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Diketene and Its Cyclic $C_4H_4O_2$ Isomers 1,3-Cyclobutanedione and 2,4-Dimethylene-1,3-dioxetane

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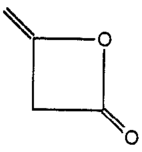
Abstract: The three title compounds are single-bonded four-membered carbon–oxygen rings with =O or =CH_2 moieties attached to diagonally opposed carbon atoms. These three isomers have been studied via ab initio quantum mechanical methods. Molecular structures, harmonic vibrational frequencies, and infrared intensities have been evaluated at the self-consistent field (SCF) level of theory with a double-ζ plus polarization (DZ+P) basis set. Relative energies have been predicted at higher levels of theory, namely single- and double-excitation configuration interaction (CISD) and coupled cluster (CCSD). Agreement with molecular structures from electron diffraction and X-ray crystallography is only fair. Direct comparison with experimental rotational constants from microwave spectroscopy suggests that the theoretical predictions are more reliable. Five of the fundamental vibrational frequencies of diketene are reassigned in light of the present theoretical predictions. For 1,3-cyclobutanedione three previously unidentified features of the IR spectrum are assigned. The 1,3-cyclobutanedione isomer is predicted to lie only 1 kcal below diketene. The unknown 2,4-dimethylene-1,3-dioxetane is predicted to lie 32 kcal above diketene and should be a makable molecule.

In his comprehensive 1986 review on the diketene molecule, Clemens[1] notes that the elucidation of the geometrical structure of diketene required 45 years, ending in 1952 with a definitive X-ray diffraction study by Katz and Lipscomb.[2] Among the alternative structures considered was the more symmetrical 1,3-cyclobutanedione.



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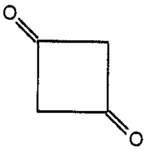

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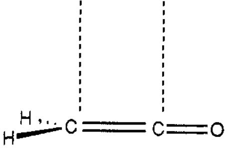
Considering that, true to its name, diketene is prepared by the dimerization of ketene, a reaction pathway of the type



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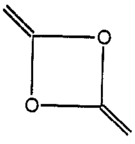
leading to **2** is potentially attractive. A third isomer that cannot be too far removed energetically is the diether structure



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which may be called 2,4-dimethylene-1,3-dioxetane. The energetic relationships between structures **1**, **2**, and **4** cannot be trivial, since one intuitively expects either the structure with zero R–O–R ether linkages (**2**) or the structure with two R–O–R moieties (**4**) to lie lowest.

As may be seen in the 77-page review by Clemens,[1] diketene (**1**) is an important and very well-characterized molecule. This view is reinforced by *Chemical Abstracts* listing of 1100 references to this molecule for the period (1986–1988) following the Clemens review.[1] Pertinent to the present theoretical study are the structural and spectroscopic studies of diketene. Following the pioneering 1952 crystallographic work by Katz and Lipscomb,[2] a refinement of the crystal structure was reported in 1958 by Kay and Katz.[3] This resulted in C—C single-bond distances of 1.54 Å (adjacent to C=C) and 1.51 Å (adjacent to C=O). The experimental C=C distance, 1.32 Å, is slightly shorter than normal for a carbon–carbon double bond. The crystallographic results[2,3] are in qualitative agreement with the electron diffraction work (1955) by Bregman and Bauer,[4] who reported both C—C single-bond distances as 1.52 Å and the C=C distance as 1.31 Å.

In light of the synthetic importance of diketene, it is surprising that no structural study has appeared since 1958, given that the experimental bond distances are stated[3] to be uncertain to ±0.03 Å. Some constraints on any experimental or theoretical molecular structure for diketene are provided by the 1967 microwave spectroscopic study by Mönnig, Dreizler, and Rudolph.[5] The latter authors report experimental rotational constants A, B, and C for the common isotopic variants of diketene. Mönnig, Dreizler, and Rudolph also report experimental dipole moment components $\mu_a = 2.28_9 \pm 0.02$ and $\mu_b = 2.66_7 \pm 0.02$ D, from which a total dipole moment of 3.51 ± 0.02 D may be deduced.

Raman[6,7] and infrared[8-12] vibrational studies of diketene go back to 1935 and 1946, respectively. The most comprehensive analysis of the fundamental vibrational frequencies of diketene is the 1966 work by Durig and Willis,[11] who also report and summarize IR and Raman spectra of the perdeuterated compound diketene-d_4. The only vibrational study of diketene since 1966 to yield new information concerning the fundamental vibrational frequencies

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is the far-IR study by Carreira and Lord.[12] The latter authors conclude that their absorption peak at 128.8 cm^{-1} is best assigned to the harmonic ring-puckering vibration.

The 1,3-cyclobutanedione molecule was first synthesized in 1962 by Wasserman and Dehmlow.[13] They also reported a strong IR band in $CHCl_3$ at 1755 cm^{-1} and a weak band at 1570 cm^{-1}, the latter identified with the C=C stretch. An apparently improved synthesis was reported in 1985 by Pericas, Serratosa, and Valenti.[14] These authors report infrared features at 1158, 1340, and 1765 cm^{-1} in $CHCl_3$. Another paper pertinent to our research is that of Chickos, Sherwood, and Jug.[15] These authors report the gas-phase heat of combustion of 1,3-cyclobutanedione ($\Delta H_c{}^{25}(g) = -468.3 \pm 1.0$ kcal/mol) and compare it with that reported earlier[16] for diketene (−467.4 kcal/mol). If both measurements[15,16] are correct, then the gas-phase enthalpy difference between diketene and 1,3-cyclobutanedione at 25 °C is 1 ± 1 kcal/mol, with the cyclobutanedione molecule lying slightly lower.

In the remainder of this paper, we will abbreviate the 1,3-cyclobutanedione molecule as simply "cyclobutanedione". That is to say, the other isomer, 1,2-cyclobutanedione, will never be considered in this research. The third diketene isomer, 2,4-dimethylene-1,3-dioxetane (**4**), has never been synthesized. For simplicity we will refer to **4** in the present research as dimethylenedioxetane, or even more simply as "the dioxetane structure".

The goal of this paper is to report a reasonably comprehensive ab initio quantum mechanical study, at a fairly substantial level of theory, of the three diketene isomers **1**, **2**, and **4**. Thus, we present molecular equilibrium structures, vibrational frequencies, infrared intensities, and relative energies for diketene, cyclobutanedione, and dimethylenedioxetane.

Previous Theoretical Work

There has been a significant amount of earlier theoretical endeavor on the diketene isomers, and this work must be mentioned. Perhaps the first modern theoretical study of any of these systems was the 1975 work of Jug and Chickos,[17] who applied a modified INDO[18] procedure to the mechanistic pathways for ketene dimerization, i.e., formation of **1**. The most interesting result of the Jug–Chickos study is their prediction that the dimerization of ketene to diketene (**1**) appears to violate the Woodward–Hoffmann rules.[19]

Quite a number of theoretical studies of diketene have been motivated by the important 1970 paper by Swenson and Hoffmann.[20] From semiempirical theoretical methods, Swenson and Hoffmann showed that there should be a sizable interaction between the nonbonding electron pairs in certain diketones. The first theoretical study to explore this "through-bond" interaction for diketene was that of Baiardo, Spafford, and Vala.[21] Using extended Hückel[22] and modified CNDO[23] methods, Baiardo concluded that through-bond effects are more important then through-space effects in explaining the photoelectron spectra of tetramethyl-1,3-cyclobutanedione.

In 1978 Jug, Dwivedi, and Chickos[24] broadened the scope of their theoretical study[17] of 3 years previous. Specifically, they examined the transition states for the isomerization of diketene to cyclobutanedione **2** and to dioxetane structure **4**. Their work utilized the semiempirical SINDO method developed by Jug's group. Perhaps the most interesting prediction by Jug, Dwivedi, and Chickos[24] was the suggestion that dimethylenedioxetane **4**, lies 12 kcal/mol below diketene (**1**). Since **4** has never been made, the theoretical prediction might appear to represent a genuine challenge to experiment. However, Jug, Dwivedi, and Chickos state that "the calculations appear to overestimate the stability of" dioxetane structure **4**.

The first ab initio quantum mechanical studies related to the diketene problem were those of Pasto, Chapman, and Worman[25] and Pasto, Chipman, and Huang.[26] In the first of these studies, the authors return to the question of through-space and through-bond interactions in cyclobutanedione **2** and related systems. With use of an STO-3G minimum basis set,[27] the molecular structure of **2** was partially optimized at the self-consistent field (SCF) level of theory. Pasto, Chipman, and Worman conclude that[25] through-bond interaction energies are 3–25 times greater than through-space interaction energies. The accompanying paper by Pasto, Chipman, and Huang[26] uses similar methods to interpret experimental photoelectron spectra. A related photoelectron spectroscopic investigation incorporating some theoretical results for cyclobutanedione appeared in 1986 by Lasne, Ripoll, Lafon, Gonbeau, and Pfister-Guillouzo.[28]

Certainly the most comprehensive theoretical study of the three ketene dimers is that reported in 1988 by the Beijing Normal University group of Fu, Decai, and Yanbo.[29] In fact, we were surprised at the appearance of their paper since it incorporates several goals of the present research, which was nearly completed when the Beijing Normal paper appeared in 1988. Fu, Decai, and Yanbo[29] report fully optimized minimum basis set[27] SCF molecular structures for diketene (**1**), cyclobutanedione **2**, and the dioxetane **4**. MBS-SCF theory predicts **2** to lie 3.0 kcal below **1**. Dioxetane molecule **4** is similarly predicted to lie 20.7 kcal above **2**. Single-point computations at the MBS-SCF stationary-point geometries were carried out with second-order perturbation theory in conjunction with the larger split-valence 4-31G basis set.[30] At this level of theory the predicted relative energies are 0.0 (**2**), 6.6 (**1**), and 48.2 (**4**) kcal/mol. The only possible experimental point of reference is the earlier discussed[15,16] conclusion that cyclobutanedione lies 1 ± 1 kcal below diketene.

Theoretical Approach

With respect to structural determinations, our work may be considered an extension of that of the Beijing Normal group.[29] While they carried out MBS-SCF geometry optimizations on **1**, **2**, and **4**, a double-ζ plus polarization (DZ+P) basis was chosen for the present work. Specifically we used the Huzinaga[31]–Dunning[32] basis, which may be technically designated

$$C(9s5p1d/4s2p1d)$$

$$O(9s5p1d/4s2p1d)$$

$$H(4s1p/2s1p)$$

Polarization function orbital exponents were $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.80$, and $\alpha_p(H) = 0.75$. For the hydrogen s functions, a scale factor of $(1.2)^2 = 1.44$ was adopted. For diketene, the DZ+P basis set includes 116 contracted Gaussian basis functions.

Here each ab initio stationary point was characterized via a harmonic vibrational analysis. This was accomplished with analytic SCF second-derivative methods.[33] Moreover, the predictions of vibrational frequencies and infrared intensities[34] were a major goal of this work.

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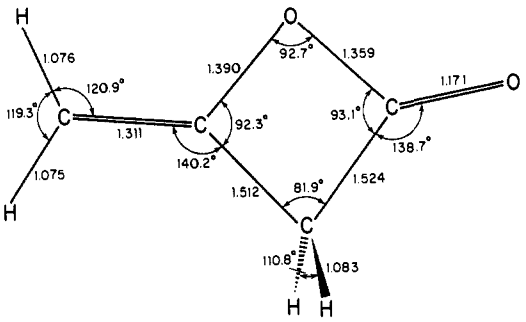

Figure 1. Theoretical equilibrium geometry for diketene (**1**), predicted at the DZ+P level of theory. All bond distances are given in angstroms.

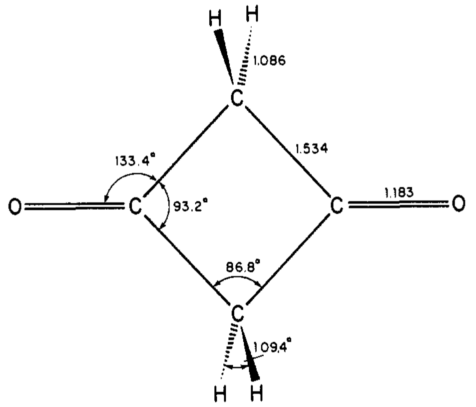

Figure 2. Theoretical equilibrium geometry for 1,3-cyclobutanedione (**2**), predicted at the DZ+P SCF level of theory. All bond distances are given in angstroms.

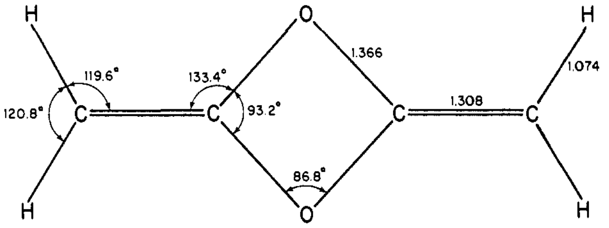

Figure 3. Theoretical equilibrium geometry for 2,4-dimethylene-1,3-dioxetane (**4**), predicted at the DZ+P SCF level of theory. All bond distances are given in angstroms.

Higher level theoretical methods were used to attempt precise predictions of the relative energies of diketene isomers **1**, **2**, and **4**. First, configuration interaction wave functions, including all single and double excitations (CISD),[35] were determined. In the CISD wave functions the six core-electron pairs (atomic 1s-like orbitals for the C and O atoms) were frozen. That is, the six lowest SCF molecular orbitals were held doubly occupied in all configurations, and the six highest molecular SCF virtual orbitals (core counterparts for a DZ or DZ+P basis set) were deleted from the CI procedure. As a simple addendum to the CISD energies, Davidson's correction[36] for unlinked quadruple excitations was attached. Finally a more complete and theoretically rigorous description of higher order correlation effects was provided by the single- and double-excitation coupled cluster method (CCSD).[37]

The largest CISD wave functions were required for diketene molecule **1**, which incorporates only a plane of symmetry, i.e., point group C_s. For diketene, there are 515 657 configurations included in the CISD wave functions.

Molecular Structures

The DZ+P SCF stationary-point geometries are shown in Figures 1–3. Subsequent vibrational analyses proved that all three structures are true minima, i.e., equilibrium geometries at this level of theory. Since only for diketene are experimental structural parameters available, we consider **1** first. The DZ+P SCF C—C single-bond distances for diketene are 1.512 Å (adjacent to C═O) and 1.524 Å (adjacent to C═O). These theoretical bond distances agree as well as could reasonably be expected with Bregman and Bauer's conclusion[4] that both C—C single-bond distances are 1.52 Å. However, the agreement between theory and the 1958 crystal structure of Kay and Katz[3] is poorer. DZ+P SCF theory predicts a difference in C—C single-bond distances of 0.012 Å, with the longer C—C bond adjacent to C═O. In contrast, Kay and Katz conclude that the C—C distance adjacent to C═C is longer (1.54 Å) than that adjacent to C═O (1.51 Å). This difference between theory and experiment is probably too large to be accounted for by crystal-packing forces or zero-point vibrational effects. Nevertheless, the two theoretical C—C bond distances do lie within the ±0.03-Å error bars given for the crystal structure.[3]

The DZ+P SCF prediction for the C═C bond distance is 1.311 Å, in perfect agreement with the 1.31 Å from the electron diffraction experiments of Bregman and Bauer. The theoretical prediction also falls within the error bars (±0.03 Å) of the *r*(C═C) = 1.32 Å from the crystal structure.[3] Thus, there is unanimous agreement that the C═C distance in diketene represents a short carbon–carbon double bond.

The predicted C—O single-bond distances are 1.359 Å (adjacent to C═O) and 1.390 Å (adjacent to C═C). Even given the generous electron diffraction error limits of ±0.04 Å, the shorter of these two distances falls below the experimental value of 1.41 Å. There exists an even more serious disagreement between theory and the experimental crystal structure for these two C—O distances. Kay and Katz[3] conclude that these distances are 1.39 Å (adjacent to C═O) and 1.47 Å (adjacent to C═C). The only comfort is the fact that theory and experiment agree on the ordering of the two carbon–oxygen single-bond distances. The fact that theory is 0.031 Å less for the shorter distance is acceptable, but the difference (1.47 − 1.39 = 0.08 Å) is surely surprising for the DZ+P SCF level of theory. Interestingly, the standard average C–O single-bond distance[38] is 1.43 Å, halfway between the theoretical prediction and experiment.

The DZ+P SCF distance for the C═O double bond is 1.171 Å, to be compared with values from electron diffraction (1.19 Å) and X-ray crystallography (1.22 Å). Theory falls comfortably within the electron diffraction bars (±0.04 Å) but outside the ±0.03-Å standard deviation for the crystallographic results. The "standard" C═O distance[38] is 1.23 Å, in closest agreement with the crystal structure.

The above discussion makes it reasonably clear that the agreement between DZ+P SCF theory and the experimental structure of Kay and Katz[3] is not good. A more rigorous check on the theory is provided by the microwave spectrum of Mönnig, Dreizler, and Rudolph.[5] They report the following rotational constants for the ground vibrational state:

$$A_0 = 12\,141.36 \pm 0.04 \text{ MHz}$$

$$B_0 = 2\,781.27 \pm 0.01 \text{ MHz}$$

$$C_0 = 2\,296.59 \pm 0.01 \text{ MHz}$$

Although these experimental results do refer to the gas-phase molecule, they are not precisely comparable to the present theoretical predictions, which refer to the equilibrium geometry:

$$A_e = 12\,430 \text{ MHz}$$

$$B_e = 2\,830 \text{ MHz}$$

$$C_e = 2\,339 \text{ MHz}$$

Nevertheless, the agreement is satisfactory, the theoretical rotational constants being 2.4%, 1.8%, and 1.8% larger than experiment. Certainly there is little indication of an error as large as

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0.08 Å in C—O bond distance, on the basis of this *direct* comparison between theory and experiment.

Since the hydrogen atom positions were not detected in the electron diffraction[4] or crystallographic[3] structure determinations, one cannot directly determine the rotational constants for these two experimental structures. However, we have made suitable rotational calculations assuming C—H parameters from the MM2 model of Allinger.[39] Specifically, the four C—H distances in diketene are assumed to be 1.09 Å and the HCH angles 108° (adjacent to two C—C single bonds) and 120° (adjacent to C=C double bond). With these assumptions the electron diffraction work of Bregman and Bauer[4] yields

$$A_{ED} = 11\,711 \text{MHz}$$

$$B_{ED} = 2\,846 \text{ MHz}$$

$$C_{ED} = 2\,323 \text{ MHz}$$

and the crystal structure of Kay and Katz[3] yields the rotational constants

$$A_x = 11\,757 \text{ MHz}$$

$$B_x = 2\,736 \text{ MHz}$$

$$C_x = 2\,250 \text{ MHz}$$

The differences with respect to the experimental A_0 constant are +289 MHz (DZ+P SCF), −430 MHz (electron diffraction), and −384 MHz (crystal structure). For B_0 the differences are +49 MHz (DZ+P SCF), +65 MHz (electron diffraction), and −45 MHz (crystal structure). For C_0 the deviations from the gas-phase experimental rotational constant are +42 MHz (DZ+P SCF), +26 MHz (electron diffraction), and −47 MHz (crystal structure). Generally speaking, these differences indicate that the theoretical equilibrium structure does the best job of reproducing the gas-phase rotational constants.

It is worth noting that all the theoretical rotational constants lie *higher* than the microwave values, while all the crystallographic derived constants lie *below* the gas-phase experimental values. Since rotational constants are generally inversely proportional to bond lengths, this means that DZ+P SCF theory predicts diketene to have bond distances too short, while the crystal structure bond distances may be too long. The latter conclusion, of course, is consistent with our earlier specific suggestion that the C—O distance of 1.47 Å adjacent to C=C is probably too long.

The predicted DZ+P SCF dipole moment μ_e is 4.08 D, compared to the experimental μ_0 value of 3.51 ± 0.02 D due to Mönnig, Dreizler, and Rudolph.[5] The theoretical prediction is a bit disappointing.

The predicted molecular structure for 1,3-cyclobutanedione is shown in Figure 2. The higher symmetry compared to diketene means that there is only one C—C distance, 1.534 Å, and only one C=O distance, 1.183 Å. The predicted carbon–carbon single-bond distances are 0.010 and 0.022 Å, respectively, longer than the two C—C lengths predicted for diketene at the same level of theory. Similarly the C=O distance 1.183 Å) is 0.012 Å longer than that predicted for diketene.

Figure 3 displays the DZ+P SCF equilibrium geometry for 2,4-dimethylene-1,3-dioxetane. This structure has four equivalent C—O single bonds of length 1.366 Å. These bonds are shorter than the standard C—O distance[38] of 1.43 Å and intermediate between the two DZ+P SCF C—O bond lengths (1.359, 1.390 Å) for diketene. The two equivalent C=C distances for the dioxetane structure are 1.308 Å, i.e., short double bonds. However, these distances are only 0.003 Å less than that predicted for diketene. Thus, although the 2,4-dimethylene-1,3-dioxetane molecule has never been prepared in the laboratory, its structural features suggest strong C—O and C=C bonds.

Some comparison with the minimum basis set SCF predictions of Fu, Decai, and Yanbo[29] is in order. This comparison is most interesting for diketene itself, where the comparison between DZ+P SCF and the available experiments[3,4] is unsettling. The STO-3G carbon–oxygen single-bond distances are both 1.421 Å, compared to 1.359 and 1.390 Å with the much larger DZ+P basis set used here. Nevertheless, the STO-3G C—O distances are in closer agreement with the experiments of Bregman and Bauer[4] (both distances 1.41 Å) and Kay and Katz (1.39 and 1.47 Å). The C=O distance from STO-3G SCF theory[29] is 1.202 Å, compared the the DZ + P value of 1.171 Å and the experimental values of 1.19 Å (electron diffraction) and 1.22 Å (X-ray crystallography). Given our above-discussed reservations concerning the two experimental structures, about all we would say is that STO-3G SCF theory is fortuitously closer to the laboratory results than is the DZ+P SCF method.

Vibrational Frequencies and Infrared Intensities

The diketene predictions from DZ+P SCF theory are summarized in Table I. There comparison is made with the experimental summary of Durig and Willis[11] and the addition ring-puckering fundamental at 128.8 cm^{-1} reported by Carreira and Lord.[12] In descending order, the differences between theory and experiment for the A′ normal modes are all positive, namely 9.6, 10.7, 9.5, 12.4, 11.8, 11.2, 10.3, 14.7, 19.2, 17.3, 10.4, 15.8, 11.8, 9.5, 9.5, and 7.1%. For the A″ frequencies the DZ+P SCF harmonic values differ from the observed fundamentals by +8.2, −11.6, −1.0, +2.6, −4.7, +12.1, 11.7, and 6.2%.

Since ab initio vibrational frequencies predicted at the DZ+P SCF level of theory usually lie higher than the experimental values,[40] the above statistics raise the possibility of a reassignment of the diketene vibrational frequencies. Most specifically, it seems unlikely that this level of theory would predict the α-CH$_2$ twist frequency (ν_{18}(A″)) to be 11.6% *below* the true fundamental.

We propose a reassignment of the A″ fundamentals of diketene. In particular, we suggest that the IR feature at 1373 cm^{-1}, assigned by Durig and Willis[11] as ν_{18}(A″), is not a fundamental of diketene. If this assumption is made, then the following correspondence between theory and experiment occurs:

	theory	expt	
ν_{18}	1214	1096	+10.8%
ν_{19}	1085	959	+13.1%
ν_{20}	984	838	+17.4%
ν_{21}	799		

The agreement between theory and experiment is quite satisfactory[40] for ν_{18} and ν_{19}, although less so for ν_{20}. In this interpretation, ν_{21} remains to be assigned experimentally.

Are the above assignments consistent with the theoretical IR intensities? The idea that ν_{21} has not been observed is eminently reasonable, since the DZ+P SCF IR intensity is only 0.06 km/mol, the smallest of all the fundamentals of diketene. Among the A″ fundamentals, theory predicts ν_{20} (γ-CH$_2$ wag) to have the highest IR intensity, namely 71 km/mol. This prediction is completely consistent with our reassignment of the experimental band at 838 cm^{-1} to ν_{20}. Durig and Willis describe the feature at 838 cm^{-1} as very strong. We assign the weak band at 959 cm^{-1} stronger than might be expected from the designation "weak". The theoretical $I(\nu_{18})$ = 2 km/mol is fully consistent with our reassignment of the weak feature observed at 1096 cm^{-1} to ν_{18}. Thus, the theoretical pattern of IR intensities agrees well with our reassignment of the fundamentals.

An interesting result of the present vibrational predictions is that they allow us to resolve a question raised by Durig and Willis.[11] Although they assign their Raman feature at 3076 cm^{-1} to ν_{17}(A″) as reported in our Table I, Durig and Willis are very clear in the tentativeness of this assignment. They state "The infrared band at 3009 cm^{-1} is considered a combination band. It is just as likely that the 3076 cm^{-1} Raman line is a combination frequency and the 3009 cm^{-1} infrared frequency is the α-CH$_2$ antisymmetric stretching vibration". We think that the latter, and not the former, assignment is correct. Our DZ+P SCF

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(39) Allinger, N. L.; Flanagan, H. L. *J. Comput. Chem.* **1983**, *4*, 399.

(40) See for example: Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *73*, 2310.

Table I. Harmonic Vibrational Frequencies, Infrared Intensities, and Potential Energy Distributions for the Diketene Molecule[a]

symmetry		description	ω (cm^{-1})	I (km/mol)
A′	1	γ-CH$_2$ antisym str (100%)	3439 (3137)	2
A′	2	γ-CH$_2$ sym str (99%)	3340 (3018)	0.3
A′	3	α-CH$_2$ sym str (99%)	3262 (2979)	4
A′	4	C=O str (77%)	2146 (1910)	581
A′	5	C=C str (67%)	1917 (1715)	390
A′	6	α-CH$_2$ deformn (83%)	1574 (1416)	18
A′	7	γ-CH$_2$ deformn (82%)	1536 (1392)	6
A′	8	C—O ring str (57%) + γ-CH$_2$ rock (14%)	1427 (1244)	142
A′	9	α-CH$_2$ wag (80%)	1339 (1123)	11
A′	10	ring deformn (str) (47%) + γ-CH$_2$ rock (20%) + C=O in-plane bend (12%)	1180 (885)	275
A′	11	ring breathing (54%) + ring deformn (bend) (29%)	1086 (673)[b]	11
A′	12	γ-CH$_2$ rock (37%) + C—C ring str (26%) + ring deformn (str) (21%)	1025 (984)	135
A′	13	C—C ring str (49%) + γ-CH$_2$ rock (17%) + ring deformn (str) (14%)	898 (1006)	4
A′	14	ring deformn (bend) (59%) + ring breathing (21%)	737 (803)[b]	3
A′	15	C=O in-plane bend (55%) + C=C in-plane bend (18%)	575 (525)	6
A′	16	C=C in-plane bend (65%)	347 (324)[b]	2
A″	17	α-CH$_2$ antisym str (100%)	3327 (3076)[b]	3
A″	18	α-CH$_2$ twist (90%)	1214 (1096)	2
A″	19	α-CH$_2$ rock (37%) + γ-CH$_2$ wag (21%) + C=O out-of-plane bend (20%)	1085 (959)	11
A″	20	γ-CH$_2$ wag (95%)	984 (838)	71
A″	21	γ-CH$_2$ twist (88%)	799 (1373)	0.06
A″	22	C=O out-of-plane bend (54%) + α-CH$_2$ rock (27%)	567 (506)	12
A″	23	C=C out-of-plane bend (55%) + γ-CH$_2$ wag (26%)	496 (444)	6
A″	24	ring puckering (42%) + C=C out-of-plane bend (32%) + γ-CH$_2$ wag (16%)	137 (129)	1

[a] Experimental frequencies, from ref 11 and 12, are given in parentheses. The prefix γ refers to the CH$_2$ group adjacent to the C=C double bond, while the prefix α refers to the CH$_2$ group adjacent to two C—C single bonds. The descriptions of the normal modes are from theory: the experimental frequencies are assigned according to ref 11. As discussed in the text, we have proposed a reassignment of seven of the experimental fundamentals. [b] Liquid-phase Raman frequencies. Obviously, the comparison between theory (gas phase) and experiment (liquid) is somewhat tenuous in these cases.

harmonic vibrational frequency ω = 3327 cm^{-1} lies 8.2% above the Raman feature at 3076 cm^{-1}. The latter difference, 10.6% (from the comparison of 3327 vs 3009 cm^{-1}), is much more typical of DZ+P SCF predictions for C—H stretching vibrational frequencies. Furthermore, the IR feature at 3009 cm^{-1} is very weak, consistent with the theoretical $I(\nu_{17}(A''))$ = 3 km/mol.

Theory and experiment agree concerning the ordering of the A′ fundamentals of diketene. However, our descriptions of the normal modes differ for ν_{10}, ν_{11}, ν_{12}, ν_{13}, and ν_{14}. It should be stated that the theoretical assignments (given in Table I) are simply the largest single contributions to the ab initio potential energy distributions (PED's). For example, DZ+P SCF theory finds that ring breathing contributes 54% to ν_{11} but only 21% to ν_{14}. Durig and Willis[11] described ν_{14} as ring breathing, while we prefer to label ν_{11} thus. Similarly, theory finds ν_{12} to be strongly mixed, 37% γ-CH$_2$ rock, 26% C—C ring stretch, and 21% ring deformation (stretch), while Durig and Willis label ν_{12} simply as "ring deformation". For a vibration as mixed as ν_{12}, it is conceivable that higher levels of theory could significantly rearrange the predicted PED's.

Some experimental data are available for the vibrational frequencies of perdeuterated diketene, i.e., diketene-d_4. The DZ+P SCF predictions are summarized in Table II. Some comment is necessary concerning the ordering of the frequencies of diketene-d_4 in Table II. Given the strong mixing of the PED's among the internal coordinates, it is no longer possible to make assignments solely on the basis of the PED's. For example, whereas for diketene-h_4, ω_7 (1536 cm^{-1}, DZ+P SCF) is characterized by its PED as 82% γ-CH$_2$ deformation; for diketene-d_4, ω_7 (1228 cm^{-1}) is 30% α-CD$_2$ deformation, 23% ring breathing, 15% γ-CD$_2$ deformation, and 13% ring deformation (stretch). To aid in the assignment of the more troublesome frequencies, use was made of the theoretical intensities. Thus, the band at 1156 cm^{-1} is assigned as ring deformation (stretch) rather than γ-CD$_2$ deformation, since its theoretical intensity (185 km/mol) corresponds more closely with ω_{10} in diketene-h_4 (275 km/mol) than with ω_7 (6 km/mol).

There also exist four pieces of experimental information concerning the infrared spectrum of 1,3-cyclobutanedione. Wasserman and Dehmlow[13] report a strong IR band in CHCl$_3$ at 1755 cm^{-1}, and Pericas, Serratosa, and Valenti[14] report what is presumably the same spectral feature at 1765 cm^{-1}. If this band is a fundamental of 1,3-cyclobutanedione, then from Table III it must be the C=O stretch (B$_{3u}$ symmetry) predicted at 2051 cm^{-1}. The DZ+P SCF harmonic vibrational frequency lies 16.5% above the observed IR band, an error somewhat larger than expected at this level of theory. However, no other allowed IR fundamental for 1,3-cyclobutanedione falls near the observed 1760-cm^{-1} band.

The weak band observed by Wasserman and Dehmlow[13] at 1570 cm^{-1} does not fit any of the predicted harmonic vibrational frequencies very well. The only conceivable correlation would be with the CH$_2$ scissor predicted at 1520 cm^{-1}. Since Pericas, Serratosa, and Valenti[14] do not observe an IR feature near 1570 cm^{-1}, it is probably the case that this band is not a fundamental of the cyclobutanedione molecule. A more reasonable correlation of the DZ+P SCF harmonic vibrational frequency predicted at 1520 cm^{-1} is with the 1340-cm^{-1} feature observed by Pericas. The difference between theoretical harmonic and experimental anharmonic frequencies would be 13.4%, an acceptable result. Similarly our predicted C—C stretching vibration (B$_{2u}$) at 1318 cm^{-1} may be plausibly identified with the observed feature at 1158 cm^{-1}, the difference between theory and experiment being 13.8%.

The proposed correlation between theory and experiment for 1,3-cyclobutanedione is particularly satisfactory in light of the theoretical infrared intensities. The three fundamentals assigned here

$$1760\ \text{cm}^{-1} \rightarrow \text{C=O stretch}$$

$$1520\ \text{cm}^{-1} \rightarrow \text{CH}_2\ \text{scissor}$$

$$1318\ \text{cm}^{-1} \rightarrow \text{C—C stretch}$$

have the three highest predicted IR intensities (823, 74, 161 km/mol). The fact that Pericas, Serratosa, and Valenti[14] observe no other IR bands fits with the theoretical prediction that the next strongest IR fundamental is weaker by a factor of 3 than the weakest of the observed features.

Diketene Isomer Relative Energies

Table V summarizes the total and relative energies predicted for diketene, cyclobutanedione, and dimethylenedioxetane. At each level of theory cyclobutanedione structure **2** is predicted to lie lowest. The energy differences between diketene (**1**) and cyclobutanedione **2** are 1.8 kcal (SCF), 0.7 kcal (CISD), and 0.8 kcal (Davidson-corrected CISD). All four levels of theory es-

Table II. Harmonic Vibrational Frequencies, Infrared Intensities, and Potential Energy Distributions for the Diketene-d_4 Molecule[a]

symmetry		description	ω (cm^{-1})	I (km/mol)	$\Delta\omega$ ($h_4 - d_4$)
A′	1	γ-CD$_2$ antisym str (98%)	2566 (2339)	1	873
A′	2	γ-CD$_2$ sym str (89%)	2454 (2257)	6	886
A′	3	α-CD$_2$ sym str (96%)	2380 (2210)	6	882
A′	4	C=O str (79%)	2141 (1910)	629	5
A′	5	C=C str (64%)	1868 (1678)	330	49
A′	6	ring deformn (str) (33%) + α-CD$_2$ deformn (22%) + α-CD$_2$ wag (17%)	1193 (944)	58	381
A′	7	α-CD$_2$ deformn (30%) + ring breathing (23%) + γ-CD$_2$ deformn (15%) + ring deformn (str) (13%)	1228 (1032)	38	308
A′	8	C—O ring str (68%) + C=O in-plane bend (15%) + C=C in-plane bend (10%)	1406 (1220)	178	21
A′	9	α-CD$_2$ wag (39%) + C—C ring str (18%) + γ-CD$_2$ deformn (17%)	1082 (895)	81	257
A′	10	γ-CD$_2$ deformn (44%) + ring deformn (str) (30%) + C—C ring str (15%)	1156 (1032)	185	24
A′	11	α-CD$_2$ deformn (35%) + ring breathing (29%) + ring deformn (bend) (24%)	990 (641)	12	96
A′	12	γ-CD$_2$ rock (27%) + C—C ring str (23%) + C=O in-plane bend (17%)	928 (695)	41	97
A′	13	γ-CD$_2$ rock (39%) + α-CD$_2$ wag (18%) + C—C ring str (15%) + ring deformn (str) (10%)	759 (1004)	0.2	139
A′	14	ring deformn (bend) (49%) + ring breathing (19%) + C=C str (15%)	703 (817)	4	34
A′	15	C=O in-plane bend (53%) + C—O ring str (11%) + C—C ring str (10%)	526 (480)	6	49
A′	16	C=C in-plane bend (65%) + γ-CD$_2$ rock (21%)	305 (281)	2	42
A″	17	α-CD$_2$ antisym str (99%)	2472 (2317)	2	855
A″	18	α-CD$_2$ twist (37%) + γ-CD$_2$ wag (31%) + C=C out-of-plane bend (26%)	933 (908)	0.07	281
A″	19	C=O out-of-plane bend (32%) + α-CD$_2$ rock (22%)	1007 (730)	12	78
A″	20	γ-CD$_2$ wag (90%)	777 (664)	40	207
A″	21	γ-CD$_2$ twist (73%) + C=C out-of-plane bend (19%)	597 (1048)	0.1	202
A″	22	C=O out-of-plane bend (39%) + C=C out-of-plane bend (19%) + α-CD$_2$ twist (18%) + α-CD$_2$ rock (14%)	491 (442)	16	76
A″	23	C=C out-of-plane bend (46%) + γ-CD$_2$ wag (18%) + α-CD$_2$ rock (18%)	408 (367)	1	88
A″	24	ring puckering (43%) + C=C out-of-plane bend (32%) + γ-CD$_2$ wag (14%)	131	0.7	6

[a] Experimental frequencies from ref 11 are given in parentheses. The prefix γ refers to the CD$_2$ group adjacent to the C=C double bond, while the prefix α refers to the CD$_2$ group adjacent to two C—C single bonds. The descriptions of the normal modes are from theory: the theoretical frequencies are reported in an order consistent with Table I. The identification of the experimental fundamentals is that of Durig and Willis.[11]

Table III. Harmonic Vibrational Frequencies and Infrared Intensities for Cyclobutanedione Molecule **2**

symmetry	description	ω (cm^{-1})	I (km/mol)
A$_g$	C—H str	3228	0
	C=O str	2137	0
	CH$_2$ scissor	1530	0
	C—C str	1007	0
	ring deformn	681	0
B$_{1g}$	CH$_2$ wag	1305	0
	C—C str	1087	0
	C—C=O wag	582	0
B$_{2g}$	CH$_2$ twist	1285	0
	C=O out-of-plane flap	470	0
B$_{3g}$	C—H str	3291	0
	CH$_2$ rock	566	0
A$_u$	CH$_2$ twist	992	0
B$_{1u}$	C—H str	3290	4
	C=O out-of-plane flap	1159	5
	CH$_2$ rock	439	2
	ring puckering	81	27
B$_{2u}$	C—H str	3224	0.01
	CH$_2$ scissor	1520	74
	C—C str	1318	161
	C—C=O wag	412	26
B$_{3u}$	C=O str	2051	823
	CH$_2$ wag	1341	0.01
	ring deformn	799	1

Table IV. Harmonic Vibrational Frequencies and Infrared Intensities for Dimethylenedioxetane Molecule **4**

symmetry	description	ω (cm^{-1})	I (km/mol)
A$_g$	C—H str	3358	0
	C=C str	2017	0
	CH$_2$ scissor	1532	0
	C—O str	1186	0
	ring deformn	783	0
B$_{1g}$	C—H str	3465.2	0
	C—O str	1226	0
	CH$_2$ rock	1033	0
	CH$_2$=C wag	483	0
B$_{2g}$	CH$_2$ twist	908	0
	CH$_2$=C out-of-plane flap	584	0
B$_{3g}$	CH$_2$ wag	736	0
A$_u$	CH$_2$ twist	745	0
B$_{1u}$	CH$_2$ wag	916	208
	CH$_2$=C out-of-plane flap	802	1
	ring puckering	154	3
B$_{2u}$	C—H str	3465.1	0.0001
	C—O str	1497	196
	CH$_2$ rock	969	26
	H$_2$C=C wag	317	0.3
B$_{3u}$	C—H str	3358	23
	C=C str	1874	1428
	CH$_2$ scissor	1513	67
	ring deformn	1008	310

Table V. Relative and Total Energies for the Three Diketene Isomers Considered in this Research (All Theoretical Studies Employed a Double-ζ Plus Polarization (DZ+P) Basis Set)

	diketene (**1**)	cyclo-butanedione **2**	dimethylene-dioxetane **3**
	Total Energies (Hartrees)		
SCF	−303.553 35	−303.556 19	−303.504 95
CISD	−304.285 40	−304.286 52	−304.235 59
CISD+Q	−304.404 83	−304.406 03	−304.354 58
CCSD	−304.446 38	−304.447 63	−304.395 67
	Relative Energies (Hartrees)		
SCF	0.0	−1.8	+30.4
CISD	0.0	−0.7	+31.3
CISD+Q	0.0	−0.8	+31.5

sentially agree with the experimental finding that **2** lies below **1** by 1 ± 1 kcal.

Not known from experiment is the energetic position of 2,4-dimethylene-1,3-dioxetane. Although cyclobutanedione molecule **2** lies slightly below **1**, we chose to make diketene (**1**) the energetic standard of comparison, because **1** is much more completely characterized experimentally than **2**. Dioxetane structure **4** is predicted to lie above diketene by 30.4 kcal (SCF), 31.3 kcal (CISD), and 31.5 kcal (Davidson-corrected CISD). These energetic predictions are surprisingly consistent, demonstrating that correlation effects are remarkably unimportant in positioning these $C_4H_4O_2$ isomers.

Relative to 1,3-cyclobutanedione the dioxetane structures lies at 32.2 kcal (SCF), 32.0 kcal (CISD), 32.3 kcal (Davidson-corrected CISD), and 32.6 kcal (CCSD). Thus, the coupled cluster results exert only a modest correction to the CISD predictions.

As noted in Previous Theoretical Work, Jug, Dwivedi, and Chickos[24] predicted dioxetane structure **4** to lie below diketene by 12 kcal. However, since the dioxetane structure had never been observed, those authors concluded that their prediction must be incorrect. We confirm this argument of Jug, Dwivedi, and Chickos in the present research by showing that the dioxetane structure lies about 31 kcal above diketene. The second-order perturbation theory prediction (4-31G basis set) of 48.2 kcal for ΔE ($1 \rightarrow 4$) by Fu, Decai, and Yanbo[29] appears somewhat high in this regard.

Concluding Remarks

We have reported a comprehensive theoretical study of diketene (**1**), 1,3-cyclobutanedione (**2**), and 2,4-dimethylene-1,3-dioxetane (**4**). Of these, diketene is well-characterized experimentally, and the theoretical predictions are broadly concordant. However, in light of differences between theory and the two existing experimental structures (both unfortunately dating from the 1950s), a precise modern structural study would be most welcome.

Most of the theoretical results for cyclobutanedione **2** and dioxetane **4** structures are true predictions; i.e., there are no experiments with which to make comparison. However, this work has allowed us to assign three previously unidentified features of the infrared spectrum of 1,3-cyclobutanedione. We hope that the present theoretical predictions will stimulate new experiments on 1,3-cyclobutanedione, which is essentially degenerate with the better known diketene molecule. The dioxetane structure lies only about 32 kcal above diketene and is a genuine minimum on the DZ+P SCF potential energy hypersurface. The synthesis of the dioxetane isomer should be achievable and would be an important scientific accomplishment.

This paper has not attempted to explain the observed primary formation of diketene over 1,3-cyclobutanedione from two ketenes. The equilibrium thermodynamic results do not seem to provide any hint concerning the answer to this question. In the future we hope to carry out detailed quantum mechanical studies of the various transition states for ketene dimerization.

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A Theoretical Study of the Reaction of Ground-State Silicon with Ethylene and Acetylene

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Abstract: It has recently been demonstrated by kinetic studies that the reaction of Si(^{3}P) with C_2H_4 proceeds at almost unit collisional efficiency. In this paper the corresponding potential surfaces have been examined by ab initio methodology, by using the UMP2 method with spin projection. It is found that the lowest triplet equilibrium structure is a silacyclopropylidene structure ($^3A_2$), for which there is no barrier to its formation. Fourteen other low-lying triplet structures are also reported. A similar study is also reported for Si(^{3}P) with C_2H_2.

I. Introduction

In a recent publication, Basu and Husain[1] reported absolute rate data for the reaction of ground-state atomic silicon, Si(^3P_J), with olefins determined by time-resolved atomic resonance absorption spectroscopy. In particular the decay of the ground-state Si was monitored in the presence of ethylene, for which the absolute second-order rate constant (k_R, T = 300 K) was measured as $8.8 \pm 1.5 \times 10^{-11}$ cm^3 mol^{-1} s^{-1}. This implies that the reaction proceeds at close to unit collisional efficiency. The evidence therefore is that one or more stable complexes are formed from the reaction of Si(^{3}P) with C_2H_4. Our purpose is to study the approach of Si(^{3}P) to C_2H_4, locating in particular minima and barriers in any reaction pathway. Basu and Husain refer to some earlier ab initio calculations. Barthelat, Trinquier, and Bertrand[2] performed pseudopotential SCF studies on SiC_2H_4, finding that silylacetylene, $SiH_3{-}C{\equiv}CH$ (**14**), was the most stable singlet structure, with silacyclopropene and silacyclopropylidene, **1**, both being 17 kcal/mol higher in energy (see Figure 1). Silaallene $CH_2{=}Si{=}CH_2$ is much higher in energy at 46 kcal/mol, and silapropyne $CH_3Si{\equiv}CH$ is 60 kcal/mol higher. Double-ζ closed shell SCF geometry optimizations were performed by Lien and Hopkinson,[3] who confirmed some of the previous findings. They found silylacetylene to be the lowest, with silacyclopropene and silacyclopropylidene being 15.2 and 17.2 kcal higher in energy. Vinylsilylene, **3** $CH_2{=}CH{-}SiH$, and ethylidenesilylene, $CH_3{-}CH{=}Si$ **6**, were also investigated and found to be 15.4 and 18.0 kcal higher in energy. They observe therefore that silacyclopropene and three divalent structures all lie within 20 kcal of the lowest state. More sophisticated calculations at the SCF level (6-31G*//3-21G) (closed shell) were carried out by Gordon and Koob,[4] who found similar results.

The situation is therefore very different to the analogous carbon structures (see Figure 3). The most detailed calculations, of relevance to this work, are by Yoshimine, Honjou, and Pacansky,[5] who report SCF and CI studies of C_3H_4. They show that the trans planar carbene **18** ($^3A''$) lies 50 kcal/mol above the almost degenerate singlet states of allene and methylacetylene, with the $^3B_1$ cyclopropylidene **15** structure lying 26 kcal/mol above the $^3A''$ **18** structure. Predominately Yoshimine et al. were concerned with singlet structures, but they state that cyclopropylidene has a singlet ground state, lying 12 kcal/mol below the $^3B_1$ **15** structure.

There are very few calculations on triplet states of SiC_2H_4. Barthelat et al.[2] report that the $^3B_1$ silacyclopropylidene (**1b**) lies 51.6 kcal/mol above the singlet silylacetylene **14**. Krogh-Jespersen[6] has performed the most accurate studies to date. In

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