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Analysis of Complexes Pairing Hydroperoxyl Radical with Peroxyformic Acid

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Ab initio quantum calculations are used to analyze the binding of complexes pairing OOH with HOOCHO. Six minima are located on the potential energy surface, all of cyclic geometry. Of particular interest are the OH···O and CH···O H-bonds that arise in the complexes and the manner in which these interactions influence the internal properties of the subunits. The analysis is complicated by the presence of an intramolecular H-bond in the unperturbed HOOCHO molecule, which must be broken in order to form the pair of intermolecular H-bonds that are responsible for the binding in the most stable complex. The CH bond of HOOCHO is contracted, and its stretching frequency undergoes a blue shift, when this group participates in a H-bond.

1. Introduction

The importance of noncovalent intermolecular interactions in many areas of contemporary chemistry has been demonstrated in numerous studies of systems that are held together by forces ranging from weak van der Waals forces, as in Ar−HF, for example, to much stronger ionic interactions.[1,2] Among all noncovalent interactions, hydrogen-bonding types are particularly significant. Although the term “hydrogen bond” is widely used, it seems that a precise definition of this phenomenon (accounting for all of its relevant aspects) has not yet been fully agreed upon. Although a rather large number of studies devoted to the H-bonding phenomenon have been published (from both experimental and theoretical viewpoints[2−7]), the great majority of these works have been devoted to interactions between closed-shell systems, whether neutral or ionic. Studies of systems involving open-shell systems (such as radicals) are much sparser. This paucity is due in part to experimental and theoretical difficulties arising in the description and characterization of the systems in question. Bearing in mind the importance of free radicals in a number of fields (e.g., atmospheric chemistry and life sciences), detailed information about intermolecular interactions involving these open-shell systems is highly desirable.

The hydroperoxyl OOH radical participates in numerous oxidation reactions.[8] Its interaction with various molecules influences the stabilization of newly formed hot radicals and may affect their reactivity. One of the more intriguing areas of radical−molecule complex studies arises from the discovery of the formation of surprisingly stable OOH complexes.[9] A number of related systems combining OOH with H_2O,[10] HNO_3,[11] H_2SO_4,[12] HC(O)OH,[13] RC(O)OH (R = H, CH_3, CF_3),[14] $CF_3C(O)OH$,[15] HOC(O)OH,[16] $RC(O)NH_2$ (R = H, CH_3, NH_2),[17] SO_3,[18] $(CH_3)_2O$,[19] CH_3X (X = F, Cl, Br),[20] NH_3,[21] HF,[22] HCl,[23] and O_3[24] have been reported in the literature.

H-bonded complexes involving peracids have become a focus of recent attention due to some fascinating chemistry.[25−37] Peracids play a vital role in several chemically important reactions such as oxidizing agents in the epoxidation type of reactions where a carbon−carbon double bond in alkenes undergoes oxidation to generate epoxides (oxiranes), as a reagent in Baeyer−Villiger oxidation type of reactions, and so forth. Peroxyformic acid (PFA) is the simplest form of this type of molecule. However, there are no theoretical or experimental data currently available concerning the interactions of peroxyformic acid with open shell species such as the OOH radical. Given the rapidly growing importance of both sorts of systems, in conjunction with the absence of experimental information about the structures or energetics of such complexes, a theoretical analysis of their properties would appear to be in order. The present work thus reports a detailed examination of the stabilities, electronic structure, and vibrational frequencies of the title complexes for the first time.

2. Computational Details

Calculations were performed using the Gaussian 03 system of codes.[38] The geometries of the isolated OOH and PFA moieties and their complexes were fully optimized at the UMP2/6-311++G(2d,2p) computational level. Optimizations were begun from a large number of different starting point structures in order to ensure sufficient coverage of the full potential energy surface to identify all minima. Harmonic vibrational frequency calculations confirmed the structures as minima and enabled the evaluation of zero-point vibrational energies (ZPE). The counterpoise (CP) procedure[39] was used to correct the interaction energy for basis set superposition error (BSSE).[40] The G3MP2[41] method permits an assessment of the magnitude of correlation effects by the QCISD approach. G3MP2 represents a modified version of the original G3[42] that reasonably approximates the full G3 method at a substantially reduced computational cost. The total G3MP2 energy is evaluated by

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$$E_0(\mathrm{G3MP2}) = E[\mathrm{QCISD(T,FC)/6\text{-}31G(d)//MP2(Full)/6\text{-}31G(d)}] + \Delta \mathrm{E(G3MP2large)} + \Delta \mathrm{E(HLC)} + E(\mathrm{ZPE}) + \Delta \mathrm{E(SO)}$$

where

$$\Delta \mathrm{E(G3MP2large)} = \mathrm{E[MP2(FC)/G3MP2large//MP2(full)/6\text{-}31G(d)]} - E[\mathrm{MP2(FC)/6\text{-}31G(d)//MP2(full)/6\text{-}31G(d)}]$$

and

$$E(\mathrm{ZPE}) = 0.8929 \times \mathrm{ZPE[HF/6\text{-}31G(d)]}$$

Spin orbit correction terms E(SO) (mainly of experimental origin) are added only for atoms and HLC is a small empirical correction, referred to as the higher-level correction. It should be noted that in calculating complexation energies, the empirical corrections cancel one another, and therefore, the complexation energies are purely ab initio.

3. Results and Discussion

3.1. Energetics and Geometries. The six minima located on the surface of OOH + HOOCHO are depicted in Figure 1. All may be categorized as cyclic in that each contains a pair of H-bonds connecting the two molecules. The numbering of these complexes conforms to the ordering of the intermolecular interaction energy (corrected for basis set superposition error), reported in bold along with the name of each structure in Figure 1. The hydrogen of OOH, denoted H_a, is involved in a OH···O H-bond in all six cases, although the particular acceptor O atom varies from one complex to the next. The OH hydrogen of HOOCHO, H_b, participates in an intermolecular OH···O bond in complexes S1, S4, and S5, but is engaged in an intramolecular H-bond in S2, S3, and S6, so it is not directly involved in the intermolecular interaction. It hence follows that H_b lies in the HOOCHO molecular plane in the latter set of structures, but rotates out of this plane, where it is better able to form the intermolecular contact, in the former group; the resulting φ-(H_bOOC) dihedral angles are displayed in Figure 1, in the range of 70°−80°. The other distinction between these two groups of complexes is that S1, S4, and S5 contain a pair of intermolecular OH···O bonds, whereas one of these H-bonds is replaced by a CH···O interaction in S2, S3, and S6 (leaving the internal OH···O bond intact).

S1 is clearly the most strongly bound of the various complexes, with a binding energy of 34 kJ/mol after correction of basis set superposition error. The hydrogen bonds are both less than 1.8 Å in length. Perhaps more importantly, there is little strain in these bonds, with both θ(OH···O) angles within 20° of linearity, as reported in the first two rows of the left side of Table 1. Such linearity has been shown to be an important component in the strength of such H-bonds.[2,43−45] The two covalent O−H bonds that are involved in the H-bonds are both stretched, one by nearly 20 mÅ and the other by 4 mÅ. In order to understand the much smaller nature of the second stretch, recall that the optimized HOOCHO monomer to which the geometry of the complex is referenced, is fully planar and contains an intramolecular OH_b···O H-bond. Therefore, the O−H_b covalent bond is already "prestretched" in the uncomplexed monomer by the internal H-bond; thus, the 3.9 mÅ value reported in Table 1 represents a *further* stretch, induced by the intermolecular, as compared to the intramolecular, bond. Also reported in Table 1 are the frequency shifts of the two O−H covalent bonds, resulting from the complexation. Both shifts are to the red, as normally anticipated for O−H bonds. Again, the lesser magnitude reported for $\Delta\upsilon(OH_b)$ reflects the shift in the complex, relative to the frequency within the planar HOOCHO molecule, wherein H_b is already engaged in an intramolecular H-bond. Hence, the smaller red shift in Table 1 is not necessarily indicative of a weaker H-bond for H_b as compared to H_a.

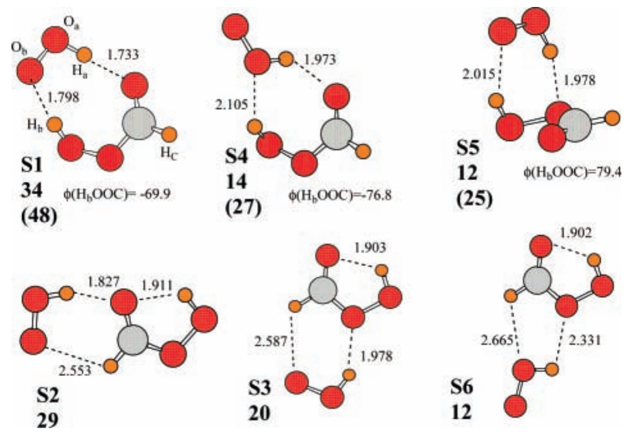

Figure 1. Complexes formed between OOH and HOOCHO. Counterpoise-corrected binding energies (kJ/mol) are displayed in bold along with the structure's label. Quantities in the upper row of structures (in parentheses) are corrected by the deformation energy of the HOOCHO molecule (see the text). Also reported are pertinent H···O distances in angstroms and dihedral angles in degrees.

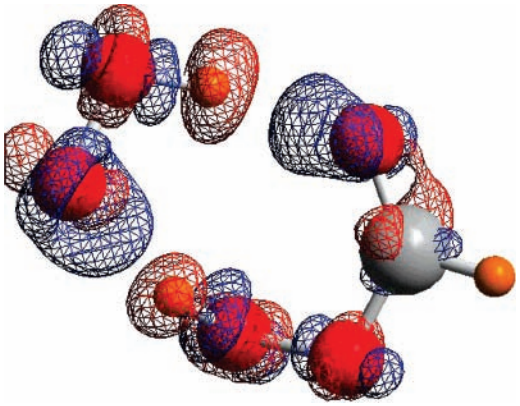

Figure 2. Electron density shifts in the S1 structure. Blue and red areas refer respectively to gains and losses of electron density within the complex, as compared to the individual, separated monomers. Contour chosen for illustration indicates changes of ±0.003 au.

Another important result of the need to break the internal HOOCHO H-bond in order to form complex S1 is that the binding energy reported represents an underestimate of the true interaction energy. More precisely, the binding energy is defined relative to the fully optimized, isolated monomers, and may thus be thought of as a two-stage process. In order to form the complex, the planar HOOCHO molecule must first distort itself by rotating its OH group, breaking the internal H-bond, and raising its energy. It is the second step, wherein the two (predistorted) molecules come together, that accounts for the true interaction energy. In order to provide an estimate of the former quantity, it was found that the energy of the HOOCHO molecule, when in its geometry within the S1 complex with a φ(H_bOOC) dihedral angle of −70°, is higher than the energy of the fully optimized planar HOOCHO subunit by 13.2 kJ/mol. (The magnitude of this quantity is consistent with the notion that it is largely due to the breaking of a OH···O H-bond.) Thus, the true binding energy of the S1 complex can be

TABLE 1: H-Bond Angles, Bond Stretches, Stretching Frequency Shifts, and Charge Transfers for Complexes Containing a Pair of OH···O H-Bonds

	S1	S4	S5		S1	S4	S5
$\theta(OH_a \cdots O)$, deg	163	134	146	$\Delta r(OH_b)$, mÅ	3.9	−7.8	−3.9
$\theta(OH_b \cdots O)$, deg	161	137	142	$\Delta \upsilon(OH_b)$ cm^{-1}	−85	145	74
$\Delta r(OH_a)$, mÅ	18.5	5.7	7.5	$q(O \rightarrow OH_a)$, me	24	6	8
$\Delta \upsilon(OH_a)$, cm^{-1}	−344	−75	−125	$q(O \rightarrow OH_b)$, me	23	3	8
				$\Delta r(O_aO_b)$, mÅ	−15	0.8	−8

TABLE 2: H-Bond Angles, O−H and C−H Bond Stretches, Frequency Shifts, and Charge Transfers for Complexes Containing Planar HOOCHO Molecule, with One OH···O and One CH···O Interaction

	S2	S3	S6		S2	S3	S6
$\theta(OH_a \cdots O)$, deg	159	146	105	$\Delta r(CH_c)$, mÅ	−1.8	−1.1	−1.1
$\theta(CH_c \cdots O)$, deg	111	120	111	$\Delta \upsilon(CH_c)$ cm^{-1}	43	28	13
$\Delta r(OH_a)$, mÅ	10.3	4.8	0.8	$q(OOH_a)$, me	18	5	0.6
$\Delta \upsilon(OH_a)$, cm^{-1}	−184	−69	−31	$q(OCH_c)$, me	0.8	0.8	0.3
				$\Delta r(O_aO_b)$, mÅ	−6	−6	0.1

considered as higher than the 34 kJ/mol listed in Figure 1 by roughly this amount. The result of this addition leads to the value of 48 kJ/mol in parentheses in Figure 1. Since the internal H-bond in HOOCHO must likewise be broken to form complexes S4 and S5, and given the similarity of their $\varphi(H_b$-OOC) dihedral angles to that in S1, a like increment can be added to their calculated binding energies.

S4 differs from S1 in that H_b of the HOOCHO molecule interacts with the hydroxyl O of OOH. This distinction introduces strain into the H-bonded ring, such that the two θ(OH···O) angles are 24−29° further from linearity as compared to those of S1. The weaker H-bonds are indicated also by reductions in the O−H covalent bond stretches. This contraction is three times smaller for O−H_a; in the case of O−H_b, this bond is shorter in the S4 complex than it is in the planar HOOCHO monomer with its internal H-bond. The corresponding O−H stretching frequencies are consequently also lowered by considerably smaller amounts in S4 as compared to S1. (It should be reiterated that the positive value for $\Delta\upsilon(OH_b)$ in Table 1 does not represent a blue shift in the usual sense, since the quantity refers to the difference between two different OH···O H-bonds, intermolecular versus intramolecular.) When coupled with the 0.2−0.3 Å longer intermolecular O···O distances, the complexation energy in S4 has been reduced by 20 kJ/mol, compared to that of S1. S5, in which the two OOH units form a cyclic structure, is comparable to S4 in binding energy. Also similar are the H-bond lengths; the θ(OH···O) angles are a little closer to linearity in S5.

A structure similar to S5 has been recently reported[46−48] in the complex pairing the OOH radical with HOOH. The OH_a stretch of 10−11 mÅ, computed at the QCISD level,[46,48] is comparable to the S5 value of 8 mÅ, and the shift of this vibrational frequency is also to the red, in the range[46−48] of 78−264 cm^{-1} in OOH···HOOH, as compared to 125 cm^{-1} in S5. Indeed, the latter value compares quite favorably with the red shift of 153 cm^{-1} computed[48] at the QCISD/6-31G** level for OOH···HOOH. This same OH stretching frequency is red-shifted also when OOH engages in cyclic complexes with H_2O[10], HNO_3,[11] RCOOH,[14] amides,[17] and SO_3.[18]

The remaining three complexes make use of the CH of HOOCHO as a proton donor. The two intermolecular H-bonds, of OH···O and CH···O character, are supplemented by a third, intramolecular OH···O bond that is also present in the uncomplexed HOOCHO molecule. Since the latter H-bond is relatively unperturbed by the complexation, the binding energies for S2, S3, and S6 represent a true assessment of the intermolecular binding itself, with no need to compensate for the loss of the internal H-bond, as in S1, S4, and S5. The OOH donates a proton to the carbonyl O of HOOCHO in the S2 complex. The strength of this interaction, making S2 second only to S1 in terms of binding energy, is perhaps surprising in view of the need for this same O atom to simultaneously accept another proton internally. One may conclude that this carbonyl O is a considerably better proton acceptor than is the peroxyl O atom to which the OOH donates a proton in the more weakly bound S3 and S6 geometries. This idea is reinforced by the shorter H_a···O distance in S2 as compared to S3 or S6. The OH···O H-bond is 0.15 Å longer in S3 than in S2, and 13° less linear. The most weakly bound complex is S6; its OH···O bond is the longest of those found here at 2.33 Å, and is severely bent, 75° from linearity.

In all three systems, the CH···O bond is considerably longer, and presumably weaker, than the intermolecular OH···O interaction. With the exception of S6, the OH···O bond is closer to linearity than is CH···O, which varies by 60°−69° from 180°, as displayed in Table 2. As in the first set of complexes, the O−H_a bond stretches in S2, S3, and S6 as well, but by smaller amounts. Consistent with this difference are the lesser red shifts in the O−H_a stretching frequencies. The next data in Table 2 demonstrate that the C−H bond is shortened when forming the intermolecular H-bond, and its stretching frequency shifted to the blue, in one case by as much as 43 cm^{-1}.

Previous calculations[10,11,13,14,17,19,20,22,24] have shown that the peroxyl O−O bond of the OOH radical contracts when engaged in H-bonding. In particular, the reduction in bond length was found to be 4 mÅ in cyclic systems,[19,20] wherein the OOH proton is donated to a good acceptor such as O or F, but the other O atom accepts a proton from a weak CH donor; the bond shortening is larger, up to 7 mÅ, when both H-bonds are of OH···O type.[13,14] The last rows of Tables 1 and 2 indicate that this pattern continues and is amplified when OOH is paired with HOOCHO. A very sizable contraction of 15 mÅ occurs in S1, verifying that this feature grows when both O atoms of OOH are involved in strong OH···O H-bonds. This contention is

TABLE 3: Energetics (kJ/mol) of Interactions between OOH and HOOCHO[a]

	D_e	$D_e^{cp\,b}$	D_0^{c}	D_0^{cp}	ΔE_0	$\Delta H(298)$	$\Delta S(298)$	$\Delta G(298)$
S1	−43.8	−34.3	−34.8	−25.3	−33.6	−34.1	−0.130	4.6
S2	−35.2	−28.8	−28.4	−22.0	−29.4	−28.7	−0.115	5.6
S3	−25.6	−19.6	−20.6	−14.6	−20.5	−19.1	−0.105	12.2
S4	−20.5	−14.1	−16.2	−9.8	−13.3	−12.7	−0.115	21.6
S5	−19.7	−11.9	−14.2	−6.4	−13.2	−12.2	−0.111	20.9
S6	−15.8	−11.6	−12.9	−8.7	−12.1	−9.7	−0.074	12.4

[a] First four columns at the MP2/6-311++G(2d,2p) level, last four at G3MP2. ΔS in units of kJ/mol K. [b] D_e^{cp} refers to the interaction energy after counterpoise correction, D_e + BSSE. [c] D_0 contains ZPE.

TABLE 4: AIM Parameters for H-Bonds in Six Complexes between HOOCHO and OOH

		ρ_{BCP}	$\nabla^2\rho$	λ_1	λ_2	λ_3	ϵ	G_{BCP}	$-V_{BCP}$	$-G_{BCP}/V_{BCP}$
S1	$H_a\cdots O{=}C$	0.0385	0.1210	−0.0618	−0.0600	0.2427	0.0294	0.0324	0.0346	0.9365
	$H_b\cdots O$	0.0365	0.1072	−0.0572	−0.0558	0.2202	0.0241	0.0294	0.0319	0.9199
S4	$H_a\cdots O{=}C$	0.0229	0.0864	−0.0293	−0.0288	0.1444	0.0154	0.0201	0.0186	1.0806
	$H_b\cdots O$	0.0169	0.0642	−0.0207	−0.0178	0.1027	0.1637	0.0146	0.0131	1.1145
S5	$H_b\cdots O$	0.0233	0.0781	−0.0310	−0.0295	0.1386	0.0484	0.0192	0.0189	1.0177
	$H_a\cdots O$	0.0230	0.0822	−0.0305	−0.0292	0.1418	0.0451	0.0197	0.0188	1.0456
S2	$H_a\cdots O{=}C$	0.0333	0.1311	−0.0426	−0.0282	0.2019	0.5131	0.0323	0.0319	1.0141
	$H_c\cdots O$	0.0094	0.0336	−0.0089	−0.0072	0.0497	0.2300	0.0074	0.0064	1.1586
	$H_b\cdots O{=}C$	0.0320	0.1050	−0.0480	−0.0463	0.1993	0.0359	0.0268	0.0274	0.9794
S3	$H_c\cdots O$	0.0086	0.0289	−0.0080	−0.0068	0.0436	0.1766	0.0064	0.0056	1.1441
	$H_a\cdots O$	0.0215	0.0822	−0.0297	−0.0266	0.1385	0.1138	0.0190	0.0174	1.0904
	$H_b\cdots O{=}C$	0.0342	0.1298	−0.0446	−0.0305	0.2049	0.4627	0.0325	0.0325	0.9988
S6	$H_c\cdots O$	0.0063	0.0256	−0.0051	−0.0022	0.0329	1.2759	0.0054	0.0045	1.2159
	$H_a\cdots O$	0.0118	0.0514	−0.0108	−0.0085	0.0706	0.2670	0.0111	0.0094	1.1832
	$H_b\cdots O{=}C$	0.0343	0.1305	−0.0447	−0.0304	0.2056	0.4731	0.0327	0.0328	0.9979

supported by a fairly large contraction in S5 as well. The weaker CH$\cdots$O bonds in S2 and S3 reduce the magnitude of this O−O bond shortening to 6 mÅ. It may be noted, however, that when the same O atom of OOH is involved as both proton donor and acceptor, as in S4 and S6, that the O−O bond contraction vanishes.

Various facets of the energetics of these six complexes are reported in Table 3. The interaction energy is reported first without, and then with, counterpoise correction of the basis set superposition error. The next two columns report these same quantities after the zero-point vibrational contributions have been added in. One may note that the ZPVE tends to diminish the binding energies by 3−9 kJ/mol, as does the counterpoise correction. The preceding quantities were computed at the MP2/6-311++G(2d,2p) level; ΔE and ΔH in the next two columns were computed at the G3MP2 level. The order of stability of the various complexes is unchanged by the introduction of counterpoise correction or of ZPE. (The only exception is the reversal between S5 and S6 in the D_0^{cp} quantity.) After full correction for the latter two quantities, the interaction energy of the OOH + HOOCHO pairing in the most stable complex S1 is 25 kJ/mol at the MP2/6-311++G(2d,2p) level. The final two columns list the computed values of ΔS and ΔG, both at the G3MP2 level. It is not surprising that the former quantity is negative for all systems, given the combination of a pair of molecules into a single dimer.

3.2. Electronic Factors. Many of the conclusions indicated above based upon interatomic distances and vibrational frequencies are supported by electronic distributions. The $q(O \rightarrow XH)$ values reported in the indicated rows of Tables 1 and 2 for each H-bond refer to the amount of electronic charge that is shifted from the proton acceptor O atom to the σ^* and Rydberg orbitals of the bridging OH or CH covalent bond, computed via natural bond orbital (NBO) analysis. The greater strength of the H-bonds in the S1 configuration is supported by these quantities, which surpass 20 me for both H-bonds. The much smaller values for S4 and S5 in Table 1 are consistent with their considerably weaker binding energies, as well as lesser degrees of O−H bond stretch and red shift of the frequencies. The OH$\cdots$O bond in S2 is stronger than the comparable bonds in S4 and S5 according to the charge shifts, again consistent with other aspects of the energetics and geometries. Finally, the charge shifts in Table 2 also confirm the much weaker nature of the CH$\cdots$O H-bonds, with magnitudes of less than 1 me.

Charge shifts may be visualized more expansively in Figure 2, which illustrates regions of gain (blue) and loss (red) of electron density. These changes are referenced to the individual, separated monomers and so indicate how the complexation affects the density patterns. Considering the H-bond regions, the red areas surrounding each bridging proton depict the typical loss of charge around this atom when a H-bond is formed. Also apparent is the gain of density in the O−H covalent bond regions of these bridges, consistent with the $q(O \rightarrow OH)$ shifts noted in Table 1.

The atoms in molecules (AIM) theory assists in analysis of the OH$\cdots$O and CH$\cdots$O H-bonds. Critical points (CPs) are classified according to their spectrum, which is the set of eigenvalues of the Hessian matrix of electron density, $\{\lambda_1 \leq \lambda_2 \leq \lambda_3\}$.[49,50] The number of nonzero eigenvalues, and their associated sign, define the CP type. A bond critical point (BCP) has two negative eigenvalues, $\lambda_1 \leq \lambda_2 \leq 0$, and one positive eigenvalue, $\lambda_3 > 0$. For weak interactions, the ellipticity, which is defined as $\epsilon = [\lambda_1/\lambda_2 - 1]$, indicates the stability of the BCP with respect to small geometrical changes such as those occurring during molecular vibrations.[49] G and V refer respectively to the kinetic and potential electron energy density. A G_C/V_C ratio greater than 1 generally indicates a noncovalent interaction, with covalent nature introduced as the ratio becomes smaller than unity.

The relevant parameters are displayed in Table 4, where the positive Laplacians at the bond critical points, $\nabla^2\rho_{BCP}$, indicate a H-bonding interaction in each case. Note also that the sets of eigenvalues all follow the pattern of two negative and one positive. There is a linear relation, albeit not a perfect one (correlation coefficient 0.97), between this Laplacian and the density at the bond critical point, ρ_{BCP}. It is interesting to point out that in the S2, S3, S6 subset, which contain an intramolecular H-bond, the latter is associated with the smallest G_{BCP}/V_{BCP} ratio, less than unity, which suggests a certain amount of covalent character, not uncommon in H-bonds. This ratio tends to be largest for the CH$\cdots$O interactions in this same group of complexes, and these same weak H-bonds also have small values of ρ_{BCP} and $\nabla^2\rho_{BCP}$.

4. Conclusions

There are six minima on the potential energy surface of the OOH + HOOCHO dimer. In three of these structures, the OOH radical pries open the internal OH$\cdots$O H-bond within the HOOCHO molecule so that it might form a pair of intermolecular OH$\cdots$O H-bonds. The other three minima are held together by one OH$\cdots$O and a weaker CH$\cdots$O bond, leaving intact the internal OH$\cdots$O H-bond of the HOOCHO monomer. The structure of lowest energy belongs in the former category, with a total binding energy of some 34 kJ/mol, reduced to 25 kJ/mol when zero-point vibrational energy is included. One of the complexes containing a OH$\cdots$O and CH$\cdots$O H-bond pair is surprisingly stable, with an interaction energy of 22 kJ/mol following ZPE correction. The C−H covalent bond is contracted when it participates in CH···O interactions, and its stretching frequency shifted to the blue, in one case by as much as 43 cm^{-1}. Electron density analyses confirm the notions of H-bond strength arising from energetic, geometric, and vibrational frequency data.

References and Notes

(1) Müller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, *100*, 143.
(2) Scheiner, S. *Hydrogen Bonding—A Theoretical Perspective*; Oxford University Press: Oxford, 1997, and references therein.
(3) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.
(4) Latajka, Z.; Scheiner, S. *J. Chem. Phys.* **1987**, *87*, 5928.
(5) Scheiner, S.; Wang, L. *J. Am. Chem. Soc.* **1993**, *115*, 1958.
(6) Orlova, G.; Scheiner, S. *J. Phys. Chem. A* **1998**, *102*, 260.
(7) Scheiner, S.; Yi, M. *J. Phys. Chem.* **1996**, *100*, 9235.
(8) Wayne, R. P. *Chemistry of Atmospheres*, 2nd ed.; Oxford University Press: Oxford, 1991.
(9) Hansen, J. C.; Francisco, J. S. *Chem. Phys. Chem.* **2002**, *3*, 833.
(10) Aloisio, S.; Francisco, J. S. *J. Phys. Chem. A* **1998**, *102*, 1899.
(11) Aloisio, S.; Francisco, J. S. *J. Phys. Chem. A* **1999**, *103*, 6049.
(12) Miller, C. E.; Francisco, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 10387.
(13) Torrent-Sucarrat, M.; Anglada, J. M. *J. Phys. Chem. A* **2006**, *110*, 9718.
(14) Parreira, R. L. T.; Galembeck, S. E. *J. Am. Chem. Soc.* **2003**, *125*, 15614.
(15) Francisco, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4570.
(16) Qu, Y.; Bian, X.; Tang, H.; Si, P. *Int. J. Quantum. Chem.* **2005**, *101*, 381.
(17) Solimannejad, M.; Azimi, G.; Pejov, Lj. *Chem. Phys. Lett.* **2004**, *400*, 185.
(18) Solimannejad, M.; Azimi, G.; Pejov, Lj. *Chem. Phys. Lett.* **2004**, *391*, 201.
(19) Solimannejad, M.; Scheiner, S. *Chem. Phys. Lett.* **2006**, *429*, 38.
(20) Solimannejad, M.; Scheiner, S. *J. Phys. Chem. A* **2006**, *110*, 5948.
(21) Bil, A.; Latajka, Z. *Chem. Phys. Lett.* **2004**, *388*, 158.
(22) Qu, Y.; Bian, X.; Tang, H.; Si, P. *J. Mol. Struct. (THEOCHEM)* **2004**, *671*, 173.
(23) Bil, A.; Latajka, Z. *J. Comput. Chem.* **2006**, *27*, 287.
(24) Mansergas, A.; Anglada, J. M. *J. Phys. Chem. A* **2007**, *111*, 976.
(25) Langley, C. H.; Noe, E. A. *THEOCHEM* **2004**, *682*, 215.
(26) Andersen, A.; Carter, E. A. *J. Phys. Chem. A* **2003**, *107*, 9463.
(27) Okovytyy, S.; Gorb, L.; Leszczynski, J. *Tetrahedron Lett.* **2002**, *43*, 4215.
(28) Yamabe, S.; Kondou, C.; Minato, T. *J. Org. Chem.* **1996**, *61*, 616.
(29) Freccero, M.; Gandolfi, R.; Sarzi-Amade, M.; Rastelli, A. *J. Org. Chem.* **2002**, *67*, 8519.
(30) Bach, R. D.; Canepa, C.; Winter, J. E.; Blanchette, P. E. *J. Org. Chem.* **1997**, *62*, 5191.
(31) Bach, R. D.; Estevez, C. M.; Winter, J. E.; Glukhovtsev, M. N. *J. Am. Chem. Soc.* **1998**, *120*, 680.
(32) Cardenas, R.; Cetina, R.; Lagunez-Otero, J.; Reyes, L. *J. Phys. Chem. A* **1997**, *101*, 192.
(33) Carlo, P. *Chem. Phys.* **1977**, *26*, 243.
(34) Bach, R. D.; Willis, C. L.; Lang, T. J. *Tetrahedron* **1979**, *35*, 1239.
(35) Bach, R. D.; Dmitrenko, O. *J. Phys. Chem. A* **2003**, *107*, 4300.
(36) Bock, C. W.; Trachtman, M.; George, P. *Chem. Phys.* **1981**, *62*, 303.
(37) Kulkarni, A. D.; Rai, D.; Bartolotti, L. J.; Pathak, R. K. *J. Phys. Chem. A* **2006**, *110*, 11855.
(38) Frisch M. J.; et al. *Gaussian 03*, Revision B02, Gaussian, Inc.: Pittsburgh, PA, 2003.
(39) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(40) Latajka, Z.; Scheiner, S. *J. Chem. Phys.* **1987**, *87*, 1194.
(41) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.
(42) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
(43) Gu, Y; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999** *121* 9411
(44) Scheiner, S.; Duan, X. *Biophys. J.* **1991**, *60*, 874.
(45) Duan, X.; Scheiner, S. *J. Mol. Struct.* **1992**, *270*, 173.
(46) Hansen, J. C.; Flowers, B. A.; Stanton, J. F. *J. Mol. Struct. (THEOCHEM)* **2006**, *768*, 111.
(47) Alikhani, M. E.; Barone, V. *Chem. Phys. Lett.* **2004**, *391*, 134.
(48) Qu, Y.; Bian, X.; Zhou, Z.; Gao, H. *Chem. Phys. Lett.* **2002**, *366*, 260.
(49) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, U.K., 1990.
(50) Popelier, P. L. A. *Atoms in Molecules, an Introduction*; Prentice Hall: Upper Saddle River, NJ, 2000.