Article

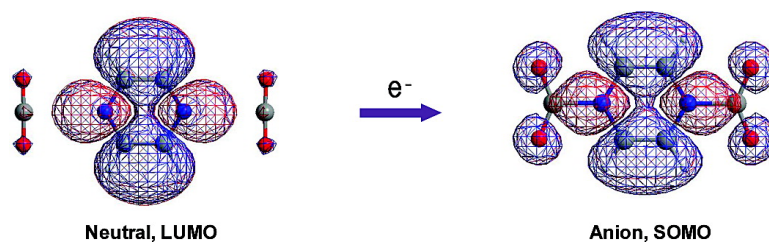# "Associative" Electron Attachment to Azabenzene#(CO) van der Waals Complexes: Stepwise Formation of Covalent Bonds with Additive Electron Affinities

Sang Hak Lee, Namdoo Kim, Dong Gyun Ha, and Seong Keun Kim

Neutral, LUMO   e⁻   Anion, SOMO

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

"Associative" Electron Attachment to Azabenzene−$(CO_2)_n$ van der Waals Complexes: Stepwise Formation of Covalent Bonds with Additive Electron Affinities

Sang Hak Lee, Namdoo Kim, Dong Gyun Ha, and Seong Keun Kim*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea

Received May 24, 2008; E-mail: seongkim@snu.ac.kr

Abstract: Electron attachment to the van der Waals complexes of azabenzene−$(CO_2)_n$ results in the formation of covalent bonds between the nitrogen atoms of azabenzene and the carbon atom of CO_2. The newly formed C−N bonds establish an extended π-orbital network over the entire moieties of the complex and thus greatly stabilize the anion, yielding a very large value of vertical detachment energy for the excess electron. The rare "associative" nature of electron attachment was found to be generally occurring in all azabenzene series, only subject to steric hindrance against the formation of the covalent C−N bond.

Introduction

Molecular anions are often less stable than their neutral counterpart, which is characterized by a potential energy surface with a smaller well depth and longer equilibrium bond distances.[1,2] Therefore, electron attachment to a stable molecule often leads to dissociation of the chemical bond due to the Franck−Condon transition to the repulsive region of the anionic potential energy surface. Dissociative electron attachment is prevalent in chemistry and plays an important role in chemical reactions, charge transfer, and biological processes.[3−7]

In rare instances, however, certain types of electron attachment can be "associative", i.e., a new chemical bond can be formed where there initially was no bond in the neutral species.[8] We observed an interesting such case that involves the van der Waals complex of pyridine and CO_2, which generates, upon electron attachment, a covalent bond between the two moieties through extended π-orbital conjugation of the extra electron between the aromatic ring and CO_2. Formation of the new covalent bond in the anion also came with formation of a wholly new anionic core, which in this case was characterized by an unexpectedly large electron affinity (measured as the vertical detachment energy (VDE) of the anion) due to the strong delocalization of the extra electron. It is also to be noted that Weber and co-workers have observed a red shift in the vibrational frequency of CO_2 in the $(O_2 \cdots CO_2)^-$ and

$(Au \cdots CO_2)^-$ complexes,[9,10] which was interpreted as a result of the formation of a covalent bond between the two moieties.

In their recent study,[11] Eustis et al. have found that an excess electron induces the hydrogen-bonded complex $NH_3 \cdots HCl$ to form the ionic salt through the dipole-bound anion of $NH_4^+Cl^-$, or a deformed Rydberg radical NH_4 polarized by Cl^-. Although this case is mechanistically different from the pyridine−CO_2 case mentioned above, it can still be regarded as another example of associative electron attachment where a new chemical bond is generated by adding an electron to a noncovalently bound complex.

In this paper, we extend our earlier study[12] on pyridine−CO_2 to the van der Waals complexes between CO_2 and other species of the azabenzene series, in particular those with two and three nitrogen atoms. The main objective of this study is to see if more than one covalent bond could be formed between multiple species (i.e., when a sufficient number of CO_2 molecules surround the azabenzene species with more than one nitrogen atom) and, if so, whether there exists a quantitative correlation between the number of covalent bonds formed and the measured electron affinity.

Experimental Methods

The details of our experimental scheme have been described elsewhere.[13,14] We generated the azabenzene−$(CO_2)_n$ complexes by expanding a gas mixture of thermally evaporated azabenzene and 2 atm of CO_2 seeded in 5 atm of Ar carrier gas through a pulsed nozzle operating at 10 Hz. Electron impact by an electron gun (400 eV, 200 μA) produced low-energy secondary electrons,

(1) Burrow, P. D. *J. Chem. Phys.* **1973**, *59*, 4922.
(2) Massey, H. S. W. *Electronic and Ionic Impact Phenomena*; 2nd ed.; Clarendon Press: Oxford, U.K., 1969; Vol. II.
(3) Illenberger, E. *Chem. Rev.* **1992**, *92*, 1589.
(4) Fabrikant, I. I.; Hotop, H. *Phys. Rev. A: At., Mol., Opt. Phys.* **2001**, *63*, 022706.
(5) Pearl, D. M.; Burrow, P. D.; Nash, J. J.; Morrison, H.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 9876.
(6) Pearl, D. M.; Burrow, P. D.; Nash, J. J.; Morrison, H.; Nachtigallova, D.; Jordan, K. D. *J. Phys. Chem.* **1995**, *99*, 12379.
(7) Zubarev, R. A.; Kelleher, N. L.; McLafferty, F. W. *J. Am. Chem. Soc.* **1998**, *120*, 3265.
(8) Tsukuda, T.; Johnson, M. A.; Nagata, T. *Chem. Phys. Lett.* **1997**, *268*, 429.
(9) Schneider, H.; Boese, A. D.; Weber, J. M. *J. Chem. Phys.* **2005**, 123.
(10) Boese, A. D.; Schneider, H.; Gloss, A. N.; Weber, J. M. *J. Chem. Phys.* **2005**, *122*, 154301.
(11) Eustis, S. N.; Radisic, D.; Bowen, K. H.; Bachorz, R. A.; Haranczyk, M.; Schenter, G. K.; Gutowski, M. *Science* **2008**, *319*, 936.
(12) Han, S. Y.; Chu, I.; Kim, J. H.; Song, J. K.; Kim, S. K. *J. Chem. Phys.* **2000**, *113*, 596.
(13) Han, S. Y.; Song, J. K.; Kim, J. H.; Oh, H. B.; Kim, S. K. *J. Chem. Phys.* **1999**, *111*, 4041.
(14) Song, J. K.; Lee, N. K.; Kim, J. H.; Han, S. Y.; Kim, S. K. *J. Chem. Phys.* **2003**, *119*, 3071.

Table 1. Calculated and Experimentally Measured Energies of Azabenzene–$(CO_2)_n^-$ Complexes[a]

	pyrazine			pyridazine			pyrimidine				triazine			
	Pz_1	$Pz_1(CO_2)_1$	$Pz_1(CO_2)_2$	Pd_1	$Pd_1(CO_2)_1$	$Pd_1(CO_2)_2$	Pm_1	$Pm_1(CO_2)_1$	$Pm_1(CO_2)_2$	$Pm_1(CO_2)_3$	Tz_1	$Tz_1(CO_2)_1$	$Tz_1(CO_2)_2$	$Tz_1(CO_2)_3$
AEA_{cal}	−0.07	1.06	1.56	−0.08	0.90	1.11	−0.30	0.77	1.04	1.16	−0.01	0.98	1.24	1.21
VDE_{cal}		2.20	3.78		2.07	2.31		1.89	2.13	3.29		2.30	2.54	3.67
VDE_{exp}	−0.01	1.98	4.35	−0.14	2.01	2.19	−0.37	1.68	1.89	4.38	0.03	2.06	2.28	4.40
ΔE		1.99	2.37		2.15	0.18		2.05	0.21	2.49		2.03	0.22	2.13

[a] All energies in eV. Calculated energies were obtained at the B3LYP/6-31++G** level, whereas the experimental VDEs were measured from photoelectron spectra, except for those of Pm and Pd which were measured by Rydberg electron transfer. ΔE represents the incremental difference in VDE from the preceding species.
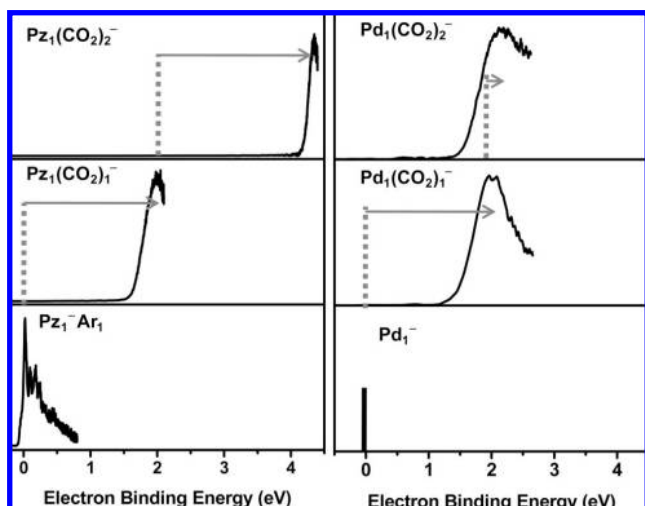

Figure 1. Photoelectron spectra of $Pz_1(CO_2)_n^-$ and $Pd_1(CO_2)_n^-$ shown against that of $Pz_1^-Ar_1$ and the known EA value of Pd (−0.14 eV measured by Rydberg electron transfer, shown as a bar) for comparison. The wavelengths used were 532 nm for $Pz_1(CO_2)_1^-$, 355 nm for $Pd_1(CO_2)_{1,2}^-$, and 266 nm for $Pz_1(CO_2)_2^-$. The arrows indicate a stepwise shift in VDE, which is nearly additive for $Pz_1(CO_2)_n^-$ with each CO_2 added but not for $Pd_1(CO_2)_n^-$.

whose attachment to neutral complexes turned them into anions. Laser irradiation at various wavelengths (532, 355, and 266 nm) produced photoelectrons whose spectrum was obtained by measuring the kinetic energy of the electron with an electron time-of-flight spectrometer.

Results and Discussion

We employed all three diazine species, i.e., pyridazine (1,2-diazine, Pd), pyrimidine (1,3-diazine, Pm), and pyrazine (1,4-diazine, Pz) as well as *s*-triazine (1,3,5-triazine, Tz) in order to investigate the effect of the number of nitrogen atoms and the substitution sites. The photoelectron spectra of $Pz_1(CO_2)_n^-$ and $Pd_1(CO_2)_n^-$ are shown in Figure 1 (for $n = 1$ and 2), along with that of $(Pz_1Ar_1)^-$ and the known electron affinity (EA) value of Pd for comparison. For $Pz_1(CO_2)_n^-$, we note that the photoelectron band shifts by about 2 eV per CO_2. The VDE values measured are 1.98 eV for $n = 1$ and 4.35 eV for $n = 2$, whereas the known VDE of Pz is −0.01 eV.[15] Since the shift in VDE when CO_2 acts as a mere solvent is of the order of 0.2 eV,[12] such a large shift indicates that the anionic core in this case is not Pz^- but something of a totally different nature. It is to be noted that the 2 eV shift is also very much the same as the change in VDE for pyridine$^-(CO_2)_1^-$,[12,13] which we had found to possess an entirely new anionic core held by a newly formed covalent bond.

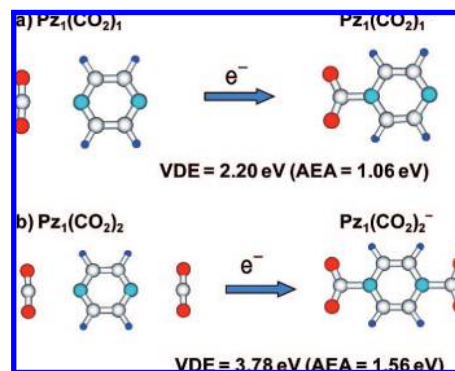(15) Song, J. K.; Lee, N. K.; Kim, S. K. *J. Chem. Phys.* **2002**, *117*, 1589.

Figure 2. Neutral (left) and anionic (right) geometries and calculated energies of $Pz_1(CO_2)_n$ optimized at the B3LYP/6-31++G** level. The van der Waals bonds in the neutral complex turn into covalent bonds in the anion.

On the other hand, the photoelectron spectra of $Pd_1(CO_2)_n^-$ shows a similar behavior with that of $Pz_1(CO_2)_n^-$ for $n = 1$ but a totally different one for $n = 2$. Since the two nitrogen atoms of Pd are adjacent to each other in the ortho position of the aromatic ring, it is intuitively clear that they would not accommodate both CO_2 molecules in their "covalent" bonding configuration lest they cause steric repulsion. The measured VDE values are 2.01 eV for $n = 1$ and 2.19 eV for $n = 2$, which is consistent with the first CO_2 forming a new anionic core (with a VDE shift of 2.15 eV from the known VDE of −0.14 eV for Pd[16]) but the second CO_2 only acting as a solvent (with a VDE shift of 0.18 eV).

These features are correctly borne out by the calculations we carried out at the level of B3LYP/6-31++G** using the Gaussian program suite.[17] The neutral and anionic geometries of $Pz_1(CO_2)_{1,2}^-$ shown in Figure 2 indicate that the addition of each CO_2 results in the formation of a new anionic core with a covalent bond between the nitrogen atom of the ring and the carbon atom of CO_2. The calculated VDE was 2.20 and 3.78 eV for $n = 1$ and 2, respectively, which are in a reasonably good agreement with our experimental values. Our Mulliken charge analysis also showed that the excess electron was completely delocalized over the entire conjugated π^* orbital of Pz and the CO_2 units through the newly formed covalent C−N bonds.

On the other hand, our calculated results for $Pd_1(CO_2)_n^-$ shown in Figure 3 suggest that neither of the two lowest energy isomers for $n = 2$ uses both CO_2 units to form an anion in the extended π^* orbital conjugation. In both isomers, only one of the two CO_2 units is involved in forming the covalent C−N

(16) Periquet, V.; Moreau, A.; Carles, S.; Schermann, J. P.; Desfrancois, C. *J. Electron Spectrosc. Relat. Phenom.* **2000**, *106*, 141.
(17) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
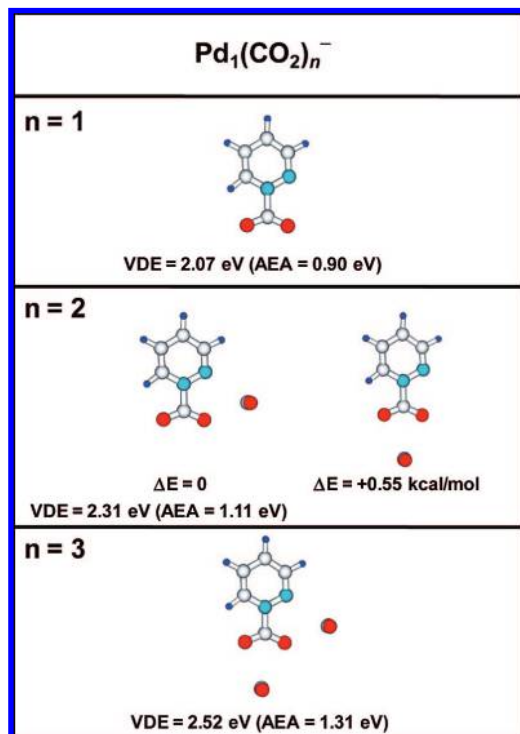
Figure 3. Calculated geometries and energies of $Pd_1(CO_2)_n^-$ optimized at the B3LYP/6-31++G** level. In $Pd_1(CO_2)_1^-$, a covalent bond is formed as in $Pz_1(CO_2)_1^-$. The two most stable isomers of $Pd_1(CO_2)_2^-$ are of nearly equal energy, but neither forms a second covalent C—N bond. The third CO_2 in $Pd_1(CO_2)_3^-$ also fails to induce the formation of the second C—N bond.
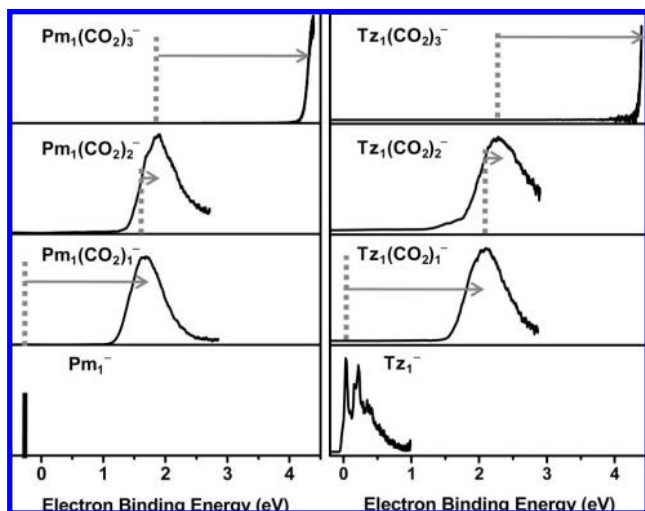

Figure 4. Photoelectron spectra of $Pm_1(CO_2)_n^-$ and $Tz_1(CO_2)_n^-$ shown against the EA value of Pm (−0.30 eV measured by Rydberg electron transfer, shown as a bar) and the photoelectron spectrum of Tz_1^- for comparison. The wavelength used was 355 nm for $n = 1$ and 2 and 266 nm for $n = 3$. The arrows indicate a stepwise shift in VDE.

bond with the ring nitrogen, whereas the other is loosely bound as a solvent to the newly formed anion core. The third CO_2 in $Pd_1(CO_2)_3^-$ also fails to induce the formation of another covalent C—N bond.

The anion complexes of $Pm_1(CO_2)_n^-$ and $Tz_1(CO_2)_n^-$ present even more intriguing cases. Figure 4 shows that the first two CO_2 units in both complexes show a similar behavior to that of $Pd_1(CO_2)_n^-$, but the third CO_2 prompts yet another CO_2 to form
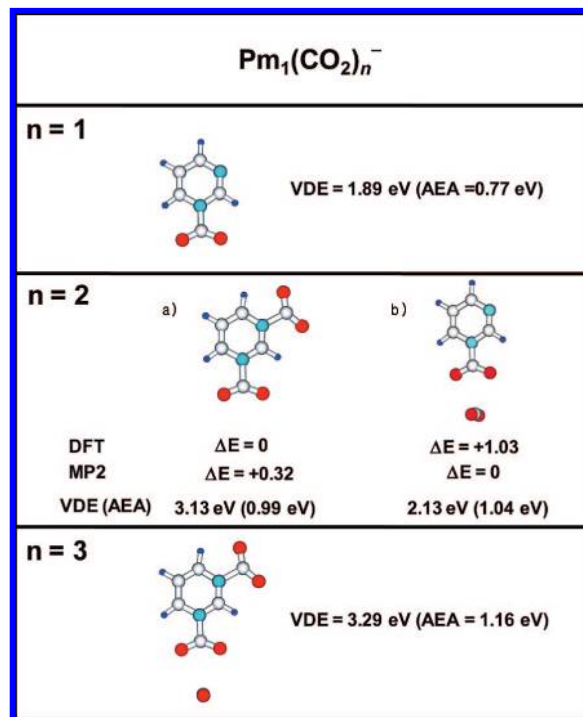

Figure 5. Calculated geometries and energies of $Pm_1(CO_2)_n^-$ optimized at the B3LYP/6-31++G** level. The first CO_2 forms a covalent C—N bond, but the second CO_2 in $Pm_1(CO_2)_2^-$ fails to form a second C—N bond in the global minimum structure at the MP2/6-31++G** level (b), in agreement with the experiment. The third CO_2 in $Pm_1(CO_2)_3^-$ induces the formation of the second C—N bond, in complete agreement with our experiment. Relative energy is in the unit of kcal/mol.

an extended π^* orbital conjugation for the anion core. The measured VDE values are 1.68, 1.89, and 4.38 eV for $n = 1, 2$, and 3 of $Pm_1(CO_2)_n^-$, and 2.06, 2.28, and 4.40 eV for $n = 1, 2$, and 3 of $Tz_1(CO_2)_n^-$, respectively. From the known VDE values of −0.37 eV for Pm[16] and 0.03 eV for Tz,[18] it is clear that the first CO_2 shifts the VDE by about 2 eV for both Pm_1^- and Tz_1^-, whereas the second CO_2 shifts it only by 0.2 eV and the third CO_2 by an additional 2 eV. The virtual "additivity" of VDEs between $n = 1$ and 3 of both complexes is quite striking, along with the "break" in the additivity at $n = 2$.

We carried out calculations for $Pm_1(CO_2)_n^-$ and $Tz_1(CO_2)_n^-$ at the level of B3LYP/6-3++G**, and the results, shown in Figures 5 and 6, are remarkably consistent with the experimental findings. The VDEs calculated are 1.89, 2.13, and 3.29 eV for $n = 1, 2$, and 3 of $Pm_1(CO_2)_n^-$, and 2.30, 2.54, and 3.67 eV for $n = 1, 2$, and 3 of $Tz_1(CO_2)_n^-$, respectively. Aside from the significant underestimation of VDE for $n = 3$ of both complexes, the overall trend is in good accord with the experimental results.

We note in Figure 5 that the two most stable isomers of $Pm_1(CO_2)_2^-$ are rather close to each other in energy. At the B3LYP/6-3++G** level, the lowest energy structure (a) seems to indicate an anion core with two CO_2 units covalently bound, but this does not agree with our experimental result that suggests only one such CO_2 unit. Upon further calculation at the MP2/6-31++G** level, however, the isomer b was found to be the global minimum geometry, which is also more consistent with our experiment both in terms of geometry and VDE. Quite remarkably, the third CO_2 in $Pm_1(CO_2)_3^-$ is found to induce

(18) Kim, J. H.; Song, J. K.; Park, H.; Lee, S. H.; Han, S. Y.; Kim, S. K. *J. Chem. Phys.* **2003**, *119*, 4320.
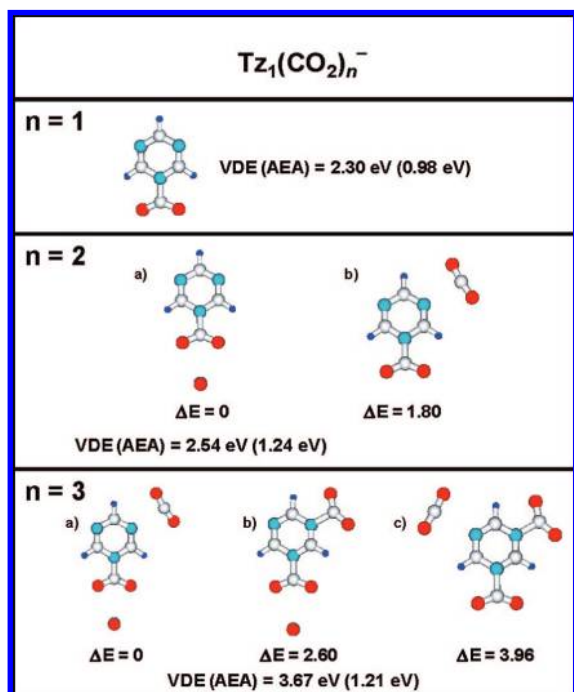
Figure 6. Calculated geometries and energies of $Tz_1(CO_2)_n^-$ optimized at the B3LYP/6-31++G** level, which are in accord with experiment for n = 1 and 2. For n = 3, our experiment suggests that two of the three CO_2 units are covalently bound, but the two structures consistent with this prediction (isomers b and c) are of higher energy than (a) at this level of calculation, possibly due to the underestimation of the π^* orbital conjugation. Relative energy is in the unit of kcal/mol.

the formation of the second C−N bond, in complete agreement with our experiment.

Figure 6 shows that $Tz_1(CO_2)_2^-$ also has two isomers at the B3LYP/6-31++G** level, but both of them have only one covalently bound CO_2. In the lower energy isomer, the second CO_2 binds to the first CO_2 rather than to the ring, as in the lowest energy isomer of $Pm_1(CO_2)_2^-$ calculated at the MP2/6-31++G** level. On the other hand, the higher energy isomer of $Tz_1(CO_2)_2^-$ shows a CO_2 positioned at the meta position but not quite making a covalent C−N bond. In $Tz_1(CO_2)_3^-$, the CO_2 in the meta position turns into a covalently bound unit in the two higher energy structures b and c, as in $Pm_1(CO_2)_3^-$. The global minimum structure a is not consistent with our experimental result, for which a higher level of calculation may be necessary.

The additivity of the VDE should stand for a virtual decoupling of covalent bond formation of the individual CO_2 units. On the other hand, the breaks in the additivity as observed in $Pm_1(CO_2)_2^-$ and $Tz_1(CO_2)_2^-$ seem to indicate that the polarization of the electron density of the ring is insufficient in these species to result in the formation of a second covalent bond. With an additional CO_2, however, the electronic polarization is sufficiently facilitated to yield the second covalent bond in both $Pm_1(CO_2)_3^-$ and $Tz_1(CO_2)_3^-$. It is quite natural that the electronic polarization plays a major role since it affects the local atomic charges and the bond distances, which in turn determines the planarity of the ring and hence the degree of
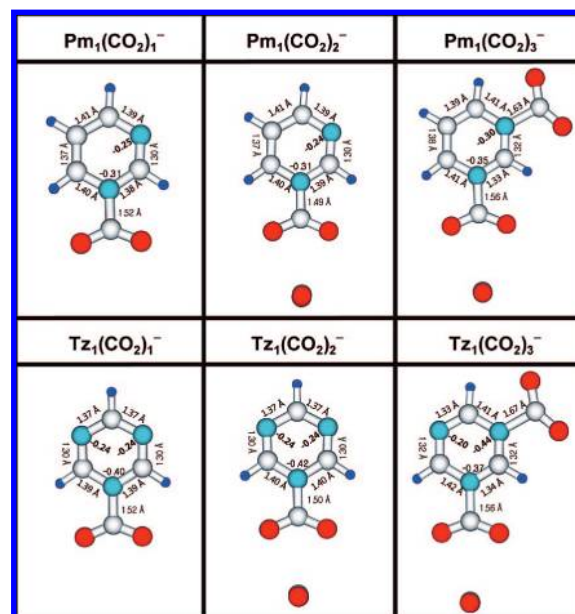

Figure 7. Bond distances and atomic charges of the nitrogen atoms for $Pm_1(CO_2)_n^-$ and $Tz_1(CO_2)_n^-$ optimized at the B3LYP/6-31++G** level. Atomic charges were extracted from the Mulliken charge analysis.

conjugation in the extended π-orbital network. Figure 7 shows the bond distances and the local atomic charges of the nitrogen atoms in the experiment-compatible structures of $Pm_1(CO_2)_n^-$ and $Tz_1(CO_2)_n^-$, whose similarities are also noteworthy for all n.

Table 1 summarizes the calculated energies (VDE and adiabatic electron affinity (AEA)) and measured energies (VDE) for all three diazine species and *s*-Tz as a function of the number of CO_2. As already mentioned, a drastic shift of the order of 2 eV in VDE indicates formation of a new anionic core with a new covalent C−N bond, whereas the much smaller change of the order of 0.2 eV represents mere solvation by CO_2.

Conclusions

In conclusion, we found that electron attachment to the van der Waals complexes of azabenzene and CO_2 is a prototypical case of *associative* electron attachment, where the excess electron is completely delocalized over the two moieties through the newly formed covalent C−N bond, resulting in a totally new anionic core with a very large electron binding energy. These changes are additive with an incremental shift of ca. 2 eV per CO_2 but subject to steric hindrance.

Supporting Information Available: Complete ref 17 and optimized geometries as Cartesian coordinates of all of calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA8039103