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Electronic Structure, Stability, and Nature of Bonding of the Complexes of C_2H_2 and C_2H_4 with H^+, Li^+, and Na^+ Ions. Extensive ab Initio and Density Functional Study

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The ground-state geometries of the complexes of C_2H_2 and C_2H_4 with H^+, Li^+, and Na^+ ions have been optimized at the B3LYP and MP2(full) levels of theory using several basis sets. The difference in the direction of tilting of the terminal H atoms noticed in $C_2H_3^+$ and $C_2H_5^+$ seems to be an artifact of the methods of calculation and basis sets. The dissociation energies (DEs) of the complexes have been calculated using B3LYP, MP2(full) and CCSD(T)=full methods. When ZPE (zero-point energy) and BSSE (basis set superposition error) corrections are included the DEs at the CCSD(T)=full level of theory are obtained for a number of basis sets in very good agreement with the experimental values, wherever available. The nature of bonding of the complexes has been deduced on the basis of charge transfer, bond indices, localized MOs, and topological properties of electron density. Both bond indices and LMOs indicate the presence of three-center bonding in all the complexes. In the protonated species the bonding is found to be predominantly covalent; in the Li^+ and Na^+ complexes also the covalent interaction plays a fairly important role.

1. Introduction

The interaction between a cation and a dipolar molecule is a particular type of acid−base interaction, where the cation acts as an acid and the dipolar molecule as a base. When both the reactants are closed-shell species, the electrostatic interaction is the main source of stability of the resulting complex. Such complexes are generally characterized[1] by high interaction energies. Nonpolar π-systems can also serve as a strong base in many cation−molecule interactions. A typical example is benzene. It was shown[2−5] to form complexes with Li^+, Na^+, and K^+ ions having stability comparable to that of the complexes of these cations with traditional ligands like water, alcohols, amines, etc. Subsequently, intermolecular complexes of a variety of π-systems (both polar and nonpolar) and cations have been characterized experimentally.[6−10] These are referred to as cation−π complexes. The cation−π interaction is recognized as a strong noncovalent binding force that plays a dominant role in a wide variety of fields ranging from material design to molecular biology.

Although the binding energies of a host of cation−π complexes have been measured experimentally,[2−10] we do not have sufficient quantitative information about their electronic structure. Consequently, a large number of theoretical studies[4,5,11−18] have been published in this field. In most of these studies, benzene was used as the π-system because it is the simplest of aromatic molecules that could mimic the binding properties of complex π-ligands that participate in the cation−π interactions operative in biological systems. The MP2 method and the 6-31G or 6-311G basis set, often augmented with one or more polarization and diffuse functions, have generally been employed in these studies. A complete basis set estimate of the binding enthalpies of alkali-metal cation−benzene complexes has been made[16,17] at the CCSD(T) (coupled cluster calculation with single, double, and perturbative triple excitations) level of theory using the hierarchy aug-cc-pVxZ ($x = D$, T, and Q) basis sets. Topological analysis[19] of electron density has also been performed for several cation−π complexes.[15]

Acetylene and ethylene are the simplest π-ligands that can participate in cation−π interactions. The pertinent complexes are amenable to more extensive and accurate theoretical calculations than is possible for larger aromatic π-complexes. Despite this advantage, only a few scattered calculations have so far been reported[5,16,20−24] on the Li^+ and Na^+ complexes of C_2H_2 and C_2H_4. The primary aim of the present study is to treat these complexes on equal footing and determine their electronic structure and binding energy using accurate density functional and ab initio post-HF methods.

The proton is not considered in cation−π interactions, presumably because the proton−π interaction is very strong and cannot be described as a noncovalent force. However, there should be some similarity between the nature of bonding of H^+ and Li^+/Na^+ complexes of C_2H_2 and C_2H_4—they should all exhibit three-center (3c) bonding. This aspect of the cation−π interaction, which has not been addressed before, has prompted us to include $C_2H_3^+$ and $C_2H_5^+$ in the list of complexes. These protonated species have been studied exhaustively[25−33] at various

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levels of theory. It was shown[28] that the terminal H atoms in $C_2H_3^+$ and $C_2H_5^+$ are tilted slightly from the CC bond, but in opposite directions. No such tilting was, however, predicted[16] in $C_2H_4Na^+$. Different basis sets and methods of calculation were employed in these studies.[16,28] This anomaly and the lack of sufficient experimental data have prompted us to undertake an extensive study of the effect of basis sets on the geometry and energetics of the YM^+ ($Y = C_2H_2$, C_2H_4; M = H, Li, Na) complexes. We have also compared their nature of bonding (with emphasis on 3c bonding) and the topological properties of their electron density.

2. Method of Calculation

The geometries of the monomers and their complexes with H^+, Li^+, and Na^+ ions were optimized with DFT/B3LYP (density functional theory/Becke[34] three-parameter nonlocal exchange functional with nonlocal correlation functional of Lee, Yang and Parr[35]) and MP2(full) methods. The following basis sets were employed in these calculations: 6-311G**, 6-311+G**, 6-311++G**, 6-311G(2d,2p), 6-311+G(2d,2p), 6-311++G(2d,2p), 6-311G(3df,3pd), 6-311+G(3df,3pd), 6-311++G(3df,3pd) and a basis set that consists of 6-311G(3df,3pd) basis for Li and Na, and cc-pVQZ basis for C and H. These basis sets are denoted by A, A+, A++, B, B+, B++, C, C+, C++, and D, respectively. The dissociation energies were calculated at the same levels of theory and also at the CCSD(T)=full//MP2(full) level. These were then corrected for ZPE (zero-point energy) and BSSE (basis set superposition error). For the latter, the counterpoise method (CP)[36] was used and the deformation of geometry of the monomers upon complexation, was taken into account.

The nature of bonding of the complexes was studied on the basis of charge-transfer calculated using NPA (natural population analysis)[37] and two-center (2c) and three-center (3c) bond indices calculated using a nonlinear version[38,39] of Mulliken population analysis (MPA). The B3LYP/6-311G** wave function was used in these calculations. To confirm the presence of 3c bonding predicted on the basis of bond indices, LMO (localized molecular orbital) calculations were performed using the Boys' method.[40] The Gaussian 98 program[41] was used to calculate the electronic structure, energetics, and NPA charges. Additional subroutines were written for the computation of bond indices. The topological analysis of the electron density obtained from HF/A and B3LYP/A (A = 6-311G**) wave functions, was performed using the MORPHY 98 program.[42]

3. Results and Discussion

While studying the effect of basis sets on various calculated qualities, it was observed that the inclusion of diffuse functions in the hydrogen basis did not have any noticeable effect on the geometries and dissociation energies. It was further noticed that basis sets A+, B+, and C+ predict these quantities in most cases in better agreement with experiment than basis sets A, B, and C, respectively. In what follows we have, therefore, presented and discussed results for basis sets A+, B+, C+, and D only. For the sake of simplicity the B3LYP method has often been referred to as DFT.

TABLE 1: Optimized Geometries (Bond Length (*R*) in Å and Tilt Angle (TA)[a] in Degrees) of C_2H_2 and $C_2H_2M^+$ (M = H, Li, and Na)

	methods and basis sets[b]							
	B3LYP				MP2(full)			
	A+	B+	C+	D	A+	B+	C+	D
C_2H_2								
R(CC)	1.199	1.196	1.196	1.195	1.215	1.208	1.208	1.204
R(CH)	1.063	1.061	1.062	1.061	1.065	1.064	1.060	1.058
$C_2H_3^+$								
R(CC)	1.221	1.217	1.218	1.217	1.234	1.226	1.225	1.221
R(CH)	1.079	1.077	1.078	1.077	1.080	1.074	1.076	1.074
R(XH_b)[c]	1.138	1.134	1.134	1.134	1.124	1.116	1.117	1.114
TA	0.50	0.35	0.47	0.47	−0.31	−0.32	−0.54	−0.70
$C_2H_2Li^+$								
R(CC)	1.205	1.201	1.202	1.201	1.221	1.214	1.213	1.208
R(CH)	1.071	1.069	1.069	1.069	1.073	1.066	1.068	1.066
R(XLi)[c]	2.217	2.212	2.211	2.212	2.221	2.217	2.181	2.191
TA	4.72	4.81	4.64	4.65	4.54	4.45	4.34	4.44
$C_2H_2Na^+$								
R(CC)	1.204	1.200	1.201	1.200	1.220	1.213	1.212	1.208
R(CH)	1.069	1.067	1.067	1.067	1.071	1.065	1.066	1.064
R(XNa)[c]	2.624	2.610	2.612	2.606	2.632	2.631	2.608	2.604
TA	4.92	4.95	4.75	4.75	4.81	4.56	4.64	4.68

[a] Tilt angle is the angle between CC and terminal CH bonds. A negative sign of TA indicates that the terminal H atoms are tilted toward M, the bridging atom. [b] A+ = 6-311+G**, B+ = 6-311+(2d,2p), C+ = 6-311+G(3df,3pd), and D consists of basis C (6-311G(3df,3pd)) for Li and Na and cc-pVQZ basis for C and H. [c] H_b is the bridging H atom, and X is the midpoint of the CC bond.

TABLE 2: Optimized Geometries (Bond Length (*R*) in Å, Bond Angle (∠HCC) and Tilt Angle (TA)[a] in Degrees) of C_2H_4 and $C_2H_4M^+$ (M = H, Li, and Na)

	methods and basis sets[b]							
	B3LYP				MP2(full)			
	A+	B+	C+	D	A+	B+	C+	D
C_2H_4								
R(CC)	1.329	1.325	1.325	1.324	1.337	1.332	1.329	1.325
R(CH)	1.085	1.082	1.082	1.082	1.085	1.079	1.079	1.077
∠HCC[c]	1.73	1.71	1.73	1.75	1.39	1.33	1.34	1.34
$C_2H_5^+$								
R(CC)	1.381	1.377	1.377	1.376	1.385	1.378	1.376	1.372
R(CH)	1.087	1.085	1.085	1.085	1.087	1.081	1.082	1.080
R(XH_b)[d]	1.128	1.125	1.125	1.124	1.113	1.108	1.109	1.104
∠HCC[c]	0.76	0.73	0.76	0.78	0.44	0.39	0.38	0.44
TA	0.53	0.43	0.44	0.46	0.29	0.15	−0.01	0.05
$C_2H_4Li^+$								
R(CC)	1.341	1.337	1.337	1.336	1.348	1.342	1.339	1.336
R(CH)	1.087	1.085	1.085	1.085	1.088	1.081	1.082	1.080
R(XLi)	2.268	2.264	2.263	2.264	2.271	2.271	2.229	2.235
∠HCC[c]	1.59	1.58	1.60	1.63	1.28	1.22	1.18	1.24
TA	2.54	2.36	2.32	2.32	2.29	2.19	2.01	2.38
$C_2H_4Na^+$								
R(CC)	1.339	1.335	1.335	1.334	1.346	1.340	1.337	1.334
R(CH)	1.087	1.085	1.084	1.084	1.087	1.081	1.081	1.079
R(XNa)	2.658	2.644	2.643	2.641	2.672	2.666	2.631	2.634
∠HCC[c]	1.61	1.58	1.60	1.63	1.46	1.24	1.20	1.27
TA	2.54	2.36	2.29	2.30	2.46	2.19	1.99	2.52

[a] See footnote *a* to Table 1. [b] See footnote *b* to Table 1. [c] The actual value of ∠HCC is $(120 + x)°$ where *x* is the entry in this table. [d] See footnote *c* to Table 1.

A. Geometries. The optimized geometries of C_2H_2 and its complexes are given in Table 1, and those for C_2H_4 and the corresponding complexes are given in Table 2. As can be seen from these tables, both methods (DFT and MP2) predict a similar type of variation in bond lengths with respect to the size and composition of the basis sets. Comparing the results for different basis sets, we note that the CC and CH bond lengths generally decrease from A+ to B+, then remain virtually constant and again decrease from C+ to D. The shortest bond lengths are predicted by basis set D since it does not contain any diffuse functions. Of all structural parameters, the XM (M = H, Li, and Na) distance, where X is the midpoint of the CC bond, is found to be most sensitive to the basis sets (the MP2 values of *R*(XLi) and *R*(XNa) decrease by about 0.03 Å from B+ to C+). No general trend is, however, observed in the variation of tilt angle (TA) and bond angle (∠HCC; see Table 2), except for the fact that the former generally varies over a wider range than the latter.

Let us now compare the geometries predicted by B3LYP and MP2 methods. As can be seen from Tables 1 and 2, the MP2 method predicts longer CC bonds and smaller tilt angles in all cases. The former trend is observed also in the CH bonds and in the XM (M = Li and Na) distances. The differences between the highest and the lowest values of *R*(CC) obtained for different basis sets are virtually constant (∼0.004 Å in DFT and ∼0.012 Å in MP2). These differences are slightly smaller (∼0.002 Å in DFT and ∼0.007 Å in MP2) in the case of CH bonds. The corresponding values for the XM distances vary from 0.004/0.009 to 0.018/0.044 Å in the DFT/MP2 methods. The differences between the highest and the lowest values of TA are most pronounced in the case of basis sets C+ (0.59°/0.63°) and D (0.66°/0.80°). These results clearly demonstrate that the geometries predicted by the B3LYP method are less sensitive to basis sets than those obtained by the MP2 method. The most prominent difference between the two sets of geometries occurs in $C_2H_3^+$ where the DFT and MP2 methods predict the tilting of the terminal H atoms in opposite directions. For basis sets C+ and D the MP2 values of the tilt angle in $C_2H_5^+$ are practically zero. In contrast, the DFT TA values are substantially high for all four basis sets. These observations indicate that the tilt angle in the protonated species is highly sensitive to basis sets and methods of calculations. It will not be out of place here to mention that the largest tilt angle predicted for the alkali-metal cation−benzene complexes[14b] is 2.5° (for the K^+ complex), while a tilt angle as high as ∼5° is predicted in the present calculations for $C_2H_2Na^+$.

The most important structural changes occurring in the *π*-ligands upon complex formation are elongation of the CC and CH bonds and tilting of the terminal H atoms either away from (downward tilting) or toward (upward tilting) the bridging atom. The upward tilting has been predicted by the MP2 method only in $C_2H_3^+$. The strong mixing of A_1 (*σ*) and A_1 (*π*) MOs in the complex has been cited[28] as one of the reasons for the upward tilting. The difference between the energies of these MOs in the complexes of both C_2H_2 and C_2H_4 increases in the order $H^+ < Li^+ < Na^+$. Thus, they cannot mix in Li^+ and Na^+ complexes as strongly as in the corresponding protonated species. Such a mixing does not occur in the single-determinant B3LYP wave function, which always predicts a downward tilting. The repulsion between the positively charged bridging atom and the terminal H atoms is mainly responsible for the downward tilting. Such tilting occurs also in alkali-metal cation−benzene complexes. The XM (or equivalently CM) distance is a new structural parameter, which increases roughly in the same order as the tilt angles.

Before we close this subsection, let us discuss the accuracy of the predicted geometries. The experimental geometry is available[43] only for C_2H_2 (*R*(CC) = 1.203 Å and *R*(CH) = 1.060 Å) and C_2H_4 (*R*(CC) = 1.339 Å, *R*(CH) = 1.086 Å, and ∠HCC = 121.2°). The MP2/C+ geometry of C_2H_2 and the MP2/A+ geometry for C_2H_4 are in very good agreement with experiment. However, in both cases a better overall agreement with experiment is achieved by the DFT geometries since they are less sensitive to basis sets. Even the CCSD(T)/cc-pVQZ method is not capable[44] of reproducing the geometry of both C_2H_2 (*R*(CC) = 1.204 and *R*(CH) = 1.061 Å) and C_2H_4 (*R*(CC) = 1.331 Å, *R*(CH) = 1.080 Å, and ∠HCC = 121.5°) with equal accuracy. The geometries predicted for the protonated species by earlier calculations[25−33] were in good agreement with the present ones when they were carried out at comparable levels of theory. However, with the exception of the work of Lammertsma and Ohwada[28] no explicit mention was made in those calculations about the difference in the nature of the tilt angles (as predicted by the MP2 method) in $C_2H_3^+$ and $C_2H_5^+$. For the Li^+ and Na complexes of C_2H_2 and C_2H_4, earlier calculations[5,20−24] were performed at lower levels of theory than employed here. Moreover, values for all the structural parameters, especially the tilt angle, were not reported. For example, the geometries (given in Å in the order, *R*(CH)/*R*(CC)/*R*(XM)) predicted by Goldfuss et al.[23] for $C_2H_2Li^+$, $C_2H_2Na^+$, and $C_2H_4Li^+$ using the B3LYP method and A+ basis for carbon and hydrogen and 6-31G* basis for Li and Na, are as follows: −/1.205/1.254, −/1.204/2.633, and 1.087/1.341/2.403. The XM distance in the Li^+ complexes is highly exaggerated even with respect to the highest values obtained by us. The most extensive calculation on these complexes is the one reported on $C_2H_4Na^+$ by Feller.[16] At the highest level of theory (MP2(FC)/aug-cc-pVQZ) he obtained *R*(CH) = 1.082 Å, *R*(CC) = 1.339 Å, *R*(XNa) = 2.641 Å, and ∠HCH = 117.3 Å. Our MP2/C+ values are in best agreement with the results of Feller. Also in good agreement are the B3LYP/D values.

B. Dissociation Energies. The dissociation energies (DE) of the complexes have been calculated at B3LYP, MP2(full), and CCSD(T)=full (henceforth referred to as CCSD(T)) levels of theory. The same basis sets that were employed to optimize geometries, have been used to calculate DEs. The raw DE values are corrected for ZPE (zero-point energy) and BSSE (basis set superposition error). For the calculation of ZPEs, the MP2 frequencies have been scaled down by 5%. The same ZPEs are used also in the CCSD(T) calculations. The DFT ZPEs are used as such since they are smaller than their MP2 counterparts.

The D_0 values thus obtained are given in Table 3. As can be seen, the BSSE corrections (ΔE_{BSSE}) to the DFT D_0 values are negligible in all cases. It has been well documented[45] that compared to DFT, the post-HF methods retrieve a significantly higher amount of ΔE_{BSSE}. The present calculations lend further support to this trend. For a given basis set very close values are predicted for ΔE_{BSSE} by MP2 and coupled cluster methods. In the protonated species the three sets of BSSE-corrected D_0 values vary in the order, DFT > CCSD(T) > MP2. For the Li^+ and Na^+ complexes this order is DFT > MP2 ≈ CCSD(T). A similar trend in the CCSD(T) and MP2 D_0 values of the complexes of benzene with alkali-metal cations was noted by Nicholas et al.[14b] No well-defined pattern is discernible in the variation of dissociation energies (unless otherwise stated, we shall use the BSSE-corrected D_0 values for discussion and comparison) of the protonated species with respect to basis sets. The DFT D_0 values of the Li^+ and Na^+ complexes also do not follow any definite trend. However, the CCSD(T) and MP2 dissociation energies of these complexes vary in a systematic manner (A+ < B+ < C+ < D). Overall, fairly convergent (within ∼1.0 kcal/mol) values of dissociation energies are predicted for the Li^+ and Na^+ complexes by the various methods and basis sets employed here.

Experimental D_0 ($-\Delta H_0$) values are available only for the protonated species ($D_0(C_2H_3^+) = 151.9$ and $D_0(C_2H_5^+) = 161.2$ kcal/mol)[26] and $C_2H_4Na^+$ ($D_0 = 10.3 \pm 1.0$ kcal/mol).[4] For the protonated species the CCSD(T) dissociation energies corresponding to all but basis set B+ are obtained in excellent agreement with the experimental estimates. However, the DFT

TABLE 3: Calculated Dissociation Energies (D_0, kcal/mol)[a] of the Complexes of C_2H_2 and C_4 with H^+, Li^+, and Na^+ Ions

	methods of calculation								
	B3LYP//B3LYP			MP2(full)//MP2(full)			CCSD(T)=full//MP2(full)		
basis sets[b]	$C_2H_3^+$	$C_2H_2Li^+$	$C_2H_2Na^+$	$C_2H_3^+$	$C_2H_2Li^+$	$C_2H_2Na^+$	$C_2H_3^+$	$C_2H_2Li^+$	$C_2H_2Na^+$
A+	152.7	20.6	13.4	151.0	20.2	12.8	153.8	20.3	12.8
	152.6	20.5	13.2	148.6	18.4	11.3	151.4	18.5	11.3
B+	153.5	21.4	14.8	149.6	19.8	12.8	152.2	20.0	13.0
	153.4	21.3	14.7	147.8	18.9	12.1	150.5	18.3	12.2
C+	153.6	21.4	14.0	151.1	21.2	14.1	153.7	21.5	14.3
	153.5	21.2	13.9	149.3	19.1	12.5	152.0	19.4	12.7
D	154.3	21.5	14.2	150.9	20.6	13.6	153.5	20.9	14.8
	154.3	21.4	14.1	149.4	19.5	12.8	152.1	19.8	14.0[c]

	methods of calculation								
	B3LYP//B3LYP			MP2(full)//MP2(full)			CCSD(T)=full//MP2(full)		
basis sets[b]	$C_2H_5^+$	$C_2H_4Li^+$	$C_2H_4Na^+$	$C_2H_5^+$	$C_2H_4Li^+$	$C_2H_4Na^+$	$C_2H_5^+$	$C_2H_4Li^+$	$C_2H_4Na^+$
A+	162.2	20.5	13.6	161.6	20.3	12.8	162.7	19.9	12.7
	162.1	20.4	13.4	159.5	18.8	11.6	160.6	18.4	11.4
B+	162.3	21.1	14.9	159.9	20.0	13.2	160.9	19.8	13.0
	162.2	21.0	14.8	158.3	19.2	12.5	159.3	19.0	12.3
C+	162.6	21.1	14.2	161.5	22.0	15.1	162.9	22.1	15.1
	162.5	21.0	14.0	159.4	19.3	12.9	160.7	19.3	12.8
D	162.6	21.0	14.1	161.2	20.7	14.0	162.4	20.8	13.9
	162.6	20.9	14.0	159.5	19.5	13.1	160.7[c]	19.6[c]	13.0[c]

[a] The second set of entries against each basis set correspond to BSSE-corrected values. The differences between these and the first set of values are BSSE corrections (Δ_{BSSE}). [b] See footnote *b* to Table 1. [c] MP2(full) BSSE correction has been used.

D_0 values are generally overestimated, and show good correspondence with experiment only for basis set A+. In contrast, the corresponding MP2 values are always underestimated. The dissociation energy of $C_2H_4Na^+$ is overestimated by DFT for all basis sets and by MP2 and CCSD(T) methods for all but basis set A+. For this basis, the post-HF methods predict D_0 of $C_2H_4Na^+$ in good agreement with experiment. It may be noted that even at the highest level of theory (CCSD(T) + CV/CBS/aug-cc-pVxZ (x = T, Q, and 5)) employed by Feller the D_0 value (13.6 ± 0.2 kcal/mol) is overestimated by ~30% with respect to the experimental value. The D_0 value predicted by basis set B+ is in very good agreement with the Gaussian-2 value reported by Feller.[16]

We now compare the BSSE-corrected D_0 values of the complexes of C_2H_2 and C_2H_4 for different cations. Of the two protonated species, $C_2H_5^+$ is predicted to be more stable than $C_2H_3^+$ by about 10 kcal/mol. This is consistent with the structural changes (see Tables 1 and 2) in the monomers (C_2H_2 and C_2H_4) occurring upon complexation. Because of higher polarizability of C_2H_4, its bonds are elongated to a greater extent than those in C_2H_2. For a given π-system the D_0 values increase in the order, $Na^+ < Li^+ \ll H^+$. Elongation of the monomer bonds also takes place in the above order. As we shall show in the following subsection, the amount of charge transfer, the bond index of the CM (M = H, Li, and Na) bond, and the change in the bond index of CC and CH bonds occurring upon complex formation generally vary in the same manner as do the D_0 values.

While it is straightforward to discriminate the strength of the interaction between C_2H_2 or C_2H_4 and H^+, Li^+, and Na^+ ions on the basis of dissociation energies, we do not get an unequivocal answer for the relative stability of $C_2H_2M^+$ and $C_2H_4M^+$ when M = Li and Na. The structural changes, the amount of charge transfer, and the bond indices (Table 4) indicate that for a given cation, $C_2H_4M^+$ should be somewhat more stable than $C_2H_2M^+$. This conclusion is supported only by the MP2 D_0 values for all four basis sets. The dissociation energies obtained by DFT and CCSD(T) methods using basis sets A+, B+, and C+ predict $C_2H_4Na^+$ to be slightly more stable than $C_2H_2Na^+$. For the Li^+ complexes the DFT and CCSD(T) methods do not predict any particular order of stability. A closer scrutiny of the results of Table 3 indicates that the difference in the stability of Li^+ and Na^+ complexes as predicted by various methods and basis sets does not generally exceed 0.5 kcal/mol (the CCSD(T) D_0 values for basis sets B+ (Li^+ complexes) and D (Na^+ complexes) provide exceptions). Since the error bar of the present calculated values is certainly greater than 0.5 kcal/mol, we did not get a unique order of stability of these complexes for all the methods and basis sets. The results of earlier calculations are less conclusive in this regard. The MP2/6-31G* calculations[12] predict a D_0 value of 24.3 kcal/mol for $C_2H_4Li^+$, which is significantly higher than almost all the values obtained in this study. According to MP2(full)/6-311+G(2d,2p)//MP2(full)/6-31G* calculations of Hoyau et al.[24] the ΔH_{298} values of $C_2H_2Na^+$ and $C_2H_4Na^+$ are −12.3 and −12.7 kcal/mol, respectively. The MP2/6-31G* calculations of Del Bene et al.[21] predicted a higher D_0 value for $C_2H_2Li^+$ (23.6 kcal/mol) than for $C_2H_4Li^+$ (23.2 kcal/mol).

TABLE 4: Charge Transfer (Δq, in au)[a] from C_2H_2 and C_2H_4 to M^+ (M = H, Li, and Na) and Bond Indices (I_{AB} and I_{ABC})[b] in $C_2H_2M^+$ and $C_2H_4M^+$ Complexes

complex	Δq_C	Δq_H	Δq^c	I_{CC}	ΔI_{CC}^d	ΔI_{CH}^d	I_{CM}	I_{CMC}
$C_2H_3^+$	0.194	0.108	0.604	2.138	0.646	0.045	0.460	0.283
$C_2H_2Li^+$	−0.040	0.052	0.024	2.548	0.236	0.020	0.198	0.174
$C_2H_2Na^+$	−0.030	0.040	0.020	2.631	0.153	0.015	0.124	0.115
$C_2H_5^+$	0.154	0.083	0.642	1.309	0.674	0.040	0.473	0.278
$C_2H_4Li^+$	−0.063	0.039	0.030	1.716	0.267	0.024	0.213	0.161
$C_2H_4Na^+$	−0.045	0.029	0.026	1.789	0.194	0.014	0.142	0.116

[a] Calculated using natural population analysis and B3LYP/6-311G** wave function. [b] Calculated using nonlinear Mulliken-type population analysis and B3LYP/6-311G** wave function. [c] Total charge transfer. [d] $\Delta I_{AB} = I_{AB}(C_2H_2/C_2H_4) - I_{AB}(\text{complex})$.

C. Nature of Bonding. To understand the nature of the interaction between C_2H_2 and C_2H_4 and H^+, Li^+, and Na^+ ions, we varied R(XM) from 0.1 to 5.0 Å (4.0 Å for M = H) in a step of 0.1 Å and fully optimized the geometry of the complexes at each value of R(XM). The B3LYP/6-311G** method was employed in these calculations. The potential energy surface thus generated shows that the approach of the cation to the ligand along the XM coordinate does not involve any energy barrier. Over the entire potential surface we calculated the Mulliken atomic charge[38] of the bridging atom (q_M) and bond indices (I_{CM} and I_{CMC}) of the 2c and 3c bonds involving the bridging atom. At R(XM) = 4.0 Å the values of q_M, I_{CM}, and I_{CMC} are 0.469, 0.388, and 0.283 in $C_2H_3^+$ and 0.388, 0.420, and 0.288 in $C_2H_5^+$, respectively. The corresponding values (separated by a slash) in $C_2H_2Li^+$, $C_2H_2Na^+$, $C_2H_4Li^+$, and $C_2H_4Na^+$ are 0.983/0.017/0.016, 0.982/0.017/0.016, 0.975/0.024/0.022, and 0.975/0.024/0.021, respectively. These values are rather close to the corresponding values in the monomers ($q_M = 1.0$, $I_{CM} = I_{CMC} = 0$). The situation is, however, quite different in the protonated species where the values of q_M, I_{CM}, and I_{CMC} at R(XM) = 4.0 are far from the above monomer values and indicate that still there is strong bonding between H^+ and the π-systems. There is another very important difference between the complexes of H^+ and those of Li^+ and Na^+. In $C_2H_3^+$ and $C_2H_5^+$ I_{CMC} varies within a very small range (from 0.27 to 0.29) over the entire potential surface while for M = Li and Na this quantity is smaller and approaches zero as R(XM) approaches ~5.0 Å. This indicates that the 3c bonding in the protonated species is exceptionally strong.

The amount of charge transfer (Δq) from the ligand to the cation and the changes in bond indices (ΔI_{AB}) occurring upon complex formation, are given in Table 4. Since Mulliken population analysis exaggerates[37,46] charge-transfer, we have calculated this quantity using NPA (natural population analysis).[37] The Δq values of Table 4 indicate that in $C_2H_3^+$ and $C_2H_5^+$ electron transfer to the bridging atom takes place from both C and H. In the Li^+ and Na^+ complexes, a fraction of the charge on the terminal H is transferred to C and the remaining portion to the bridging atom. At the equilibrium geometry of the complexes the amount of positive charge carried by the bridging atoms (in the order $H^+/Li^+/Na^+$) is 0.396/0.976/0.982 and 0.358/0.970/0.973 in $C_2H_2M^+$ and $C_2H_4M^+$, respectively. For the terminal hydrogen atoms the corresponding figures are 0.330/0.274/0.262 and 0.358/0.219/0.210, respectively. For a given π-ligand Δq varies in the order $H^+ \gg Li^+ > Na^+$ and ΔI_{CC}, ΔI_{CH}, I_{CM}, and I_{CMC} vary in the order $H^+ > Li^+ > Na^+$. The decrease in the CC and CH bond indices is consistent with the lengthening of these bonds upon complex formation (see Tables 1 and 2). The amount of charge transfer and changes in the CC and CH bond indices indicate that for a given cation the complex of C_2H_4 should be slightly more stable than that of C_2H_2. As we have observed in the previous subsection, this is indeed the case with most of the calculated D_0 values. The I_{ABC} value of a 3c single bond (a 3c bond can be also of multiple type[47]) can have a maximum value[39c,48a] of 0.296 (as in H_3^+). The 3c bond in $C_2H_3^+$ and $C_2H_5^+$ appears to be as strong as that in H_3^+. It may be noted that the unit positive charge in $C_2H_3^+$ is almost equally distributed among the three H atoms. The 3c bond indices in the Li^+ and Na^+ complexes are about one-half of the corresponding values in the protonated species. These values are, however, still substantially high, and on the basis of the empirical criterion (a genuine 3c bond (ABC) that can be detected by LMO calculations has $I_{ABC} \geq 0.1$[39a,48b]), they are sufficiently indicative of the presence of 3c bonding, albeit weak.

The present analysis made on the basis of charge transfer and bond indices suggests that bonding in $C_2H_3^+$ and $C_2H_5^+$ is predominantly covalent. In the Li^+ and Na^+ complexes also the covalent interaction plays a fairly important role. Quantum mechanical energy component analysis[12] using the Morokuma decomposition scheme[49] finds that for $C_2H_4Li^+$ the electrostatic energy is only ~60% of the total energy. According to Tsuzuki et al.,[18] induction (polarization and charge transfer) and electrostatic interactions are the major sources of stability of alkali-metal cation−π complexes; the contribution of the former outweighs that of the latter by a significant margin in the case of Li^+ and Na^+ complexes of benzene.

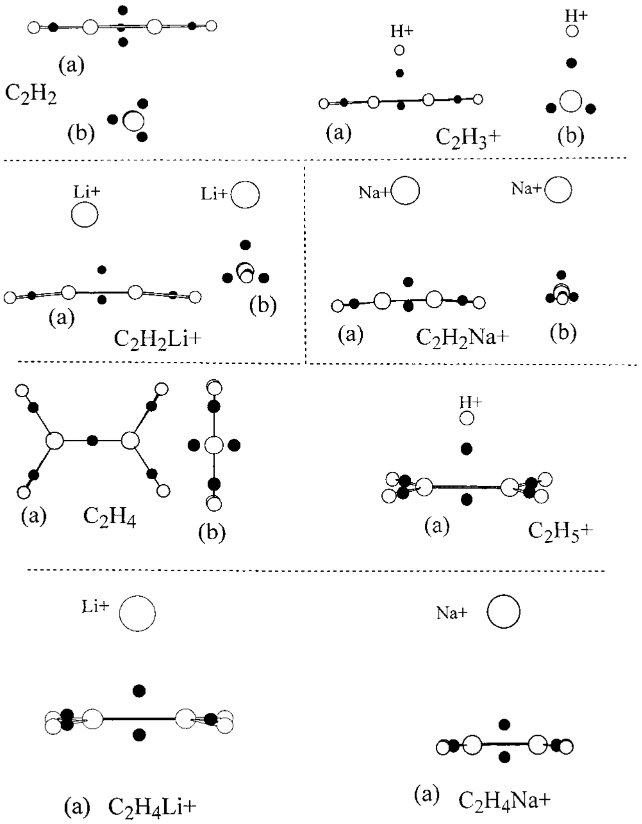

Figure 1. Charge centroids (solid circles) of the valence LMOs of C_2H_2,C_2H_4 and their complexes with H^+, Li^+, and Na^+ ions. The frontal view is shown in (a), and the view through the CC bond is shown in (b).

To lend further support to the presence of 3c bonding, we transformed the B3LYP/6-311G** CMOs (canonical MOs) to a set of LMOs (localized MOs) using Boys' method.[40] Following Kar and Jug,[50] we used the positions of charge centroids rather than populations of the LMOs to identify the bonds (both 2c and 3c). They observed that the charge centroid of the LMO corresponding to a 3c bond is located at the surface of the triangle formed by the constituent atoms of the bond. The charge centroids of the valence LMOs in C_2H_2, C_2H_4 and their complexes are shown in Figure 1 ((a) for frontal view and (b) for viewing through the CC bond). It can be seen that the centroids of the LMOs describing 3c bonds are located at the surface of a triangle in each case. In $C_2H_3^+$ the centroid of the CHC bond is located almost at the midpoint of the triangle (the centroids of HHH bond in H_3^+ and CCC bond in $C_3H_3^+$ ions are located exactly at the midpoint of the corresponding triangle[50]). In $C_2H_5^+$ the centroid is displaced slightly toward the bridging hydrogen. The centroids of the CMC bonds (M = Li and Na) are located near the CC bond (they are, however, slightly further away from the centroid of the CC π bond in the monomers) implying thereby that these bonds are mainly composed of the CC π bond with sufficient contribution from the bridging atom.

A great deal of information about the nature of bonding in a molecule can also be obtained from the topological analysis[19]

TABLE 5: Topological Properties (au) of the Electron Densities[a] at Bond Critical Points (CP) of C_2H_2 and $C_2H_2M^+$ (M = H, Li, and Na) Complexes

system	bond	CP	ρ	$\nabla^2\rho$	λ_1	λ_2	λ_3	ϵ
C_2H_2	CC	(3, −1)	0.407	−1.202	−0.660	−0.660	0.118	0.0
			0.411	−1.232	−0.669	−0.669	0.107	0.0
	CH	(3, −1)	0.291	−1.064	−0.813	−0.813	0.561	0.0
			0.288	−1.045	−0.801	−0.801	0.559	0.0
$C_2H_3^+$	CC	(3, −1)	0.417	−1.375	−0.809	−0.612	0.046	0.321
			0.403	−1.239	−0.773	−0.622	0.160	0.244
	CH_b[b]	(3, −1)	0.209	−0.350	−0.421	−0.269	0.340	0.568
			0.205	−0.278	−0.424	−0.237	0.383	0.787
	CH	(3, −1)	0.293	−1.242	−0.909	−0.893	0.562	0.018
			0.286	−1.117	−0.877	−0.860	0.619	0.020
$C_2H_2Li^+$[c]	CC	(3, −1)	0.422	−1.349	−0.695	−0.858	0.004	0.056
			0.411	−1.248	−0.699	−0.669	0.121	0.046
	CLi	(3, −1)	0.019	0.091	−0.024	−0.019	0.135	0.215
			0.020	0.092	−0.025	−0.020	0.137	0.273
	CH	(3, −1)	0.295	−1.171	−0.850	−0.850	0.528	0.0
			0.284	−1.044	−0.814	−0.814	0.583	0.0
$C_2H_2Na^+$	CC	(3, −1)	0.416	−0.773	−0.654	−0.609	0.489	0.075
			0.411	−1.246	−0.628	−0.596	0.038	0.054
	CNa	(3, −1)	0.013	0.057	−0.011	−0.008	0.076	0.318
			0.014	0.062	−0.012	−0.008	0.085	0.465
	CH	(3, −1)	0.301	−1.329	−0.859	−0.858	0.388	0.001
			0.285	−1.044	−0.808	−0.806	0.446	0.001

[a] Calculated from HF/6-311G** (upper entries against each CP) and B3LYP/6-311G** (lower entries) wave functions. [b] H_b is the bridging hydrogen atom. [c] Poincare−Hopf relationship is not satisfied for the B3LYP density.

TABLE 6: Topological Properties (au) of the Electron Densities[a] at Bond Critical Points (CP) of C_2H_4 and $C_2H_4M^+$ (M = H, Li, and Na) Complexes

system	bond	CP	ρ	$\nabla^2\rho$	λ_1	λ_2	λ_3	ϵ
C_2H_4	CC	(3, −1)	0.360	−1.198	−0.803	−0.566	0.171	0.418
			0.345	−1.033	−0.747	−0.559	0.273	0.338
	CH	(3, −1)	0.291	−1.083	−0.760	−0.740	0.427	0.013
			0.280	−0.957	−0.740	−0.730	0.513	0.013
$C_2H_5^+$[b]	CC	(3, −1)	0.327	−1.043	−0.696	−0.568	0.220	0.226
			0.315	−0.887	−0.652	−0.546	0.311	0.196
	CH_b	(3, −1)	0.191	−0.293	−0.410	−0.166	0.283	1.462
			0.181	−0.219	−0.386	−0.135	0.302	1.863
	CH	(3, −1)	0.301	−1.192	−0.877	−0.855	0.535	0.020
			0.288	−1.049	−0.832	−0.816	0.600	0.020
$C_2H_4Li^+$[c]	CC	(3, −1)	0.353	−1.168	−0.778	−0.573	0.183	0.358
			0.338	−1.002	−0.724	−0.561	0.283	0.291
	CLi	(3, −1)	0.018	0.069	−0.022	−0.016	0.107	0.397
			0.019	0.071	−0.024	−0.016	0.111	0.458
	CH	(3, −1)	0.293	−1.098	−0.786	−0.777	0.465	0.011
			0.281	−0.971	−0.760	−0.753	0.542	0.010
$C_2H_4Na^+$[d]	CC	(3, −1)	0.355	−1.175	−0.784	−0.573	0.181	0.367
			0.339	−1.007	−0.727	−0.562	0.282	0.294
	CNa	(3, −1)	0.012	0.046	−0.011	−0.007	0.064	0.505
			0.014	0.052	−0.012	−0.008	0.072	0.649
	CH	(3, −1)	0.292	−1.093	−0.779	−0.770	0.456	0.012
			0.281	−0.969	−0.756	−0.745	0.537	0.010

[a] Calculated from HF/6-311G** (upper entries against each CP) and B3LYP/6-311G** (lower entries) wave functions. [b] H_b is the bridging hydrogen atom. [c] Poincare−Hopf relationship is not satisfied for the B3LYP density. [d] The HF density predicts a (3, −3) CP (nonnuclear attractor) at the midpoint of the CC bond with $\rho = 0.419$, $\nabla^2\rho = -1.317$, $\lambda_1 = -0.635$, $\lambda_2 = -0.598$, and $\lambda_3 = -0.085$.

of its electron density. The topological properties of HF/6-311G** and B3LYP/6-311G** densities at the respective bond critical points are given in Table 5 for C_2H_2 and its complexes; the corresponding quantities for C_2H_4 and its complexes are listed in Table 6. The Poincare−Hopf relationship is satisfied in all but two cases (B3LYP density of $C_2H_2Li^+$ and $C_2H_4Li^+$). It has been pointed out by Cubero et al.[15] that the number of critical points and their quality is not quite sensitive to electron correlation. We have also observed that the MP2/6-311G** critical point data of Lammertsma and Ohwada[28] for $C_2H_3^+$ and $C_2H_5^+$ are comparable to the present values. All the bond critical points (BCP) are of (3, −1) type and are characterized by negative values of the Laplacian of the electron density for CC, CH, and CH_b bonds. This is indicative of covalent interaction. In contrast, the Laplacian of the density at the BCPs of CM (M = Li and Na) bonds is positive. This is a characteristic of closed-shell interactions and indicates a depletion of electron density from the interatomic surface to the interacting nuclei. The relatively large value of λ_3 (compared to λ_1 and λ_2) in these cases denotes a sort of structural instability. The HF density predicts a (3, −3) CP at the midpoint of the CC bond in $C_2H_4Na^+$. Similar observation was made in a number of 3c bonded systems by Lammertsma and Ohwada.[28] The dissociation energies of the complexes vary almost linearly with ρ and $\nabla^2\rho$ (absolute values) at the CP of the CM bonds. The cylindrical symmetry ($\epsilon = 0$) of the CH bonds is more or less maintained in all the complexes.

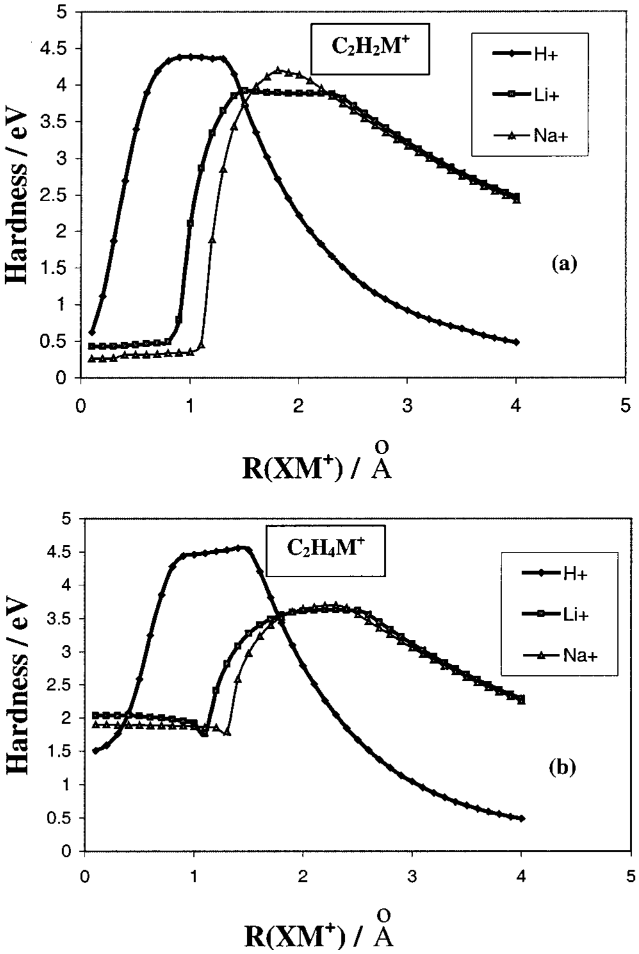

Figure 2. Hardness profiles of (a) $C_2H_2M^+$ and (b) $C_2H_4M^+$.

The topological analysis of the electron density, although it is capable of accounting for the essential features of bonding in the present complexes, is not free from inadequacies. For example, the weakening of the CC bonds upon complexation is reflected from the corresponding ρ values in the complexes of C_2H_4, but not in those of C_2H_2, where they remain virtually constant at the corresponding monomer value. The ρ value at the BCP of CH_b indicates that $C_2H_3^+$ should be more stable than $C_2H_5^+$, which is not true. It may be noted in this context that the CH_b (b denotes bridging) BCP in the $H^+...C_6H_6$ complex is associated[15] with a much smaller value of ρ (∼0.07) and a positive value of $\nabla^2\rho$ (+0.08), which implies rather unstable structure. This does not conform to the very high value (∼−122 kcal/mol) of the interaction energy in this complex. As shown in the same work,[15] it is difficult to accommodate in the topological analysis the changes in electron density raised by heteroatoms and substitutents in five-membered rings. That AIM[19] exaggerates electron density on electronegative atoms has been pointed out also by Van Alem et al.[51] in the course of their studies on the electronic properties of α-substituted vinyl cations.

We conclude our discussion on bonding by referring to a somewhat different observation. While scanning the potential energy surfaces of the complexes using the B3LYP/6-311G* method, we calculated their hardness ($\eta = (I - A)/2$, where I, the ionization potential, and A, the electron affinity, were evaluated using Koopmans' approximation) over the entire potential surface. The hardness profiles thus generated are shown in Figure 2 ((a) for $C_2H_2M^+$ and (b) for $C_2H_4M^+$). These profiles shown in (a) and (b) are quite similar; all of them exhibit a maximum. Only in $C_2H_3^+$ and $C_2H_4Li^+$ are the positions of the maxima obtained in good agreement with the calculated equilibrium XM distances. This observation may be a qualitative manifestation of the principle of maximum hardness.[52]

D. Concluding Remarks. The present numerical experiments carried out to determine the electronic structure and stability of the complexes of C_2H_2 and C_2H_4 with H^+, Li^+, and Na^+ ions demonstrate that the direction of tilting of the terminal H atoms in the protonated species is highly sensitive to the levels of theory and basis sets. Of the several basis sets employed in this study, the 6-311+G**(A+) appears to be the most balanced one. Basis set D, although it is the largest one considered here, does not perform satisfactorily. It may be due to the noninclusion of any diffuse functions on the heavy atoms. The CCSD(T) calculations predict the dissociation energies of $C_2H_3^+$ and $C_2H_5^+$ in excellent agreement with experiment; a good agreement is obtained also in the case of $C_2H_4Na^+$. Barring a few exceptions provided mainly by the DFT and CCSD(T) D_0 values for the Li^+ complexes, $C_2H_4M^+$ (M = Li, Na) is predicted to be slightly more stable than $C_2H_2M^+$. The nature of bonding of the complexes can be fairly quantitatively understood on the basis of charge transfer, bond indices, LMOs, and topological properties of electron density.

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References and Notes

(1) (a) Castleman, A. W.; Keese, R. G., Jr. *Chem. Rev.* **1986**, *86*, 589. (b) Sannigrahi, A. B.; Nandi, P. K.; Schleyer, P. v. R *J. Am. Chem. Soc.* **1994**, *116*, 7225. (c) Sannigrahi A. B.; Nandi, P. K.; Kar, T. *J. Mol. Struct. (THEOCHEM)* **1994**, *306*, 85.

(2) (a) Woodin, R. L.; Bauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501. (b) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem*. **1981**, *85*, 1814.

(3) Guo, B. C.; Purnell, J. W.; Castleman, A. W., Jr.; *Chem. Phys. Lett.* **1990**, *168*, 155.

(4) Armentrout, P. B.; Rodgers, M. T. *J. Phys. Chem. A* **2000**, *104*, 2238.

(5) Deakyne, C. A.; Meotner (Mautner), M. *J. Am. Chem. Soc.* **1985**, *107*, 469.

(6) (a) Deakyne, C. A. In *Molecular Interactions. From van der Waals to strongly Bound Complexes*; Scheiner, S., Ed.; Wiley: Chichester, U.K., 1997; pp 265−296. (b) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.

(7) Amicangelo, J. C.; Armentrout, P. B. *J. Phys. Chem. A* **2000**, *104*, 11420.

(8) Mavri, J.; Koller, J.; Hadzi, D. *J. Mol. Struct. (THEOCHEM)* **1993**, *281*, 305.

(9) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708.

(10) (a) Meccozi, S.; West, A. P., Jr.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 2307. (b) Mecozzi, S.; West, A. P., Jr.; Dougherty, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 10556.

(11) (a) Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T.-K.; Kim, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 7399. (b) Lee, J. Y.; Lee, S. J.; Choi, H. S.; Cho, S. J.; Kim, K. S.; Ha, T.-K. *Chem. Phys. Lett.* **1995**, *232*, 67.

(12) Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 4177.

(13) Basch, H.; Stevens, W. J. *J. Mol. Struct. (THEOCHEM)* **1995**, *338*, 303.

(14) (a) Nicholas, J. B.; Hay, B. P. *J. Phys. Chem. A* **1999**, *103*, 9815. (b) Nicholas, J. B.; Hay, B. P.; Dixon, D. A *J. Phys. Chem. A* **1999**, *103*, 1394.

(15) Cubero, E.; Orozco, M.; Lugue, F. L. *J. Phys. Chem. A* **1999**, *103*, 315 and references therein.

(16) Feller, D. *Chem. Phys. Lett.* **2000**, *322*, 543.

(17) Feller, D.; Dixon, D, A.; Nicholas, J. B. *J. Phys. Chem. A* **2000**, *104*, 11414.

(18) Tsuzuki, S.; Yoshida, M.; Uchimaru, T.; Mikami, M. *J. Phys. Chem. A* **2001**, *105*, 769.

(19) Bader, R. F. W *Chem. Rev.* **1991**, *91*, 893.

(20) Sauer, J.; Delnlnger, D. *J. Phys. Chem.* **1982**, *86*, 1327.

(21) Del Bene, J. E.; Frisch, M. J.; Raghavachari, K.; Pople, J. A. *J. Phys. Chem.* **1983**, *87*, 73.

(22) Rodriguez-Monge, L.; Larsson, S. L. *J. Chem. Phys.* **1996**, *105*, 7857.

(23) Goldfuss, B.; Schleyer, P.v. R.; Hampel, F. *J. Am. Chem. Soc.* **1996**, *118*, 12183; **1997**, *119*, 1072.

(24) Hoyu, S.; Norrman, K.; McMahon, T. B.; Ohanessiau, G. *J. Am. Chem. Soc.* **1999**, *121*, 8864.

(25) Liang, C.; Hamilton, T. P.; Schefer, H. F., III. *J. Chem. Phys.* **1990**, *92*, 3653.

(26) Ochterski J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299.

(27) Perera, S. A.; Bartlett, R. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 8476.

(28) Lammertsma, K.; Ohwada, T. *J. Am. Chem. Soc.* **1996**, *118*, 7247.

(29) Morgon, N. H. *J. Phys. Chem. A* **1998**, *102*, 2050.

(30) Del Rio, E.; Lopez, R.; Sordo, T. L. *J. Phys. Chem. A* **1998**, *102*, 6831.

(31) East, A. L. L.; Liu, Z. F.; McCagne, C.; Perez-Jorde, J. M.; San-Fabian, E. *J. Phys. Chem. A* **1998**, *102*, 903.

(32) Alem, K. V.; Sudholter, E. J. R.; Zuilhof, H. *J. Phys. Chem. A* **1998**, *102*, 10860.

(33) Minoux, H.; Chipot, C. *J. Am. Soc.* **1999**, *121*, 10366.

(34) Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155; **1993**, *98*, 5648.

(35) Lee, H.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(36) Boys, S. F.; Bernardi, M. *Mol. Phys.* **1970**, *19*, 353.

(37) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Weinhold, F.; Curtiss, L. A. *Chem. Rev.* **1988**, *88*, 899.

(38) (a) Mulliken, R. S.; *J. Chem. Phys.* **1955**, *23*, 1833 and 1841. (b) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270; *Int. J. Quantum Chem.* **1986**, *29*, 73 and 477. (c) Sannigrahi, A. B. *Adv. Quantum. Chem.* **1992**, *23*, 301.

(39) (a) Sannigrahi, A. B.; Kar, T. *Chem. Phys. Lett.* **1990**, *173*, 569. (b) Giambiagi, M.; de Giambiagi, M. S.; Mundin, K. C. *Struct. Chem.* **1990**, *1*, 423. (c) Sannigrahi, A. B.; Kar, T. *Chem. Phys. Lett.* **1999**, *299*, 518.

(40) Boys, S. F. In *Quantum Theory of Atoms, Molecules and the Solid State*; Lowdin, P.-O., Ed.; Academic Press: New York, 1966; p 253.

(41) Frisch, M. J.; Trucks, G. W.; Schlegel H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Petersson, G. A.; Montegomery, J. A., Jr.; Strartmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin K. N.; Strain M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Geomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Baboul, A. G.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andreas, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Version A 7; Gaussian Inc.: Pittsburgh, PA, 1998.

(42) Popelier, P. L. A. *Theor. Chim. Acta* **1994**, *87*, 465; *Can. J. Chem.* **1996**, *74*, 829; *Mol. Phys.* **1996**, *87*, 1169; *Comput. Phys. Commun.* **1996**, *93*, 212; **1998**, *108*, 180; MORPHY98, a topological analysis program

written by P. L. A. Popelier with contribution from R. G. A. Bone; UMIST, England, EU, 1998.

(43) Stewart, J. J. P. *J. Computer-Aided Mol. Design* **1990**, *4*, 1.

(44) Gauss, J.; Cremer, D.; Stanton, J. F. *J. Phys. Chem. A* **2000**, *104*, 1319.

(45) Rosa, A.; Ehlers, A. W.; Baerends, E. J.; Snidjers, J. G.; Velde, *G. J. Phys. Chem.* **1996**, *100*, 5690.

(46) Sannigrahi, A. B.; Nandi, P. K.; Kar, T. *J. Mol. Struct. (THEOCHEM)* **1994**, *306*, 85.

(47) Ponec, R.; Roithova, J.; Sannigrahi, A. B.; Lain, L.; Torre, A.; Bochicchio, R. *J. Mol. Struct. (THEOCHEM)* **2000**, *505*, 283.

(48) (a) Sannigrahi, A. B.; Nandi, P. K.; Behera, L.; Kar, T. *J. Mol. Struct. (THEOCHEM)* **1992**, *276*, 259. (b) Sannigrahi, A. B.; Kar, T. *J. Mol. Struct. (THEOCHEM)* **2000**, *496*, 1.

(49) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325.

(50) Kar, T.; Jug, K. *Int. J. Quantum Chem.* **1995**, *53*, 407; *Chem. Phys. Lett.* **1996**, *256*, 201.

(51) Van Alem, K.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2000**, *104*, 2780.

(52) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561; *Acc. Chem. Res.* **1993**, *26*, 250.