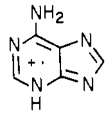
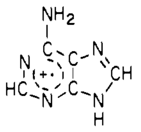
thus shows structural equivalence of the populations that contribute to m/z 135. Examination of a space-filling CPK model of adenosine shows that N-9 is sterically inaccessible to the transfer of labeled hydrogen directly from O-2′ in the absence of ribose ring opening, suggesting that the initial common structure of m/z 135 may be **23** rather than **22**. Other interconverting forms are



23

also possible, including ring-opened species (a–d) through which dissociation occurs.



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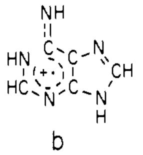

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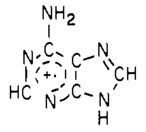

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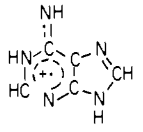

d

As a consequence of their identical molecular ion structures, there exists the possibility that adenine- and adenosine-produced m/z 135 ions may follow sufficiently similar decomposition paths to permit extrapolation of established label-retention patterns in adenine to those of m/z 135 from adenosine, or other adenine nucleosides. This question would best be pursued by examination of one or more [^{15}N]adenosine models but is not presently being investigated.

Conclusions

More than two-thirds of the ion current produced by electron ionization of adenine is carried by fragment ions, the formation of most of which requires rupture of one or both rings. The dominant reaction sequence is initiated by expulsion of HCN, which is approximately 90% site specific for N-1, C-2. Positional selectivity is also exhibited in the formation of $M - NH_2$ and $M - NH_3$ ions (retention of N-7 and N-9) and in $C_2H_4N_3^+$ (retention of C-2, C-4, N-1, N-3, and N-9). Mass spectrometry may thus provide a useful method for location of biologically incorporated heavy isotopes in studies of purine metabolism and turnover and in detecting unusual isotopic enrichment patterns that would reflect alterations in the de novo purine biosynthesis pathway.[6,25] Although the sample for such measurements must be relatively pure and enrichments of several percent or greater must be present, the microgram-level sample requirement is more favorable by a factor of 10^3–10^4 than conventional stepwise chemical degradation methods.[26]

The complex decomposition pathways represented by ions that were found to exhibit largely random isotopic retention patterns in this and earlier work[11] are a reminder of the speculative nature of assignments of structures to fragment ions from complex heteroaromatic compounds. Numerous examples of such assignments are found in the literature.[27]

Acknowledgment. This work was supported by Grants CA 28381 (L.B.T.) and GM 21584 (J.A.M.) from the National Institutes of Health. Collisional-activation mass spectra were determined at the Midwest Center for Mass Spectrometry at the University of Nebraska, supported by National Science Foundation Grant CHE 78-18572. The authors are grateful for assistance and suggestions from Drs. David L. Smith and T. Kinoshita.

Registry No. 1, 5098-11-3; **2**, 23142-10-1; **3**, 79364-53-7; **4**, 2302-25-2; **5**, 79364-58-2; **6**, 79364-59-3; **7**, 79364-60-6; **8**, 79364-61-7; **9**, 81602-56-4; **10**, 81602-57-5; **11**, 79364-54-8; **12**, 87-42-3; **13**, 19713-11-2; **14**, 2434-56-2; **15**, 79364-64-0; **16**, 79364-65-1; **17**, 79364-55-9; **18**, 5413-85-4; **19**, 56777-11-8; **19a**, 81602-58-6; **20**, 56777-12-9; **21**, 56777-22-1; diethoxymethyl acetate, 14036-06-7.

Supplementary Material Available: Equations for calculation of heavy isotope retention in ions $M - 2(HCN)$, $M - 3(HCN)$, $M - HCN - NH_2CN$, $M - NH_2$, and NH_3; compositional list of all ions in the mass spectrum of adenine; ion abundance data from [^{15}N]- and [^{13}C]adenines (Table 3); calculated ^{15}N retentions in ions $M - HCN$, $M - 2(HCN)$, $M - 3(HCN)$, $M - HCN - NH_2CN$ (Table 4); and experimental details for preparation of [3-^{15}N]adenine and [6-*amino*-^{15}N]adenine (10 pages). Ordering information is given on any current masthead page.

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[25] "Purine and Pyrimidine Metabolism", Ciba Foundation Symposium 48 (new series); Elsevier: Amsterdam, 1977.

[26] For example: (a) Smulson, M. E.; Suhadolnik, R. J. *J. Biol. Chem.* **1967**, *242*, 2872–2876. (b) Isono, K.; Suhadolnik, R. J. *Ann. N.Y. Acad. Sci.* **1975**, *255*, 390–401.

[27] For an extensive compilation of polynitrogen heterocycle fragmentation schemes (text in Japanese) taken from the literature, see: Goto, M. In "Kagaku no Ryoiki"; Nankodo: Tokyo, 1968; Special Issue No. 85, pp 141–180.

Cis–Trans Equilibria in Aliphatic Semidiones[1]

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Received November 30, 1981

Abstract: Ion pairing and cis–trans equilibria of the dimethylsemidiones in Me_2SO in the presence of K^+ has been analyzed in terms of four equilibrium constants which at 25 °C are as follows: trans free ion/cis free ion = 125 ($\Delta H°$(trans–cis) = −2.5 kcal/mol); trans ion pair/cis ion pair = 2 ($\Delta H°$(trans–cis) = −1.4 kcal/mol); K(ion pairing) for the cis semidione = 250 M^{-1} ($\Delta H°$ = −1.1 kcal/mol); K(ion pairing) for the trans semidione = 4 M^{-1} ($\Delta H°$ = 0). In cyclic C_{11}–C_{15} semidiones the cis and trans isomers can be detected. The cis isomers are favored by high [K^+] whereas in the presence of K^+[2.2.2]-cryptand the trans isomers are preferred. The cyclic trans 1,2-semidiones exist in an asymmetric conformation with four magnetically nonequivalent α-hydrogen atoms which become time averaged to two pairs of hydrogen atoms at higher temperatures (>25 °C for C_{15} and >170 °C for C_{11}). Internal rotation in the trans 1,2-cyclic semidiones is quite slow but can be detected for the *trans*-cyclopentadecane-1,2-semidione at 130 °C.

Dialkyl semidiones ($RC(O\cdot)=C(O^-)R$) exhibit cis–trans equilibria which are established in a matter of seconds or less in Me_2SO at 25 °C but are slow on the ESR time scale.[3] Cis semidiones have values of a_α^H considerably greater than their trans

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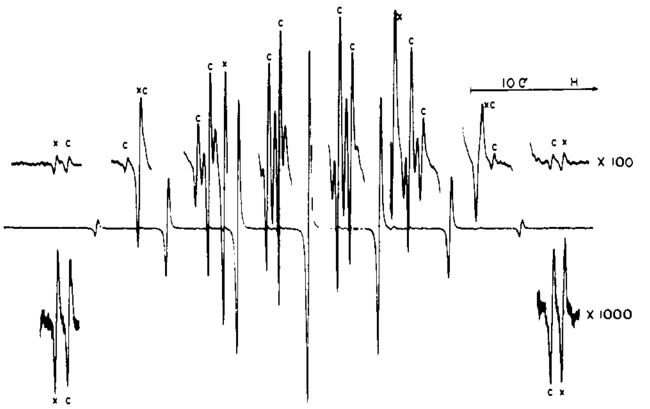
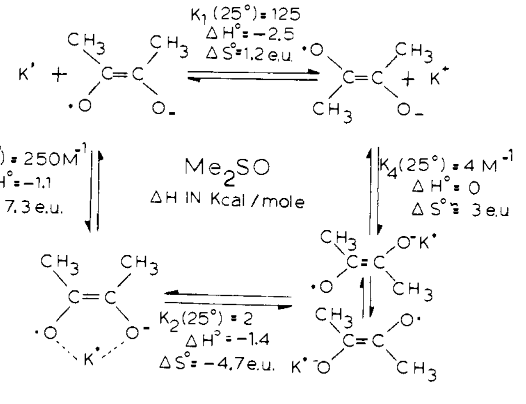


Figure 1. ESR spectrum of dimethyl semidiones (Me_2SO, 25 °C, K^+,[2.2.2]-cryptand). The predominant species is the trans isomer whose ^{13}C satellites are labeled C. Lines for the cis isomer are labeled X.

Scheme I



isomers.[3] It has also been noted that under certain conditions cis semidiones have higher g values than the trans isomers.[3-5] Ion pairing is important in determining the cis/trans ratios as well as the a^H and g values, even in Me_2SO.[6] The cis/trans ratio increases as the counterion is changed from R_4N^+ to Cs^+ to K^+ to Na^+ to Li^+ or (for the alkali-metal cations) as the dielectric constant of the solvent is decreased.[3-6]

We have investigated the equilibria of Scheme I for R = Me with K^+ as the counterion in Me_2SO by ESR spectroscopy.

The equilibrium constant K_1 was obtained by observation of the semidiones generated by the action of Me_3COK in the presence of an excess of [2.2.2]-cryptand upon 2,3-bis(trimethylsiloxy)-2-butene in Me_2SO (Figure 1). The trans/cis ratio (K_1) varied from 143 at 15 °C to 74 at 70 °C with $\Delta H°$(trans–cis) = −2.5 kcal/mol and $\Delta S°$ = 1.2 eu. The values of a^H of 5.67 and 6.75 G for the trans and cis semidiones were independent of temperature and were not affected by the addition of $Me_4N^+I^-$ to the solution. The g values were essentially the same: 2.005 07 (trans) and 2.005 10 (cis). Earlier reports[4] and ab initio molecular orbital calculations,[7] indicating a much lower g value for the cis isomer, were based on a comparison of the cis and trans semidiones in the presence of K^+ which preferentially complexes with the cis isomer so that essentially the cis ion pair and the free trans semidione were being compared. Upon the addition of alkali-metal cations in the form of their iodide salts the trans/cis ratio decreases (Figure 2), the values of g decrease (Figure 3), and the values of a^H increase. In the presence of 1.31 M KI the trans/cis ratio was 1.1, $a_{trans}{}^H$ = 5.89 G, $a_{cis}{}^H$ = 7.21 G, g(trans) = 2.004 982, g(cis) = 2.004 899. These are time-averaged values for the mixture of free ion and ion pairs determined by the values of K_3 and K_4. From Figure 3 it is obvious that at 1.3 M KI the cis semidione is essentially completely ion paired while the trans semidione is only partially complexed. Other values of a^H, g, and the trans/cis ratio in the presence of various alkali-metal iodides in Me_2SO are given in Table I.

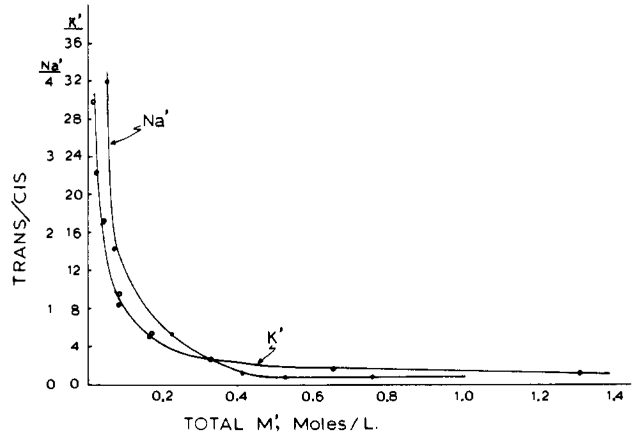


Figure 2. Cis/trans ratios of dimethylsemidiones at 25 °C in Me_2SO containing NaI or KI.

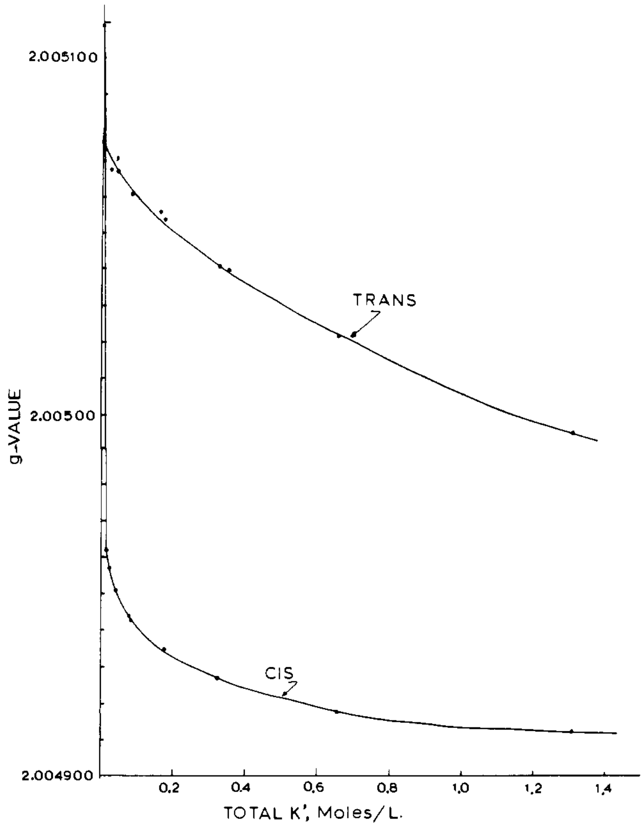


Figure 3. g values observed for cis and trans dimethyl semidiones in Me_2SO at 25 °C in the presence of KI.

It was impossible to obtain in the presence of Li^+ or Na^+ well-resolved spectra of the semidiones at low temperatures where time averaging between the free ions and the ion pairs might be slow on the ESR time scale. Lowering the temperature causes a reversible loss of the ESR signal due to disproportionation of the semidione to biacetyl and enediol dianion. This disproportionaton is more important when ion pairing occurs which greatly limits the solvents and counterions for low-temperature work. However, at −90 °C in DMF with Cs^+ or K^+ as the counterion

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[1] Aliphatic Semidiones. 42. This work was supported by a grant from the National Science Foundation (CHE-7823866).

[2] National Science Foundation Pre-doctoral Fellow, 1976–1979.

[3] Russell, G. A.; Lawson, D. F.; Malkus, H. L.; Stephens, R. D.; Underwood, G. R.; Takano, T.; Malatesta, V. *J. Am. Chem. Soc.* **1974**, *96*, 5830.

[4] Corvaja, C.; Nordio, P. L.; Giacometti, G. *J. Am. Chem. Soc.* **1967**, *89*, 1751. We have found that R_4N^+ salts often contain alkali-metal impurities which can significantly affect cis/trans ratios of aliphatic semidiones.

[5] Russell, G. A.; Lawson, D. F. *J. Am. Chem. Soc.* **1972**, *94*, 1699.

[6] Russell, G. A.; Osuch, C. *J. Am. Chem. Soc.* **1978**, *100*, 5979.

[7] McCain, D. C.; Hayden, D. W. *J. Magn. Reson.* **1973**, *12*, 312.

Table I. Values of g, a^H (in G), and Trans/Cis Ratio for Dimethylsemidione in Me_2SO Containing Alkali-Metal Iodides at 25 °C

MI (M)	g_{trans}	a_{trans}^H	g_{cis}	a_{cis}^H	[trans]/[cis]
LiI (0.7)	2.004 90	6.17	2.004 76	7.70[a]	0.2
NaI (0.8)	2.004 94	5.96	2.004 81	7.40	0.2
KI (1.31)	2.004 982	5.89	2.004 899	7.21	1.1
KI (0.66)	2.005 008	5.82	2.004 904	7.17	1.6
KI (0.35)	2.005 026	5.77	2.004 914	7.13	3.2
KI (0.33)	2.005 027	5.77	2.004 913	7.13	2.7
KI (0.17)	2.005 040	5.74	2.004 921	7.10	5.3
KI (0.16)	2.005 042	5.73	2.004 925	7.09	5.1
KI (0.088)	2.005 047	5.71	2.004 929	7.08	9.6
KI (0.082)	2.005 047	5.71	2.004 930	7.03	8.4
KI (0.044)	2.005 053	5.70	2.004 937	7.06	17.3
KI (0.022)	2.005 053	5.69	2.004 943	7.04	23.0
KI (0.011)	2.005 051	5.69	2.004 948	7.02	30–35
RbI (0.61)	2.005 013	5.77	2.004 785	7.08	19.0
RbI (0.30)	2.005 027	5.74	2.004 800	7.05	30.0
RbI (0.15)	2.005 037	5.72			
RbI (0.076)	2.005 034	5.71			
RbI (0.038)	2.005 035	5.70			
CsI (1.0)	2.005 089	5.80	*b*	*b*	40–50
CsI (0.59)	2.005 067	5.76			
CsI (0.30)	2.005 057	5.73			
CsI (0.15)	2.005 053	5.72			
CsI (0.074)	2.005 059	5.71			
CsI (0.037)	2.005 077	5.70			
CsI (0.018)	2.005 054	5.69			
KI (0.1)[c]	2.005 046	5.71	2.004 979	7.00	24
KI (0.1)[d]	2.005 061	5.67	2.005 095	6.75	125

[a] $a^{Li} = 0.5$ G. [b] The spectrum of the cis isomer consists of lines too broad for an accurate measurement of g or a^H values. [c] Containing excess 18-crown-6 ether. [d] Containing excess [2.2.2]-cryptand. a^H and g values are for the free ions.

two trans semidione species can be resolved which we assign to the free ion ($g = 2.00506$; $a^H = 5.66$ (6 H) G) and to the ion pair ($g(Cs^+) = 2.00495$; $a^H(Cs^+) = 6.6$ (3 H), 5.5 (3 H) G). With perfluorobiacetyl radical anion, where ion pairing is less important than for biacetyl radical anion, we have previously reported a slow intramolecular migration of Li^+ in THF at 25 °C for the trans semidione and a sharp quartet of quartets for $(CF_3C(OLi){=}C(O\cdot)CF_3)$ at −80 °C.[8]

If, as shown in Scheme I, only two forms of each dimethylsemidione are present (free ion and ion pair), g(obsd) in Figure 2 should be equal to fg(ion pair) + $(1 - f)g$(free ion) where f is the fraction of the semidione which is complexed with the cation. This leads to the expression $1/[g(\text{free ion}) - g(\text{obsd})] = \{1/[g(\text{free ion}) - g(\text{ion pair})](1 + 1/K(\text{ion pair})a^{M^+})\}$. Extrapolation of plots $1/[g(\text{free ion}) - g(\text{obsd})]$ vs. $1/[\text{KI}]$ to $[\text{KI}] = \infty$ leads to the g values of the ion pairs listed in Table II. A similar treatment of the data for a^H yielded values for the ion pairs (the values listed in Table II of 6.23 G (trans) and 7.26 G (cis) were obtained by a least-squares fit of the linear correlation between a^H and g). Values of K_3 and K_4 ([ion pair]/[free ion][a^{K^+}]) could be calculated at [KI] < 0.01 M or over the entire concentration range of [KI] by using the a^{K^+} values previously determined for KI in Me_2SO by using cyclopentane-1,2-semidione.[9] At 25 °C, K_3 was 250 and K_4 4.0 M^{-1} which leads to a value of K_2 of 2 ± 1 (experimental uncertainties in K_1, K_3, and K_4 are ~±10%). An approximate value of $\Delta H°$ for K_2 was measured in Me_2SO saturated with KI as $\Delta H_2° = -1.4$ kcal/mol and $\Delta S_2° = -4.7$ eu.

At a given KI concentration the g(obsd) and a^H(obsd) values for the time-averaged trans semidiones were essentially independent of temperature (i.e., $\Delta H_4° = 0$). Thus, from the value $K_4 = 4$ M^{-1} at 25 °C, $\Delta S_4° = 3$ eu. These values require that $\Delta H_3° = -1.1$ kcal/mol since K_1–K_4 form a cycle. Calculation of $\Delta S_3°$ from $\Delta S_1° + \Delta S_4° - \Delta S_2°$ leads to $\Delta S_3° = 8.9$ eu, whereas the value of $K_3 = 250$ M^{-1} at 25 °C and $\Delta H_3° = -1.1$ kcal/mol leads to $\Delta S_3° = 7.3$ eu. The value of $\Delta S_3°$ is consistent with the requirement that ion pairing of the cis semidione will free solvent molecules from solvated K^+.

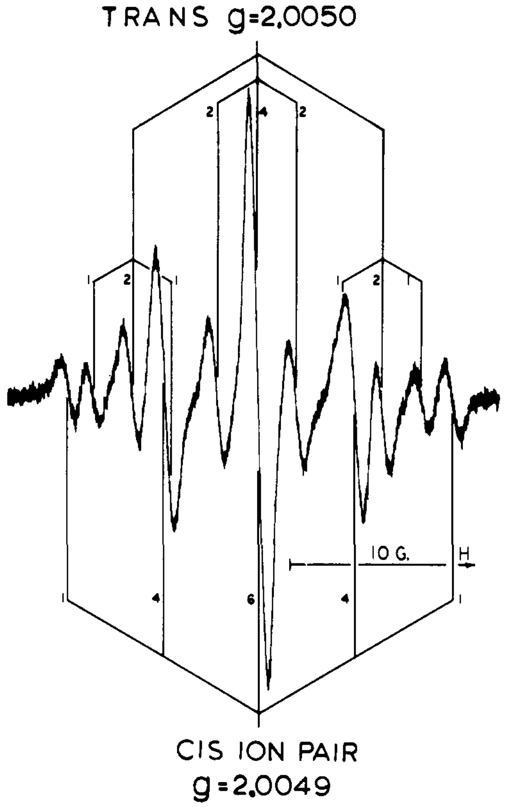

Figure 4. ESR spectrum of cyclopentadecane-1,2-semidiones in the presence of 0.47 M KI (80 °C, Me_2SO).

Cyclic Trans 1,2-Semidiones. The C_4–C_9 cyclic semidiones exist as the cis isomers with ion-pairing constants (K^+, 25 °C, Me_2SO) increasing from 14 (C_4) to 87 (C_5) to 220 (C_6), 190 (C_7), and 260 (C_9) M^{-1}.[9] Although the trans semidione could not be detected for the C_9 carbocycle, 6,6-dimethyl-6-silacyclononane-1,2-semidione exists in cis and trans forms.[10] For the free ions (K^+, [2.2.2]-cryptand), the trans structure was preferred, but in the presence of excess KI the cis structure predominated. A similar situation exists for the C_{11}–C_{15} carbocycles. In the presence of K^+, [2.2.2]-cryptand the trans structure predominates or is the only isomer present, whereas in the presence of K^+ the cis isomer is preferred in some instances. Because of conformational motions in both the cis and trans semidiones and the equilibria between the free ions and ion pairs, the ESR spectra of the C_{11}–C_{15} cyclic semidiones are somewhat complex and in general yield rather intractable spectra below room temperature. The problem of low-temperature spectra is exacerbated by the fact that $\Delta H°$ for disproportionation of the semidione to the dione and dianion of the enediol is negative, and a reversible loss of signal is observed upon cooling. Figures 4 and 5 illustrate the situation for cyclopentadecane-1,2-semidione where conformational equilibria are relatively fast. Figure 4 (80 °C) observed in the presence of 0.5 M K^+ shows two species assigned to the trans (t of t) and cis (1:4:6:4:1, pentet) semidiones at about equal concentrations. Additional K^+ increases the percent of the pentet spectrum while in the presence of excess [2.2.2]-cryptand the tt predominates and only a trace of the pentet can be detected at 40 °C (Figure 5). From our experience with other systems, including 6,6-dimethyl-6-silacyclononane-1,2-semidione,[10] we feel that the tt does not represent two pairs of statically equivalent hydrogen atoms but is instead the result of time averaging of H_1 with H_4 and H_2

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[8] Russell, G. A.; Gerlock, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 5830.

[9] Russell, G. A.; Osuch, C. *J. Org. Chem.* **1980**, *45*, 1242.

[10] Russell, G. A.; Osuch, C. E.; Chau, W. *Heterocycles* **1978**, *11*, 165. Russell, G. A.; Osuch, C. E.; Senatore, G.; Morita, T.; Yamashita, M. *J. Org. Chem.* **1979**, *44*, 2780.

Table II. Values of g and a^{H} (in G) for Free and Ion-Paired Cis and Trans Dimethylsemidiones at 25 °C in Me_2SO

cation	g_{cis}	g_{trans}	$a_{\mathrm{cis}}^{\mathrm{H}}$	$a_{\mathrm{trans}}^{\mathrm{H}}$	$K_{\mathrm{ip}}{}^{a}$
K, [2.2.2]-cryptand	2.005 10	2.005 06	6.76	5.66	
Cs^{b}		2.004 95		6.6 (3 H), 5.5 (3 H)	
K	2.004 90^{c}	2.004 87^{c}	7.26^{c}	6.23^{c}	250 (cis), 4 (trans)
K (18-crown-6)	2.004 88^{c}		6.97^{c}		124 (cis)
Na	2.004 84		7.40		>500 (cis)
Li	2.004 76		7.70		>500 (cis)

[a] [Ion pair]/[free ion] [a^{K^+}]. [b] −90 °C in DMF; spectrum was a mixture of trans free ion (1:6:15:20:15:6:1) and trans ion pair (q × q). [c] Extrapolated value, see text.

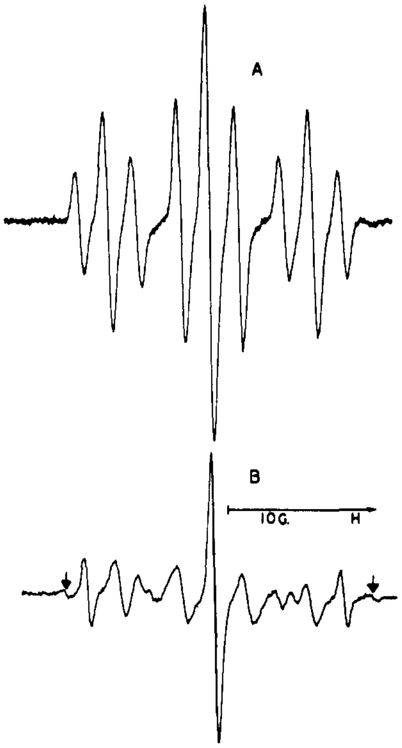
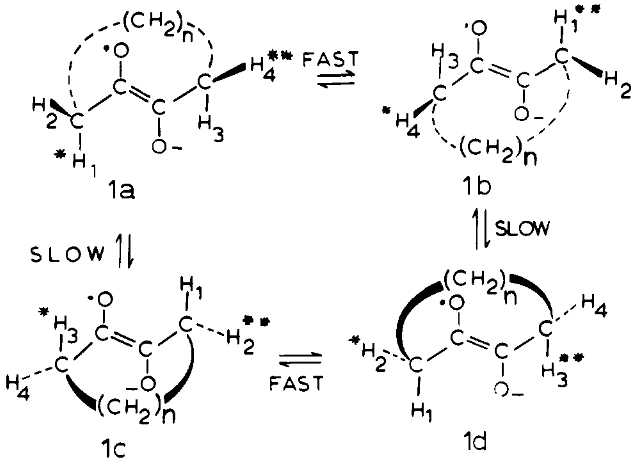


Figure 5. ESR spectrum of *trans*-cyclopentadecane-1,2-semidione in Me_2SO (K^+[2.2.2]-cryptand): A, 40 °C; B, 130 °C (↓ indicates wing peaks of cis isomer).

Scheme II^{a}



[a] H_1–H_4 refer to the magnetic environments of the protons; * and ** are specific protons. In 1a, H_1 and H_3 are in the plane of the semidione double bond. 1a and 1b are superimposable, while 1a(b) and 1c(d) are enantiomers.

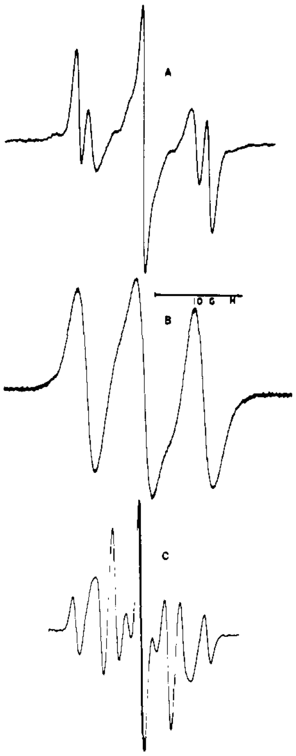


Figure 6. ESR spectra of *trans*-cycloundecane-1,2-semidione (Me_2SO, K^+[2.2.2]-cryptand): A, 100 °C; B, 25 °C; C, 170 °C.

with H_3 in structure **1** by the process converting **1a** to **1b** and **1c** to **1d** (Scheme II). Internal rotation converting **1a** ⇄ **1b** to **1c** ⇄ **1d** should lead to four equivalent α-hydrogen atoms. Spectrum B of Figure 5 at 130 °C shows specific line broadening and peak shifts consistent with the onset of such a process. From the line broadening, the rate constant for the process **1a(b)** ⇄ **1c(d)** is of the order of 10^7 s^{-1} at 130 °C. The absence of time averaging between the cis and trans semidiones, and the sharpness of lines for the cis semidione under conditions where the trans semidione shows selective line broadening, demonstrates that the cis semidione is not an intermediate in the **1a(c)** ⇄ **1b(d)** or **1a(b)** ⇄ **1c(d)** interconversions.

The C_{11}–C_{14} cyclic semidiones yield similar spectra to cyclopentadecanesemidione which become progressively more complicated the smaller the ring. In addition, the overall spectral width for the trans isomers varied slightly with temperature, suggesting that the system may not be explained by only the conformers **1a–d**. Figure 6 shows the *trans*-cycloundecane-1,2-semidione observed with K^+,[2.2.2]-cryptand. At 170 °C the spectrum approaches a tt expected for **1a(c)** ⇄ **1b(d)**, but line broadening is still apparent and k for the interconversion is $\sim 10^{7-8}$ s^{-1}. The rate of **1a(c)** ⇄ **1b(d)** is obviously slower for the C_{11} than for the C_{15} semidione. In the presence of K^+, cycloundecane-1,2-semidione gives a complicated spectrum (Figure 7), but at 160 °C the tt of the trans isomer can be identified. The cis isomer appears to have a spectrum more complex that a 1:4:6:4:1 pentet and may possess four nonequivalent α-hydrogen atoms. The C_8 cyclic semidione exists only as the cis isomer and below 25 °C yields a spectrum consistent with magnetically nonequivalent α-hydrogen atoms, but in the presence of K^+,[2.2.2]-cryptand yields a sharp 1:4:6:4:1 pentet at 100 °C (a^{H} = 3.48 G).[11]

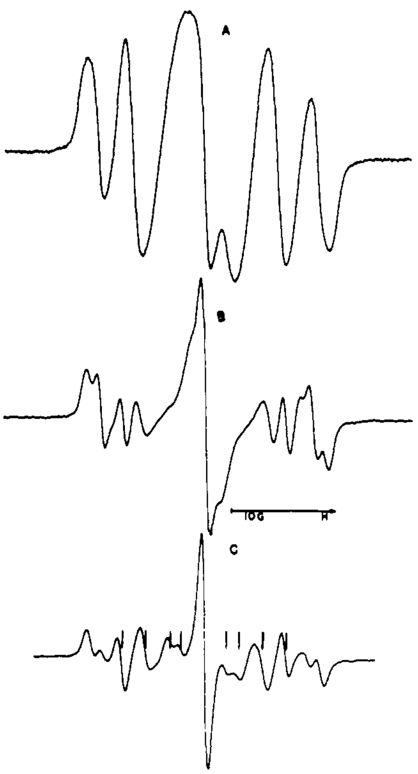


Figure 7. ESR spectra of cycloundecane-1,2-semidiones in the presence of KI: A, 25 °C; B, 100 °C, C, 160 °C (vertical lines identify the tt of the trans isomer seen in Figure 6C).

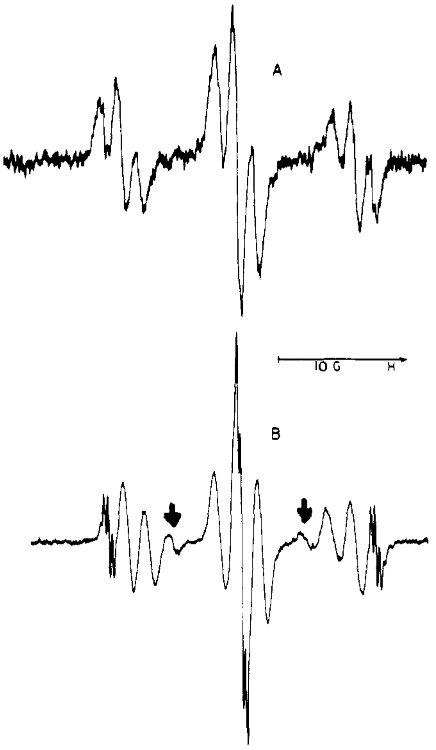


Figure 8. ESR spectrum of 7,7-dimethyl-7-silacycloundecane-1,2-semidione in Me_2SO containing KI: A, 45 °C, B, 90 °C (↓ lines due to cis isomer).

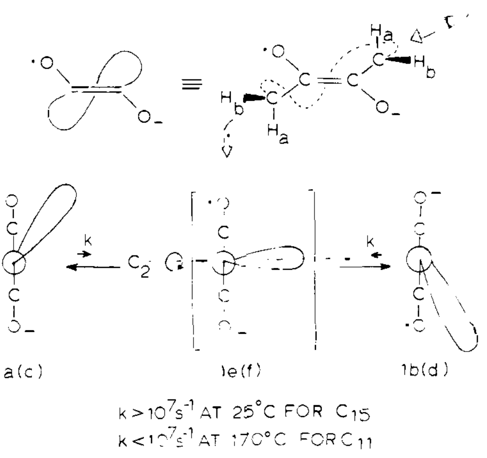


Figure 9. Conformational motion observed for C_{11}–C_{15} trans 1,2-semidiones.

Table III lists the ESR parameters for the cyclo-C_{11} to cyclo-C_{15} semidiones and for 7-Me_2Si and 7-Me_2Ge derivatives of cycloundecane-1,2-semidione and the 8-Me_2Si derivative cyclotridecane-1,2-semidione. For these semidiones the cis isomers were barely detectable even in the presence of excess K^+ and the trans isomers still displayed some selective line broadening at 100 °C of the tt from the **1a(c)** ⇄ **1b(d)** process. Figure 8 illustrates the situation for 7,7-dimethyl-7-silacycloundecane-1,2-semidione where a small pentet splitting by β-hydrogens can be resolved at 90 °C for the wing and center peak of the tt but cannot be resolved for other lines in the spectrum which are still broadened by the rate of interconversion of **1a(c)** ⇄ **1b(d)**.[12]

All of the cyclic trans semidiones examined have the common feature that the preferred conformation (**1a–d**) is asymmetric and does not possess a C_2 axis of symmetry as might have been expected (see structure **1e** in Figure 9). Eclipsing effects between the α-C-H bond and the C–O bond in the semidione, as well as between the α- and α'-CH_2 groups of the polymethylene chain, would favor **1e** (or its enantiomer **1f**) over **1a–d**. Although other nonbonding interactions in the polymethylene chain cannot be ignored (and may in fact contribute to the broadness of the lines in the low temperature spectra), it appears from the partial Newman projections of Figure 9 that in conformation **1a–d** that one of the oxygen atoms can be solvated in an unrestricted fashion. Perhaps this solvation effect overcomes the eclipsing effects and leads to structure **1e(f)** (where neither oxygen atom can be completely solvated) being several kilocalories per mole less stable than the asymmetric conformations **1a–d**.

Experimental Section

ESR Spectra. Spectra were obtianed with a Varian V-4500 spectrometer with Fieldial control and 100-KHz modulation of a 9-in. mag-

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[11] A 1:4:6:4:1 pentet does not require four chemically equivalent (on a time average) hydrogen atoms. If four magnetically nonequivalent hydrogen atoms are time averaged to yield two pairs of equivalent hydrogens (H_1 and H_4, H_2 and H_3), a 1:4:6:4:1 pentet will fortuitously result if $a_1^H + a_4^H = a_2^H + a_3^H$.

[12] The trans semidiones of 11-membered sila- and germacycles (Table III) show a large effect of temperature and counterion upon a_α^H. This suggests the presence of two or more conformations whose proportions change with temperature and with counterion. With Cs^+ in DMF the *trans*-7,7-dimethyl-7-silacycloundecane-1,2-semidione gave a broad triplet at −70 °C (g = 2.00501, a^H = 9.7 G), perhaps with selective line broadening, which sharpened to a t × t at 0 °C (a^H = 8.9, 1.2 G). Warming caused the wing triplets to broaden at 50 °C and then to sharpen by 80 °C (g = 2.005 17, a^H = 6.99 (2 H), 1.62 (2 H) G). Further heating caused the values of a_α^H to decrease: 110 °C, a^H = 6.72 (2 H), 1.46 (2 H) G; 140 °C, a^H = 6.6 (2 H), 1.8 (2 H) G. It appears that a conformation not important at −70 °C is being populated and is time averaged with the low-temperature conformation above 80 °C. In the presence of K^+ in Me_2SO (Table III) the spectra between 25 and 140 °C were better resolved and gave no indication of time averaging between different species although the values of a_α^H did decrease significantly as the temperature was increased. The spectra in the presence of K^+ appear to most closely resemble the spectra observed in the presence of Cs^+ at low temperature. The trans semidione of the 11-membered germacycle in the presence of K^+ in Me_2SO also shows a wide variation in a_α^H with temperature (Table III) but now without any obvious effect of complexing the K^+ with [2.2.2]-cryptand. The trans 1,2-semidione of tridecane did not display any appreciable variation in $\sum a_\alpha^H$ between −100 °C (THF, K^+) and 140 °C (Me_2SO, K^+, with and without [2.2.2]-cryptand). This suggests that perhaps the additional equilibria involving the sila- or germacycle may involve the heteroatom directly, perhaps by an intramolecular interaction with a semidione oxygen atom (i.e., internal solvation). Such an interaction is readily appreciated from the conformational drawing of **1a–d** in Figure 9.

Table III. Values of g and a^H (in G) in Me_2SO for Cyclic 1,2-Semidiones Displaying Cis–Trans Isomers

ring size	temp, °C	a_{cis}^H	g_{cis}	g_{trans}	a_{trans}^H
11	170	~5.6 (4 H)[a]	2.004 89[a]	2.005 06[b]	4.7 (2 H), 3.1 (2 H)[b,c]
12	100[a]	8.3 (2 H)	2.004 91	2.005 0	*c*
	130[b]	*d*	*d*	2.005 11	6.1 (2 H), 1.9 (2 H)[c]
13	100	5.2 (4 H)[a]	2.004 90[a]	2.005 12[b]	6.3 (2 H), 1.7 (2 H)[b,c]
14	100	4.7 (4 H)[a]	2.004 94[a]	2.005 13[b]	6.3 (2 H), 1.7 (2 H)[b]
15	100	5.2 (4 H)[a]	2.004 90[a]	2.005 07[b]	6.7 (2 H), 2.1 (2 H)[b]
6-Me_2Si-9[e]	25	7.3 (2 H), 1.35 (2 H), 0.32 (2 H)[b]	2.004 96[b]	2.005 08[b]	3.5 (2 H), 2.5 (2 H)[b]
7-Me_2Si-11	0[f]	*d*	*d*	*g*	8.9 (2 H), 1.2 (2 H)[f]
	25[a]	*d*	*d*	2.005 01[a]	8.8 (2 H), 1.3 (2 H)[a]
	80[a]	*d*	*d*	*g*	8.8 (2 H), 1.5 (2 H), 0.3 (4 H)[d]
	120[a]	4.8 (4 H)[a]	*h*	*g*	8.3 (2 H), 1.8 (2 H), 0.3 (4 H)[a]
	140[a]	4.6 (4 H)[a]	*h*	*g*	8.1 (2 H), 1.8 (2 H), 0.3 (4 H)[a]
7-Me_2Ge-11	25[a]	*d*	*d*	*g*	7.8 (2 H), 1.6 (2 H)[a]
	60[b]	*d*	*d*	2.005 03	6.6 (2 H), 1.7 (2 H)[b]
	80[i]	4.7 (4 H)[i]	2.004 95[i]	2.005 03[i]	6.3 (2 H), 1.8 (2 H)[i]
	100[b]	*d*	*d*	2.005 04[b]	6.3 (2 H), 1.8 (2 H)[b]
	130[i]	4.6 (4 H)[i]	*g*	*g*	6.0 (2 H), 1.8 (2 H)[i]
8-Me_2Si-13	40[a]	4.9 (4 H)[a]	*g*	*g*	7.0 (2 H), 1.7 (2 H)[a]
	90[f]	*d*	*d*	2.005 06[f]	6.7 (2 H), 1.8 (2 H)[f]
	130[a]	5.1 (4 H)[a]	*h*	*g*	6.6 (2 H), 2.0 (2 H)[a]

[a] In the presence of KI; presumably highly or completely ion paired. [b] In the presence of K^+,[2.2.2]-cryptand; presumably free ion. [c] Spectra show selective line broadening consistent with the time averaging of four different hydrogen atoms to yield two pairs of equivalent α-hydrogen atoms. [d] Not detected. [e] Reference 10. [f] *t*-BuOCs in DMF. [g] Not measured. [h] Lower than trans isomer. [i] In the presence of excess *t*-BuOK.

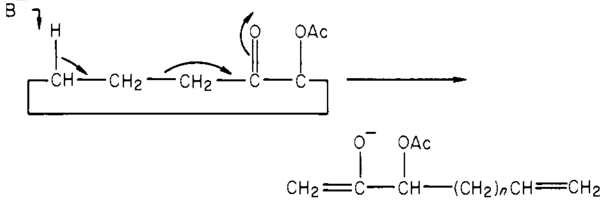
net. The magnetic field experienced by the dual cavity was measured with a modified Alfa Scientific NMR gaussmeter. The NMR frequency was measured to eight significant figures with a Hewlett-Packard counter and with care the magnetic fields could be measured reproducibly to within 1 ppm. The dual cavity was calibrated at the beginning of each experiment with perylene radical cation in H_2SO_4 ($g = (2.002\,569 \pm 6) \times 10^{-6}$).[13] Typically the correction between cavities was 60 mG. Semidione g values were then measured relative to perylene radical cation in the calibrated system. Relative concentration of cis and trans semidiones were measured from relative peak heights for ratios >10:1 and by double integration using LM-301A operational amplifiers for ratios <10:1.

Semidiones were prepared in flat quartz cells using an H cell mixing chamber[14] in which deoxygenated solutions (~0.5 mL) of an acyloin or bis(trimethylsiloxy)alkene or cycloalkanone in Me_2SO were mixed with an alkoxide base or potassium dimsylate in Me_2SO to give a solution ~0.1 M in base and ~0.05 M in the semidione precursor. When the cycloalkanone precursor was employed, oxygen was introduced into the cell either through incomplete deoxygenation or by syringe. Added reagents such as cryptands, crown ethers, or alkali-metal iodides were added with the semidione precursor when the H cell was prepared in a nitrogen glovebag. Dilution experiments were performed by removal of 0.50 mL of the thoroughly mixed semidione solution by syringe and replacement by an equal volume of deoxygenated Me_2SO.

Reagents. Alkali-metal *tert*-butoxides (K^+, Na^+, Li^+) were vacuum sublimed. The alkali-metal iodides were purchased as anhydrous salts (Alfa-Ventron) and with the exception LiI were dried at 125 °C before use. Potassium dimsylate in Me_2SO was prepard from KH and dry Me_2SO, titrated for total base concentration, and stored frozen under argon in ampules. Solvents were dried with CaH_2 (Me_2SO, DMF) or $LiAlH_4$ (THF).

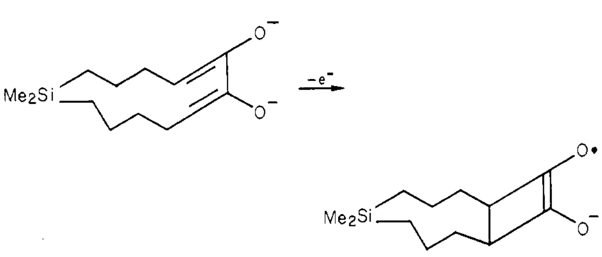
The known bis(trimethylsiloxy)alkenes[15] were used as the precursors to dimethyl, cycloundecyl, and cyclotridecyl semidiones. The cyclodecyl, cyclododecyl, cyclotetradecyl, and cyclopentadecyl semidiones were prepared from oxygenation of the commercial ketones.[16] The semidiones of the 9-, 11-, and 13-membered silacycles and the 11-membered germacycle were prepared from the α-hydroxy ketones.[17,18]

Attempts to use α-acetoxy ketones as semidione precursors for the 9-membered and larger carbocycles gave rise to cis and trans acyclic semidiones of the structure $CH_3C(O\cdot){=}C(O^-)CH_2X$. Apparently the ring is cleaved by nucleophilic attack, e.g., eq 1.



(1)

With the 11-membered silacycle on one occasion the action of Me_3COK on the acyloin led to a spectrum consistent with a cyclobutanesemidione (a^H = 13 (2 H), 0.54 (4 H), 0.24 (2 H) G). Apparently isomerization occurred by reaction 2.[19]



(2)

Acknowledgment. We thank Professor P. Mazerolles for samples of the acyloins of the 9-, 11-, and 13-membered silacycles and the 11-membered germacycle.[17,18]

Registry No. **1** (n = 7) K, 70136-07-1; **1** (n = 8) K, 81572-63-6; **1** (n = 9) K, 70136-08-2; **1** (n = 10) K, 81583-51-9; **1** (n = 11) K, 81572-64-7; dimethylsemidione Li, 34510-77-5; dimethylsemidione Na, 81572-65-8; dimethylsemidione K, 18851-56-4; dimethylsemidione Rb, 81572-66-9; dimethylsemidione CS, 81572-67-0; [2.2.2]-cryptand, 23978-09-8; 7,7-dimethyl-7-silacyloundecane-1,2-semidione K, 81572-68-1; 7,7-dimethyl-7-germanoundecane-1,2-semidione K, 81572-69-2; 8,8-dimethyl-8-silacylotridecane-1,2-semidione K, 81572-70-5.

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(13) Segal, B. G.; Kaplan, M.; Frankel, G. K. *J. Chem. Phys.* **1965**, *43*, 4191. Allendorfer, R. D. *J. Chem. Phys.* **1971**, *55*, 3615.

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

(15) Rühlmann, K. *Synthesis*, **1971**, 236.

(16) Russell, G. A.; Strom, E. T. *J. Am. Chem. Soc.* **1946**, *86*, 5345.

(17) Mazerolles, P.; Faucher, A. *Bull. Soc. Chim. Fr.* **1967**, 2131.

(18) Mazerolles, P.; Faucher, A.; Laporterie, A. *Bull. Soc. Chim. Fr.* **1969**, 887.

(19) Russell, G. A. "Aspects of Mechanism and Organometallic Chemistry"; Brewster, J. H., Ed.; Plenum Press: New York, 1978, p 59.