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# Thermochemical Properties and Contribution Groups for Ketene Dimers and Related Structures from Theoretical Calculations

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This research's main goals were to analyze ketene dimers' relative stability and expand group additivity value (GAV) methodology for estimating the thermochemical properties of high-weight ketene polymers (up to tetramers). The CBS-Q multilevel procedure and statistical thermodynamics were used for calculating the thermochemical properties of 20 cyclic structures, such as diketenes, cyclobutane-1,3-diones, cyclobut-2-enones and pyran-4-ones, as well as 57 acyclic base compounds organized into five groups. According to theoretical heat of formation predictions, diketene was found to be thermodynamically favored over cyclobutane-1,3-dione and its enol-tautomeric form (3-hydroxycyclobut-2-enone). This result did not agree with old combustion experiments. 3-Hydroxycyclobut-2-enone was found to be the least stable dimer and its reported experimental detection in solution may have been due to solvent effects. Substituted diketenes had lower stability than substituted cyclobutane-1,3-diones with an increased number of methyl substituents, suggesting that cyclobutane-1,3-dione type dimers are the major products because of thermodynamic control of alkylketene dimerization. Missing GAVs for the ketene dimers and related structures were calculated through linear regression on the 57 acyclic base compounds. Corrections for non next neighbor interactions (such as gauche, eclipses, and internal hydrogen bond) were needed for obtaining a highly accurate and precise regression model. To the best of our knowledge, the hydrogen bond correction for GAV methodology is the first reported in the literature; this correction was correlated to MP2/6-31G† and HF/6-31G† derived geometries to facilitate its application. GAVs assessed by the linear regression model were able to reproduce acyclic compounds' theoretical thermochemical properties and experimental heat of formation for acetylacetone. Ring formation and substituent position corrections were calculated by consecutively replacing the GAVs regarding the 20 cyclic structures' thermochemical properties.

## Introduction

Ketenes are versatile compounds due to the class of products they can yield in broad types of reactions.[1] Ketenes are of major importance as starting materials in $\beta$-lactam formation (leading to penicillins by [2 + 2] cycloaddition with imines[1a−c]) and prostaglandin precursor formation[1d] and in the synthesis of $\alpha$-amino acid derivatives[1e] and ketene heterodimer production for proteasome inhibitor synthesis.[1f] Ketenes can also be polymerized in different routes due to their structures' double conjugated bonds ($nR_1R_2C{=}C{=}O$). Diketenes (4-methyleneoxetan-2-ones) ($n = 2$), cyclobutane-1,3-diones ($n = 2$) and their enol-tautomeric forms (3-hydroxycyclobut-2-enones) and pyran-4-ones ($n = 3$) are among the cyclic structures which can be generated from ketene polymerization.[1a,2] Spontaneous alkylketene dimerization generally yields a greater percentage of cyclobutane-1,3-diones whereas parent ketene dimerization yields diketene.[1a] Cyclobutane-1,3-dione can be used in polymerization[3a,b] and squaric acid production, this being an intermediate reagent for producing pharmaceuticals, dyes, and herbicides.[3c] Depending on the substituted groups, this ketene type dimer can isomerize to its enol-tautomeric form either by spontaneous means[4] or by using basic catalysts such as thrietylamine[5a] and aqueous sodium hydroxide.[5b,c] Diketene is an industrially important raw material used in preparing acetoacetates and acetoacetamides.[6] Diketene is also used for introducing functionalized C2, C3, and C4 units into organic compounds.[1a] High molecular weight alkyl diketene dimers are used as moisture-proof agents in the paper and painting industries.[7] Further ketene incorporation into dimer compounds can yield ketene trimers[5] and ketene tetramers,[2] which are both constituted by the pyran-4-one ring. The pyran-4-one ring is an important component of many biologically active molecules, pharmaceutical substances, and versatile building blocks in synthetic organic chemistry.[8] For example, the pyran-4-one ring has been detected as an odor-active component in the aroma of foods such as in cooked clam soup,[8a] microwaved rainbow trout,[8b] and yogurt.[8c] The pyran-4-one ring has been used in deriving vanadyl complexes with insulin-like properties for diabetes therapy[8d] and new types of solvatochromic merocyanine dyes having potential applications for colorimetric sensor arrays for volatile organic compounds.[8e]

There are only a few experimental thermochemical property measurements for ketene dimers,[9,10] scarcely helping to evaluate these compounds' relative energetics. No experimental estimation for several other ketene polymer structures' thermochemical properties has been reported, and an alternative method must therefore be used for predicting them. Benson's group additivity values (GAVs)[11−14] is one of the low computational cost and highly accurate methods (about 1 kcal/mol[11,12] for the heat of formation) for estimating thermochemical properties. However, several GAVs for estimating ketene polymer structures' ther-

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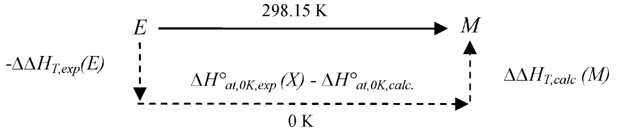


**Figure 1.** Atomization reaction procedure. X are the atoms of the E elements. M is the target compound.

mochemical properties are missing, including ring corrections and substituent positions.[14] GAV methodology is based on the lineal adjustment of a set of reliable thermochemical data. It has been demonstrated that quantum mechanical and statistic thermodynamic calculations are able to reproduce thermochemical properties, having excellent agreement with experiments.[11,15−17] The following section analyzes the thermochemical properties of ketene dimers and related structures and assesses the GAVs missing for this class of cyclic compounds based upon theoretical procedures using a set of acyclic base molecules.

**Theoretical Calculations.** ***Molecular Properties.*** Conformational isomers were calculated for the acyclic base compounds by using molecular mechanics' universal force field method, due to its broadly proven performance in obtaining conformers at low computational cost.[18] The conformers were reoptimized at the B3LYP/6-31+G(d) level of theory for discharging the most unstable isomers. The most stable isomers so obtained were further calculated with the CBS-Q multilevel method to assess accurate values for their molecular energies. CBS-Q level energies showed mean absolute deviations for the heat of formation at 0 K of ca. 1 kcal/mol, which was better than the value of ca. 1.5 kcal/mol performed by the B3LYP method (B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)).[19b] The CBS-Q method involves a sequence of optimizations using the restricted Hartree−Fock procedure and the second-order Moller−Plesset perturbational theory (MP2); the wave function is approximated in both levels by using the 6-31G† basis set. This basis set follows the 6-31G(d) mathematical structure and also includes d-type polarization functions on the heavy atoms, as in the 6-311G(d) basis set. After geometry optimization calculations, the energy is obtained by combining the extrapolated complete basis set second-order limit (CBS2) with higher order correlation (MP3, MP4, QCISD(T)) energies derived from a relatively smaller basis set. The method can be improved by an empirical correction due to bond additivity methodology and a correction for spin contamination.[19a,b] All the theoretical procedures were carried out using Gaussian package version 03W.[20] Harmonic vibrational frequencies and moments of inertia were estimated at HF/6-31G† and MP2/6-31G† levels, respectively. Zero point vibrational energies and vibrational frequencies were scaled by a factor of 0.918 44 because of systematic overestimation of HF derivate frequencies.[15,19]

***Thermochemical Properties.*** Standard heats of formation were calculated within the atomization reaction framework.[21a,b] The experimental enthalpy change from 0 to 298 K for the elements in their standard state,[21c] the heats of formation at 0 K for the atoms[21d] and the theoretical enthalpy change from 0 to 298 K for the compounds being studied were used in this reaction (Figure 1). Total partition function for all the substances was taken within the rigid-rotor-harmonic-oscillator framework corrected by hindered internal rotation contributions. Anharmonic frequencies specifying internal rotations around single bonds were determined by Ayala and Schlegel's procedure.[22] The conformational ring movements (i.e., ring puckering and pseudorotations) were assumed to be harmonic. Such an assumption was in good agreement with the diketene ring vibrational data;[23] no known studies have revealed the anharmonicity committed by ring movements for the other cyclic structures analyzed in this work.

Potential energy surfaces ($V$ vs $\phi$) for the torsional movements were obtained at the HF/6-31G† level by optimized internal coordinate sequences, except for the corresponding dihedral angle, which was varied in increments of 15° or 20°. The HF/6-31G(d) results have been shown to properly reproduce internal rotations' potential energy surface.[15b,24] Hindered rotor energies were subsequently obtained by solving the following Schrödinger equation:[25,26]

$$-\frac{\hbar^2}{2I_r}\frac{\mathrm{d}^2\psi(\phi)}{\mathrm{d}\phi^2} + V(\phi)\,\psi(\phi) = E\psi(\phi) \tag{1}$$

$$\psi_n(\phi) = \sum_m a_{nm}\mathrm{e}^{-\mathrm{i}m\phi} \tag{2}$$

The reduced moment of inertia, $I_r$, was taken as the reduced moment for both the rotating group and the remainder molecule according to East and Radom's[27] $I(2,3)$ method; in this method, $I_r$ is calculated on an axis passing through the center of gravity of both the rotating group and the other site. Though $I_r$ is actually a function of dihedral angle, $\phi$, it has been shown that a constant value for $I_r$ can achieve acceptable approximations to hindered rotor contributions.[15b,26−28] The Schrödinger equation (eq 1) was solved within the variational method's framework by the lineal combination of rigid-rotor basis functions (eq 2, $m = 0, \pm1, ..., \pm200$).[26] The torsional partition function ($Q_{\mathrm{int}}$) and torsional contribution to the thermochemical properties were calculated by directly counting the energy levels (eq 3) and by using the following widely acknowledged statistical expressions (eqs 4−6):[29,30]

$$Q_{\mathrm{int}} = \frac{1}{\sigma_{\mathrm{int}}}\sum \mathrm{e}^{-E_i/RT} \tag{3}$$

$$S = Nk\left[\ln Q + T\frac{\partial}{\partial T}(\ln Q)\right] \tag{4}$$

$$C = NkT\frac{\partial^2}{\partial T^2}(T\ln Q) \tag{5}$$

$$H(T) - H(0) = \frac{RT^2}{Q}\frac{\partial Q}{\partial T} \tag{6}$$

***Contribution Groups.*** The procedure for obtaining the thermochemical properties stated was applied to ketene dimers and related structures (Table 1) as well as to acyclic base compounds (Table 2). The cyclic compounds (Table 1) contained some GAVS in their structure (Table 3) whose values had not been issued before; 57 acyclic compounds were thus calculated by the theoretical procedure to obtain these unknown GAVs (Table 3), covering a wide range of ketene polymer related structures. These compounds were classed into 5 groups (Table 2): group 1 contained alcohol and ether compounds, group 2 consisted of molecules containing carboxyl functional groups, group 3 comprised molecules with carbonyl, hydroxyl and alkoxyl functional

**TABLE 1: Ketene Dimers and Related Structures Analyzed in This Work**

| | |
|---|---|
| Diketenes | |
| (1c) $-CH_2-CO-O-C(CH_2)-$ | diketene (4-methyleneoxetan-2-one) |
| (2c) $-C(CH_3)H-CO-O-C(CH_2)-$ | 3-methyl-4-methyleneoxetan-2-one |
| (3c) $-C(CH_3)_2-CO-O-C(CH_2)-$ | 3,3-dimethyl-4-methyleneoxetan-2-one |
| Cyclobutane-1,3-diones | |
| (4c) $-CH_2-CO-CH_2-CO-$ | cyclobutane-1,3-dione |
| (5c) $-C(CH_3)H-CO-CH_2-CO-$ | 2-methylcyclobutane-1,3-dione |
| (6c) $-C(CH_3)_2-CO-CH_2-CO-$ | 2,2-dimethylcyclobutane-1,3-dione |
| (7c) $-C(CH_3)H-CO-C(CH_3)H-CO-$ | (*Z*)-2,4-dimethylcyclobutane-1,3-dione |
| Pyran-4-ones | |
| (8c) $-CO-CH=CH-O-CH=CH-$ | pyran-4-one |
| (9c) $-CO-C(CH_3)=CH-O-CH=CH-$ | 3-methylpyran-4-one |
| (10c) $-CO-CH=C(CH_3)-O-CH=CH-$ | 2-methylpyran-4-one |
| (11c) $-CO-CH=C(OH)-O-CH=CH-$ | 2-hydroxypyran-4-one |
| Cyclobut-2-enones | |
| (12c) $-CH_2-CO-CH=CH-$ | cyclobut-2-enone |
| (13c) $-C(CH_3)H-CO-CH=CH-$ | 4-methylcyclobut-2-enone |
| (14c) $-CH_2-CO-C(CH_3)=CH-$ | 2-methylcyclobut-2-enone |
| (15c) $-C(CH_3)_2-CO-CH=CH-$ | 4,4-dimethylcyclobut-2-enone |
| (16c) $-CH_2-CO-CH=C(OH)-$ | 3-hydroxycyclobut-2-enone |
| (17c) $-CH_2-CO-C(CH_3)=C(OH)-$ | 3-hydroxy-2-methylcyclobut-2-enone |
| (18c) $-C(CH_3)H-CO-CH=C(OH)-$ | 3-hydroxy-4-methylcyclobut-2-enone |
| (19c) $-C(CH_3)H-CO-C(CH_3)=C(OH)-$ | 3-hydroxy-2,4-dimethylcyclobut-2-enone |
| (20c) $-C(CH_3)_2-CO-CH=C(OH)-$ | 3-hydroxy-4,4-dimethylcyclobut-2-enone |

groups, group 4 contained ester compounds, and group 5 comprised molecules containing carboxylic functional groups.

Non next interactions or interactions between nonbonded atoms are not explicitly considered in the GAV methodology; several correction values (8 in total) were thus introduced, on the basis of the most stable conformers' calculated thermochemical properties and geometries. Unknown or missing groups for ketene dimers and related structures were obtained by using both cyclic (Table 1) and acyclic compounds (Table 2). A multivariate linear regression (MVLR) procedure was applied to the set of acyclic compounds; meanwhile, a sequential solving procedure assessed the corrections for ring formation (RC) and substituent position (SP) on the basis of the set of cyclic structures. This procedure for obtaining the missing GAVs was carried out to avoid possible alterations in GAV values due to ring formation strain forces.

## Results and Discussion

**Geometries and Energies.** The parent ketene structure has been experimentally studied in some detail,[1a] and it has been demonstrated that calculated geometries at the MP2 level are in good agreement with such experimental measurements.[15,31] Diketene has also been studied at both theoretical[32] and experimental[33] levels. The MP2/6-31G† geometrical parameters obtained in the current research were found to be in excellent agreement with theoretical calculations at different levels of theory (Figure 2). The theoretical predictions for the diketene ring were all found to disagree with both electron diffraction experiments and X-ray diffraction measurements. Electron diffraction-derived geometries predicted the same length for the C−C and C−O ring bonds, whereas X-ray data predicted much larger values for both bonds than other estimates. A more detailed discussion about differences in geometry predictions for diketene can be found in Seidl and Schaefer's work.[32] Discrepancies regarding geometric parameters for diketene can be resolved by comparing the predicted rotational constants with those directly obtained from microwave spectra.[33a] The rotational constants at the MP2/6-31G† level obtained in this research reproduced the values obtained from microwave spectrum experiments, having excellent agreement (Table 4). This result meant that the geometrical parameters obtained at this level suitably represented the diketene molecular structure.

No experiments have been reported in the literature for cyclobutane-1,3-dione; however, the geometrical parameters obtained at the MP2/6-31G† level coincided with other theoretical estimations[34] (Figure 2). Regarding the acyclic compounds, the geometrical parameters for acrolein and ethoxyethene[35] found in this work agreed with experimental measurements[36,37] (Figure S1 in the Supporting Information material). For the other compounds, the theoretical measurements found in this work agreed with theoretical estimations at different levels of theory; ethyl vinyl ether, ethylene ether, geometrical parameters were in excellent agreement with geometrical parameters at other levels of theory.[35]

According to the current research's geometrical results, the diketene (1c) and cyclobut-2-one rings (12c) as well as the pyran-4-one ring (8c), maintained their planarity independently of the number and characteristics of the substituent groups (Me or OH) (Figure 3). The symmetric cyclobutane-1,3-dione ring (4c) slightly puckered when it had either one or two Me substituents in the cis or (*Z*) 2,4 position (Table S1 in the Supporting Information material). For the acyclic compounds, the group 2 molecules (i.e., aldehydes and ketones) showed conformations of the oxygen atom from the CO functional group eclipsing the carbon atom. The oxygen atom preferred eclipsing the carbon atom in the following order CO > CH3 > Cd > H. Exceptions to this rule were acrolein, 17, and but-3-en-2-one, 26, due to them preferring the CO−H eclipse to the CO−Cd eclipse. Compounds having branches in the main backbond, as happens in compounds 25 and 27, also showed alterations to this rule. Group 3 molecules exhibited internal hydrogen bonds having less than 1.8 Å lengths. Tables S1 and S2 of the Supporting Informa-

**TABLE 2: Acyclic Base Compounds Calculated in This Work**

| | |
|---|---|
| Group 1. Ethers and Alcohols | |
| (1) $CH_2C(OH)_2$ | ethene-1,1-diol |
| (2) $CH_2C(OH)OCH_3$ | 1-methoxyethenol |
| (3) $CH_2CHOC(OH)CH_2$ | 1-(vinyloxy)ethenol |
| (4) $CH_2CHOC(CH_2)OCH_3$ | 1-methoxy-1-(vinyloxy)ethene |
| (5) $CH_2C(OH)OC(OH)CH_2$ | 1-[(1-hydroxyvinyl)oxy]ethenol |
| (6) $CH_3OC(CH_2)OC(CH_2)(OH)$ | 1-[(1-methoxyvinyl)oxy]ethenol |
| (7) $CH_2CHOCHCH_2$ | vinyloxyethene |
| (8) $CH_3OCHCH_2$ | methoxyethene |
| (9) $(HO)CHC(OH)CH_3$ | propene-1,2-diol |
| (10) $CH_2CHOH$ | ethenol |
| (11) $CH_2C(OH)CH_3$ | propen-2-ol |
| (12) $CH_3CH_2OCHCH_2$ | ethoxyethene |
| (13) $(HO)CHCHOC(CH_2)OH$ | 1-[(2-hydroxyvinyl)oxy]ethenol |
| (14) $CH_3OC(CH_2)OCH_3$ | 1,1-dimethoxyethene |
| (15) $CH_3CH_2OC(CH_2)OCH_3$ | 1-ethoxy-1-methoxyethene |
| Group 2. Aldehydes and Ketones | |
| (16) $CH_2CHCOCHCH_2$ | penta-1,4-dien-3-one |
| (17) $HCOCHCH_2$ | propenal |
| (18) $HCOC(CH_2)CH_3$ | 2-methylpropenal |
| (19) $HCOCH_2CHCH_2$ | but-3-enal |
| (20) $HCOCH_2COH$ | malonaldehyde |
| (21) $HCOCH(CH_3)CHCH_2$ | 2-methylbut-3-enal |
| (22) $HCOC(CH_3)_2CHCH_2$ | 2,2-dimethylbut-3-enal |
| (23) $HCOCH_2COCH_3$ | 3-oxobutyraldehyde |
| (24) $HCOCH(CH_3)COH$ | 2-methylmalonaldehyde |
| (25) $HCOC(CH_3)COH$ | 2,2-dimethylmalonaldehyde |
| (26) $CH_3CHOCHCH_2$ | but-3-en-2-one |
| (27) $CH_2CHCOCH(CH_3)COH$ | 2-methyl-3-oxopent-4-enal |
| (28) $CH_2CHCOCH_2CHCH_2$ | hexa-1,5-dien-3-one |
| (29) $CH_3C(CH_2)COCHCH_2$ | 2-methylpenta-1,4-dien-3-one |
| (30) $HCOCH_2COCH_2CHCH_2$ | 3-oxohex-5-enal |
| (31) $CH_2CHCOCH_2CH_3$ | pent-1-en-3-one |
| (32) $CH_3C(CH_2)COC(CH_2)CH_3$ | 2,4-dimethylpenta-1,4-dien-3-one |
| (33) $CH_3C(CH_2)COCH_2CHCH_2$ | 2-methylhexa-1,5-dien-3-one |
| Group 3. Carbonyl, Hydroxyl, and Alkoxyl Groups | |
| (34) $CH_3C(OH)CHCOCHCH_2$ | (*Z*)-5-hydroxyhexa-1,4-dien-3-one |
| (35) $(HCO)CH(CH_3)C(OH)CH_2$ | 3-hydroxy-2-methylbut-3-enal |
| (36) $(HCO)C(CH_3)_2C(OH)CH_2$ | 3-hydroxy-2,2-dimethylbut-3-enal |
| (37) $(HO)CHCHCOCH_2COH$ | (*Z*)-5-hydroxy-3-oxopent-4-enal |
| (38) $(HO)_2CCHCOH$ | 3,3-dihydroxypropenal |
| (39) $CH_2CHOCHCHCOH$ | (*Z*)-3-vinyloxypropenal |
| (40) $(HCO)C(CH_3)HCHCH(OH)$ | 4-hydroxy-2-methylbut-3-enal |
| (41) $(HO)CHCHC(COH)(CH_3)_2$ | 4-hydroxy-2,2-dimethylbut-3-enal |
| (42) $CH_2CH(OH)CH_2COH$ | 3-hydroxybut-3-enal |
| (43) $(HO)CHCHCH_2COH$ | 4-hydroxybut-3-enal |
| (44) $(HCO)_2C(CH_3)CH_2(OH)$ | 2-(hydroxymethyl)-2-methyl malonaldehyde |
| (45) $(HO)_2CCHCOCH_2CH_3$ | 1,1-dihydroxypent-1-en-3-one |
| (46) $(HO)CHCHCOCH_2CH_3$ | (*Z*)-1-hydroxypent-1-en-3-one |
| (47) $(HO)CHCHCOCH_3$ | (*Z*)-4-hydroxybut-3-en-2-one |
| (48) $(HO)CHCHCOH$ | (*Z*)-3-hydroxypropenal |
| (49) $(HO)_2CCHCOCH_3$ | 4,4-dihydroxybut-3-en-2-one |
| (50) $(HO)_2CCHCOCHCH_2$ | 1,1-dihydroxypenta-1,4-dien-3-one |
| (51) $CH_3C(OH)CHCOH$ | (*Z*)-3-hydroxybutenal |
| Group 4. Ester Group | |
| (52) $HCOOCHCH_2$ | formic acid vinyl ester |
| (53) $CH_2CHOCOCH_2COH$ | 3-oxopropionic acid vinyl ester |
| (54) $CH_2CHCOOC(CH_2)CH_3$ | 2-methylacrylic acid vinyl ester |
| Group 5. Carboxylic Acids | |
| (55) $CH_2CHCOOH$ | acrylic acid |
| (56) $HOCOC(CH_3)_2COH$ | 2,2-dimethyl-3-oxopropionic acid |
| (57) $HOCOCH_2CHCH_2$ | but-3-enoic acid |

tion show the most stable conformers and their Cartesian coordinates obtained at the MP2/6-31G† level for the ketene cyclic structures and the acyclic base compounds calculated in this work.

**Hindered Rotor Potentials.** Internal rotations' energetic barriers were calculated as being the difference between restricted optimized geometry and global equilibrium conformers. Potential surfaces were interpolated by using a finite Fourier series containing the minimum number of terms possible (eq 7). The usefulness of the Fourier series in quantum chemistry is widely acknowledged not only for the proper representation of internal rotation potential but also as a means of elucidating the computed potential functions' electronic molecular features.[38,39]

$$V(\phi) = \sum_{i=0}^{k} a_i \cos(i\phi) + b_i \sin(i\phi) \tag{7}$$

Figure 4 illustrates the potential energy surfaces calculated at the HF/6-31G(d′) level for some rotors accounted for by the single bonds of the compounds listed in Table 2. Tables S15−S19 in the Supporting Information show the Fourier-series coefficients for the adjusted internal rotor surfaces for the acyclic compounds. According to the internal rotation potentials obtained in this work, some rotors can be acceptably approximated within the frame of harmonic vibrations due to the large value of their energy barriers. This is the case for compounds undergoing internal hydrogen bond rotation; e.g., the Cd−OH internal rotation in 3-hydroxypropenal (compound 48 from group 3) occurred at 819 $cm^{-1}$ frequency (Figure 4), exhibiting a ca. 65 kJ/mol energy barrier that forced the rotamer to stay in the well potential in a position very close to the lowest energy point ($\phi = 0°$).

**Heats of Formation.** Tables 5 and 6 show the calculated values for the thermodynamic properties of the compounds studied in this work. The heats of formation for the studied compounds were also assessed by using the widely known heat of formation for several reference compounds (Table 7) in isodesmic reaction methodology (Table 8).[40] Isodesmic reactions are usually fictitious reactions conserving the type of chemical bonds and their numbers; this quality cancels out computational errors that can arise from a lack of electron correlation and deficiencies in the basis sets in both reactants and products.[40] The heat of formation values obtained with the isodesmic reactions for each compound analyzed here (Tables 8 and S15, Supporting Information) were in excellent agreement (±1 kcal/mol of deviation) with the results obtained by using atomization reaction methodology (Tables 5 and 6). Such agreement between both methodologies provided confidence in the theoretical calculation results since the isodesmic reaction procedure made use of the experimental heat of formation for the reference compounds (Table 7). The correct heats of formation values for the analyzed compounds were taken as being those assessed by the atomization reaction procedure (Tables 5 and 6).

Diketene (1c) appeared to be the most stable ketene dimer according to the heat of formation values for the different cyclic structures analyzed in this work (Table 5). This dimer's relative stability contradicted experimental measurements by Chickos et al.,[9] who claimed that cyclobutane-1,3-dione dimer (4c) was more stable than diketene (1c) by about 1 kcal/mol. The reportedly favorable experimental stability of cyclobutane-1,3-dione over diketene was based on both combustion and sublimation data that might have been erroneous due to this compound's tautomeric instability in the condensed phase.[4] Several investigations have recently criticized such experimental relative stability and it seems that the heat of formation for both compounds must be reassessed.[34,42] The values calculated in this research coincided with theoretical works[34,42] regarding diketene's relative stability over cyclobutane-1,3-dione. In fact, diketene was found to have a −47.81 kcal/mol heat of formation at the CBS-Q level which is ca. 2 kcal/mol more stable than the −45.47 ± 0.3 kcal/mol experimental value.[10] Likewise, cyclobutane-1,3-dione was found to have a −44.34 kcal/mol heat

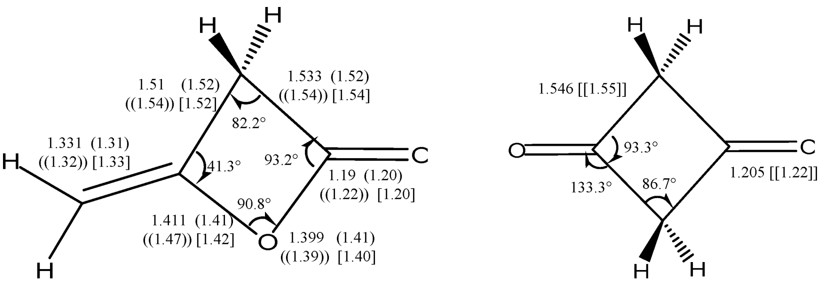
**TABLE 3: List of Unknown GAVS for the Ketene Cyclic Structures and the Acyclic Base Compounds**[a]

| | O/ Cd/C | CO/ O/Cd | O/ Cd2 | O/ CO/Cd | CO/ Cd2 | C/(CO)2/ C/H | C/ (CO)2/C2 | C/(CO)2/ H2 | C/CO/ Cd/C/H | C/CO/ Cd/C2 | C/CO/ Cd/H2 | Cd/ CO/C | Cd/ CO/H | Cd/ O/C | Cd/ O/H | Cd/ O2 | CO/ Cd/C | O/ Cd/H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (1c) diketene (4-methyleneoxetan-2-one) | | | | 1 | | | | | | | 1 | | | 1 | | | | |
| (2c) 3-methyl-4-methyleneoxetan-2-one | | | | 1 | | | | | 1 | | | | | 1 | | | | |
| (3c) 3,3-dimethyl-4-methyleneoxetan-2-one | | | | 1 | | | | | | 1 | | | | 1 | | | | |
| (4c) cyclobutane-1,3-dione | | | | | | | | 2 | | | | | | | | | | |
| (5c) 2-methylcyclobutane-1,3-dione | | | | | | 1 | | 1 | | | | | | | | | | |
| (6c) 2,2-dimethylcyclobutane-1,3-dione | | | | | | | 1 | 1 | | | | | | | | | | |
| (7c) (*E*)-2,4-dimethylcyclobutane-1,3-dione | | | | | | 2 | | | | | | | | | | | | |
| (8c) pyran-4-one | | | 1 | | 1 | | | | | | | | 2 | | 2 | | | |
| (9c) 3-methylpyran-4-one | | | 1 | | 1 | | | | | | | | 2 | 1 | 1 | | | |
| (10c) 2-methylpyran-4-one | | | 1 | | 1 | | | | | | | 1 | 1 | | 2 | | | |
| (11c) 2-hydroxypyran-4-one | | | 1 | | 1 | | | | | | | | 2 | | 1 | 1 | | 1 |
| (12c) cyclobut-2-enone | | | | | | | | | | | 1 | | 1 | | | | 1 | |
| (13c) 4-methylcyclobut-2-enone | | | | | | | | | 1 | | | | 1 | | | | 1 | |
| (14c) 2-methylcyclobut-2-enone | | | | | | | | | | | 1 | 1 | | | | | 1 | |
| (15c) 4,4-dimethylcyclobut-2-enone | | | | | | | | | | 1 | | | 1 | | | | 1 | |
| (16c) 3-hydroxycyclobut-2-enone | | | | | | | | | | | 1 | | 1 | 1 | | | 1 | 1 |
| (17c) 3-hydroxy-2-methylcyclobut-2-enone | | | | | | | | | | | 1 | 1 | | 1 | | | 1 | 1 |
| (18c) 3-hydroxy-4-methylcyclobut-2-enone | | | | | | | | | 1 | | | | 1 | 1 | | | 1 | 1 |
| (19c) 3-hydroxy-2,4-dimethylcyclobut-2-enone | | | | | | | | | 1 | | | 1 | | 1 | | | 1 | 1 |
| (20c) 3-hydroxy-4,4-dimethylcyclobut-2-enone | | | | | | | | | | 1 | | | 1 | 1 | | | 1 | 1 |
| (1) ethene-1,1-diol | | | | | | | | | | | | | | | | 1 | | 2 |
| (2) 1-methoxyethenol | 1 | | | | | | | | | | | | | | | 1 | | 1 |
| (3) 1-(vinyloxy)ethenol | | | 1 | | | | | | | | | | | | 1 | 1 | | 1 |
| (4) 1-methoxy-1-(vinyloxy)ethene | 1 | | 1 | | | | | | | | | | | | 1 | 1 | | |
| (5) 1-[(1-hydroxyvinyl)oxy]ethenol | | | 1 | | | | | | | | | | | | | 2 | | 2 |
| (6) 1-[(1-methoxyvinyl)oxy]ethenol | 1 | | 1 | | | | | | | | | | | | | 2 | | 1 |
| (7) (vinyloxy)ethene | | | 1 | | | | | | | | | | | | 2 | | | |
| (8) methoxyethene | 1 | | | | | | | | | | | | | | 1 | | | |
| (9) propene-1,2-diol | | | | | | | | | | | | | | 1 | 1 | | | 2 |
| (10) ethenol | | | | | | | | | | | | | | | 1 | | | 1 |
| (11) propen-2-ol | | | | | | | | | | | | | | 1 | | | | 1 |
| (12) ethoxyethene | 1 | | | | | | | | | | | | | | 1 | | | |
| (13) 1-[(2-hydroxyvinyl)oxy]ethenol | | | 1 | | | | | | | | | | | | 2 | 1 | | 2 |
| (14) 1,1-dimethoxyethene | 2 | | | | | | | | | | | | | | | 1 | | |
| (15) 1-ethoxy-1-methoxyethene | 2 | | | | | | | | | | | | | | | 1 | | |
| (16) penta-1,4-dien-3-one | | | | | 1 | | | | | | | | 2 | | | | | |
| (17) propenal | | | | | | | | | | | | | 1 | | | | | |
| (18) 2-methylpropenal | | | | | | | | | | | | 1 | | | | | | |
| (19) but-3-enal | | | | | | | | | | | 1 | | | | | | | |
| (20) malonaldehyde | | | | | | | | 1 | | | | | | | | | | |
| (21) 2-methylbut-3-enal | | | | | | | | | 1 | | | | | | | | | |
| (22) 2,2-dimethylbut-3-enal | | | | | | | | | | 1 | | | | | | | | |
| (23) 3-oxobutyraldehyde | | | | | | | | 1 | | | | | | | | | | |
| (24) 2-methylmalonaldehyde | | | | | | 1 | | | | | | | | | | | | |
| (25) 2,2-dimethylmalonaldehyde | | | | | | | 1 | | | | | | | | | | | |
| (26) but-3-en-2-one | | | | | | | | | | | | | 1 | | | | 1 | |
| (27) 2-methyl-3-oxopent-4-enal | | | | | | 1 | | | | | | | 1 | | | | 1 | |
| (28) hexa-1,5-dien-3-one | | | | | | | | | | | 1 | | 1 | | | | 1 | |

TABLE 3: Continued

| | O/ Cd/C | CO/ O/Cd | O/ Cd2 | O/ CO/Cd | CO/ Cd2 | C/(CO)2/ C/H | C/ (CO)2/C2 | C/(CO)2/ H2 | C/CO/ Cd/C/H | C/CO/ Cd/C2 | C/CO/ Cd/H2 | Cd/ CO/C | Cd/ CO/H | Cd/ O/C | Cd/ O/H | Cd/ O2 | CO/ Cd/C | O/ Cd/H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (29) 2-methylpenta-1,4-dien-3-one | | | | | 1 | | | | | | | 1 | 1 | | | | | |
| (30) 3-oxohex-5-enal | | | | | | | | 1 | | | 1 | | | | | | | |
| (31) pent-1-en-3-one | | | | | | | | | | | | | 1 | | | | 1 | |
| (32) 2,4-dimethylpenta-1,4-dien-3-one | | | | | 1 | | | | | | | 2 | | | | | | |
| (33) 2-methylhexa-1,5-dien-3-one | | | | | | | | | | | 1 | 1 | | | | | 1 | |
| (34) 5-hydroxyhexa-1,4-dien-3-one | | | | | 1 | | | | | | | | 2 | 1 | | | | 1 |
| (35) 3-hydroxy-2-methylbut-3-enal | | | | | | | | | 1 | | | | | 1 | | | | 1 |
| (36) 3-hydroxy-2,2-dimethylbut-3-enal | | | | | | | | | | 1 | | | | 1 | | | | 1 |
| (37) 5-hydroxy-3-oxopent-4-enal | | | | | | | | 1 | | | | | 1 | | 1 | | 1 | 1 |
| (38) 3,3-dihydroxypropenal | | | | | | | | | | | | | 1 | | | 1 | | 2 |
| (39) 3-(vinyloxy)propenal | | | 1 | | | | | | | | | | 1 | | 2 | | | |
| (40) 4-hydroxy-2-methylbut-3-enal | | | | | | | | | 1 | | | | | | 1 | | | 1 |
| (41) 4-hydroxy-2,2-dimethylbut-3-enal | | | | | | | | | | 1 | | | | | 1 | | | 1 |
| (42) 3-hydroxybut-3-enal | | | | | | | | | | | 1 | | | 1 | | | | 1 |
| (43) 4-hydroxybut-3-enal | | | | | | | | | | | 1 | | | | 1 | | | 1 |
| (44) 2-hydroxymethyl-2-methylmalonal | | | | | | | 1 | | | | | | | | | | | |
| (45) 1,1-dihydroxypent-1-en-3-one | | | | | | | | | | | | | 1 | | | 1 | 1 | 2 |
| (46) 1-hydroxypent-1-en-3-one | | | | | | | | | | | | | 1 | | 1 | | 1 | 1 |
| (47) 4-hydroxybut-3-en-2-one | | | | | | | | | | | | | 1 | | 1 | | 1 | 1 |
| (48) 3-hydroxypropenal | | | | | | | | | | | | | 1 | | 1 | | | 1 |
| (49) 4,4-dihydroxybut-3-en-2-one | | | | | | | | | | | | | 1 | | | 1 | 1 | 2 |
| (50) 1,1-dihydroxypenta-1,4-dien-3-one | | | | | 1 | | | | | | | | 2 | | | 1 | | 2 |
| (51) 3-hydroxybutenal | | | | | | | | | | | | | 1 | 1 | | | | 1 |
| (52) formic acid vinyl ester | | | | 1 | | | | | | | | | | | 1 | | | |
| (53) 3-oxopropionic acid vinyl ester | | | | 1 | | | | 1 | | | | | | | 1 | | | |
| (54) 2-methylacrylic acid vinyl ester | | 1 | | 1 | | | | | | | | | 1 | 1 | | | | |
| (55) acrylic acid | | 1 | | | | | | | | | | | 1 | | | | | |
| (56) 2,2-dimethyl-3-oxopropionic acid | | | | | | | 1 | | | | | | | | | | | |
| (57) but-3-enoic acid | | | | | | | | | | | 1 | | | | | | | |

[a] CO/O/Cd, O/Cd2, and O/CO/Cd are unknown GAVs for both entropy and specific heat. O/Cd/C is an unknown GAV for specific heat.



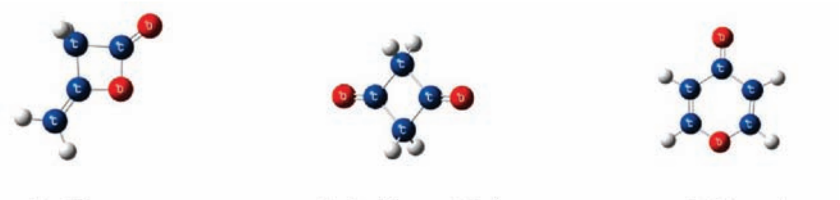
**(a)** 4-methyleneoxetan-2-one **(b)** Cyclobutane-1,3-dione

**Figure 2.** Some geometrical parameters for ketene dimers (lengths in Å) compared to other estimates: electron diffraction,[33b] in parentheses; X-ray structures,[33d] in double parentheses; Seidl and Schaefer's theoretical predictions,[32] in brackets; theoretical predictions at MP2/aug-cc-pVDZ level,[34a] in double brackets.

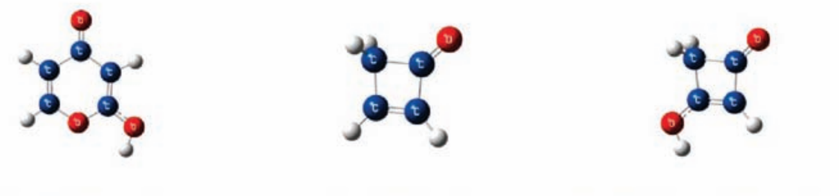
**TABLE 4: Rotational Constants for the d−I Dimer (MHz)**[a]

| method | *A* | *B* | *C* | absolute deviation |
|---|---|---|---|---|
| microwave spectrum[33a] | 12141.36 ± 0.04 | 2781.27 ± 0.01 | 2296.59 ± 0.01 | |
| electron diffraction[33b] | 11711 (−430) | 2846 (65) | 2323 (26) | 521 |
| X-ray crystallography[33d] | 11757 (−387) | 2736 (−45) | 2250 (−47) | 479 |
| MP2/aug-cc-pVDZ[34a] | 12053 (−88) | 2716 (−65) | 2249 (−47) | 200 |
| CCSD/DZd[32] | 12051 (−90) | 2747 (−34) | 2270 (−27) | 151 |
| MP2/6-31G† | 12063 (−78) | 2766 (−14) | 2283 (−13) | 105 |

[a] Numbers in parentheses indicate the deviation from experimental microwave results. Rotational constants for the electron diffraction and X-ray structures were taken from ref 32.



1c) Diketene 4c) Cyclobutane-1,3-dione 8c) Pyran-4-one



11c) 2-Hydroxy-pyran-4-one 12c) Cyclobut-2-enone 16c) 3-hydroxy-cyclobut-2-enone

**Figure 3.** Cyclic structures analyzed in this work.

of formation which is ca. 2 kcal/mol less stable than the experimentally obtained value.[9] Experimental and theoretical heat of formation values for ketene compounds have typically been in contradiction. So far, theoretical calculations have appeared to properly assess the heat of formation for this class of compounds.[15] Experimental discrepancies in determining the heat of formation is proof of the inherent difficulties of working with ketenes and ketene derivative compounds. Generating cyclobutane-1,3-dione structure ketene dimers has also been a matter of controversy due to it being unknown whether they are produced as just a result of a kinetic effect.[1a] On the basis of this work's results, diketene was found to be the major product of ketene dimerization in the gas phase due to thermodynamic control of the reaction. This conclusion is in excellent agreement with the results obtained by Morales et al.[42] at the MPW1K/DZP//PW86x+PBEc/DZP level.

The 3-hydroxycyclobut-2-enone (16c) was found to be the least stable ketene dimer that has been reported (Tables 5 and 8). 3-Hydroxycyclobut-2-enone can be generated by tautomerization of cyclobutane-1,3-dione[4] (4c). On the basis of the values calculated in this work, the appearance of the cyclobutane-1,3-dione acidic or enolized form was thermodynamically disfavored in gas phase; the gas phase heat of tautomerization for cyclobutane-1,3-dione to 3-hydroxycyclobut-2-enone was calculated to be 6.0 kcal/mol. In comparison, the tautomerization enthalpy of acetaldehyde ($\Delta H_f° = -40.80$ kcal/mol[35]) to ethenol ($\Delta H_f° = -28.89$ kcal/mol, Table 6) is ca. 12 kcal/mol (enthalpy was subsequently lowered to 10.9 kcal/mol when considering the reviewed value for acetaldehyde by Holmes et al.[41b]), while the tautomerization enthalpy of propanal ($\Delta H_f° = -45.10$ kcal/mol[35]) to propen-1-ol ($\Delta H_f° = -41.60$ kcal/mol[43]) is 3.5 kcal/mol (ca. 8 kcal/mol when considering $\Delta H_f° = -36.20$ kcal/mol[41c] for propen-1-ol) and the tautomerization enthalpy of acetone ($\Delta H_f° = -51.9$ kcal/mol[35]) to propen-2-ol ($\Delta H_f° = -40.1$ kcal/mol, Table 6) is 11.8 kcal/mol. The carbonyl form was more stable than the hydroxide form in the gas phase in all the preceding cases. On the other hand, tautomeric cyclobutane-1,3-dione species have been reported in substantial amounts in polar solvents.[4] This favorable

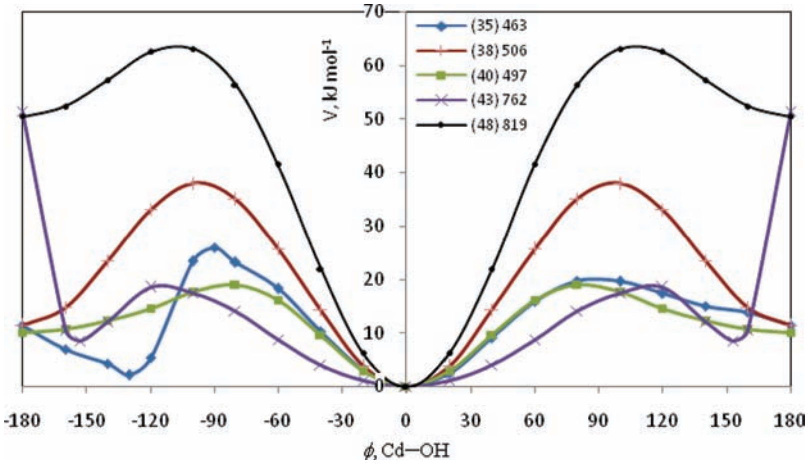


**Figure 4.** PES for internal rotations around Cd−OH bonds for some group 3 compounds (ZPE correction included). The legend illustrates the number of compounds with corresponding vibrational frequencies given in cm$^{-1}$.

**TABLE 5: Thermochemical Properties for Ketene Cyclic Structures from Quantum Mechanical Calculations**

| | | | $C_p$, cal/(mol K) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Delta H_f°$, kcal/mol | $S°$, cal/(mol K) | 300 K | 400 K | 500 K | 600 K | 800 K | 1000 K | 1500 K |
| | | Diketenes | | | | | | | |
| (1c) diketene (4-methyleneoxetan-2-one) | −47.81 | 72.64 | 20.40 | 25.79 | 30.29 | 33.92 | 39.30 | 43.05 | 48.51 |
| (2c) 3-methyl-4-methyleneoxetan-2-one | −57.46 | 81.98 | 26.09 | 32.78 | 38.49 | 43.19 | 50.27 | 55.29 | 62.72 |
| (3c) 3,3-dimethyl-4-methyleneoxetan-2-one | −67.37 | 87.22 | 32.35 | 40.45 | 47.34 | 53.01 | 61.63 | 67.80 | 77.05 |
| | | Cyclobutane-1,3-diones | | | | | | | |
| (4c) cyclobutane-1,3-dione | −44.34 | 74.57 | 21.26 | 26.43 | 30.75 | 34.27 | 39.56 | 43.27 | 48.68 |
| (5c) 2-methylcyclobutane-1,3-dione | −54.02 | 82.83 | 26.88 | 33.21 | 38.67 | 43.24 | 50.25 | 55.28 | 62.75 |
| (6c) 2,2-dimethylcyclobutane-1,3-dione | −72.26 | 90.40 | 33.14 | 40.81 | 47.45 | 52.99 | 61.56 | 67.75 | 77.06 |
| (7c) (*E*)-2,4-dimethylcyclobutane-1,3-dione | −68.24 | 91.50 | 32.57 | 40.10 | 46.72 | 52.32 | 61.04 | 67.36 | 76.86 |
| | | Pyran-4-ones | | | | | | | |
| (8c) pyran-4-one | −39.19 | 73.97 | 21.65 | 27.93 | 33.19 | 37.43 | 43.62 | 47.83 | 53.86 |
| (9c) 3-methylpyran-4-one | −50.00 | 81.86 | 27.70 | 34.90 | 41.17 | 46.38 | 54.27 | 59.82 | 67.93 |
| (10c) 2-methylpyran-4-one | −54.13 | 81.91 | 27.69 | 35.00 | 41.31 | 46.53 | 54.40 | 59.91 | 67.97 |
| (11c) 2-hydroxypyran-4-one | −86.87 | 79.30 | 26.61 | 33.31 | 38.77 | 43.06 | 49.13 | 53.16 | 58.91 |
| | | Cyclobut-2-enones | | | | | | | |
| (12c) cyclobut-2-enone | 10.32 | 67.70 | 16.87 | 21.69 | 25.83 | 29.20 | 34.23 | 37.75 | 42.91 |
| (13c) 4-methylcyclobut-2-enone | 0.98 | 76.83 | 22.80 | 28.91 | 34.20 | 38.59 | 45.25 | 50.01 | 57.11 |
| (14c) 2-methylcyclobut-2-enone | −6.39 | 76.77 | 22.28 | 28.10 | 33.33 | 37.77 | 44.63 | 49.56 | 56.90 |
| (15c) 4,4-dimethyl-cyclobut-2-enone | −68.31 | 84.91 | 33.85 | 41.93 | 48.66 | 54.14 | 62.38 | 68.19 | 76.82 |
| (16c) 3-hydroxycyclobut-2-enone | −38.32 | 72.10 | 21.79 | 27.08 | 31.44 | 34.93 | 39.99 | 43.41 | 48.28 |
| (17c) 3-hydroxy-2-methylcyclobut-2-enone | −56.59 | 82.03 | 26.88 | 33.11 | 38.60 | 43.19 | 50.12 | 54.97 | 62.08 |
| (18c) 3-hydroxy-4-methylcyclobut-2-enone | −54.70 | 81.15 | 27.69 | 34.35 | 39.90 | 44.40 | 51.09 | 55.74 | 62.52 |
| (19c) 3-hydroxy-2,4-dimethylcyclobut-2-enone | −68.60 | 89.76 | 32.94 | 40.41 | 47.03 | 52.60 | 61.14 | 67.22 | 76.27 |
| (20c) 3-hydroxy-4,4-dimethylcyclobut-2-enone | −68.31 | 84.91 | 33.85 | 41.93 | 48.66 | 54.14 | 62.38 | 68.19 | 76.82 |

appearance of 4c enol-tautomeric species in polar solvents can only be plausibly explained due to the lack of kinetic information. From the thermodynamic point of view (and in the absence of any catalyst) favorable interactions in polar media mainly due to the OH group may enable cyclobutane-1,3-dione to afford its enol-tautomeric species.

The more relative stability of cyclobutane-1,3-dione compared to its enol tautomer is not characteristic of acyclic $\beta$-diketones (Figure 5). Both the symmetrical and unsymmetrical enol-tautomeric forms of $\beta$-diketones generally appear to be more stable than the keto form.[44] Such relatively more stable enol forms may be explained by the fact that nonbonding orbitals can interact by connecting $\sigma$ bonds (through-bond interaction) in these tautomers to a greater extent than interactions by direct overlap (through-space interaction).[45] Despite experimental and theoretical analysis finding that the symmetrical enol-tautomer for acyclic $\beta$-diketones is the most stable,[45b,46] the unsymmetrical one was analyzed in this work (in group 3) to enable correct O/Cd/H and CO/Cd/C group calculations.

Substituent methyl groups modify relative energies for different dimer species as well as for the tautomeric reaction in gas phase (Table 5). Figure 6 shows the different stabilizations achieved by the dimers with H, Me and 2Me substituents. On the basis of these results, the increased number of Me substituents lowered the energy gap between the different dimers. When the rings contained 2Me substituents, the diketene form became thermodynamically unfavorable. This fact suggests that the greater the alkyl substituents' molecular weight the more the relative stabilization of the cyclobutane-1,3-diones and their enol-tautomeric forms compared to the corresponding diketene forms. The relative stabilization of cyclobutane-1,3-diones and their enol-tautomeric forms by the methyl groups could be due to increased through-bond interactions.[45c] Accordingly, spontaneous alkylketene dimerization toward cyclobutane-1,3-dione forms tended to be thermodynamically favored over dimerization toward 4-methyleneoxetan-2-one forms having increased alkyl substituent weight (Table 5).

**Entropies and Specific Heats.** The entropies and specific heats assessed by using MP2/6-31G† geometries and scaled frequencies

**TABLE 6: Thermochemical Properties for Acyclic Base Compounds from Quantum Mechanical Calculations**

| | | | $C_p$, cal/(mol K) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Delta H_f°$, kcal/mol | $S°$, cal/(mol K) | 300 K | 400 K | 500 K | 600 K | 800 K | 1000 K | 1500 K |
| Group 1. Ethers and Alcohols | | | | | | | | | |
| (1) ethene-1,1-diol | −75.62 | 64.98 | 18.97 | 23.27 | 26.50 | 28.77 | 31.61 | 33.45 | 36.46 |
| (2) 1-methoxyethenol | −71.84 | 72.73 | 23.75 | 29.30 | 33.88 | 37.42 | 42.35 | 45.71 | 50.89 |
| (3) 1-(vinyloxy)ethenol | −48.39 | 81.60 | 27.27 | 33.45 | 38.12 | 41.65 | 46.72 | 50.33 | 56.03 |
| (4) 1-methoxy-1-(vinyloxy)ethene | −42.78 | 91.04 | 30.18 | 37.42 | 43.58 | 48.59 | 56.14 | 61.57 | 69.89 |
| (5) 1-[(1-hydroxyvinyl)oxy]ethenol | −91.75 | 93.71 | 27.08 | 33.05 | 38.45 | 43.06 | 50.33 | 55.72 | 64.03 |
| (6) 1-[(1-methoxyvinyl)oxy]ethenol | −88.05 | 100.96 | 37.18 | 44.34 | 50.03 | 54.60 | 61.54 | 66.64 | 74.70 |
| (7) (vinyloxy)ethene | −2.09 | 73.76 | 21.53 | 26.67 | 31.04 | 34.65 | 40.21 | 44.30 | 50.66 |
| (8) methoxyethene | −25.05 | 67.58 | 20.13 | 24.26 | 27.83 | 30.87 | 35.75 | 39.44 | 45.31 |
| (9) propene-1,2-diol | −78.77 | 76.90 | 25.00 | 29.06 | 32.59 | 35.59 | 40.34 | 43.93 | 49.75 |
| (10) ethenol | −28.89 | 60.22 | 14.69 | 18.15 | 20.81 | 22.80 | 25.67 | 27.77 | 31.23 |
| (11) propen-2-ol | −40.10 | 66.32 | 19.97 | 25.05 | 29.13 | 32.28 | 36.84 | 40.14 | 45.48 |
| (12) ethoxyethene | −33.15 | 73.95 | 26.57 | 32.14 | 36.89 | 40.90 | 47.34 | 52.23 | 59.95 |
| (13) 1-[(2-hydroxyvinyl)oxy]ethenol | −88.66 | 87.35 | 31.30 | 38.73 | 44.34 | 48.40 | 53.59 | 56.81 | 61.66 |
| (14) 1,1-dimethoxyethene | −65.72 | 84.24 | 27.08 | 33.05 | 38.45 | 43.06 | 50.33 | 55.72 | 64.03 |
| (15) 1-ethoxy-1-methoxyethene | −74.06 | 90.52 | 33.69 | 40.52 | 46.96 | 52.57 | 61.51 | 68.14 | 78.38 |
| Group 2. Aldehydes and Ketones | | | | | | | | | |
| (16) penta-1,4-dien-3-one | −0.83 | 76.96 | 25.60 | 31.01 | 35.86 | 39.91 | 46.06 | 50.41 | 56.89 |
| (17) propenal | −15.08 | 65.16 | 16.80 | 20.37 | 23.46 | 26.06 | 30.09 | 32.97 | 37.23 |
| (18) 2-methylpropenal | −25.02 | 73.23 | 21.53 | 26.67 | 31.04 | 34.65 | 40.21 | 44.30 | 50.66 |
| (19) but-3-enal | −17.69 | 80.95 | 21.39 | 26.14 | 30.44 | 34.11 | 39.90 | 44.17 | 50.72 |
| (20) malonaldehyde | −60.60 | 75.47 | 18.62 | 22.35 | 25.71 | 28.60 | 33.14 | 36.43 | 41.33 |
| (21) 2-methylbut-3-enal | −25.82 | 83.64 | 29.06 | 34.40 | 39.40 | 43.82 | 51.01 | 56.44 | 64.88 |
| (22) 2,2-dimethylbut-3-enal | −34.48 | 92.94 | 33.16 | 40.69 | 47.51 | 53.32 | 62.43 | 69.12 | 79.38 |
| (23) 3-oxobutyraldehyde | −74.53 | 86.50 | 23.99 | 29.11 | 33.74 | 37.71 | 43.95 | 48.51 | 55.40 |
| (24) 2-methylmalonaldehyde | −67.96 | 86.60 | 25.40 | 30.13 | 34.44 | 38.20 | 44.23 | 48.71 | 55.52 |
| (25) 2,2-dimethylmalonaldehyde | −77.19 | 90.91 | 31.62 | 37.82 | 43.33 | 48.05 | 55.57 | 61.18 | 69.80 |
| (26) but-3-en-2-one | −26.46 | 73.82 | 21.61 | 26.41 | 30.77 | 34.50 | 40.31 | 44.54 | 50.94 |
| (27) 2-methyl-3-oxopent-4-enal | −57.75 | 98.44 | 34.20 | 41.04 | 47.22 | 52.51 | 60.76 | 66.72 | 75.65 |
| (28) hexa-1,5-dien-3-one | −5.84 | 90.07 | 31.89 | 38.15 | 43.91 | 48.85 | 56.56 | 62.19 | 70.77 |
| (29) 2-methylpenta-1,4-dien-3-one | −10.53 | 86.14 | 31.34 | 38.41 | 44.30 | 49.15 | 56.62 | 62.11 | 70.62 |
| (30) 3-oxohex-5-enal | −53.76 | 103.45 | 32.92 | 40.05 | 46.39 | 51.74 | 60.04 | 66.08 | 75.20 |
| (31) pent-1-en-3-one | −32.60 | 80.17 | 29.06 | 34.92 | 40.14 | 44.62 | 51.76 | 57.07 | 65.26 |
| (32) 2,4-dimethylpenta-1,4-dien-3-one | −19.10 | 95.07 | 36.80 | 44.96 | 51.95 | 57.84 | 67.09 | 73.97 | 84.63 |
| (33) 2-methylhexa-1,5-dien-3-one | −15.74 | 96.69 | 37.49 | 45.73 | 52.85 | 58.79 | 67.97 | 74.71 | 85.07 |
| Group 3. Carbonyl, Hydroxyl, and Alkoxyl Groups | | | | | | | | | |
| (34) (*Z*)-5-hydroxyhexa-1,4-dien-3-one | −71.16 | 85.55 | 33.38 | 41.06 | 47.76 | 53.37 | 62.04 | 68.46 | 78.79 |
| (35) 3-hydroxy-2-methylbut-3-enal | −71.91 | 92.54 | 32.25 | 38.83 | 44.58 | 49.35 | 56.64 | 61.92 | 70.06 |
| (36) 3-hydroxy-2,2-dimethylbut-3-enal | −83.37 | 98.36 | 37.81 | 46.28 | 53.49 | 59.39 | 68.33 | 74.75 | 84.59 |
| (37) (*Z*)-5-hydroxy-3-oxopent-4-enal | −101.83 | 90.33 | 30.03 | 36.73 | 42.53 | 47.37 | 54.92 | 60.58 | 69.45 |
| (38) 3,3-dihydroxy-propenal | −119.12 | 72.70 | 22.62 | 28.02 | 32.47 | 35.99 | 41.08 | 44.60 | 50.19 |
| (39) (*Z*)-3-(vinyloxy)propenal | −31.72 | 84.59 | 27.71 | 33.74 | 39.06 | 43.50 | 50.25 | 55.03 | 62.01 |
| (40) 4-hydroxy-2-methylbut-3-enal | −67.66 | 91.50 | 35.10 | 41.51 | 46.61 | 50.74 | 57.21 | 62.12 | 70.00 |
| (41) 4-hydroxy-2,2-dimethylbut-3-enal | −77.72 | 96.04 | 37.28 | 46.74 | 55.02 | 61.62 | 70.93 | 77.12 | 86.09 |
| (42) 3-hydroxybut-3-enal | −63.43 | 83.91 | 26.22 | 31.95 | 36.83 | 40.82 | 46.77 | 50.90 | 56.90 |
| (43) 4-hydroxybut-3-enal | −61.04 | 82.69 | 24.33 | 29.93 | 34.74 | 38.71 | 44.77 | 49.12 | 55.70 |
| (44) 2-(hydroxymethyl)-2-methylmalonal | −114.04 | 96.53 | 37.53 | 45.39 | 51.72 | 56.73 | 63.99 | 68.99 | 76.37 |
| (45) 1,1-dihydroxypent-1-en-3-one | −140.54 | 88.21 | 33.11 | 41.28 | 48.24 | 53.93 | 62.44 | 68.48 | 77.95 |
| (46) (*Z*)-1-hydroxypent-1-en-3-one | −85.58 | 83.55 | 29.36 | 36.42 | 42.68 | 48.01 | 56.47 | 62.92 | 73.31 |
| (47) (*Z*)-4-hydroxy-but-3-en-2-one | −78.94 | 75.79 | 23.52 | 29.25 | 34.35 | 38.66 | 45.45 | 50.62 | 59.10 |
| (48) (*Z*)-3-hydroxypropenal | −65.23 | 68.10 | 18.52 | 22.84 | 26.68 | 29.95 | 35.17 | 39.17 | 45.28 |
| (49) 4,4-dihydroxybut-3-en-2-one | −133.13 | 80.73 | 27.41 | 34.28 | 40.04 | 44.70 | 51.54 | 56.32 | 63.84 |
| (50) 1,1-dihydroxypenta-1,4-dien-3-one | −110.12 | 82.67 | 32.01 | 39.59 | 45.77 | 50.66 | 57.70 | 62.53 | 70.03 |
| (51) (*Z*)-3-hydroxybutenal | −78.98 | 75.33 | 24.24 | 29.72 | 34.64 | 38.87 | 45.64 | 50.82 | 59.12 |
| Group 4. Ester Group | | | | | | | | | |
| (52) formic acid vinyl ester | −61.94 | 70.29 | 19.51 | 24.08 | 28.00 | 31.19 | 35.86 | 39.03 | 43.27 |
| (53) 3-oxopropionic acid vinyl ester | −96.92 | 93.56 | 31.69 | 38.30 | 43.92 | 48.54 | 55.63 | 60.77 | 68.16 |
| (54) 2-methylacrylic acid vinyl ester | −58.27 | 94.07 | 33.74 | 41.15 | 47.86 | 53.67 | 62.76 | 69.09 | 77.58 |
| Group 5. Carboxylic Acids | | | | | | | | | |
| (55) acrylic acid | −76.88 | 69.86 | 30.86 | 38.47 | 44.15 | 48.24 | 53.48 | 56.74 | 61.63 |
| (56) 2,2-dimethyl-3-oxopropionic acid | −140.11 | 97.64 | 33.25 | 40.46 | 46.86 | 52.31 | 60.89 | 67.22 | 76.52 |
| (57) but-3-enoic acid | −81.49 | 82.13 | 24.86 | 30.34 | 35.18 | 39.29 | 45.77 | 50.56 | 57.53 |

at HF/6-31G† level are summarized in Tables 5 and 6. Tables S11 and S12 of the Supporting Information summarize contributions to entropy and specific heat from each class of movement, namely translation, rotation, and normal vibrations (TRV) and internal rotations (IR). Final values for the compounds' entropies must consider the mixture of energetically equivalent conformers. An additional mixture entropy term corrects the entropy for properly estimating this property; the entropy generated by 1 mol of mixture

**TABLE 7: Experimental $\Delta H_f^\circ$ (kJ/mol)[a] and CBS-Q Energies (au) at 298 K for the Reference Species in the Isodesmic Reactions**

| species | $\Delta H_f^\circ$, kJ/mol | $E^{298}$, au | species | $\Delta H_f^\circ$, kJ/mol | $E^{298}$, au |
|---|---|---|---|---|---|
| CH4 | −74.60 | −40.405770 | $(CH_3)_2CHCHCH_2$ | −27.20 | −196.091909 |
| $CH_3CHO$ | −166.10[b] | −153.575967 | $(CH_3)_2CHCHO$ | −213.17[c] | −232.026087 |
| $CH_2CHOCH_3$ | −104.60 | −231.999290 | $H_2O$ | −241.83 | −76.332730 |
| $C_2H_6$ | −84.00 | −79.625293 | $CH_3CHCO$ | −63.35[c] | −191.592801 |
| $CH_3COC_2H_5$ | −238.60 | −232.036918 | HCOOH | −378.65 | −189.521474 |
| $CH_2CHOC_2H_5$ | −140.16 | −231.999290 | $CH_3COOCH_3$ | −413.30 | −267.967415 |
| $CH_2CHCH_3$ | 19.70 | −117.639993 | $CH_2CHCHCH_2$ | 108.78 | −155.660066 |
| $CH_2CHCH_2CH_3$ | −0.50 | −156.863963 | oxetane | −80.50[d] | −192.759516 |
| $H_2CO$ | −108.60 | −114.338952 | oxirane | −52.60[d] | −153.533011 |
| $C_2H_4$ | 52.40 | −78.411728 | propiolactone | −282.90[d] | −266.757641 |
| $HCOOCH_3$ | −352.40 | −228.731354 | cyclobutene | 156.70[d] | −155.640421 |
| $H_2$ | 0.00 | −1.162781 | cyclobutane | 28.40[d] | −156.854156 |
| $CH_3COCH_3$ | −217.10 | −192.812053 | cyclobutanone | −101.25[d] | −230.819403 |
| $CH_3OH$ | −201.00 | −115.534033 | cyclohexane | −123.14[d] | −235.344221 |
| $C_2H_5OC_2H_5$ | −252.10 | −233.198893 | cyclohexanone | −226.10[d] | −309.305669 |
| $CO_2$ | −393.51 | −188.367756 | furan | −34.89[d] | −229.635986 |
| $H_2CCO$ | −47.70[c] | −152.370823 | 3,4-dihydro-2*H*-pyran | −125.10[d] | −270.045343 |
| $CH_3CH_2CHO$ | −188.66 | −192.800567 | tetrahydro-2*H*-pyran | −223.38[d] | −271.247122 |

[a] Reference 35. [b] References 41a and 41b. [c] Reference 15. [d] Reference 41d.

**TABLE 8: Checking of $\Delta H_f^\circ$ (kcal/mol) for Some Compounds by Using Isodesmic Reactions[a]**

| | $\Delta H_{rxn}^{298}$ | $\Delta H_f^\circ$ |
|---|---|---|
| (1c) diketene (Dik) → $2H_2C{=}C{=}O$ | 24.59 | −47.39 |
| Dik + $3CH_4$ → $CH_3CHO$ + $CH_3OCHCH_2$ + $C_2H_6$ | 17.00 | −48.03 |
| Dik + $2C_2H_6$ → $CH_2CHCH_2CH_3$ + $CH_3COOCH_3$ | −18.17 | −48.10 |
| Dik + $2CH_4$ → oxetane + $H_2CO$ + $C_2H_4$ | 51.56 | −48.60 |
| Dik + $3C_2H_6$ → oxetane + $CH_3COCH_2CH_3$ + $C_2H_4$ + $CH_4$ | 26.84 | −48.18 |
| Dik + $CH_4$ → oxetan-2-one + $C_2H_4$ | 10.81 | −48.07 |
| average (−47.81) | | −48.06 |
| (4c) cyclobutane-1,3-dione (Cy13one) → $2H_2C{=}C{=}O$ | 20.49 | −43.28 |
| Cy13one + $2CH_4$ → cyclobutane + $2H_2CO$ | 33.74 | −43.26 |
| Cy13one + $CH_4$ → cyclobutanone + $2H_2CO$ | 13.62 | −45.97 |
| Cy13one + $2CH_4$ → cyclobutane + OCHCHO | 19.54 | −43.35 |
| Cy13one + $CH_4$ → $CH_3CH{=}C{=}O$ + $CH_3CHO$ | 7.10 | −44.24 |
| average (−44.34) | | −44.02 |
| (16c) 3-hydroxycyclobut-2-enone (3HCy): | | |
| 3HCy + $2CH_4$ → $CH_3COCH_2CH_3$ + $CH_2CHOH$ | −12.28 | −37.97 |
| 3HCy + $3CH_4$ → $CH_3CHC{=}C{=}O$ + $CH_3CH_2OH$ + $C_2H_6$ | 0.88 | −38.77 |
| 3HCy + $C_2H_6$ → cyclobutanone + $CH_2CHOH$ | 7.33 | −40.34 |
| 3HCy + $H_2CO$ → cyclobutanone + HCOOH + $CO_2$ | −54.34 | −40.80 |
| average (−38.32) | | −39.47 |

[a] Results from atomization reaction procedure shown in parentheses.

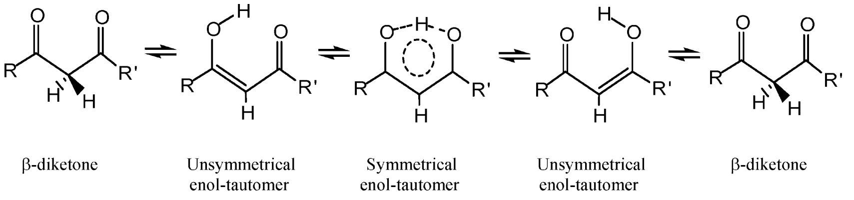


**Figure 5.** β-diketone tautomerization.

can be calculated according to[14] $\Delta S_{mix} = -R\Sigma n_i \ln(n_i)$, where $n_i$ corresponds to the equilibrium mol fraction of the *i*th conformer in the mixture. The entropy of mixture was reduced to the well-known formula of $\Delta S_{mix} = -R \ln(2)$ for the mixture of two energetically equivalent conformers. It is worth mentioning that the effects of hindrance potential were prominent in calculating entropy and low temperature specific heat (see Table S6, Supporting Information). This is a consequence of both potential barrier medium values in most of the rotors and low internal rotator frequency values. The symmetry numbers and other information, such as optical conformers, hindered frequencies, and the potential energy barriers required for calculating the entropies of the analyzed compounds, can be consulted in Table 9.

**Non Next Neighbor Interactions.** The corrections for the proper GAV calculations were based on final thermochemical property values (Table 6). The first correction analyzed here concerns the preferable spatial configuration of ether compounds (Figure 7). Group 1 ether compounds 14 and 15 showed different eclipsed atom trends, increasing from hydrogen to methyl substituent in the alkoxy group. The 14 and 15 dioxy compounds possessed the methyl group eclipsed by the methylene group; the methoxyl substituents were thus in syn position (Figure 7). The most stable conformers having low molecular weight for this group were 1 and 2; in line with expressing these molecules in terms of GAVs, the Cd/O2 group took the O−H eclipse into account. Thus, the GAVs for compounds 14 and 15 had to be corrected for the

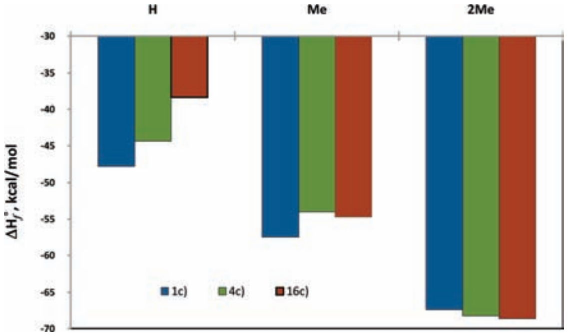


**Figure 6.** Substituent stabilization in (1c) diketene, (2c) cyclobutane-1,3-dione, and (16c) 3-hydroxy-cyclobut-2-enone.

lack of this eclipse ($NN_{G1}^{I}$). Likewise, ether compounds 4, 5, 6, and 13, which included another methylene group, showed spatial distortions ($NN_{G1}^{II}$) compared to most stable low-weight diether conformers. GAV corrections for the heat of formation (kcal/mol) in the preceding ether compounds were obtained as follows: $NN_{G1}^{I} = T14 + (T1 - 2{*}T2)$, $NN_{G1}^{I} = 2.34$; $NN_{G1}^{I} = T15 + T1 - 2{*}T2 - T12 + T8$, $NN_{G1}^{I} = 2.1$; $NN_{G1}^{II\text{-}4} = T4 - T7 + T10 - T2$, $NN_{G1}^{II\text{-}4} = 2.27$; $NN_{G1}^{II\text{-}5} = T5 - T1 + T10 - T2 + T8 - T7$, $NN_{G1}^{II\text{-}5} = 3.87$; $NN_{G1}^{II\text{-}6} = T6 - T1 + 2{*}T10 - T2 - T7$, $NN_{G1}^{II\text{-}6} = 3.73$; $NN_{G1}^{II\text{-}13} = T13 - T1 - T7 + 2{*}Cd/H2$, $NN_{G1}^{II\text{-}13}{=}1.58$.

The correction for the lack of the O−H eclipse, $NN_{G1}^{I}$, thus corresponded to the mean value of 2.22 kcal/mol for the heat of formation for compounds 14 and 15. Similarly, group 2 compounds 27, 28, and 31 and group 3 compounds 37, 45, and 46 as well as compound 55 belonging to group 5 took different conformations from those exhibited by the corresponding low-weight compounds; i.e., low-weight compounds such as 17, 18, and 26 showed that the carbonyl group preferred the syn position and the CO group (Figure 8) therefore appeared to eclipse the hydrogen and methyl group instead of the methylene group. In contrast, compounds 27, 28, 31, 37, 45, 46, and 55 showed the anti conformation to be the most stable (Figure 8 and Table S2, Supporting Information). The correction for the heat of formation in these compounds due to this class of non next neighbor interaction corresponded to $NN_{G2}^{I} + C/CO/C/H_2 = T31 - T26$, $NN_{G2}^{I} = -0.96$ kcal/mol. Likewise, the most stable conformers for 23, 27, 30, 44, and 56 compounds exhibited nonbonding interactions that were different to that in the syn and anti position; this type of correction was due to the CO−X eclipse where X = {H, CO} (in kcal/mol): $NN_{G2}^{II\text{-}23} + C/CO/H_3 + CO/C_2 - CO/C/H = T23 - T20$, $NN_{G2}^{II\text{-}23} = -1.43$; $NN_{G2}^{II\text{-}27} - CO/C/H - C/CO/H_3 + NN_{G2}^{I} = T27 - T24 - T26$, $NN_{G2}^{II\text{-}27} = -1.67$; $NN_{G2}^{II\text{-}30} + CO/C_2 - 2{*}CO/C/H = T30 - T20 - T19$, $NN_{G2}^{II\text{-}30} = -2.25$; $NN_{G2}^{II\text{-}44} + O/C/H - C/C/H_3 = T44 - T25 - T12 + T8$, $NN_{G2}^{II\text{-}44} = -1.04$; $NN_{G2}^{II\text{-}56} - CO/C/H + CO/O/C + O/C/H = T56 - T25$, $NN_{G2}^{II\text{-}56} = 1.20$.

Group 3 presented molecules with an internal hydrogen bond (internal H-bond) having appreciably short distances of less than 1.8 Å at the MP2/6-31G† level. Molecules 34, 37, 38, 43, 45, 46, 47, 48, 49, 50, and 51 exhibited short C=O−H−O distances, further contributing toward their stability (see the unsymmetrical enol-tautomer depicted in Figure 5). Among these compounds, molecules 34, 46, 47, and 48 increased their stability by adopting the cis or (*Z*) conformation (Figure 9). Cis conformations were preferred due to both a resonance effect of the C=C and C=O bonds and the interaction between the hydroxyl hydrogen orbitals and the π-CO systems.[5b−d,47] Effects and interactions of this type (known as resonance-assisted hydrogen bonding) are significant for strengthening hydrogen bonding and increasing the resonance energy of many systems having biological activity, such as several enzymatic reaction mechanisms[48a−c] and chemical inversion of L-amino acids to D-amino acids which are important neurotransmitters (D-serine)[48d,e] and building blocks (D-alanine) for bacterial cell wall synthesis.[48f] Considering the extra stability in the cis or (*Z*) conformers for molecules 34, 46, 47, and 48 ($NN_{CIS}^{OH}$ in kcal/mol), it was possible to estimate H-bond interactions, $NN_{x}^{OH}$ (in kcal/mol), in *x* distances as follows:

$$NN_{CIS}^{OH} + NN_{1.725}^{OH\text{-}34} = T34 - T11 - T16 + 2{*}Cd/H_2 = -17.70$$

$$NN_{1.652}^{OH\text{-}38} - 2{*}Cd/H_2 = T38 - T1 - T17,\ NN_{1.652}^{OH\text{-}38} = -15.9$$

$$NN_{1.788}^{OH\text{-}43} - 2{*}Cd/H_2 = T43 - T19 - T10,\ NN_{1.788}^{OH\text{-}43} = -1.94$$

$$NN_{1.643}^{OH\text{-}45} - 2{*}Cd/H_2 + C/CO/C/H_2 + NN_{G2}^{I} = T45 - T1 - T26,\ NN_{1.635}^{OH\text{-}45} = -19.78$$

$$NN_{CIS}^{OH} + NN_{1.775}^{OH\text{-}46} = T46 - T31 - T10 + 2{*}Cd/H_2 = -11.59$$

$$NN_{CIS}^{OH} + NN_{1.771}^{OH\text{-}47} = T47 - T26 - T10 + 2{*}Cd/H_2 = -11.03$$

$$NN_{CIS}^{OH} + NN_{1.792}^{OH\text{-}48} = T48 - T17 - T10 + 2{*}Cd/H_2 = -8.81$$

$$NN_{1.635}^{OH\text{-}49} - 2{*}Cd/H_2 = T49 - T1 - T26,\ NN_{1.635}^{OH\text{-}49} = -18.53$$

$$NN_{1.615}^{OH\text{-}50} - 2{*}Cd/H_2 = T50 - T1 - T16,\ NN_{1.615}^{OH\text{-}50} = -21.15$$

$$NN_{CIS}^{OH} + NN_{1.759}^{OH\text{-}51} = T51 - T17 - T11 + 2{*}Cd/H_2 = -11.28$$

Assessment of both $NN_{CIS}^{OH}$ and $NN_{x}^{OH}$ for compounds 34, 46, 47, 48, and 51 involved a linear system of equations. The value of one variable had to be defined to solve this linear system. This can be done by assuming a distance for a null value for the internal H-bond interaction. Figure S12 of the Supporting Information shows the correction values for the distances calculated by using compounds 38, 43, 45, 49, and 50 (Figure 9). According to linear fitting with the H-bond interaction values in the preceding compounds, it could be assumed that there were null interactions in distances greater than ca. 1.79 Å (at the MP2/6-31G† level). Therefore, $NN_{1.792}^{OH\text{-}48}$ was assumed to be null and the linear system could be solved to assess the following values in kcal/mol: $NN_{CIS}^{OH} = -8.81$, $NN_{1.725}^{OH\text{-}34} = -8.89$, $NN_{1.759}^{OH\text{-}51} =$

**TABLE 9: Symmetry Numbers, Optical Isomers, Hindered Internal Frequencies, Reduced Moment of Inertia and Potential Energies**

|  | $\sigma_{\text{int}}$ | $\sigma_{\text{ext}}$ | OI | hind. freq, cm$^{-1}$ | $I_r$, amu Å | $V_{\max}$, kcal/mol |
|---|---|---|---|---|---|---|
| Group 1. Ethers and Alcohols |  |  |  |  |  |  |
| (1) ethene-1,1-diol | 2 | 1 | 1 | 257 (Cd−O); 417 (Cd−O) | 0.755; 0.657 | 5.13; 8.76 |
| (2) 1-methoxyethenol | 6 | 2 | 1 | 131 (Cd−OCH3); 254 (O−C); 298 (Cd−OH) | 2.8; 8.156; 0.814 | 9.0; 3.54; 5.62 |
| (3) 1-(vinyloxy)ethenol | 1 | 1 | 2 | 86 (O−Cd); 116 (O−Cd); 301 (Cd−O) | 0.83; 9.74; 5.81 | 3.11; 5.13; 5.10 |
| (4) 1-methoxy-1-(vinyloxy)ethene | 6 | 1 | 2 | 45 (O−Cd); 64 (Cd−O); 123 (O−Cd); 266 (O−C) | 4.25; 11.84; 4.71; 3.05 | 3.84; 1.67; 3.11; 3.43 |
| (5) 1-[(1-hydroxy-vinyl)oxy]-ethenol | 1 | 2 | 2 | 65 (O−Cd); 71 (Cd−O); 256 (Cd−O); 257 (Cd−O) | 25.8; 25.8; 0.83; 0.83 | 2.52; 2.52; 3.43; 3.43 |
| (6) 1-[(1-methoxy-vinyl)oxy]ethenol | 3 | 1 | 2 | 44 (O−Cd); 70 (O−Cd); 105 (O−Cd); 262 (O−C); 282 (O−H) | 29.82; 31.42; 5.56; 3.02; 0.84 | 3.61; 2.18; 3.57; 2.91; 4.49 |
| (7) (vinyloxy)ethene | 1 | 2 | 1 | 57 (Cd−O); 78 (Cd−O) | 3.60; 3.60 | 2.36; 2.36 |
| (8) methoxyethene | 6 | 2 | 1 | 237 (O−Cd); 269 (O−C) | 6.53; 2.60 | 4.5; 3.73 |
| (9) propene-1,2-diol | 3 | 1 | 2 | 209 (Cd−C); 321 (Cd−O); 555 (Cd−O) | 2.96; 0.54; 0.84 | 2.74; 3.52; 3.54 |
| (10) ethenol | 2 | 1 | 1 | 476 (Cd−O) | 0.76 | 5.29 |
| (11) propen-2-ol | 6 | 2 | 1 | 204 (Cd−C); 463 (O−H) | 2.93; 0.66 | 2.32; 5.18 |
| (12) ethoxyethene | 6 | 2 | 1 | 115 (O−C); 214 (O−Cd); 287 (C−C) | 5.10; 7.13; 2.71 | 11.8; 4.21; 3.58 |
| (13) 1-[(2-hydroxy-vinyl)oxy]ethenol | 4 | 1 | 2 | 59 (O−Cd); 92 (O−Cd); 309 (Cd−O); 461 (Cd−O) | 19.4; 21.05; 0.83; 0.61 | 6.20; 4.80; 4.51; 6.0 |
| (14) 1,1-dimethoxyethene | 9 | 1 | 1 | 100 (Cd−O); 141 (Cd−O); 265 (O−C); 282 (O−C) | 2.83; 2.83; 7.46; 7.46 | 3.03; 3.03; 3.89; 3.89 |
| (15) 1-ethoxy-1-methoxyethene | 9 | 2 | 1 | 79 (Cd−O); 127 (O−C); 135 (Cd−O); 274 (O−C); 276 (C−C) | 6.36; 11.3; 10.55; 2.91; 2.76 | 2.96; 2.76; 5.92; 3.68; 3.91 |
| Group 2. Aldehydes and Ketones |  |  |  |  |  |  |
| (16) penta-1,4-dien-3-one | 4 | 2 | 1 | 71 (Cd−CO); 119 (Cd−CO) | 7.22; 7.22 | 5.70; 5.70 |
| (17) propenal | 2 | 1 | 1 | 173 (Cd−CO) | 2.76 | 7.67 |
| (18) 2-methylpropenal | 6 | 2 | 1 | 158 (Cd−O); 189 (Cd−C) | 6.44; 2.90 | 8.04; 1.86 |
| (19) but-3-enal | 1 | 1 | 2 | 85 (C−CO); 156 (C−Cd) | 5.59; 7.61 | 2.91; 2.86 |
| (20) malonaldehyde | 1 | 1 | 2 | 66 (CO−C); 129 (CO−C) | 3.86; 7.48 | 2.89; 2.56 |
| (21) 2-methylbut-3-enal | 3 | 1 | 2 | 84 (C−CO); 96 (C−Cd); 237 (C−C) | 5.67; 6.13; 3.00 | 2.87; 3.07; 3.22 |
| (22) 2,2-dimethylbut-3-enal | 9 | 1 | 2 | 78 (C−CO); 100 (C−Cd); 254 (C−C); 292 (C−C) | 5.29; 7.18; 3.06; 3.06 | 2.91; 2.60; 3.80; 4.73 |
| (23) 3-oxobutyraldehyde | 3 | 1 | 2 | 34 (C−CO); 69 (C−CO); 125 (CO−CH3) | 13.44; 4.48; 2.94 | 3.29; 1.90; 0.77 |
| (24) 2-methylmalonaldehyde | 3 | 1 | 2 | 79 (CO−C); 96 (CO−C); 222 (C−C) | 8.40; 5.93; 2.91 | 2.88; 3.62; 2.88 |
| (25) 2,2-dimethylmalonaldehyde | 9 | 2 | 2 | 62 (CO−C); 68 (CO−C); 222 (C−C); 254 (C−C) | 5.48; 5.48; 3.06; 3.06 | 2.63; 2.65; 3.29; 3.29 |
| (26) but-3-en-2-one | 6 | 2 | 1 | 128 (CO−Cd); 160 (CO−C) | 8.07; 2.95 | 5.49; 1.44 |
| (27) 2-methyl-3-oxopent-4-enal | 3 | 1 | 2 | 53 (CO−C); 65 (CO−C); 98 (CO−Cd); 223 (C−C) | 5.57; 41.22; 7.55; 2.97 | 3.95; 2.61; 6.51; 3.03 |
| (28) hexa-1,5-dien-3-one | 2 | 1 | 2 | 54 (CO−C); 81 (Cd−C); 119 (CO−Cd) | 14.50; 6.60; 7.10 | 2.78; 3.21; 5.36 |
| (29) 2-methylpenta-1,4-dien-3-one | 3 | 1 | 1 | 55 (CO−Cd); 78 (CO−Cd); 191 (Cd−C) | 26.43; 6.77; 2.85 | 4.10; 3.71; 2.01 |
| (30) 3-oxohex-5-enal | 1 | 1 | 2 | 39 (CO−C); 44 (CO−C); 68 (CO−C); 98 (Cd−C) | 16.50; 14.72; 5.20; 7.47 | 2.14; 3.31; 2.21; 3.34 |
| (31) pent-1-en-3-one | 6 | 2 | 1 | 68 (CO−Cd); 113 (CO−C); 236 (C−C) | 11.33; 7.31; 2.66 | 3.69; 5.32; 2.87 |
| (32) 2,4-dimethylpenta-1,4-dien-3-one | 9 | 2 | 2 | 47 (CO−Cd); 92 (CO−Cd); 181 (Cd−C); 188 (Cd−C) | 34.54; 34.54; 2.89; 2.89 | 5.12; 5.12; 1.96; 1.96 |
| (33) 2-methylhexa-1,5-dien-3-one | 3 | 1 | 2 | 49 (CO−Cd); 74 (CO−C); 101 (Cd−C); 195 (Cd−C) | 29.65; 16.30; 7.40; 2.81 | 4.80; 5.36; 3.56; 2.07 |
| Group 3. Carbonyl, Hydroxyl, and Alkoxyl Groups |  |  |  |  |  |  |
| (34) (*Z*)-5-hydroxyhexa-1,4-dien-3-one | 12 | 2 | 1 | 71 (CO−Cd); 159 (Cd−C); 210 (CO−Cd); 649 (CO−H) | 7.49; 3.01; 21.64; 0.66 | 5.86; 1.64; 14.92; 18.64 |
| (35) 3-hydroxy-2-methylbut-3-enal | 3 | 1 | 2 | 67 (Cd−C); 94 (CO−C); 245 (C−C); 463 (Cd−OH) | 28.02; 5.38; 2.94; 0.17 | 3.54; 4.10; 3.10; 5.58 |
| (36) 3-hydroxy-2,2-dimethylbut-3-enal | 9 | 1 | 2 | 70 (Cd−C); 89 (CO−C); 261 (C−C); 321 (C−C); 455 (Cd−OH) | 34.3; 5.04; 3.03; 3.07; 0.21 | 3.36; 4.35; 3.49; 5.20; 5.42 |
| (37) (*Z*)-5-hydroxy-3-oxopent-4-enal | 4 | 1 | 2 | 36 (CO−C); 57 (CO−C); 116 (CO−Cd); 802 (Cd−OH) | 15.00; 4.62; 18.80; 0.52 | 3.55; 2.03; 15.80; 15.52 |
| (38) 3,3-dihydroxy-propenal | 4 | 1 | 1 | 313 (CO−Cd); 506 (Cd−OH); 901 (Cd−OH) | 8.91; 0.69; 0.84 | 22.70; 9.09; 22.51 |
| (39) (*Z*)-3-(vinyloxy)propenal | 2 | 1 | 1 | 47 (Cd−O); 92 (Cd−O); 168 (Cd-CO) | 4.23; 4.62; 3.14 | 2.06; 4.25; 9.76 |
| (40) 4-hydroxy-2-methylbut-3-enal | 6 | 1 | 2 | 74 (CO−C); 203 (Cd−C); 228 (C−C); 497 (Cd−OH) | 4.78; 7.93; 2.97; 0.84 | 3.05; 3.80; 3.40; 4.53 |
| (41) 4-hydroxy-2,2-dimethylbut-3-enal | 9 | 1 | 2 | 104 (CO−C); 112 (Cd−C); 253 (C−C); 291 (C−C); 623 (C−C) | 9.25; 31.26; 2.84; 3.05; 0.60 | 6.40; 7.03;3.75; 4.60; 4.88 |
| (42) 3-hydroxybut-3-enal | 1 | 1 | 2 | 87 (CO−C); 143 (Cd−C); 522 (Cd−OH) | 9.36; 20.10; 0.79 | 6.12; 7.57; 6.50 |
| (43) 4-hydroxybut-3-enal | 1 | 1 | 1 | 52 (Cd−C); 159 (CO−C); 762 (Cd−OH) | 22.88; 10.0; 0.56 | 3.71; 3.66; 12.28 |
| (44) 2-hydroxymethyl-2-methylmalonal | 3 | 1 | 2 | 73 (CO−C); 102 (CO−C); 152 (C−C); 230 (C−C); 549 (C−OH) | 7.54; 7.58; 15.58; 3.08; 0.84 | 7.10; 4.52; 9.34; 3.85; 6.63 |

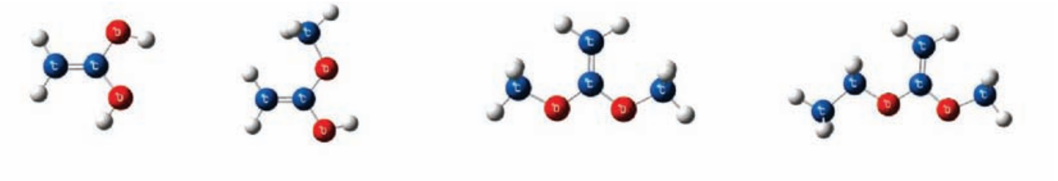
**TABLE 9: Continued**

| | $\sigma_{int}$ | $\sigma_{ext}$ | OI | hind. freq, $cm^{-1}$ | $I_r$, amu Å | $V_{max}$, kcal/mol |
|---|---|---|---|---|---|---|
| (45) 1,1-dihydroxypent-1-en-3-one | 12 | 1 | 1 | 45(CO−C); 118 (CO−Cd); 243 (C−C); 491 (Cd−OH); 782 (Cd−OH) | 12.62; 21.44; 2.67; 0.65; 0.57 | 1.20; 21.90; 2.96; 23.10; 8.87 |
| (46) (*Z*)-1-hydroxypent-1-en-3-one | 12 | 1 | 1 | 62 (CO−C); 106 (CO−Cd); 238 (C−C); 822 (Cd−OH) | 12.45; 17.96; 2.62; 0.45 | 1.28; 15.64; 2.92; 15.96 |
| (47) (*Z*)-4-hydroxybut-3-en-2-one | 12 | 1 | 1 | 101 (CO−C); 122 (CO−Cd); 834 (Cd−H) | 2.97; 17.33; 0.63 | 0.80; 16.10; 16.25 |
| (48) (*Z*)-3-hydroxypropenal | 4 | 1 | 1 | 251 (CO−Cd); 819 (Cd−OH) | 8.78; 0.65 | 15.80; 15.06 |
| (49) 4,4-dihydroxy-but-3-en-2-one | 12 | 1 | 1 | 69 (CO−C); 137 (CO−Cd); 494 (Cd−OH); 908 (Cd−OH) | 2.99; 20.62; 0.60; 0.76 | 0.33; 22.34; 8.91; 23.30 |
| (50) 1,1-dihydroxypenta-1,4-dien-3-one | 8 | 1 | 1 | 77 (CO−Cd); 150 (CO−Cd); 502 (Cd−OH); 939 (Cd−OH) | 7.54; 20.55; 0.57; 0.67 | 6.05; 22.60; 9.05; 23.86 |
| (51) (*Z*)-3-hydroxybutenal | 12 | 1 | 1 | 155 (Cd−C); 186 (CO−Cd); 828 (Cd−OH) | 2.98; 8.91; 0.81 | 1.63; 17.40; 16.96 |
| | | | | Group 4. Ester Group | | |
| (52) formic acid vinyl ester | 4 | 1 | 1 | 69 (CO−O); 304 (O−Cd) | 3.83; 5.75 | 3.83; 11.66 |
| (53) 3-oxopropionic acid vinyl ester | 4 | 1 | 2 | 33 (CO−C); 52 (CO−C); 71 (O−Cd); 152 (CO−O) | 12.08; 4.50; 5.72; 7.37 | 2.26; 2.98; 3.93; 11.97 |
| (54) 2-methylacrylic acid vinyl ester | 6 | 1 | 2 | 70 (CO−Cd); 72 (O−Cd); 144 (CO−O); 205 (Cd−C) | 25.11; 24.61; 7.35; 2.61 | 9.84; 2.97; 6.92; 2.23 |
| | | | | Group 5. Carboxylic Acids | | |
| (55) acrylic acid | 4 | 1 | 1 | 124 (CO−Cd); 706 (CO−OH) | 7.50; 0.60 | 6.89; 13.86 |
| (56) 2,2-dimethyl-3-oxopropionic acid | 9 | 1 | 2 | 44 (CO−C); 68 (CO−C); 235 (C−C); 280 (C−C); 655 (CO−OH) | 31.60; 5.40; 3.03; 3.05; 0.30 | 2.24; 2.56; 3.75; 3.66; 14.27 |
| (57) but-3-enoic acid | 2 | 1 | 2 | 54 (CO−C); 95 (Cd−C); 560 (CO−OH) | 14.00; 6.33; 0.53 | 2.13; 3.05; 13.71 |

$-2.47$, $NN_{1.771}{}^{OH\text{-}47} = -2.22$, $NN_{1.775}{}^{OH\text{-}46} = -2.78$. The values obtained for the H-bond correction including the resonance effect of the cis conformers in enol form of $\beta$-diketones were in the intramolecular hydrogen bond energy range in malonaldehyde enol derivatives assessed by Musin and Mariam.[49] Parts a and b of Figure 10 show the adjustment for the $NN_x{}^{OH}$ correction found in this work. Figure 10a presents the results for the distances based on the MP2/6-31G† level whereas Figure 10b presents the results for the distances based on the HF/6-31G† level. This last adjustment can be used for preliminary evaluations of this interaction at low levels of theory.

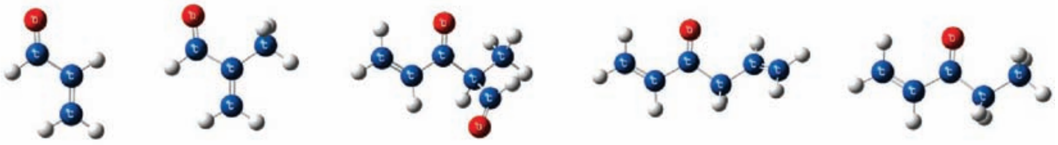
Compounds 37 and 43 from group 3 possessed internal H-bonds (Figure 9). Molecule 37 contained several non next neighbor corrections. H-bond correction for compound 37 at 1.783 Å can be calculated to be $NN_{1.783}{}^{OH\text{-}37} = -1.45$ kcal/mol by using the linear fitting shown in Figure 10a. Correction due to the CO−CO eclipse for this molecule could be calculated as $NN_{G2}{}^{II\text{-}37} - C/CO/H_3 - CO/C/H - 2Cd/H_2 + NN_{CIS}{}^{OH} + NN_{1.783}{}^{OH\text{-}37} + NN_{G2}{}^{I} = T37 - T20 - T10 - T26$, $NN_{G2}{}^{II\text{-}37} = -1.45$ kcal/mol. The $NN_x{}^{OH}$ value for a 1.788 Å distance occurring in compound 43 was assessed as being −1.61 kcal/mol. The most stable conformer for compound 43 shows that the NN value also contained some correction for methylene distortion. The CO−Cd eclipse for the $C/CO/Cd/H_2$ group possessed the normal orientation as shown in compound 19 (Table S2, Supporting Information) whereas it had ca. 160° distortion in compound 43. This distortion prolonged the H−H distances, thereby giving extra stability which was already included in the $NN_x{}^{OH}$ correction. The true value for this $NN_x{}^{OH}$ for a 1.788 Å distance was less than the value supposed in this work, as shown by linear adjustment tendency in Figure 10a,b. This supports the consideration that the H-bond GAV correction was null at distances greater than 1.79 Å (Figure 10a). It should be mentioned that contributions to molecular stability from weak internal H-bonding (such as contributions in polyols[13c]) have already been considered in the value of the constituent GAVs.

Appreciable magnitude non next neighbor interactions were also present in compounds 9, 32, and 53. Compound 9 needed a non next neighbor correction due to the hydroxyl groups' cis position. This interaction can be assessed as follows: $NN_{G1}{}^{I\text{-}9} = T9 - T10 - T11 + 2{*}Cd/H2$, $NN_{G1}{}^{I\text{-}9} = 2.74$ kcal/mol. Compound 32 had to be corrected due to the $CH_3{-}CO{-}CH_3$ eclipse that differed from the Cd−CO−Cd eclipse of the lowest isomer of compound 16: $NN_{G2}{}^{II\text{-}32} = T32 - 2{*}T18 - T16 + 2{*}T17$, $NN_{G2}{}^{II\text{-}32} = 1.61$ kcal/mol. Compound 53 presented the CO−CO eclipse as in compounds 23 and 37 (Group 2); however, its value was a little lower than in this group due to the oxy group attached to one of the CO groups: $NN_{G2}{}^{I\text{-}53} + C/O/H_3 + CO/C/H + O/Cd/C - CO/O/C - O/CO/Cd = T53 - T20 - T8$, $NN_{G4}{}^{I\text{-}53} = -0.48$ kcal/mol. Likewise, compounds 3, 33, 35, 36, 41, 42, and 54 were corrected by including gauche interactions ($NN_{GE}$). The corresponding non next neighbor corrections could be obtained by using the following figures (in kca/mol): $NN_{GE}{}^{3} = T3 - T2 + T8 - T7$, $NN_{GE}{}^{3} = 0.50$; $NN_{GE}{}^{33} = T33 - T19 - T18 - CO/Cd/C + 2{*}CO/Cd/H$, $NN_{GE}{}^{33} = -0.90$; $NN_{GE}{}^{35} = T35 - T21 - T11 + Cd/H_2 + C/Cd/H_3 + Cd/C/H$, $NN_{GE}{}^{35} = -1.32$; $NN_{GE}{}^{36} = T36 - T22 - T11 + Cd/H_2 + C/Cd/H_3 + Cd/C/H$, $NN_{GE}{}^{36} = -4.13$; $NN_{GE}{}^{41} = T41 - T22 - T10 + 2{*}Cd/H_2$, $NN_{GE}{}^{41} = -1.83$; $NN_{GE}{}^{42} = T42 - T19 - T11 + Cd/H_2 + C/Cd/H_3 + Cd/C/H$, $NN_{GE}{}^{42} = -0.97$; $NN_{GE}{}^{54} = T54 - T11 + T10 - T52 + O/CO/H + CO/O/H + NN_{G2}{}^{I}$, $NN_{GE}{}^{54} = 0.61$.



(1) Ethene-1,1-diol (2) 1-Methoxy-ethenol (14) 1,1-Dimethoxy-ethene (15) 1-Ethoxy-1-methoxy-ethene

**Figure 7.** Conformers for some group 1 compounds.



(17) Acrolein (18) 2-Me-propenal (27) 2-Me-3-oxo-pent-4-enal (28) Hexa-1,5-dien-3-one (31) Pent-1-en-3-one

**Figure 8.** Conformers for some group 2 compounds.

(34) 5-hydroxy-hexa-1,4-dien-3-one (37) (Z)-5-hydroxy-3-oxo-pent-4-enal (38) 3,3-dihydroxy-propenal (43) 4-hydroxy-but-3-enal (49) 4,4-dihydroxy-but-3-en-2-one

**Figure 9.** Conformers for some group 3 compounds.

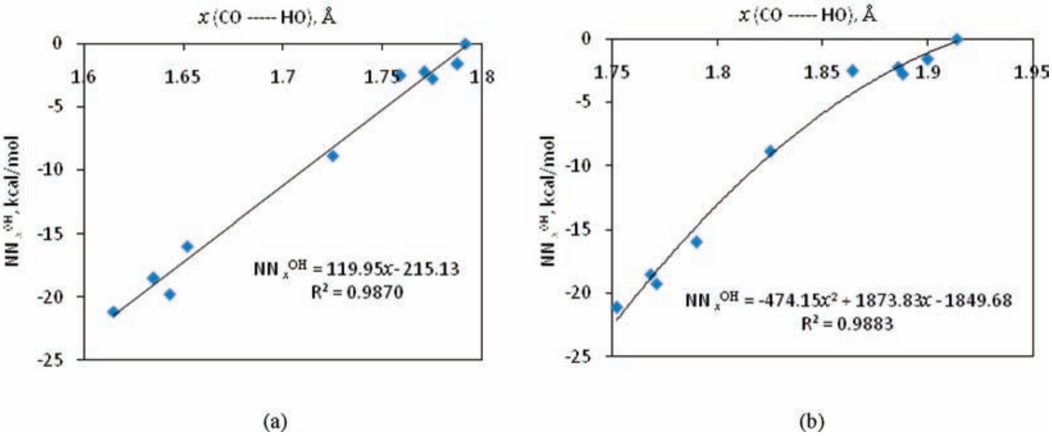


**Figure 10.** Correction for $\Delta H_f$ in molecules with both $NN_x^{OH}$ and $NNcis^{OH}$ interactions. Distances based on (a) MP2/6-31G† and (b) HF/6-31G† calculations.

An additional improvement to the equations so derived must be considered for correctly assessing the unknown GAVS. Correction due to possible errors accounted for by CBS-Q energy predictions ($NN_{CBS-Q}$) were considered for compounds 7, 17, and 39. The balance of heat of formation values for these related compounds by using GAVs must fulfill T39 − T17 − T7 + 2*Cd/$H_2$ = 0. Nevertheless, heat of formation values with CBS-Q energies gave T39 − T17 − T7 + 2*Cd/$H_2$ = −2.03 kcal/mol. This error in predicting these compounds' heat of formation can be set up as a correction ($NN_{CBS-Q}$) for compound 39. Some other appreciable deviations in predicting the heat of formation based on energies at the CBS-Q multilevel have been reported elsewhere.[15,19] Table S8A of the Supporting Information gives a summary of the non next neighbor corrections for calculating heat of formation GAVs. The preceding corrections were also applied for the calculation of GAVS for intrinsic entropy and specific heat at different temperatures. Tables S7−S14 and Figures S2−S18 of the Supporting Information summarize and illustrate the correction values for the non next neighbor interactions. It should be stressed that $NN_x^{OH}$ corrections for specific heat at different temperatures agreed with the assumption that internal hydrogen bonds become weakened with increasing temperature.[50]

**Acyclic Compound-Based GAVS.** Estimating entropy by the GAV method (so-called intrinsic entropy) needs correction due to high temperatures (statistical thermodynamic classical limits) in addition to non next neighbor interactions.[14] Such correction is obtained by considering both the number of indistinguishable configurations which the compounds may have and the contribution from the mixture of energetically equivalent conformers. The correction can be done mathematically by using the following expression:

$$S^\circ_{\mathrm{int}} = S^\circ_{\mathrm{calc}} + R\sum \ln\left(\frac{\sigma_i}{n_i}\right) \qquad (8)$$

where $\sigma_i$ corresponds to the total symmetry number ($\sigma_i^{\mathrm{ext}}\sigma_i^{\mathrm{int}}$) and $n_i$ corresponds to the number of energetically equivalent conformers (Table 9). The calculated total entropy was thus further modified while deriving GAVs to work with the intrinsic value instead (eq 8). All final thermochemical properties were expressed in terms of GAVs and the corresponding non next neighbor corrections. The values for known GAVs can be found in Table 10. The unknown groups were assumed to be the independent variables of the derived linear systems of equations, one for each property. MVLR methodology was used for determining values for the unknown groups which best fit the systems of equations. The common feature for all groups of acyclic compounds when using the MVLR method was that estimating the thermochemical properties was successful. The data's agreement indicated that GAV methodology was applicable for calculating standard enthalpies of formation, standard entropies, and specific heat at several temperatures and suggested that it could provide reliable data for other ketene polymer structures that were not considered in this study.

GAV methodology was capable of reproducing the 57 ab initio thermochemical data having 0.065 kcal/mol, 0.12 cal/(mol K), 0.09 cal/(mol K) average deviation for heat of formation at 298 K, 298 K standard entropy, and 300 K specific heat (Table 11). The highest deviation was found to be 0.25 kcal/mol for heat of formation, 0.6 cal/(mol K) for entropy, and 0.48 cal/(mol K) for specific heat at 300 K. Table 11 gives a summary of main regression process features; it also shows a comparison between the fitting process without non next neighbor corrections (NN) and with them. The fitting process without NN showed good $R^2$ coefficient, although the deviations were appreciable for all properties and this model was therefore inaccurate; for example, maximum positive deviation for 9 kcal/mol heat of formation cannot be accepted for reproducing this property. The fitting process with the use of NN showed both good $R^2$ coefficient and very low deviation; Table 11 shows a 0.66 kcal/mol root-mean-square deviation for adjusting heat of formation for the process with NN. Considering NN gives both a precise and accurate model. This improvement suggested that including the NN interactions derived in this work (Tables S7−S14, Supporting Information) in regression were essential for correctly determining the unknown GAVs (Table 3). Table 12 compares the values for the unknown GAVs obtained with and without NN. The main differences in the values of the different GAVS obtained without NN and with NN were found in Cd/CO/H, Cd/O/C, Cd/O/H, Cd/O2, and O/Cd/H due to these groups being involved in most compounds corrected by interactions. The inductive and resonance effects,[51] which might have been present in the molecules analyzed here containing these GAVS, may have been responsible for the NN interactions. Table 13 presents the final values for the GAVs calculated in this work (standard error at 99% confidence). The confidence intervals showed that the model is very precise (0.48 kcal/mol as maximum confidence size for heat of formation). The condition number, defined as $\|\mathbf{A}\|\|\mathbf{A}^{-1}\|$, where $\mathbf{A}$ is the coefficient matrix associated with the GAV-adjusting problem, indicates how well-defined the regression problem was.[52] The condition number was calculated to be 9.4 and therefore indicated that errors in predicting theoretical properties would be amplified by up to 9 times in derived Benson group values; for example, the lack of $\mathrm{NN_{CBS\text{-}Q}}$ for compound 39 would assess a ca. 1.5 kcal/mol value for heat of formation for this compound, this being greater than that estimated from the CBS-Q energies. It seems that values for the condition number less than 10 were sufficient for considering the GAV-regression problem as being well conditioned (see ref 15b). The randomly distributed residuals, found when predicting thermochemical properties from GAVs, suggested that error deviations were uncorrelated (Figures 11, 12, and 13, and Figures S19−S24, Supporting Information); the Durbin−Watson test[53] score ($d = 1.78$) was found to be inconclusive in identifying the autocorrelation in the residuals for this regression model.

Some heat-of-formation GAVs assessed in this work have been reported elsewhere. The 8.27 kcal/mol value for Cd/O/C (Table 13) was in excellent agreement with the value calculated by Sebbar et al. (8.20 kcal/mol).[54] Likewise, the −44.43 kcal/mol value for O/Cd/H is in excellent agreement with the −44.80 kcal/mol value recently calculated by da Silva et al.[55a] The O/Cd/H value has been recalculated several times since being first estimated by Benson et al. on the basis of alcohols (−37.9 kcal/mol).[13a] Several newer more stable values for O/Cd/H have been reported by other authors[41c,55b−f] and it has been found that these estimations differed from those of Benson et al. by values ranging from −6.7 to −11.4 kcal/mol, into which the data calculated in the current research fall precisely (Table 13). Similarly, the 9.21 kcal/mol value for Cd/O/H differed from the value initially obtained by Benson et al.[13a,14] (8.60 kcal/mol), presumably due to differences in O/Cd/H group.

The 7.79 kcal/mol value for Cd/CO/H assessed in the current research differed from that calculated by Benson et al. (4.32 kcal/mol) on the basis of crotonaldehyde.[13a] Differences in Cd/CO/H values were mainly due to uncertainties in heat of formation for this compound. Benson et al.[13a] used a −25.5 kcal/mol value whereas a recent experiment assessed −24.36 ± 0.12 kcal/mol for crotonaldehyde's heat of formation.[56] This recent experimental data suggested (agreeing with the results of this research) that the actual Cd/CO/H group value must be greater than 4.32 kcal/mol. The 6.49 kcal/mol value for $\mathrm{Cd/O_2}$ diverged from that assessed by Sebbar et al.[57] (12.41 kcal/mol) at the B3LYP/6-311G(d,p) level. Differences in $\mathrm{Cd/O_2}$ group values were related to ethane-1,1-diol heat of formation[57] (Table 2) and assumed O/Cd/H group value, which was reduced to ethenol heat of formation[55e] (Table 2). Experiments for determining ethene-1,1-diol and ethenol heat of formation are called for to assign correct figures for O/Cd/H and $\mathrm{Cd/O_2}$.

The validity of the GAVs calculated in the current research can be verified by comparing the results regarding heats of formation for acetylacetone ($\mathrm{CH_3COCH_2COCH_3}$) and malonic acid ($\mathrm{HOCOCH_2COOH}$). According to GAV methodology (Tables 10 and 13), these compound's heats of formation were −85.6 and −188.8 kcal/mol, respectively. The result for acetylacetone was in excellent agreement with the −85.78 kcal/mol reported by Temprado et al.[58a] on the basis of analyzing recent NMR studies and correlations for pure tautomer vaporization enthalpies in gas chromatography experiments. Likewise, the result for malonic acid was in excellent agreement with the −187.8 kcal/mol value based on both experimental heat of sublimation (105.1 ± 0.8 kJ/mol)[59a] and experimental $\Delta H_{\mathrm{f}}$ in solid phase (−891 kJ/mol).[59b] Such agreements between the GAV methodology and experiments suggested that the $\mathrm{C/(CO)_2/H_2}$ value must be −2.4 kcal/mol instead of the data initially estimated by Benson et al. (−7.6 kcal/mol).[13a,14] Discrepancies in Benson et al.'s estimation can be explained by errors in the acetylacetone thermo-

**TABLE 10: Known GAVS[14]**

| | $\Delta H_f^\circ$, kcal/mol | $S_{intr}$, cal/(mol K) | $C_p$, cal/(mol K) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 300K | 400K | 500K | 600K | 800K | 1000K | 1500K |
| C/C/H3 | −10.2 | 30.4 | 6.2 | 7.8 | 9.4 | 10.8 | 13.0 | 14.8 | 17.6 |
| C/Cd/H3 | −10.2 | 30.4 | 6.2 | 7.8 | 9.4 | 10.8 | 13.0 | 14.8 | 17.6 |
| C/CO/H3 | −10.2 | 30.4 | 6.2 | 7.8 | 9.4 | 10.8 | 13.0 | 14.8 | 17.6 |
| C/O/H3 | −10.2 | 30.4 | 6.2 | 7.8 | 9.4 | 10.8 | 13.0 | 14.8 | 17.6 |
| Cd/C/H | 8.6 | 8.0 | 4.2 | 5.0 | 5.8 | 6.5 | 7.6 | 8.5 | 9.6 |
| Cd/H2 | 6.3 | 27.6 | 5.1 | 6.4 | 7.5 | 8.5 | 10.1 | 11.3 | 13.2 |
| C/CO/C/H2 | −5.2 | 9.6 | 6.2 | 7.7 | 8.7 | 9.5 | 11.1 | 12.2 | 13.5[a] |
| CO/C/H | −29.1 | 34.9 | 7.0 | 7.8 | 8.8 | 9.7 | 11.2 | 12.2 | 13.6[a] |
| CO/C2 | −31.4 | 15.0 | 5.6 | 6.3 | 7.1 | 7.8 | 8.9 | 9.6 | 10.1[a] |
| CO/Cd/H | −29.1 | 34.9 | 7.0 | 7.8 | 8.8 | 9.7 | 11.2 | 12.2 | 13.6[a] |
| CO/O/C | −35.1 | 14.8 | 6.0 | 6.7 | 7.3 | 8.0 | 8.9 | 9.4 | 10.4[a] |
| CO/O/H | −32.1 | 34.9 | 7.0 | 7.9 | 8.8 | 9.7 | 11.2 | 12.2 | 13.6[a] |
| O/C/H | −37.9 | 29.1 | 4.3 | 4.4 | 4.8 | 5.2 | 6.0 | 6.6 | 7.6[a] |
| O/CO/H | −58.1 | 24.5 | 3.8 | 5.0 | 5.8 | 6.3 | 7.2 | 7.8 | 8.2[a] |

[a] Values estimated from extrapolation.

**TABLE 11: Summary of Regressions Processes' Main Features**

| | $\Delta H_f^\circ$, kcal/mol | | $S_{intr}$, cal/(mol K) | | $C_p$ at 300 K, cal/(mol K) | |
|---|---|---|---|---|---|---|
| | without NN | with NN | without NN | with NN | without NN | with NN |
| average deviation | 0.294 | 0.010 | 0.097 | 0.002 | 0.107 | −0.001 |
| mean absolute deviation | 2.669 | 0.065 | 1.102 | 0.120 | 1.080 | 0.092 |
| maximum positive deviation | 9.060 | 0.266 | 3.992 | 0.556 | 4.336 | 0.374 |
| maximum negative deviation | −7.493 | −0.245 | −3.249 | −0.598 | −4.336 | −0.486 |
| root mean square deviation | 26.876 | 0.664 | 10.902 | 1.411 | 10.356 | 1.087 |
| *R2*coefficient | 0.989 | 0.999 | 0.981 | 0.999 | 0.950 | 0.999 |

**TABLE 12: Comparison between the Assessed GAVs without NN and with NN**

| | $\Delta H_f^\circ$, kcal/mol | | $S_{intr}$, cal/(mol K) | | $C_p$ at 300 K, cal/(mol K) | |
|---|---|---|---|---|---|---|
| | without NN | with NN | without NN | with NN | without NN | with NN |
| CO/Cd2 | −28.3 | −28.9 | 17.2 | 17.9 | 8.0 | 5.9 |
| C/(CO)2/C/H | 2.4 | 0.4 | −11.5 | −12.8 | 5.8 | 5.2 |
| C/(CO)2/C2 | 1.5 | 1.4 | −36.5 | −35.4 | 5.3 | 5.2 |
| C/(CO)2/H2 | −4.4 | −2.4 | 7.5 | 7.0 | 5.5 | 4.6 |
| C/CO/Cd/C/H | −0.1 | −1.5 | −13.1 | −13.7 | 7.2 | 6.6 |
| C/CO/Cd/C2 | 0.0 | 0.2 | −36.1 | −35.4 | 5.0 | 4.5 |
| C/CO/Cd/H2 | −2.3 | −3.5 | 9.1 | 9.1 | 6.1 | 5.1 |
| Cd/CO/C | 8.9 | 8.1 | −15.6 | −14.7 | 3.5 | 3.6 |
| Cd/CO/H | 3.0 | 7.8 | 2.9 | 4.1 | 3.2 | 4.7 |
| Cd/O/C | 11.2 | 8.3 | −14.1 | −16.7 | 3.5 | 1.8 |
| Cd/O/H | 11.1 | 9.2 | 5.1 | 4.2 | 5.0 | 2.8 |
| Cd/O2 | 10.6 | 6.9 | −16.8 | −19.9 | 5.1 | 0.0 |
| CO/Cd/C | −32.1 | −30.3 | 15.0 | 16.7 | 6.2 | 5.6 |
| O/Cd/H | −49.6 | −44.4 | 27.7 | 29.9 | 4.0 | 6.9 |

chemical data, which seemingly referred to its enol-tautomeric form instead (Figure 5). Additional calculations in current research at CBS-Q multilevel have predicted −17.6 kJ/mol tautomerization enthalpy for acetylacetone, agreeing with a −19.3 ± 2.8 kJ/mol experimental value by Temprado et al.[58a] and −19.5 ± 0.75 kJ/mol by Folkendt et al.[58b]

**Ring and Substituent Position Corrections for Ketene Dimers and Related Structures.** Ring corrections (RC) derived in this work had a high confidence level due to the CBS-Q method's good performance.[19] Ring strain energies calculated by the CBS-Q model, particularly in four-membered rings, had one of the best performances, according to Petersson et al.'s evaluation.[19] RC for ketene dimers and related structures derived with the GAVs listed in Tables 10 and 13 are shown in Table 14 and Tables S21 and S22 (Supporting Information). The RC value for diketene was found to be 1 kcal/mol more stable than the 22.5 kcal/mol value estimated by Månsson et al.[10] The RC values for the other ring compounds assessed in the current work represent the first ones reported in the literature. Enthalpy corrections for the four-membered ring compounds had positive values, whereas the enthalpy corrections for pyran-4-one type ring compounds had negative values (Table 14). According to Benson, the ring correction derived from GAVs reflects the strain energy of the corresponding cyclic compound since group values were derived from open-chain-zero-strained compounds.[14] However, this RC value may also contain contributions from resonance energy. The pyran-4-ones negative enthalpy corrections may have resulted from combining resonance energy and ring strain energy, such as that occurring in furan, phenol, and other vinyl or unsaturated ether compounds.[15] Resonance through chemical bonds on unsaturated carbon and adjacent oxygen atoms was evidenced by the weaker O−H bonds (ca. 85 kcal/mol[60a]) in $\mathrm{CH_2{=}CHOH}$, $\mathrm{CH{\equiv}COH}$ and phenol, compared to that in $\mathrm{CH_3OH}$ and $\mathrm{CH_3CH_2OH}$ (ca. 104 kcal/mol[60b]).

Regarding cyclobut-2-enones, resonance energy's effect on total correction value for heat of formation could be partly seen in the OH value and methyl substituent corrections (Table 14, column SP). 3-Hydroxycyclobut-2-enone lowered its energy by

**TABLE 13: GAVs Calculated in This Work (Standard Errors 99% Confidence)**

| | $\Delta H_f°$, kcal/mol | $S_{intr}$, cal/(mol K) | $C_p$, cal/(mol K)<br>300 K | 400 K | 500 K | 600 K | 800 K | 1000 K | 1500 K |
|---|---|---|---|---|---|---|---|---|---|
| C/O/C/H2[c] | −8.1[a] | 7.8 | 6.5 | 7.9 | 9.1 | 10.0 | 11.6 | 12.8 | 14.6 |
| O/Cd/C[b] | −30.5[a] | 9.7[a] | 5.7 ± 0.4 | 6.7 ± 0.5 | 6.7 ± 0.4 | 6.5 ± 0.5 | 6.6 ± 0.5 | 6.0 ± 0.5 | 5.2 ± 0.5 |
| CO/O/Cd | −32.0[a] | 18.4 ± 0.6 | 16.0 ± 0.4 | 20.6 ± 0.6 | 23.5 ± 0.5 | 25.3 ± 0.5 | 27.2 ± 0.6 | 28.0 ± 0.5 | 29.6 ± 0.6 |
| O/CO/Cd | −45.2[a] | 6.4 ± 0.5 | 4.6 ± 0.4 | 6.2 ± 0.6 | 6.9 ± 0.5 | 7.3 ± 0.5 | 7.6 ± 0.5 | 7.6 ± 0.5 | 6.7 ± 0.5 |
| O/Cd2 | −33.0[a] | 14.1 ± 0.5 | 5.7 ± 0.4 | 6.7 ± 0.5 | 6.7 ± 0.4 | 6.5 ± 0.5 | 6.3 ± 0.5 | 6.0 ± 0.5 | 5.2 ± 0.5 |
| CO/Cd2 | −28.9 ± 0.2 | 17.9 ± 0.6 | 5.9 ± 0.5 | 5.9 ± 0.6 | 6.5 ± 0.5 | 7.1 ± 0.6 | 8.1 ± 0.6 | 8.7 ± 0.6 | 9.4 ± 0.6 |
| C/(CO)2/C/H | 0.4 ± 0.2 | −12.8 ± 0.4 | 5.2 ± 0.3 | 6.7 ± 0.5 | 7.5 ± 0.4 | 8.0 ± 0.4 | 8.8 ± 0.4 | 9.5 ± 0.4 | 10.7 ± 0.4 |
| C/(CO)2/C2 | 1.4 ± 0.2 | −35.4 ± 0.4 | 5.2 ± 0.3 | 6.9 ± 0.4 | 7.2 ± 0.3 | 7.3 ± 0.3 | 7.3 ± 0.4 | 7.4 ± 0.3 | 7.4 ± 0.4 |
| C/(CO)2/H2 | −2.4 ± 0.1 | 7.0 ± 0.3 | 4.6 ± 0.2 | 6.8 ± 0.3 | 8.1 ± 0.3 | 9.2 ± 0.3 | 10.8 ± 0.3 | 12.1 ± 0.3 | 14.1 ± 0.3 |
| C/CO/Cd/C/H | −1.5 ± 0.2 | −13.7 ± 0.4 | 6.6 ± 0.3 | 7.4 ± 0.4 | 7.9 ± 0.3 | 8.4 ± 0.4 | 9.1 ± 0.4 | 9.8 ± 0.4 | 10.9 ± 0.4 |
| C/CO/Cd/C2 | 0.2 ± 0.2 | −35.4 ± 0.4 | 4.5 ± 0.3 | 5.8 ± 0.4 | 6.6 ± 0.3 | 7.1 ± 0.4 | 7.5 ± 0.4 | 7.7 ± 0.4 | 7.8 ± 0.4 |
| C/CO/Cd/H2 | −3.5 ± 0.1 | 9.1 ± 0.2 | 5.1 ± 0.2 | 6.9 ± 0.3 | 8.3 ± 0.2 | 9.4 ± 0.2 | 11.0 ± 0.3 | 12.3 ± 0.2 | 14.3 ± 0.3 |
| Cd/CO/C | 8.1 ± 0.2 | −14.7 ± 0.3 | 3.6 ± 0.3 | 5.0 ± 0.4 | 5.9 ± 0.3 | 6.4 ± 0.3 | 7.0 ± 0.3 | 7.1 ± 0.3 | 7.1 ± 0.3 |
| Cd/CO/H | 7.8 ± 0.1 | 4.1 ± 0.3 | 4.7 ± 0.2 | 6.2 ± 0.3 | 7.1 ± 0.2 | 7.9 ± 0.3 | 8.8 ± 0.3 | 9.5 ± 0.3 | 10.4 ± 0.3 |
| Cd/O/C | 8.3 ± 0.1 | −16.7± 0.3 | 1.8 ± 0.4 | 2.5 ± 0.5 | 3.6 ± 0.4 | 4.3 ± 0.5 | 5.1 ± 0.5 | 5.6 ± 0.5 | 6.2 ± 0.5 |
| Cd/O/H | 9.2 ± 0.1 | 4.2 ± 0.2 | 2.8 ± 0.3 | 3.6 ± 0.4 | 4.7 ± 0.3 | 5.6 ± 0.3 | 6.9 ± 0.3 | 7.9 ± 0.3 | 9.5 ± 0.3 |
| Cd/O2 | 6.9 ± 0.1 | −19.9 ± 0.3 | 0.0 ± 0.6 | 0.4 ± 0.8 | 1.8 ± 0.6 | 3.0 ± 0.7 | 4.5 ± 0.7 | 5.2 ± 0.7 | 6.4 ± 0.7 |
| CO/Cd/C | −30.3 ± 0.1 | 16.7 ± 0.3 | 5.6 ± 0.3 | 6.0 ± 0.4 | 6.7 ± 0.3 | 7.3 ± 0.3 | 8.4 ± 0.3 | 9.0 ± 0.3 | 9.7 ± 0.3 |
| O/Cd/H | −44.4 ± 0.1 | 29.9 ± 0.2 | 6.9 ± 0.3 | 8.3 ± 0.4 | 8.6 ± 0.4 | 8.7 ± 0.4 | 8.6 ± 0.4 | 8.5 ± 0.4 | 8.5 ± 0.4 |

[a] From ref 10. [b] Estimated to be equal to O/Cd₂. [c] Recalculated for $S_{int}$ and $C_p$ based upon compounds **12** and **8**.

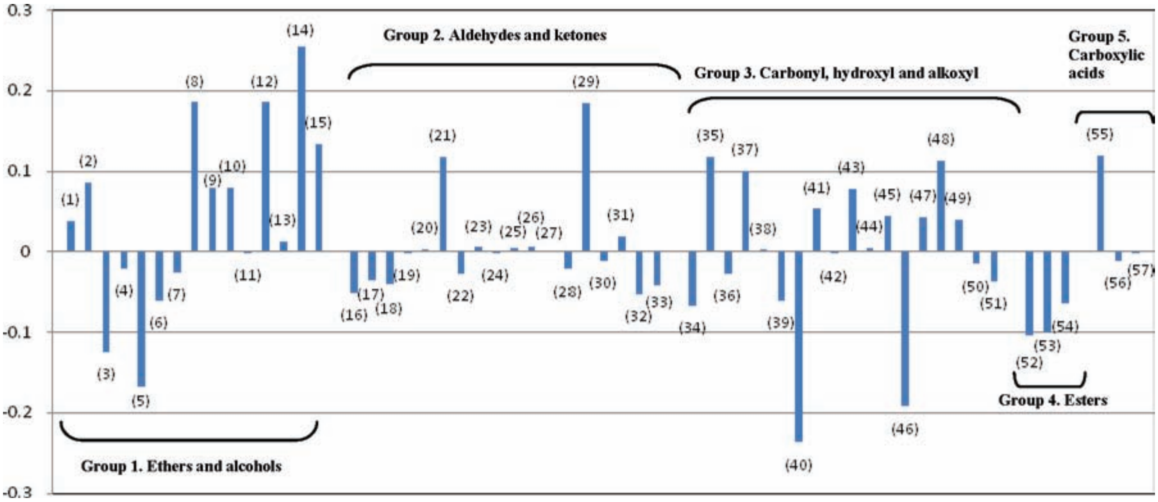


**Figure 11.** Deviations in $\Delta H_f$ (in kcal/mol) predictions for the acyclic base compounds from GAVs.

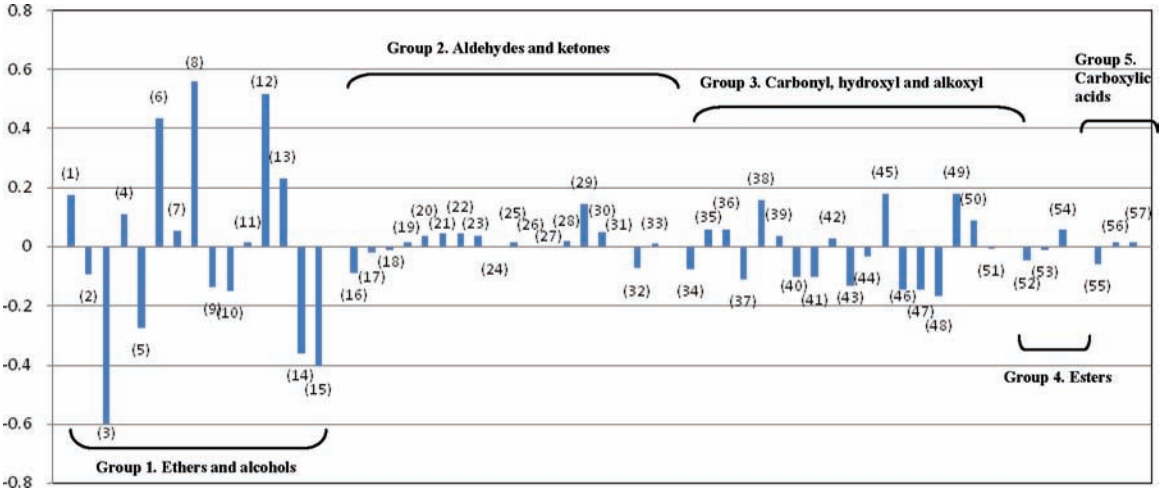


**Figure 12.** Deviations in intrinsic entropy (in cal/(mol K)) predictions for the acyclic base compounds from GAVs.

ca. 12 kcal/mol in the presence of a methyl substituent (Table 5), whereas two methyl substituent groups lowered energy by ca. 16 kcal/mol. Better electron-withdrawing groups presumably further stabilize 3-hydroxycyclobut-2-enones. It is also worth mentioning that substituent position corrections (SP) were more important in cyclobutane-1,3-dione than in the diketene ring.

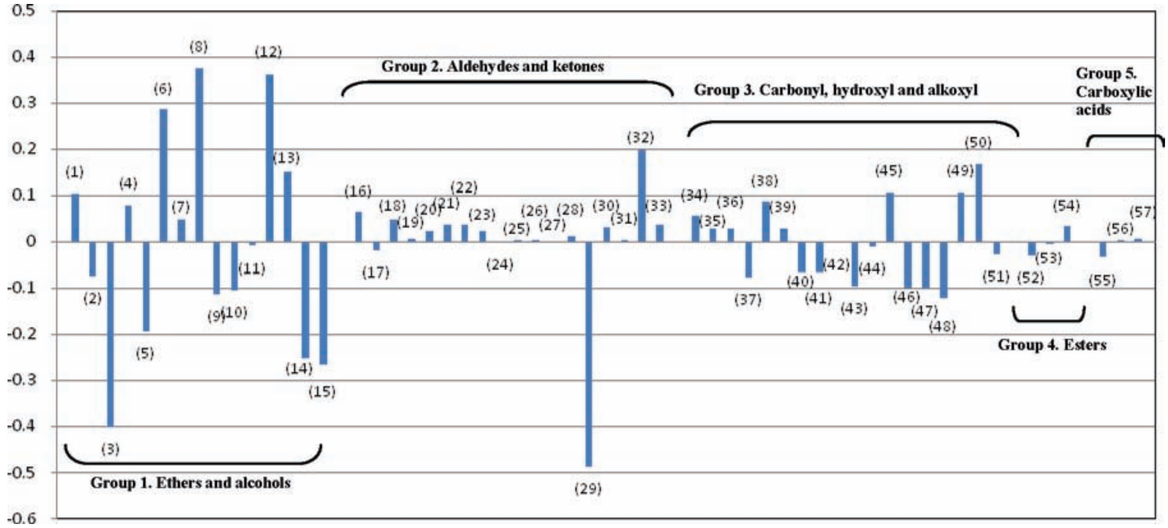


**Figure 13.** Deviations in $C_p$ at 300 K (in cal/(mol K)) predictions for the acyclic base compounds from GAVs.

**TABLE 14: Ring Formation (RC) and Substituent Position (SP) Corrections for Ketene Dimers and Related Cyclic Structures**

| | $\Delta H_f°$, kcal/mol | | $S_{intr}$, cal/(mol K) | | $C_p$ 300 K, cal/(mol K) | |
|---|---|---|---|---|---|---|
| | RC | SP | RC | SP | RC | SP |
| Diketenes | | | | | | |
| (1c) diketene (4-methyleneoxetan-2-one) | 21.4 | | 31.5 | | −2.3 | |
| (2c) 3-methyl-4-methyleneoxetan-2-one | 21.4 | −1.4 | 31.5 | 2.6 | −2.3 | −2.0 |
| (3c) 3,3-dimethyl-4-methyleneoxetan-2-one | 21.4 | −2.8 | 31.5 | 2.6 | −2.3 | 0.2 |
| Cyclobutane-1,3-diones | | | | | | |
| (4c) cyclobutane-1,3-dione | 23.3 | | 30.5 | | 0.9 | |
| (5c) 2-methylcyclobutane-1,3-dione | 23.3 | −2.3 | 30.5 | −0.2 | 0.9 | −1.2 |
| (6c) 2,2-dimethylcyclobutane-1,3-dione | 23.3 | −11.3 | 30.5 | 1.7 | 0.9 | −1.1 |
| (7c) (*E*)-2,4-dimethylcyclobutane-1,3-dione | 23.3 | −9.2 | 30.5 | 0.1 | 0.9 | −2.3 |
| Pyran-4-ones | | | | | | |
| (8c) pyran-4-one | −11.3 | | 25.4 | | −5.0 | |
| (9c) 3-methylpyran-4-one | −11.3 | −3.8 | 25.4 | 0.6 | −5.0 | 0.9 |
| (10c) 2-methylpyran-4-one | −11.3 | −0.7 | 25.4 | −1.5 | −5.0 | 1.0 |
| (11c) 2-hydroxypyran-4-one | −11.3 | −1.0 | 25.4 | 0.9 | −5.0 | 0.9 |
| Cyclobut-2-enones | | | | | | |
| (12c) cyclobut-2-enone | 27.7 | | 29.9 | | −2.7 | |
| (13c) 4-methylcyclobut-2-enone | 27.7 | −1.1 | 29.9 | 2.3 | −2.7 | −1.7 |
| (14c) 2-methylcyclobut-2-enone | 27.7 | −6.8 | 29.9 | −0.4 | −2.7 | 0.4 |
| (15c) 4,4-dimethylcyclobut-2-enone | 27.7 | −8.3 | 29.9 | 2.5 | −2.7 | 0.5 |
| (16c) 3-hydroxycyclobut-2-enone | 27.7 | −3.9 | 29.9 | 0.5 | −2.7 | 0.4 |
| (17c) 3-hydroxy-2-methylcyclobut-2-enone | 27.7 | −12.2 | 29.9 | 1.0 | −2.7 | 0.4 |
| (18c) 3-hydroxy-4-methylcyclobut-2-enone | 27.7 | −12.0 | 29.9 | 2.8 | −2.7 | −1.4 |
| (19c) 3-hydroxy-2,4-dimethylcyclobut-2-enone | 27.7 | −16.0 | 29.9 | 1.2 | −2.7 | −1.1 |
| (20c) 3-hydroxy-4,4-dimethylcyclobut-2-enone | 27.7 | −17.1 | 29.9 | 0.6 | −2.7 | 0.7 |

The tendency of these SP agreed with the conclusion that alkylketene dimerization produced cyclobutane-1,3-dione structure as being the major product because of thermodynamic control of the reaction. Ketene dimerization tendencies cannot be explained and separated within the GAV framework in terms of strain and resonance energy or steric effects. As Lay et al.[61] have stated, additional studies are needed to separate and identify ring strain and resonance effects in oxygenated hydrocarbon species.

Substituent position corrections for intrinsic entropy and specific heat were particularly lower than for heat of formation. Such low substituent effect values showed that the main concern in intrinsic entropy and specific heat corrections for ring formation is the loss of acyclic compounds' internal rotation modes.[14] The RC and SP corrections assessed in this work clearly helped in calculating the thermochemical data for ketene dimers and related structures and were particularly valuable when no other data were available.

## Conclusions

The most relevant results concerning ketene dimers' geometries and thermochemistry have been discussed above. According to the thermochemical data in the gas phase assessed in this work, the diketene dimer was more stable than the cyclobutane-1,3-dione dimer by ca. 3.5 kcal/mol and therefore the diketene dimer was found to be the major product for parent ketene dimerization due to thermodynamic control of the reaction. Such relative stability for ketene dimers found at CBS-Q multilevel contradicts combustion experiments. New experimental measurements regarding parent ketene dimer thermochemistry are called for to clarify dimerization energetics. On the other hand, alkylketene dimer stability was found to favor cyclobutane-1,3-dione structure and its enol-tautomeric species when increasing the number of methyl substituents. Such relative alkyl dimer stability suggested that alkylketene dimerization was thermodynamically controlled regarding cyclobutane-1,3-dione structure and its enol tautomer.

Despite its relatively simple approach, the GAV method proved to be a powerful and relatively accurate technique for estimating heat of formation, entropy, and specific heat for ketene dimers and other cyclic structures. The GAV method was particularly useful when no other data or theoretical methods were available. This work has led to 19 new GAVs, 4 ring corrections, and 16 substituent position corrections needed for estimating the thermochemical properties of ketene dimers and related structures (i.e., cyclobut-2-enones and pyran-4-ones) based on quantum chemical calculations using a set of 57 acyclic compounds and 20 cyclic molecules. NN interactions derived from gauche positions, eclipse positions, and hydrogen internal bonds were found to significantly affect the properties of the compounds analyzed here. The GAVs assessed by using such NN corrections accurately reproduced the theoretical thermochemical properties for the set of 57 acyclic compounds and experimental heat of formation for acetylacetone. Ring and substituent corrections derived from the new GAV values were found to contain resonance and strain energies reflecting the relative stability of the different cyclic species. The protocol outlined here provides support for applying GAVs to high-weight ketene polymers and for expanding this methodology to other polymer structures which were not considered in this research.

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**Supporting Information Available:** Twenty-two tables: the structures, geometries and rotational constants calculated at MP2/6-31G† level; a list of known GAVs for acyclic base compounds; the contribution of each movement to the thermochemical properties for both cyclic and acyclic compounds; the non next neighbor corrections for intrinsic entropy at 298.15 K and specific heat at different temperatures; heat of formation calculated from isodesmic reaction methodology; Fourier coefficients for the hindered potential of internal rotations around single bonds; thermochemical properties for acyclic base compounds from the GAVs calculated in this work; corrections for ring formation and substituent position for specific heat at different temperatures. Twenty-four figures: some parameters calculated for acrolein and ethoxy-ethene geometries; the tendencies for non next neighbor corrections due to hydrogen bonding for heat of formation at 298.15 K, intrinsic entropy at 298.15 K and specific heat at different temperatures; deviations for predicting specific heat from the GAVs calculated in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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