

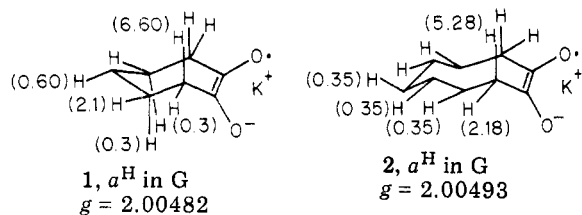
Aliphatic Semidiones. 39. Cyclononane-1,2-semidione and Derivatives<sup>1</sup>Glen A. Russell,\* C. E. Osuch,<sup>2</sup> G. Senatore, T. Morita, and M. Yamashita

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received January 29, 1979

Cyclononane-1,2-semidione exists as the (*Z*) isomer with a preferred chair-like conformation. Ring inversion has been detected by ESR spectroscopy with  $\Delta H^\ddagger = 5$  kcal/mol and  $\Delta S^\ddagger = -15$  eu. 6,6-Dimethyl-6-silacyclononane-1,2-semidione exists as (*E*) and (*Z*) isomers. For the free ions, the (*E*) isomer is the preferred structure, but in the presence of  $K^+$ , the (*Z*) isomer is more stable because of ion pairing. The (*Z*) isomer gives ring inversion with  $\Delta H^\ddagger = 2.3$  kcal/mol and  $\Delta S^\ddagger = -23$  eu. The (*E*) isomer at low temperatures exists as a pair of superimposable conformations possessing four different  $\alpha$ -hydrogen atoms which are time averaged at  $+50$  °C to give an ESR spectrum with hyperfine splitting from two pairs of  $\alpha$ -hydrogen atoms. The (*E*) isomer does not undergo internal rotation (which would make all four  $\alpha$ -hydrogen atoms equivalent) up to  $110$  °C.

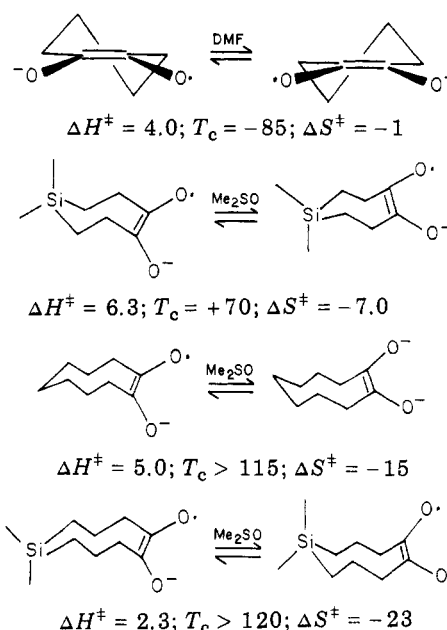
We have previously reported that cyclobutane- and cyclopentane-1,2-semidiones give no evidence of conformational motion by ESR spectroscopy,<sup>3,4</sup> that cyclohexane-1,2-semidione exists as a half-chair conformation with  $\Delta H^\ddagger$  for ring inversion = 4.0 kcal/mol,<sup>5</sup> and that cycloheptane-1,2-semidione exists as a frozen staggered conformation (1) in the ESR time frame ( $\tau > 10^{-6}$  s at  $100$



°C).<sup>6</sup> The paramagnetic 1,2-semidiones appear to be reasonable conformational models for the parent olefins.

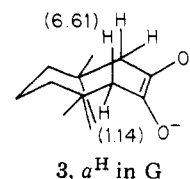
Cyclooctane-1,2-semidione (and the larger even-membered ring semidiones) is conformationally complex, but at  $+50$  °C the four  $\alpha$ -hydrogen atoms are time averaged in the ESR measurement. Cyclononane-1,2-semidione (2) is of considerable interest because of the possibility of observing a cyclic *trans*-1,2-semidione. However, we have found no evidence for the (*E*) isomer of 2. From  $-30$  to  $+50$  °C, 2 is conformationally stable as judged by the rich hyperfine (hf) structure of the ESR spectrum (Figure 1a). At higher temperatures, the ESR spectrum of 2 is a triplet of triplets from the  $\alpha$ -hydrogen atoms which coalesces (Figure 1b) to a quintet above  $115$  °C (the highest temperature at which the  $\alpha$ -axial and  $\alpha$ -equatorial hyperfine splitting (hfs) can be visually resolved). From peak separation as a function of temperature,  $\Delta H^\ddagger$  for ring inversion of 2 is 5.0 kcal/mol (Chart I, an error limit of  $\pm 0.3$  kcal/mol in  $\Delta H^\ddagger$  and  $\pm 0.5$  eu in  $\Delta S^\ddagger$  results if the rate constants measured are in error by a factor of 2). In a similar fashion, the 5,5-dimethyl-5-sila derivative of 1 gave a coalescence of the  $\alpha$ -hydrogens at  $+70$  °C with  $\Delta H^\ddagger = 6.3$  kcal/mol (Chart I).<sup>7</sup> The silacycloalkane-1,2-semi-

Chart I. Ring Inversion of Cyclic 1,2-Semidiones,  $\Delta H^\ddagger$  in kcal/mol,  $T_c$  = coalescence temperature ( $\pm 5$  °C),  $\Delta S^\ddagger$  in cal/(°C mol) ( $K^+$  Counterion in All Cases)



diones have conformational stabilities roughly equivalent to the carbocyclic analogues with two more atoms in the ring.

The two largest hfsc's in 2 were assigned to the  $\alpha$  equatorial and axial hydrogen atoms (C-3,9) on the basis of the synthesis of 3 (4,4,8,8-tetramethylcyclononane-



1,2-semidione). The staggered conformation of 2 was assigned on the basis of the similarity of the hfsc at the  $\beta$ ,  $\gamma$ , and  $\delta$  positions with 1, and on the basis of predictions made on the zig zag or W-plan rule for long range hfsc's.<sup>6,8,9</sup> The assigned hfsc's for 2 are in agreement with the hfsc's

(1) Application of ESR Spectroscopy to Problems of Structure and Conformation. 32. This work was partially supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgement is made to the donors of this fund.

(2) N.S.F. Predoctoral Fellow, 1977-1979.

(3) G. A. Russell, P. R. Whittle, R. G. Keske, G. Holland, and C. Aubuchon, *J. Am. Chem. Soc.*, **94**, 1693 (1972).

(4) G. A. Russell, E. R. Talaty, and R. H. Horrocks, *J. Org. Chem.*, **32**, 353 (1967).

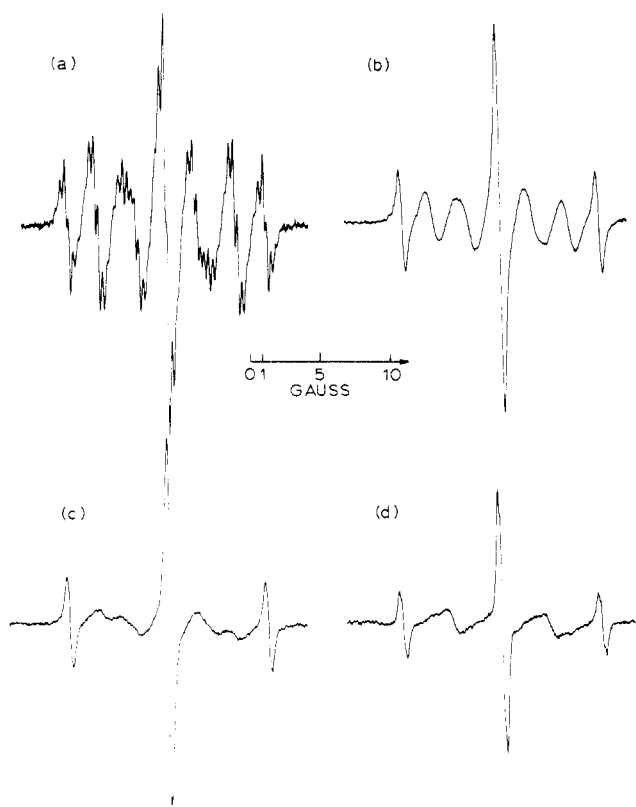
(5) G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Am. Chem. Soc.*, **89**, 6623 (1967).

(6) G. A. Russell, R. G. Keske, G. Holland, J. Mattox, R. S. Givens, and K. Stanley, *J. Am. Chem. Soc.*, **97**, 1892 (1975).

(7) G. A. Russell, C. E. Osuch, and W. Chau, *Heterocycles*, **11**, 165 (1978).

(8) G. A. Russell and K.-Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965); G. A. Russell, K.-Y. Chang, and C. Jefford, *ibid.*, **87**, 4383 (1965).

(9) G. A. Russell, G. W. Holland, K.-Y. Chang, R. G. Keske, J. Mattox, C. S. C. Chung, K. Stanley, K. Schmitt, R. Blankespoor, and Y. Kosugi, *J. Am. Chem. Soc.*, **96**, 7237 (1974).



**Figure 1.** Ring inversions of cyclononane-1,2-semidione observed by ESR spectroscopy in  $\text{Me}_2\text{SO}$ ,  $\text{K}^+$  counterion. (a) Spectrum at 30 °C showing triplet, triplet, sextet splitting. (b) Spectrum with selective line broadening at +70 °C. (c) Spectrum at +100 °C, slightly below coalescence point. (d) Spectrum at +125 °C, slightly above the coalescence temperature.

in a series of rigid polycyclic semidiones where the nine-membered ring is constrained to conformations A-D.

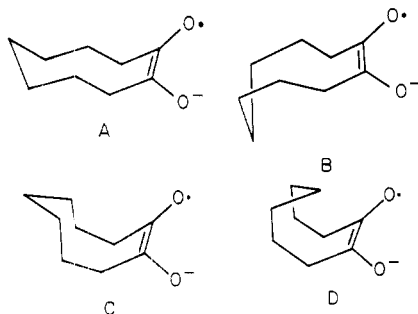


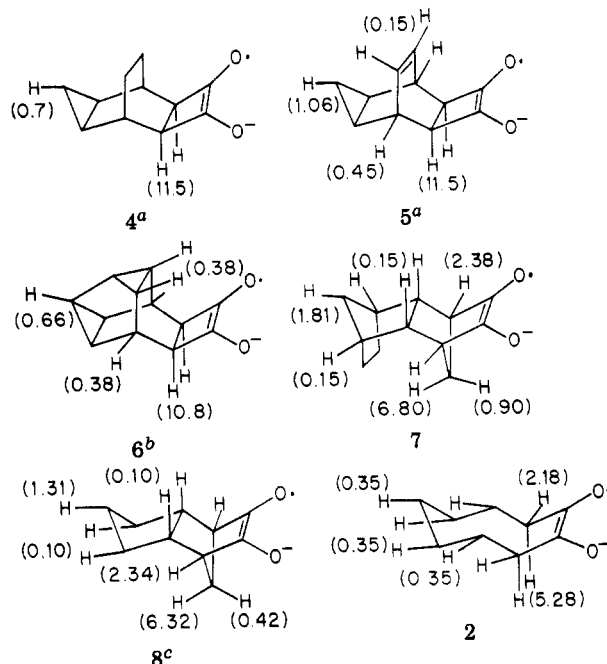
Chart II lists mainly previously described semidiones possessing a nine-membered ring in conformation A. From these model compounds, it is clear that equatorial hydrogen atoms at the  $\beta$ -,  $\gamma$ -, or  $\delta$ -carbon atoms (C(4)-C(6)) have larger hfsc's than axial hydrogen atoms at these positions.

Chart III lists two semidiones possessing the nine-membered ring in conformation B. No doublet hfs is observed for the  $\delta$ -hydrogen atom of the nine-membered ring as is observed for 1.

Chart IV lists two semidiones in which the nine-membered ring possesses structure C. Structure C is also present in the semidione 6 of Chart I. Again, no hfs is noted for the  $\delta$ -hydrogen atom. Chart V gives two structures, one rigid and one conformationally mobile, which possess structure D. Here, hfs can be observed for one or both  $\delta$ -hydrogen atoms in the nine-membered ring.

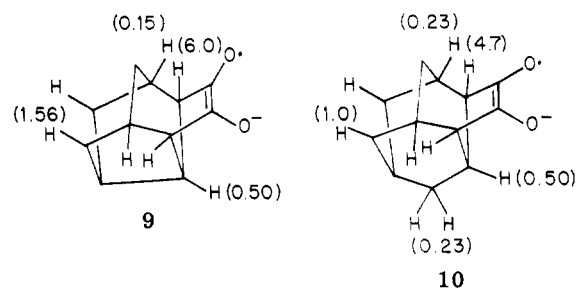
The 6,6-dimethyl-6-sila derivative of 2, prepared from the  $\alpha$ -hydroxy ketone plus potassium dimethylsilylate in  $\text{Me}_2\text{SO}$ ,

**Chart II. Polycyclic Semidiones Containing a Nine-Membered Ring in the Staggered Configuration (A) (Hyperfine Splitting Constants in G)**

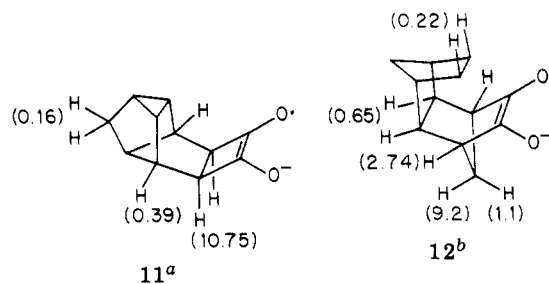


<sup>a</sup> Reference 3. <sup>b</sup> Reference 6. <sup>c</sup> Reference 9.

**Chart III. Polycyclic Semidiones Containing the Nine-Membered Ring in Configuration B (Hyperfine Splitting Constants in G)**



**Chart IV. Polycyclic Semidiones Having the Nine-Membered Ring in Sickle Conformation (C) (Hyperfine Splitting Constants in G)**



<sup>a</sup> References 3 and 6. <sup>b</sup> Reference 9.

gave a mixture of semidiones (Figure 2a) which we have identified as the (*E*) and (*Z*) isomers 15 and 16.

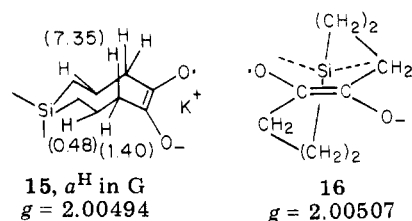
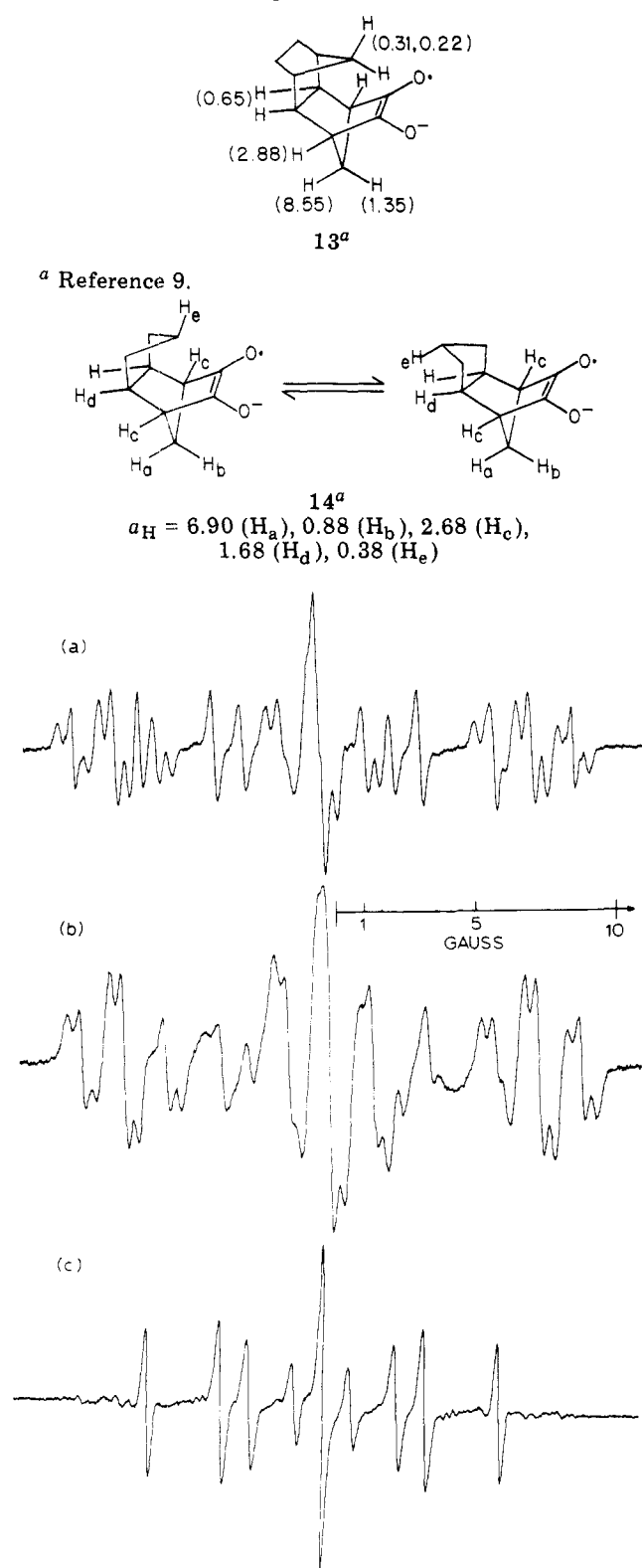
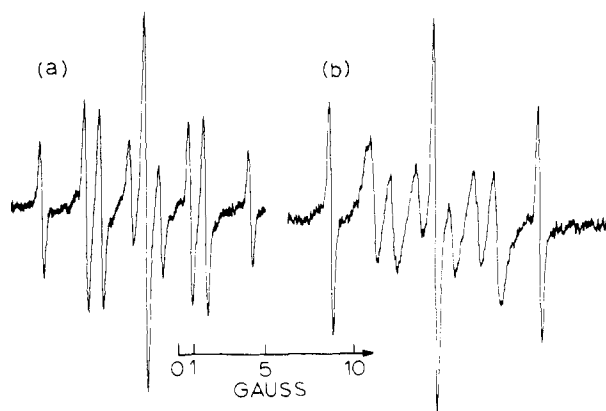


Chart V. Polycyclic Semidiones Containing the Nine-Membered Ring in the Cup Configuration (D) (Hyperfine Splitting Constants in G)



**Figure 2.** ESR spectra of the mixture of (*E*)- and (*Z*)-6,6-dimethyl-6-silacyclononane-1,2-semidione at 25 °C in  $\text{Me}_2\text{SO}$ : (a) mixture of isomers observed with 0.1 M  $\text{K}^+$ ; (b) mainly *Z* isomer observed with KI added; (c) *E* isomer observed upon the addition of an excess of [2.2.2]cryptand.

The structural assignments hinge partially upon the effect of ion pairing upon  $g$  values<sup>10</sup> and the greater



**Figure 3.** ESR spectra of (*E*)-6,6-dimethyl-6-silacyclononane-1,2-semidione in DMF: (a) +80 °C showing a time averaged triplet of triplets; (b) -20 °C showing a sharp 1:2:1 triplet with other lines broadened.

tendency of a *cis*-1,2-semidione than of a *trans*-1,2-semidione to undergo ion pairing with  $\text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$ .<sup>11</sup> Cyclononane-1,2-semidione itself in the presence of excess  $\text{K}^+$  gives the ion pair with  $g = 2.00493$ ,  $a^{\text{H}}_{\alpha} = 5.28$  (2 H), 2.18 (2 H) G. In the presence of an excess of [2.2.2]-cryptand, the free ion is observed with  $g = 2.00513$ ,  $a^{\text{H}}_{\alpha} = 5.10$  (2 H), 2.14 (2 H) G. The two radical ions observed with the 6,6-dimethylsila derivative have different  $g$  values suggesting a *cis* and a *trans* structure. Addition of excess  $\text{K}^+$  favors one of these species to which we ascribe the *cis* structure (15,  $g = 2.00494$ , Figure 2b). Treatment of the solution with an excess of [2.2.2]cryptand gives mainly the other isomer which we assign as the *trans* isomer (16,  $g = 2.00507$ , Figure 2c).

At 25 °C, 15 gives an ESR spectrum with  $a^{\text{H}}_{\alpha} = 7.35$  (axial), 1.40 (equatorial) and  $a^{\text{H}}_{\beta} = 0.48$  (equatorial) G. Upon warming, the peaks of the triplet of triplets for the  $\alpha$  hydrogens shift and approach a pentet from four equivalent (time averaged)  $\alpha$ -hydrogen atoms. From the shifts in the position of the peaks, a  $\Delta H^{\ddagger}$  for ring flip of 15 of 2.3 kcal/mol can be calculated (Chart I, an error limit of  $\pm 0.3$  kcal/mol and  $\pm 0.5$  eu results if the rate constants measured are in error by a factor of 2).

Chart I shows the expected variation in  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  for the ring inversions of the seven- and nine-membered rings. Increasing ring size lowers  $\Delta H^{\ddagger}$  but makes  $\Delta S^{\ddagger}$  more negative. The floppy large rings have a very low energy barrier for ring flip, but to avoid nonbonded interactions the configurational pathway is a tortuous one of low probability involving rotations among the single bonds in the ring in a rigid time sequence.

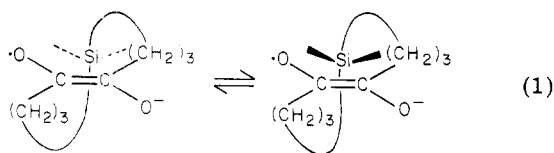
Addition of [2.2.2]cryptand converts 15 to 16. A transient spectra (apparently when a very slight deficiency of the cryptand was employed) for the free ion of the (*Z*) semidione was detected with  $g = 2.00507$  and  $a^{\text{H}}_{\alpha} = 6.47$  (2 H), 1.45 (2 H),  $a^{\text{H}}_{\beta} = 0.37$  (2 H),  $a^{\text{H}}_{\gamma} = 0.16$  (2 H) G. For the ion pair 15,  $a^{\text{H}}_{\gamma}$  could not be resolved.

Conformational motion can be detected for 16 also. Above 50 °C, the hfs pattern is a triplet of triplets ( $a^{\text{H}} = 2.3, 3.6$  G) from the  $\alpha$ -hydrogen atoms (Figure 3a). Upon cooling, selective line broadening is observed, and at -30 °C only the wing peaks and center line remain sharp to give a 1:2:1 triplet (Figure 3b). This behavior is also observed for the *trans*-1,2-semidiones in the 11-, 13-, and 15-membered carbocyclic rings. Heating 16 to 110 °C does

(11) G. A. Russell, D. F. Lawson, H. L. Malkus, R. D. Stephens, G. R. Underwood, T. Takano, and V. Malatesta, *J. Am. Chem. Soc.*, **96**, 5830 (1974); G. A. Russell, G. Wallraff, and J. L. Gerlock, *J. Phys. Chem.*, **82**, 1161 (1978).

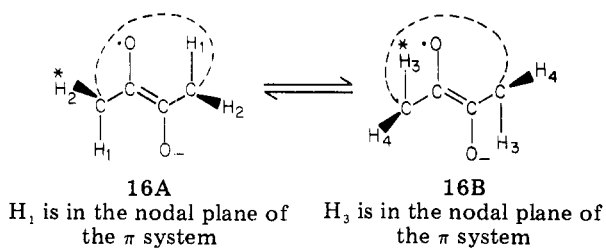
(10) G. A. Russell and C. E. Osuch, *J. Am. Chem. Soc.*, **100**, 5979 (1978).

not give any indication that all four of the  $\alpha$ -hydrogen atoms are being time averaged, and we conclude that internal rotation (eq 1) for **16** must be quite a high-energy



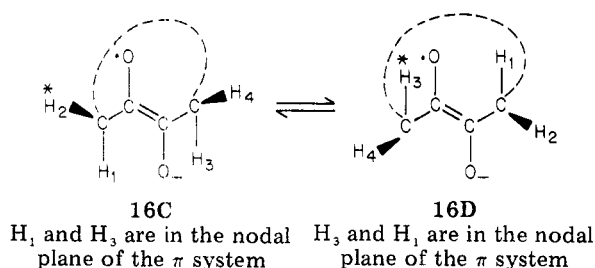
process ( $\tau > 10^{-6}$  s at 110 °C).

The low-temperature conformational equilibrium observed for **16** and other trans cyclic-1,2-semidiones<sup>12</sup> excludes structures **16A** and **16B** or their time average. In structures **16A-D** the four chemically and magnetically different kinds of hydrogen atoms are labeled  $H_1$ - $H_4$ . Equilibrium between **16A** and **16B** would maintain sharp



wing peaks in the spectrum only under the unlikely event that  $\sum a^H(16A) = \sum a^H(16B)$ . However, even in this event the spectrum with selective line broadening (Figure 3b) should be a 1:4:1 triplet of sharp lines rather than the 1:2:1 triplet observed.

The observed effect of temperature on the ESR spectrum of **16** strongly suggests that a pair of equivalent conformations (topomers) are involved as is the case for **15**, **2**, or the 6,6-dimethyl-6-silacycloheptane-1,2-semidione wherein achiral diastereotopomers possessing a plane of symmetry are observed. The observed spectra can be nicely accommodated by conformational equilibrium between the superimposable structures **16C** and **16D**.



Each of these chiral topomers contains four different  $\alpha$ -hydrogen atoms, but equilibration between them time averages  $H(1)$  with  $H(4)$  and  $H(2)$  with  $H(3)$  to give the observed triplet of triplets at +50 °C (Figure 3a). The wing peaks will remain sharp irrespective of the rate of interconversion because both topomers contain the same ensemble of  $\alpha$ -hydrogen atoms. A 1:2:1 triplet of sharp lines can occur in the low-temperature spectrum with selective line broadening, if the ESR spectrum for conformationally frozen **16C,D** contains fortuitous overlap at the center of the spectrum to give a line of intensity two whose ESR

transition does not change in energy when  $H(1)$ ,  $H(4)$  and  $H(2)$ ,  $H(3)$  are interchanged. The only possibility for this situation is the overlap of the lines with nuclear spin orientations  $\alpha, \beta, \beta, \alpha$  and  $\beta, \alpha, \alpha, \beta$  where the four spins are arranged in order of decreasing  $a^H$ . The hydrogen atoms  $H(2)$  and  $H(4)$  most removed from the nodal plane of the spin label will have hfsc greater than hydrogen atoms  $H(1)$  and  $H(3)$ .<sup>13</sup> To explain the observed spectrum, the ordering of these hfsc must be  $H(2) > H(4) > H(1) > H(3)$ . Only in this case does the conversion of **16C** to **16D** (which converts  $H(2)$  to  $H(3)$  and  $H(1)$  to  $H(4)$ ) have no effect on the energies of the  $\alpha, \beta, \beta, \alpha$  and  $\beta, \alpha, \alpha, \beta$  states. Conversion of **16C** to **16D** converts the  $\alpha_2, \beta_4, \beta_1, \alpha_3$  spin state in **16C** to the isoergic  $\alpha_3, \beta_1, \beta_4, \alpha_2$  spin state in **16D**, while the  $\beta_2, \alpha_4, \alpha_1, \beta_3$  state in **16C** is converted to the isoergic  $\beta_3, \alpha_1, \alpha_4, \beta_2$  state in **16D**. At temperatures below -30 °C, **16** gives a spectrum which is not inconsistent with structure **16CD** (four doublet splittings), but broadening of the lines and the possibility for asymmetric ion pairing in a trans semidione<sup>12</sup> eliminate the possibility of a definitive analysis.

### Experimental Section

Cyclononane-1,2-semidione was prepared by mixing equal volumes of a solution of the 1,2-bis(trimethylsiloxy)cyclononene (0.1 M) with potassium dimsylate (0.2 M) in  $Me_2SO$  in an inverted H cell which had been thoroughly deoxygenated by prepurified nitrogen.<sup>14</sup> The 6,6-dimethyl-6-silacyclononane-1,2-semidione was prepared in a similar fashion from the  $\alpha$ -hydroxy ketone.<sup>15</sup> For low-temperature studies, the semidiones were prepared in DMF using potassium *tert*-butoxide (0.5 M). The  $g$  values were measured using a dual cavity with a Varian V-4500 spectrometer.

Semidione **7** was prepared from the dione<sup>16</sup> in  $Me_2SO$  by electron transfer from propiophenone in the presence of potassium *tert*-butoxide.<sup>13</sup> Semidione **9** was prepared from tetracyclo[5.3.1.0<sup>2,6</sup>.0<sup>3,9</sup>]undec-4-ene<sup>17</sup> (0.04 g) by treatment with potassium permanganate in acetic anhydride to form the dione.<sup>18</sup> The crude dione was treated with potassium *tert*-butoxide in  $Me_2SO$  containing propiophenone to form **9**. Semidione **10** was prepared from the monoketone, tetracyclo[6.3.1.0<sup>2,8</sup>.0<sup>5,10</sup>]dodecan-3-one,<sup>19</sup> by treatment with a trace of air in  $Me_2SO$  containing potassium *tert*-butoxide.

4,4,8,8-Tetramethylcyclononane-1,2-semidione was prepared from the corresponding acyloin<sup>20</sup> or bis(trimethylsiloxy)alkene obtained by acyloin condensation of 3,3,7,7-tetramethylazelaic dimethyl ester.<sup>20</sup>

**Acknowledgments.** 2-Hydroxy-7,7-dimethyl-7-silacyclononane was kindly furnished by Professor P. Mazerolles.<sup>21</sup> The dione precursor to **7** was supplied by Professor H.-D. Scharf,<sup>16</sup> the olefin precursor to **9** was supplied by Professor M. Kawanishi,<sup>17</sup> and the ketone precursor to **10** (ethanoadamantan-3-one) was supplied by Professor T. Sasaki.<sup>19</sup>

**Registry No.** **2**, 70136-05-9; **3**, 70524-36-6; **7**, 70561-38-5; **9**, 70562-09-3; **10**, 70524-37-7; **15**, 70136-06-0; 1,2-bis(trimethylsiloxy)cyclononene, 70524-38-8.

(13) G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 714 (1964).

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

(15) R. A. Benkeser and R. F. Cunico, *J. Org. Chem.*, **32**, 395 (1967).

(16) H.-D. Scharf, P. Friedrich, and A. Linckens, *Synthesis*, 256 (1976).

(17) T. Katsushima, R. Yamaguchi, M. Kawanishi, and E. Osawa, *Chem. Commun.*, 39 (1976).

(18) K. B. Sharpless, R. F. Lauer, O. Repik, A. Y. Teranishi and D. R. Williams, *J. Am. Chem. Soc.*, **93**, 3303 (1971).

(19) T. Sasaki, S. Eguchi, and Y. Hirako, *J. Org. Chem.*, **42**, 298 (1977).

(20) A. T. Blomquest and G. A. Miller, *J. Am. Chem. Soc.*, **83**, 243 (1961).

(21) P. Mazerolles and A. Faucher, *Bull. Soc. Chim. Fr.*, 2134 (1967); P. Mazerolles, A. Faucher, and A. Laporterie, *ibid.*, 887 (1969).

(12) Unpublished work with C. E. Osuch.