The OCS Trimer: Isotopic Studies, Structure, and Dipole Moment

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The rotational spectra of $(^{18}OCS)_3$ and $(O^{13}CS)_3$ have been assigned using a pulsed-nozzle Fourier transform microwave spectrometer. The data for these isotopic species have been combined with normal species data from a paper by Connelly et al. [Connelly, J. P., et al. *Mol Phys.* **1996**, *88*, 915] to determine the nine structural parameters of the trimer. The carbon atoms form a triangle with the axes of the monomer units roughly parallel to each other (barrel-like structure). The monomers have an antiparallel-like arrangement, with the dipole moment of one monomer opposing those of the other two monomers. The dipole moment of the complex has been measured, giving values of $\mu_a = 0.537(10)$ D, $\mu_c = 0.373(2)$ D, and $\mu_{total} = 0.653(8)$ D. The *b* component of the dipole moment was too small to determine from our data but is predicted to be about 0.02 D. The structure of $(OCS)_3$ has been compared with similar trimers involving linear triatomic molecules and with the OCS dimer. Semiempirical calculations have been performed on the $(OCS)_3$ system, and they show good qualitative agreement with the experimental structure.

Introduction

The spectra of many weakly bound dimers have been studied by microwave spectroscopy. In recent years, a number of trimers have been added to the list of complexes whose structures have been determined by this technique. The structure of trimers is of interest to compare with known related dimers. The growing body of information on trimers allows patterns to be identified and testing of theoretical models which describe intermolecular forces. Although most theoretical models have been applied primarily to dimer systems, they must also predict the behavior when a third body is added to the system if they are to be successfully extended to even larger aggregates and to liquids.

In this work, the structure of OCS trimer has been determined. This complex was previously studied by Connelly et al.[1] Their data from a single isotopomer did not permit a unique structure determination, and two possible isomers consistent with the observed rotational constants were identified. Semiempirical modeling of the intermolecular forces for the two structures pointed to a preference for an antiparallel barrel-like structure over a parallel model. We report in this paper the assignment of two additional isotopomers of the trimer, measurement of the dipole moment, and additional semiempirical calculations which confirm this prediction. The observed barrel-like structure is similar to other mixed trimers of linear triatomic molecules recently studied in this laboratory and elsewhere. These include $(CO_2)_2OCS$,[2,3] $(OCS)_2CO_2$,[4] $(CO_2)_2N_2O$,[5] and $(CO_2)_2HCN$.[6] As with these and other previously studied homogeneous trimers, such as $(CO_2)_3$[7] and $(N_2O)_3$,[8] the relationship of known dimers to the structure of the larger complex is easily recognized and will be discussed.

Experimental Section

The spectra of two isotopomers of $(OCS)_3$ were observed in the 5.5−12.0 GHz range on the Balle−Flygare-type Fourier transform microwave spectrometers[9] at the University of Michigan.[10,11] The $(^{18}OCS)_3$ isotopomer was generated by expanding a mixture of 1% ^{18}OCS and 99% first run He/Ne (10% He/90% Ne) into the evacuated spectrometer chamber through a General Valve Series 9 nozzle, while the $(O^{13}CS)_3$ isotopomer was generated by expanding a similar 2% $O^{13}CS$ mixture into the spectrometer cavity through a modified Bosch fuel injector valve. The ^{18}OCS (93.4% ^{18}O) and $O^{13}CS$ (99% ^{13}C, 12% ^{18}O) were obtained from Isotec. A He/Ne backing pressure of 2−3 bar was used. The nozzles were aligned perpendicular to the direction of microwave propagation, which essentially eliminates the usual Doppler doublets observed in the parallel configuration. The perpendicular arrangement has higher sensitivity in the Michigan spectrometer for inexplicable reasons, unlike the experience in other labs. Line widths were approximately 30 kHz full width at half-maximum, and center frequencies were reproducible to about 4 kHz. A typical transition of the $(^{18}OCS)_3$ isotopomer had a signal-to-noise ratio of about 7 in 300 gas pulses, while transitions of the $(O^{13}CS)_3$ isotopomer generally required about 500 gas pulses to obtain the same quality of signal. Several transitions of both species were considerably weaker, requiring about 1000 gas pulses to obtain a good signal-to-noise ratio. The difference in intensity between the two isotopes can be attributed to the lower isotopic enrichment in the $O^{13}CS$ sample. Although transitions of the normal species show a small splitting (usually a few tens of kilohertz) due to interconversion between the two enantiomers of the chiral complex,[1] no splitting was observed for the two isotopes assigned in this work.

Stark effect measurements were carried out by applying voltages of up to ±9 kV to a pair of parallel 50 cm × 50 cm steel mesh plates separated by about 30 cm and located just outside the Fabry−Perot cavity. The electric field was calibrated by measuring the Stark effect of the $J = 1 \leftarrow 0$ transition of OCS at 12162.980 MHz and assuming an OCS dipole moment of 0.7152 D.[12]

Results

A. Spectra. For $(^{18}OCS)_3$, 21 *a*-type and 10 *c*-type transitions were observed, while for $(O^{13}CS)_3$ 22 *a*-type and 9 *c*-type transitions were observed. The frequencies of these transitions

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TABLE 1: Frequencies of Measured Rotational Transitions for $(^{18}OCS)_3$

J_{upper}	K_a	K_c	J_{lower}	K_a	K_c	frequency (MHz)	$\Delta\nu$ (MHz)[a]
5	1	5	4	1	4	5731.850	0.001
5	0	5	4	0	4	5733.384	0.000
5	2	4	4	2	3	6117.078	0.002
5	1	4	4	1	3	6160.769	−0.001
5	3	3	4	3	2	6399.617	0.001
5	4	2	4	4	1	6498.074	−0.002
5	4	1	4	4	0	6584.159	0.002
5	2	3	4	2	2	6605.207	0.001
5	4	1	4	3	1	7587.620	−0.002
5	4	2	4	3	2	7692.189	−0.002
5	5	0	4	4	0	7962.711	0.001
5	5	1	4	4	1	7971.907	0.001
6	1	6	5	1	5	6838.528	−0.001
6	0	6	5	0	5	6838.810	−0.001
6	2	5	5	2	4	7237.156	−0.001
6	1	5	5	1	4	7249.494	−0.001
6	3	4	5	3	3	7588.809	0.000
6	2	4	5	2	3	7717.317	−0.001
6	3	3	5	3	2	8073.109	−0.002
6	5	1	5	4	1	9228.634	0.002
6	5	2	5	4	2	9287.679	−0.001
6	6	0	5	5	0	9592.597	−0.001
6	6	1	5	5	1	9595.606	0.001
7	1	7	6	1	6	7944.720	0.001
7	0	7	6	0	6	7944.767	0.000
7	2	6	6	2	5	8346.827	0.000
7	1	6	6	1	5	8349.677	0.001
7	3	5	6	3	4	8734.287	−0.001
7	3	4	6	3	3	9270.808	0.001
7	7	0	6	6	0	11220.187	−0.001
7	7	1	6	6	1	11221.096	0.000

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

TABLE 2: Frequencies of Measured Rotational Transitions for $(O^{13}CS)_3$

J_{upper}	K_a	K_c	J_{lower}	K_a	K_c	frequency (MHz)	$\Delta\nu$ (MHz)[a]
5	1	5	4	1	4	5863.310	0.004
5	0	5	4	0	4	5864.888	0.004
5	2	4	4	2	3	6267.016	−0.001
5	1	4	4	1	3	6312.245	−0.002
5	3	3	4	3	2	6563.758	0.000
5	4	2	4	4	1	6667.702	−0.001
5	4	1	4	4	0	6758.810	0.001
5	2	3	4	2	2	6778.400	0.003
5	3	2	4	3	1	6924.375	0.000
5	3	2	4	2	2	7560.878	0.002
5	4	1	4	3	1	7805.238	0.002
5	4	2	4	3	2	7915.015	0.000
5	5	0	4	4	0	8196.863	0.001
5	5	1	4	4	1	8206.595	−0.002
6	1	6	5	1	5	6994.381	−0.001
6	0	6	5	0	5	6994.668	−0.003
6	1	5	5	1	4	7424.677	−0.002
6	2	5	5	2	4	7411.978	−0.001
6	3	4	5	3	3	7780.888	−0.002
6	2	4	5	2	3	7914.295	0.002
6	3	3	5	3	2	8288.963	−0.002
6	6	0	5	5	0	9875.275	0.001
6	6	1	5	5	1	9878.467	−0.004
7	2	6	6	2	5	8546.132	0.002
7	1	6	6	1	5	8549.048	0.001
7	3	5	6	3	4	8952.239	−0.003
7	2	5	6	2	4	9005.194	0.000
7	3	4	6	3	3	9513.868	0.001
7	7	0	6	6	0	11551.262	−0.003
7	7	1	6	6	1	11552.239	0.002
8	1	7	7	1	6	9677.717	0.001

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

are given in Tables 1 and 2. The transitions of each isotopomer were fit to a Watson A-reduced Hamiltonian in the I^r representation. The resulting spectroscopic constants for both isotopes and the normal species are given in Table 3. For the $(O^{13}CS)_3$ isotopomer, δ_K was not well determined, so it was fixed at the value of δ_K of the $(^{18}OCS)_3$ isotopomer. This improved the quality of the fit slightly and had little effect on the other distortion constants. Two lines believed to be the $5_{05}-6_{06}$ and $5_{15}-6_{16}$ transitions of $(^{18}O^{13}CS)_3$ were observed in the $O^{13}CS$ sample (which is estimated to be about 12% $^{18}O^{13}CS$), but the rest of the spectrum of this isotope remains unassigned due to the very low intensity of the lines.

TABLE 3: Spectroscopic Constants for the Assigned Isotopes of $(OCS)_3$

	$(^{16}O^{12}CS)_3$ [a]	$(^{18}O^{12}CS)_3$	$(^{16}O^{13}CS)_3$
A/MHz	847.97958(2)	813.3787(2)	837.5555(3)
B/MHz	736.17579(2)	708.4134(2)	728.1778(3)
C/MHz	574.32591(1)	553.1467(2)	565.3423(2)
Δ_J/kHz	0.45440(9)	0.4134(22)	0.4566(27)
Δ_{JK}/kHz	0.1571(5)	0.1822(91)	0.129(16)
Δ_K/kHz	0.3013(5)	0.2309(79)	0.301(15)
δ_J/kHz	0.06797(4)	0.0583(12)	0.0680(17)
δ_K/kHz	0.0339(3)	0.0545(59)	0.0545[d]
N[b]	137	31	31
$\Delta\nu_{rms}$[c]	0.51	1.16	2.19

[a] From ref 1. [b] N = number of lines in fit. [c] $\Delta\nu_{rms}$ in kHz where $\Delta\nu = \nu_{obs} - \nu_{calc}$. [d] Fixed at value from $(^{18}OCS)_3$.

TABLE 4: Stark Coefficients for OCS Trimer Transitions

frequency/MHz	$J'_{Ka'Kc'}-J''_{Ka''Kc''}$	$\lvert M\rvert$	$\Delta\nu/\epsilon^2$ [a]	obsd − calcd[a]
6355.5492	$5_{24}-4_{23}$	1	2.301	0.025
		2	8.666	−0.446
6369.5275	$4_{32}-3_{22}$	3	−5.360	−0.189
6648.6140	$5_{33}-4_{32}$	1	0.652	0.045
		2	2.463	0.091
		3	5.187	−0.125
7852.9891	$5_{33}-4_{23}$	3	−9.001	−0.149
		4	−15.836	−0.106
7885.3043	$6_{34}-5_{33}$	2	1.212	0.082
		3	2.692	0.149

[a] Units of 10^{-5} MHz cm^2 V^{-2}.

B. Dipole Moment. To guide the assignment of the isotopic species, the dipole moment of the normal isotopic species was measured since this should provide insight on the preferred isomer. Stark effect measurements on 10 components of 5 transitions were least-squares fit to calculate the dipole moment of the complex. We chose to measure transitions with intermediate K values to reduce possible complication from nonlinear second-order Stark effects. These transitions should be the least affected by such behavior, and when plotted, showed little if any deviation from linearity. The b component of the dipole moment was predicted to be very small and, when it was included in the fit, resulted in a small, negative value for μ_b^2. This indicated that the component was, indeed, too small to be determined from the data available. The fact that b-type transitions were not seen after 60 000 gas pulses was further indication of the small value of μ_b. A maximum possible value of μ_b is 0.2 D, based on the assumption that this dipole moment component could contribute no more that 20 kHz of a total 1 MHz shift for the fastest moving Stark effect measured. It was found that $\mu_a = 0.537(10)$ D, $\mu_c = 0.373(2)$ D, and $\mu_{tot} = 0.653(8)$ D. The Stark coefficients for the measured transitions are summarized in Table 4, and the dipole moment data is shown in Table 5. The experimentally determined dipole moment components give values consistent with the antiparallel model identified in both this and the previous work.[1] In these models, the experimental monomer dipole moments are projected onto

TABLE 5: Dipole Moment Components for OCS Trimer

		projected values[a]			ORIENT values[b]	
	experiment	experimental structure [c]	antiparallel model Connelly et al.[d]	parallel model Connelly et al.[d]	no polarization	polarization
μ_a/D	0.537(10)	0.391	0.6	1.5	0.681	0.507
μ_b/D	0.00(20)[e]	0.023	0.05	0.02	0.025	0.060
μ_c/D	0.373(2)	0.517	0.4	1.4	0.400	0.299
μ_{tot}/D	0.653(8)	0.649	0.72	2.1	0.790	0.592

[a] Projection of OCS monomer dipole moments onto principal axes of experimental or semiempirical structure. [b] Structure in Table 7, column 2. This structure changes slightly with polarization terms. [c] Structure in Table 7, column 1. [d] Reference 1. [e] Uncertainty based on assumption that the *b* component of the dipole moment contributes at most 20 kHz of 1 MHz total shift to the fastest Stark effect measured.

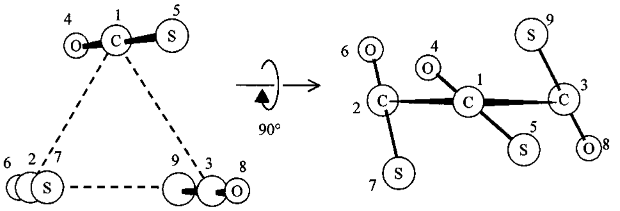

Figure 1. The antiparallel structure of the OCS trimer. In the left-hand view, the three carbon atoms are in the plane of the page. A rotation of 90° about an axis in the C−C−C plane brings the top OCS above the page and the other two below, giving the view on the right. In this view, all three OCS molecules are nearly parallel to the plane of the page.

the principal axes of a plausible trimer structure. The dipole moment components predicted by projecting the monomer moments onto the principal axes of our experimental structure (see below) and the parallel and perpendicular models of Connelly[1] are given in Table 5 for comparison. The possibility that the structure can be the parallel form is essentially eliminated by the dipole moment data. The results also suggest small polarization effects which increase μ_a and decrease μ_c by about 0.15 D compared to the experimental structure.

C. Structure. Figure 1 illustrates a model and numbering scheme for the experimental antiparallel structure. The parallel structure is similar with all three OCS dipoles approximately parallel. The (^{18}OCS)$_3$ isotopic shift data, and the dipole moment data, are only consistent with the antiparallel form.

Nine parameters defining the structure of the OCS trimer were fit to the nine moments of inertia from the normal species and the two enriched isotopomers using techniques for solving a set of nonlinear simultaneous equations. The structures of the OCS monomers were held fixed at their experimental values, with $r_{O-C} = 1.1561$ Å and $r_{C-S} = 1.5651$ Å.[13,14] The fitted parameters were the C1−C2 and C2−C3 distances, the angles C1−C2−C3, S5−C1−C3, S7−C2−C1, and O8−C3−C2, and the dihedral angles S5−C1−C3−C2, S7−C2−C1−C3, and O8−C3−C2−C1. Since this is a minimum data set, the fit is exact, with no statistical fitting errors or redundancy checks from fitting extra equations. The principal axis coordinates derived from the fit are given in Table 6, and the nine fitted parameters are given in Table 7 where they are compared with bond distances and angles derived from semiempirical calculations (described later). It should be noted that an uncertainty can be estimated by holding one structural parameter fixed while fitting the other eight parameters to the nine moments of inertia. This was carried out for both C−C distances and for the C1−C2−C3 angle, and the calculation generally led to a standard deviation of between 0.001 and 0.003 amu Å^2 in the fitted moments. This suggests that statistical errors arising from contamination of the effective moments by large amplitude motions is not a complication. Nevertheless, the derived parameters are so-called effective parameters in the ground state, which may deviate markedly from equilibrium values. We expect the equilibrium values to be within 0.05 Å for distances and about 5° in angles.

TABLE 6: Principal Axis Coordinates (Å) for the Experimentally Fitted Structure of OCS Trimer

	a	*b*	*c*
C1[a]	1.08070	1.68607	−0.64283
C2	−2.25260	0.31900	−0.03202
C3	0.88452	−1.98819	0.29479
O4	0.25388	1.92442	−1.41492
S5	2.20003	1.36340	0.40240
O6	−2.55231	0.16991	−1.13859
S7	−1.84685	0.52082	1.46604
O8	1.37954	−2.04039	1.33824
S9	0.21438	−1.91753	−1.11782
M1[b]	1.45697	1.57760	−0.29149
M2	−2.11620	0.38684	0.47155
M3	0.65925	−1.96444	−0.18006

[a] Atom numbering as in Figure 1. [b] M1, M2, and M3 are the center of mass of each OCS.

As a redundancy check of the derived structure, the spectrum of the (^{18}O^{13}CS)$_3$ species was predicted. Two transitions believed to belong to this species were found at 6737.035 and 6737.337 MHz ($6_{06}-5_{05}$ and $6_{16}-5_{15}$), approximately 800 kHz from the predicted frequencies. Their low intensity discouraged us from further exploring this assignment.

Discussion

A. Experimental Summary. The original study of OCS trimer[1] established that the complex had a structure in which the three monomers are aligned roughly side-by-side, but there was insufficient experimental data to determine whether the three sulfur atoms were pointing in the same direction (parallel structure) or whether one of the sulfur atoms pointed in the opposite direction to the other two (antiparallel structure). The new isotopic shift data reported here clearly establishes that the antiparallel conformer has been observed. The dipole moment results also confirm this. Table 5 compares the experimental values of the dipole moments with the values projected for this structure on the principal axes using the dipole moments of the OCS monomers (0.7152 D[12]). These results are in reasonable agreement but indicate that some modest polarization effects also occur. If point polarizabilities of OCS[15] and electric fields and dipole moments from the semiempirical ORIENT model described below are used, the predicted dipole moments more closely reproduce those measured experimentally.

B. Semiempirical Modeling. The previous report[1] predicted, via semiempirical calculations, that the antiparallel structure was of lower energy and, thus, the more likely of the two possibilities. We performed semiempirical calculations which also favored the antiparallel configuration, although our modeling with the ORIENT program[16] gave slightly different structural parameters than that of Connelly et al. who used a procedure

TABLE 7: Comparison of Structural Parameters with Those Predicted by ORIENT Calculations (Bond Lengths in Å, Angles in Degrees)

	experimental	DMMs at atom centers[a]	DMMs at atom and bond centers[a]	DMMs (ref 1)[b]	DMMs atom centers, $K = 0.00083E_h$[a]	Muenter model[c]
C1−C2[d]	3.654	3.653	3.658	3.685	3.544	3.816
C1−C3	3.797	3.731	3.694	3.692	3.621	3.778
C2−C3	3.908	3.908	3.853	3.811	3.802	3.891
C1−C2−C3	60.2	59.0	58.9	59.0	59.0	58.7
C2−C3−C1	56.6	57.1	57.9	58.8	57.0	59.7
C3−C1−C2	63.2	63.9	63.2	62.2	64.1	61.6
S5−C1−C3	70.9	70.8	71.0	73.7	70.3	74.8
S7−C2−C1	82.8	71.3	70.5	72.7	70.8	72.7
O8−C3−C2	116.5	116.0	115.4	111.3	116.6	110.2
S5−C1−C3−C2[e]	136.4	139.9	138.0	133.3	140.6	133.9
S7−C2−C1−C3	80.0	72.0	73.5	76.1	71.4	77.5
O8−C3−C2−C1	89.9	97.5	97.3	96.4	97.8	96.0
S5−C1−C3−S9	−156.2	−148.9	−150.7	−152.2	−148.6	−151.0
S7−C2−C1−S5	32.7	27.2	27.3	24.5	27.5	25.7
S9−C3−C2−S7	−178.8	−164.7	−163.5	−165.2	−164.2	−165.1

[a] DMM = distributed multipole moments in Table 8. $K = 0.001$ in eq 1 unless otherwise noted. [b] DMMs (with bond centers) from ref 1, used through hexadecapoles. [c] DMMs and model from ref 1. [d] Atom numbering as in Figure 1. [e] The signs of the dihedral angles are consistent with the definition in ref 30.

TABLE 8: Distributed Multipole Moments for OCS Calculated with and without Bond Centers (in au)

	Q_{00}	Q_{10}	Q_{20}	Q_{30}	Q_{40}
O	−0.519	−0.083	0.277	0.437	0.708
C	0.646	−0.458	0.287	1.753	7.088
S	−0.127	0.080	1.659	−0.755	2.341
O	−0.169	0.218	0.354	0.185	0.068
O−C[a]	−0.672	0.024	0.476	0.054	0.066
C	1.186	−0.668	0.416	0.189	0.634
C−S[a]	−0.778	0.212	0.848	−0.305	0.669
S	0.433	−0.720	2.371	−0.704	0.209

[a] Calculated at the bond center.

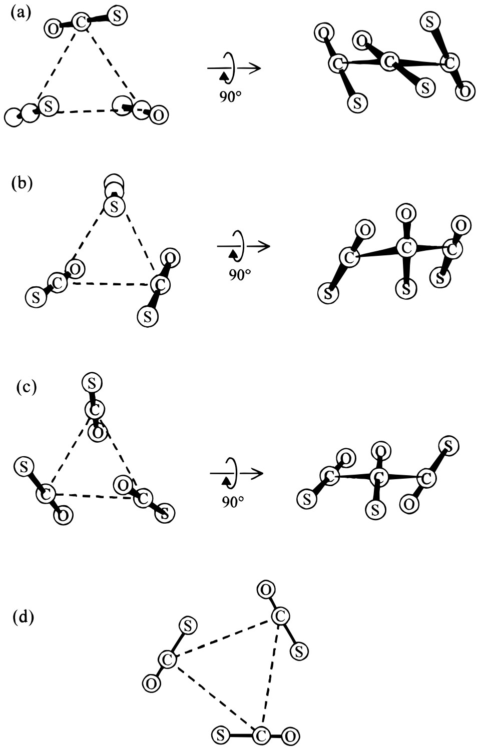

Figure 2. The four OCS trimer structures obtained with the ORIENT modeling program using the default value of K and distributed multipole moments only at atom centers: (a) $E = -0.00760E_h$; (b) $E = -0.00712E_h$; (c) $E = -0.00689E_h$; (d) $E = -0.00517E_h$. The same comments as in Figure 1 apply to the viewing perspectives except that the three OCS molecules are no longer nearly parallel to the plane of the page in the right-side view.

that has been described in detail by Muenter.[17] Muenter's method uses distributed multipole moments (DMMs) to describe electrostatic interactions and atom−atom Lennard-Jones potentials to describe dispersion and repulsion.[1] The semiempirical model used in ORIENT also uses DMMs to describe the electrostatic part of the intermolecular interaction potential and analytic terms of the form

$$U_{\text{exp}-6} = \sum_{i,j} K \exp[-\alpha_{ij}(R_{ij} - \rho_{ij})] - \frac{C_6^{ij}}{R_{ij}^6} \tag{1}$$

to describe dispersion and repulsion.[18] The effects of induction were not treated in either set of calculations, except for one calculation by us mentioned in the previous section. The DMMs of OCS were calculated at the SCF level using the CADPAC suite of programs with a TZ2P basis set from the CADPAC library.[19] The multipoles are given in Table 8. The necessary parameters for the dispersion and repulsion atom−atom terms were obtained from Mirsky[20] in Table 11.2 of ref 18. The preexponential factor K was set at the default value of $0.001E_h$ for the initial calculations, where $E_h = 1$ hartree = 27.2 eV.

Initially, DMMs were calculated only at the atom centers in the OCS molecule, and structure optimizations run using these DMMs led to four minima (see Figure 2). The lowest energy structure (Figure 2a) corresponds to the antiparallel arrangement of molecules that has been confirmed experimentally ($E = -0.00760E_h$). The next lowest energy structure (Figure 2b) has a parallel barrel-shaped arrangement ($E = -0.00712E_h$) which roughly agrees with the parallel structure also proposed by Connelly et al. The next highest energy structure (Figure 2c) again has an antiparallel arrangement of monomers ($E = -0.00689E_h$), but in this structure the oxygen atom of one OCS is opposite the carbon atom of the second OCS. The fourth structure has the highest energy ($E = -0.00517E_h$) and is a planar cyclic structure (Figure 2d) with the carbon atoms arranged in an equilateral triangle.

To test the sensitivity of the calculation to the DMMs, the calculations were rerun with a new set of DMMs that included additional multipoles located at the bond centers of the OCS. Again, four structures were found, and they differed little from those predicted without bond centers. The structural parameters of the minimum energy antiparallel arrangement of molecules

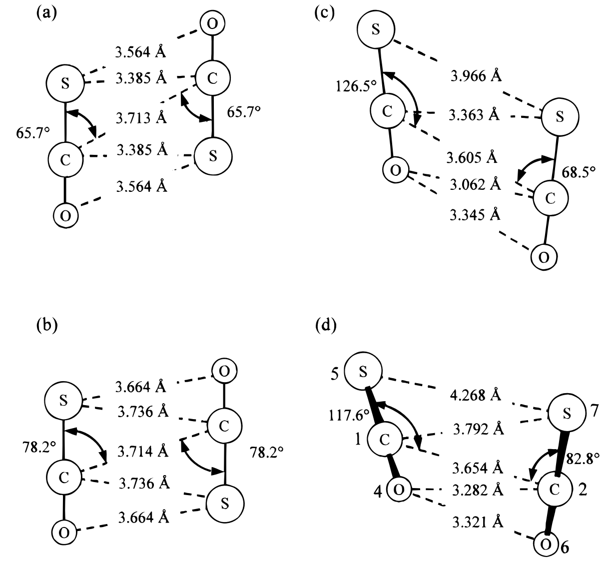

Figure 3. OCS dimer structures: (a) ORIENT, nonpolar; (b) experimental (ref 21); (c) ORIENT, polar; (d) the parallel $(OCS)_2$ face of OCS trimer. The trimer face has a S7−C2−C1−S5 dihedral angle of 32.7°.

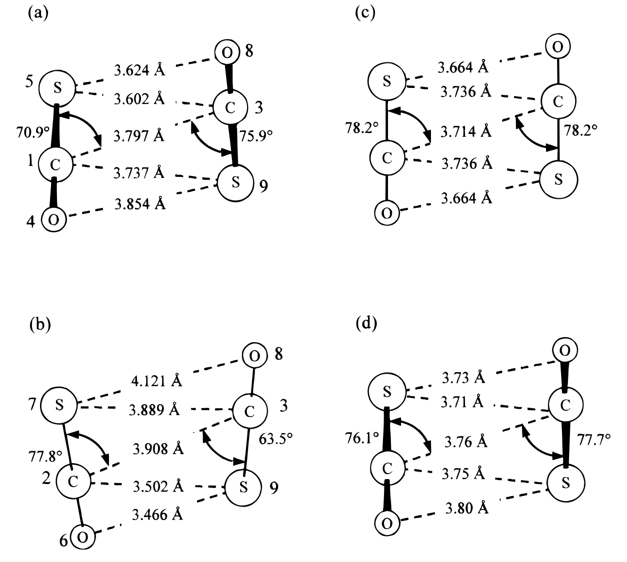

Figure 4. (a,b) The two antiparallel $(OCS)_2$ faces of OCS trimer. The S5−C1−C3−S9 dihedral angle is −156.2°, and the S9−C3−C2−S7 dihedral angle is −178.8°. (c) The experimental structure of OCS dimer (ref 21). (d) The $(OCS)_2$ face of $(OCS)_2CO_2$. The S−C−C−S dihedral angle is 34.0° (ref 4).

are given for the calculations with and without bond centers in Table 7.

A third set of calculations used the DMMs (truncated at the hexadecapole level) that were calculated by Connelly et al. and used in their structural predictions.[1] These DMMs also included bond centers. Again, similar minimum energy structures were found, but one of the barrel-like structures showed noticeable changes from the structure obtained in the first set of calculations. This structure is comparable to Figure 2c, but the central OCS in the view on the left is shifted up the page to put the sulfur atom between the carbons of the other two OCS molecules. Table 7 lists both the Connelly et al. lowest energy structural parameters and those from ORIENT using their DMMs.

Finally, the sensitivity of the calculation to the preexponential factor K was tested. When the OCS dimer was modeled with $K = 0.00083E_h$, the C−C distance was reproduced to within 0.001 Å[21] (see Figure 3). The OCS trimer optimizations were repeated with this value of K in the hope that this might lead to a better reproduction of the experimental OCS trimer structure. This did not materialize, however, as these calculations gave bond lengths considerably shorter than those observed experimentally for the OCS trimer. Again, four minimum energy structures were found which were roughly the same as the structures found in the previous calculations, although the C−C distances were considerably shorter than those obtained with the default value of K (see Table 7). With this value of $K = 0.00083E_h$, a parallel, polar form of the OCS dimer was also predicted to be 0.094 cal higher in energy than the known antiparallel form. It is shown in Figure 3c. Although the spectrum of the polar OCS dimer has not been assigned in the microwave region, there has been evidence of its existence in other work.[22]

In summary, Table 7 indicates a small variance in structural details for the lowest energy conformer depending on the parameters which are used. It is pleasing that all of the calculations suggest the same low-energy form. Given the simplicity of the model, the neglect of polarization, and anisotropic effects in the dispersion and repulsion terms, this variation in details is not surprising. It would appear from this study and others which use similar semiempirical modeling recipes that such calculations give a qualitatively correct structural prediction for trimers of three linear molecules. In some cases, the predicted structure is good enough to significantly assist the spectroscopic assignment.

C. Empirical Structure Trends. It is of interest to study the small changes that occur in dimers upon addition of a third body to the system. For this reason, we compare each of the three faces of the OCS trimer to the corresponding dimer. First we examine the parallel face, where both sulfur atoms are pointing in the same direction. As mentioned in the previous paragraph, an experimental structure is not available for the parallel OCS dimer, so a comparison with the semiempirically determined structure is made instead. This structure was predicted using parameters that accurately reproduce the known, nonpolar OCS dimer center of mass separation. Both the trimer and the predicted dimer structure have the two OCS units tipped away from a parallel arrangement, with the sulfur atoms farther apart than the oxygen atoms, a logical size effect. Various distances and angles are compared in Figure 3 (parts c and d). While the dimer is predicted to have a planar structure, the trimer face is twisted noticeably from planarity with a S5−C1−C2−S7 dihedral angle of 32.7°.

The two antiparallel faces of the trimer are compared with the nonpolar dimer structure in Figure 4. It can be seen that both trimer faces have the OCS molecules tipped away from the parallel alignment that is seen in the dimer. Also, the planar structure of the dimer is lost in the trimer faces, although the change is significantly larger on the face in Figure 4a than that of Figure 4b. The former deviates from planarity by 33.8°, while the latter deviates by only 1.2°. It is interesting to note that the face that is nearly planar has a much larger tilt away from the parallel structure of the dimer than the face that has a large dihedral angle but which otherwise reproduces the intermolecular C−C and C−S distances of the parallel dimer more closely.

The phenomenon of one face of a trimer having significantly larger changes from the comparable dimer structure than a second face of the trimer has been seen in other, similar trimer complexes. Some examples are $(CO_2)_2N_2O$,[5] $(OCS)_2CO_2$,[4] and $(CO_2)_2OCS$,[2,3] all recently studied in this laboratory. In the first of these trimers, one CO_2-N_2O face has a $C-N_{central}$ distance of 3.427 Å, while the distance on the other face is 3.638 Å compared to 3.473 Å in the $CO_2 \cdot N_2O$ dimer.[23] The $(OCS)_2$-CO_2 trimer shows similar effects on its two OCS−CO_2 faces, although the differences are smaller than those in $(OCS)_3$ and $(CO_2)_2N_2O$. The $C_{OCS}-C_{CO_2}$ distance in the dimer is 3.69 Å,[24] while the distances on the two faces of the trimer are 3.57 and 3.77 Å. The differences are still smaller in the $(CO_2)_2OCS$ trimer where the two $C_{OCS}-C_{CO_2}$ distances are 3.59 and 3.66 Å.

The dihedral angles between adjacent monomers on the trimer faces that most closely resemble the known dimer structure can also be compared. The dihedral angle of the $(OCS)_2$ face of $(OCS)_2CO_2$ is 34.0° (O−C−C−S), which is only 0.2° different from the 33.8° angle seen in $(OCS)_3$. The C−O−O−C angle of the $(CO_2)_2$ portion of $(CO_2)_2N_2O$ is also very similar to these two dihedrals with a value of 33.4°. This trend is broken by the C−O−O−C dihedral angle in $(CO_2)_2OCS$, which has the considerably smaller value of 7.7°. Other trimers with similar structures, such as $(CO_2)_2HCN$,[6] $(CO_2)_2H_2O$,[25,26] $(N_2O)_3$,[7] and $(CO_2)_3$,[8] also have dihedral angles that are considerably different from the ~34° angle seen in the complexes discussed here. Thus, perhaps the similarity between the dihedral angles of $(OCS)_3$, $(CO_2)_2N_2O$, and $(OCS)_2CO_2$ is no more than a coincidence. It is possible that the angle of ~34° might be common in other trimers containing an $(OCS)_2$ face, but there are presently no other known trimers containing two OCS molecules to compare.

The OCS dimer portion of $(OCS)_2CO_2$ (Figure 4d) can be compared with the OCS dimer face of $(OCS)_3$ that is shown in Figure 4a. While no parameters differ very greatly, "third body effects" in the OCS dimer unit of $(OCS)_3$ are readily apparent. The larger sulfur in OCS and the electrical asymmetry cause the dimer structure to be more distorted than in $(OCS)_2CO_2$.

Summary

It has been determined that the OCS trimer has a barrel-like antiparallel structure. This structure is similar to that proposed by Connelly et al. in a previous paper and it conforms to a pattern of structures seen in other trimers of linear monomers. Structures with this triangular arrangement of monomers are common and include CO_2 trimer,[7] N_2O trimer,[8] $(CO_2)_2H_2O$,[25,26] $(CO_2)_2HCN$,[6] $(CO_2)_2N_2O$,[5] $(CO_2)_2OCS$,[2,3] and $(OCS)_2CO_2$,[4] for example. The structures in which the three monomer units are roughly parallel maximize the dispersion interactions, while the slipping and twisting of the sticks enhances the attractive electrostatic forces. There is also a planar, cyclic structure for CO_2 trimer,[27] which has not been observed for any other homomolecular trimers except $(HCN)_3$[28] and $(HCCH)_3$.[29] Semi-empirical modeling using analytic dispersion and repulsion terms and distributed multipole analysis to model the electrostatic interaction terms has been a helpful tool for predicting the structure of OCS trimer. The model predicted three other higher energy structures in addition to the experimentally determined antiparallel barrel structure. The first of these structures is the parallel analogue of the structure that was determined experimentally; the second structure is another antiparallel structure with the oxygen of one OCS interacting with the carbon of the adjacent OCS, and the final structure is a planar, equilateral triangular structure. The ORIENT program was run using various sets of input parameters, and it was found that adding bond centers when calculating the DMMs or using the DMMs of Connelly et al. made only small differences to the global minimum structures. Decreasing the value of K in the expression defining dispersion and repulsion had a larger effect on the predicted structures, making the monomer distances much shorter than the other predictions. This was a surprising result, because a value of K that almost exactly reproduced the experimental C−C distance of the nonpolar OCS dimer gave poorer predictions than larger values. Thus, it can be concluded that values of the parameter K that are appropriate for predicting accurate dimer structures are not necessarily appropriate for trimers. This is a phenomenon that has yet to be explored with other trimer systems, and further calculations may lead to a better understanding of how to adjust a useful K for a dimer to accurately predict a trimer structure. The changes in structural parameters that are seen in comparing the OCS dimer structure to the three dimer faces of the trimer are similar to the changes seen in other trimer complexes. In general, one trimer face more closely resembles the known dimer than the other trimer face. Also, the planarity that is common in dimers of linear triatomic molecules is lost in all faces of the trimer. This reflects the fact that the balance between electrostatic, dispersion, and repulsive forces in the trimers is different from that in the corresponding dimers. The addition of a third body to the complex leads to a loss of some of the dispersion forces that cause the dimers to have the planar slipped parallel structure. This loss is compensated for by additional favorable electrostatic and dispersion interactions caused by the third body.

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