[2] For a review, see T. Bach, *Liebigs Ann.* **1997**, 1627 – 1634.
[3] a) T. Bach, *Tetrahedron Lett.* **1994**, *35*, 1855 – 1858; b) T. Bach, *Liebigs Ann.* **1995**, 1045 – 1053; c) T. Bach, K. Jödicke, K. Kather, R. Fröhlich, *J. Am. Chem. Soc.* **1997**, *119*, 2437 – 2445.
[4] a) R. E. Schwartz, J. Liesch, O. Hensens, L. Zitano, S. Honeycutt, G. Garrity, R. A. Fromtling, J. Onishi, R. Monaghan, *J. Antibiot.* **1988**, *41*, 1774 – 1779; b) J. H. Johnson, D. W. Phillipson, A. D. Kahle, *J. Antibiot.* **1989**, *42*, 1184 – 1185.
[5] For previous syntheses of preussin, see A. Kanazawa, S. Gillet, P. Delair, A. E. Greene, *J. Org. Chem.* **1998**, *63*, 4660 – 4663, and references therein.
[6] For examples, see a) C. Rivas, R. A. Bolivar, *J. Heterocyclic Chem.* **1976**, *13*, 1037 – 1040; b) D. R. Morton, R. A. Morge, *J. Org. Chem.* **1978**, *43*, 2093 – 2101; c) S. R. Thopate, M. G. Kulkarni, V. G. Puranik, *Angew. Chem.* **1998**, *110*, 1144 – 1147; *Angew. Chem. Int. Ed.* **1998**, *37*, 1110 – 1112.
[7] For examples, see a) J. D. White, D. N. Gupta, *J. Am. Chem. Soc.* **1968**, *90*, 6171 – 6177; b) J. J. Partridge, N. K. Chadha, M. R. Uskokovic, *J. Am. Chem. Soc.* **1973**, *95*, 532 – 540; c) S. W. Baldwin, M. T. Crimmins, *J. Am. Chem. Soc.* **1980**, *102*, 1198 – 1201; d) T. Hansson, B. Wickberg, *J. Org. Chem.* **1992**, *57*, 5370 – 5376; e) A. B. Smith III, G. A. Sulikowski, M. M. Sulikowski, K. Fujimoto, *J. Am. Chem. Soc.* **1992**, *114*, 2567 – 2576.
[8] M. J. S. Carpes, P. C. M. L. Miranda, C. R. D. Correia, *Tetrahedron Lett.* **1997**, *38*, 1869 – 1872.
[9] A. L. J. Beckwith, C. L. L. Chai, *J. Chem.* Soc *Chem. Commun.* **1990**, 1087 – 1088.
[10] a) S. C. Freilich, K. S. Peters, *J. Am. Chem. Soc.* **1981**, *103*, 6255 – 6257; b) S. C. Freilich, K. S. Peters, *J. Am. Chem. Soc.* **1985**, *107*, 3819 – 3822.
[11] For a review, see H. Buschmann, H.-D. Scharf, N. Hoffmann, P. Esser, *Angew. Chem.* **1991**, *103*, 480 – 518; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 477 – 515.
[12] S. Saijo, M. Wada, J. Himizu, A. Ishida, *Chem. Pharm. Bull.* **1980**, *28*, 1449 – 1458.
[13] E. Hardegger, H. Ott, *Helv. Chim. Acta* **1955**, *38*, 312 – 320.
[14] J. Ackermann, M. Matthes, C. Tamm, *Helv. Chim. Acta* **1990**, *73*, 122 – 132.
[15] P. G. Gassman, S. J. Burns, *J. Org. Chem.* **1988**, *53*, 5574 – 5578.
[16] T. Bach, *Angew. Chem.* **1996**, *108*, 976 – 977; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 884 – 886.
[17] The force field calculations (MM3*) were conducted with Macromodel 4.5 (G. Chang, W. C. Guida, W. C. Still, *J. Am. Chem. Soc.* **1989**, *111*, 4379 – 4386). The coupling constants were calculated by an extended Karplus function. The ratio of the various conformers was deduced from a Boltzmann distribution at 373 K. As a simplification a butyl side chain at C5 was assumed instead of a nonyl group. We thank Dipl.-Chem. Thomas Trieselmann (research group of Prof. Hoffmann) and Dr. Ruth Gschwind cordially for their help in the course of the structure elucidation.
[18] D. P. Curran, N. A. Porter, B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, **1995**, pp. 120 – 121.
[19] T. Bach, *Liebigs Ann.* **1995**, 855 – 866.

Ethenedithione (S=C=C=S): Does It Obey Hund's Rule?**

Ngai Ling Ma and Ming Wah Wong*

One of the fundamental rules governing the electronic structure of molecules is Hund's rule of maximum multiplicity. In order to minimize Coulombic repulsion, two electrons in a pair of degenerate orbitals prefer to be unpaired. Thus, for a molecule like O_2, the stability of the three lowest electronic states is in the order $^3\Sigma_g^- > {}^1\Delta_g > {}^1\Sigma_g^+$.

For the linear cumulated carbon oxides and carbon sulfides, XC_nX (X = O and S; n is even), such species have two electrons in the degenerate π HOMO, and hence are expected to have a triplet ground state. However, for the smallest member of the cumulated carbon sulfides, ethenedithione (S=C=C=S), the nature of its ground state remains controversial. C_2S_2 was first predicted by Schaefer et al. to be an experimentally accessible species in the gas phase that should have a triplet ground state.[1] The existence of this transient molecule has been demonstrated by mass spectrometry[2–4] and matrix isolation IR[3, 5] and UV[3, 5, 6] spectroscopy. Based on the unusual thermodynamic stability and extreme intermolecular activity, Wentrup et al. suggested that C_2S_2 is a triplet species.[3] On the other hand, Maier et al. observed a very weak signal in the ESR spectrum of C_2S_2, which indicated that it could possess a singlet ground state. In addition, they performed complete active space (CAS) SCF and CISD calculations and found that the ground state of C_2S_2 is $^1\Delta_g$, with a singlet – triplet (S – T) gap estimated to be 3 and 9 kJ mol^{-1}, respectively. Hence, C_2S_2 was suggested by Maier et al. to be one of the first examples for the "violation of Hund's rule in an equilibrium structure".[5]

Given that the reported S – T gap is rather small using moderate levels of theory, whether C_2S_2 is exists as a singlet or triplet remains uncertain. Herein we report ab initio calculations that are at a significantly higher level of theory than those reported previously in order to establish definitively the nature of the ground electronic state for ethenedithione.

First, we examined the energy difference of the three lowest states of C_2S_2, namely $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$, using various single-determinant methods (Table 1). The $^3\Sigma_g^-$ and $^1\Delta_g$ states were obtained by using an unrestricted Hartree – Fock (UHF) starting point. At the HF/6-31G* level, the $^1\Delta_g$ and $^1\Sigma_g^+$ states lie 31 and 98 kJ mol^{-1}, respectively, above the $^3\Sigma_g^-$ state. Inclusion of electron correlation at the MP2 level significantly lowers the energy gap by 15 and 61 kJ mol^{-1}, respectively. It is important to note that the $\langle S^2 \rangle$ values of the UHF wavefunctions of the $^3\Sigma_g^-$ (2.10) and $^1\Delta_g$ (1.07) states are significantly different from that of the corresponding pure spin states. In particular, the $^1\Delta_g$ state is severely spin contaminated

[*] Prof. Dr. M. W. Wong, Dr. N. L. Ma
Department of Chemistry,
National University of Singapore
Kent Ridge, Singapore 119260 (Singapore)
Fax: (+65) 7791691
E-mail: chmwmw@nus.edu.sg

[**] M.W.W. would like to thank the National University of Singapore for financial support (grant no. 970620).

  1433-7851/98/3724-3402 $ 17.50+.50/0

Table 1. Calculated energies of the three lowest states of C_2S_2 by using various single-determinant methods.

Level[a,b]	E ($^3\Sigma_g^-$)[c]	ΔE($^1\Delta_g$)[d]	ΔE($^1\Sigma_g^+$)[d]
HF/6-31G*[e]	− 870.69070	31.1	98.4
B3-LYP/6-31G*[e]	− 872.52277	15.2	62.3
MP2/6-31G*[e]	− 871.16455	15.9	37.2
MP3/6-31G*	− 871.18191	16.8	40.0
MP4/6-31G*	− 871.21973	10.9	27.9
MP5/6-31G*	− 871.21033	14.0	37.3
PMP4/6-31G*	− 871.22323	20.0	37.1
RCISD/6-31G*[e, f]	− 871.11441	38.4	87.5
CISD/6-31G*[e]	− 871.11956	21.7	60.5
CCSD/6-31G*[e]	− 871.18955	16.3	39.8
QCISD/6-31G*	− 871.19249	16.2	40.1
QCISD(T)/6-31G*	− 871.21790	12.7	33.9
QCISD(TQ)/6-31G*	− 871.21670	12.7	34.3
QCISD(T)/6-311G*	− 871.30014	13.2	35.0
QCISD(T)/6-311 + G(2d)	− 871.35673	13.5	35.8
QCISD(T)/6-311 + G(2df)	− 871.44071	13.1	35.3

[a] Based on QCISD/6-31G*-optimized geometries (r(C=C) = 1.281, 1.283, and 1.287 Å, respectively, for $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$; r(C=S) = 1.580, 1.581, and 1.585 Å, respectively, for $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$), unless otherwise noted. [b] Frozen-core approximation for all correlated calculations. [c] Total energy [Hartree]. [d] Energy [kJ mol^{-1}] relative to the $^3\Sigma_g^-$ state. [e] Fully optimized at the level specified. [f] Based on a restricted Hartree–Fock (RHF) starting point.

by the triplet state. Thus, we would expect the stability of the $^1\Delta_g$ state to be overestimated by the UMP methods. This is readily indicated by the fact that the projected MP4 (PMP4)[7] relative energy is 9 kJ mol^{-1} higher than the UMP4 values (Table 1).

Maier et al. reported RCISD/6-31G* calculations with an active space of 9 occupied and 21 virtual orbitals, and they found that the $^1\Delta_g$ state is 9 kJ mol^{-1} more stable than the $^3\Sigma_g^-$ state. However, since the detail of the calculations was not reported, we have not been able to repeat their calculations. Instead, we have carried out full-valence RCISD calculations but the result is in distinct contrast to that reported previously.[5] The calculated relative stabilities of the $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$ states are 0, 38, and 88 kJ mol^{-1}, respectively. Both QCISD[8] and CCSD[9] methods predict similar relative energies for the $^1\Delta_g$ (16 kJ mol^{-1}) and $^1\Sigma_g^+$ (40 kJ mol^{-1}) states. Inclusion of triple excitations (QCISD(T)) reduces the relative energies by 4–6 kJ mol^{-1}, while further inclusion of quadruple excitations (QCISD(TQ)) has virtually no effect on the relative energies. Table 1 shows that the effect of basis set on the calculated relative energies is rather small. The relative energies computed with the 6-31G* basis set lie within 1 kJ mol^{-1} of the 6-311 + G(2df) values. Thus, based on single-determinant methods, our best estimate of the energy difference between the $^1\Delta_g$ and $^3\Sigma_g^-$ states is 13 kJ mol^{-1}, in favor of the triplet state. In summary, all the single-determinant methods predict the stability of the three lowest states of C_2S_2 is in the order of $^3\Sigma_g^- > {}^1\Delta_g > {}^1\Sigma_g^+$, and there is no evidence for the Hund's rule being violated.

Next, we examined the relative stability of the three states of C_2S_2 using the multiconfiguration (MC) SCF approach, which was expected to provide a proper description of the degeneracy problem involved. We have carried out a series of CASSCF[10] calculations with active space systematically expanded from the two-electron, two-orbital CAS (CASSCF(2,2)) to the twelve-electron, ten-orbital CAS (CASSCF(12,10)). The active orbitals involved are given in Table 2. For all the CASSCF calculations, we found that molecular orbitals lower than and including $7\sigma_g$ are always doubly occupied. The dominant configuration of the three states is identical to that of the HF reference state with coefficient > 0.7. Other dominant configurations with coefficients > 0.1 arise only from the excitation of the π electrons, $2\pi_u$, $2\pi_g$, and $3\pi_u$. Hence, we would expect an active space including all π orbitals, for example CASSCF(10, 8), to yield a reliable result. In fact, further expansion of the active space beyond CASSCF(10, 8) leads to small changes in the relative energies (Table 2). For our largest CASSCF calculation, CASSCF(12,10), the $^1\Delta_g$ and $^1\Sigma_g^+$ states lie 17 and 31 kJ mol^{-1}, respectively, above the $^3\Sigma_g^-$ ground state. As for the CISD calculation, we have not been able to reproduce the CASSCF(6,6) result of Maier et al.,[5] which suggests that the $^1\Delta_g$ state is more stable than the $^3\Sigma_g^-$ state.

Dynamic electron correlation effects were included by carrying out third-order multireference perturbation (CASPT3)[11] or multiconfiguration reference configuration interaction (MRCI)[12] single-point energy calculations at the CASSCF-optimized geometries. As with the single-determinant methods, inclusion of dynamic electron correlation stabilizes the singlet states. However, the $^3\Sigma_g^-$ state is still significantly more stable than the $^1\Delta_g$ state. Our best estimate of the relative energies of the $^1\Delta_g$ and $^1\Sigma_g^+$ states, based on MRCI-CASSCF(10,8) calculations with a significantly larger cc-pVQZ basis set, are 24 and 45 kJ mol^{-1}, respectively.

In conclusion, based on the various sophisticated single-determinant and multiconfiguration methods, we found no evidence that C_2S_2 violates Hund's rule. We hope that our theoretical prediction will stimulate further experimental

Table 2. Calculated energies[a] of the three lowest states of C_2S_2 by using various multiconfiguration methods, with the 6-31G* basis set.

CAS[b]	Active orbital	$^3\Sigma_g^-$[c]			$^1\Delta_g$[d]			$^1\Sigma_g^+$[d]		
		CASSCF	CASPT3	MRCI	CASSCF	CASPT3	MRCI	CASSCF	CASPT3	MRCI
(2,2)	$3\pi_u^2$	− 870.67221	− 871.16825	− 871.10762	49.9	30.7	37.9	99.5	50.4	69.5
(2,4)	$3\pi_u^2\ 3\pi_g^0$	− 870.67990	− 871.17004	− 871.11128	40.9	28.1	34.9	79.9	47.7	64.2
(6,4)	$2\pi_g^4\ 3\pi_u^2$	− 870.68239	− 871.17430	− 871.11295	32.5	28.6	30.1	59.4	53.6	56.4
(10,6)	$2\pi_u^4\ 2\pi_g^4\ 3\pi_u^2$	− 870.68574	− 871.17578	− 871.11421	30.8	25.8	27.5	57.5	45.8	50.6
(6,6)	$2\pi_g^4\ 3\pi_u^2\ 3\pi_g^0$	− 870.71394	− 871.18116	− 871.12876	44.9	30.9	33.3	83.0	52.7	57.8
(10,8)	$2\pi_u^4\ 2\pi_g^4\ 3\pi_u^2\ 3\pi_g^0$	− 870.75973	− 871.19034	− 871.14457	19.3	24.7	23.7	36.1	43.3	41.8
(12,10)	$7\sigma_g^2\ 2\pi_u^4\ 2\pi_g^4\ 3\pi_u^2\ 3\pi_g^0\ 7\sigma_u^0$	− 870.78861	− 871.18989	− 871.15226	16.6	24.9	23.0	31.2	43.0	40.3

[a] Based on the CASSCF optimized geometry. [b] Number electrons and number of orbitals in the active space. Note that full-valence CAS corresponds to CAS(20,16). [c] Total energy [Hartree]. [d] Energy [kJ mol^{-1}] relative to the $^3\Sigma_g^-$ state.

  1433-7851/98/3724-3403 $ 17.50+.50/0

studies on this elusive molecule. To assist future characterization of the ground-state of C_2S_2, the predicted geometry, vibrational spectrum, rotational constants, heat of formation, ionization energy, and proton affinity are summarized in Table 3.

Table 3. Calculated properties for the C_2S_2 ground state ($^3\Sigma_g^-$).

Property	Value
geometry[a]	r(C=C) = 1.277 Å, r(C=S) = 1.579 Å
rotational constant[a]	$B_e = 1.5587$
IR spectrum[b]	2036 (0), 1198 (244), 561 (0), 364 (0), 175 cm^{-1} (0 $km\,mol^{-1}$)
heat of formation	380.1 (ΔH°_{f0}), 383.1 $kJ\,mol^{-1}$ (ΔH°_{f298})
ionization energy[c]	8.3 (adiabatic), 8.4 eV (vertical)
proton affinity[c, d]	731.8 $kJ\,mol^{-1}$
dissociation energy[c]	$C_2S_2 \rightarrow CS(^1\Sigma_g^+) + CS(^1\Sigma_g^+)$: $\Delta E = 138.6$ $kJ\,mol^{-1}$
	$C_2S_2 \rightarrow CS(^1\Sigma_g^+) + CS(^3\Pi)$: $\Delta E = 589.8$ $kJ\,mol^{-1}$

[a] QCISD/6-311 + G(2d)-optimized geometry. [b] QCISD/6-31G* values. Intensity values are given in parentheses. [c] G2//QCI[13] value. [d] The protonated C_2S_2 ion (SCC(H)S^+) has a singlet ground state. Proton affinity of SCCS ($^3\Sigma_g^-$) + $H^+ \rightarrow$ SCC(H)S^+ ($^1A'$) = 812.1 $kJ\,mol^{-1}$.

Received: June 30, 1998 [Z 12074 IE]
German version: *Angew. Chem.* **1998**, *110*, 3587 – 3589

Keywords: ab initio calculations · cumulenes · electronic structure · ethenedithione

[1] G. P. Raine, H. F. Schaefer, R. C. Haddon, *J. Am. Chem. Soc.* **1983**, *105*, 194 – 198.
[2] D. Sülzle, H. Schwarz, *Angew. Chem.* **1988**, *100*, 1384 – 1386; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1337 – 1339.
[3] C. Wentrup, P. Kambouris, R. A. Evans, D. Owen, G. Macfarlane, J. Chuche. J. C. Pommelet, A. Ben Cheikh, M. Plisnier, R. Flammang, *J. Am. Chem. Soc.* **1991**, *113*, 3130 – 3135.
[4] M. W. Wong, C. Wentrup, R. Flammang, *J. Phys. Chem.* **1995**, *99*, 16849 – 16856.
[5] G. Maier, H. P. Reisenauer, J. Schrot, R. Janoschek, *Angew. Chem.* **1990**, *102*, 1475 – 1477; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1464 – 1466.
[6] R. B. Bohn, Y. Hannachi, L. Andrews, *J. Am. Chem. Soc.* **1992**, *114*, 6452 – 6459.
[7] H. B. Schlegel, *J. Chem. Phys.* **1986**, *84*, 4530 – 4534.
[8] J. A. Pople, M. Head-Gordon, K. Raghavachari, *J. Chem. Phys.* **1987**, *87*, 5968 – 5975.
[9] A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, H. F. Schaefer, *J. Chem. Phys.* **1987**, *87*, 5361 – 5373.
[10] B. O. Roos, *Adv. Chem. Phys.* **1987**, *69*, 399 – 446.
[11] H.-J. Werner, *Mol. Phys.* **1996**, *89*, 645 – 661.
[12] H.-J. Werner, P. J. Knowles, *J. Chem. Phys.* **1988**, *89*, 5803 – 5817.
[13] L. A. Curtiss, K. Raghavachari, J. A. Pople, *J. Chem. Phys.* **1995**, *103*, 4192 – 4200.

Closure of the Cavity in Permethylated Cyclodextrins through Glucose Inversion, Flipping, and Kinking**

Thomas Steiner* and Wolfram Saenger*

Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday

Cyclodextrins (CDs) or cycloamyloses (CA) are macrocyclic oligosaccharides produced by enzymatic degradation of amylose; they can contain up to 100 or more $\alpha(1-4)$-linked glucose units.[1, 2] The well known smallest members with six to eight glucose residues called α-, β-, and γ-cyclodextrin are annular in shape (doughnut-form) reminiscent of a hollow, truncated cone. Their narrower side are formed by primary O6 hydroxyl groups and the wider side by secondary O2 and O3 hydroxyl groups. All the glucose residues are found exclusively in the $^4C_1$ chair form and are oriented *syn* about the glycosidic link so that all O2 and O3 hydroxyl groups are on the same side and connected by intramolecular $O2(n)\cdots O3(n-1)$ hydrogen bonds that stabilize the macrocyclic structures. The *anti* form with the O2 and O3 hydroxyl groups of adjacent glucose units on opposite sides has not yet been observed in any of the crystal structures of the common CDs.

Surprisingly, the solubility of the cyclodextrins in water increases manyfold if only O2 and O6 or all three of the hydroxyl groups of the glucose residues are methylated. Furthermore, the temperature coefficient of the solubility becomes negative, that is their solubility in water is lower at elevated temperatures and crystals can be grown by heating the solutions.[3] To shed light on these peculiar properties several partially and fully methylated CDs (that have practical importance as bioorganic host molecules) were crystallized from hot and cold water and analyzed by X-ray crystallography.[4–8]

Of particular structural interest are the fully methylated α-, β-, and γ-cyclodextrins hexakis-(2,3,6-tri-*O*-methyl)-α-, β-, and γ-CD (TRIMEA, TRIMEB, and TRIMEG, respectively) because intramolecular $O2(n)\cdots O3(n-1)$ hydrogen bonds cannot form. Crystals that have been grown from hot water include anhydrous TRIMEA,[6] TRIMEB monohydrate,[4] and TRIMEG dihydrate.[9] In all three cases the CD molecules adopt conformations characterized by greatly reduced cavity volumes. The remaining shallow cavities are only filled by O6 methyl groups of adjacent molecules and not by water, which occupies interstices in the crystal lattices of the hydrate forms. It is remarkable that the cavities are closed by three completely different structural mechanisms, which are discussed below. Because the molecular structure of

[*] Prof. Dr. W. Saenger, Dr. T. Steiner
Institut für Kristallographie der Freien Universität
Takustrasse 6, D-14195 Berlin (Germany)
Fax: (+49) 30-838-6702
E-mail: saenger@chemie.fu-berlin.de

[**] Topography of Cyclodextrin Inclusion Complexes, Part 43. This work was supported by the Deutsche Forschungsgemeinschaft (Sa 196/25-1) and Fonds der Chemischen Industrie. For Part 42, see T. Aree, J. Jacob, W. Saenger, H. Hoier, *Carbohyd. Res.* **1998**, *307*, 191 – 197.

  1433-7851/98/3724-3404 $ 17.50+.50/0