

Structure and Conformational Properties of Diacetyl Sulfide in the Gaseous and Condensed Phases Explored by Gas Electron Diffraction, Single-Crystal X-ray Diffraction, Vibrational Spectroscopy, and Quantum Chemical Calculations

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Abstract: On the evidence of the electron diffraction pattern of the vapor, of the IR spectrum of the matrix-isolated molecule, and of quantum chemical calculations, the diacetyl sulfide molecule, $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$, adopts a planar heavy-atom skeleton with the [sp,ap] conformation. Other conformations contribute little (<1%) to the population of the gaseous molecules at normal temperatures. Salient structural parameters (r_a structure, distances (in Å), angles (in deg), and 3σ uncertainties in parentheses) were as follows: $r(\text{C}=\text{O})$ 1.198(2)/1.196(2), $r(\text{C}-\text{S})$ 1.787(3)/1.808(3), $r(\text{C}-\text{C})$ 1.483(4)/1.472(4), $\angle\text{C}-\text{S}-\text{C}$ 108.8(9), $\angle\text{S}-\text{C}=\text{O}$ 125.7(6)/115.1(6), and $\angle\text{S}-\text{C}-\text{C}$ 121.1(7)/111.2(7). The structure of a single crystal at 150 K [monoclinic, $P2_1/n$, $a = 4.2230(7)$ Å, $b = 11.2105(17)$ Å, $c = 12.332(2)$ Å, $\beta = 94.544(16)^\circ$] also reveals planar molecules with the same conformation and dimensions close to those of the gaseous molecule. Changes in the vibrational spectra of the compound accompanying the transition from the vapor to the condensed phases are attributed not to the presence of more than one conformer but to differences in the local environment of the two carbonyl groups. The properties deduced are compared with those of other compounds of the type $\text{CH}_3\text{C}(\text{O})\text{XC}(\text{O})\text{CH}_3$ ($\text{X} = \text{CH}_2, \text{NH}, \text{or O}$).

Introduction

Compounds having the framework $\text{CH}_3\text{C}(\text{O})\text{XC}(\text{O})\text{CH}_3$, with two acetyl groups linked to a common atom X, excite attention because of the variety of conformational opportunities they afford. Such compounds include the keto form of 2,4-pentanedione, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$, *N*-acetylacetamide, $\text{CH}_3\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_3$, acetic anhydride, $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_3$, and diacetyl sulfide, $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$. The different possible conformations can be characterized in terms of the two dihedral or torsion angles ϕ_1 and ϕ_2 defined by each of the $\text{C}-\text{X}-\text{C}=\text{O}$ units. Hence, we can distinguish a number of planar or nonplanar rotamers with the numbering scheme and labels, e.g., [sp,sp], [sp,ap], [sc,sc], etc., given in Figure 1.

Experimental studies of the conformational behaviors of these molecules have been concerned mainly with electron diffraction measurements on the vapors^{1–4} and with the vibrational spectra

of the vapors and condensed phases.^{4–7} Both methods have their limitations. For example, torsional motions that have large amplitudes and low wavenumbers create “shrinkage” problems in the analysis of the electron diffraction patterns. Moreover, the relative complexity and low symmetry of the molecules are liable to frustrate any definitive interpretation of their vibrational spectra; most studies of this sort have concentrated on the regions of the spectra where the $\nu(\text{CO})$ fundamentals occur, but even here ambiguities may arise as a result of factors such as intermolecular perturbations or Fermi resonance. In these circumstances, there is clearly much scope for quantum chemical methods which have developed apace in their ability to simulate the equilibrium structure, vibrational force field, and thermodynamic properties of such molecules.⁸ Such studies as have been carried out do not reveal any clear pattern of behavior with regard to conformational preference of the molecules.

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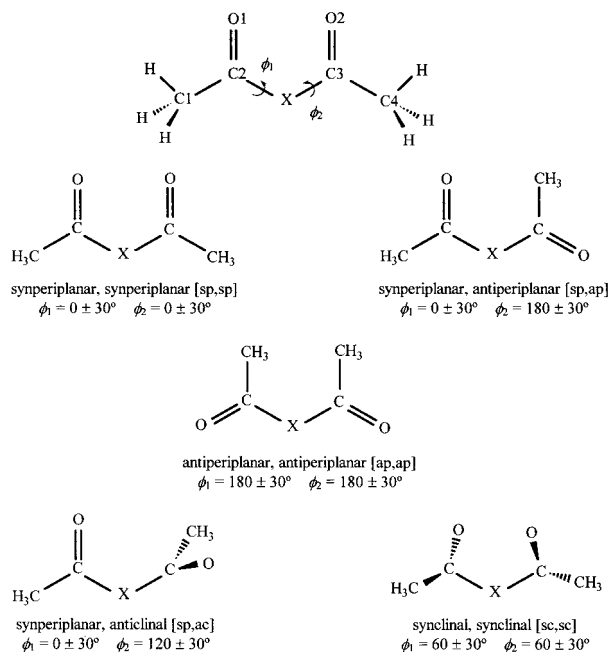
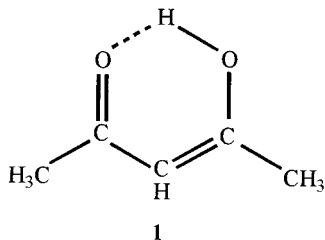


Figure 1. Different possible planar and nonplanar conformations for a molecule of the type $\text{CH}_3\text{C}(\text{O})\text{XC}(\text{O})\text{CH}_3$ in terms of the two dihedral or torsion angles ϕ_1 and ϕ_2 defined by each of the $\text{C}-\text{X}-\text{C}=\text{O}$ units.

2,4-Pentadione is unusual since the vapor normally consist of an equilibrium mixture of the keto form of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ and the more abundant enol form **1**, which is stabilized



by intramolecular hydrogen bonding.^{1,9,10} The compound crystallizes exclusively as the enol form.¹¹ In these circumstances, the keto form is difficult to characterize, but the electron diffraction pattern of the vapor at 105 °C has been interpreted on the basis of a single nonplanar [sp,sp] conformer,¹ and despite possible misgivings about overinterpretation of the results, this is not far out of line with the results of more recent ab initio calculations (which actually favor an [sc,sc] conformation).¹²

N-Acetylacetamide, $\text{CH}_3\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_3$, which is of considerable interest as a reference point for molecules such as polypeptides, is more straightforward. Experiment² and theory¹³

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both come out in favor of a planar [sp,ap] (i.e., *E,Z*) conformer as the global minimum on the potential energy surface of the molecule. Any deviation from planarity suggested by an analysis of the electron diffraction pattern of the vapor taken at face value is likely to reflect the shallowness of the surface with respect to the torsional coordinates ϕ_1 and ϕ_2 . However, the fineness of the energy balance between the [sp,ap] (*E,Z*) and [sp,sp] (*Z,Z*) conformers and its susceptibility to environment is demonstrated by studies involving solutions and systematic changes of solvent permittivity,¹⁴ and also the solid where both conformers are found to exist and the change for the metastable [sp,sp] to the [sp,ap] form give rise to a polymorphic transition.¹⁵

Acetic anhydride, $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_3$, is another matter. Earlier studies of the electron diffraction pattern of the vapor³ and the vibrational spectra of the compound⁶ led to the conclusion that there is under normal conditions a single molecular conformer which is nonplanar with an [sc,sc] structure and torsional angles $\phi_1 = \phi_2 = \sim 50^\circ$ (conforming to C_2 symmetry). More recent measurements of the electron diffraction pattern and vibrational spectra have been interpreted,⁴ however, in the light of extensive ab initio calculations, on the basis of a model in which the vapor consists of a mixture of two nonplanar conformers, one possessing the [sp,sp] and the other the [sp,ac] configuration in a proportions of roughly 1:2. The two conformers are calculated to differ in energy by only 1 kcal mol⁻¹ or less, and the potential energy surface linking them appears to offer low-energy rotation barriers that imply large-amplitude torsional motions.

In the case of diacetyl sulfide, $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$, the picture hitherto has been unclear in that molecular polarizability measurements made with C_6H_6 or CCl_4 solutions¹⁶ appear to be at odds with the vibrational spectra of the compound in the vapor and condensed phases.⁷ The first are most readily reconciled with a nonplanar [ac,ac] structure with C_2 symmetry, whereas the second have been interpreted in terms of a single flexible conformer with only C_1 symmetry and the $\text{C}=\text{O}$ vectors subtending an angle between 110 and 180°. Here we report the results of a detailed study drawing on (i) quantum chemical calculations at different levels of theory, (ii) new measurements of the vibrational spectra (including studies of the matrix-isolated molecule), (iii) electron diffraction analysis of the vapor, and (iv) an X-ray crystallographic study of a single crystal at 150 K. Hence we shall show that a single conformer does indeed predominate but that this is planar with an [sp,ap] configuration. The increased complexity of the $\nu(\text{C}=\text{O})$ region of the vibrational spectra of the compound in the condensed phases we believe to reflect not conformational changes but the innately different environmental responses of the two carbonyl groups.

Experimental Section

Sample Preparation and Purification. Diacetyl sulfide, $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$, was prepared by the reaction of thioacetic acid, $\text{CH}_3\text{C}(\text{O})\text{SH}$, with acetyl chloride, according to the published procedure.¹⁷ The compound was isolated by distillation at low pressure and subsequently purified by repeated trap-to-trap condensation in vacuo until it appeared colorless. Its purity was checked by reference to its IR, Raman, and ¹H and ¹³C NMR spectra.⁷

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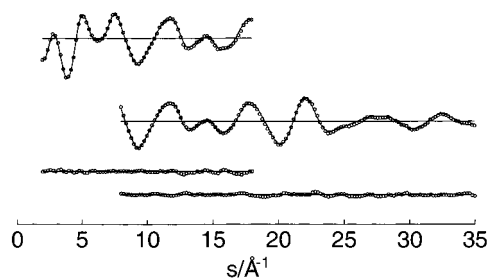


Figure 2. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

Vibrational Spectroscopy. The Raman spectrum of the liquid was recorded with a Jobin-Yvon U-1000 spectrophotometer. It was excited at $\lambda = 457.9, 488.0,$ or 514.5 nm by the output from a Spectra-Physics model 165 Ar⁺ laser, and measurements were made with a spectral resolution of 5 cm^{-1} while the sample was maintained at three different temperatures, viz. $55\text{ }^{\circ}\text{C}$, ambient temperature ($22\text{ }^{\circ}\text{C}$), and $-60\text{ }^{\circ}\text{C}$. Gas mixtures of diacetyl sulfide with argon or nitrogen (BOC, "Research" grade) in the proportions $\sim 1:1000$, prepared by standard manometric methods, were deposited on a CsI window cooled to $\sim 15\text{ K}$ by means of a Displex closed-cycle refrigerator (Air Products model CS202) using the pulsed deposition technique.^{18,19} IR spectra of the matrix samples were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 0.5 cm^{-1} , with 256 scans and a wavenumber accuracy of $\pm 0.1\text{ cm}^{-1}$, using a Nicolet Magna 560 FTIR instrument equipped with an MCTB detector.

Electron Diffraction. Electron diffraction measurements on the vapor of the compound were made with a Gasdiffraktograph KD-G2²⁰ at nozzle-to-plate distances of 25 and 50 cm and with an accelerating voltage of $\sim 60\text{ kV}$. The sample temperature was kept at $40\text{ }^{\circ}\text{C}$ (giving a vapor pressure estimated to be $\sim 3\text{ Torr}$), and the inlet system, including the nozzle, was heated to $50\text{ }^{\circ}\text{C}$. The experiments were carried out with a nozzle having an internal diameter of 0.6 mm. The photographic plates were analyzed by the usual procedures²¹ to give molecular intensities spanning the s ranges 2–18 and 18–35 \AA^{-1} in intervals D_s of 0.2 \AA^{-1} [$s = (4\pi/\lambda) \sin\theta/2$, where λ is the electron wavelength and θ the scattering angle]; the averaged intensities are shown in Figure 2.

Crystal Structure. A single crystal of diacetyl sulfide was grown by careful cooling of a sample contained in a Pyrex glass capillary 0.38 mm in external diameter that was mounted on the diffractometer. A stable solid/liquid phase boundary was established at a temperature just below the melting point and crystal growth effected from this boundary by cooling the sample at a rate of $\sim 50\text{ K h}^{-1}$. The yellow cylindrical crystal thus formed was then cooled to 150 K , and diffraction data were collected with a Stoe Stadi 4 four-circle diffractometer, an Oxford Cryosystems low-temperature device²² providing the appropriate temperature control. Crystal data and data collection details are listed in Table 1. For the purposes of an absorption correction, ψ -scan data were collected, but since they showed no significant variation, no correction was applied. This is not unexpected in an essentially cylindrical sample. Slightly more than one hemisphere of reflections was collected to $2\theta = 50^{\circ}$ using Mo K α radiation; these 3192 data were merged to give 1020 unique data ($R_{\text{int}} = 0.0381$), of which 881 had $F > 4\sigma(F)$. The structure was solved by direct methods and refined against F^2 (SHELXTL).²³ H atoms were located in a difference synthesis

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Table 1. Crystal Data for $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$

empirical formula	$\text{C}_4\text{H}_6\text{O}_2\text{S}$ (CH_3CO) ₂ S
formula weight	118.15
wavelength	0.71073 \AA
temperature	150(2) K
crystal system	monoclinic
space group	$P2_1/n$
unit cell dimensions	$a = 4.2230(7)\text{ \AA}$ $b = 11.2105(17)\text{ \AA}$ $c = 12.332(2)\text{ \AA}$ $\beta = 94.544(16)^{\circ}$
volume	581.98(16) \AA^3
no of reflections for cell	63 ($15 \leq \theta \leq 16^{\circ}$)
Z	4
density (calculated)	1.348 Mg/m^3
absorption coefficient	0.445 mm^{-1}
$F(000)$	248

performed about the locus of possible H positions; the methyl groups were thereafter treated as rotating rigid bodies. All non-H atoms were refined with anisotropic displacement parameters. The final conventional R factor (based on F) was 0.0276; wR_2 was 0.0664. The ultimate difference map extremes were $+0.20$ and -0.23 e \AA^{-3} , respectively. Supplemental data in the form of a cif file have been deposited.

Theoretical Calculations. All the quantum chemical calculations were performed using the GAUSSIAN 98 program package²⁴ under the Linda parallel execution environment using two coupled PCs. Geometry optimizations were sought (i) with the HF approximation and (ii) with the MP2 and B3LYP methods; in all cases, the calculations employed 6-31+G* basis sets and standard gradient techniques with simultaneous relaxation of all the geometric parameters. The vibrational properties cited in detail hereafter corresponded to minimums in the potential energy surface and included no imaginary frequencies. The wavenumbers of the vibrational fundamentals calculated with the HF method were scaled by a factor of 0.9 to take some account of the overestimation prevalent in such estimates.

Results and Discussion

1. Quantum Chemical Calculations. Using different starting values for the dihedral angles ϕ_1 and ϕ_2 ($\angle\text{C3-S-C2=O1}$ and $\angle\text{C2-S-C3=O2}$, respectively; see Figure 1) ranging from 0 to 360° in steps of 10° , we encountered three stable structures for the $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$ molecule no matter which method was used to optimize the geometry. These are as follows: (i) [sp,ap] with $\phi_1 = 0$ and $\phi_2 = 180^{\circ}$ having C_s symmetry, (ii) [sp,sp] with $\phi_1 = \phi_2$ near 20° having C_2 symmetry, and (iii) [ap,ap]. For the last rotamer, the HF and MP2 methods predict C_2 symmetry with $\phi_1 = \phi_2$ near 155° , whereas the B3LYP method predicts C_{2v} symmetry with $\phi_1 = \phi_2 = 180^{\circ}$. The energies of the three conformers calculated relative to one another are given in Table 2. Hence, it appears that the [sp,sp] and [ap,ap] forms lie at higher energies than the [sp,ap] one, by $1.0\text{--}2.4$ and $6.5\text{--}7.6\text{ kcal mol}^{-1}$, respectively.

The vibrational properties of the [sp,ap] and [sp,sp] conformers have been calculated by the HF and B3LYP methods. The results are noteworthy mainly in relation to the two $\nu(\text{CO})$

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Table 2. Calculated Relative Energies (kcal mol⁻¹) of the Three Stable Conformers of CH₃C(O)SC(O)CH₃

theoretical model	[sp,ap]	[sp,sp]	[ap,ap]
HF/6-31+G*	0.00	2.43	7.34
MP2/6-31+G*	0.00	1.01	7.60
B3LYP/6-31+G*	0.00	1.96	6.57

fundamentals, which are likely to be the modes most responsive to the conformation of the molecule. For the [sp,ap] form, these vibrations are predicted to be uncoupled and to occur close together with similar intensities (B3LYP estimates 1788/1802 cm⁻¹ and 314/302 km mol⁻¹; HF estimates 1781/1785 cm⁻¹ and 486/257 km mol⁻¹). By contrast, the corresponding vibrations of the [sp,sp] form are expected to be coupled and to be well separated as a result. According to the B3LYP calculations, the in-phase $\nu(\text{CO})$ mode occurs at 1857 cm⁻¹ with an intensity of 376 km mol⁻¹ and the out-of-phase mode at 1793 cm⁻¹ with an intensity of 146 km mol⁻¹; the corresponding values given by the HF calculations are 1843 (476 km mol⁻¹) and 1780 cm⁻¹ (151 km mol⁻¹). Vibrational amplitudes for the most stable [sp,ap] form were derived from the Cartesian force constants (B3LYP), which were transformed to symmetry force constants. Stretching and bending constants were scaled with a factor of 0.95 and the program ASYM40²⁵ was used.

In summary, our calculations indicate that the global minimum for the diacetyl sulfide molecule corresponds to an [sp,ap] conformer with a planar heavy-atom skeleton and the dimensions included in Table 3. About 1–2.5 kcal mol⁻¹ higher in energy comes a second minimum corresponding to an [sp,sp] conformer in which the heavy-atom skeleton deviates somewhat from planarity. Still higher in energy is an [ap,ap] form, which is unlikely to be more than a minor component of the vapor under normal conditions. The calculations lead us therefore to expect that the dominant component of the vapor at ambient temperatures will be the [sp,ap] molecule with between 1 and 16% of the less stable [sp,sp] molecule. The two are expected to differ in the wavenumbers and intensity patterns displayed by their $\nu(\text{CO})$ modes in IR absorption, the two transitions appearing as bands that are similar in wavenumber and intensity in one case ([sp,ap]) but different in both particulars in the other ([sp,sp]). These conclusions find little common ground with earlier interpretations of polarization¹⁶ and spectroscopic⁷ measurements confined, admittedly, mainly to the condensed phases. It is appropriate, therefore, to consider next the new measurements we have carried out on the vibrational spectra of diacetyl sulfide.

2. Vibrational Spectra. The IR spectrum of diacetyl sulfide in the vapor and condensed phases has been reported previously.⁷ While confirming the essential details of the vapor spectrum, we have concentrated on the spectrum of the molecule isolated at high dilution in a solid argon or nitrogen matrix at ~15 K to take advantage of the superior definition of the vibrational transitions made possible (i) by the quenching of rotational motion and (ii) by the inclusion of the molecule in a more or less isotropic but weakly interacting environment.²⁶

The IR spectrum of such a matrix is most immediately notable for what it shows in the region associated with the $\nu(\text{CO})$ fundamentals (see Figure 3). In the event, there is a *single* intense absorption centered at 1725.0 or 1724.0 cm⁻¹ according to whether the host is Ar or N₂, respectively. The absorption

carries a shoulder at higher wavenumber (at 1731 cm⁻¹ for Ar, and 1729 cm⁻¹ for N₂). In light of the calculations described in the preceding section, the present results are clearly consistent with the predominance of a single conformer recognizable on the evidence of the $\nu(\text{CO})$ region as being the [sp,ap] one. The observed separation of the two $\nu(\text{CO})$ modes (6 and 5 cm⁻¹ for Ar and N₂ matrixes, respectively) compares with a predicted splitting of 14 (B3LYP) or 4 cm⁻¹ (HF).

No other absorption could be discerned in this region in the spectrum of the N₂ matrix, but the spectrum of the Ar matrix included two weak features at 1783 and 1811 cm⁻¹ at least one of which is a possible candidate for the in-phase $\nu(\text{CO})$ fundamental of the [sp,sp] conformer (predicted wavenumber 1857 cm⁻¹). Unlike the other bands associated with diacetyl sulfide,²⁷ however, these two features underwent no decay when the matrix was irradiated with broad-band UV–visible light ($\lambda = 200$ –800 nm). The most likely explanation is that they originate not in diacetyl sulfide but in some unidentified impurity. In summary, therefore, we find no spectroscopic sign of a second conformer and on the evidence of this and related¹⁸ studies it would appear that any such conformer makes up less than 1% of the vapor molecules at ambient temperatures.

In this and other respects, the observed spectra are well reproduced by the results of the theoretical calculations on the [sp,ap] conformer (see Table 3). Hence, it has been possible to assign all the features displayed by the matrix-isolated molecules. For example, the wavenumbers measured for an argon matrix are replicated by the B3LYP calculations with an rms deviation of only 3.08% (the HF calculations do even better with an rms deviation of 1.49%). Hence, we conclude that the assignments proposed in Table 3 are reasonable and that the spectra are wholly consistent with a molecule having an [sp,ap] conformation and C_s symmetry, although a change of conformation would have little effect on many of the vibrational transitions.

The IR spectrum we measured for the vapor of the compound is very similar to the matrix spectrum, with due allowance for the appreciably broader absorptions; the $\nu(\text{CO})$ region features just a single band centered at 1739 cm⁻¹. A previous report of this spectrum and of the spectrum of a cyclohexane solution included in addition to an intense band at 1724–1739 cm⁻¹ a much weaker band near 1780 cm⁻¹.⁷ Fortunato et al.⁷ attributed the weak and strong bands to the in-phase and out-of-phase $\nu(\text{CO})$ vibrations of a single conformer and then deduced from their relative intensities that the CO groups subtend an angle approaching 180° to each other. In the course of purification of diacetyl sulfide, we found that samples of the vapor did indeed display a weak IR absorption near 1780 cm⁻¹. However, since the intensity of this feature decreased almost to vanishing point on repeated fractionation of the sample, we are left to infer that it must be associated with an impurity.

The liquid compound presents a rather different picture in its IR spectrum as reported previously.⁷ Here we note two regions of strong absorption attributable to $\nu(\text{CO})$ modes, one centered at 1769 and the other at 1712 cm⁻¹. The solid presents a similar pattern, the absorptions now being centered at about 1730 and 1703 cm⁻¹. The change in intensity pattern was explained earlier⁷ on the basis of a change in the mutual orientation of the two CO groups, with the angle subtended by the two vectors closing down from nearly 180° in the vapor to roughly 110° in the liquid (i.e., close to the value expected for the [sp,ap] conformer). Such an explanation cannot, however,

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Table 3. Calculated and Observed IR Spectrum of CH₃C(O)SC(O)CH₃ (Wavenumbers in cm⁻¹)

mode	HF/6-31+G ^{*a,b}		B3LYP/6-31+G ^{*a,b}		Ar matrix ^b obs	N ₂ matrix ^b obs	assignment
	[sp,ap]	[sp,sp]	[sp,ap]	[sp,sp]			
ν_1	2999 (2)	2993 (10)	3166 (2)	3161 (3)	3016.8 (3)	3017.9 (3)	$\nu_{as}C(4)H_3$
ν_2	2995 (2)	2993 (3)	3162 (2)	3161 (<1)			$\nu_{as}C(1)H_3$
ν_3	2992 (1)	2958 (2)	3147 (<1)	3125 (1)			$\nu_{as}C(4)H_3$
ν_4	2960 (1)	2958 (1)	3128 (1)	3125 (<1)		3002.9 (<1)	$\nu_{as}C(1)H_3$
ν_5	2918 (1)	2898 (<1)	3074 (1)	3058 (<1)	2944.1 } (1)	2945.9 } (1)	$\nu_sC(4)H_3$
ν_6	2900 (<1)	2898 (1)	3060 (<1)	3057 (<1)	2939.7 } (1)	2938.1 } (1)	$\nu_sC(1)H_3$
ν_7	1785 (53)	1843 (100)	1802 (96)	1857 (100)	1731 (79)	1729 (84)	$\nu C(3)=O(2)$
ν_8	1781 (100)	1780 (32)	1788 (100)	1793 (39)	1725.0 (100)	1724.0 (100)	$\nu C(2)=O(1)$
ν_9	1449 (2)	1451 (<1)	1494 (4)	1494 (<1)			$\delta_{as}C(1)H_3$
ν_{10}	1448 (3)	1450 (5)	1486 (5)	1493 (7)	1420.1 } (11)	1419.5 (11)	$\delta_{as}C(4)H_3$
ν_{11}	1443 (3)	1441 (5)	1485 (6)	1484 (7)	1416.4 } (11)		$\delta_{as}C(1)H_3$
ν_{12}	1433 (3)	1441 (<1)	1469 (5)	1484 (<1)	1406.8 (6)	1409.7 (6)	$\delta_{as}C(4)H_3$
ν_{13}	1395 (3)	1390 (1)	1414 (7)	1409 (3)	1361.0 } (10)	1361.1 } (8)	$\delta_sC(4)H_3$
					1360.1 } (10)	1359.7 } (8)	
ν_{14}	1391 (4)	1390 (7)	1408 (8)	1408 (10)	1353.5 (10)	1357.4 } (10)	$\delta_sC(1)H_3$
						1356.7 } (10)	
ν_{15}	1138 (8)	1126 (4)	1153 (12)	1141 (4)	1143.7 } (31)	1143.7 } (35)	ρCH_3
					1138.3 } (31)	1136.1 } (35)	
ν_{16}	1117 (62)	1103 (68)	1126 (86)	1116 (78)	1101.8 (92)	1124.0 } (96)	ρCH_3
						1102.4 } (96)	
ν_{17}	1031 (<1)	1030 (<1)	1045 (<1)	1044 (<1)			ρCH_3
ν_{18}	1025 (1)	1021 (1)	1038 (1)	1035 (1)			ρCH_3
ν_{19}	956 (19)	953 (4)	969 (35)	975 (4)	956.3 } (31)	956.1 (33)	$\nu C(3)-C(4)$
					951.9 } (31)		
ν_{20}	927 (4)	920 (25)	947 (9)	935 (41)	929.2 (8)	936.8 } (3)	$\nu C(1)-C(2)$
						931.2 } (3)	
ν_{21}	628 (14)	616 (42)	627 (5)	602 (59)	625.5 (9)	629.0 (7)	$\nu C(2)-S$
ν_{22}	615 (20)	596 (2)	611 (53)	601 (3)	614.1 (93)	615.2 (62)	$\nu C(3)-S$
ν_{23}	517 (<1)	553 (<1)	524 (<1)	548 (<1)			$\delta C(2)-O(1)$ out-of-plane
ν_{24}	506 (1)	508 (2)	509 (1)	517 (2)	506.3 (1)	529.6 (1)	$\delta O(1)-C(2)-S$
ν_{25}	501 (2)	480 (<1)	496 (4)	482 (<1)	499.4 (<1)	511.1 (1)	$\delta C(3)-O(2)$ out-of-plane
ν_{26}	440 (1)	431 (1)	436 (1)	426 (1)	440.8 } (<1)	439.4 (1)	δ
					438.4 } (<1)		
ν_{27}	316 (<1)	304 (<1)	316 (1)	310 (<1)			δ
ν_{28}	286 (<1)	291 (1)	295 (1)	297 (1)			δ
ν_{29}	189 (<1)	149 (<1)	170 (2)	147 (<1)			δ
ν_{30}	171 (2)	102 (<1)	159 (<1)	96 (<1)			$\rho C(4)H_3$
ν_{31}	82 (<1)	102 (<1)	79 (<1)	95 (<1)			$\rho C(1)H_3$
ν_{32}	42 (<1)	49 (1)	45 (1)	54 (1)			τ
ν_{33}	20 (2)	40 (<1)	30 (2)	46 (<1)			τ

^a Scaled by a factor of 0.90. ^b Intensities in parentheses normalized relative to that of the most intense band set equal to 100.

be reconciled with the vibrational properties we predict for the [sp,ap] conformer. The change in this region of the spectrum brought about by condensation from the vapor is too marked to be caused by impurity. There are thus two possible reasons for it. (i) Condensation results either in a change of conformation or at least in a significant population of a conformer other than the [sp,ap] one (cf. *N*-acetylacetamide^{14,15}). (ii) Intermolecular forces discriminate between the two CO groups of the CH₃C(O)SC(O)CH₃ molecule and thereby modify their properties. The evidence currently available offering no obvious way of deciding which of these reasons is correct; we have appealed to the Raman spectrum of the liquid, which lends itself more readily than the IR spectrum to studies at different temperatures.

We found the Raman spectrum of the liquid at ambient temperatures to be identical in all important respects with that reported by Fortunato et al.⁷ The $\nu(CO)$ region thus resembles that of the IR spectrum, with medium-to-strong scattering centered at 1712 cm⁻¹, a shoulder at 1730 cm⁻¹, and medium-to-weak scattering at 1769 cm⁻¹. Of more immediate concern is our finding that the spectrum underwent no significant change when the temperature of the sample was varied in the range 213–328 K. With an energy of interconversion between the [sp,ap] and [sp,sp] conformers estimated to be 1–2.5 kcal mol⁻¹, an appreciable change in the proportions of these conformers would be expected were they to coexist in equilibrium over this

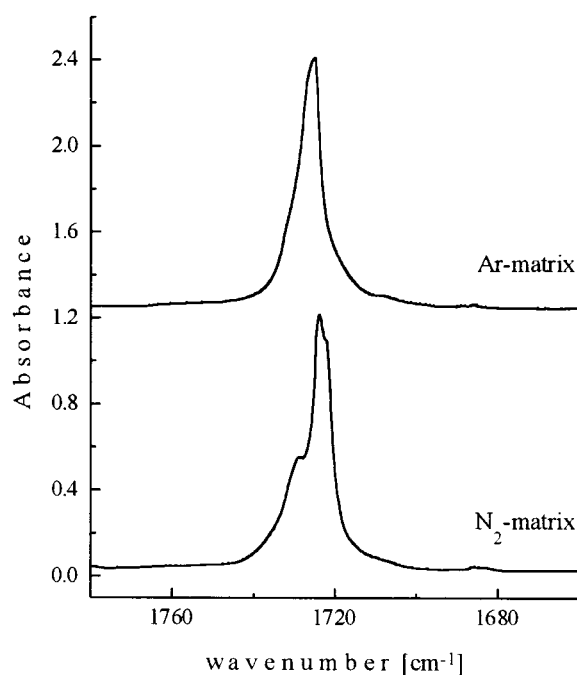


Figure 3. FTIR spectra in the $\nu(CO)$ region of the CH₃C(O)SC(O)CH₃ molecule isolated in an Ar or N₂ matrix (1:1000) at ~15 K.

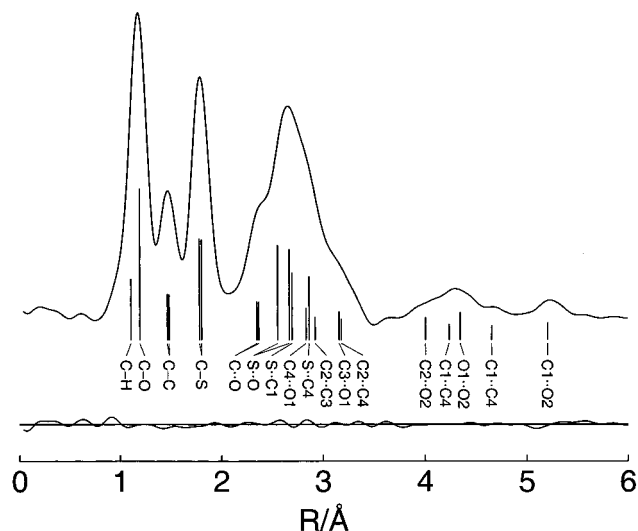


Figure 4. Experimental radial distribution function and difference curve. Important interatomic distances are shown with vertical bars.

range. It seems unlikely therefore that the liquid consists of a mixture of such conformers. Hence, we conclude either that the molecule changes conformation, presumably from the [sp,-ap] to the [sp,sp] rotamer, or that the exposure of the [sp,ap] molecule to an interacting, anisotropic environment perturbs the two CO groups to different degrees. Without additional information from a source other than vibrational spectroscopy, however, there is no way of proceeding beyond this point, to which we will return following the characterization of diacetyl sulfide by its crystal structure.

3. Structure of the Gaseous Molecule: Electron Diffraction Studies. The experimental radial distribution function (RDF), which was derived by Fourier transformation of the experimental molecular intensities, is shown in Figure 4. The principal peaks, occurring at distances near 1.2, 1.5, and 1.8 Å, are assigned to the bonded atom-pairs C=O, C-C, and C-S, respectively. A large number of different structures with C_2 , C_s , or C_1 symmetry and with different dihedral angles $\angle C-S-C=O$, ϕ_1 , and ϕ_2 were considered. The experimental RDF could be reproduced satisfactorily only with a model having an [sp,ap] conformation, a result in pleasing agreement with the predictions of the quantum chemical calculations. The geometric parameters were refined by least-squares fitting of the molecular intensities. The following assumptions were made: (i) The molecule was supposed to possess C_s overall symmetry and each of the methyl groups to possess local C_{3v} symmetry. (ii) The differences between analogous bond distances and angles of the syn- and anti-oriented acetyl groups were constrained to the calculated (MP2) values. (iii) Vibrational amplitudes that either cause large correlations between geometric parameters or are poorly determined in the electron diffraction experiment were set equal to the calculated (B3LYP) values. With these assumptions, it was possible to refine simultaneously eight geometric parameters, viz. $r(C-H)$, $r(C=O)$, $r(C-C)$, $r(C-S)$, $\angle C-S-C$, $\angle S-C=O$, $\angle C-C-S$, and $\angle H-C-H$ (p_1-p_8), and eight vibrational amplitudes (l_1-l_8). The following correlation coefficients had values larger than |0.6|: $p_6/p_7 = -0.76$, $p_6/l_4 = 0.63$, $p_6/l_5 = 0.74$, and $p_7/l_4 = -0.71$. The geometric parameters are listed, together with the X-ray and quantum chemical results in Table 4 and the vibrational amplitudes in Table 5. The structure of the molecule in the optimum refinement is illustrated in Figure 5.

Table 4. Experimental and Calculated Geometric Parameters of Diacetyl Sulfide^a

	GED ^b	X-ray ^c	MP2/ 6-31+G* ^e	B3LYP/ 6-31+G* ^e
C-H	1.109(9)	p_1	1.092	1.094
C2=O1	1.198(2)	p_2	1.196(2)	1.219
C3=O2	1.196(2) ^f		1.199(2)	1.217
C1-C2	1.483(4)	p_3	1.494(2)	1.512
C3-C4	1.472(4) ^f		1.488(2)	1.501
S-C2	1.787(3)	p_4	1.808(2)	1.805
S-C3	1.808(3) ^f		1.805(2)	1.826
C-S-C	108.8(9)	p_5	109.4(1)	108.9
S-C2=O1	125.7(6)	p_6	124.2(1)	125.5
S-C3=O2	115.1(6) ^f		114.3(1)	114.9
S-C2-C1	111.2(7)	p_7	110.9(1)	111.1
S-C3-C4	121.1(7) ^f		121.8(1)	121.0
H-C-H	109.8(20)	p_8	109.5	109.1
$\phi(C3-S-C2=O1)$	0.0 ^d	-	0.0	0.0
$\phi(C2-S-C3=O2)$	180.0 ^d	-	180.0	180.0

^a Distances in angstroms; angles in degrees. For atom numbering, see Figure 5. ^b r_a values with 3σ uncertainties. ^cDifference to preceding value constrained to calculated value (MP2). ^dNot refined. ^eMean values for parameters that are not unique.

Table 5. Interatomic Distances and Experimental and Calculated (B3LYP/6-31+G*) Vibrational Amplitudes (Excluding Distances Involving Hydrogen Atoms)^a

atom pair	distance	exptl amplitude ^b		calcd amplitude
C=O	1.20	0.037(3)	l_1	0.038
C-C	1.47-1.48	0.052(4)	l_2	0.052
S-C	1.79-1.81	0.055(3)	l_3	0.058
S...O1	2.67	0.082(11)	l_4	0.061
S...O2	2.56	0.082(11)	l_4	0.067
S...C1	2.70	0.084(19)	l_5	0.075
S...C4	2.87	0.084(19)	l_5	0.072
O1...C1	2.36	0.068(7)	l_6	0.060
O2...C4	2.36	0.068(7)	l_6	0.060
O1...C4	2.83	0.136 ^c		0.136
C2...C3	2.92	0.084 ^c		0.084
O1...C3	3.16	0.126(16)	l_7	0.113
C2...C4	3.18	0.126(16)	l_7	0.105
C2...O2	4.01	0.104(25)	l_8	0.080
O1...O2	4.35	0.126(16)	l_7	0.109
C1...C3	4.24	0.104(25)	l_8	0.085
C1...C4	4.66	0.126(16)	l_7	0.108
C1...O2	5.21	0.104(25)	l_8	0.086

^a Values in angstroms. For atom numbering, see Figure 5. ^bError limits are 3σ values. ^cNot refined.

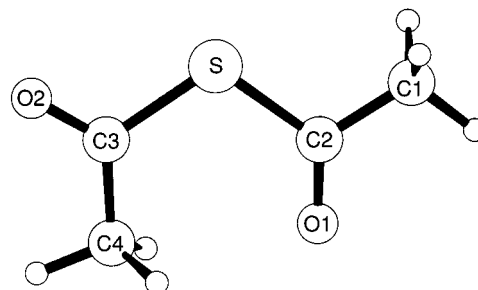


Figure 5. Optimum molecular model associated with the gas electron diffraction pattern of $CH_3C(O)SC(O)CH_3$.

Inclusion of small contributions (<10%) of a [sp,sp] conformer in the electron diffraction analysis did not improve the fit of the experimental intensities; inclusion of larger contributions led to an increase of the agreement factor. Taken alone, the electron diffraction method cannot exclude small contributions from other conformers; the results, however, are consistent with the conclusions drawn from the quantum chemical analysis

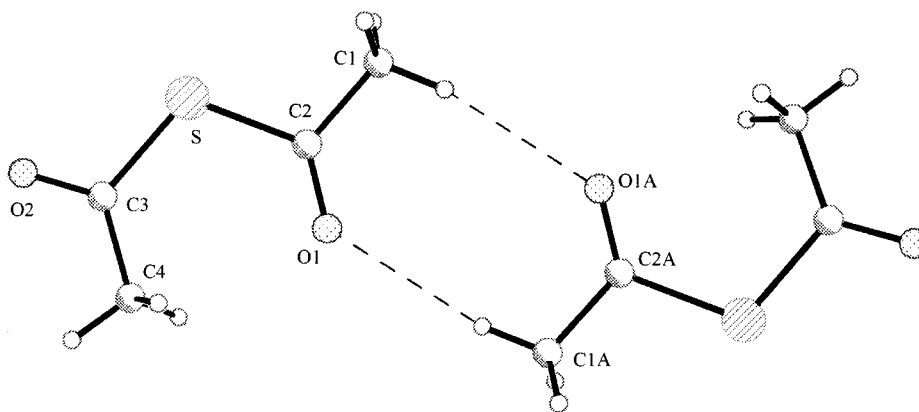


Figure 6. Dimeric assembly in the crystal structure of $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$.

and vibrational spectroscopic studies, namely, that the [sp,ap] conformer outstrips any other for the molecules that make up the vapor at ambient temperatures.

While theory has played a part in constraining the analysis of the electron diffraction pattern, there is satisfactory agreement between the equilibrium dimensions delivered by the calculations and the vibrationally averaged ones delivered by experiment. The dimensions themselves are unremarkable. Within experimental error, for example, the $\text{C}=\text{O}$ and $\text{C}-\text{C}$ distances are not significantly different from those in other molecules of the type $\text{CH}_3\text{C}(\text{O})\text{XC}(\text{O})\text{CH}_3$, where $\text{X} = \text{CH}_2$,¹ NH ,² and O ,^{3,4} with values falling in the ranges 1.18–1.23 and 1.49–1.54 Å, respectively. The $\text{C}-\text{S}$ distances in $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$ [1.787(3) and 1.808(3) Å] are on average somewhat shorter than those in $(\text{CH}_3)_2\text{S}$ [1.807(2) Å]²⁸ and distinctly shorter than those in $(\text{Me}_3\text{C})_2\text{S}$ [1.854(5) Å].²⁹ By contrast, the $\text{C}-\text{S}-\text{C}$ bond angle appears to open out from 99.1(1)° in $(\text{CH}_3)_2\text{S}$ ²⁸ to 108.8(9)° in the acetyl derivative, and to 113.2(12)° in $(\text{Me}_3\text{C})_2\text{S}$.²⁹ The corresponding angles in other molecules of the type $\text{CH}_3\text{C}(\text{O})\text{XC}(\text{O})\text{CH}_3$ are reported to be 114.0(36)°, 129.2(10)°, and 116.5(20)/121.0(15)° for $\text{X} = \text{CH}_2$,¹ NH ,² and O ,⁴ respectively. No very clear pattern emerges from these values, and it is impossible to judge the relative importance of steric and electronic effects, particularly when the pattern itself may be appreciably perturbed by “shrinkage”, allowance for which has rarely been ventured.

The asymmetry of the $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$ molecule in the [sp,ap] conformation, with one $\text{C}=\text{O}$ group syn and the other anti to the methyl group of the adjacent acetyl fragment, is reflected in the slightly different distances and angles calculated for the two acetyl functions. According to the MP2 calculations, for example, the acetyl group featuring the anti $\text{C}=\text{O}$ group has a $\text{C}=\text{O}$ bond 0.002 Å shorter, a $\text{C}-\text{C}$ bond 0.011 Å shorter, and a $\text{C}-\text{S}$ bond 0.021 Å longer than its syn counterpart. This suggests that the carbonyl groups differ slightly in their electronic makeup, as well as being more obviously different in their environmental aspect. How the variance might operate with regard to intermolecular interactions in the condensed phases is revealed in the next section, where we discuss the crystal structure of the compound.

4. Crystal Structure. Diacetyl sulfide crystallizes in the monoclinic space group $P2_1/n$ with four $\text{CH}_3\text{C}(\text{O})\text{SC}(\text{O})\text{CH}_3$ molecules per unit cell. The more or less discrete molecules have a planar skeleton with the [sp,ap] conformation favored

by the gaseous molecules. Selected bond distances and angles, included in Table 4, reveal only minor changes of dimensions compared with the gaseous molecule, although comparisons are clouded somewhat by differences of temperature and technique, with X-ray diffraction, unlike electron diffraction, measuring distances between centers of maximum electron density. How the molecules are packed in the crystal is illustrated in Figure 6.

It is Figure 6 that reveals perhaps the most significant aspect of the crystal structure, namely, that the molecules aggregate loosely to form *dimeric* assemblies, the two molecules being related by a crystallographic inversion center. The interaction depends on what might be regarded as weak hydrogen bridging between an sp $\text{C}=\text{O}$ group of one molecule and the CH_3 group of an sp acetyl substituent carried by a second molecule, to complete an eight-membered ring. The $\text{C}\cdots\text{O}$ and $\text{H}\cdots\text{O}$ separations and $\text{C}-\text{H}\cdots\text{O}$ angle associated with the interaction are found to be 3.502(2) Å, 2.53 Å, and 171°, respectively. The effect of the interaction is also apparent through the dimensions of the relevant (sp) acetyl groups compared with those of the noninteracting ap acetyl groups: while the $\text{C}=\text{O}$ bond distances do not change significantly, the $\text{C}-\text{C}$ bonds are 0.006 Å shorter, and the $\text{C}-\text{S}$ bonds are not longer (as in the gaseous molecule) but 0.003 Å shorter.

The short $\text{C}-\text{H}\cdots\text{O}$ contacts evident in the crystal structure of diacetyl sulfide are certainly not unprecedented. Indeed, there has been a wave of interest in the past decade in weak “hydrogen bonds” in general,³⁰ and $\text{C}-\text{H}\cdots\text{O}$ interactions in particular.³¹ The energy of a $\text{C}-\text{H}\cdots\text{O}$ interaction is difficult to determine experimentally, but on the evidence of quantum chemical estimates, it is judged typically to be ≤ 2 kcal mol⁻¹,³¹ and there has been considerable debate about whether the interaction should be categorized as a true hydrogen bond.^{31,32} Whatever its origin, the interaction is now generally recognized as having a potentially significant influence on crystal packing, molecular conformation, molecular recognition, and stabilization of inclusion complexes. A survey of $\text{C}-\text{H}\cdots\text{O}=\text{C}$ contacts finds $\text{C}\cdots\text{O}$ and $\text{H}\cdots\text{O}$ separations and $\text{C}-\text{H}\cdots\text{O}$ angles typically in the ranges 3.1–3.5 Å, 2.2–2.6 Å, and 150–160°, respectively. While the characteristics of the $\text{C}-\text{H}\cdots\text{O}$ contacts in crystalline diacetyl sulfide at 150 K may suggest a directional interaction

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consistent with hydrogen bonding, this interaction is plainly only weak, even by C—H \cdots O standards. It is, for example, comparable with that in the stable orthorhombic phase of solid acetone for which the shortest H \cdots O contacts, measuring 2.51 Å at 150 K, are judged to be important only at 5 K.³³

Weak the C—H \cdots O=C intermolecular interaction may be in solid diacetyl sulfide, but it operates for one acetyl group and not the other. Now that the structure has been shown to consist exclusively of the [sp,ap] rotamer, it is necessary to reconsider the interpretation of the IR spectrum exhibited by the solid and, particularly, the two absorption bands appearing in the $\nu(\text{CO})$ region.⁷ Conformational change now being excluded, it seems much more likely that the two bands relate to the sp and ap acetyl fragments. The $\nu(\text{CO})$ mode of the noninteracting ap unit then occurs at wavenumbers close to that of the gaseous molecule (about 1730 vs 1739 cm⁻¹), whereas the corresponding mode of the interacting sp unit is shifted to lower wavenumber (1703 cm⁻¹). This interpretation is in agreement with the expected behavior of a dimeric unit, as modeled in B3LYP/6-31+G*. For a dimeric assembly with the C \cdots O and H \cdots O distances and C—H \cdots O angle of 3.604 Å, 2.511 Å, and 177.4°, respectively, the $\nu(\text{CO})$ mode of the noninteracting ap acetyl group is predicted to be at 1801 cm⁻¹ with an intensity of 595 km mol⁻¹ and the $\nu(\text{CO})$ mode of the interacting sp unit at 1779 cm⁻¹ with an intensity of 811 km mol⁻¹. The calculated separation between the two is thus 22 cm⁻¹, as against the experimentally observed one of 36 cm⁻¹.

We cannot be sure that the same applies to the liquid, which also displays two bands in the $\nu(\text{CO})$ region of the IR and Raman spectra (centered at 1769 and 1712 cm⁻¹).⁷ The change of wavenumber undoubtedly reflects the (unknown) permittivity of the medium, but it seems quite plausible that the carbonyl groups of the sp and ap acetyl substituents should again respond differently to the environment of the molecule, irrespective of whether this results in the formation of specific aggregates of the sort identified by the crystal structure. Overall, then, our findings must serve as a warning against undue reliance on vibrational spectroscopy as a probe of molecular conformation, especially in the condensed phases. At the same time, they highlight the importance of quantum chemical calculations as a guide to the interpretation of these and other experimental results.

Conclusions

We have carried out a study of the structural and vibrational properties of diacetyl sulfide with particular reference to the conformation favored by the CC(O)SC(O)C skeleton. For this purpose we have drawn on both experiment for measurements of the vibrational spectra, of the electron diffraction pattern of the vapor, and of X-ray diffraction for a single crystal at 150 K, and theory for HF, MP2, and density functional theory (DFT) calculations. All the evidence points to a situation dominated by a single rotamer having a planar [sp,ap] configuration not only in the vapor at normal temperatures but also in the crystalline solid at 150 K. The experiments give no sign of any other rotamer, the IR spectrum of the vapor trapped in a solid Ar or N₂ matrix implying that at least 99% of the vapor molecules have the [sp,ap] form. The quantum chemical calculations identify two other stable, nonplanar rotamers, one with an [sp,sp] and the other with an [ap,ap] skeleton. The potential energy minimums of these are estimated to lie above the global minimum representing the [sp,ap] configuration by

1.0–2.4 and 6.5–7.6 kcal mol⁻¹, respectively. While the [ap,ap] conformer is unlikely on this basis to make a significant contribution to the vapor, the [sp,sp] one might be expected to account for 1–16% of the gaseous molecules at room temperature. It is probable, therefore, that the theoretical methods we have used have underestimated somewhat the energy separation between the [sp,ap] and [sp,sp] conformers.

Changes in the vibrational spectra of the compound accompanying the transition from the vapor to the condensed phases we attribute to the different environmental responses of the sp and ap carbonyl functions. The crystal structure gives specific notice of this with the revelation that the molecules aggregate loosely in dimer pairs with weak but significant C—H \cdots O=C interactions between the ap acetyl groups of the two molecules.

The conformational behavior of diacetyl sulfide is therefore not very different from that of the rather thinly characterized CH₃C(O)CH₂C(O)CH₃ molecule^{1,12} and the better characterized CH₃C(O)NHC(O)CH₃ molecule.^{2,13–15} Curiously, though, acetic anhydride, CH₃C(O)OC(O)CH₃, behaves differently, the vapor consisting, it appears,⁴ of a mixture of nonplanar conformers of the types [sp,ac] and [sp,sp]. It thus stands apart not only from the sulfide but also from the anhydrides HC(O)OC(O)-H³⁴ and CH₃C(O)OC(O)H,³⁵ which have both been reported to favor planar [sp,ap] conformations. The preference of the formyl compounds for this particular configuration is judged to be a result, at least in part, of an attractive interaction between the formyl H atom and the oxygen of the distal carbonyl group.^{34,35} For a molecule of the type YC(O)OC(O)Y, the conformational choice appears to involve a tradeoff between the dipole–dipole interaction between the O=C(Y)O groups on one hand and nonbonded Y \cdots Y or Y \cdots O repulsions on the other. The [sp,-ap] form is superior to the [sp,sp] form in affording dipole–dipole attraction between the O=C(Y)O groups but inferior in the nonbonded Y \cdots O repulsions it produces (see Figure 1). Only for the smallest Y groups, e.g., Y = H, is the attractive interaction expected to prevail. Larger Y groups without the potential for any secondary bonding, e.g., Y = CH₃, will otherwise generate Y \cdots O repulsions sufficient to disfavor the planar [sp,ap] conformation, causing the molecule to seek out alternatives to achieve its minimum energy. It is for this reason presumably that acetic anhydride behaves differently from its formyl analogues.

Extension of these arguments to molecules of the type YC(O)XC(O)Y introduces at least two additional factors. First, there is the mesomeric effect, which stabilizes a planar skeleton and which varies with the nature of the central atom or group X. In the case of diacetyl sulfide, for example, there is some potential for conjugation between the $\pi(\text{lp})$ orbital of the sulfur atom and the two C=O π bonds. Second, the dimensions of the C—X—C unit affect critically the O=C(Y)X dipole–dipole interactions and the Y \cdots Y or Y \cdots O nonbonded repulsions. As the C—X distance increases, the C—X—C bond angle expands, or both occur, the energies of the two interactions inevitably decrease, but the short-range repulsion term at a much faster rate than the long-range dipolar term. Hence, the dipolar term may be expected to assume greater influence in these circumstances. It is noteworthy, then, that the separation between the two carbon atoms of the carbonyl groups in CH₃C(O)XC(O)CH₃ molecules ranges from 2.330/2.416 Å for X = O [sp,sp]/[sp,ac],⁴ through 2.732 Å for X = CH₂ [sp,ap]¹ and 2.743 for X = NH [sp,ap],²

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to 2.923 Å for X = S [sp,ap]. Accordingly, the anomalous status of acetic anhydride appears to depend mainly on steric factors arising from the shortness of the central C—O bonds.

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Supporting Information Available: X-ray crystallographic data for diacetyl sulfide (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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