AM1 and PM3 Calculations on the Effect of Substituents on the Stabilities of Carbocations in the Gas Phase and in Solution

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The effect of substituents on the stability of $Ph_nC^+H_{2-n}X$ (n = 0–2) carbocations, X = F, OH, OCH_3, NH_2, CH_3, C_6H_5, CH=CH_2, C≡CH, CN, CHO, COOH, and NO_2, has been studied with AM1 and PM3 semiempirical molecular orbital theories both in the gas phase and in solution. The results indicate that the amino group gives the most stabilization by π-electron donation, whereas the nitro group is most destabilizing because of its strong σ- and π-accepting nature. Carbocation substituent stabilization energies decrease with increasing number of phenyl rings directly attached to the cation center. Electron-withdrawing substituents, (CN, CHO, and COOH) destabilize the cation center to a lesser extent than might be expected because they act as π-electron donors when directly attached to a cation center. On going from the gas phase to solution, the stabilization energies of primary carbocations decrease, whereas for tertiary cations they increase. The secondary carbocations are of intermediate behavior.

Introduction

Carbocations are involved as intermediates in many rearrangement, elimination, and substitution reactions of organic compounds.[1–9] Because of their electron-deficient nature, carbocations should be particularly susceptible to substituent effects. Taft, Martin, and Lampe[6] in an early mass spectroscopic study showed that the stabilizing effect of substituents ranges from 10.0 kcal/mol destabilization to −106.0 kcal/mol stabilization. Alkyl, aryl, amino, hydroxy, alkoxy, and halogens are examples of groups that stabilize the cationic center.[6,10–31] Experimental hydride ion affinities of C^+H_2X cations showed the stability order to be X = C_6H_5 > CH=CH_2 > C≡CH > CH_3 > F.[31b] The stabilizing effects of π-donor substituents have been the subject of many theoretical studies.[10–30] Hyperconjugation is also an important factor in stabilizing carbocations.[10] Electron-withdrawing groups might be expected to destabilize carbocations, but experimental studies show that the cationic center is stabilized to some extent by an adjacent electron-withdrawing group and that such carbocations can indeed be generated, studied, and used in synthetic applications.[32–38] Experimental work has indicated that the nitro, cyano, and carbonyl groups destabilize cations less than would be expected only on the basis of their inductive effects.[32–38] Theoretical studies indicate that this attenuated destabilization arises from resonance delocalization of the π-orbital on the electron-withdrawing substituent to the cation center.[39–45] This involves conjugation (back-donation) of the substituent with the empty orbital of the carbocation. In this paper, the results of semiempirical molecular orbital calculations at the AM1[46] and PM3[47] levels on the carbocations $Ph_nC^+H_{2-n}X$ (n = 0–2), X = F, OH, OCH_3, NH_2, CH_3, C_6H_5, CH=CH_2, C≡CH, CN, CHO, COOH, and NO_2, are presented. Comparison is made with the available experimental heats of formation of the neutral species and carbocations to assess the performance of the theory. The effect of substituents on the stabilities of these carbocations is investigated.

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Table 1. Heats of Formation (kcal/mol) of Neutral Compounds at AM1 and PM3 Levels

	CH_3X		$PhCH_2X$		Ph_2CHX	
X	AM1	PM3	AM1	PM3	AM1	PM3
H	−8.80	−13.02	14.40	14.11	42.10	42.79
F	−61.00	−53.80	−32.40	−25.97	0.90	3.15
OH	−57.00	−51.88	−28.40	−22.38	1.70	5.59
OCH_3	−51.86	−46.94	−24.50	−24.50	7.40	11.32
NH_2	−6.10	−4.00	19.80	21.94	49.10	49.38
CH_3	−17.40	−18.13	8.60	9.88	39.70	39.57
C_6H_5	14.40	14.11	42.10	42.79	74.90	74.97
$CH{=}CH_2$	6.60	6.40	33.20	34.59	64.90	65.62
$C{\equiv}CH$	43.41	40.22	71.00	69.64	103.20	100.17
CN	19.30	23.29	46.70	46.74	78.60	82.92
CHO	−41.60	−44.20	−15.40	−15.42	16.50	14.24
COOH	−97.14	−99.41	−75.50	−75.47	−43.40	−41.35
NO_2	−9.90	−15.94	16.64	16.56	48.30	42.13

Table 2. Heats of Formation (kcal/mol) of Neutral Compounds at AM1 and PM3 Levles in H_2O

	CH_3X		$PhCH_2X$		Ph_2CHX	
X	AM1	PM3	AM1	PM3	AM1	PM3
H	−10.19	−17.14	13.09	7.03	29.45	24.52
F	−61.94	−56.49	−32.58	−26.87	−10.64	−5.51
OH	−59.37	−56.16	−30.33	−26.49	−11.23	−7.71
OCH_3	−53.98	−51.38	−26.95	−24.81	1.53	5.26
NH_2	−9.29	−8.24	16.58	18.87	40.20	39.42
CH_3	−18.30	−21.39	7.93	8.05	29.96	28.13
C_6H_5	13.09	7.03	29.45	24.52	78.97	79.11
$CH{=}CH_2$	5.86	4.05	30.39	30.80	61.89	62.21
$C{\equiv}CH$	41.37	37.48	66.57	67.69	97.08	92.46
CN	13.86	16.07	41.17	43.96	69.67	73.55
CHO	46.00	−50.50	−20.40	−22.63	10.47	7.62
COOH	−104.16	−109.21	−82.45	−83.04	−45.98	−44.56
NO_2	−19.58	−31.14	6.94	−3.76	41.13	33.33

Table 3. Heats of Formation (kcal/mol) of Carbocations at AM1 and PM3 Levels

	C^+H_2X		PhC^+HX		Ph_2C^+X	
X	AM1	PM3	AM1	PM3	AM1	PM3
H	252.35	256.55	222.11	227.42	232.29	237.35
F	180.35	200.27	169.96	183.02	187.95	196.97
OH	161.31	166.29	161.10	166.81	178.56	183.47
OCH_3	157.99	165.08	162.10	169.67	184.20	190.65
NH_2	176.26	185.34	184.94	194.67	206.57	214.26
CH_3	216.79	222.47	206.20	210.57	223.76	227.49
C_6H_5	222.11	227.42	232.29	237.35	259.55	258.95
$CH{=}CH_2$	226.21	232.70	225.09	234.57	245.77	251.74
$C{\equiv}CH$	273.67	275.34	267.80	269.99	286.10	287.59
CN	282.55	287.89	260.39	269.48	275.06	284.41
CHO	221.42	223.63	197.22	199.59	211.68	214.26
COOH	181.66	181.66	140.70	146.51	155.90	160.69
NO_2	283.16	284.38	244.74	242.78	258.14	255.49

Methods of Calculations

All computations used the VAMP program.[48] The geometries of the neutral compounds and their carbocations were fully optimized with AM1 and PM3. Solvent effects in aqueous solution at these levels were performed using the self-consistent reaction field (SCRF) method[49] available in the VAMP5.5 program.[50] The stabilization energies of the investigated carbocations are calculated from the following isodesmic[10] equation:

$$Ph_nC^+H_{3-n} + Ph_nCH_{3-n}X \rightarrow Ph_nC^+H_{2-n}X + Ph_nCH_{4-n},\ n = 0{-}2$$

Results and Discussion

The standard heats of formation of the neutral compounds and their carbocations are shown in Tables 1–4. Experimental heats of formation in comparison with AM1 and PM3 values are listed in Table 5. In Tables 6 and 7 the carbocation stabilization energies are presented. Comparison of stabilization energies with experimental and *ab initio* data is collected in Table 8. In Tables 9 and 10 the calculated C–X bond lengths on the neutral species and carbocations are listed. The C–X bond variations on going from neutral compounds to carbocations are given in Table 11.

Table 4. Heats of Formation (kcal/mol) of Carbocations at AM1 and PM3 Levels in H_2O

	C^+H_2X		PhC^+HX		Ph_2C^+X	
X	AM1	PM3	AM1	PM3	AM1	PM3
H	172.02	171.78	169.46	173.01	183.45	186.88
F	101.26	118.09	117.22	128.45	143.52	140.02
OH	84.75	86.64	107.56	111.04	130.44	134.57
OCH_3	89.99	92.74	113.01	118.24	142.93	146.03
NH_2	104.07	106.14	130.53	134.08	159.72	162.08
CH_3	147.01	149.22	155.48	158.41	180.28	178.62
C_6H_5	169.46	173.01	183.45	186.88	214.74	219.41
$CH{=}CH_2$	162.03	165.78	175.44	183.14	200.72	208.45
$C{\equiv}CH$	207.60	208.00	218.10	219.93	243.98	244.28
CN	205.04	209.15	203.58	210.73	228.20	235.23
CHO	143.85	143.77	142.38	141.56	164.36	164.37
COOH	100.98	93.90	85.68	89.30	109.98	112.27
NO_2	192.31	185.60	182.18	171.91	207.48	198.23

Table 5. Heats of Formation (kcal/mol) of Neutral Compounds and Their Carbocations at AM1 and PM3 Levels in Comparison with the Experimental Values[a]

molecules	AM1	error	PM3	error	exp
CH_4	−8.8	9.1	−13.0	4.9	−17.9
CH_3OH	−57.0	−8.9	−51.9	−3.8	−48.1
CH_3NH_2	−6.1	−0.6	−4.0	1.5	−5.5
CH_3CH_3	−17.4	2.8	−18.1	2.1	−20.2
$CH_3CH{=}CH_2$	6.6	1.7	6.4	1.5	4.9
CH_3CN	19.3	−1.6	23.3	2.4	20.9
CH_2COOH	−97.1	2.8	−99.4	0.5	−99.9
CH_3OCH_3	−51.9	−7.9	−46.9	−2.9	−44.0
$CH_3C{\equiv}CH$	43.4	−1.0	40.2	−42.	44.4
C^+H_3	252.4	−8.7	256.6	−4.5	261.0
C^+H_2F	180.4	−20.0	200.3	0.0	200.3
C^+H_2OH	161.3	−6.7	166.3	−1.7	168.0
$C^+H_2CH_3$	316.8	−2.2	222.5	3.5	219.0
$C^+H_2C_6H_5$	222.1	10.1	227.4	15.4	212.0
$C^+H_2CH{=}CH_2$	226.2	0.2	232.7	6.7	226.0
$C^+H_2C{\equiv}CH$	273.7	−7.3	275.3	−5.7	281.0
$C_6H_5C^+HCH_3$	206.2	6.1	210.6	10.5	200.1
$(C_6H_5)_2C^+CH_3$	223.8	10.2	227.5	13.9	213.6

[a] Reference 52.

Before going into a detailed discussion of our results, we consider first the comparison of experimental heats of formation of the neutral compounds and their carbocations and the calculated values shown in Table 5. The average errors in the cation heats of formation using AM1 and PM3 are 7.9 and 6.9 kcal/mol, respectively. These errors are lower in the neutral compounds. Therefore, AM1 and PM3 describe substituent effects at least qualtitatively well.

The amino group gives the most stabilization by effective π-electron donation to the empty p orbital of the cation center. At the other extreme, the nitro group is most destabilizing because of its strong σ- and π-electron-accepting nature. Hyperconjugation is responsible for a moderate stabilization by the methyl group. The X substituents have a smaller effect on stability for the Ph-substituted compounds due to reduced electronic demand.

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In other words, the effect of X is less pronounced because Ph already significantly stabilizes the cation. However, the effect of substituents on carbocation stabilities decreases with increasing number of phenyl groups attached to the central carbon as a result of repulsion between phenyl rings and substituents. This behavior has been observed before for the effect of substituents on the stability of C^+HX, C^+H_2X, CH_3C^+HX, and $(CH_3)_2C^+X$ systems (X = F, OH, NH_2, CN, and NC).[16] With the exception of the NO_2 group, the C−X bond lengths in carbocations are generally shorter than in the corresponding neutral species as a result of the π-interaction between substituents and the cation center. We can classify substituents into four categories: (1) lone pair electron donors (F, OH, OCH_3, and NH_2), (2) conjugated systems (C_6H_5, $CH{=}CH_2$, and $C{\equiv}CH$), (3) hyperconjugative groups (CH_3), and (4) σ- and π−acceptors (CN, CHO, COOH, and NO_2).

Lone Pair Groups. Despite their σ-withdrawing nature, F, OH, OCH_3, and NH_2 give large stabilizations, with the amino group being the most effective. The stability of these carbocations decreases with increasing substituent electronegativities. The stability order has been emphasized by both theoretical and experimental methods.[6,10,13,16,18,51] The reduction in the C−X bond lengths in the cation compared to the neutral species decreases with increasing electronegativity of the substituents. As stated before, the stabilizing effect of these groups of substituents decreases from primary to secondary to tertiary carbocations.

Conjugated Systems. These groups have double bonds which can resonate with the adjacent cation center. The stabilizing order is C_6H_5 > $CH{=}CH_2$ > $C{\equiv}CH$ in line with the ability of these substituents to donate their π-electrons. The extent of such π-interaction is reflected in the shortening of the C−X bond lengths in the cation compared to the neutral species, 0.111 > 0.096 > 0.080 Å, respectively. The same stability order was obtained experimentally from hydride ion affinities of these carbocations.[31b] The stabilities of this category are higher, and the effect of C_6H_5 and $CH{=}CH_2$ is comparable to that of OCH_3 and OH groups, respectively. Experimental investigations demonstrated the presence of such π-interactions in 1,1-diaryl-2-butynyl and butynyl cations.[34b] The substituent stabilization energies of these carbocations decrease with increasing number of phenyl rings at the cation center.

Table 6. Stabilization Energies (kcal/mol) of Carbocations at AM1 and PM3 Levels

	C^+H_2X		PhC_+HX		Ph_2C^+X	
X	AM1	PM3	AM1	PM3	AM1	PM3
F	−19.76	−5.50	−5.34	−4.32	−3.18	−0.74
OH	−42.79	−51.40	−18.14	−24.12	−13.34	−16.68
OCH_3	−51.30	−57.55	−21.10	−19.14	−13.40	−15.23
NH_2	−78.76	−80.23	−42.52	−40.58	−32.74	−29.68
CH_3	−26.93	−28.97	−10.14	−12.62	−6.08	−6.64
C_6H_5	−53.43	−56.26	−17.52	−18.75	−5.52	−10.58
$CH{=}CH_2$	−41.49	−43.27	−15.77	−13.33	−9.34	−8.44
$C{\equiv}CH$	−30.90	−34.45	−10.90	−12.96	−7.30	−7.14
CN	2.14	−4.97	5.95	9.43	6.30	6.93
CHO	1.85	−1.74	4.95	1.70	5.03	5.46
COOH	17.70	11.50	8.50	8.67	9.10	7.48
NO_2	31.99	30.75	20.48	12.91	19.66	18.80

Table 7. Stabilization Energies (kcal/mol) of Carbocations at AM1 and PM3 Levels in H_2O

	C^+H_2X		PhC^+HX		Ph_2C^+X	
X	AM1	PM3	AM1	PM3	AM1	PM3
F	−19.01	−14.34	−6.57	−10.66	0.16	−16.83
OH	−38.09	−46.67	−18.48	−28.45	−12.28	−20.08
OCH_3	−38.24	−44.80	−16.41	−22.93	−12.60	−21.59
NH_2	−68.85	−74.54	−42.42	−50.77	−34.48	−39.70
CH_3	−16.90	−18.31	−8.82	−15.62	−3.68	−11.87
C_6H_5	−25.84	−22.94	−2.37	−3.62	−18.23	−22.06
$CH{=}CH_2$	−26.04	−27.19	−11.32	−13.64	−15.17	−16.12
$C{\equiv}CH$	−15.98	−18.40	−4.84	−13.74	−7.10	−10.54
CN	8.97	4.16	6.04	0.79	4.53	−0.68
CHO	7.64	5.35	6.41	−1.79	−0.11	−5.61
COOH	22.93	14.19	11.76	6.36	1.96	−5.53
NO_2	29.68	27.82	18.87	9.69	12.35	2.54

Hyperconjugative Groups. The methyl group shows a moderate stabilizing effect due to its π-electron donation through hyperconjugation. It has been previously indicated that the ability of XH_3 (X = C, Si, Ge, and Sn) to hyperconjugate with the adjacent cation center decreases down the group.[51] This hyperconjugation is reflected in the reduction of the C−X bond lengths in the cations compared to the neutral counterparts. The methyl group effect also decreases with increasing crowding at the cation center. In the condensed phase, hyperconjugation is strong and increases the stability of the secondary and tertiary cations at PM3, but at AM1 the effect of the methyl group decreases as usual with increasing substituents.

***σ*- and *π*-Acceptors.** An inspection in Tables 6 and 7 indicates that these groups give a destabilizing effect but much less so than expected from their strong electron-

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Table 8. Comparisons of Stabilization Energies (kcal/mol) of C^+H_2X at AM1 and PM3 Levels and *ab Initio*[a] and Experimental Values

						/6-31G*//6-31G*				
X	AM1	PM3	STO-3G	3-21G//3-21G	3-21G*//3-21G*	HF	MP2	MP4SDT	QCISD(T)[b]	exp[c]
F	−19.8	−5.5	−32.1	−8.7	−2.1	−14.9	−25.3	−25.9	−17.8	−27 ± 3
OH	−42.8	−51.4	−66.0	−52.6	−47.8	−53.7	−66.0	−66.3	−60.7	−60−64
OCH_3	−51.3	−57.6								−69.0
NH_2	−78.8	−80.2	−93.8	−93.5	−93.3	−86.5	−100.0	−99.6	−95.6	−95−97
CH_3	−26.9	−29.0	−30.9	−29.1	−29.9	−29.5	−35.0	−35.5	−34.2	−37 ± 3
C_6H_5	−53.4	−56.3								−55.0
CN	2.1	−5.0				12.8 (9.9)[d]				10.0
CHO	1.9	−1.7				6.1[d]				

[a] Reference 18. [b] //MP2/6-31+G, ref 51. [c] Reference 6. [d] 4-31G//4-31G, ref 45.

Table 9. C−X Bond Lengths (Å) in Neutral Compounds and Their Carbocations at the AM1 Level

X	CH_3X	C^+H_2X	$PhCH_2X$	PhC^+HX	Ph_2CHX	Ph_2C^+X
F	1.375	1.271	1.382	1.314	1.390	1.334
OH	1.411	1.284	1.421	1.325	1.426	1.336
OCH_3	1.416	1.281	1.429	1.319	1.435	1.330
NH_2	1.435	1.293	1.446	1.316	1.453	1.330
CH_3	1.524	1.414	1.510	1.455	1.519	1.474
C_6H_5	1.481	1.370	1.491	1.410	1.502	1.437
$CH{=}CH_2$	1.476	1.380	1.486	1.418	1.497	1.440
$C{\equiv}CH$	1.427	1.347	1.435	1.382	1.444	1.401
CN	1.439	1.383	1.448	1.413	1.457	1.429
CHO	1.490	1.457	1.502	1.487	1.516	1.502
COOH	1.490	1.480	1.498	1.484	1.510	1.498
NO_2	1.500	1.503	1.524	1.499	1.546	1.525

Table 10. C−X Bond Lengths (Å) in Neutral Compounds and Their Carbocations at the PM3 Level

X	CH_3X	C^+H_2X	$PhCH_2X$	PhC^+HX	Ph_2CHX	Ph_2C^+X
F	1.351	1.265	1.359	1.306	1.368	1.327
OH	1.395	1.255	1.411	1.302	1.417	1.318
OCH_3	1.404	1.257	1.429	1.302	1.432	1.316
NH_2	1.473	1.295	1.482	1.321	1.487	1.332
CH_3	1.504	1.412	1.514	1.456	1.523	1.475
C_6H_5	1.486	1.367	1.497	1.411	1.509	1.439
$CH{=}CH_2$	1.480	1.379	1.491	1.421	1.501	1.438
$C{\equiv}CH$	1.433	1.353	1.440	1.390	1.449	1.408
CN	1.440	1.375	1.448	1.412	1.460	1.429
CHO	1.499	1.461	1.502	1.495	1.528	1.516
COOH	1.503	1.479	1.498	1.497	1.524	1.512
NO_2	1.514	1.636	1.524	1.541	1.556	1.557

accepting character. Consequently, these groups when attached to a cation center act as π-electron donors. The cyano group is more electron withdrawing than CF_3. Despite this fact, a number of cations have been generated with the cyano group directly attached to the cation center.[32−38] This stability was attributed to the mesomeric interaction involving the cyano group, which is absent in CF_3.[3] The destabilization of the CN group was estimated to be 9.9 kcal/mol compared to 37.3 kcal/mol destabilization for CF_3.[41] The geometric difference between the neutral compounds and the corresponding carbocations indicates the presence of a significant π-interaction between these groups (CN, CHO, and COOH) and the vacant p orbital at the cation center. In these cations, the C−X bond lengths are significantly shorter than in the neutral species with the reduction order CN > CHO > COOH indicating the degree of π-contribution. The strongest electron-withdrawing group, NO_2, give the most destabilized carbocations in the whole series. In this case, the C−X bond lengths in the carbocations are usually longer than in the neutral species. Solvolytic studies[35c] have shown that a cyano group bonded to a cationic center stabilizes it through resonance interactions, despite the strong inductive electron-withdrawing effect. This is supported by ^{15}N NMR spectroscopy of the cyanodiarylmethyl cation in which electron-donor substituents shielded both the cyano nitrogen and C^+.[32] The importance of mesomeric charge delocalization increases with increasing phenyl substitution. This may explain the experimental accessibility of Ph_2C^+X (X = CN, COR, and NO_2).[32−38]

Table 11. C−X Bond Length Differences (Å) between Neutral Compounds and Their Carbocations at AM1 and PM3 Levels

	C^+H_2X		PhC^+HX		Ph_2C^+X	
X	AM1	PM3	AM1	PM3	AM1	PM3
F	0.104	0.086	0.068	0.053	0.056	0.041
OH	0.127	0.140	0.096	0.109	0.090	0.099
OCH_3	0.135	0.147	0.110	0.127	0.105	0.116
NH_2	0.142	0.178	0.130	0.161	0.123	0.155
CH_3	0.110	0.092	0.055	0.058	0.045	0.048
C_6H_5	0.111	0.119	0.081	0.086	0.065	0.070
$CH{=}CH_2$	0.096	0.101	0.068	0.070	0.057	0.063
$C{\equiv}CH$	0.080	0.080	0.053	0.050	0.043	0.041
CN	0.056	0.056	0.035	0.036	0.028	0.031
CHO	0.0333	0.038	0.015	0.007	0.014	0.012
COOH	0.010	0.024	0.014	0.001	0.012	0.012
NO_2	−0.003	−0.122	0.025	−0.017	0.021	−0.001

Solvent Effects in Aqueous Solution. Inspection of Tables 6 and 7 indicates that, with the exception of X = F, the stabilization energies of primary carbocations in the condensed phase are lower than in the gas phase. On the other hand, for most tertiary cations the stabilization energies are higher in solution than in the gas phase. The seconday carbocations are of intermediate behavior between the two extremes. In the condensed phase, the stabilization energies of electron-withdrawing-substituted carbocations increase. This may reflect the experimental observation of these carbocations in solution.[32−38]

Comparison of Experimental and Theoretical Stabilization Energies. Our calculated stabilization energies are about 15.0 kcal/mol lower than the experimental values, but the agreement with different *ab initio* data is good. The experimental stability of $C_6H_5C^+H_2$ is in a good agreement with our calculated values (Table 8).

Conclusions

From this study we can conclude the following. (1) The substituent stabilization energies of the $Ph_nC^+H_{2-n}X$ carbocations decreases with increasing number of phenyl groups because of increasing electron crowding at the cation center. (2) The amino group is the most stabilizing, and the nitro group is the most destabilizing. (3) Lone pair interaction and double-bond conjugation give strong stabilization, while hyperconjugation is moderate. (4) The electron-withdrawing groups (CN, CHO, and COOH) destabilize carbocations but to a much lower extent than would be expected from only their electron-withdrawing effect. This can be attributed to the fact that these substituents act as π-donors when directly attached to a cation center. (5) Geometric differences between the neutral species and their carbocations, particularly the C−X bond lengths, reflect the strength of the π-interactions between substituents and the empty p orbital on the cation center. (6) The performance of AM1 and PM3 methods is qualitatively good and can reproduce the experimental findings. (7) In solution, the stabilities of electron-withdrawing-substituted carbocations increase.

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