

A Density Functional Study of Sulfoxy Anions Containing Sulfur–Sulfur Bonds

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Abstract: Density functional calculations using the LCAO- $X\alpha$ method have been performed on the series $S_2O_4^{2-}$, $S_2O_5^{2-}$, and $S_2O_6^{2-}$. In the absence of external charge stabilization, the dithionite ion is predicted to be unbound with respect to electron loss by both limited-basis Hartree–Fock and LCAO- $X\alpha$ methods. Hartree–Fock calculations predict that the gas-phase dithionite ion has a 2.13-Å sulfur–sulfur internuclear distance, while the shortest experimentally observed S–S bond is 2.26 Å in length for $S_2O_4^{2-}$. In contrast LCAO- $X\alpha$ calculations indicate that the gas-phase dithionite ion is unstable toward dissociation. A method for charge stabilization using point charge envelopes is described which produces sulfur–sulfur bond lengths and force constants in good agreement with those determined experimentally.

Introduction

The structure of the dithionite ion has been a subject of interest and controversy since the first crystal structure of $Na_2S_2O_4$ was published by Dunitz¹ in 1956. The ion was reported to be in an eclipsed C_{2v} conformation, although only the C_2 axis coincided with a crystallographic symmetry element and the sulfur–sulfur bond length was much longer than expected at 2.39 Å. A more recent and accurate determination of this structure² shows that the ion is only approximately eclipsed, with a torsional angle of 16° about the sulfur–sulfur bond; the sulfur–sulfur bond length is confirmed to be 2.393 ± 0.002 Å.

Structures of several other dithionite salts confirm this unexpected conformation of the ion. In 1978 the dithionite ion in ZnS_2O_4 -pyridine was again found to have a 2.39-Å sulfur–sulfur bond length and approximate C_{2v} symmetry.³ In this case, the mirror plane was a crystallographic symmetry element and the C_2 axis was noncrystallographic. A slightly distorted C_{2v} conformation was again observed for the dithionite ion in $Sn_2(S_2O_4)_2$ in 1982.⁴ The structure was composed of ring-shaped dimers. Each Sn^{2+} ion is coordinated to four oxygen atoms, with one oxygen atom bonded to each of the four sulfur atoms in two dithionite ions. The sulfur–sulfur bond length is somewhat shorter at 2.35 Å.

Initially, in view of the long sulfur–sulfur bond length, the dithionite ion was described as two SO_2^- radicals weakly linked, and attempts were made to explain the apparent preference of the dithionite ion for the eclipsed conformation. However, in 1982 convincing spectroscopic evidence was obtained indicating that the dithionite ion was centrosymmetric in solution, adopting the staggered conformation,^{5,6} and it was suggested that some shortening of the sulfur–sulfur bond length might accompany this change in conformation. We have also published recent spectroscopic evidence for the staggered conformation in *solid* $((C_2H_5)_3N)_2S_2O_4$.⁷

In 1992 we reported a structural investigation of the dithionite ion in other than the approximately eclipsed conformation.² In $Na_2S_2O_4 \cdot 2H_2O$ the dithionite ion has a torsional angle of 56° about the sulfur–sulfur bond, very near to the 60° of an idealized gauche conformation. The sulfur–sulfur bond length is 2.298 ± 0.004 Å, 0.1 Å shorter than that in anhydrous $Na_2S_2O_4$. The crystal structure of $Na_2S_2O_4$ strongly indicated that the dithionite ion adopts conformations in response to external perturbations and that it is readily distorted in different environments. In view of this, several years ago we set out to perform molecular orbital calculations in order to ascertain the nature of the electronic structure of the dithionite ion and compare it to that of other sulfoxy anions containing sulfur–sulfur bonds. Such a study demands a relatively rigorous computational model, and we elected to perform ab-initio Hartree–Fock calculations, using the GAMESS⁸ program at the STO-3G and 431-G levels. In these studies we found the gauche conformation at a shallow minimum on the potential energy surface, with the ion exhibiting a rotational barrier of only 13 kJ mol⁻¹ at a length of 2.16 Å (the equilibrium bond length for the gauche conformer). However, we elected to refrain from publishing these results because the calculations universally resulted in a number of positive eigenvalues for occupied orbitals. In 1989 limited-basis Hartree–Fock geometry optimization calculations on the dithionite ion using the Gaussian 86 program were published.⁹ In these studies the staggered conformation was determined to be the most stable. The equilibrium sulfur–sulfur bond lengths were 2.13 Å for the staggered conformation and 2.21 Å for the eclipsed. Although higher energy D_{2h} (planar) and D_{2d} (perpendicular) conformations were calculated, the gauche conformation was apparently not a stationary point on the potential energy surface and no bond length for this conformation was calculated. There is no indication by the authors that positive eigenvalues were encountered, but their results (as ours) clearly do not agree well with experiment.

Density functional methods such as the LCAO- $X\alpha$ method used in the studies reported here generally give results comparable in quality to those of Hartree–Fock calculations with a slower increase in computational time as the number of basis functions increases. Since calculations on anions routinely require larger basis sets to model diffuse electron density, density functional models present distinct practical advantages over ab-initio methods. In this report we present the results of a density functional study of the dithionite ($S_2O_4^{2-}$), metabisulfite ($S_2O_5^{2-}$),

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(1) Dunitz, J. D. *Acta Crystallogr.* **1956**, *9*, 579–586.

(2) Weinrach, J. B.; Meyer, D. R.; Guy, J. T., Jr.; Michaelis, P. E.; Carter, K. L.; Grubisha, D. S.; Bennett, D. W. *J. Crystallogr. Spectrosc. Res.* **1992**, *22*, 291–301.

(3) Kiers, C. T.; Vos, A. *Acta Crystallogr.* **1978**, *B34*, 1499–1504.

(4) Magnusson, A.; Johansson, L. *Acta Chem. Scand.* **1982**, *A36*, 429–433.

(5) Peter, L.; Meyer, B. *J. Mol. Struct.* **1982**, *95*, 131–139.

(6) Takahashi, H.; Kaneko, N.; Miwa, K. *Spectrochim. Acta* **1982**, *38A*, 1147–1153.

(7) Hodgeman, W. C.; Weinrach, J. B.; Bennett, D. W. *Inorg. Chem.* **1991**, *30*, 1611–1614.

(8) Guest, M. F. Daresbury Laboratory, Warrington WA4 4AD, U.K.

(9) Leszczynski, J.; Zerner, M. C. *Chem. Phys. Lett.* **1989**, *159*, 143–147.

and dithionate ($\text{S}_2\text{O}_6^{2-}$) ions using the LCAO- $X\alpha$ method with moderately large Gaussian basis sets.

Computational Details

The computer program used in this study was developed by Dunlap,¹⁰ from a model originally formulated by Sambe and Felton.¹¹ Convergence criteria were chosen to ensure six-digit precision in the orbital energies and eight-digit precision in total energy.¹¹ The values of the parameter α were taken from Schwartz.¹² For total energy, α was weighted by the number of electrons on the neutral oxygen and sulfur atoms in the ions. For ionization energies, α was weighted by the number of valence electrons on the neutral atoms in the ion. Ionization energies were calculated using the transition-state method.¹³ A relatively large basis set was used, (5211/41) for oxygen and (62111/6111) for sulfur, plus d functions on both oxygen and sulfur.¹⁴ The same functions, with appropriate exponents were used for the orbital and exchange basis sets. Bond-directed functions along the S-O bonds and bond-centered functions at the S-S midpoint were also employed.

As discussed in the results section which follows, initial LCAO- $X\alpha$ calculations on the gas-phase $\text{S}_2\text{O}_4^{2-}$ ion indicated that the ion was unbound with respect to electron loss and unstable with respect to dissociation into two SO_2^- radical anions. In addition, the equilibrium sulfur-sulfur bond length for the gas-phase dithionite ion was calculated at 2.50 Å, a value substantially longer than any observed experimentally. While these results are in agreement with experiments performed on the ion in nonstabilizing environments (see below), we sought to study the ion as it might exist in a stabilizing environment in solution or in the solid state.

A similar problem was encountered by Watson¹⁵ in 1958, in studies of the oxide ion. O^{2-} is not bound in the absence of positive charge, and Watson wished to obtain wave functions for the ion which would be suitable for calculations on solids. He was able to accomplish this by surrounding the ion with a sphere of uniform positive charge. The sphere, given a net +1 charge, surrounded the ion at its ionic radius, allowing each of the two "extra" electrons to see an effectively neutral entity. A shouldered potential well was created with well-behaved wave functions within the charged sphere.

We desired to take the same approach with the LCAO- $X\alpha$ program, which calculates charge density on points on a grid surrounding each atom. This precluded the use of a uniform charge distribution about each atom. Fortunately, the software allows for the inclusion of point charges of any magnitude and at any location. We therefore began by surrounding the ions with point charge distributions designed to approximate a charged sphere.¹⁶ Configurations of up to 50 points were investigated, and a 32-point icosahedral arrangement (point group I_h) was chosen to combine a relatively high number of points with high symmetry.

The dithionite ion is not spherical, but the excess charge resides on the oxygen atoms; surrounding the entire ion with a sphere which would approach the oxygen atoms more closely than the sulfur atoms did not seem unreasonable. However, a +2 total charge on the surface of a sphere of radius 5 Å resulted in short sulfur-sulfur bond lengths similar to those obtained by the Hartree-Fock method. Surrounding the ion with a rigid pseudosphere of point charges distorts the ion because the interactions between the atoms and the point charges change as the sulfur-sulfur bond length is varied. It followed that, in order to obtain results comparable to those obtained in Watson's oxide ion studies, a charge envelope adapted to the geometry of the ion was necessary.

We returned to Watson's original use of a +1 charge at the ionic radius. Each atom in an ion was surrounded by a 32-point pseudosphere at its ionic radius, 1.4 Å for oxygen and 1.7 Å for sulfur. Any pseudosphere points lying within another sphere were then deleted, eliminating all points lying within 1.4 Å of an oxygen atom or within 1.7 Å of a sulfur atom. This removed all point charges from the bonding regions for each sulfoxy anion and left a charge envelope around the ion. At equilibrium sulfur-sulfur bond lengths, the envelopes consisted of 111-122 points for $\text{S}_2\text{O}_4^{2-}$, depending on the conformation of the ion, 132 points for $\text{S}_2\text{O}_5^{2-}$, and 146

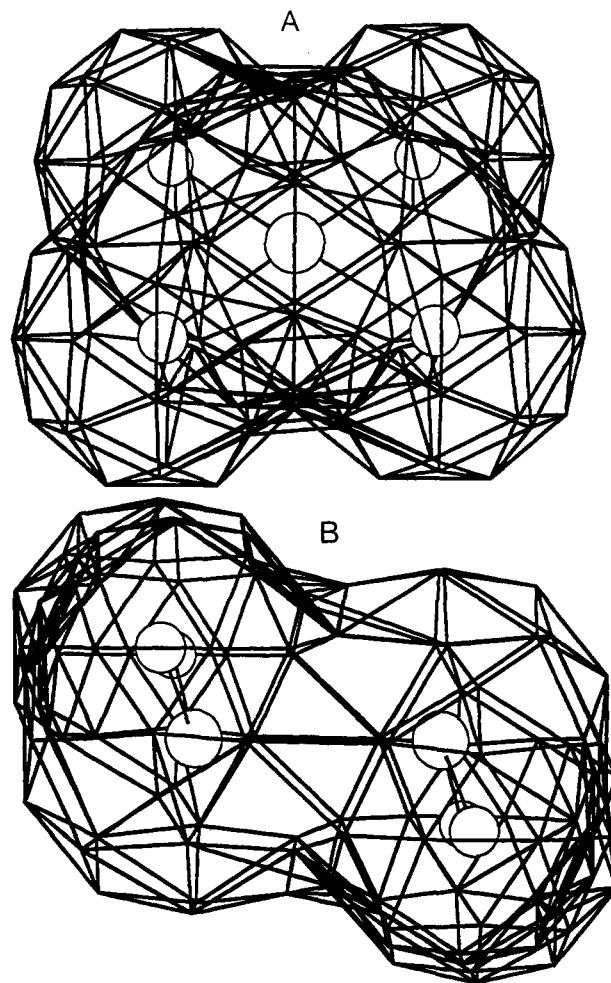


Figure 1. Staggered dithionite ion in the point charge envelope. Adjacent point charges are connected to illustrate the shape of the envelope. (A) View down the sulfur-sulfur bond. (B) View down the C_2 axis.

points for $\text{S}_2\text{O}_6^{2-}$. With a total +1 charge divided among these points, the maximum charge on any one point was less than +0.01. The form of the charge envelope for the dithionite ion in the staggered conformation is shown in Figure 1. Adjacent point charges are connected in the figure to illustrate the shape of the charge envelope; the point charges lie at the vertices of the polygon.

Since the pseudosphere around each atom moves with the atom, the interactions of the nearest point charges with each atom remain constant. In fact, each SO_2^- or SO_3^- unit remains rigid, and the interaction of each atom with all points on the half of the charge envelope in which it resides will remain constant. The only exception to this occurs when a substantial increase in sulfur-sulfur bond length causes extra points on the sulfur atoms to appear as their spheres overlap less. It is important to note this did not happen in the vicinity of the equilibrium bond lengths calculated. Interactions between an atom and envelope point charges surrounding the other half of the molecule gradually change as the sulfur-sulfur distance varies, but this effect is comparatively small. The repulsions among the point charges of the envelope itself change similarly, but the total repulsive energy of the charge envelope is readily computed and subtracted out to leave only the energy of the ion. Subtraction of the electrostatic energy of the charge envelope changes the equilibrium sulfur-sulfur bond lengths by a maximum of 0.02 Å (generally less), but it is in principle correct to subtract this energy, since it is an artifact of the method.

While the charge envelopes do not represent physical reality, it was hoped that they might lend a generalized "solvent-like" stabilization to the ions and facilitate calculations on systems which are physically more realistic than isolated gas-phase ions. Indeed, this proved to be the case, as the computational results will show. Although the method was developed for unbound, doubly negative ions, calculations were also performed on SO_2^- and SO_3^- in charge envelopes with a total +1/2 charge for comparison purposes.

(10) Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71* (8), 3396-3402.

(11) Sambe, H.; Felton, R. H. *J. Chem. Phys.* **1975**, *63* (3), 1122-1126.

(12) Schwartz, K. *Phys. Rev. B* **1972**, *5* (7), 2466-2468.

(13) Beebe, N. H. F. *Chem. Phys. Lett.* **1973**, *19* (2), 290-294.

(14) Huzinaga, S.; Yoshimine, M. *J. Chem. Phys.* **1978**, *68* (10), 4486-4489.

(15) Watson, R. E. *Phys. Rev.* **1958**, *111*, 1108-1110.

(16) Weinrach, J. B.; Carter, K. L.; McDowell, H. K.; Bennett, D. W. *J. Chem. Educ.* **1990**, *69*, 995-999.

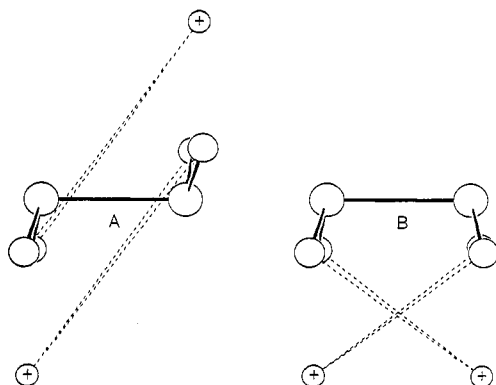


Figure 2. Staggered (A) and eclipsed (B) conformations of the dithionite ion with +1 point charges.

In addition to the charge envelope method, some calculations were also performed without charge stabilization and others with two +1 point charges. In the latter case the +1 charges were placed on the intersection of the mirror plane between two oxygen atoms and a plane passing through the oxygen atoms perpendicular to the sulfur-sulfur bond, as shown in Figure 2. This "mid-point" location was chosen to minimize distortion of the S-S bond length through electrostatic attraction between the negative oxygen atoms and the positive ions. The distance between the oxygen centers and the positive ion was chosen to be that observed for the Na-O distance in the crystal structure of $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$.² Initial calculations were performed using C_2 symmetry for both the staggered and eclipsed forms of $\text{S}_2\text{O}_4^{2-}$ as well as $\text{S}_2\text{O}_5^{2-}$ and $\text{S}_2\text{O}_6^{2-}$. During the course of these calculations we determined the crystal structure of $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (s) and discovered that the dithionite ion had the gauche conformation.² With an experimental value for the sulfur-sulfur bond length of the $\text{S}_2\text{O}_4^{2-}$ ion in this less constrained conformation available, we extended our studies to the gauche form of the dithionite ion in the charge envelope. Since the gauche conformation of the dithionite ion does not have a mirror plane along the sulfur-sulfur bond as all of the other ions in this series do, the calculations were performed using C_1 symmetry. To enable comparisons to be made, calculations were then performed in the region of the equilibrium sulfur-sulfur bond length for all of the ions in the charge envelope using C_1 symmetry. It was found that removing the symmetry constraint resulted in a very slight decrease in the sulfur-sulfur bond length, generally 0.01 Å for each ion. The change in symmetry resulted in a systematic lowering of the total energy of each ion by about 40 kJ mol⁻¹. Although the difference in the results using these two symmetries is minimal and the potential energy curves would remain essentially the same, the energy differences between the three conformations of the dithionite ion are sufficiently small that they must be compared in the same symmetry for meaningful results. A few calculations were performed for each ion using a +2 envelope charge at configurations close to their equilibrium geometries. In all cases the sulfur-sulfur bond lengths decreased negligibly, and the relative ordering of the occupied and virtual orbitals remained unchanged.

Graphical representations of electron density maps and difference electron densities were made using PSI/77,¹⁷ modified extensively to accommodate LCAO- $X\alpha$ wave functions consisting of linear combinations of Hermite Gaussians.

Results and Discussion

As mentioned above, initial calculations of the gas-phase dithionite anion using the LCAO- $X\alpha$ method produced sulfur-sulfur bond lengths much longer than those observed experimentally. While these deviations were actually larger than those determined in the limited-basis Hartree-Fock calculations,⁹ the very long sulfur-sulfur bond length in the LCAO- $X\alpha$ method may reflect recent evidence¹⁸ that the dithionite ion is predominantly dissociated in solvents with low dielectric constants.

In addition to the possibility that the dithionite ion is not stable to dissociation without charge stabilization, the ion would probably be unbound with respect to electron loss as an isolated gas-phase ion. Positive eigenvalues are obtained in limited-basis Hartree-

Table I. Dependence of Equilibrium Sulfur-Sulfur Bond Lengths on Charge Stabilization

ion	sulfur-sulfur bond lengths, Å ^a			
	no charge	+1 point charges	charge envelope	experiment
eclipsed $\text{S}_2\text{O}_4^{2-}$	>2.75	2.31	2.43	2.39
staggered $\text{S}_2\text{O}_4^{2-}$	2.50	2.34	2.35	
$\text{S}_2\text{O}_5^{2-}$	2.42	2.32	2.35	2.21
$\text{S}_2\text{O}_6^{2-}$	2.20	2.15	2.16	2.14

^a C_2 symmetry in all cases. An experimental value for staggered $\text{S}_2\text{O}_4^{2-}$ is not available; the bond length is not expected to be longer than 2.30 Å.

Fock calculations, and although this does not guarantee that the free ion is unstable with respect to electron loss, the generally more reliable LCAO- $X\alpha$ transition-state method predicts that the ion is unbound. Since the ion is observed experimentally, it is clearly stabilized in aqueous solution and in the solid state, thus requiring the computational method to reflect such stabilization as described in the previous section. The point charge stabilization method was also applied to the metabisulfite and dithionate ions to test its validity. The dithionate ion ($\text{S}_2\text{O}_6^{2-}$) is an excellent candidate, since it has been the subject of numerous crystal structure investigations. A high-resolution structure of $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ was published in 1980.¹⁹ The ion is staggered with a sulfur-sulfur bond length of 2.14 Å, and examination of a number of published structures indicates that the sulfur-sulfur bond length does not vary by more than 0.02 Å from this value. The metabisulfite ion has only been observed in the staggered conformation, with sulfur-sulfur bond lengths of 2.17 Å in $(\text{NH}_4)_2\text{S}_2\text{O}_5$ ²⁰ and 2.21 Å in $\text{K}_2\text{S}_2\text{O}_5$.²¹ Preliminary studies in our laboratories indicate that the bond length also is about 2.21 Å in $\text{Na}_2\text{S}_2\text{O}_5$, but this structure has not been fully solved.

The results of initial calculations designed to ascertain the necessity of charge stabilization are shown in Table I. It is clear that some form of charge stabilization is desirable when applying the LCAO- $X\alpha$ method to these doubly negative gas-phase ions. The isolated ions, particularly the dithionite ion, are predicted to have much longer sulfur-sulfur bond lengths than are actually observed. For the eclipsed dithionite ion, distances up through 2.75 Å were calculated without finding a minimum; greater distances would not indicate a bond. The results deviate from experiment in the opposite direction to the Hartree-Fock results and are even greater in magnitude, although C_1 symmetry would be expected to shorten the distances slightly as it does in the charge envelopes. The bond lengthening is much greater for the dithionite ion than it is for the dithionate ion.

At first glance the results with pseudo Na^+ ions, +1 charges at the sodium-oxygen distances observed in $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, appear to be qualitatively the same as those with the ions in the charge envelopes. However, the weakness in this approach is apparent in an analysis of the results for the two conformations of $\text{S}_2\text{O}_4^{2-}$. The eclipsed form is calculated to have a shorter sulfur-sulfur bond length than the staggered form; it is also considerably shorter than the experimental value. The use of two +1 point charges for charge stabilization does not provide a series which is valid for comparison of conformations because of the difference in the ion-point charge interactions. Figure 2 shows that in the eclipsed conformation the point charge aligned with the opposite end of the ion is likely to present a significant attractive force to an oxygen atom. This shortens the sulfur-sulfur bond of the eclipsed form relative to the staggered conformation.

Table II compares the equilibrium sulfur-sulfur bond lengths obtained in the LCAO- $X\alpha$ calculations with previous limited-basis Hartree-Fock results and experimental results from X-ray

(17) Jorgensen, W. A. *QCPE* 1977, 11, 340.

(18) Lough, S. M.; McDonald, J. W. *Inorg. Chem.* 1987, 26, 2024-2027.

(19) (a) Kirfel, A.; Will, G. *Acta Crystallogr.* 1980, B36, 223-228. (b) Kirfel, A.; Will, G. *Acta Crystallogr.* 1980, B36, 512-523.

(20) Baggio, S. *Acta Crystallogr.* 1971, B27, 517-522.

(21) Lindqvist, I.; Mortzell, M. *Acta Crystallogr.* 1957, 10, 406-409.

Table II. Comparison of Charge-Stabilized LCAO-X α Results with Experiment and Limited-Basis Hartree-Fock Results

ion	sulfur-sulfur bond lengths, Å ^a		
	Hartree-Fock	LCAO-X α	experiment
eclipsed S ₂ O ₄ ²⁻	2.21	2.41	2.39
gauche S ₂ O ₄ ²⁻	2.16	2.33	2.30
staggered S ₂ O ₄ ²⁻	2.13	2.34	
S ₂ O ₅ ²⁻		2.33	2.21
S ₂ O ₆ ²⁻		2.15	2.14

^a C₁ symmetry in all cases.

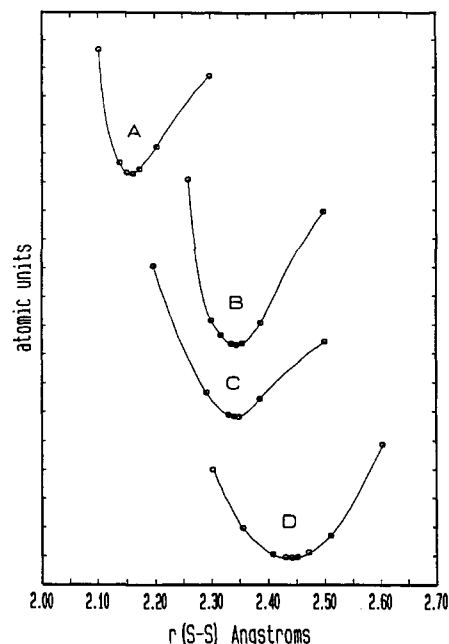
crystallography. All of the LCAO-X α results in this table are the minima obtained using C₁ symmetry to assure a valid comparison; the Hartree-Fock calculations were not symmetry constrained, and the gauche form of the dithionite ion was only calculated in the C₁ point group. In each case the ion was stabilized by an envelope of +1 total charge as previously described.

It is obvious from the results in Tables I and II that the charge-stabilized LCAO-X α results are in much better agreement with experiment for the dithionite ion than those from limited-basis Hartree-Fock or LCAO-X α calculations without such stabilization. For the gauche and eclipsed conformations, the LCAO-X α sulfur-sulfur bond lengths are only 0.03 Å longer than experiment. The bond shortening from eclipsed to gauche conformations is 0.09 Å, both experimentally and computationally. Unfortunately, the experimental sulfur-sulfur bond length for the staggered configuration is not yet available. Since the geometries of the thionite and thionate units remain essentially constant, an estimate of 2.20–2.26 Å has been published⁵ by assuming a constant increase in the sulfur-sulfur bond length in the series S₂O₆²⁻, S₂O₅²⁻, S₂O₄²⁻. Values of up to 2.28 Å may be obtained in this way. However, these extrapolations cannot be considered experimental values. A sulfur-sulfur bond length of 2.266 Å has been observed for staggered dithionite as a bridging ligand between two metal centers in a neutral complex,²² but the ion is no longer a discrete unit in this case.

Figure 3 illustrates the total energies of each of the ions as a function of sulfur-sulfur bond length. It is immediately obvious that S₂O₄²⁻ has a very flat potential well when compared to S₂O₆²⁻, with S₂O₅²⁻ intermediate but resembling S₂O₄²⁻ more closely. The steep potential curve for the dithionate ion illustrates why it was relatively insensitive to the presence or absence of charge, while the dithionite ion requires charge stabilization to produce a reasonable sulfur-sulfur bond length, particularly for the eclipsed conformation.

Since the force constant of the sulfur-sulfur bond depends only upon the shape of its potential energy curve at the bottom of the potential well, a polynomial was fit to this area of each curve. Five points were used in each case, the minimum and the two nearest points that had been computed on each side of the minimum. The data was least-squares fitted to both quadratic (harmonic oscillator) and cubic polynomials. The force constant is the second derivative of the curve at the minimum: For $y = a + bx + cx^2$, $y'' = 2c$. For $y = a + bx + cx^2 + dx^3$, $y'' = 2c + 6dx$, where x is the equilibrium sulfur-sulfur bond length.

The results of the force constant calculations and a comparison with values determined from the Raman and infrared spectra of the ions are given in Table III. The quadratic and cubic fits gave the same values for force constants for the staggered and eclipsed conformations of the dithionite ion; the quadratic equation provided the best fit to the potential well for the gauche conformation. For the metabisulfite ion, the results are similar but not identical, and the cubic equation provides the better fit. The harmonic oscillator model breaks down completely for the dithionate ion. The energies used were for sulfur-sulfur bond lengths of 2.14, 2.15, 2.16, 2.17, and 2.20 Å. When the point at

**Figure 3.** Total energy of dithionate (A), metabisulfite (B), staggered dithionite (C), and eclipsed dithionite (D) ions with charge stabilization as a function of sulfur-sulfur bond lengths. Sulfur-sulfur bond lengths are in Å; vertical scale is marked in increments of 0.001 atomic units. The position of each curve on the energy axis is arbitrary.**Table III.** Force Constants of Sulfur-Sulfur Bonds from Charge-Stabilized LCAO-X α Calculations

ion	force constants, mdyn/Å		
	quadratic	cubic	experiment
eclipsed S ₂ O ₄ ²⁻	0.80	0.80	
gauche S ₂ O ₄ ²⁻	0.90	0.90	
staggered S ₂ O ₄ ²⁻	1.56	1.56	1.34 ^a
S ₂ O ₅ ²⁻	1.71	1.86	1.65 ^b
S ₂ O ₆ ²⁻	3.27	5.43	2.02 ^b

^a Calculated from the solid-state spectra of (Et₄N)₂S₂O₄, ref 7.
^b Calculated from aqueous Raman and infrared spectra, ref 6. A force constant of 1.08 mdyn/Å was calculated for aqueous S₂O₄²⁻ using a 2.39-Å bond length for the staggered conformation.

2.20 Å was omitted, the quadratic force constant more than doubled. The cubic equation was a better fit, as might be expected from the curve in Figure 2d, and the cubic force constant is probably the best value from this curve. Since the dithionate curve was difficult to fit, the force constant was also computed from the results for S₂O₆²⁻ with two +1 charges. The result is very similar to the cubic fit of the curve in the charge envelope, 5.36 mdyn/Å. Although this result is more than twice as large as the force constant calculated from experiment, it is in better agreement than the value obtained by fitting the curve for the dithionite ion without charge stabilization—only 0.36 mdyn/Å.

The agreement between experimental and calculated force constants for charge-stabilized dithionite and metabisulfite ions is surprisingly good. In general, the qualitative ordering of the magnitudes of the force constants derived from the LCAO-X α calculations using the charge envelope is correct, and the results are quantitatively reasonable. The metabisulfite ion is intermediate in both the magnitude of its force constant and the degree of shortening of the sulfur-sulfur bond length with charge stabilization. However, the force constant is nearer to that of the dithionite ion, while the bond shortening is more similar to that in the dithionate ion. The bonds decrease in the charge envelope by 0.04 Å for S₂O₆²⁻, 0.07 Å for S₂O₅²⁻, and 0.15 Å for staggered S₂O₄²⁻. Force constants for the dithionate and dithionite ions appear to vary reciprocally with the degree to which charge stabilization affects the bond length. This is not totally unex-

Table IV. Total Energy of Ions in Charge Envelopes

ion	energy, au
eclipsed S ₂ O ₄ ²⁻	-1095.678 008 36
gauche S ₂ O ₄ ²⁻	-1095.686 637 23
staggered S ₂ O ₄ ²⁻	-1095.687 652 51
S ₂ O ₅ ²⁻	-1170.764 389 38
S ₂ O ₆ ²⁻	-1245.813 718 94
SO ₂ ⁻	-547.822 828 224
SO ₃ ⁻	-622.861 879 341

ion	total energy less energy of components, kJ mol ⁻¹
eclipsed S ₂ O ₄ ²⁻	84.94
gauche S ₂ O ₄ ²⁻	107.62
staggered S ₂ O ₄ ²⁻	209.20
S ₂ O ₆ ²⁻	236.19

pected, since the steepness of the potential well determines the force constant and the susceptibility of the bond length to external influences. While at this stage the analysis is essentially empirical, the product of the force constant and the bond shortening would be expected to be constant. This product, in millidynes, is 0.22 for S₂O₆²⁻, 0.23 for S₂O₄²⁻, and only 0.13 for S₂O₅²⁻. Thus a shortening of the sulfur–sulfur bond of the metabisulfite ion by 0.12 Å with charge stabilization would be more consistent with the results for the other ions.

The only obvious difference between the metabisulfite ion and the other ions is the asymmetry between the two ends of the ion, resulting in a dipole along the sulfur–sulfur bond. The charge envelope would decrease this dipole by placing more point charges around the thionate group than the thionite group. Since it seemed possible that decreasing the dipole could result in a longer bond length, a few calculations were performed with the magnitudes of the point charges adjusted so that half of the positive charge was on each end of the ion. This did not result in a shortening of the sulfur–sulfur bond, and no reasons for the less satisfactory sulfur–sulfur bond length of the metabisulfite ion have been determined.

It becomes difficult to obtain convergence in the calculations when the sulfur–sulfur internuclear distances increase significantly past their equilibrium bond lengths; thus dissociation energies could not generally be obtained directly. Some indication of the stability of the ions to dissociation may be obtained by comparison of the total energy of the ions with the sum of the energies of their SO₂⁻ and/or SO₃⁻ components. The results, using C₁ symmetry and a total electron-weighted α , are given in Table IV. The trend is correct; S₂O₄²⁻ is the most dissociated in solution, while S₂O₆²⁻ dissociates least. However, these results overestimate the stability of the ions toward dissociation. Approximate equilibrium constants for the dissociations have been calculated from the data in Table IV. Since the major contribution to the entropy of dissociation in all cases considered here is the formation of two ions from a single ion, the entropy of dissociation was estimated²³ to be 48 J mol⁻¹ K⁻¹. For the staggered dithionite ion in aqueous solution at 25 °C, the calculation gives an equilibrium constant of 1.6 × 10⁻¹⁴ mM, as opposed to experimental values^{24,25} of 1.4 × 10⁻⁶ to 5.1 × 10⁻⁷ mM for the reaction S₂O₄²⁻ → 2SO₂⁻ in water. This exaggeration of the stability of the dithionite ion to dissociation arises because SO₂⁻ is not as well stabilized by the charge envelope as S₂O₄²⁻. Since the negative charges of the ions reside primarily on the oxygen atoms, placing the positive charges around the oxygen atoms has a greater stabilizing effect than placing them around the sulfur atoms. To correct this discrepancy, the four envelope points around the sulfur atom of SO₂⁻, which

Table V. Ionization Potentials Calculated in Charge Envelopes

ion	ionization potentials, eV
eclipsed S ₂ O ₄ ²⁻	1.45
gauche S ₂ O ₄ ²⁻	1.55
staggered S ₂ O ₄ ²⁻	1.58
S ₂ O ₅ ²⁻	2.83
S ₂ O ₆ ²⁻	4.42
SO ₂ ⁻	3.79 (0.39) ^a
SO ₃ ⁻	5.80 (2.57) ^a

^a Values in parentheses are ionization potentials without charge stabilization. The other ions are not bound in the absence of charge stabilization.

disappear when the sulfur–sulfur bond of S₂O₄²⁻ forms, were excluded from the SO₂⁻ envelope and the total charge was distributed equally among the remaining points. The energy calculated for SO₂⁻ with this change was -547.832 101 54 au, which gives a dissociation constant of 5.2 × 10⁻⁶ mM. Since the sulfur atoms are essentially neutral and would not greatly polarize a solvent, it is possible that better results for this series of ions would be obtained by placing the charge envelopes around only the oxygen atoms. However, this would render the method less general for application to a wide range of negative ions. Furthermore, the SO₂⁻ calculations did not converge as readily in the incomplete charge envelope, and other convergence problems could be encountered. In any case, it is only in comparisons of very different ions that serious quantitative problems arise, and even this is not a major problem if an investigator is aware of possible problems and the reasons for them. The ordering of the stabilities with respect to dissociation is qualitatively correct. When comparisons of the energies of ions as dissimilar as S₂O₄²⁻ and SO₂⁻ are not involved, good quantitative results are obtained for geometry optimization of sulfur–sulfur bond lengths, force constants of the sulfur–sulfur bonds, etc.

Comparison of the total energies of the three conformations of the dithionite ion in Table IV also gives an indication of the rotational barrier, although the values in the table also include changes in sulfur–sulfur bond length. The staggered conformation is lowest in energy, but it lies only 2.68 kJ mol⁻¹ below the gauche conformation. The eclipsed form is 25.31 kJ mol⁻¹ above the staggered form at their respective equilibrium bond lengths. This indicates that the barrier to rotation is very small, and the energy required to go from the staggered configuration to the eclipsed configuration with a longer sulfur–sulfur bond will be readily provided by the lattice energy as a solid is formed. The very low rotational barrier is reasonable in view of the apparent ease with which the ion can adopt any of the three observed conformations.

SO₂⁻ and SO₃⁻ are predicted to be bound ions, with ionization potentials of 0.39 and 2.57 eV, respectively, in the absence of charge stabilization. S₂O₄²⁻, S₂O₅²⁻, and S₂O₆²⁻ are all predicted to be unbound in the absence of charge stabilization, but all of the ions are bound in the charge envelopes. This allows calculation of relative ionization potentials as shown in Table V. Unlike the metabisulfite and dithionate ions, the dithionite ion is widely used as a reducing agent. Many suggested mechanisms for dithionite reduction involve the dissociation of S₂O₄²⁻ to SO₂⁻ and subsequent reduction by the sulfur dioxide anion. The dithionite ion has the lowest ionization potential in Table V, indicating that the dithionite ion itself has the potential to act as the reducing agent and that the dissociation step may not be necessary.

Figure 4 shows the electron density of the highest occupied molecular orbitals (HOMOs) of staggered and eclipsed dithionite in the charge envelope. While there is electron density in the sulfur–sulfur bonding region, there is also a considerable sulfur “lone pair” component. The electron density on the oxygen atoms resides essentially in lone pair orbitals, and there is no appreciable sulfur–oxygen bond. Overall, the orbitals may be described as

(23) Laidler, K. J.; Meiser, J. H. *Physical Chemistry*; Benjamin/Cummings, Inc.: Menlo Park, CA, 1982; p 387.

(24) Lambeth, D. O.; Palmer, G. J. *Biol. Chem.* 1973, 248, 6095–6103.

(25) Burlamacchi, L.; Casini, G.; Fagioli, O.; Tiezzi, E. *Scienze Chimiche* 1967, 7 (2), 97–101.

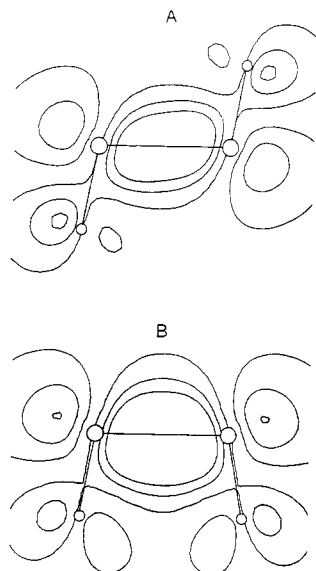


Figure 4. Electron density contours of the highest occupied molecular orbital of the dithionite ion in the O–S–S–O plane for the staggered conformation (A) and the eclipsed conformation (B).

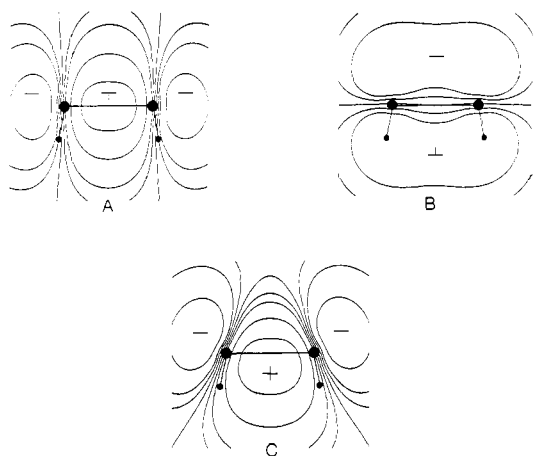


Figure 5. Sulfur contributions to the HOMO on the mirror plane of the eclipsed dithionite ion: σ functions (A), π functions (B), and the total sulfur contribution (C).

effectively nonbonding. The HOMOs of the staggered and eclipsed forms are similar.

When Dunitz¹ discovered in 1956 that dithionite was eclipsed in $\text{Na}_2\text{S}_2\text{O}_4(\text{s})$, it was not yet known that the ion adopted other conformations. He suggested that dp_x orbitals formed from the HOMOs of SO_2^- would be bonding in the eclipsed dithionite ion and antibonding in the staggered form, leading to increased stability for the eclipsed conformation. The signs of the orbitals were chosen so that the dp hybrids were directed away from the S–O bonds. No calculations were done, and the necessity of this choice for the signs of the wave functions was not clear. However, Figures 5 and 6 show that Dunitz was correct in asserting that the dp_x orbitals are bonding in the eclipsed form and antibonding in the staggered form of the dithionite ion. The figures show the sulfur σ (A), π (B), and total (C) contributions to the HOMOs. The reason for the signs of the π orbitals becomes clear; they serve to polarize the total wave functions, and thus the charge density, into the regions between the two oxygen atoms bonded to the same sulfur atom. It should be noted that this does not require the eclipsed conformation to be more stable; the eclipsed form of the dithionite ion is still calculated to have a longer sulfur–sulfur bond and higher total energy than the staggered conformation.

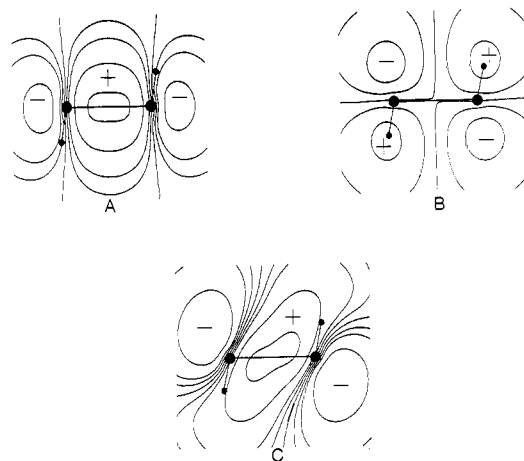


Figure 6. Sulfur contributions to the HOMO on the mirror plane of the staggered dithionite ion: σ functions (A), π functions (B), and the total sulfur contribution (C).

Difference electron density plots were also prepared to examine the way in which the charge distribution changes when $\text{S}_2\text{O}_4^{2-}$ is formed from two SO_2^- ions. The calculated electron density of two SO_2^- units was subtracted from the electron density of $\text{S}_2\text{O}_4^{2-}$. When this was first attempted, the electron density appeared to move out of the sulfur–sulfur bonding region when the dithionite ion was formed. While this was surprising, it did seem plausible in view of the dissociation of $\text{S}_2\text{O}_4^{2-}$. To check this, a similar calculation was performed on the dithionate ion, which is very stable to dissociation. The loss of electron density in the sulfur–sulfur bonding region as $\text{S}_2\text{O}_6^{2-}$ was formed from two SO_3^- units indicated that these results were not reliable. Further consideration made it clear that the problem again arose from the difference in the effect of the charge envelope on ions such as $\text{S}_2\text{O}_4^{2-}$ and $\text{S}_2\text{O}_6^{2-}$ and its effect on SO_2^- and SO_3^- . It was mentioned earlier that comparisons of these very different ions overestimated the stability of the dithionite ion to dissociation when total energies were compared. A similar effect causes the difference electron density to underestimate the stability of $\text{S}_2\text{O}_4^{2-}$. The four charge envelope points on each SO_2^- unit which disappear when $\text{S}_2\text{O}_4^{2-}$ is formed polarize charge onto the sulfur atoms. In fact, these charges polarize more charge into what will become the sulfur–sulfur bonding region than actual bond formation does. Again, a comparison of very different ions becomes unreliable.

Although the charge envelope calculations did not produce satisfactory difference electron densities, the calculations performed with pseudo sodium ions, +1 point charges, were suitable for this purpose. The result for the staggered dithionite ion is shown in Figure 7. Increased electron density is found along the sulfur–sulfur bond direction, including in the bonding region, and on the oxygen atoms in “lone pair” orbitals. Electron density is drawn away from the sulfur atoms and their orbitals in the O–S–S–O planes, particularly in the S–O bonding regions. A sulfur–sulfur bond is formed; experimentally the sulfur–oxygen bond length increases from 1.43 Å in SO_2^- to 1.50 Å in $\text{S}_2\text{O}_4^{2-}$.

Conclusions

Results of LCAO- $X\alpha$ calculations show that the dithionite ion exhibits a very flat potential energy well along the sulfur–sulfur bond coordinate. This allows the bond length to respond readily to crystal packing forces and other external perturbations. The rotational barrier is also very low; this may account for the facile dehydration of $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ to $\text{Na}_2\text{S}_2\text{O}_4(\text{s})$ and the accompanying change from a gauche to approximately eclipsed conformation of the dithionite ion with a 0.1-Å increase in the sulfur–sulfur bond length. While the staggered conformation of the dithionite ion was calculated to be the lowest energy

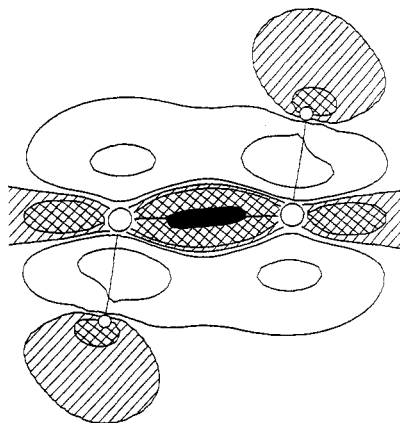


Figure 7. Difference electron density contours for the dithionite ion. Electron density increases in the shaded regions and decreases in the white areas as $S_2O_4^{2-}$ is formed from two SO_2^- units.

conformation, in agreement with spectroscopic evidence for this form in solution, both the differences in total energy and sulfur-sulfur bond length between the gauche and staggered forms were not significant. It appears that the repulsions between sulfur atom lone pairs in the eclipsed form are essentially relieved by assuming the gauche configuration. This leads to the expectation that the sulfur-sulfur bond length in the staggered dithionite ion will be somewhat longer than the previous prediction⁵ of 2.20–2.26 Å. From the calculations, together with the crystal structure of $Na_2S_2O_4 \cdot 2H_2O$, a range of 2.27–2.30 Å now seems more likely.

Geometry optimization produced excellent results for the sulfur-sulfur bond lengths of the dithionate and dithionite ions, the latter of which were handled well by the Hartree-Fock method, at least in the case where the basis sets were relatively limited. That the calculated sulfur-sulfur bond lengths for both the eclipsed and gauche conformations of the dithionite ion are only 0.03 Å longer than experiment is particularly impressive. The sulfur-sulfur bond length for the metabisulfite ion was less satisfactory, but the error was less than 6%. Force constants for the sulfur-sulfur bonds of all of the ions were in good agreement with experiment. Charge stabilization has also allowed comparative ionization potentials to be obtained for species which would otherwise be unbound. The ordering of the stability of the ions to dissociation is in agreement with experimentally measured dissociation constants. Thus the LCAO- $X\alpha$ method using charge envelope stabilization is a promising technique for electronic structure studies of anions which are not amenable to other computational methods.

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