide (DMSO), potassium *tert*-butoxide, 4-methoxy-1-indanone, 5-methoxy-1-indanone, 6-methoxy-1-indanone, 5,6-dimethoxy-1-indanone, and 5-amino-1-indanone came from Aldrich Chemical Co. 4-Methyl-1-indanone was obtained from Alfa Chemical Co. and 2-indanone from Lancaster Chemical Co. The 5-amino-1-indanone was obtained from the Sigma-Aldrich rare chemical collection, so its structure was verified by ^{13}C and ^{1}H NMR measurements. The NMR spectra were completely consistent with the 5-amino-1-indanone structure. The derivatives 5-, 6-, and 7-methyl-1-indanone were a gift from Professor E. J. Eisenbraun. Their synthesis has been described.[11]

Instrumentation. Early experiments were carried out with a Varian V-4500-10 ESR spectrometer. Later experiments utilized a Bruker ER-300 ESR spectrometer.

Procedures. The semidione radicals were generated by base-catalyzed oxidation in DMSO of the appropriate indanone derivative. The base used was potassium *tert*-butoxide, and the oxidant was the normal dissolved oxygen in the DMSO. Approximately 6−12 mg of indanone derivative and 2−8 mg of potassium *tert*-butoxide were weighed into each side of the "H-cell" of Russell and co-workers.[12] One mL of DMSO was then added to each side. An ESR aqueous sample cell was mounted on a jointed connection on top of the H-cell, and the two compartments of the H-cell were sealed with rubber septa. The solutions were mixed, and the reaction mixture was shaken down into the ESR cell. Best results were obtained with a 2-fold excess of indanone to base, as an excess of base led to complex spectra, complicated by other radicals. Russell and co-workers[7] found that large excesses of base gave radical condensation products.

Results

Usually the indanone derivatives gave green solutions on mixing with the base. Exceptions will be noted below. In most instances ESR spectra were obtained which had a good signal-to-noise ratio and were well resolved. The

---

[†] Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday and in memory of Dr. Robert F. Bridger.

(1) Part 4: Bridger, R. F.; Strom, E. T. *J. Org. Chem.* **1971**, *36*, 560.

(2) Presented in part at the Southwest Regional ACS Meeting, Nov 13−16, 1994, Ft. Worth, TX.

(3) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *38*, 773.

(4) Whiffen, D. H. *Mol. Phys.* **1963**, *6*, 223.

(5) Krusic, P. J.; Jesson, J. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 4566.

(6) Strom, E. T.; Janzen, E. G.; Gerlock, J. L. *Mol. Phys.* **1970**, *19*, 577.

(7) Russell, G. A.; Myers, C. L.; Bruni, P.; Neugebauer, F. A.; Blankespoor, R. *J. Am. Chem. Soc.* **1970**, *92*, 2762.

(8) Russell, G. A.; Blankespoor, R. L.; Trahanovsky, K. D.; Chung, C. S. C.; Whittle, P. R.; Mattox, J.; Myers, C. L.; Penny, R.; Ku, T.; Kosugi, Y.; Givens, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 1906.

(9) Strom, E. T. *J. Am. Chem. Soc.* **1966**, *88*, 2065.

(10) Strom, E. T.; Norton, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 2327.

(11) Boykin, D. W.; Hertzler, R. L.; Delphon, J. K.; Eisenbraun, E. J. *J. Org. Chem.* **1989**, *54*, 1418.

(12) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807.

0022-3263/95/1960-5686$09.00/0

expected uncertainty in the analyzed splitting constants is ±0.03 G.

Oxidation of 2-Indanone. An ESR spectrum was obtained in which 42 of the expected 48 lines were resolved. The analysis gave a methylene splitting of 2.66 G with ring proton splittings of 0.53, 0.74, 2.82, and 2.92 G. These numbers differ slightly from those we obtained earlier[6] in the methylene splitting (2.80 vs 2.66 G), although the ring splittings are close to our previous values (0.56, 0.73, 2.80, and 2.95 G). These new values are extremely close to those obtained by Russell and coworkers[7] (methylene 2.64 G; ring protons 0.56, 0.73, 2.83, and 2.95 G.). Our new methylene splitting perhaps reflects improved resolution with a more modern ESR spectrometer.

Oxidation of 4-Methyl-1-indanone. About 70 of the 96 expected lines could be discerned. The methyl splitting was clearly the smallest, 0.51 G. The methylene splitting was 2.53 G, while the remaining ring proton splittings were 0.71, 2.60, and 2.74 G.

Oxidation of 5-Methyl-1-indanone. Only 35 of the expected 96 lines could be resolved. The spectrum consisted of seven main multiplets, with the wing multiplets being 1:2:1 triplets. The center peak of the triplet showed a tendency to break, but it could not be resolved into a doublet. Therefore, the average splitting for the triplet, clearly from the 4 and 6 protons, was 0.65 G. The next splitting constant was derived from a single proton, and it was 2.77 G. This should be assigned to the proton at position 7. The splittings from the 5-methyl and the methylene protons were too close to be distinguished. The average splitting for these five protons was 2.96 G.

Oxidation of 6-Methyl-1-indanone. Here, 47 of the expected 96 lines were resolved. The smallest splitting of 0.54 G came from a single proton. The next largest splitting came from the methyl group, 0.73 G. One ring splitting and the methylene splitting were equivalent at 2.69 G. The remaining ring splitting was 2.92 G.

Oxidation of 7-Methyl-1-indanone. Again, only 47 of the expected 96 lines could be resolved. Like the 5-methyl derivative, the spectrum consisted of seven main multiplets. Here, the wing multiplets, however, could be resolved into approximately 1:1:1:1 quartets, giving splitting constants of 0.66 and 0.74 G for the 4 and 6 protons. The next larger splitting 2.78 G came from three protons. The remaining three protons gave a splitting of 2.94 G. Reasoning from the results for the 5-methyl derivative, the 2.78 G splitting would be assigned to the 7-methyl. Therefore, the 5 proton and methylene splittings must be approximately equal with a value of 2.94 G.

Oxidation of 4-Methoxy-1-indanone. This radical gave a rather poorly resolved spectrum, although the spectrum could be analyzed. There were 10 basic multiplets with some fine structure in between plus a very small quartet splitting from the methoxy group. The methoxy splitting was 0.12 G. The methylene splitting was 2.17 G. The remaining ring proton splittings were 0.68, 2.24, and 2.46 G.

Oxidation of 5-Methoxy-1-indanone. On mixing with base this compound gave the usual green color, but no stable free radical could be observed.

Oxidation of 6-Methoxy-1-indanone. On mixing with base this compound gave first a yellow color, then green, and then yellow-brown. There was no evidence of any methoxy splitting. All 24 expected peaks were resolved. The methylene splitting was 2.26 G, while the ring proton splittings were 0.49, 2.68, and 3.10 G.

Oxidation of 5,6-Dimethoxy-1-indanone. The predominant splitting pattern was a 1:3:3:1 multiplet, while the smallest splitting was a methyl quartet, made more complex because a ring splitting was approximately double the value of the small methyl splitting. The small methyl splitting, presumably from the 5-methoxy group, was 0.31 G. The small ring proton splitting was 0.66 G. The value of the methylene splitting equaled that of the other ring proton, giving the large 1:3:3:1 quartet. These splittings were 2.32 G.

Oxidation of 5-Chloro-1-indanone. A complex, unsymmetrical spectrum was obtained. Presumably, condensation radicals were present. Although the ratio of ketone to base was increased in an attempt to obtain just the simple semidione, no spectrum that could be attributed to just the monomeric radical could be obtained. No convincing analysis for the simple semidione could be found.

Oxidation of 5-Fluoro-1-indanone. This spectrum was quite simple because of the accidental degeneracy of the methylene splitting and one ring proton splitting and because of the accidental degeneracy of the two small ring proton splittings. Therefore, the spectrum consisted of two sets of 1:3:3:1 triplets, overlapped from the 6.14 G fluorine splitting. The methylene and one ring proton splitting were 2.98 G, and the remaining two proton splittings were 0.64 G.

Oxidation of 5-Amino-1-indanone. On mixing with base this compound gave a red-brown color. This material gave a very complex spectrum, which could not be solved in its entirety. In theory this spectrum should have 216 lines, but only about 70 peaks and shoulders could be resolved. Fortunately, the methylene splitting was quite prominent, and its value was 4.01 G. The smallest splitting appeared to be a quintet. Most likely this came from the amino nitrogen and the amino hydrogens with approximately equal splittings. This value was 0.35 G. The only other splitting that could be identified was a 0.86 G splitting, presumably from a ring proton.

Discussion

Substituent effects on the methylene hyperfine splittings in 1,2-indansemidiones can first be addressed by discussing the spin densities in the unsubstituted radical **3**. For **3**, any simple consideration of spin delocalization indicates that the two larger splittings must come from protons at positions 5 and 7 and the two smaller splittings from protons at positions 4 and 6. An unambiguous assignment of splitting constants would entail synthesis of specifically deuterated indanones. Fortunately, methyl substitution provides an easier way to make these assignments. Substitution of a methyl group for a proton results in a methyl splitting constant very close to that of the original proton,[13] provided that the odd electron is not in a nearly degenerate molecular orbital. For example, in the closely related 1-phenyl-1,2-propanesemidione system, where the assignments for the *para*-substituted compounds can be readily made by reason of symmetry, the splitting for the *para*-hydrogen in the

---

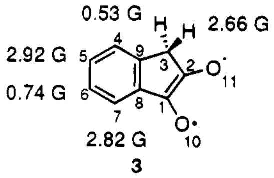
[13] Sullivan, P. D. *J. Magn. Reson.* **1983**, *54*, 314.

unsubstituted compound is 1.84 G, while the methyl splitting for the *para*-methyl derivative is 1.78 G.[14]

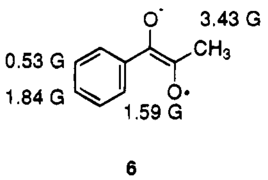
The ring splitting constants in **3** are 0.53, 0.74, 2.82, and 2.92 G. For the methyl-substituted compounds, the methyl splitting for the 4 derivative is 0.51 G, that for the 5 derivative 2.96 G, and that for the 6 derivative 0.73 G. Assignment of the methyl splitting for the 7-methyl derivative is admittedly more ambiguous, but, on the basis of the results for the 5-methyl radical, a value of 2.78 G is reasonable. Therefore, I will assign in **3** the 0.53 G splitting to position 4, the 0.74 G splitting to position 6, the 2.82 G splitting to position 7, and the 2.92 G splitting to position 5.

We note here the salient results of our earlier Hückel molecular orbital calculation on semidione **3**,[6] using McLachlan's modification of Hückel theory.[15] That calculation predicted the hyperfine splitting in position 4 to be greater than that in position 6, in accord with our results, and the hyperfine splitting in position 7 to be greater than that in position 5, the reverse of our assignment. Most important, the calculation showed that the Hückel coefficients at positions 2 and 9 in the SOMO were of *opposite* sign. If the methylene hyperfine splitting is calculated from the McLachlan equation,[16] modified for the $\cos^2\theta$ dependence[17] for methylene splitting, but by just squaring the coefficients without allowing for cancellation effects, the calculated splitting is 7.68 G. If the coefficients are algebraically summed and then squared, the calculated splitting is 1.83 G, much closer to the experimental value of 2.66 G.

These molecular orbital calculations together with just a simple comparison of the α-methylene splittings in 1,2-indansemidione (**3**) and 1,2-tetralinsemidione (**4**) show the substantial decrease in methylene splitting in the indansemidione caused by the orbital symmetry cancellation effects. Next we directly compare the substituent effects in the 1,2-indansemidione system with those found in the *trans*-1-phenyl-1,2-propanesemidiones (**6**).[9,10] We make the reasonable assumption that a 5 substituent in **3** is equivalent to a *para*-substituent in **6** and that a 4 or 6 substituent in **3** is equivalent to a *meta*-substituent in **6**. For systems **3** and **6** we then calculate the percent change the substituent has caused in the methylene splitting in **3** or the methyl splitting in **6**, as compared to the unsubstituted radicals. These calculations are given in Table 1.



3



6

Table 1. Per Cent Changes in Methylene or Methyl Hyperfine Splittings Caused by Substituents

substituent	$-CH_2-$ splitting	% change	substituent	Me splitting	% change
unsubst.	2.66 G		unsubst.	3.43 G	
4-Me	2.53 G	−4.9	*m*-Me	3.52 G	+2.6
5-Me	2.96 G	+11.3	*p*-Me	3.63 G	+5.8
6-Me	2.69 G	+1.1	*m*-Me	3.52 G	+2.6
4-OMe	2.17 G	−18.4	*m*-OMe	3.39 G	−1.2
5-OMe	no radical		*p*-OMe	3.88 G	+13.1
6-OMe	2.26 G	−15.0	*m*-OMe	3.39 G	−1.2
5,6-diOMe	2.32 G	−12.8	*m,p*-diOMe	3.84 G	+12.0
5-F	2.94 G	+10.5	*p*-F	3.59 G	+4.7
5-NH_2	4.01 G	+50.8	*p*-NH_2	4.30 G	+25.4

The data of Table 1 clearly show significant differences in substituent effects in semidiones **3** as compared to semidiones **6**. First of all, the methylene splittings in semidiones **3** are much more sensitive to substituents than the methyl splittings in semidiones **6**. For some electron-donating substituents, the effect in semidiones **3** is about twice as great as for semidiones **6**. For example: 5-Me, +11.3%, *p*-Me, +5.8%; 5-fluoro, +10.5%, *p*-fluoro, +4.7%; 5-NH_2, +50.8%, *p*-NH_2, +25.4%. Differences are even more pronounced for the single electron-withdrawing group studied, the −OMe group in a meta-type position. For the 6-OMe group and the *m*-OMe group the corresponding differences are −15.0% and −1.2%, respectively. Second, there are reversals in substituent effects. A 4-Me group reduces methylene splitting in **3**; a *m*-Me group increases side chain Me splitting in **6**. The 5,6-diOMe unit reduces methylene splitting in **3**; the *m,p*-diOMe unit substantially increases methyl splitting in **6**. Note that the increase in methyl splitting caused by the *m,p*-diOMe unit in **6** is exactly equal to the increase caused by a *p*-OMe group minus the decrease caused by a *m*-OMe group.

Our past work[9,10] has shown that the methyl hyperfine splitting in semidiones **6**, which reflects the spin density at the β carbonyl carbon, gives an excellent correlation with σ constants. (Obviously, the 5- or *p*-F group is an exception, but there are many examples of substituted aromatic radical systems where the fluorine atom raises the hyperfine splitting of a reporter atom in the side chain.[18]) There seems to be no valid reason why the spin density at the β carbonyl carbon in the related semidione **3** should not follow the same pattern as in **6**. Therefore, the discontinuities in the substituent pattern for semidiones **3** *must* arise from orbital symmetry effects engendered by changes in spin densities at the methylene substituted ring position, position 9.

The way that orbital symmetry effects can enhance substituent effects in semidiones **3** is quite straightforward. Consider an electron-donating group which pushes electron spin out of the aromatic ring into the semidione side chain. The methylene splitting will go up because the spin density at the β carbonyl carbon increases, but the effect will be *enhanced* because the spin density at the attached *ortho* position goes *down*, with a concomitant decrease in its spin density and molecular orbital coefficient. The amount of cancellation of the molecular orbital coefficients at the β carbonyl carbon and the attached *ortho*-carbon is *decreased*. With an electron-withdrawing group the decrease in methylene splitting will be *enhanced* because the spin density and molecular orbital coefficient goes up as the attached *ortho* position goes *up*, while the β carbonyl carbon spin density and coefficient go down. The amount of cancellation of the molecular orbital coefficients at the β carbonyl carbon and the attached *ortho*-carbon is *increased*.

To illustrate, let us consider the most anomalous of our results, the reversal of the substituent effect in the 5,6-dimethoxy derivative in **3**, as compared to the substituent effect of the *m,p*-dimethoxy unit in **6**. The splitting constants for the two dimethoxy semidiones **3a** and **6a**

---

[14] Strom, E. T.; Petkun, R. I. Unpublished results.

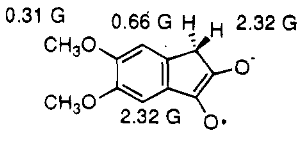
[15] McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.

[16] McLachlan, A. D. *Mol. Phys.* **1958**, *1*, 233.

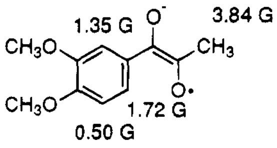
[17] Heller, H. C.; McConnell, H. M. *J. Chem. Phys.* **1960**, *32*, 1535.

[18] Strom, E. T.; Bluhm, A. L.; Weinstein, J. *J. Org. Chem.* **1967**, *32*, 3853.

are shown below. Radical **6a** was reported by Strom and



3a



6a

Norton.[10] They found that the spectrum could be analyzed in terms of a methyl side chain splitting of 3.84 G, a *meta* splitting of 0.50 G, and two *ortho* splittings of 1.35 and 1.72 G. Compared to the *ortho* splitting in unsubstituted radical **6** (1.59 G), one *ortho* splitting in **6a** has gone up and one has gone down. Strom and Norton were unable to make a definitive assignment for the *ortho* splittings in **6a**, but the results for **3a** now make the correct assignment clear. The 5,6-dimethoxy unit has decreased the splitting from the *ortho*-like 7 proton from 2.82 to 2.32 G. Therefore, in **6a** the 1.35 G splitting has to be assigned to the *ortho* position next to the *m*-methoxy. The 1.72 G splitting comes from the cross-ring *ortho* position in **6a**. The corollary is that in semidione **3a**, the 5,6-dimethoxy unit, while increasing the spin density at the β carbonyl carbon, has also increased the spin density at the methylene-attached *ortho* position. Because of the difference in signs of the molecular orbital coefficients, enough cancellation occurs to actually cause the methylene splitting to decrease rather than increase.

Summary and Conclusions

The methylene hyperfine splitting constant in 1,2-indansemidione radical is anomalously low because the molecular orbital coefficients in the SOMO at the π atoms bridged by the methylene group are of opposite sign. Eleven aromatic substituted derivatives of this system were studied. These derivatives showed a heightened sensitivity of methylene splitting to substituent when compared to the side chain methyl splitting in the related 1-phenyl-1,2-propanesemidione system. This sensitivity is caused by substituent effects at the substituted *ortho* position enhancing the substituent effect at the semidione side chain.

Acknowledgment. I am grateful to the National Biomedical Center for Spin Trapping and Free Radicals, Oklahoma Medical Research Foundation (OMRF), Oklahoma City, OK, for use of their ESR spectrometer. I am grateful to OMRF staff Dr. Edward G. Janzen, Dr. Yashige Kotake, Mrs. Melinda West, Dr. Lee Poyer, and Dr. Yongkang Zhang and to Dr. Kirk Schmitt of Mobil's Central Research Laboratory for technical assistance. I thank Professor Edmund Eisenbraun, Oklahoma State University, for a gift of methylindanones. I also thank Mobil Research and Development Corp. for permission to publish this work.

JO9502312