erable excess energy. However, it lies below the lowest fragmentation barrier, consistent with its experimental observation via charge stripping. A striking additional result is that double ionization of the ethyl radical also produces an ethyl dication (**1a**$^{2+}$) which lies below the lowest fragmentation barrier. It should therefore be possible to produce the ethyl dication from the ethyl radical in the source of a mass spectrometer. This contrasts with the situation for molecules such as methane for which double ionization in the source does not lead to a stable dication but for which production of the dication can be achieved through charge stripping of the methane monocation.[29a-c,30]

Concluding Remarks

Several important points emerge from this study.

(i) In contrast to the ethyl cation, which has a bridged (or nonclassical) structure, the ethyl dication has an open (or classical) structure, returning in a qualitative sense to the preference found in the ethyl radical.

(ii) The ethyl dication lies in a moderately deep potential well, being prevented by barriers of more than 100 kJ mol^{-1} from undergoing highly exothermic fragmentation reactions to $CH_2^{\bullet+}$ + CH_3^+ and $C_2H_4^{\bullet+}$ + H^+.

(iii) The various forms of the ethyl dication display unusual structural features (e.g., long β C–H bonds in the open forms) which may be readily rationalized with use of qualitative orbital arguments.

(iv) The calculated difference between vertical and adiabatic ionization energies for the ethyl radical, reflecting the difference in structures for these two species, is somewhat larger than the value originally reported from photoelectron spectroscopy but is in good agreement with more recent experimental thermochemical data.

Acknowledgment. We thank Dr. Eric Kingston for some stimulating discussions regarding the charge-stripping process.

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Ylides and Ylidions: A Comparative Study of Unusual Gas-Phase Structures

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Received September 18, 1986

Abstract: Ab initio molecular orbital calculations with split-valence plus polarization basis sets and incorporating electron correlation and zero-point energy corrections have been used to study the structures and stabilities of prototype ylides CH_2XH and ylidions $\dot{C}H_2X^+H$ (X = NH_2, OH, F, PH_2, SH, Cl). Detailed potential energy surfaces are presented for the 12 systems studied, and comparisons are made across the periodic table, between first- and second-row compounds and between the ylides and ylidions. The ylidions are confirmed to be much more stable with respect to unimolecular rearrangement or decomposition than their neutral counterparts. For both ylides and ylidions, this stability decreases across a row of the periodic table. For the ylides, the first-row species tend to be less stable energetically than the second-row species, while the reverse is true for the ylidions. The effects of higher level calculations have been examined for ylides, ylidions, and their conventional isomers, and the results are compared with recent experimental data.

Experimental and theoretical studies have firmly established the existence in the gas phase of simple organic ions with unusual structures whose neutral counterparts are unknown or extremely reactive. One of the earliest examples to receive high-level treatment both theoretically[2] (by using ab initio calculations) and experimentally[3] (by using collisionally activated dissociation (CAD) mass spectrometry) was the methyleneoxonium radical cation, $CH_2OH_2^{\bullet+}$. This species has quite a short C–O bond and, perhaps surprisingly, lies lower in energy than the methanol radical cation, $CH_3OH^{\bullet+}$. In contrast, the neutral ylide (CH_2OH_2) resembles a weak complex of methylene with water.[4]

We have introduced[5] the term *ylidion* to describe the class of radical cations corresponding to such ionized ylides.[6] The ylidions may be written with the charge and radical sites on adjacent centers (e.g., $\dot{C}H_2O^+H_2$) and are members of the more general class of *distonic*[7] radical cations in which the charge and radical sites are formally separated.

In this paper, we present a comprehensive survey of the first- and second-row ylidions $\dot{C}H_2X^+H$ (X = NH_2, OH, F, PH_2, SH, Cl) and their corresponding ylides CH_2XH.[8] The main emphasis is on the ylidions, with the ylides being briefly included largely for comparison purposes. Our general aim is to compare structural features and relative stabilities of the various species at uniform and moderately high levels of ab initio theory. In particular, we wish to elucidate trends in these properties in three specific areas: (i) across a row of the periodic table, (ii) between first- and second-row compounds, and (iii) between neutral and charged species.

Method

Standard ab initio molecular orbital calculations were carried out with modified versions[9,10] of the Gaussian 80[11] and Gaussian 82[12] programs.

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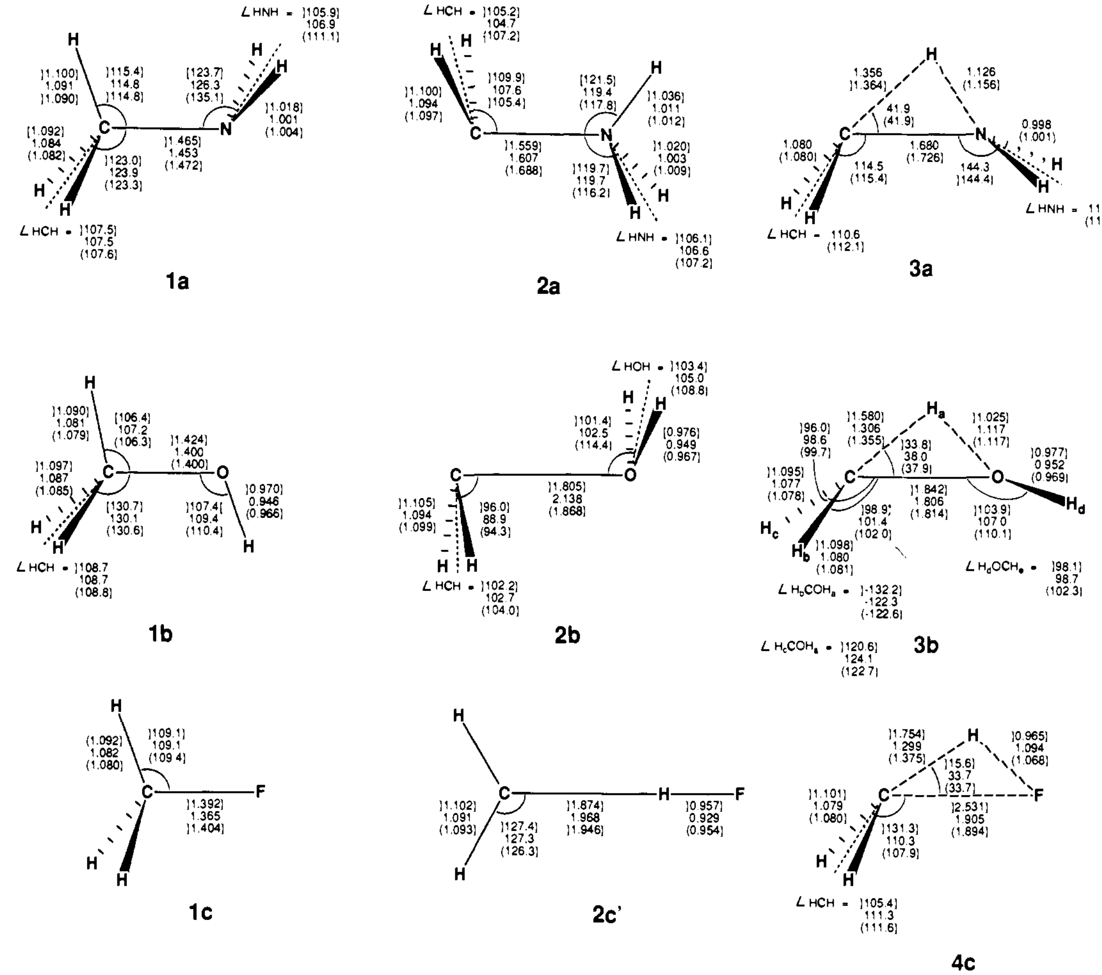

Figure 1a. Optimized structures for the first-row neutral ylides (2), their conventional isomers (1), and related systems.

Optimized structures were obtained initially with the 3-21G$^{(*)}$[13] and 6-31G*[14] basis sets by using gradient procedures.[11,12,15] The spin-unrestricted Hartree–Fock (UHF) formalism was used for all open-shell systems. Improved relative energies were obtained with the larger 6-31G** basis set[14] and with valence-electron correlation, incorporated with Møller–Plesset perturbation theory terminated at second (MP2) and third (MP3) order.[16] Vibrational frequencies were calculated at the 3-21G$^{(*)}$//3-21G$^{(*)}$ level in order to characterize stationary points on the surface as minima (representing equilibrium structures) or saddle points (representing transition structures) and to allow zero-point vibrational contributions to relative energies to be evaluated. The latter were scaled by 0.9 to account for the overestimation of vibrational frequencies at this level of theory.

Application of these procedures yielded relative energies at a uniform level corresponding to MP3/6-31G**//6-31G* values with zero-point correction, either calculated directly for first-row systems or estimated for second-row systems by assuming the additivity of basis set enhancement and electron correlation effects[17] (eq 1). Unless otherwise noted,

$$\Delta E(\text{MP3/6-31G**}) \approx \Delta E(\text{MP3/6-31G*}) + \Delta E(\text{HF/6-31G**}) - \Delta E(\text{HF/6-31G*}) \quad (1)$$

these are the values referred to in the text. Results at this level, which we refer to as our standard level of theory, are reported for the ylides (CH_2XH), the ylidions ($\dot{C}H_2X^+H$), their conventional isomers (CH_3X and $CH_3X^{•+}$, respectively), several pairs of fragmentation products, and the various transition structures for rearrangement and fragmentation.

For the ylides, ylidions, and their conventional isomers, additional calculations at higher levels of theory were performed. Geometries were reoptimized at the MP2/6-31G* level by using analytical gradients,[18] and improved relative energies were obtained, firstly at the MP2 level with the larger 6-311G(*df,p*)[19] and 6-31G(*df,p*)[19b] basis sets (for first- and second-row systems, respectively) and secondly at the MP4 level with full fourth-order Møller–Plesset theory (MP4SDTQ)[20] and the 6-31G(*d,p*) (synonymous with 6-31G**) basis set. For these systems, our best relative energies were estimated from the additivity relationships given in eq 2 and 3.

$$\Delta E(\text{MP4/6-311G}(df,p)) \approx \Delta E(\text{MP4/6-31G}(d,p)) + \Delta E(\text{MP2/6-311G}(df,p)) - \Delta E(\text{MP2/6-31G}(d,p)) \quad (2)$$

$$\Delta E(\text{MP4/6-31G}(df,p)) \approx \Delta E(\text{MP4/6-31G}(d,p)) + \Delta E(\text{MP2/6-31G}(df,p)) - \Delta E(\text{MP2/6-31G}(d,p)) \quad (3)$$

In the open-shell systems, calculated expectation values of S^2 (which should be 0.75 for a pure doublet) are between 0.753 and 0.765 for equilibrium species (including fragmentation products), between 0.769 and 0.822 for the transition structures for 1,2-hydrogen rearrangement, and between 0.782 and 1.016 for the transition structures for fragmen-

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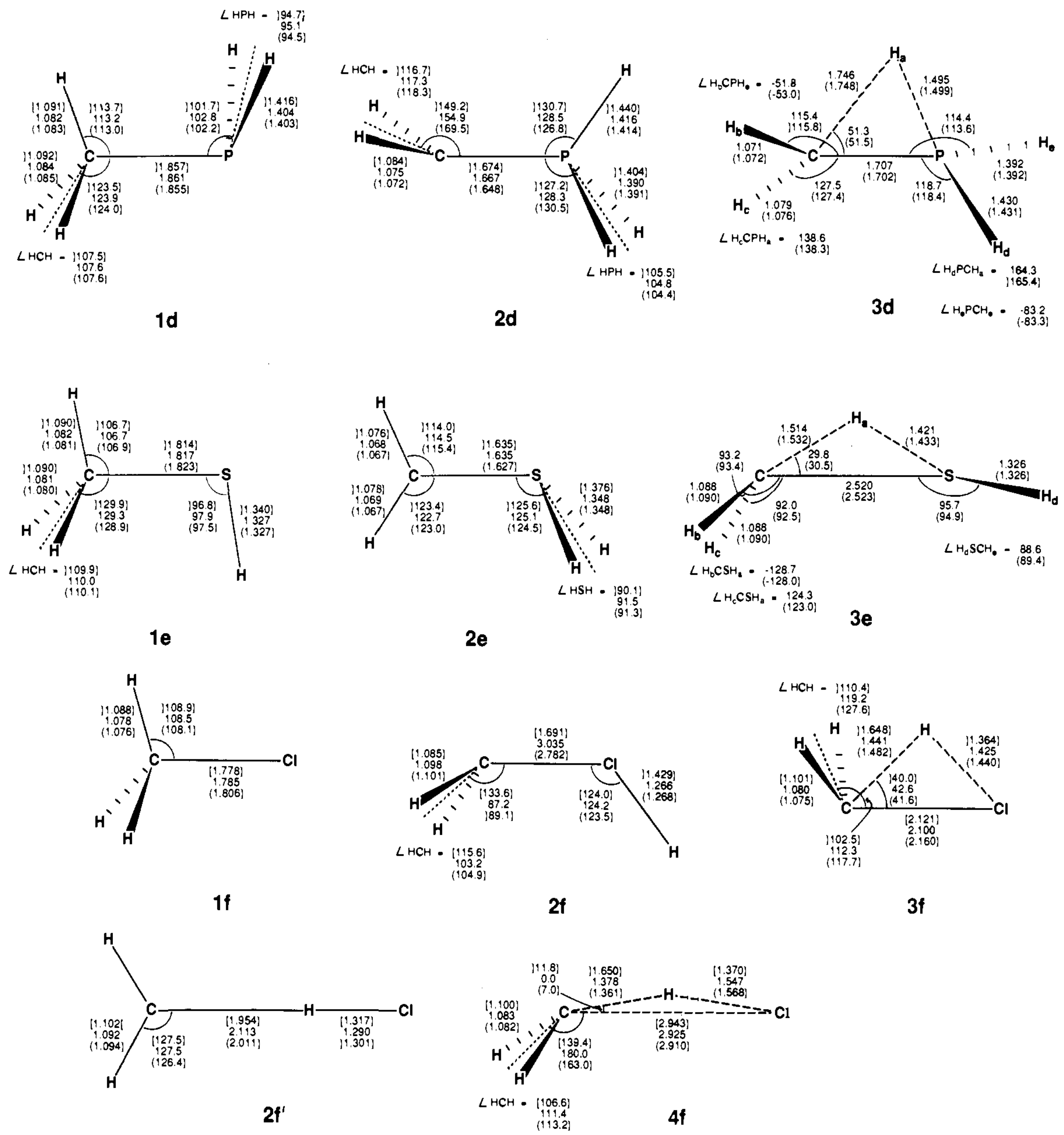

Figure 1b. Optimized structures for the second-row neutral ylides (**2**), their conventional isomers (**1**), and related systems.

tation. These values suggest[21] that relative energies for the equilibrium structures are probably not significantly affected by spin contamination in the UHF wave function but that the barriers for rearrangement and fragmentation may be overestimated at our highest levels.

Optimized HF/6-31G* structures are displayed for the ylides and related systems in Figure 1 and for the ylidions and related systems in Figure 3;[22] HF/3-21G$^{(*)}$ values are given in parentheses and MP2/6-31G* values (where available) in square brackets. Bond lengths are given in angstroms and angles in degrees. Total energies for our standard calculations are contained in the supplementary material, experimental heats of formation[23] corrected to 0 K[24] are presented in Table I, and relative energies are in Tables II and III. Schematic energy profiles (based on the results in Tables II and III) are displayed in Figures 2 and 4 for the ylides and ylidions, respectively. For the higher-level calculations, total and relative energies are presented in Tables IV and V, re-

Table I. Experimental Heats of Formation ($\Delta H_f{}^\circ{}_0$, kJ mol^{-1})^a for First- and Second-Row Systems

species	$\Delta H_f{}^\circ{}_0$	species	$\Delta H_f{}^\circ{}_0$
$CH_3NH_2{}^{\bullet+}$	857^b	$\dot{C}H_2N^+H_3$	$972^{b,c}$
$CH_2NH_2{}^+$	757^b	NH_3	-39
$\dot{N}H_2$	193^d	$CH_3OH^{\bullet+}$	856
$\dot{C}H_2O^+H_2$	$825^{b,e}$	CH_2OH^+	720
OH_2	-239	$\dot{O}H$	39
$CH_3F^{\bullet+}$	981^b	$\dot{C}H_2F^+H$	$913^{b,c}$
CH_2F^+	842^b	FH	-271
$F^\bullet$	77	$CH_3SH^{\bullet+}$	899
$\dot{C}H_2S^+H_2$	$925^{b,c}$	CH_2SH^+	870^f
SH_2	-18	$\dot{S}H$	142
$CH_3Cl^{\bullet+}$	1014	$\dot{C}H_2Cl^+H$	$1034^{b,c}$
CH_2Cl^+	$966^{b,g}$	ClH	-92
$Cl^\bullet$	120	$CH_3{}^+$	1095
$CH_2{}^{\bullet+}$	1398	$H^\bullet$	216

[a] From ref 23a unless otherwise noted. [b] $\Delta H_f{}^\circ{}_{298}$ value corrected to 0 K by using standard formulas from ref 24 and calculated vibrational frequencies. [c] $\Delta H_f{}^\circ{}_{298}$ value from ref 56b. [d] From ref 23b. [e] $\Delta H_f{}^\circ{}_{298}$ value from ref 3b. [f] From ref 58. [g] $\Delta H_f{}^\circ{}_{298}$ value from ref 23c.

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Table II. Calculated[a] and Experimental[b] Relative Energies (kJ mol^{-1}) for First-Row Systems

		HF/ 3-21G	HF/ 6-31G*	HF/ 6-31G**	MP2/ 6-31G**	MP3/ 6-31G**	MP3/ 6-31G**[c]	exptl
CH_3NH_2	**1a**	0	0	0	0	0	0	
CH_2NH_3	**2a**	278	308	303	310	308	304	
TS(**2a** → **1a**)	**3a**	378	420	403	376	383	366	
$CH_2NH_2^\bullet + H^\bullet$		321	328	330	408	413	377	
$CH_2 + NH_3$		414	402	394	472	452	418	
CH_3OH	**1b**	0	0	0	0	0	0	
CH_2OH_2	**2b**	336	364	351	397	384	372	
TS(**2b** → **1b**)	**3b**	394	428	411	375	386	367	
$CH_2OH^\bullet + H^\bullet$		336	337	340	419	424	387	
$CH_2 + OH_2$		421	400	385	459	439	403	
CH_3F	**1c**	0	0	0	0	0	0	
H_2CHF	**2c'**	391	372	354	417	400	376	
TS(**2c'** → **1c**)	4c	405	427	413	392	400	377	
$CH_2 + FH$		446	418	432	467	448	412	
$CH_3NH_2^{\bullet+}$	**5a**	0	0	0	0	0	0	0
$\dot{C}H_2N^+H_3$	**6a**	−3	4	−1	−19	−12	−8	115
TS(**6a** → **5a**)	**7a**	246	232	218	165	178	168	
TS(**5a** → $CH_2NH_2^+ + H^\bullet$)	**8a**	167	160	161	136	154	140	
TS(**6a** → $CH_2NH_2^+ + H^\bullet$)	**9a**	212	208	211	195	209	194	
$CH_2NH_2^+ + H^\bullet$		150	133	136	108	131	113	116
$CH_3^+ + \dot{N}H_2$		424	378	377	457	442	412	431
$CH_2^{\bullet+} + NH_3$		516	477	469	520	520	491	502
$CH_3OH^{\bullet+}$	**5b**	0	0	0	0	0	0	0
$\dot{C}H_2O^+H_2$	**6b**	−39	−18	−34	−68	−51	−50	−31
TS(**6b** → **5b**)	**7b**	222	190	175	94	118	108	
TS(**5b** → $CH_2OH^+ + H^\bullet$)	**8b**	159	108	107	50	81	68	
TS(**6b** → $CH_2OH^+ + H^\bullet$)	**9b**	225	201	201	141	167	151	
$CH_2OH^+ + H^\bullet$		148	85	87	45	80	61	80
$CH_3^+ + \dot{O}H$		229	194	194	277	265	243	278
$CH_2^{\bullet+} + OH_2$		350	289	274	303	313	285	303
$CH_3F^{\bullet+}$ ($^2A''$)	**5c**	0	0	0	0	0	0	0
$CH_3F^{\bullet+}$ ($^2A'$)	**5c'**	0	0	0	6	6	7	
$\dot{C}H_2F^+H$	**6c**	−22	−36	−54	−33	−46	−49	−68
TS(**6c** → **5c**)	**7c**	193	142	130	94	90	79	
TS(**6c** → $CH_2F^+ + H^\bullet$)	**9c**	231	190	191	162	158	142	
$CH_2F^+ + H^\bullet$		139	41	45	64	66	47	77
$CH_3^+ + F^\bullet$		60	31	31	187	139	130	191
$CH_2^{\bullet+} + FH$		182	101	81	161	137	113	146

[a] Based on the total energies in the supplementary material. [b] Based on the $\Delta H_f{}^\circ{}_0$ values in Table I. [c] With zero-point vibrational energy correction (see text).

spectively, and the highest level results incorporated, where appropriate, in Figures 2 and 4.

Results and Discussion

1. Ylides and Related Systems. A number of previous studies on the simple ylides have used assumed or partially optimized geometries to calculate a wide range of properties.[25] More recently, various aspects of ylide chemistry have also been investigated in several comprehensive studies using complete geometry optimizations and higher levels of theory.[4,26-30]

In one of these recent studies, Mitchell et al.[27a] investigated the structures and energies of CH_2PH_3 and CH_2SH_2 with the 4-31G* basis set and carried out a detailed perturbational molecular orbital (PMO) analysis. Eades et al.[29a] have also reported high-level calculations for CH_2NH_3, CH_2OH_2, CH_2PH_3, and CH_2SH_2. They performed full geometry optimizations with double-ζ basis sets supplemented by polarization functions on heavy atoms and diffuse *s* and *p* functions on carbon. Energies relative to the conventional isomers were reported at this level (DZP + diffuse functions) and refined estimates obtained[29b] through the use of the generalized valence bond and POL-CI approaches. In another recent paper,[30a] the first-row prototype ylides, CH_2XH (X = NH_2, OH, F), and their related systems were comprehensively studied at the MP4SDQ(T)/6-31G**//6-31G* level of theory.[30b] Despite these extensive previous studies, we have carried out an additional set of calculations in order that we can make a uniform comparison among the various species. Where appropriate, we will compare our present results with those of the earlier studies.

First-Row Ylides. The methyleneammonium ylide (CH_2NH_3, **2a**) has a C–N bond length of 1.607 Å at HF/6-31G*[31] (1.591 Å with DZP + diffuse functions[29a]), somewhat longer than the C–N bond length of 1.453 Å in methylamine[31] (**1a**, Figure 1a).

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Table III. Calculated[a] and Experimental[b] Relative Energies (kJ mol^{-1}) for Second-Row Systems

		HF/ 3-21G$^{(*)}$	HF/ 6-31G*	HF/ 6-31G**	MP2/ 6-31G*	MP3/ 6-31G*	MP3/ 6-31G**[c]	MP3/ 6-31G**[d]	exptl
CH_3PH_2	**1d**	0	0	0	0	0	0	0	
CH_2PH_3	**2d**	241	247	244	238	247	244	237	
TS(**2d** → **1d**)	**3d**	457	460	452	388	399	392	378	
$CH_2PH_2^\bullet + H^\bullet$		343	344	347	413	413	416	378	
$CH_2 + PH_3$		460	436	433	524	502	499	464	
CH_3SH	**1e**	0	0	0	0	0	0	0	
CH_2SH_2	**2e**	344	354	348	334	339	334	327	
TS(**2e** → **1e**)	**3e**	434	432	418	452	441	428	402	
$CH_2SH^\bullet + H^\bullet$		340	341	344	403	405	408	369	
$CH_2 + SH_2$		435	422	414	510	487	479	442	
CH_3Cl	**1f**	0	0	0	0	0	0	0	
CH_2ClH	**2f**	416	418	404	495	472	458	429	
H_2CHCl	**2f′**	386	392	376	466	446	430	403	
TS(**2f** → **1f**)	**3f**	557	550	527	527	525	502	477	
TS(**2f′** → **1f**)	**4f**	410	418	403	480	468	454	421	
$CH_2Cl^\bullet + H^\bullet$		353	351	354	416	417	420	381	
$CH_2 + ClH$		425	422	408	505	481	467	430	
$CH_3PH_2^{\bullet+}$	**5d**	0	0	0	0	0	0	0	
$\dot{C}H_2P^+H_3$	**6d**	20	22	21	54	49	48	40	
TS(**6d** → **5d**)	**7d**	268	265	256	253	249	240	220	
$CH_2PH_2^+ + H^\bullet$		291	294	297	257	266	269	240	
$CH_3^+ + \dot{P}H_2$		327	309	310	395	377	377	352	
$CH_2^{\bullet+} + PH_3$		495	483	482	588	571	570	535	
$CH_3SH^{\bullet+}$	**5e**	0	0	0	0	0	0	0	0
$\dot{C}H_2S^+H_2$	**6e**	84	86	81	103	100	95	86	26
TS(**6e** → **5e**)	**7e**	249	243	229	217	218	205	189	
TS(**5e** → $CH_2SH^+ + H^\bullet$)	**8e**	231	235	238	223	232	236	213	
TS(**6e** → $CH_2SH^+ + H^\bullet$)	**9e**	234	241	244	242	248	251	227	
$CH_2SH^+ + H^\bullet$		231	231	235	201	215	219	194	187
$CH_3^+ + \dot{S}H$		264	258	256	353	341	339	318	338
$CH_2^{\bullet+} + SH_2$		422	419	411	520	510	502	466	481
$CH_3Cl^{\bullet+}$ ($^2A'$)	**5f**	0	0	0	0	0	0	0	0
$CH_3Cl^{\bullet+}$ ($^2A''$)	**5f′**	0.0	0.1	0.1	0.1	0.1	0.1		
$\dot{C}H_2Cl^+H$	**6f**	71	68	56	66	67	55	46	20
TS(**6f** → **5f**)	**7f**	220	205	184	161	168	148	133	
TS(**6f** → $CH_2Cl^+ + H^\bullet$)	**9f**	222	218	218	190	201	201	182	
$CH_2Cl^+ + H^\bullet$		190	174	178	144	163	167	144	168
$CH_3^+ + Cl^\bullet$		91	94	92	182	173	171	163	201
$CH_2^{\bullet+} + ClH$		226	231	217	313	309	294	265	292

[a] Based on the total energies in the supplementary material. [b] Based on the $\Delta H_f°_0$ values in Table I. [c] Estimated by using the additivity approximation of eq 1. [d] MP3/6-31G** value with zero-point vibrational energy correction (see text).

At the MP2/6-31G* level, the length of the C–N bond in **2a** shortens (to 1.559 Å) while that in **1a** lengthens (to 1.465 Å[31]). The ylide **2a** lies in a well with moderate barriers to rearrangement (62 kJ mol^{-1}) and fragmentation (≥73 kJ mol^{-1}) processes (Table II, Figure 2a). At our standard level of theory, CH_2NH_3 is calculated to lie 304 kJ mol^{-1} above CH_3NH_2. Higher level calculations (Table V) reduce this energy difference to 277 kJ mol^{-1}, which coincides with the POL–CI value.[29b]

The methyleneoxonium ylide (**2b**, Figure 1a) is calculated to be a minimum on the HF/6-31G* potential energy surface and has a C_s structure with an anti arrangement of the hydrogen atoms. Eades et al.[29a] found that a C_1 structure was 5 kJ mol^{-1} more stable at the SCF level, but we have optimized this conformation at various levels of theory (including MP2/6-31G*) and have found that it returns to the C_s structure, **2b**. The ylide **2b** has a long C–O bond at HF/6-31G* (2.138 Å compared with the C–O bond of 1.400 Å in methanol),[31] and at our standard level of theory lies 372 kJ mol^{-1} above CH_3OH (Figure 2b). Harding et al.[4] found that the C–O bond length in **2b** is reduced significantly in the MP2/6-31G*-optimized structure to 1.805 Å (which is close to the DZP + diffuse functions value of 1.825 Å[29a]). Our higher level calculations based on MP2/6-31G* geometries (Table V) reveal, however, only a small consequential lowering in the relative energy of the ylide to 351 kJ mol^{-1}, which may be compared with the POL–CI value of 388 kJ mol^{-1}. Although CH_2OH_2 corresponds to a minimum on the HF/6-31G* surface, the barrier for rearrangement (via **3b**) disappears when single-point calculations that include electron correlation are carried out (Table II and ref 30a). At our highest level in Table V, we again find a barrier for rearrangement, but it is only 4 kJ mol^{-1}.

The methylenefluoronium ylide (CH_2FH) is found to be unstable at HF/6-31G* and MP2/6-31G*,[32] rearranging without a barrier to the much lower energy isomer fluoromethane. A second minimum on the surface was found by Pople et al.,[30a] corresponding to a hydrogen-bonded complex $H_2C\cdots HF$ with C_{2v} symmetry (**2c′**, Figure 1a). However, the barrier separating this structure from rearrangement (via **4c**) to fluoromethane (**1c**) is only 1 kJ mol^{-1} (Figure 2c). Single-point MP4 calculations on **4c**[30a] lower the "barrier" by 30 kJ mol^{-1}, with nearly half of this lowering coming from the triple substitutions in the correlation method (see column five, Table II of ref 30a). MP2 optimizations and higher level single-point calculations have little effect on the relative energy of **2c′** (Table V). At our highest level in Table V, we again find a barrier for rearrangement, but it is only 6 kJ mol^{-1}.

Second-Row Ylides. We have previously reported preliminary results for these systems.[5]

The methylenephosphonium ylide (**2d**) is found to have a C–P bond length of 1.667 Å at HF/6-31G* and 1.674 Å at MP2/6-31G* (Figure 1b), compared with values of 1.668 (DZP + diffuse functions)[29a] and 1.652 Å (4-31G*)[27a] from other theoretical studies, as well as compared with an experimental value of 1.661

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[31] Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*; Department of Chemistry: Carnegie-Mellon University, Pittsburgh, PA, 1983.

[32] An ylide-like structure with C_s symmetry was found at HF/6-31G* and MP2/6-31G* (with C–F bond lengths of 2.514 and 2.207 Å, respectively), but vibrational frequency calculations show that this corresponds to a saddle point on both surfaces.

Table IV. Higher Level Calculations for the Ylides and Ylidions: Total Energies[a] (hartrees)

		MP2/6-31G*[b]	MP2/6-31G**	MP2/6-311G(*df,p*)[c]	MP3/6-31G**	MP4/6-31G**
CH_3NH_2	**1a**	-95.514 44	-95.550 20	-95.618 14	-95.574 08	-95.585 76
CH_2NH_3	**2a**	-95.395 91[d]	-95.432 73	-95.510 36	-95.456 99	-95.469 56
NH_3		-56.357 38	-56.383 15	-56.425 51	-56.395 90	-56.401 38
CH_3OH	**1b**	-115.353 29	-115.381 91[e]	-115.471 68	-115.399 39[e]	-115.411 70
CH_2OH_2	**2b**	-115.203 29[d]	-115.235 60[f]	-115.330 07	-115.255 10[f]	-115.269 44
TS(**2b** → **1b**)	**3b**	-115.198 29	-115.232 37	-115.325 15	-115.249 43	-115.266 18
OH_2		-76.199 24[e]	-76.219 67[e]	-76.283 75	-76.225 89[e]	-76.231 14[e]
CH_3F	**1c**	-139.342 65	-139.360 06	-139.477 59	-139.373 40	-139.386 58
H_2CHF	**2c'**	-139.178 46[d]	-139.200 85	-139.321 20	-139.220 49	-139.231 03
TS(**2c'** → **1c**)	**4c**	-139.176 54	-139.199 12	-139.318 97	-139.217 84	-139.229 54
FH		-100.184 16	-100.194 46[e]	-100.289 16	-100.196 13[e]	-100.201 24[e]
CH_3PH_2	**1d**	-381.736 89	-381.763 70	-381.797 74	-381.795 53	-381.807 30
CH_2PH_3	**2d**	-381.646 96	-381.674 83	-381.712 92	-381.703 41	-381.716 56
PH_3		-342.562 26	-342.578 49	-342.597 22	-342.599 93	-342.606 02
CH_3SH	**1e**	-437.967 88	-437.987 71	-438.027 59	-438.016 81	-438.027 95
CH_2SH_2	**2e**	-437.841 71	-437.863 52	-437.907 41	-437.890 22	-437.903 64
SH_2		-398.798 70	-398.810 00	-398.834 27	-398.828 82	-398.833 79
CH_3Cl	**1f**	-499.369 08	-499.378 18	-499.422 86	-499.403 88	-499.413 71
CH_2ClH	**2f**	-499.188 19[d]	-499.201 20	-499.249 34	-499.225 24	-499.240 32
H_2CHCl	**2f′**	-499.191 17[d]	-499.207 43	-499.246 45	-499.240 29	-499.248 94
TS(**2f** → **1f**)	**3f**	-499.163 43	-499.182 58	-499.226 10	-499.210 67	-499.223 72
TS(**2f′** → **1f**)	**4f**	-499.188 55	-499.205 38	-499.244 99	-499.237 12	-499.246 40
ClH		-460.202 15[e]	-460.205 37	-460.234 34	-460.220 59	-460.223 90
CH_2 ($^1A_1$)		-38.974 01[e]	-38.987 17[e]	-39.014 23[g]	-39.006 29[e]	-39.011 96
$CH_3NH_2^{\bullet+}$	**5a**	-95.199 32	-95.230 78[h]	-95.290 83[h]	-95.258 63[h]	-95.269 48
$\dot{C}H_2N^+H_3$	**6a**	-95.205 40	-95.237 80[h]	-95.298 82[h]	-95.262 95[h]	-95.273 01
$CH_3OH^{\bullet+}$	**5b**	-114.961 60	-114.986 66	-115.070 73	-115.010 27	-115.023 07
$\dot{C}H_2O^+H_2$	**6b**	-114.981 55	-115.010 35	-115.095 85	-115.028 37	-115.039 67
$CH_3F^{\bullet+}$ ($^2A''$)	**5c**	-138.891 21[d]	-138.904 98[i]	-139.020 99	-138.913 10[i]	-138.931 03
$\dot{C}H_3F^+H$	**6c**	-138.899 00	-138.917 96[i]	-139.026 92	-138.930 63[i]	-138.943 67
TS(**6c** → **5c**)	**7c**	-138.852 04	-138.869 43	-138.980 99	-138.879 07	-138.896 93
$CH_3PH_2^{\bullet+}$	**5d**	-381.426 63	-381.450 78	-381.482 23	-381.480 64	-381.491 30
$\dot{C}H_2P^+H_3$	**6d**	-381.405 81	-381.430 48	-381.463 00	-381.462 88	-381.472 80
$CH_3SH^{\bullet+}$	**5e**	-437.637 27	-437.654 74	-437.690 41	-437.684 85	-437.696 02
$\dot{C}H_2S^+H_2$	**6e**	-437.597 99	-437.617 23	-437.654 44	-437.648 40	-437.658 75
$CH_3Cl^{\bullet+}$ ($^2A'$)	**5f**	-498.963 69	-498.971 41	-499.013 13	-498.999 74	-499.010 16
$\dot{C}H_2Cl^+H$	**6f**	-498.936 87	-498.949 08	-498.991 87	-498.977 18	-498.986 45

[a] Based on MP2/6-31G*-optimized geometries. [b] Full range of molecular orbitals used for correlation. [c] For second-row systems the underlying 6-31G(*df,p*) basis set was used. [d] MP2/6-31G*//MP2/6-31G* zero-point vibrational energies are 170.4 (CH_2NH_3), 127.2 (CH_2OH_2), 82.6 (H_2CHF), 83.0 (CH_2ClH), 74.1 (H_2CHCl), and 89.5 ($CH_3F^{\bullet+}$) kJ mol^{-1}. [e] From ref 31. [f] From ref 4. [g] For second-row energy comparisons, the MP2/6-31G(*df,p*) value is -38.996 91 hartrees. [h] From ref 39b. [i] From ref 41.

Å for the central C–P bond in CH_2PPh_3.[33] The C–P bond in **2d** is considerably shorter than the C–P single bond of methylphosphine (**1d**) (1.861 Å at HF/6-31G*,[14c] 1.857 Å at MP2/6-31G*). At our standard level of theory (Table III), CH_2PH_3 is found to lie 237 kJ mol^{-1} above methylphosphine (Figure 2d), a value which is reduced slightly by higher level calculations (Table V) to 220 kJ mol^{-1}. This may be compared with values of 220 (POL–CI)[29b] and 247 (4-31G*)[27a] kJ mol^{-1} from other studies. There is a large barrier (141 kJ mol^{-1}, Table III) for the exothermic rearrangement via **3d** to methylphosphine (**1d**), and with a binding energy with respect to $CH_2(^1A_1)$ + PH_3 of 227 kJ mol^{-1} (256 kJ mol^{-1} at our highest level, Table V), CH_2PH_3 is the most stable of the prototype ylides reported here.

The rearrangement of **2d** to **1d** proceeds via a transition structure (**3d**) with C_1 symmetry, in contrast to the C_s symmetry found for the transition structure in the nitrogen system. It has been noted previously[34] that under C_s symmetry the 1,2-hydrogen shift formally involves a repulsive four-electron interaction. The symmetry breaking that occurs in the phosphorus but not in the nitrogen case suggests a stronger interaction between the two participating pairs of electrons in the former situation.

The methylenesulfonium ylide (**2e**, Figure 1b) has a C–S bond (1.635 Å at HF/6-31G* and MP2/6-31G*, 1.646 Å with the DZP + diffuse functions basis set[29a]) which is significantly shorter than the C–S single bond in methanethiol (1.817 Å at HF/6-31G*,[31] 1.814 Å at MP2/6-31G*). Nevertheless, at our standard level of theory the ylide **2e** lies 327 kJ mol^{-1} above the conventional isomer (Figure 2e), compared with values of 347 (POL–CI)[29b] and 349 (4-31G*)[27a] kJ mol^{-1} from other studies. This energy difference is only slightly reduced (to 309 kJ mol^{-1}) by the higher level calculations (Table V). The barrier for CH_2CH_2 to rearrange to CH_3SH via **3e** is 75 kJ mol^{-1} (Table III), and the binding energy with respect to $CH_2(^1A_1)$ + SH_2 is 115 kJ mol^{-1}. This binding energy is increased by the higher level calculations (Table V) to 148 kJ mol^{-1}.

The methylenechloronium ylide (**2f**, Figure 1b) has a C_s structure with a syn arrangement of the hydrogen atoms, in contrast to the fluorine system where no ylide-like structure could be found. The ylide has a long C–Cl bond length of 3.035 Å at HF/6-31G*. At our standard level of theory (Table III), it is bound by just 1 kJ mol^{-1} with respect to $CH_2(^1A_1)$ + ClH and lies some 429 kJ mol^{-1} above CH_3Cl (Figure 2f). Nevertheless, the barrier for CH_2ClH to rearrange to CH_3Cl is 46 kJ mol^{-1}, and analytical frequency calculations show that the ylide corresponds to a true minimum on both the HF/3-21G$^{(*)}$ and HF/6-31G* potential surfaces. MP2/6-31G* reoptimization has a dramatic effect on the geometry of **2f**, reducing the C–Cl bond length to 1.691 Å,[35a] which is even shorter than the C–Cl bond in chloromethane (1.778 Å at MP2/6-31G*). However, this result

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(33) Bart, J. C. J. *J. Chem. Soc. B* **1969**, 350.

(34) (a) Raghavachari, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 5853. (b) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1971; p 131.

(35) (a) This is somewhat surprising since the MP2/3-21G$^{(*)}$-optimized structure for **2f** still has a long (2.413 Å) C–Cl bond. (b) To test the reliability of the MP2/6-31G* result we have optimized **2f** at MP2/6-31+G*, MP2/6-31G**, CISD/6-31G*, MP3/6-31G*, and MP4/6-31G* and have found the C–Cl length to be 1.730, 1.728, 2.610, 2.495, and 2.373 Å, respectively. (c) Use of the MP4- rather than the MP2-optimized geometry for CH_2ClH in the first term of eq 3 increases the binding energy of CH_2ClH to 22 kJ mol^{-1}.

Table V. Higher Level Calculations for the Ylides and Ylidions: Relative Energies[a] (kJ mol^{-1})

		MP2/6-31G*	MP2/6-31G**	MP2/6-311G(*df,p*)[b]	MP3/6-31G**	MP4/6-31G**	MP4/6-311G(*df,p*)[b,c]	MP4/6-311G(*df,p*)[d]
CH_3NH_2	**1a**	0	0	0	0	0	0	0
CH_2NH_3	**2a**	311	308	283	307	305	280	277[e]
$CH_2 + NH_3$		481	472	468	451	453	449	415
CH_3OH	**1b**	0	0	0	0	0	0	0
CH_2OH_2	**2b**	394	384	372	379	373	361	351[e]
TS(**2b** → **1b**)	**3b**	407	393	385	394	382	374	355
$CH_2 + OH_2$		473	460	456	439	443	439	403
CH_3F	**1c**	0	0	0	0	0	0	0
H_2CHF	**2c'**	431	418	411	401	408	401	378[e]
TS(**2c'** → **1c**)	**4c**	436	423	416	408	412	406	384
$CH_2 + FH$		484	468	457	449	455	444	408
CH_3PH_2	**1d**	0	0	0	0	0	0	0
CH_2PH_3	**2d**	236	233	223	242	238	228	220
$CH_2 + PH_3$		527	520	535	497	497	512	476
CH_3SH	**1e**	0	0	0	0	0	0	0
CH_2SH_2	**2e**	331	326	316	332	326	316	309
$CH_2 + SH_2$		512	500	516	477	478	494	457
CH_3Cl	**1f**	0	0	0	0	0	0	0
CH_2ClH	**2f**	475	465	456	469	455	446	427[e]
H_2CHCl	**2f'**	467	448	463	429	433	447	421[e]
TS(**2f** → **1f**)	**3f**	540	514	517	507	499	502	477
TS(**2f'** → **1f**)	**4f**	474	454	467	438	439	453	420
$CH_2 + ClH$		507	487	503	465	467	483	445
$CH_3NH_2^{\bullet+}$	**5a**	0	0	0	0	0	0	0
$\dot{C}H_2N^+H_3$	**6a**	−16	−18	−21	−11	−9	−12	−8
$CH_3OH^{\bullet+}$	**5b**	0	0	0	0	0	0	0
$\dot{C}H_2O^+H_2$	**6b**	−52	−62	−66	−48	−44	−47	−46
$CH_3F^{\bullet+}$	**5c**	0	0	0	0	0	0	0[e]
$\dot{C}H_2F^+H$	**6c**	−20	−34	−16	−46	−33	−15	−14
TS(**6c** → **5c**)	**7c**	103	93	105	89	90	101	95
$CH_3PH_2^{\bullet+}$	**5d**	0	0	0	0	0	0	0
$\dot{C}H_2P^+H_3$	**6d**	55	53	50	47	49	46	38
$CH_3SH^{\bullet+}$	**5e**	0	0	0	0	0	0	0
$\dot{C}H_2S^+H_2$	**6e**	103	98	94	96	98	94	85
$CH_3Cl^{\bullet+}$	**5f**	0	0	0	0	0	0	0
$\dot{C}H_2Cl^+H$	**6f**	70	59	56	59	62	59	51

[a] Based on the total energies in Table IV. [b] For second-row systems the underlying 6-31G(*df,p*) basis set was used. [c] Estimated by using the additivity approximations of eq 2 and 3 for first- and second-row systems, respectively. [d] MP4/6-311G(*df,p*) or MP4/6-31G(*df,p*) value with zero-point vibrational energy correction. [e] MP2/6-31G* ZPVE used (after scaling by 0.93, ref 51).

is not maintained at still higher levels of theory, which again yield long-bond structures for CH_2ClH.[35b] At our highest level of theory (MP4/6-31G*), the C–Cl length is 2.373 Å.

The corresponding changes in the energy of the ylide **2f** relative to **1f** are much less pronounced, amounting at our highest level in Table V to a lowering of only 2 kJ mol^{-1}. There is a somewhat greater effect on calculated binding energies, our best estimate in Table V yielding a binding energy with respect to $CH_2(^1A_1)$ + ClH of 18 kJ mol^{-1}.[35c] The barrier for rearrangement of the ylide to CH_3Cl is raised slightly to 50 kJ mol^{-1}.

A possible third minimum on the $[CH_3Cl]$ surface is the hydrogen-bonded complex $H_2C{\cdots}HCl$ with C_{2v} symmetry (**2f'**). At our standard level of theory (Table III), this lies 403 kJ mol^{-1} above chloromethane, and the barrier for rearrangement of **2f'** to **1f** (via **4f**) is 18 kJ mol^{-1}. This barrier disappears, however, at our highest level in Table V.

Comparisons across the Periodic Table. A number of general observations can be made concerning the properties of ylides as we move from left to right across the first or second row of the periodic table: (i) the C–X bond in the ylide CH_2XH tends to get longer relative to the C–X bond in CH_3X, (ii) the energy difference between the ylide and its conventional isomer increases, (iii) the barrier for rearrangement of the ylide to its conventional isomer decreases, and (iv) the binding energy of the ylide with respect to $CH_2(^1A_1)$ + XH decreases. Overall, these trends reflect a general decrease in the stability of the ylides in the order, group V > group VI > group VII (group 15 > group 16 > group 17).[61] This ordering is consistent with the differing ease with which the XH can share a lone pair of electrons (and so form the C–X bond in the ylide).

Comparisons between First- and Second-Row Ylides. The differences in structure and bonding between first- and second-row ylides have been discussed at some length previously,[25j,q,29,36,37] and we will only note a few of the more important features here.

For the first-row systems, the C–X bonds in the ylides (CH_2XH) are all longer than those in the conventional isomers. The CH_2X groups are markedly nonplanar, and the ylides tend to resemble donor–acceptor complexes. The ylides lie considerably higher in energy than their conventional isomers, and the barriers for rearrangement are small or nonexistent. The binding energies of the ylides with respect to $CH_2(^1A_1)$ + XH are also generally small.

For the second-row systems, the C–X bonds in the ylides are shorter (except possibly for CH_2ClH) than those in the conventional isomers. The bonds at carbon are more nearly coplanar than in the first-row ylides, supporting previous suggestions that multiple bonding might be involved (resulting from p_π–d_π back-bonding).[38] The ylides still lie much higher in energy than their conventional isomers, but on the whole the energy difference is less than in the first row. The barriers for rearrangement of the second-row ylides are larger than in the first row, and their binding energies also tend to be greater.

We may conclude from these comparisons that our results support the established notion that the second-row ylides are overall more stable than their first-row counterparts.

2. Ylidions and Related Systems. We have previously reported preliminary results from our theoretical studies on the first-row ylidions $\dot{C}H_2N^+H_3$,[2b,39] $\dot{C}H_2O^+H_2$,[2,40] and $\dot{C}H_2F^+H$[41] and on

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(36) Johnson, A. W. *Ylid Chemistry*; Academic: New York, 1966.

(37) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(38) Supporting evidence comes from comparisons of gross *d*-orbital populations and bond orders for the first- and second-row ylides. See also ref 25a, 25o, and 37.

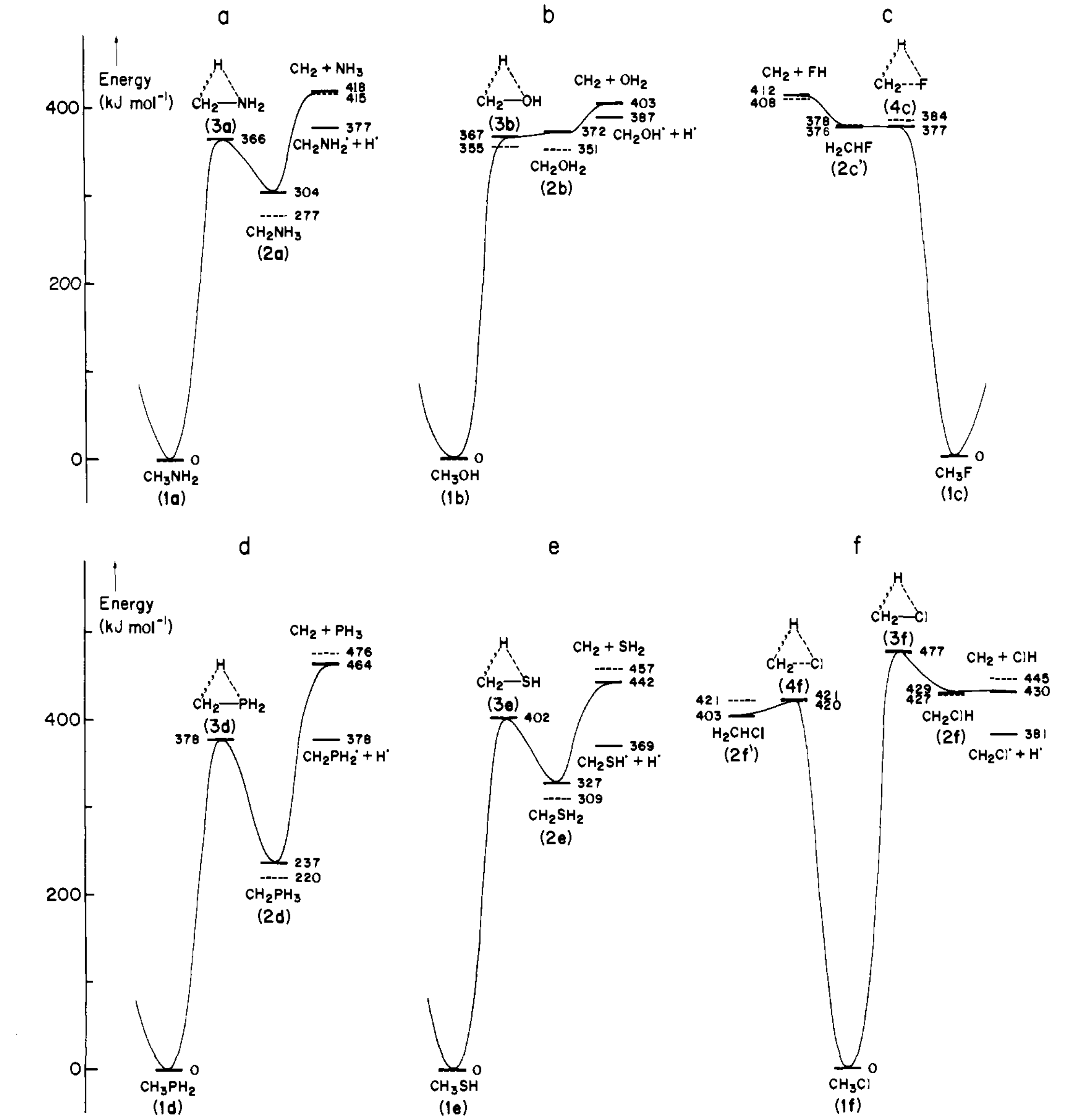

Figure 2. Schematic energy profiles for rearrangement and fragmentation processes of the neutral ylides based on the highest level results in Table II or III (—) and Table V (- - -).

related systems. Some of these systems have also been studied at lower levels of ab initio theory[7a,42] or with semiempirical methods.[42b,d,43] For the second-row systems, the only ab initio calculations published previously are an earlier study of the $\dot{C}H_2S^+H_2$ ylidion and related systems[44] and brief reports[5,6a,7a] of some of our results from this current study. In addition, there have been two semiempirical studies on the $\dot{C}H_2P^+H_3$ ylidion.[25s,45]

First-Row Ylidions. The methyleneammonium ylidion (**6a**, Figure 3a) is found to have a C–N bond length of 1.470 Å at both HF/6-31G*[2b,39a] and MP2/6-31G*,[39b] which is slightly longer than the C–N bond length in $CH_3NH_2^{\cdot+}$ (**5a**) (1.458 Å at HF/6-31G*, 1.431 Å at MP2/6-31G*). At our standard level of theory (Table II), the ylidion **6a** is predicted to lie 8 kJ mol^{-1} lower in energy than the methylamine radical cation (Figure 4a) and to have substantial barriers for rearrangement (176 kJ mol^{-1}) and fragmentation (202 kJ mol^{-1}) processes. The lowest energy decomposition pathway for $\dot{C}H_2N^+H_3$ has a barrier of 176 kJ mol^{-1} and involves hydrogen migration (via **7a**) followed by loss of a hydrogen radical to give $CH_2NH_2^+$ + H˙. The highest level calculations on **5a** and **6a** (Table V) produce no change in the value obtained for the relative energy of the ylidion.

The methyleneoxonium ylidion (**6b**, Figure 3a) has a C–O bond length (1.459 Å at HF/6-31G*,[2a] 1.468 Å at MP2/6-31G*) which is only slightly different from that in the methanol radical cation **5b** (1.474 Å at HF/6-31G*, 1.383 Å at MP2/6-31G*) but which is considerably shorter than the C–O bond in neutral CH_2OH_2. At our standard level of theory (Table II), the ylidion **6b** is calculated to lie 50 kJ mol^{-1} below the methanol radical cation (Figure 4b). The barrier for rearrangement of $\dot{C}H_2O^+H_2$ to

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(39) (a) Bouma, W. J.; Dawes, J. M.; Radom, L. *Org. Mass Spectrom.* **1983**, *18*, 12. (b) Yates, B. F.; Nobes, R. H.; Radom, L. *Chem. Phys. Lett.* **1985**, *116*, 474.

(40) (a) Nobes, R. H.; Radom, L. *Org. Mass Spectrom.* **1982**, *17*, 340. (b) Bouma, W. J.; MacLeod, J. K.; Nobes, R. H.; Radom, L. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 235.

(41) Bouma, W. J.; Yates, B. F.; Radom, L. *Chem. Phys. Lett.* **1982**, *92*, 620.

(42) (a) Lathan, W. A.; Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *11*, 175. (b) Bonazzola, L.; Iacona, C.; Michaut, J. P.; Roncin, J. *J. Chem. Phys.* **1980**, *73*, 4175. (c) Bonazzola, L.; Lerary, N.; Ellinger, Y. *Chem. Phys.* **1982**, *73*, 145. (d) Halim, H.; Ciommer, B.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 528. (e) Frenking, G.; Koch, W. *THEOCHEM* **1984**, *110*, 49.

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(44) Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 2774.

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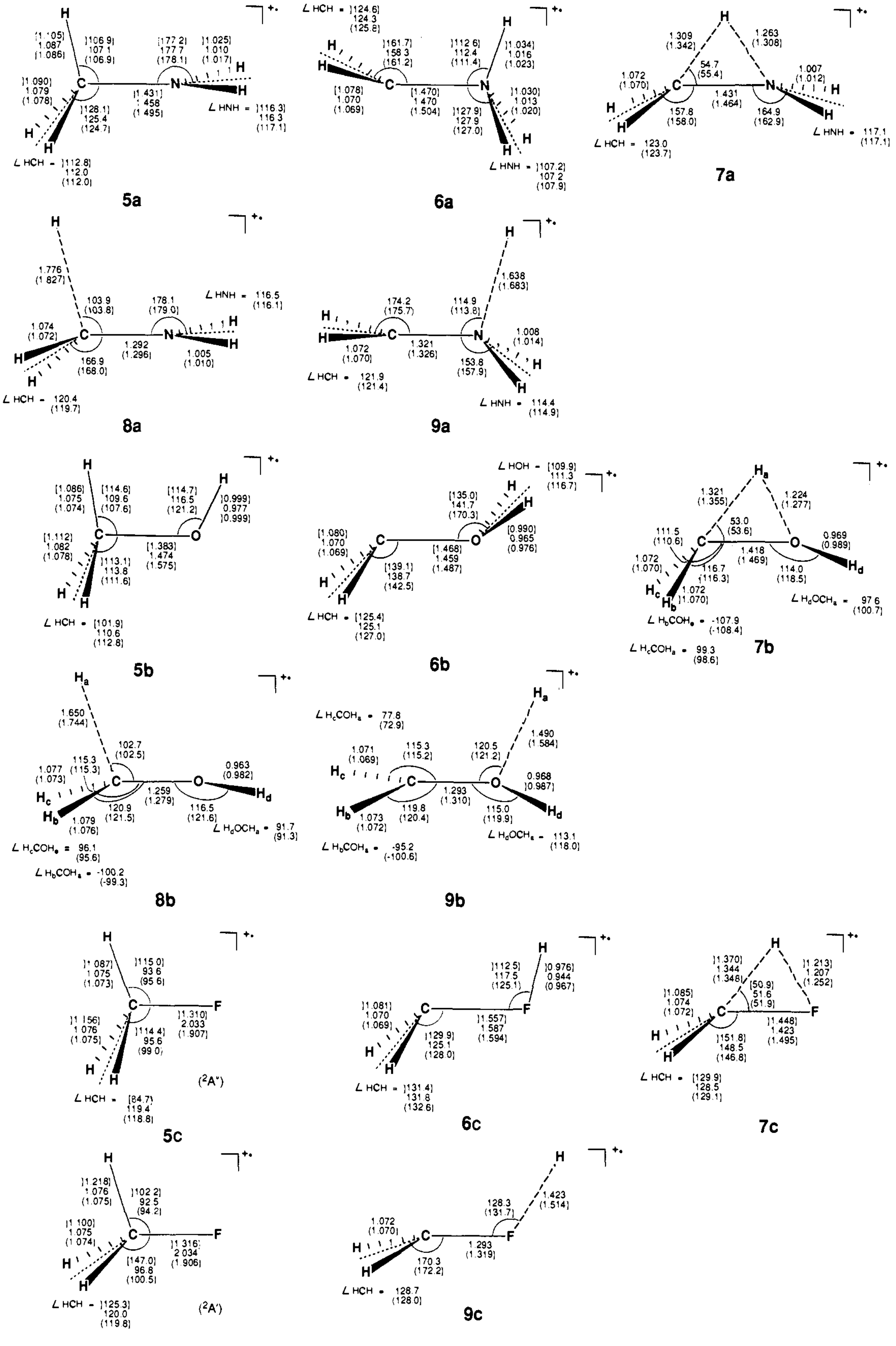

Figure 3a. Optimized structures for the first-row ylidions (6), their conventional isomers (5), and related systems.

$CH_3OH^{•+}$ is 158 kJ mol^{-1}, and the lowest energy decomposition pathway for the ylidion is via this 1,2-hydrogen shift (i.e., via **7b**) followed by hydrogen radical loss. Higher level calculations (Table V) slightly reduce the energy difference between **5b** and **6b** to 46 kJ mol^{-1}.

The methylenefluoronium ylidion (**6c**, Figure 3a) has a moderately long C–F bond at the HF/6-31G* level (1.587 Å[41]) compared with that in neutral fluoromethane (1.365 Å), and there is a slight shortening (to 1.557 Å) upon reoptimization at MP2/6-31G*. The conventional isomer, $CH_3F^{•+}$ (**5c**), also has

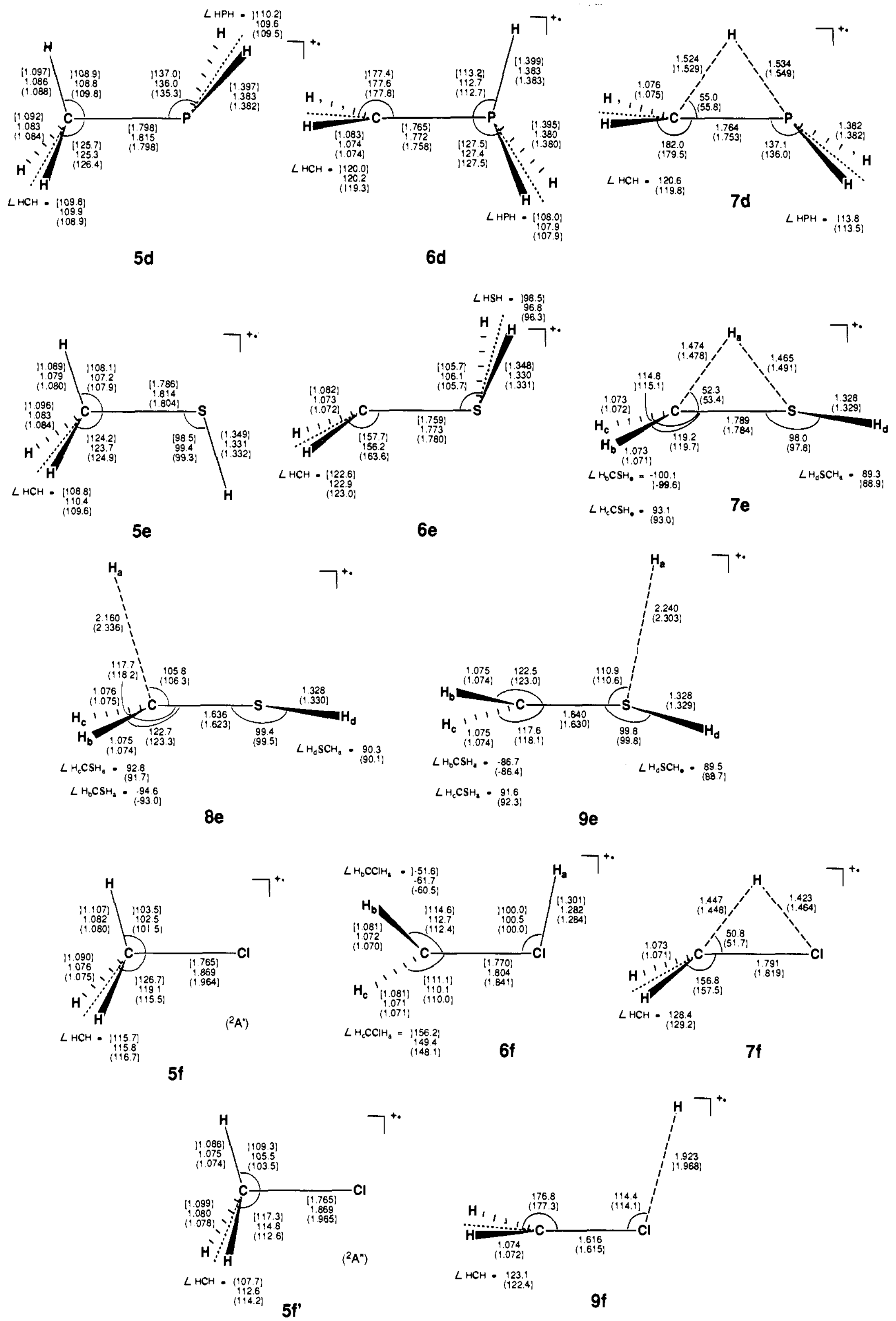

Figure 3b. Optimized structures for the second-row ylidions (6), their conventional isomers (5), and related systems.

an unusually long C–F bond at the HF/6-31G* level (2.033 Å), but in this case there is a dramatic contraction to 1.310 Å when correlation is included.[46] Because of the large effect this has on the energy of **5c**, we have based our standard calculations (Table II) on the MP2/6-31G*-optimized structure for $CH_3F^{\bullet+}$. At this level, the ylidion **6c** is calculated to lie 49 kJ mol^{-1} lower in energy than **5c** (Figure 4c).[47] The barrier for rearrangement of the

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[46] We note in passing that reoptimization at MP3/6-31G* of the complete [$CH_3F^{\bullet+}$] surface, including the two transition structures **7c** and **9c**, leads to only minor further structural changes. See: Baker, J., unpublished results.

[47] A zero-point vibrational energy correction for this relative energy was not included in our earlier study[41] due to difficulties in calculating numerically the vibrational frequencies for **5c**. A detailed discussion of the theoretical problem has been presented by Colwell et al.[48] for the isoelectronic methoxy radical.

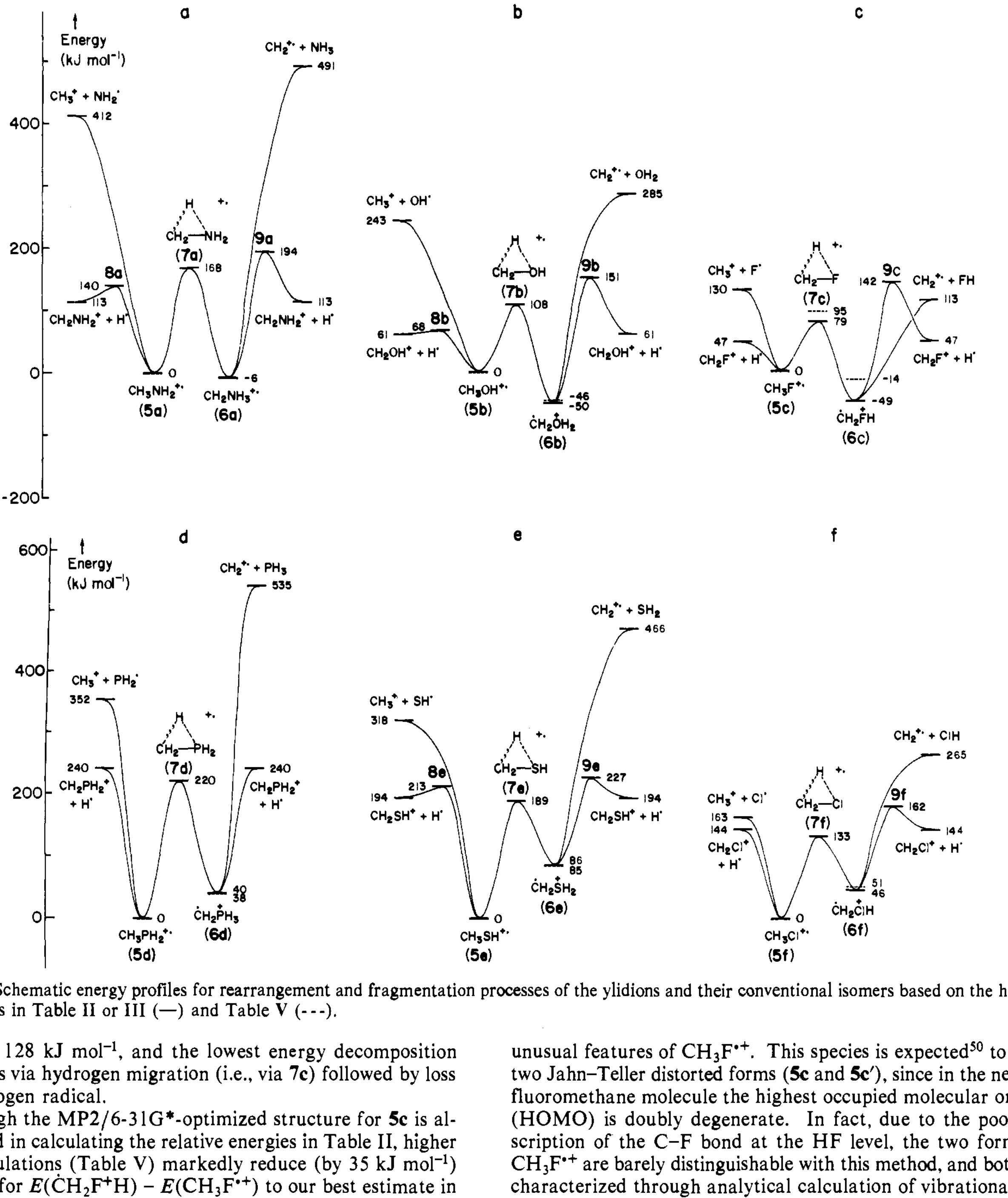

Figure 4. Schematic energy profiles for rearrangement and fragmentation processes of the ylidions and their conventional isomers based on the highest level results in Table II or III (—) and Table V (---).

ylidion is 128 kJ mol^{-1}, and the lowest energy decomposition pathway is via hydrogen migration (i.e., via **7c**) followed by loss of a hydrogen radical.

Although the MP2/6-31G*-optimized structure for **5c** is already used in calculating the relative energies in Table II, higher level calculations (Table V) markedly reduce (by 35 kJ mol^{-1}) the value for $E(\dot{C}H_2F^+H) - E(CH_3F^{\cdot+})$ to our best estimate in Table V of −14 kJ mol^{-1}. Approximately 18 kJ mol^{-1} of this change is due to the larger basis set, and 13 kJ mol^{-1} is due to the MP4 treatment of electron correlation, both effects favoring the conventional isomer $CH_3F^{\cdot+}$. Higher level calculations on the transition structure **7c** also lower the barrier for rearrangement of the ylidion to 109 kJ mol^{-1}. Thus, not only is inclusion of electron correlation important for obtaining good geometries for the $CH_3F^{\cdot+}$ system, it seems that large basis sets and extensive treatments of electron correlation are also important in obtaining good estimates of the relative energies involved. We cannot exclude the possibility that more sophisticated calculations will further change these relative energies.[49]

Although attention in this section is focused on the ylidions, it is appropriate at this juncture to point out some additional unusual features of $CH_3F^{\cdot+}$. This species is expected[50] to have two Jahn–Teller distorted forms (**5c** and **5c′**), since in the neutral fluoromethane molecule the highest occupied molecular orbital (HOMO) is doubly degenerate. In fact, due to the poor description of the C–F bond at the HF level, the two forms of $CH_3F^{\cdot+}$ are barely distinguishable with this method, and both are characterized through analytical calculation of vibrational frequencies as being minima on the HF/3-21G potential surface. With the inclusion of electron correlation, the C–F bond shortens, and the Jahn–Teller distortion is consequently much larger.

The poor geometries obtained at HF/3-21G for $CH_3F^{\cdot+}$ suggest that the vibrational frequency analyses at this level may be inappropriate. However, it turns out that after recalculating vibrational frequencies at MP2/6-31G* for the $^2A''$ form and scaling by an appropriate factor (0.93),[51] the calculated ZPVE is only 4 kJ mol^{-1} lower than the HF/3-21G value. These MP2/6-31G* calculations also confirm that the $^2A''$ state of $CH_3F^{\cdot+}$ corresponds to a minimum on the potential surface. At our highest level in Table V (without inclusion of zero-point correction), the $^2A'$ state (**5c′**) lies 8.7 kJ mol^{-1} higher than the $^2A''$ state (**5c**). By analogy with the methoxy radical,[48] this higher state would probably have

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(48) Colwell, S. M.; Amos, R. D.; Handy, N. C. *Chem. Phys. Lett.* **1984**, *109*, 525.

(49) Still higher level calculations give a value of −23 kJ mol^{-1} for the energy of **6c** relative to **5c**: Yates, B. F.; Radom, L., unpublished results.

(50) (a) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, A* **1937**, *161*, 220. (b) Moffitt, W.; Liehr, A. D. *Phys. Rev.* **1957**, *106*, 1195.

(51) (a) Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234. (b) DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

one imaginary frequency at MP2/6-31G* (i.e., it represents the transition structure for rearrangement between two equivalent $^2A''$ forms).

Second-Row Ylidions. The methylenephosphonium ylidion (**6d**) has a preferred staggered conformation (Figure 3b) and is nearly planar at carbon. The alternative eclipsed conformation lies higher in energy by just 0.1 kJ mol^{-1} and is confirmed by frequency calculations to be located at a saddle point on the surface. At the HF/6-31G* level, the C–P bond length of 1.772 Å in $\dot{C}H_2P^+H_3$ (**6d**) is shorter than the 1.815 Å in $CH_3PH_2^{\bullet+}$ (**5d**) and the 1.861 Å in neutral CH_3PH_2 (**1d**). These observations are confirmed with MP2/6-31G* reoptimization (where there is a slight shortening of each of these bond lengths). At our standard level of theory (Table III), $\dot{C}H_2P^+H_3$ is found to lie higher in energy than its conventional isomer (**5d**) by 40 kJ mol^{-1} (Figure 4d), which is nearly double the value obtained from MNDO calculations.[25g] The ylidion lies in a deep potential well with substantial barriers for rearrangement and fragmentation processes (180 and 200 kJ mol^{-1}, respectively). Decomposition of $\dot{C}H_2P^+H_3$ is predicted to occur most easily by loss of a hydrogen radical, either directly or via an initial isomerization (i.e., via **7d**). The higher level calculations on **5d** and **6d** (Table V) result in a slight lowering of the relative energy of the ylidion to 38 kJ mol^{-1}.

The methylenesulfonium ylidion is found to have two structures which are almost equivalent energetically. The preferred conformation is an anti (C_s) structure (**6e**, Figure 3b), but this lies just 0.1 kJ mol^{-1} lower in energy than the alternative C_s structure with the CH_2 group rotated by 90°. $\dot{C}H_2S^+H_2$ (**6e**) has a C–S bond length of 1.773 Å at HF/6-31G*, which is shorter than the C–S bond in either $CH_3SH^{\bullet+}$ (**5e**) (1.814 Å) or neutral methanethiol (1.817 Å). Reoptimization at the MP2/6-31G* level leads to a slight shortening of each of these bond lengths (to 1.759, 1.786, and 1.814 Å, respectively), but the general trend remains the same. At our standard level of theory (Table III), the ylidion **6e** is predicted to lie 86 kJ mol^{-1} higher in energy than its conventional isomer (Figure 4e); however, the barriers for rearrangement and fragmentation processes are still significant at 103 and 127 kJ mol^{-1}, respectively. The lowest decomposition pathway for $\dot{C}H_2S^+H_2$ involves hydrogen migration (via **7e**) followed by loss of a hydrogen radical, although this route is only slightly preferable to direct loss of $H^\bullet$. Higher level calculations on **5e** and **6e** (Table V) have a negligible effect on the relative energy of the ylidion, lowering it to 85 kJ mol^{-1}.

The methylenechloronium ylidion (**6f**, Figure 3b) is found to have a C_1 structure with the CH_2 group twisted significantly away from C_s symmetry. This contrasts with the orthogonal C_s structure predicted for $\dot{C}H_2F^+H$ (**6c**). Frequency calculations indicate that the $\dot{C}H_2Cl^+H$ structure with C_s symmetry lies at a saddle point on the potential energy surface, although at our highest level in Table V it is only 2.1 kJ mol^{-1} higher in energy than **6f**. $\dot{C}H_2Cl^+H$ has a C–Cl bond length of 1.804 Å at HF/6-31G*, which is shorter than the C–Cl bond in $CH_3Cl^{\bullet+}$ (**5f**) (1.869 Å) but slightly longer than that in neutral chloromethane (1.785 Å). MP2/6-31G* optimizations shorten each of these bonds (to 1.770, 1.765, and 1.778 Å, respectively), but the effect is largest for $CH_3Cl^{\bullet+}$, and the ordering of the C–Cl bond lengths is reversed. The ylidion is predicted (Table III) to lie 46 kJ mol^{-1} higher in energy than **5f** (Figure 4f), and the barriers for rearrangement and fragmentation processes are 87 and 98 kJ mol^{-1}, respectively. Higher level calculations (Table V) slightly increase the energy difference between **5f** and **6f** to 51 kJ mol^{-1}.

The chloromethane radical cation ($CH_3Cl^{\bullet+}$) is apparently better described at the HF level than $CH_3F^{\bullet+}$, with MP2 optimizations altering the structure much less than in the fluorine case. Like the fluoromethane radical cation, $CH_3Cl^{\bullet+}$ is expected to have two Jahn–Teller distorted forms (**5f** and **5f′**). Indeed, a small distortion is observed at the HF level, but even when the structures are reoptimized at MP2/6-31G*, the distortion in less than in $CH_3F^{\bullet+}$. The observation that the distortion is smaller for X = Cl than for X = F has previously beeen rationalized[52] in terms of the degree of localization of the HOMO ("lone pair on X") in the neutral: the greater the localization, the smaller the Jahn–Teller distortion. In contrast to $CH_3F^{\bullet+}$, the lowest energy structure of $CH_3Cl^{\bullet+}$ corresponds to the $^2A'$ state (**5f**), although it lies only 0.3 kJ mol^{-1} below the $^2A''$ state (**5f′**) at our highest level in Table V (without inclusion of zero-point correction). The higher lying $^2A''$ state has one imaginary frequency at the HF/3-21G$^{(*)}$ level.[53]

We note in passing that the lower energy structure ($^2A''$) of $CH_3F^{\bullet+}$ resembles a complex of H_2 with $HCF^{\bullet+}$ in that the two symmetry-equivalent C–H bonds are quite long (1.156 Å) and the angle between them is just 84.7° (at MP2/6-31G*). When viewed in this manner, the geometry of $CH_3F^{\bullet+}$ is analogous to the preferred C_{2v} structure of $CH_4^{\bullet+}$.[54] This resemblance does not carry over, however, to the MP2-optimized structures of $CH_3NH_2^{\bullet+}$, $CH_3OH^{\bullet+}$, $CH_3PH_2^{\bullet+}$, $CH_3SH^{\bullet+}$, and $CH_3Cl^{\bullet+}$, where the angles between the symmetry-equivalent C–H bonds are 112.8°, 101.9°, 109.8°, 108.8°, and 107.7°, respectively. Indeed, these species resemble the less stable C_{3v} structure of $CH_4^{\bullet+}$. It would seem that for X = NH_2, OH, PH_2, SH, and Cl, the positive charge in $CH_3X^{\bullet+}$ tends to be localized on the substituent X, reversing the relative stabilities that exist in $CH_4^{\bullet+}$ of the C_{2v} and C_{3v} forms. For the more electronegative X = F, however, significant electron depletion occurs from the CH_3 moiety.

Comparisons across the Periodic Table. From left to right across the first and second rows of the periodic table the following trends in the ylidions may be noted: (i) the C–X bond in the ylidion ($\dot{C}H_2X^+H$) gets longer relative to the C–X bond in $CH_3X^{\bullet+}$, (ii) the degree of nonplanarity at carbon in the ylidion increases, (iii) the barrier for rearrangement of the ylidion to its conventional isomer decreases, (iv) the barrier for the lowest energy decomposition of the ylidion decreases, and (v) the binding energy of the ylidion with respect to $CH_2^{\bullet+}$ + XH dramatically decreases. These trends reflect a decrease in the overall stability of the ylidions in the order, group V > group VI > group VII (group 15 > group 16 > group 17).[61]

Comparisons between First- and Second-Row Ylidions. For the first-row systems, the C–X bonds in the ylidions ($\dot{C}H_2X^+H$) are all longer than those in the conventional isomers (provided MP2-optimized structures are used for the comparison). These ylidions are all fairly "bent" at carbon. They are lower in energy than their conventional isomers, and the barriers to rearrangement are quite large.

For the second-row systems, the C–X bonds in the ylidions tend to be shorter than those in the conventional isomers. These ylidions have a greater tendency to be planar at carbon than their first-row counterparts. They lie higher in energy than their conventional isomers, and the barriers to rearrangement tend to be lower than in the first row.

These comparisons can lead to two different conclusions. On the one hand, the relative bond lengths suggest that the ylidions are more tightly bound in the second row than in the first row. Thus, whereas $\dot{C}H_2P^+H_3$ appears to have quite a strong C–P bond, the $\dot{C}H_2F^+H$ ylidion might be regarded as more of a complex between $CH_2^{\bullet+}$ and FH.[55] On the other hand, comparison of the energy data suggests that the first-row ylidions are relatively more stable than their second-row counterparts.

3. Comparisons between Ylides and Ylidions. From the comparisons already presented, it is apparent that some of the trends in the ylides and ylidions are very similar. For example, the trends in relative bond lengths, rearrangement barriers, and binding energies observed for the ylidions parallel those observed for the ylides. However, quantitatively the neutral and charged species behave quite distinctly.

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(52) Glidewell, C. *Inorg. Chim. Acta* **1982**, *64*, L59.

(53) Frequencies calculated by using a numerical gradient procedure are, however, all real, a deficiency which has been previously noted for the methoxy radical.[48]

(54) See: Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21 and references therein.

(55) This stability ordering based on relative bond lengths may be rationalized in terms of the donor ability of XH.[42e]

The ylides CH_2XH have a long C–X bonds in the first-row systems and in extreme cases resemble very weak complexes of methylene and XH. All the ylides lie much higher in energy than their conventional isomers (the smallest energy difference is still 220 kJ mol^{-1}). The binding energies of the ylides with respect to $CH_2(^1A_1)$ + XH are modest (the largest is 256 kJ mol^{-1}), and the lowest energy decomposition barriers are quite small.

The ylidions ($\dot{C}H_2X^+H$) from the first row have shorter C–X bonds than their corresponding ylides, while those from the second row have longer C–X bonds. All the ylidions lie fairly close in energy to their conventional isomers (the largest energy difference being 85 kJ mol^{-1}), and they tend to have large barriers to rearrangement. The binding energies of the ylidions with respect to $CH_2^{\bullet+}$ + XH are quite substantial (the largest is 499 kJ mol^{-1}), and the lowest energy decomposition barriers are fairly large.

4. Effects of the Higher Level Calculations. Differences between the HF/6-31G*- and MP2/6-31G*-optimized geometries are quite large in a number of the ylides CH_2XH (average change in C–X length = 0.340 Å, maximum = 1.344 Å) but are much less pronounced in the conventional isomers CH_3X (average change in C–X length = 0.013 Å, maximum = 0.027 Å). For the charged species, on the other hand, the effect of electron correlation on the optimized geometries is much larger in the conventional isomers $CH_3X^{\bullet+}$ (average change in C–X length = 0.165 Å, maximum = 0.723 Å) than in the ylidions $\dot{C}H_2X^+H$ (average change in C–X length = 0.016 Å, maximum = 0.034 Å). The effect of electron correlation on geometry for both CH_2XH and $CH_3X^{\bullet+}$ systems appears to be most important for electronegative X.

Single-point calculations on these MP2-optimized structures result in relative energies of the ylides at the MP4/6-311G(*df,p*) or MP4/6-31G(*df,p*) levels (Table V) which are generally 10–30 kJ mol^{-1} lower than the values in Tables II and III. This effect is largely due, however, to the larger basis set and more complete incorporation of electron correlation and only to a minor extent to the use of the improved MP2 geometries. For the ylidions, the effect on relative energies, with the exception of the fluorine system, is rather smaller.

5. Comparisons with Experiment. Experimental confirmation of the stability of the ylidions in the gas phase has come from several CAD mass spectrometric studies.[3,42d,56] The CAD mass spectra of all the ylidions ($\dot{C}H_2X^+H$) show intense peaks corresponding to $CH_2^{\bullet+}$ and $XH^{\bullet+}$ fragments and show little or no sign of CH_3^+. There is greater evidence of formation of CH_3^+ for the second-row ylidions, consistent with the theoretical finding that the fragmentation to $CH_3^+ + X^\bullet$ compared with $CH_2^{\bullet+}$ + XH is more favorable in the second-row than in the first-row systems (Figure 4). Furthermore, measurement of the kinetic energy release for loss of $H^\bullet$ from the ylidions[56b] confirms that this process tends to occur indirectly. Other experimental evidence for the existence of the ylidions has come from ion cyclotron resonance,[57] photoionization,[58] and electron paramagnetic resonance (EPR)[42b,59] studies.

Our best values for the energy differences $E(\dot{C}H_2X^+H) - E(CH_3X^{\bullet+})$ of −8, −46, −14, 85, and 51 kJ mol^{-1} for X = NH_2, OH, F, SH, and Cl, respectively (Table V), may be compared with experimental estimates of 115, −31, −68, 26, and 20 kJ mol^{-1}, respectively (Tables II and III). The agreement can at best be described as fair. The discrepancies are somewhat surprising since we have shown in preceding sections that, with the exception of the fluorine system, the theoretical energy differences do not change greatly as we move to increasingly sophisticated levels of theory. The disagreement is extreme in the case of the $CH_3NH_2^{\bullet+}/\dot{C}H_2N^+H_3$ pair, for which we have suggested[39b] that a reinterpretation of the experimental data may be in order.

Better agreement between theory and experiment is found for the various fragmentation products in Tables II and III, particularly for the nitrogen system. For the oxygen, fluorine, and chlorine systems, the theoretical relative energies of the fragments are consistently lower than the experimental values, suggesting that in these cases the absolute energy of the $CH_3X^{\bullet+}$ species may be too high. To some extent, this error is corrected by the more sophisticated calculations.

We have commented recently[5] on the relationship between theoretical results, such as those presented here, and neutralization–reionization mass spectrometry (NRMS) experiments.[60] The mechanism of NRMS suggests that the ylidions could be used as a starting point to investigate the stability of the less readily accessible ylides. Our calculations show that CH_2NH_3, CH_2PH_3, and CH_2SH_2 lie in moderately deep wells and suggest that they have sufficiently long lifetimes to be observable in an NRMS experiment. However, CH_2OH_2, CH_2ClH, and even the hydrogen-bonded species H_2CHF and H_2CHCl have rather small binding energies (52, 18, 30, and 24 kJ mol^{-1}, respectively), and the barriers for rearrangement (which for these systems were recalculated at our highest level) are only 4, 50, 6, and 0 kJ mol^{-1}, respectively. In addition, the large differences in equilibrium geometries of the charged and neutral species mean firstly that the vertically neutralized ylides will be formed with considerable excess energy, thus facilitating their rearrangement or fragmentation, and secondly that the likelihood of adiabatic neutralization is reduced. Although still higher level calculations may shorten the long bonds in some of these structures, our present experience with progressively more sophisticated calculations suggests that these species should, at best, lie in only shallow wells on their respective ground-state potential surfaces. On this basis, it seems likely that neutralization of $\dot{C}H_2O^+H_2$, $\dot{C}H_2F^+H$, and $\dot{C}H_2C^+H$ would result in products with fairly short lifetimes, and we are therefore unable to explain their detection in NRMS experiments.[60]

Conclusions

In this paper, we have presented a broad survey of the structures and stabilities of prototype ylides and ylidions. Our results confirm previous suggestions that the simple ylides CH_2XH are generally unstable species which often have little or no barrier to rearrangement or fragmentation. In contrast, the ylidions $\dot{C}H_2X^+H$ lie in moderately deep potential wells and are of comparable stability to their conventional isomers. For both ylides and ylidions, the stability decreases in progressing from group V (group 15)[61] to group VII (group 17)[61] of the periodic table. On moving from the first row to the second row, the stability (based on energy

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(61) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and AC nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

criteria) appears to increase for the neutral ylides but to decrease for the charged ylidions.

Our calculations also reveal the importance of including electron correlation in calculating the structural features of some of the systems considered here, particularly those involving the more electronegative elements. The effect is most noticeable in the CH$_2$XH and CH$_3$X$^{\bullet+}$ species. On the whole, MP2/6-31G* optimizations tend to shorten the C–X bonds (relative to HF/6-31G*) with the largest reductions being 1.344 Å in CH$_2$ClH and 0.723 Å in CH$_3$F$^{\bullet+}$. On the other hand, the effects on the relative energies of using large basis sets and of using MP4 instead of MP3 are much less dramatic. Our highest level calculations reveal some significant discrepancies between theoretical and experimental relative energies.

Acknowledgment. We are pleased to acknowledge continuing, stimulating interaction with Professors F. W. McLafferty and J. L. Holmes.

Registry No. 1a, 74-89-5; **1b**, 67-56-1; **1c**, 593-53-3; **1d**, 593-54-4; **1e**, 74-93-1; **1f**, 74-87-3; **2d**, 36429-11-5; **5a**, 34516-31-9; **5b**, 12538-91-9; **5c**, 59122-96-2; **5d**, 91391-14-9; **5e**, 53369-41-8; **5f**, 12538-71-5; **6a**, 21444-88-2; **6b**, 25765-84-8; **6c**, 84609-27-8; **6d**, 56898-66-9; **6e**, 81255-83-6; **6f**, 81255-84-7; HF, 7664-39-3; HCl, 7647-01-0; H$_2$C:, 2465-56-7.

Supplementary Material Available: Total energies for the standard calculations for the first- and second-row systems (Tables VI and VII, respectively) (6 pages). Ordering information is given on any current masthead page.

Structure and Aromaticity of 14-Annulene and 18-Annulene[†]

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Received September 16, 1986

Abstract: The ground-state structures of 14- and 18-annulene were calculated for localized and delocalized geometries with the semiempirical MO method SINDO1 on the SCF and CI level. The results for geometry and energy are in agreement with other available theoretical and experimental data. The delocalized structures are obtained as most stable only if interpair correlation is included and the Davidson correction added. These structures can be called aromatic.

I. Introduction

The larger annulenes have been the subject of much discussion. Initially they served as objects of demonstration for the famous Hückel rule of aromaticity which classifies annulenes with $(4n + 2)$ π electrons as aromatic and with $(4n)$ π electrons as antiaromatic.[1] Since then it became clear that not only topology but also geometry has a decisive influence on the properties of such compounds. Dewar and Gleicher[2] suggested on the basis of PPP calculations a damped oscillation of resonance energies with increasing ring size. In their scheme the 22-annulene would present the limit for aromaticity with a positive resonance energy. All annulenes with more than 22 atoms were predicted to have negative resonance energies. Later Dewar[3] corrected this picture by suggesting that annulenes with an even number of 20 or more atoms would approach a common limit of resonance stabilization of about 2.8 kcal/mol. This small resonance energy implies bond alternation. Dewar estimated that an alternation of bond lengths would occur with limiting values for minimal bond lengths of 1.35 Å and maximal bond lengths of 1.46 Å under the assumption of an inverse linear relationship between bond order and bond length. Resonance energy methods advanced by Hess and Schaad[4] and Trinajstic et al.[5] on the Hückel electron level arrived at almost the same conclusions with respect to aromaticity as Dewar. More recently the structure of these compounds became the object of increased attention. Molecular mechanics calculation[6,7] on 14- and 18-annulenes and ab initio SCF calculations[8] on 10- and 18-annulenes determined the structures for alternative symmetries.

In this paper we wish to unify the view points of structure and aromaticity of annulenes. Here the question of bond alternation is most important. Experiments suggest that 14-annulene is nonplanar with very little bond alternation[9] and 18-annulene is planar also with very little bond alternation.[10] A summary of previous discussion on the structure of 18-annulene with particular reference to the electronic spectrum was given by Baumann and Oth.[11] Most previous calculations on the stability of 18-annulene are in disagreement with the experimental result. Using MINDO/3 Dewar[12] reported that a planar structure with D_{3h} symmetry and localized bonds is 26 kcal/mol more stable than the D_{6h} structure with delocalized bonds. But Binsch et al.[13] had already arrived qualitatively at a delocalized structure. More recently Baumann[14] predicted more definitively a delocalized structure by using MINDO/2 with correlation correction. In the following we wish to contribute to the discussion with the presentation of SINDO1[15] calculations on the structure of these two annulenes. The question of aromaticity is investigated with the bond order index recently introduced.[16]

Table I. Energy Lowering (kcal/mol) of Relevant Structures by CI Calculations with the Most Important Double Excitations

	14-annulene			18-annulene	
size of CI	D_2	C_{2h}	C_s	D_{3h}	D_{6h}
20	36.8	36.5			37.5
40	43.3	41.3			45.5
60	46.3	43.7	7.1	9.4	50.7

[†] Dedicated to Prof. R. G. Parr on the occasion of his 65th birthday.

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