

Table 5. Enthalpies of disproportionation $2\text{AMgCl}_3(\text{s}) = \text{A}_2\text{MgCl}_4(\text{s}) + \text{MgCl}_2(\text{s})$, (estimated uncertainties ± 1 kcal).

Reaction	$\frac{\Delta H_{700}}{\text{kcal mol}^{-1}}$	$\frac{\Delta H_{298.15}}{\text{kcal mol}^{-1}}$
$2\text{KMgCl}_3(\text{s}) = \text{K}_2\text{MgCl}_4(\text{s}) + \text{MgCl}_2(\text{s})$	+ 1.3	- 1.1
$2\text{RbMgCl}_3(\text{s}) = \text{Rb}_2\text{MgCl}_4(\text{s}) + \text{MgCl}_2(\text{s})$	+ 3.9	+ 1.3
$2\text{CsMgCl}_3(\text{s}) = \text{Cs}_2\text{MgCl}_4(\text{s}) + \text{MgCl}_2(\text{s})$	+ 10.0	+ 8.0

considerably from the potassium to the cesium compound.

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Calculation of C=C and C—F Bond Lengths in $\text{CH}_2=\text{CH}_2$, $\text{CH}_2=\text{CHF}$, *cis*- $\text{CHF}=\text{CHF}$, and $\text{CH}_2=\text{CF}_2$

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Experimental observations of C=C and C—F bond lengths in ethylene and fluorinated ethylenes (Table 1) indicate decreasing lengths with progressing fluorination. Earlier "resonance" structures such

as $\bar{\text{C}}\text{H}_2-\text{CH}=\overset{\dagger}{\text{F}}$ would seem to connect increasing C=C length with decreasing C—F length. This communication reports results of *ab initio* calculations of the molecules of Table 1 in which the molecular energy was separately minimized with respect to the C=C and C—F bond(s) in that order, taking remaining geometrical parameters from Refs. 1–3. A relatively small, Gaussian basis set⁴ (*s,p* = 7,3 contracted to 4,2) was used. The set was tested to see how well the experimental carbon-carbon distances in ethane ($r_c = 1.532 \text{ \AA}$),⁵ in ethylene ($r_c = 1.335 \text{ \AA}$),¹ and in acetylene ($r_c = 1.203 \text{ \AA}$)⁶ were reproduced. The results (r_c) were 1.554, 1.314, and 1.188 Å, respectively. Obviously, to assign significance to what follows one must assume that somehow the molecules of Table 1 are more "related" than C_2H_6 , C_2H_4 , and C_2H_2 .

The results of Table 2 are a minor part of a more comprehensive investigation.⁷ To the best of our knowledge only one paper⁸ based on the experimental structure of $\text{CH}_2=\text{CHF}$ (Table 1) has appeared earlier. At the present level of approximation the calculated bond lengths of Table 2 show the same trends as the experiments. The computed gross atomic charges show that carbon in ethylene, when binding fluorine instead of hydrogen, donates ca. 0.6 e (~ 6.3965 (col. 1) – 5.7818 (col. 2) ~ 6.3965 – 5.8433 (col. 3) $\sim 0.5(6.3965 - 5.2163)$ (col. 4)) to fluorine, the hydrogen gross electronic charges (not quoted) being practically constant (0.8 e). Unsubstituted C prac-

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Table 1. Experimental geometric parameters of ethylene and three fluorinated ethylenes as taken from Refs. 1–3. Distances in Å.

Molecule	$R_{C=C}^a$	R_{C-F}^a	Reference
$CH_2=CH_2$	1.335 ± 0.003		1
$CH_2=CHF$	1.329 ± 0.006	1.347 ± 0.009	2
$CHF=CHF$ (<i>cis</i>)	1.324 ± 0.004	1.335 ± 0.004	3
$CH_2=CF_2$	1.315 ± 0.002	1.325 ± 0.002	3

^a Largely R_z parameters.

Table 2. Calculated equilibrium distances, σ - and π -overlap charges and σ - and π -gross atomic charges for $CH_2=CH_2$, $C(2)H_2=C(1)HF$, *cis*- $C(2)HF=C(1)HF$, and $C(2)H_2=C(1)F_2$. Distances in Å, charges in units of electronic charge.

	$CH_2=CH_2$	$CH_2=CHF$	<i>cis</i> - $CHF=CHF$	$CH_2=CF_2$
C=C distance	1.315	1.306	1.305	1.300
σ -Overlap	0.6286	0.5404	0.3612	0.4205
π -Overlap	0.5300	0.5114	0.4974	0.4850
$\sigma + \pi$ -Overlap	1.1585	1.0518	0.8586	0.9055
C(1), σ -gross	5.3965	4.7805	4.7798	4.2644
C(1), π -gross	1.0000	1.0013	1.0635	1.0019
($\sigma + \pi$)-Gross	6.3965	5.7818	5.8433	5.2163
C(2), σ -gross	5.3965	5.4093	4.7798	5.3839
C(2), π -gross	1.0000	1.0639	1.0635	1.1342
($\sigma + \pi$)-Gross	6.3965	6.4732	5.8433	6.5103
C-F distance		1.370	1.357	1.350
σ -Overlap		0.4123	0.4216	0.4682
π -Overlap		0.0115	0.0102	0.0300
$\sigma + \pi$ -Overlap		0.4238	0.4318	0.4982
F, σ -gross		7.4789	7.4576	7.4530
F, π -gross		1.9348	1.9365	1.9320
($\sigma + \pi$)-Gross		9.4137	9.3941	9.3850

tically retains its gross charge (6.3965 compared to 6.4732 and 6.5103). The role of fluorine as a donor to the "conjugated" π -system is rather modest ($2.00 - 1.93 = 0.07 e$). If the overlap charges of the C=C and C-F bonds were the main factors determining bond lengths our calculations would be contradictory. However, other factors may probably be important emerging, perhaps, when a larger basis set is applied.

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