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Probing the Low-Barrier Hydrogen Bond in Hydrogen Maleate in the Gas Phase: A Photoelectron Spectroscopy and ab Initio Study

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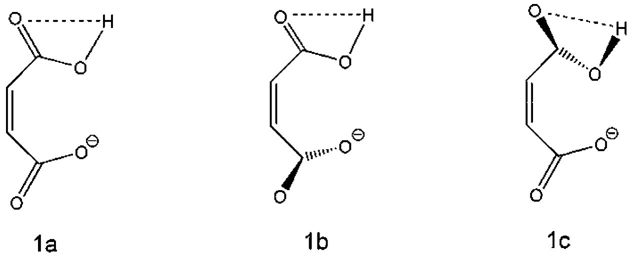
The strength of the low-barrier hydrogen bond in hydrogen maleate in the gas phase was investigated by low-temperature photoelectron spectroscopy and ab initio calculations. Photoelectron spectra of maleic and fumaric acid monoanions (*cis*-/*trans*-$HO_2CCH{=}CHCO_2^-$) were obtained at low temperatures and at 193 nm photon energy. Vibrational structure was observed for *trans*-$HO_2CCH{=}CHCO_2^-$ due to the OCO bending modes; however, *cis*-$HO_2CCH{=}CHCO_2^-$ yielded a broad and featureless spectrum. The electron binding energy of *cis*-$HO_2CCH{=}CHCO_2^-$ is about 1 eV blue-shifted relative to *trans*-$HO_2CCH{=}CHCO_2^-$ due to the formation of intramolecular hydrogen bond in the *cis*-isomer. Theoretical calculations (CCSD(T)/aug-cc-pVTZ and B3LYP/aug-cc-pVTZ) were carried out to estimate the strength of the intramolecular hydrogen bond in *cis*-$HO_2CCH{=}CHCO_2^-$. Combining experimental and theoretical calculations yields an estimate of 21.5 ± 2.0 kcal/mol for the intramolecular hydrogen bond strength in hydrogen maleate.

The study of the hydrogen bond has long been a topic of intensive scientific research due to its relevance in materials science, biochemistry, organic chemistry, inorganic chemistry, solid-state physics, and molecular medicine.[1−5] In recent years, the short-strong hydrogen bond, usually referred as the low-barrier hydrogen bond (LBHB), has attracted considerable attention because of its possible role in enzyme catalysis.[6−9] It has been suggested that LBHB can supply up to 20 kcal/mol to stabilize the transition states in enzymatic reactions.[7] However, the importance of LBHBs in enzyme catalysis has been a controversial issue,[10−12] although the LBHBs have been shown to be involved in several enzyme systems.[13−15]

CHART 1



One system that has been widely studied for LBHB is the maleic/fumaric acid monoanion (*cis*-/*trans*-$HO_2CCH{=}CHCO_2^-$),[8,16−23] due to the existence of a LBHB in the maleic acid monoanion (hydrogen maleate). Several experimental and theoretical studies have been designed to measure the hydrogen bond strength in hydrogen maleate.[20−23] The reported values cover a rather wide energy range. Schwartz and Drueckhammer[20] measured the equilibrium constant between hydrogen maleate and the corresponding trans-monoanion isomer, as well as the cis-/trans-neutral diacids. The difference in the relative free energies of the cis- and trans-isomers was used as an estimate of the relative strength of the intramolecular hydrogen bond in hydrogen maleate. Their equilibrium measurement showed that the energy difference between the cis- and trans-forms of hydrogen maleate ranged from 0.5 to 5.5 kcal/mol, depending on the solvent used, with lower polarity solvents favoring stronger hydrogen bonding. However, this estimate of the hydrogen bond strength is significantly lower than the 20 kcal/mol value suggested for a LBHB. Theoretically, Lluch et al.[21] have calculated that the hydrogen maleate is 14.14 kcal/mol more stable than the fumarate. The gas-phase hydrogen bond strength in the monoanion was estimated to be 18.35 kcal/mol higher than that of the normal hydrogen bond in the neutral diacid. Using **1a** in Chart 1 as the reference structure (non-hydrogen bond case in hydrogen maleate), McAllister[22] calculated the gas-phase hydrogen bond strength to be approximately 27 kcal/mol. Bach et al.[23] have computed the hydrogen bond strength on the basis of different reference structures (**1a**, **1b**, and **1c** in Chart 1). They concluded that the gas-phase intramolecular hydrogen bond strength in hydrogen maleate is in the range 14−28 kcal/mol, depending on the choice of reference structures.

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Thus, better experiments are needed to determine the hydrogen bond strength in hydrogen maleate. In the current study, we report a photoelectron spectroscopic study of the hydrogen maleate and fumarate systems. Hydrogen maleate is significantly stabilized, and higher electron binding energy was observed due to the formation of a LBHB. The difference in electron binding energies between hydrogen maleate and fumarate gives an intuitive perception on the strength of LBHB.

The experiments were performed with a recently constructed apparatus that couples electrospray ionization (ESI) with photoelectron spectroscopy (PES).[24-26] The key feature of this apparatus is a temperature-controlled ion trap, where ions are accumulated and cooled by a background gas. The ion trap is attached to a closed-cycle helium refrigerator, which can reach 10 K. The anions of interest, *cis*-/*trans*-$HO_2CCH{=}CHCO_2^-$, were produced using the ESI source from $\sim 1.0 \times 10^{-3}$ M solutions of the corresponding sodium salts in a mixture of methanol/water solvent (3/1 volume ratio). Anions produced were guided by a RF-only octopole into a quadrupole mass filter. Following the mass filter, the ions were directed by a 90° ion bender to the temperature-controlled ion trap, where ions were cooled via collisions with N_2 as background gas at a 70 K trapping temperature. Ions were trapped and cooled for a period of 20−80 ms before being pulsed (10 Hz) into the extraction zone of a time-of-flight mass spectrometer.

During the PES experiment, the ions of interest were mass-selected and decelerated before being intercepted by the probe laser beam in the photodetachment zone of the magnetic-bottle photoelectron analyzer. A photodetachment energy of 193 nm (6.424 eV) from an excimer laser was used in the current experiment. The lasers were operated at a 20 Hz repetition rate with the ion beam off at alternating laser shot for shot-by-shot background subtraction. Photoelectrons were collected at nearly 100% efficiency by the magnetic-bottle and analyzed in a 5.2-m electron flight tube. Time-of-flight photoelectron spectra were collected and converted to kinetic energy spectra, calibrated by the known spectra of I^- and ClO_2^-.[27] The electron binding energy spectra were obtained by subtracting the kinetic energy spectra from the detachment photon energy. The energy resolution ($\Delta E/E$) was about 2%, i.e., ~20 meV for 1 eV electrons.

Figure 1 displays the 193 nm photoelectron spectra of (a) fumarate (*trans*-$HO_2CCH{=}CHCO_2^-$) and (b) hydrogen maleate (*cis*-$HO_2CCH{=}CHCO_2^-$) measured at a 70 K ion trap temperature. No detachment transition occurs below 3 eV, so the binding energy scale is plotted from 3.0 to 6.4 eV for clearer presentation. Spectra for the two anions exhibit different spectral patterns and binding energies, although both are primarily due to detachment channels from the $-CO_2^-$ derived molecular orbitals.[28] Vibrational structures are observed in *trans*-$HO_2CCH{=}CHCO_2^-$, whereas the *cis*-$HO_2CCH{=}CHCO_2^-$ spectrum is basically structureless.

In *trans*-$HO_2CCH{=}CHCO_2^-$, the broad peak between 4.0 and 5.5 eV is due to removing electrons from the $-CO_2^-$ group and the higher binding energy peak (C band) at about 6 eV is due to detachment of the π electrons of the C=C double bond. From previous works,[26,29,30] it is known that there are three closely spaced detachment channels involving the $-CO_2^-$ moiety, all due to removal of oxygen 2p lone pair electrons. Because of the elimination of vibrational hot bands in the current low-temperature conditions, the tail at the low binding energy side suggested a broad ground-state detachment transition, as shown more clearly in our recent study of benzoate ($C_6H_5CO_2^-$).[26] The broad and weak ground-state transition (X) is due to the large geometry change between the ground states of the anion and neutral. In this case, the threshold detachment energy (TDE) may not represent the adiabatic detachment energy (ADE) of the parent anion. Instead, the TDE should be considered as the upper limit for the ADE, or the electron affinity (EA) of the neutral. Due to the low signal-to-noise ratio and lack of vibrational resolution in the lower binding energy side, we were only able to estimate the TDE from the onset of appreciable photoelectron signals. The TDE of *trans*-$HO_2CCH{=}CHCO_2^-$ was estimated to be 3.91 eV. Partially resolved vibrational structures were obtained in the A and B bands. The vibrational frequencies for the A and B bands are characteristic of the OCO bending mode: 645 cm^{-1} for the A band and 565 cm^{-1} for the B band (Table 1). Because of the congestion of bands X, A, B and limited spectral resolution, we were not able to identify the 0−0 transitions for bands A and B. We were only able to estimate their VDEs, as given in Table 1.

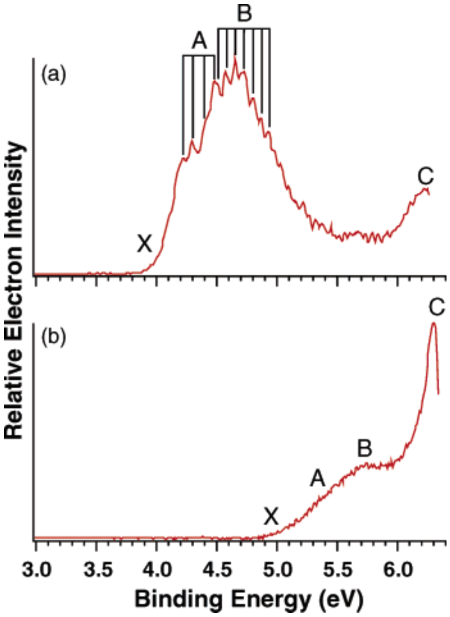

Figure 1. Photoelectron spectra of (a) *trans*-$HO_2CCH{=}CHCO_2^-$ and (b) *cis*-$HO_2CCH{=}CHCO_2^-$ at 193 nm (6.424 eV) and 70 K ion trap temperature.

In the case of *cis*-$HO_2CCH{=}CHCO_2^-$, the photoelectron spectrum shows a completely different pattern. The low binding energy region involving the detachment from the $-CO_2^-$ moiety is featureless and dramatically blue-shifted as compared to that of *trans*-$HO_2CCH{=}CHCO_2^-$. The room-temperature spectrum (not shown) is identical to the 70 K spectrum. There is no improvement in spectral resolution when the ion trap is lowered to 70 K, suggesting the broad spectrum is due to large geometry changes upon photodetachment. The blue shift in binding energy is due to the formation of intramolecular hydrogen bond between the $-CO_2H$ and $-CO_2^-$ groups, which greatly stabilizes the anion. However, the hydrogen bond strength is expected to be significantly reduced in neutral *cis*-$HO_2CCH{=}CHCO_2$, thus inducing a large geometry change along the hydrogen bond coordinate and completely smearing out the OCO bending vibrational progression. The labels (X, A, B) in Figure 1 are simply to indicate three bands are expected in this spectral region. The estimated TDE of *cis*-$HO_2CCH{=}CHCO_2^-$ is 4.93 eV (Table 1).

The C band due to the π electrons of the C=C double bond is much sharper for the *cis*-$HO_2CCH{=}CHCO_2^-$ than for the trans-isomer. This is because the strong hydrogen bond makes the cis-isomer very rigid and the ionization of the π electron is

TABLE 1: Experimental and Theoretical Adiabatic Detachment Energies (ADEs), Vertical Detachment Energies (VDEs), and Vibrational Frequencies of the OCO Bending Mode

		ADE (eV)		VDE (eV)		vibrational frequency (cm^{-1})
		exp[a]	theo	exp[a]	theo	exp[a]
trans-$HO_2CCH{=}CHCO_2^-$	X	3.91(5)[b]	3.80[c] 3.89[d]		4.30[c]	
	A			4.22(4)		645 (20)
	B			4.51(4)		565 (20)
	C			6.23(6)		
cis-$HO_2CCH{=}CHCO_2^-$	X	4.93(5)[b]	4.72[c] 4.85[d]		5.19[c]	
	C			6.31(4)		

[a] Numbers in parentheses are uncertainties in the last digits. [b] Threshold detachment energy (TDE), representing the upper limit for ADE. [c] Computed at the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level plus ZPVE corrections. No ZPVE corrections were made on VDE values. [d] Computed at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level plus ZPVE corrections at the B3LYP/aug-cc-pVTZ level.

not able to induce significant structural changes. However, in the trans-isomer ionization of a π electron, which weakens the C═C π bonding, may induce significant torsional distortion, giving rise to a much broader C band for the trans-isomer.

From the photoelectron spectra in Figure 1, the hydrogen bond strength in hydrogen maleate can be roughly estimated. The difference in TDE values of *trans*-/*cis*-$HO_2CCH{=}CHCO_2^-$, which is 1.02 eV (23.5 kcal/mol), can be viewed as the hydrogen bond strength. This estimation is based on two assumptions: (1) the trans-/cis-isomerization energies are similar in both anion and neutral and (2) the hydrogen bond strength in the *cis*-$HO_2CH{=}CHCO_2$ neutral is negligible. This estimated value of the hydrogen bond strength (23.5 kcal/mol) falls within the range of the theoretical calculations (14−28 kcal/mol) by Bach et al.,[23] but it is lower than the value (27 kcal/mol) calculated by McAllister.[22]

To gain further insight into the nature of the hydrogen bonding in hydrogen maleate, theoretical calculations were performed. Similar to previous theoretical investigations,[21−23] a reference structure is needed to estimate the hydrogen bond strength. In the present work, structure **1b** is used as the reference. We chose **1b** as the reference because its energy is the lowest among the three non-hydrogen bond structures (**1a**, **1b**, and **1c**). In addition, we found that the neutrals of **1a** and **1c** are not minima on the potential energy surface and they relax back to **1b** in our calculations.

Density functional theory was used to determine the geometries and electronic structures of *trans*-/*cis*-$HO_2CCH{=}CHCO_2^-$, and the corresponding neutrals. Structures were optimized at the B3LYP[31]/aug-cc-pVTZ level using the Gaussian 03 package of programs[32] and the subsequent single-point energy calculations were done at the CCSD(T)/aug-cc-pVTZ level using Molpro2002.6.[33] The CCSD(T) electronic energies were corrected with zero-point vibrational energy (ZPVE) using harmonic vibrational frequencies calculated at the B3LYP/aug-cc-pVTZ level. To estimate the hydrogen bond strength in *cis*-$HO_2CCH{=}CHCO_2^-$, we also performed the same procedures on **1b**. However, for the neutral of **1b**, which possesses no symmetry, the single-point energy calculation can only be obtained at the CCSD/aug-cc-pVTZ level because the CCSD(T)/aug-cc-pVTZ energy involves extensive computational resources. The vertical detachment energies (VDEs) were obtained by the energy difference between the anions and the ground state of the neutrals with its geometry fixed at that of the anions. The ADEs were obtained by taking the energy difference between the anions and the ground state of the neutrals in its optimized geometry.

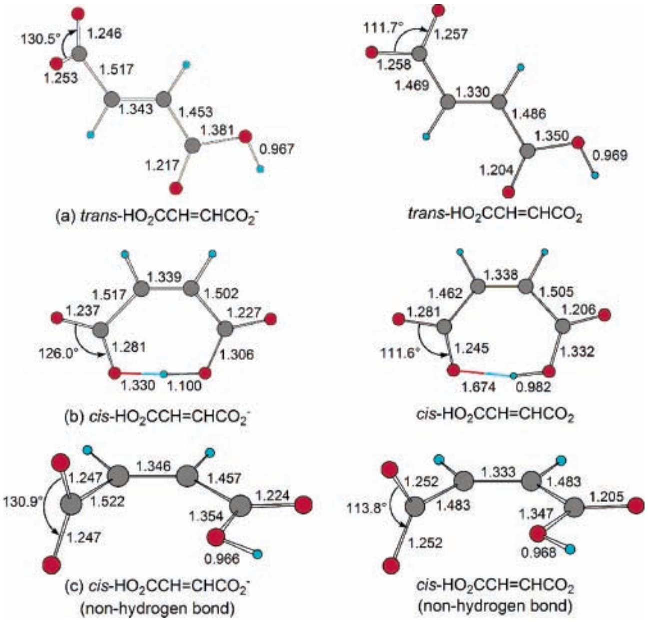

Figure 2. Optimized geometries of (a) *trans*-$HO_2CCH{=}CHCO_2^-$ and *trans*-$HO_2CCH{=}CHCO_2$, (b) *cis*-$HO_2CCH{=}CHCO_2^-$ and *cis*-$HO_2CCH{=}CHCO_2$, and (c) *cis*-$HO_2CCH{=}CHCO_2^-$ (non-hydrogen bond) and *cis*-$HO_2CCH{=}CHCO_2$ (non-hydrogen bond). Selected bond lengths are given in angstroms.

The optimized geometries of *trans*-/*cis*-$HO_2CCH{=}CHCO_2^-$, reference structure **1b** and their corresponding neutrals are shown in Figure 2. In both *trans*-/*cis*-$HO_2CCH{=}CHCO_2^-$, the negative charge is delocalized in the carboxylate OCO group. Due to electron repulsion, the OCO moiety is expected to adapt a larger interatomic angle (∠OCO) than the typical angle of 120° in a sp^2 hybridized carboxylic group. This expectation is supported by the predicted ∠OCO angles at B3LYP/aug-cc-pVTZ, ranging from 126 to 131°, for all three $HO_2CCH{=}CHCO_2^-$ isomers. These ∠OCO angles are also similar to that of benzoate that we studied recently.[26] Photodetachment removes the delocalized electron from the $-CO_2^-$ moiety of $HO_2CCH{=}CHCO_2^-$ and results in a large geometry change between the anions and neutrals. At the B3LYP/aug-cc-pVTZ level, significant changes in the angle ∠OCO from the anions (∠OCO ≈ 126−131°) to the neutrals (∠OCO ≈ 111−114°) are observed for all three $HO_2CCH{=}CHCO_2^-$ species. A similar angular change is also observed in our previous study on the benzoate anion.[26] Other than the angular changes, there are additional noticeable geometrical changes between the anions and neutrals. For example, the $-CO_2^-$ group has an out-of-plane orientation in *trans*-$HO_2CCH{=}CHCO_2^-$ but it becomes planar in the neutral. The bond distances of $C-CO_2^-$ are decreased by ~0.05 Å upon photodetechment for both isomers. The large geometry

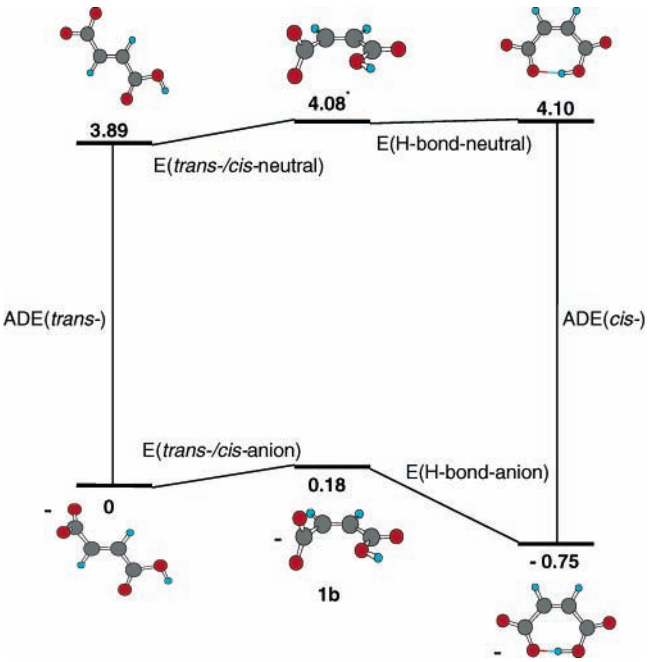

Figure 3. Estimation of hydrogen bond strength based on theoretical calculations. The energies (eV) calculated at the CCSD(T)/aug-cc-pVTZ + ZPVE(B3LYP/aug-cc-pVTZ) level are shown. *Energy computed at CCSD/aug-cc-pVTZ + ZPVE(B3LYP/aug-cc-pVTZ) level.

change between the anion and neutral ground states confirmed our experimental observation of the broad photoelectron spectra in Figure 1.

The cis-orientation between $-CO_2^-$ and $-CO_2H$ groups favors the formation of intramolecular hydrogen bonding in both the *cis*-$HO_2CCH{=}CHCO_2^-$ anion and its neutral. The intramolecular $CO_2^-\cdots HOOC$ distance in *cis*-$HO_2CCH{=}CHCO_2^-$ is 1.330 Å at the B3LYP/aug-cc-pVTZ level. However, the intramolecular distance is found to significantly increase by ~0.35 Å to 1.674 Å in the *cis*-$HO_2CCH{=}CHCO_2$ neutral. The nature of a hydrogen bond is mostly dependent on the electron densities of the donor and acceptor atoms. The acceptor (CO_2^-) in the *cis*-$HO_2CCH{=}CHCO_2^-$ anion is much more electron-rich than the acceptor (CO_2) in the neutral; thus the *cis*-$HO_2CCH{=}CHCO_2^-$ anion is expected to form a much stronger intramolecular hydrogen bond than the neutral counterpart and this results in the extremely short intramolecular $CO_2^-\cdots HOOC$ distance in *cis*-$HO_2CCH{=}CHCO_2^-$. Both the *cis*-$HO_2CCH{=}CHCO_2^-$ anion and its neutral adapt a seven-membered ring conformation for the formation of the intramolecular hydrogen bond. The $\angle O\cdots H-O$ angle in the *cis*-$HO_2CCH{=}CHCO_2^-$ anion is almost linear (176.9°) whereas the $\angle O\cdots H-O$ angle in the *cis*-$HO_2CCH{=}CHCO_2$ neutral is slightly nonlinear (167.6°). The theoretical ADEs predicted at the DFT and CCSD(T) levels for *trans-/cis*-$HO_2CCH{=}CHCO_2^-$ are compared with the experimental threshold values in Table 1. The CCSD(T) values should be more reliable than the DFT predictions because it is generally expected that the CCSD(T) theory is more capable of describing electron correlation effects than the DFT method. We note that the CCSD(T) ADE for the trans-isomer is very close to the measured TDE, suggesting that the TDE can probably be taken as the ADE in this case. However, the CCSD(T) ADE for the cis-isomer is lower than the estimated TDE, suggesting that indeed the large geometry change upon detachment probably yielded a negligible Franck−Condon factor for the 0−0 transition for the cis-isomer.

Figure 3 displays an energy diagram relating the detachment energies of the *trans-/cis*-$HO_2CCH{=}CHCO_2^-$ isomers to the hydrogen bond energies via the reference **1b**. Energies calculated at the CCSD(T) level are shown. The calculated trans-/cis-isomerization energy in the anion is 0.18 eV [*E*(trans-/cis-anion)] whereas for the neutral (non-hydrogen bond) it is 0.19 eV [*E*(trans-/cis-neutral)]. Our calculations show that the **1b** neutral is slightly more stable than the hydrogen-bonded cis-neutral, suggesting that the hydrogen bond strength in the *cis*-$HO_2CCH{=}CHCO_2$ neutral [*E*(H-bond-neutral)] is negligible. The similar [*E*(trans-/cis-anion)] and [*E*(trans-/cis-neutral)] energies and the weak hydrogen bonding in *cis*-$HO_2CCH{=}CHCO_2$ also concurred with our assumptions used in estimating the hydrogen bond strength by the experimental TDE values. Taking the energy difference between hydrogen maleate and **1b** in Figure 3, the calculated hydrogen bond strength [*E*(H-bond-anion)] at the CCSD(T)/aug-cc-pVTZ level is 0.93 eV (21.4 kcal/mol). This value is close to a previous theoretical estimation (20.6 kcal/mol) using the same reference structure.[23]

Experimentally, the ADE difference between the trans- and cis-isomer should give a very good value of the hydrogen bond strength in the hydrogen maleate, given the fact that the trans-/cis-isomerization energies are similar in the anion and neutral and the hydrogen bond strength in neutral hydrogen maleate is negligible. From the comparison between the TDEs and the CCSD(T) predictions, we note that the TDE for the trans-isomer is very likely to represent the true ADE. However, the TDE for the cis-isomer is higher than the CCSD(T) prediction by ~0.08 eV (Table 1), suggesting that the TDE is likely the upper limit for the true ADE. The 0.08 eV difference between the CCSD(T) prediction and the TDE for the cis-isomer represent one vibrational quanta in the OCO bending mode. Thus, the true ADE of the cis-isomer is likely to be 4.85 eV; i.e., the CCSD(T) prediction for the ADE of the cis-isomer is very accurate, as is the case for the trans-isomer. Using this estimated ADE for the cis-isomer, we obtain an ADE difference between the trans-/cis-isomer of 0.94 eV (21.6 kcal/mol), which is in excellent agreement with the CCSD(T) prediction of the hydrogen bond strength in hydrogen maleate (21.4 kcal/mol). Considering the experimental and theoretical results and accuracies, our best estimate for the LBHB in hydrogen maleate is 21.5 ± 2.0 kcal/mol, which is comparable to other strong hydrogen bond strength formed between a $-CO_2H$ and $-CO_2^-$ group.[34−36]

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References and Notes

(1) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
(2) Scheiner, S. *Hydrogen Bonding*; Oxford University Press: New York, 1997.
(3) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: Oxford, U.K., 1999.
(4) Steiner, T. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 48.
(5) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.
(6) Gerlt, J. A.; Gassman, P. G. *Biochemistry* **1993**, *32*, 11943.
(7) Cleland, W. W.; Kreevoy, M. M. *Science* **1994**, *264*, 1887.
(8) Frey, P. A.; Whitt, S. A.; Tobin, J. B. *Science* **1994**, *264*, 1927.
(9) Shan, S. O.; Loh, S.; Herschlag, D. *Science* **1996**, *272*, 97.
(10) Scheiner, S.; Kar, T. *J. Am. Chem. Soc.* **1995**, *117*, 6970.
(11) Guthrie, J. P. *Chem. Biol.* **1996**, *3*, 163.
(12) Warshel, A.; Papazyan, A. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 13665.

(13) Zhao, Q.; Abeygunawarana, C.; Talalay, P.; Mildvan, A. S. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 8220.

(14) We, Z. R.; Ebrahimian, S.; Zawrotny, M. E.; Thornburg, L. D.; Perez-Alvarado, G. C.; Brothers, P.; Pollack, R. M.; Summers, M. F. *Science* **1997**, *276*, 415.

(15) Frey, P. A. *Magn. Reson. Chem.* **2001**, *39*, S190.

(16) George, P.; Bock, C. W.; Trachtman, M. *J. Phys. Chem.* **1983**, *87*, 1893.

(17) Rios, M. A.; Rodriguez, J. *Can. J. Chem.* **1992**, *71*, 303.

(18) Perrin, C. L.; Thoburn, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 8559.

(19) Lin, J.; Frey, P. A. *J. Am. Chem. Soc.* **2000**, *122*, 11258.

(20) Schwartz, B.; Drueckhammer, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 11902.

(21) Garcia-Viloca, M.; Gonzalez-Lafont, A.; Lluch, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 1081.

(22) McAllister, M. A. *Can. J. Chem.* **1997**, *75*, 1195.

(23) Bach, R. D.; Dmitrenko, O.; Glukhovtsev, M. N. *J. Am. Chem. Soc.* **2001**, *123*, 7134.

(24) Wang, X. B.; Woo, H. K.; Kiran, B.; Wang, L. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 4968.

(25) Wang, X. B.; Woo, H. K.; Wang, L. S. *J. Chem. Phys.* **2005**, *123*, 051106.

(26) Woo, H. K.; Wang, X. B.; Kiran, B.; Wang, L. S. *J. Phys. Chem. A*, Articles ASAP, Web Release Date: 21-Sep-2005.

(27) Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *J. Chem. Phys.* **1992**, *96*, 8012.

(28) Wang, X. B.; Nicholas, J. B.; Wang, L. S. *J. Chem. Phys.* **2000**, *113*, 653.

(29) Kim, E. H.; Bradforth, S. H.; Arnold, D. W.; Metz, R. B.; Neumark, D. M. *J. Chem. Phys.* **1995**, *103*, 7801.

(30) Lu, Z.; Continetti, R. E. *J. Phys. Chem. A* **2004**, *108*, 9962.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(32) Frisch, M. J.; et al. *Gaussian 03*, Rev. B. 05; Gaussian, Inc.: Pittsburgh, PA, 2003.

(33) MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos et al.

(34) Basch, H.; Stevens, W. J. *J. Am. Chem. Soc.* **1991**, *113*, 95.

(35) Kumar, G. A.; McAllister, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 3159.

(36) Meot-Ner (Mautner), M. *Chem. Rev.* **2005**, *105*, 213.