JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 109, NUMBER 11 MAY 27, 1987

Substituted Methylene Dications (HCX^{2+}): Some Remarkably Short Bonds to Carbon

Ming Wah Wong, Brian F. Yates, Ross H. Nobes, and Leo Radom*

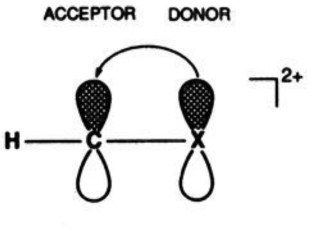
Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia. *Received October 30, 1986*

Abstract: Ab initio molecular orbital calculations have been carried out for the substituted methylene dications HCX^{2+} (X = F, OH, NH_2, CH_3, Cl, SH, PH_2, and SiH_3), for a number of possible isomeric structures of these species, and for transition structures for rearrangement and fragmentation. Geometry optimizations have been performed at MP2/6-31G* and higher levels, and energy comparisons obtained at the MP4/6-31G** level together with zero-point vibrational corrections. The HCX^{2+} dications are characterized generally by extremely short C–X bonds. In the case of HCF^{2+} and $HCCl^{2+}$, the calculated C–X bond lengths (1.138 and 1.459 Å, respectively) are the shortest yet reported for a gas-phase species containing a C–F or C–Cl bond. The calculated formal single C–C bond length in $HCCH_3^{2+}$ is also remarkably short (1.299 Å) as a result of strong hyperconjugative interaction. With the exception of $HCCH_3^{2+}$, $HCPH_2^{2+}$, and $HCSiH_3^{2+}$, which are found to have little or no barrier to rearrangement to more stable isomers, the remaining HCX^{2+} dications are predicted to be experimentally observable. The calculations reveal several interesting, stable isomers of the various HCX^{2+} dications. These include COH_2^{2+}, CH_2NH^{2+}, CNH_3^{2+}, $CH_2CH_2^{2+}$, HCH_2CH^{2+}, CCH_4^{2+}, $CClH^{2+}$, CSH_2^{2+}, CH_3P^{2+}, CPH_3^{2+}, CH_4Si^{2+}, CH_3SiH^{2+}, and $CH_2SiH_2^{2+}$. Adiabatic and vertical ionization energies have been predicted for the production of several of the HCX^{2+} dications from $HCX^{\bullet+}$ monocations for comparison with possible future experimental data.

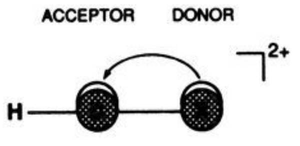
There has been considerable recent interest in the chemistry of gas-phase dications[1] as a result of the development of sophisticated experimental techniques[2] and the application of high-level theoretical procedures.[3] Highly exothermic fragmentations are possible for many of these species, but such fragmentations are often inhibited by large barriers, leading to stable, observable dications. A striking example is the dihelium dication (He_2^{2+})[4] which, despite an exothermicity for fragmentation to two helium monocations of 836 kJ mol^{-1}, resides in a well of depth 145 kJ mol^{-1}, and boasts the shortest known bond length of 0.703 Å.

In the course of our own studies of dications, we have found that substituted methylene dications (HCX^{2+}) often exhibit remarkably short C–X bonds. Our observations in this regard, reported to date[5] for the case of $HCOH^{2+}$, parallel similar observations by Lammertsma et al.[6] on $HCCH_3^{2+}$ and by Koch and Frenking[7] on the disubstituted system FCF^{2+}.

The origin of the bond shortening is clear: the dicationic carbon center has a pair of formally vacant p orbitals which may interact conjugatively or hyperconjugatively with an appropriate π-electron-donor substituent X (**1a**, **1b**), leading to partial double-bond or triple-bond character in the C–X bond. Conversely, the dicationic carbon may be considered an extremely sensitive probe of the conjugative or hyperconjugative electron-donating ability of X.



1a



1b

In order to examine in detail these phenomena, we have carried out a systematic study of substituted methylene dications HCX^{2+} with X = F, OH, NH_2, CH_3, Cl, SH, PH_2, and SiH_3. Results are reported for the structures of these systems and for their stabilities with respect to unimolecular rearrangement and fragmentation.

---

[1] For recent reviews, see: (a) Koch, W.; Maquin, F.; Stahl, D.; Schwarz, H. *Chimia* **1985**, *39*, 376. (b) Koch, W.; Schwarz, H. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, 1987.

[2] For leading references, see: (a) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77. (b) Kingston, E. E.; Beynon, J. H.; Ast, T.; Flammang, R.; Maquestiau, A. *Org. Mass Spectrom.* **1985**, *20*, 546. (c) Thompson, M.; Baker, M. D.; Christie, A.; Tyson, J. F. *Auger Electron Spectroscopy*; Wiley: New York, 1985. (d) Millie, P.; Nenner, I.; Archirel, P.; Lablanquie, P.; Fournier, P.; Eland, J. H. D. *J. Chem. Phys.* **1986**, *84*, 1259.

[3] For leading references, see: (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1986**, *108*, 6545. (b) Lammertsma, K.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1986**, *108*, 7. (c) Koch, W.; Maquin, F.; Schwarz, H.; Stahl, D. *Ibid.* **1985**, *107*, 2256.

[4] (a) Yagisawa, H.; Sato, H.; Watanabe, T. *Phys. Rev. A* **1977**, *16*, 1352. (b) Guilhaus, M.; Brenton, A. G.; Rabrenovic, M.; Beynon, J. H.; Schleyer, P. v. R. *J. Phys. B* **1984**, *17*, L605. (c) Guilhaus, M.; Brenton, A. G.; Beynon, J. H.; Rabrenovic, M.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 210. (d) Gill, P. M. G.; Radom, L. *Chem. Phys. Lett.* **1986**, *132*, 16.

[5] Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 5484.

[6] Lammertsma, K.; Brazaghi, M.; Olah, G. A.; Pople, J. A.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 5252.

[7] Koch, W.; Frenking, G. *Chem. Phys. Lett.* **1985**, *14*, 178.

0002-7863/87/1509-3181$01.50/0

Table I. Calculated C–X Bond Lengths (Å) for CH_3–X, CH_2–X^+, and HC–X^{2+}

X	CH_3–X[a] (6-31G*)	CH_2–X^{+}[a] (6-31G*)	HC–X^{2+}[b] (6-31G*)	HC–X^{2+}[b] (MP3/6-31G**)
F	1.365	1.220	1.111	1.128
OH	1.400	1.232	1.102	1.120
NH_2	1.453	1.263	1.191	1.209
CH_3	1.528	1.432	1.308	1.299
Cl	1.785	1.593	1.450	1.459
SH	1.817	1.616	1.539	1.519
PH_2	1.861	1.624	1.627	1.658
SiH_3	1.888	1.963	c	c

[a] Data for CH_3–X and CH_2–X^+ from ref 18 unless otherwise noted. [b] Present work. [c] Unstable at this level of theory; see text.

Method and Results

Standard ab initio molecular orbital calculations[8] were carried out with a modified version[9,10] of the Gaussian 82 system of programs.[11] Geometry optimizations for the HCX^{2+} dications were performed at the 3-21G(*),[12] 6-31G*,[13] 6-31G**,[13] MP2/6-31G*,[14] MP3/6-31G*,[14] MP3/6-31G**,[14] and, in one case, MP4/6-311G*[15,16] levels. Optimized structures at two of these levels, MP2/6-31G* and MP3/6-31G**, are displayed in Figure 1. A comparison of C–X lengths in the CH_3–X, CH_2–X^+, and HC–X^{2+} systems, calculated at the 6-31G* level, is presented in Table I.[17] Unless otherwise stated, geometric parameters in the text refer to the MP2/6-31G* values.

In order to assess the stabilities of the HCX^{2+} dications, calculations were performed on possible rearrangement and fragmentation products and on transition structures for such processes which are exothermic or only slightly endothermic. Geometry optimizations in these cases were carried out at the MP2/6-31G* level. Improved relative energies were obtained through single-point MP4/6-31G** energy calculations, together with zero-point vibrational energy corrections calculated at the 6-31G*//6-31G* level and scaled by 0.9.[19] The vibrational frequencies calculated for this purpose also served to characterize the stationary points on the surface as minima (representing equilibrium structures) or saddle points (representing transition structures). Our best relative energies correspond to MP4/6-31G**//MP2/6-31G* values with zero-point corrections. Unless otherwise noted, these are the values referred to in the text.

Calculated total energies and relative energies are presented in Table II. Optimized structures, other than for the HCX^{2+} dications themselves (which are collected in Figure 1), are displayed within the text. Calculated vibrational frequencies are contained in the supplementary material.

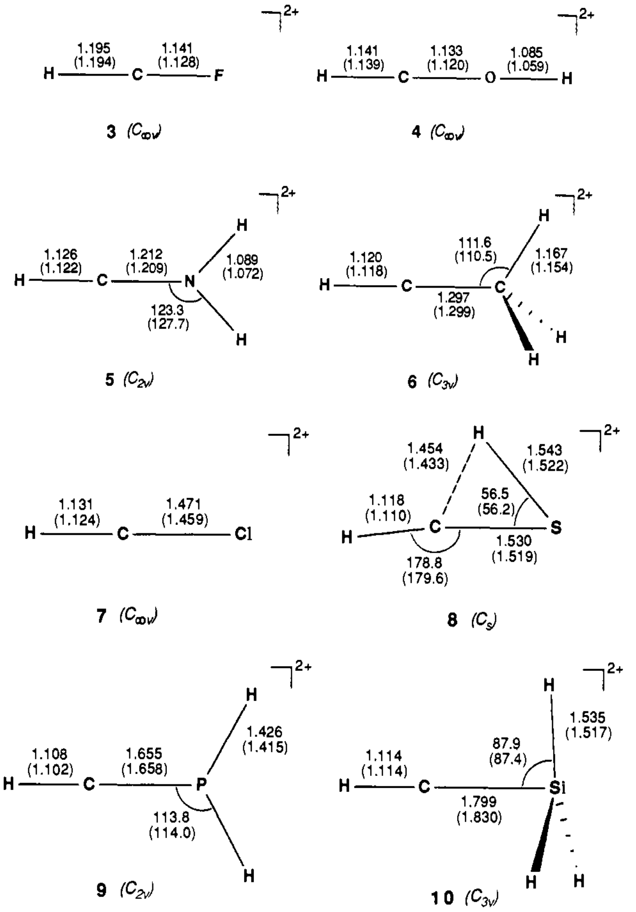
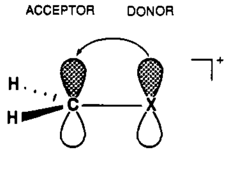


Figure 1. Optimized structures (MP2/6-31G*, MP3/6-31G** values in parentheses) for HCX^{2+} dications. The $HCSiH_3^{2+}$ structure is C_{3v} constrained (see text).

Discussion

Structural Considerations: C–X Bond Lengths. The principal structural feature of interest in the HCX^{2+} dications is the C–X bond length. In order to provide a basis for discussion, we initially compare (at the 6-31G* level) the C–X lengths in the HCX^{2+} dications with corresponding values for the monocations CH_2X^+ and the neutrals CH_3X (Table I). For the HCX^{2+} dications, our highest level results from Figure 1 (MP3/6-31G**) are also included in Table I.

It is well known[20] that in the monocations, CH_2X^+, π-electron-donor substituents X interact favorably with the formally vacant 2p orbital at the cationic center (**2**). Such an interaction leads to a stronger and shorter C–X bond. Thus, substantial bond-length reductions compared with CH_3X are generally observed, ranging from 0.096 (X = CH_3) to 0.237 Å (X = PH_2) (Table I). The only exception is X = SiH_3, for which a slight increase in C–X length is observed, suggesting that hyperconjugative interaction in $SiH_3CH_2^+$ is not particularly favorable.[21,22]



2

---

(8) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(9) Baker, J.; Nobes, R. H.; Wong, M. W., unpublished.

(10) (a) Baker, J. *J. Comput. Chem.* **1986**, *7*, 385. (b) Baker, J. *Ibid.* in press.

(11) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon University, Pittsburgh, PA 15213.

(12) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *Ibid.* **1982**, *104*, 5039.

(13) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(14) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(15) (a) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. (b) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem Phys.* **1980**, *72*, 4244.

(16) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(17) Data for the neutral and singly charged systems taken from ref 18 unless otherwise noted.

(18) 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.

(19) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(20) See, for example: (a) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291. (b) Hopkinson, A. C.; Lien, M. H. *Can. J. Chem.* **1985**, *63*, 3582 and references therein. (c) Bernardi, F.; Bottoni, A.; Venturini, A. *J. Am. Chem. Soc.* **1986**, *108*, 5395.

Table II. Calculated Total Energies[a] (Hartrees), Zero-Point Vibrational Energies[b] (ZPVE, kJ mol^{-1}), and Relative Energies[a] (kJ mol^{-1})

		total energy			relative energy	
species	symmetry	MP2/6-31G*[c]	MP4/6-31G**[d]	ZPVE[e]	MP4/6-31G**	MP4/6-31G**[f]
HCF^{2+} (**3**)	$C_{\infty v}$	−136.963 70	−136.994 19	37.9	0	0
TS: **3** → $H^+ + CF^+$ (**12**)	$C_{\infty v}$	−136.933 94	−136.960 98	18.4	87	70
$H^+ + CF^+$		−137.107 04	−137.133 98	11.8	−367	−391
$CH^+ + F^+(^3P)$		−136.831 57	−136.877 25	19.2	307	290
$HCOH^{2+}$ (**4**)	$C_{\infty v}$	−113.139 69	−113.177 63	66.6	0	0
CH_2O^{2+}[g] (**13**)	C_{2v}	−113.007 70	−113.041 68	35.4	357	329
COH_2^{2+} (**14**)	C_{2v}	−113.036 23	−113.085 54	60.8	242	237
TS: **4** → $HCO^+ + H^+$ (**15**)	$C_{\infty v}$	−113.111 58	−113.140 37	49.4	98	82
TS: **4** → $H^+ + COH^+$ (**16**)	$C_{\infty v}$	−113.059 22	−113.094 31	43.2	219	198
$HCO^+ + H^+$		−113.258 68	−113.285 66	47.5	−284	−301
$H^+ + COH^+$		−113.184 16	−113.221 23	36.5	−114	−142
$CH^+ + OH^+$ ($^3\Sigma^-$)		−113.027 51	−113.087 52	39.3	237	212
$HCNH_2^{2+}$ (**5**)	C_{2v}	−93.338 08	−93.389 53	98.8	0	0
CH_2NH^{2+} (**17**)	C_{2v}	−93.264 88	−93.313 39	84.3	200	187
CNH_3^{2+} (**18**)	C_{3v}	−93.252 26	−93.313 07	101.8	201	204
CH_3N^{2+}[h] (**19**)	C_{3v}	−93.152 52	−93.212 03	63.4	466	434
TS: **5** → $HCNH^+ + H^+$ (**20**)	C_s	−93.274 32	−93.313 98	78.4	198	180
TS: **5** → $H^+ + CNH_2^+$ (**21**)	C_{2v}	−93.228 27	−93.276 90	76.0	296	275
$HCNH^+ + H^+$		−93.434 57	−93.473 02	80.1	−219	−236
$H^+ + CNH_2^+$		−93.340 95	−93.391 36	73.3	−5	−28
$CH^+ + NH_2^+$ ($^3B_1$)		−93.265 54	−93.333 69	67.0	147	118
$HCCH_3^{2+}$ (**6**)	C_{3v}	−77.245 77	−77.308 58	113.0	0	0
$CH_2CH_2^{2+}$ (**22**)	D_{2d}	−77.273 17	−77.336 56	128.4	−73	−60
HCH_2CH^{2+} (**23**)	C_{2v}	−77.243 59	−77.305 87	108.1[i]	7	6
CCH_4^{2+} (**24**)	C_{4v}	−77.121 85	−77.191 75	108.6	307	303
TS: **6** → **22** (**25**)	C_s	−77.244 98	−77.307 98	112.1	2	1
TS: **6** → $HCCH_2^+ + H^+$ (**26**)	C_s	−77.169 34	−77.224 71	102.1	220	210
TS: **6** → $CH^+ + CH_3^+$ (**27**)	C_{3v}	−77.124 72	−77.197 34	123.4	292	302
TS: **6** → $H^+ + CCH_3^+$ (**28**)	C_{3v}	−77.118 43	−77.178 75	95.3	341	325
$HCCH_2^+ + H^+$		−77.307 08	−77.363 83	100.2	−145	−157
$CH^+ + CH_3^+$		−77.287 12	−77.363 32	107.7	−144	−149
$H^+ + CCH_3^+$		−77.230 95	−77.293 01	95.5	41	25
$HCCl^{2+}$ (**7**)	$C_{\infty v}$	−497.095 25	−497.138 46	37.2	0	0
$CClH^{2+}$ (**29**)	C_s	−497.952 23	−497.008 64	24.0	341	329
TS: **7** → $H^+ + CCl^+$ (**30**)	$C_{\infty v}$	−496.994 40	−497.033 58	12.2	275	253
$H^+ + CCl^+$		−497.113 66	−497.154 01	7.7	−41	−67
$CH^+ + Cl^+$ (^3P)		−497.062 24	−497.113 92	19.2	64	48
$HCSH^{2+}$ (**8**)	C_s	−435.748 16	−435.803 08	55.1	0	0
CH_2S^{2+} (**31**)	C_{2v}	−435.737 63	−435.792 03	59.1	29	33
TS: **8** → **31** (**32**)	C_s	−435.737 49	−435.791 65	51.1	30	26
CSH_2^{2+} (**33**)	C_s	−435.626 50	−435.693 38	52.2	288	285
TS: **8** → $HCS^+ + H^+$ (**34**)	C_s	−435.706 90	−435.749 12	40.5	142	129
TS: **8** → $H^+ + CSH^+$ (**35**)	C_s	−435.611 12	−435.663 17	30.5	367	345
TS: **8** → $CH^+ + SH^+$ ($^1\Sigma^+$) (**36**)	C_s	−435.544 36	−435.610 35	45.6	506	497
$HCS^+ + H^+$		−435.861 03	−435.900 33	41.0	−255	−268
$H^+ + CSH^+$		−435.715 60	−435.769 79	27.5	87	63
$CH^+ + SH^+$ ($^1\Sigma^+$)		−435.689 32	−435.758 57	36.3	117	100
$CH^+ + SH^+$ ($^3\Sigma^-$)		−435.768 07	−435.832 03	36.3	−76	−93
$HCPH_2^{2+}$ (**9**)	C_{2v}	−379.517 35	−379.580 77	79.6	0	0
CH_3P^{2+} (**37**)	C_{3v}	−379.587 77	−379.646 95	86.3	−174	−168
CPH_3^{2+} (**38**)	C_{3v}	−379.433 67	−379.505 95	78.8	197	196
TS: **9** → **37** (**40**)	C_1	−379.509 43	−379.576 08	71.9	12	6
TS: **9** → $CH^+ + PH_2^+$ (**41**)	C_s	−379.411 28	−379.483 93	70.1	254	246
$H^+ + CPH_2^+$		−379.446 22	−379.508 53	48.7	190	162
$CH^+ + PH_2^+$ ($^1A_1$)		−379.548 20	−379.624 12	58.8	−114	−132
$HCSiH_3^{2+}$[j] (**10**)	C_{3v}	−328.210 04	−328.288 59	80.9[i]	0	0
CH_3SiH^{2+} (**42**)	C_{3v}	−328.408 91	−328.469 51	116.4	−475	−443
$CSiH_4^{2+}$ (**43**)	C_{4v}	−328.392 07	−328.460 67	104.7	−452	−430
$CH_2SiH_2^{2+}$ (**44**)	C_{2v}	−328.365 88	−328.430 52	108.6	−373	−348
$CH^+ + SiH_3^+$		−328.353 11	−328.429 05	82.5	−369	−367

[a] MP2/6-31G* optimized structures. All total energies refer to frozen-core calculations.

[b] 6-31G*//6-31G* level unless otherwise noted.

[c] Calculated MP2/6-31G* total energies include −37.961 74 (CH^+), −98.869 83 (F^+, ^3P), −75.065 77 (OH^+, $^3\Sigma^-$), −55.303 80 (NH_2^+, $^3B_1$), −39.325 38 (CH_3^+), −459.100 50 (Cl^+, ^3P), −397.727 58 (SH^+,$^1\Sigma^+$), −397.806 33 (SH^+, $^3\Sigma^-$), −341.586 46 (PH_2^+, $^1A_1$), and −290.391 37 (SiH_3^+).

[d] Calculated MP4/6-31G** total energies include −37.994 41 (CH^+), −98.882 84 (F^+, ^3P), −75.093 11 (OH^+, $^3\Sigma^-$), −55.339 28 (NH_2^+, $^3B_1$), −39.368 91 (CH_3^+), −459.119 51 (Cl^+, ^3P), −397.764 16 (SH^+, $^1\Sigma^+$), −397.837 62 (SH^+, $^3\Sigma^-$), −341.629 71 (PH_2^+, $^1A_1$), and −290.434 64 (SiH_3^+).

[e] Calculated zero-point vibrational energies (kJ mol^{-1}) include 19.2 (CH^+), 20.2 (OH^+), 47.8 (NH_2^+, $^3B_1$), 88.5 (CH_3^+), 17.1 (SH^+, $^1\Sigma^+$ and $^3\Sigma^-$), 39.6 (PH_2^+, $^1A_1$), and 63.3 (SiH_3^+).

[f] Including zero-point vibrational correction.

[g] This structure is a saddle point on the surface and collapses on removal of the C_{2v} constraint to $HCOH^{2+}$ (**4**).

[h] This structure is a saddle point on the surface and collapses on removal of the C_{3v} constraint to CH_2NH^{2+} (**17**).

[i] Calculated at the MP2/6-31G*//MP2/6-31G* level.

[j] This structure is a second-order saddle point on the surface and collapses on removal of the C_{3v} constraint to CH_3SiH^{2+} (**42**).

For the remaining substituents, the bond-shortening effect increases in the order F < OH < NH_2 and Cl < SH < PH_2, reflecting the π-donating abilities of the substitutents.

For the HCX^{2+} dications, further substantial bond-length reductions are observed in most cases, although the situation for X = SiH_3 requires qualification (see below). For the first-row substituents, the effects are largest for the three axially symmetrical groups F, OH, and CH_3 since these allow π-electron donation into *both* of the formally vacant orbitals at the positive carbon (cf. **1a** and **1b**).

Some of the results are quite astounding. Our best estimate of the C–F length in HCF^{2+} (1.138 Å at MP4/6-311G*) is shorter by more than 0.1 Å than any C–F length in any molecule whose experimental gas-phase structure has been reported![23] It is even shorter than that recently calculated[7] for CF^{2+} (1.146 Å at MP2/6-31G*) which was noted at that stage to be "the shortest ever reported".

We have remarked previously[5] on the C–O bond in $HCOH^{2+}$. The calculated bond length (1.120 Å at MP3/6-31G**) is even slightly less than the C–O length in carbon monoxide (1.135 Å at MP3/6-31G**).[18] The C–N bond in $HCNH_2^{2+}$ is rather short (1.209 Å at MP3/6-31G**) for a formal C–N single bond and lies between the lengths of C–N double (1.275 Å at MP3/6-31G* for CH_2NH[18]) and triple (1.158 Å at MP3/6-31G* for HCN[18]) bonds.

The C–C length in $HCCH_3^{2+}$, reported previously by Lammertsma et al.,[6] is also quite remarkable. There is a massive *hyperconjugative* C–C bond shortening of more than 0.2 Å, leading to a value of 1.299 Å (MP3/6-31G**) for the length of a *formal single* C–C bond.

Even the second-row systems show strikingly short C–X bonds. The C–Cl length in $HCCl^{2+}$ (1.459 Å at MP3/6-31G**) is shorter by ~0.2 Å than any known experimental gas-phase value[23] for such a bond. The C-X bonds in $HCSH^{2+}$ and $HCPH_2^{2+}$ are also very short.

Complete Structures. The complete HCX^{2+} structures (Figure 1) reveal some additional interesting features. HCF^{2+} (**3**), isoelectronic with hydrogen cyanide, and $HCOH^{2+}$ (**4**), isoelectronic with acetylene, both have linear structures. The C–H bonds are quite long (1.194 and 1.139 Å at MP3/6-31G**), suggesting possible decomposition modes involving loss of the carbon-bound proton. These will be explored below. Both $HCNH_2^{2+}$ (**5**) and $HCCH_3^{2+}$ (**6**) show the effects of strong hyperconjugative interaction with the dicationic center: the N–H and C(Me)–H bonds are lengthened considerably to 1.072 and 1.154 Å (MP3/6-31G**), respectively.

Among the second-row systems, $HCCl^{2+}$ (**7**) is similar to HCF^{2+} (**3**) with a linear structure having a very short C–Cl bond and a somewhat elongated C–H bond (1.124 Å at MP3/6-31G**).

$HCSH^{2+}$ has a most unusual *bridged* structure (**8**) with almost equal C- - -H (1.433 Å) and S- - -H (1.522 Å) bonds (MP3/6-31G**). The degree of bridging increases substantially when electron correlation is introduced: calculated CSH bond angles are 91.6° (3-21G$^{(*)}$), 90.1° (6-31G*), 88.6° (6-31G**), 56.5° (MP2/6-31G*), 56.6° (MP3/6-31G*), and 56.2° (MP3/6-31G**). For the related CSH^+ system, a strongly bent structure is found at the Hartree–Fock level,[24,25] but on the basis of calculations which include electron correlation, it has been suggested[24a,d] that CSH^+ may collapse without a barrier to HCS^+. We find, however, that at our highest levels of theory (MP2/6-31G(2d,2p) and MP4/6-31G**), CSH^+ still resides in a (shallow) potential well and has a strongly bent structure.[25]

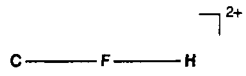
The nonlinear structure of $HCSH^{2+}$ (**8**) is somewhat surprising since it does not allow the optimum π-electron delocalization which we have just seen for (linear) $HCOH^{2+}$ (**4**). It is, however, consistent with the known reduced tendency for π-electron delocalization and the increased tendency for bending for second-row molecules compared with their first-row counterparts.[26] If the $HCSH^{2+}$ dication is constrained to linearity, the C–S bond is reduced in length from 1.530 to 1.493 Å, but the energy is increased by 103 kJ mol^{-1}.

The $HCPH_2^{2+}$ dication has a structure (**9**) with C_{2v} symmetry, analogous to that of $HCNH_2^{2+}$ (**5**). The C–P bond length (1.658 Å at MP3/6-31G**) is comparable to that in the monocation $CH_2PH_2^+$.

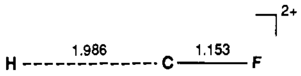
Our results for the $HCSiH_3^{2+}$ dication are rather interesting. Optimization under a C_{3v} symmetry constraint yields a structure (**10**) with a quite short C–Si bond length: 1.799 Å at MP2/6-31G* and 1.830 Å at MP3/6-31G** compared with 1.884 and 1.883 Å at corresponding levels for CH_3SiH_3. These results thus show a bond shortening, presumably hyperconjugative in origin, that is not found in the monocation $CH_2SiH_3^+$. The C_{3v} structure (**10**), however, has a degenerate pair of imaginary frequencies, indicating a second-order saddle point. Rearrangement of **10** along the normal coordinates representing these frequencies leads without a barrier to CH_3SiH^{2+}, discussed in more detail below. Thus, $HCSiH_3^{2+}$ is not an equilibrium structure on the potential energy surface and should not be observable.

Stability Considerations. In order to assess which, if any, of the HCX^{2+} dications are likely to be experimentally observable, it is necessary to determine the barriers for possible rearrangement or fragmentation processes.

HCF^{2+}. For HCF^{2+} (**3**), the alternative isomer CFH^{2+} (**11**) is unstable (with respect to $CF^+ + H^+$) so we have not examined in detail the rearrangement of **3** to **11**. Dissociation to CH^+ + F^+ also does not need to be considered in detail since it is highly endothermic (by 290 kJ mol^{-1}). On the other hand, direct fragmentation of **3** to $H^+ + CF^+$ is exothermic by 391 kJ mol^{-1}. However, the barrier to such a fragmentation, via the transition structure **12**, is 70 kJ mol^{-1}, sufficiently large that **3** should be detectable in, for example, mass-spectrometry-based experiments. The C–F bond in **12** (1.153 Å) is only slightly longer than that in **3**, but the C- - -H bond (1.986 Å) is strikingly elongated.[27]



11



12 ($C_{\infty v}$)

We have calculated the vertical (IE_v) and adiabatic (IE_a) ionization energies corresponding to production of the HCF^{2+} dication from $HCF^{\cdot+}$ for comparison with possible future experimental values. The calculated values[28] are 21.0 (IE_v) and 19.7 (IE_a) eV.

$HCOH^{2+}$. We have previously commented[5] on the stability of $HCOH^{2+}$ (**4**) with respect to rearrangement and fragmentation.[29]

---

(21) The destabilizing effect of the SiH_3 substituent on an adjacent carbocation center has been noted previously: (a) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998. (b) Pople, J. A. ; Apeloig, Y.; Schleyer , P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 489.

(22) We have carried out further calculations on $CH_2SiH_3^+$ at the (higher) MP2/6-31G* level and find that, at this level, the orthogonal conformation of $CH_2SiH_3^+$ collapses without a barrier to $CH_3SiH_2^+$. The (constrained) eclipsed structure has a C–Si bond length of 1.929 Å compared with 1.884 Å in CH_3SiH_3 (MP2/6-31G*).

(23) As listed in the compendium: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem Ref. Data* **1979**, *8*, 619.

(24) (a) Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1978**, *27*, 33. (b) Berthier, G.; Chekir, S.; Jaidane, N.; Pauzat, F.; Yuanqi, T.; Vermeulin, P. *J. Mol. Struct.* (THEOCHEM) **1983**, *94*, 327. (c) Berthier, G.; Pauzat, F.; Yuanqi, T. *Ibid.* **1984**, *107*, 39. (d) Pope, S. A.; Hillier, I. H.; Guest, M. F. *J. Am. Chem. Soc.* **1985**, *107*, 3789.

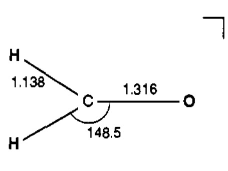
(25) At our highest levels of theory, the calculated bond angle in CSH^+ is 62.6° (MP2/6-31G(2d,2p)) or 71.6° (MP4/6-31G(d,p)), and the calculated barrier (MP4/6-31G(2d,2p) using additivity, together with an MP2/6-31G** zero-point vibrational correction) for the rearrangement of CSH^+ to HCS^+ is 5 kJ mol^{-1}. For a detailed discussion of the CSH^+ and $HCSH^{2+}$ systems, see: Wong, M. W.; Nobes, R. H.; Radom, L., to be published.

(26) Kutzelnigg, W. *Agnew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

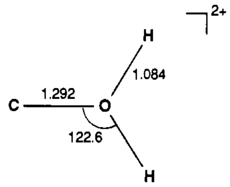
(27) For a rationalization of the surprisingly long C- - -H bond lengths in transition structures for deprotonation of dications, see: Gill, P. M. W.; Radom, L. *Chem. Phys. Lett.*, in press.

(28) The MP2/6-31G* structural parameters for $HCF^{\cdot+}$ (C_s) are r(HC) = 1.107 Å, r(CF) = 1.215 Å, and ∠HCF = 124.3°. MP4/6-31G** total energies for this structure are −137.71746 ($HCF^{\cdot+}$) and −136.94703 (HCF^{2+}) hartrees.

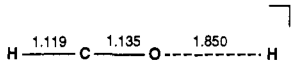
The slightly higher level calculations of the present study confirm in the first instance that the conventional formaldehyde dication (CH_2O^{2+}) is not stable. The C_{2v} structure (**13**) has one imaginary frequency and corresponds to a saddle point for hydrogen scrambling in **4**. We have, however, found an interesting new structure (COH_2^{2+}, **14**) which *is* located at a minimum on the surface, 237 kJ mol^{-1} above **4**. There are two exothermic dissociations for **4**, leading to $HCO^+ + H^+$ and $COH^+ + H^+$ with barriers via transition structures **15** and **16** of 82 and 198 kJ mol^{-1}, respectively. These barrier values are very similar to those which we obtained previously[5] and again indicate that $HCOH^{2+}$ (**4**) lies in a significant potential well. Indeed, **4** has recently been observed in charge-stripping experiments.[30] Our calculated ionization energies[31] of 18.9 (IE$_v$) and 17.2 (IE$_a$) eV may be compared with the experimental Q_{min} value of 17.7 eV.



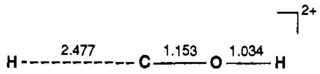
13 (C_{2v})



14 (C_{2v})

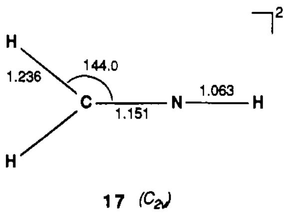


15 ($C_{\infty v}$)

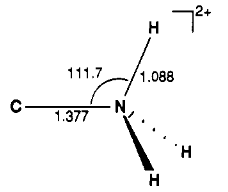


16 ($C_{\infty v}$)

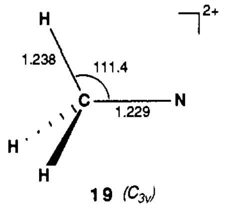
$HCNH_2^{2+}$. We have found two stable isomers of $HCNH_2^{2+}$ (**5**), namely CH_2NH^{2+} (**17**) and CNH_3^{2+} (**18**), lying respectively 187 and 204 kJ mol^{-1} above **5**.[32,33] The CH_2NH^{2+} structure (**17**) is interesting, the very short C–N bond (1.151 Å) and long C–H bonds (1.236 Å) suggesting strong hyperconjugative interaction. On this basis, however, the HCN angle is surprisingly large (144.0°). Hyperconjugative interaction is also evident in CNH_3^{2+} (**18**) which displays long N–H bonds (1.088 Å). A third possible isomer, CH_3N^{2+} (**19**), was examined initially with a C_{3v} symmetry constraint. However, the C_{3v} structure (**19**) has one imaginary frequency and collapses to CH_2NH^+ (**17**) when the constraint is relaxed to C_s. It thus represents a saddle point for scrambling of the hydrogen atoms of **17**.



17 (C_{2v})

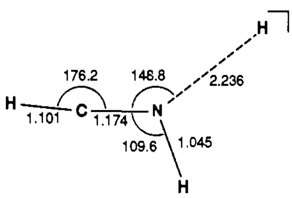


18 (C_{3v})

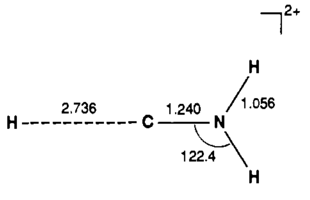


19 (C_{3v})

Exothermic dissociations of $HCNH_2^{2+}$ (**5**) can lead to $HCNH^+ + H^+$ and $H^+ + CNH_2^+$. The barriers for both processes are, however, substantial at 180 and 275 kJ mol^{-1}, respectively, via **20** and **21**.

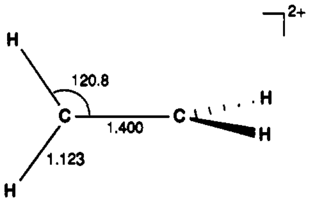


20 (C_s)

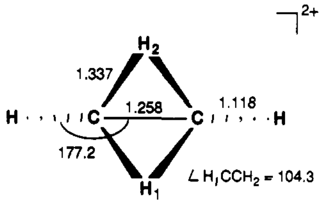


21 (C_{2v})

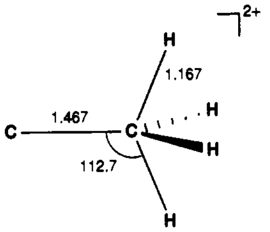
$HCCH_3^{2+}$. For $HCCH_3^{2+}$ (**6**), we find three stable isomeric structures: $CH_2CH_2^{2+}$ (**22**), the doubly bridged structure **23**, and CCH_4^{2+} (**24**). Although the last of these (**24**) does indeed lie at a minimum on the surface, it has a high energy (303 kJ mol^{-1} above **6**) and is not considered further. Explicit calculation of vibrational frequencies at the MP2/6-31G*//MP2/6-31G* level confirms that **6**, **22**, and **23** represent minima on the MP2/6-31G* potential energy surface.[34] The lowest energy structure is the ethylene dication (**22**). This is found to lie 60 kJ mol^{-1} *below* **6**, which may be compared with a value of 89 kJ mol^{-1} obtained at a somewhat lower level of theory in a previous study.[6] Rearrangement of $HCCH_3^{2+}$ (**6**) to $CH_2CH_2^{2+}$ (**22**) via the singly bridged transition structure **25** requires only 1 kJ mol^{-1}, suggesting that experimental observation of **6** is most unlikely. The doubly bridged structure (**23**), in contrast to the singly bridged structure (**25**), does represent an equilibrium structure on the MP2/6-31G* surface, as pointed out above.[35] Rearrangement of **23** to both **6** and **22** is currently being studied and will be reported elsewhere.[34]



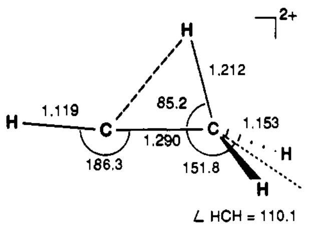
22 (D_{2d})



23 (C_{2v})



24 (C_{4v})



25 (C_s)

A recent MINDO/3 study[36] indicated that the doubly bridged and singly bridged structures are the lowest energy isomers on the $C_2H_4^{2+}$ surface. We find, however, that while the doubly bridged structure **23** does represent a minimum on the surface, it lies substantially higher in energy than **22** (by 65 kJ mol^{-1}). We find, in addition, no evidence for a singly bridged *equilibrium* structure; the singly bridged structure **25** is, as noted above, a transition structure for interconversion of **6** and **22**.

---

(29) For leading references to studies of the $HCOH^{\cdot+}$ monocation, see: Bouma, W. J.; Burgers, P. C.; Holmes, J. L.; Radom, L. *J. Am. Chem. Soc.* **1986**, *108*, 1767.

(30) Stahl, D.; Maquin, F. *Chem. Phys. Lett.* **1984**, *106*, 531.

(31) The MP2/6-31G* structural parameters for $HCOH^{\cdot+}$ (anti, C_s) are r(HC) = 1.097 Å, r(CO) = 1.230 Å, r(OH) = 1.002 Å, ∠HCO = 123.9°, and ∠COH = 117.7°, MP4/6-31G** total energies for this structure are −113.81204 ($HCOH^{\cdot+}$) and −113.11404 ($HCOH^{2+}$) hartrees.

(32) For leading references to studies of the $HCNH_2^{\cdot+}$ monocation, see: Uggerud, E.; Schwarz, H. *J. Am. Chem. Soc.* **1985**, *107*, 5046.

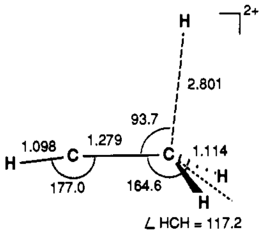
(33) Since completion of the present work, a detailed study of the CH_3N^{2+} potential surface has been reported with results in substantial agreement with those presented here: Koch, W.; Heinrich, N.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 5400.

(34) Nobes, R. H.; Wong, M. W.; Radom, L. *Chem. Phys. Lett.*, in press.

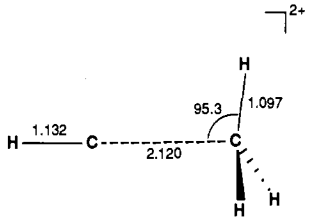
(35) Note, however, that frequency calculations indicate the doubly bridged structure **23** to be a first-order saddle point on the HF/6-31G* surface.

(36) Dewar, M. J. S.; Reynolds, C. H. *J. Mol. Struct.* (THEOCHEM) **1986**, *136*, 209.

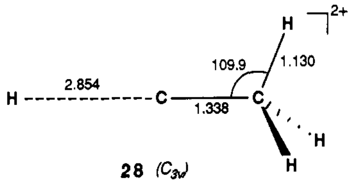
We have also determined the transition structures (**26**, **27**, and **28**) for fragmentation of $HCCH_3^{2+}$ (**6**) to $HCCH_2^+ + H^+$, $CH^+ + CH_3^+$, and $H^+ + CCH_3^+$. The calculated barriers for these processes are all substantial at 210, 302, and 325 kJ mol^{-1}, respectively.



26 (C_s)

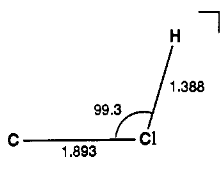


27 (C_{3v})

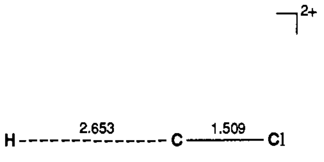


28 (C_{3v})

$HCCl^{2+}$. Rearrangement of $HCCl^{2+}$ (**7**) to its isomer $CClH^{2+}$ (**29**) is highly endothermic (by 329 kJ mol^{-1}). In addition, although dissociation of $HCCl^{2+}$ (**7**) to $H^+ + CCl^+$ is exothermic (by 67 kJ mol^{-1}), the barrier for this process, via transition structure **30**, is very large (253 kJ mol^{-1}). Thus, $HCCl^{2+}$ (**7**) is predicted to lie in a deep potential well and should be readily observable. We have calculated ionization energies[37] for production of $HCCl^{2+}$ (**7**) from $HCCl^{\bullet+}$ of 17.8 (IE_v) and 17.0 (IE_a) eV.

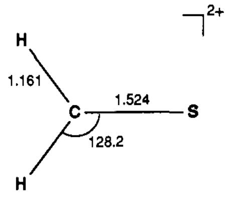


29 (C_s)

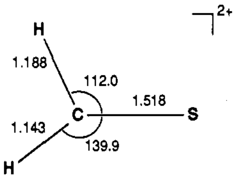


30 ($C_{\infty v}$)

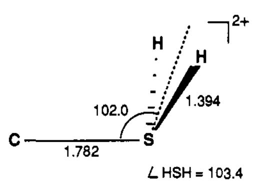
$HCSH^{2+}$. Although at the Hartree–Fock level both $HCSH^{2+}$ and the thioformaldehyde dication (CH_2S^{2+}) represent distinct equilibrium structures, each lying in significant potential wells, reoptimization at MP2/6-31G* leads to an $HCSH^{2+}$ dication of intermediate structure (**8**) and a thioformaldehyde cation (**31**) lying in a very shallow potential well, 33 kJ mol^{-1} above **8**. At the MP2/6-31G* level, we find a transition structure (**32**) for the 1,2-hydrogen shift connecting **31** and **8**, but the barrier at this level is very small (<1 kJ mol^{-1}). Indeed, at higher levels (in particular when zero-point vibrational energies are included), this barrier may disappear entirely. A third minimum on the surface, with a CSH_2^{2+} structure (**33**), is predicted to lie very high in energy (285 kJ mol^{-1} above **8**).



31 (C_{2v})

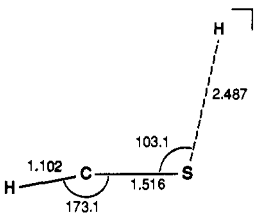


32 (C_s)

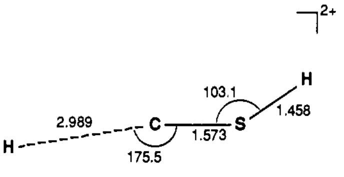


33 (C_s)

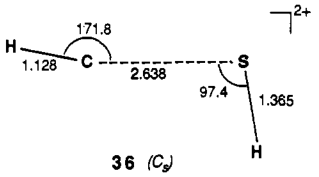
We have examined transition structures (**34**, **35**, and **36**) for the dissociations of **8** leading to $HCS^+ + H^+$, $H^+ + CSH^+$, and $CH^+ + SH^+$ ($^1\Sigma^+$), respectively. The first of these processes has a large exothermicity (268 kJ mol^{-1}), but the calculated barrier is substantial (129 kJ mol^{-1}). Fragmentation to $CH^+ + SH^+$ ($^3\Sigma^-$) is also predicted to be exothermic (by 93 kJ mol^{-1}), but this would involve intersystem crossing and we would not expect it to be a facile process. Fragmentation to $H^+ + CSH^+$ both is endothermic (by 63 kJ mol^{-1}) and is inhibited by a large barrier (345 kJ mol^{-1}).



34 (C_s)

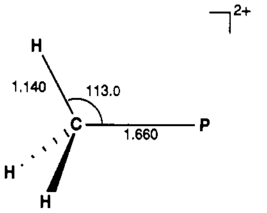


35 (C_s)

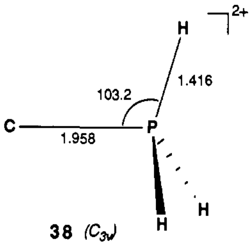


36 (C_s)

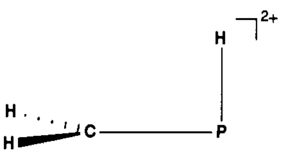
$HCPH_2^{2+}$. Several isomers of the $HCPH_2^{2+}$ dication (**9**) were examined, including CH_3P^{2+} (**37**), CPH_3^{2+} (**38**), and CH_2PH^{2+} (**39**). The most stable of these is CH_3P^{2+} (**37**), which lies substantially lower in energy (168 kJ mol^{-1}) than **9**. Rearrangement of **9** to **37** may occur via transition structure **40**, the calculated barrier for this process being very low (6 kJ mol^{-1}). It would seem, therefore, that experimental observation of $HCPH_2^{2+}$ (**9**) will not be straightforward. The CPH_3^{2+} isomer (**38**) is found to lie high in energy, 196 kJ mol^{-1} above **9**. For the final isomer which we considered, CH_2PH^{2+} (**39**), minima were found at lower levels of theory (e.g., HF/6-31G*). However, optimization at MP2/6-31G* led directly to the more stable structure CH_3P^{2+} (**37**).



37 (C_{3v})



38 (C_{3v})



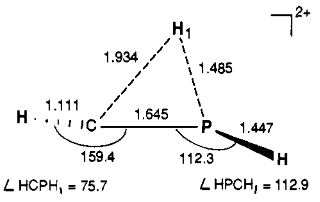
39

Dissociations of $HCPH_2^{2+}$ (**9**) to $H^+ + CPH_2^+$ and $CH^+ + PH_2^+$ were also examined. Loss of a proton is highly endothermic (by 162 kJ mol^{-1}). Fission of the C–P bond (via transition structure **41**), on the other hand, is exothermic by 132 kJ mol^{-1} but requires substantial activation energy (246 kJ mol^{-1}).

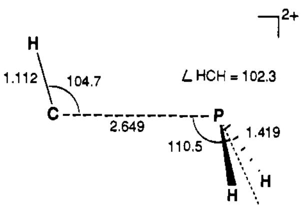
$HCSiH_3^{2+}$. The final HCX^{2+} structure to be considered, namely $HCSiH_3^{2+}$, is, as noted above, not stable. The constrained C_{3v} structure (**10**) has two imaginary frequencies and collapses under

---

(37) The MP2/6-31G* structural parameters for $HCCl^{\bullet+}$ (C_s) are $r(HC) = 1.095$ Å, $r(CCl) = 1.548$ Å, and $\angle HCCl = 131.8°$. MP4/6-31G** total energies for this structure are −497.76100 ($HCCl^{\bullet+}$) and −497.10985 ($HCCl^{2+}$) hartrees.

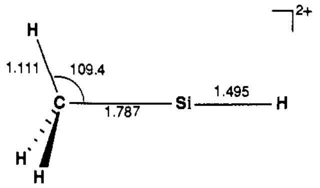


40 (C_1)

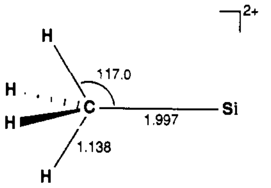


41 (C_s)

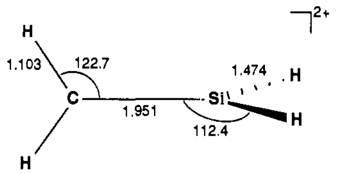
C_s symmetry to CH_3SiH^{2+} (**42**). The latter (**42**) is the lowest energy structure which we have found, lying 443 kJ mol^{-1} below **10**. It is characterized by a quite short C–Si bond (1.787 Å). Another low-lying isomer is $SiCH_4^{2+}$ (**43**) (430 kJ mol^{-1} below **10**), while the silaethylene dication (**44**) lies somewhat higher in energy (but still 348 kJ mol^{-1} below **10**). A detailed study of the $CSiH_4^{2+}$ surface will be presented elsewhere.[38]



42 (C_{3v})



43 (C_{4v})



44 (C_{2v})

Concluding Remarks

Several important points emerge from this study.

(1) The HCX^{2+} dications are characterized in general by remarkably short C–X bond lengths. In the case of HCF^{2+} and $HCCl^{2+}$, the C–X bonds are the shortest yet reported for these types of bonds in gas-phase molecules.

(2) The shortening of the C–X bonds may be attributed to conjugative or hyperconjugative electron donation from X into the *pair* of formally vacant orbitals at X.

(3) Conversely, the HCX^{2+} system provides a sensitive probe of the conjugative or hyperconjugative electron-donating ability of X.

(4) With the exception of $HCCH_3^{2+}$, $HCPH_2^{2+}$, and $HCSiH_3^{2+}$, which show little or no barrier to rearrangement to more stable isomers, the remaining HCX^{2+} isomers are predicted to be experimentally observable.

Supplementary Material Available: Calculated vibrational frequencies for the HCX^{2+} dications and their isomers (Table III) (2 pages). Ordering information is given on any current masthead page.

---

(38) Wong, M. W.; Nobes, R. H.; Radom, L., to be published.

Reactions of Isolated Bicyclic Hydrocarbon Ions Excited by Different Methods

Pirjo Vainiotalo,*[†] Hilkka I. Kenttämaa,*[‡§] Md. Abdul Mabud,[‡] John R. O'Lear,[‡] and R. Graham Cooks*[‡]

Contribution from the Department of Chemistry, University of Joensuu, Joensuu, Finland, and the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.

Received December 8, 1986

Abstract: The molecular ions of the isomeric hydrocarbons 2-methylbicyclo[2.2.1]hept-2-ene and 2-methylenebicyclo[2.2.1]heptane retain their structural identities at low internal energies, while fragmentation of the isomers proceeds through intermediates of identical structure (e.g., ionized methylcyclopentadiene) at higher energies. Reaction intermediate scans were used to identify fragmentation intermediates not evident in other types of MS/MS data. Structures were assigned to the major odd-electron fragments on the basis of energy-resolved mass spectrometry. Activation methods which deposit a *broad range* of internal energies (electron ionization and high-energy collisional activation with a gas-phase target) or *low average* internal energies (collisional activation, surface-induced dissociation at low translational energies) produce distinct dissociation product distributions. In contrast, methods which selectively deposit high internal energies (>50 eV collisions with a surface) or which deposit relatively high energies in several steps (multiple collisions with a gaseous target at 30 eV laboratory collision energy) fail to differentiate the isomers. It is concluded that the way in which ions are energized can be a crucial factor in successful isomer distinction by mass spectrometry. Moreover, activation methods which deposit a narrow distribution of internal energies, and which are therefore desirable in isomer differentiation, should be applied over a wide range of energies if information is not to be lost.

Characterization of the numerous methods of activating ions in tandem mass spectrometry[1,2] is important for analytical applications as well as for investigations into the fundamentals of ionic processes.[3] Fragmentation of the excited ions usually takes place from a vibrationally excited ground state and may be described within the framework of the quasi-equilibrium theory.[1-3] The relative abundances of the product ions obtained by using different methods are thus expected[1-3] to differ mainly because of differences in the internal energy distributions, P(*E*), of the fragmenting ions. Recently, various qualitative and semiquan-

---

[†] University of Joensuu.

[‡] Purdue University.

[§] On leave from the Department of Chemistry, University of Helsinki, Finland.

(1) *Tandem Mass Spectrometry*; McLafferty, F. W. Ed.; John Wiley & Sons, Inc.: New York, 1983.

(2) (a) McLafferty, F. W.; Bente III, P. F.; Kornfeld, R.; Tsai, S. C.; Howe, I. *J. Am. Chem. Soc.* **1973**, *95*, 2120. (b) Cody, R. B.; Freiser, B. S. *Anal. Chem.* **1979**, *51*, 547. (c) Mabud, Md. A.; DeKrey, M. J.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 285.

(3) Levsen, K. *Fundamental Aspects of Organic Mass Spectrometry*; Verlag Chemie: New York, 1978.

0002-7863/87/1509-3187$01.50/0 © 1987 American Chemical Society