Reference Data

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^{13}C NMR Chemical Shift Assignments for Some Carbazole Derivatives

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^{13}C NMR chemical shift assignments have been made for a series of 1-substituted carbazoles, 8-substituted 1,2,3,4-tetrahydrocarbazoles, 1-substituted benzo[*a*]-carbazoles and 6-substituted dibenzo-[*c*,*g*]carbazoles. Single examples were examined of other classes of substituted carbazoles: 3-butylcarbazole and its tetrahydro precursor 6-butyl-1,2,3,4-tetrahydrocarbazole, 8-butyl- and 8,10-diethylbenzo[*a*]carbazoles and their 5,6-dihydro precursors, dibenzo[*a*,*i*]carbazole and its 5,6,7,8-tetrahydro precursor, benzo[*c*]-carbazole and its 6-chloro derivatives and 5,6-dihydrobenzo[*c*]carbazole and 5,6,8,9-tetrahydrodibenzo[*c*,*g*]carbazole and their *N*-methyl derivatives. In addition, the *N*-(1-pyrrolidinomethyl) derivatives of carbazole, 1,2,3,4-tetrahydrocarbazole, benzo[*c*]carbazole and dibenzo[*c*,*g*] carbazole were also studied.

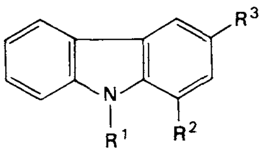
KEY WORDS ^{13}C NMR Chemical shift assignments Carbazole derivatives.

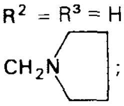
INTRODUCTION

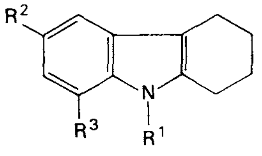
Although several publications are available on the ^{13}C NMR chemical shift assignments of carbazoles, these mainly deal with *N*-substituted or symmetrically substituted compounds,[1–4] and the amount of data for unsymmetrical *C*-substituted derivatives is limited.[5,6] We now report the analyses of the ^{13}C NMR spectra of a range of unsymetrically substituted carbazoles, including some benzo and dibenzo derivatives, which allow considerable insight into the pattern of chemical shifts in these compounds.

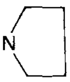
EXPERIMENTAL

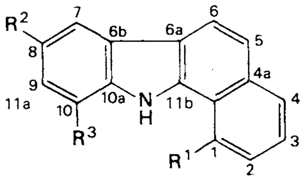
The compounds studied were prepared by procedures described elsewhere.[7,8] Thus, **3**–**11**, **16**, **17**, **31**, **36** and **37** were prepared via lithiation of the respective aminal derivatives **2**, **14**, **30** and **35**, and **19**–**21** were prepared from benzo[*a*]carbazole-1,11-dianion.[7] 6-Chlorobenzo[*c*]carbazole (**31**) was available only as a mixture containing a smaller amount of the 8-isomer, but the signals due to the major component were readily identi-



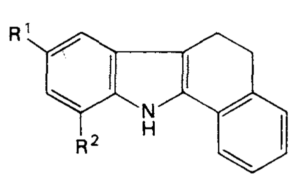
1 $R^1 = R^2 = R^3 = H$
2 $R^1 = CH_2N$  $; R^2 = R^3 = H$
3 $R^1 = R^3 = H; R^2 = CH_3$
4 $R^1 = R^3 = H; R^2 = CH_2CH_2CH_2CH_3$
5 $R^1 = R^3 = H; R^2 = OH$
6 $R^1 = R^3 = H; R^2 = Cl$
7 $R^1 = R^3 = H; R^2 = NO_2$
8 $R^1 = R^3 = H; R^2 = CO_2H$
9 $R^1 = R^3 = H; R^2 = COC_6H_5$
10 $R^1 = R^3 = H; R^2 = COC_6H_4-p-CH_3$
11 $R^1 = R^3 = H; R^2 = C(OH)(C_6H_5)_2$
12 $R^1 = R^2 = H; R^3 = CH_2CH_2CH_2CH_3$



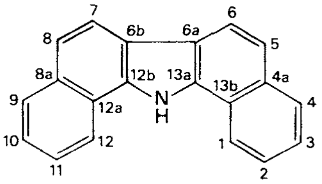
13 $R^1 = R^2 = R^3 = H$
14 $R^1 = CH_2N$  $; R^2 = R^3 = H$
15 $R^1 = R^3 = H; R^2 = CH_2CH_2CH_2CH_3$
16 $R^1 = R^2 = H; R^3 = D$
17 $R^1 = R^2 = H; R^3 = CO_2H$



18 $R^1 = R^2 = R^3 = H$
19 $R^1 = D; R^2 = R^3 = H$
20 $R^1 = Cl; R^2 = R^3 = H$
21 $R^1 = CO_2H; R^2 = R^3 = H$
22 $R^1 = R^3 = H; R^2 = CH_2CH_2CH_2CH_3$
23 $R^1 = H; R^2 = R^3 = CH_2CH_3$



24 $R^1 = R^2 = H$
25 $R^1 = CH_2CH_2CH_2CH_3; R^2 = H$
26 $R^1 = R^2 = CH_2CH_3$



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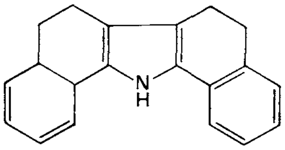

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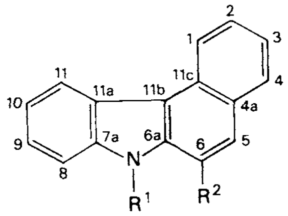
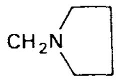
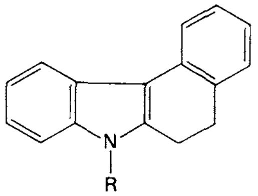
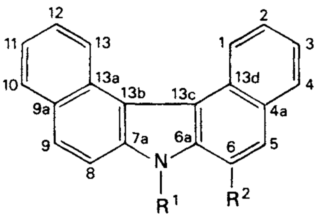


29 $R^1 = R^2 = H$
30 $R^1 = CH_2N$  $; R^2 = H$
31 $R^1 = H; R^2 = Cl$

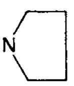


32 $R = H$
33 $R = CH_3$

Reference Data

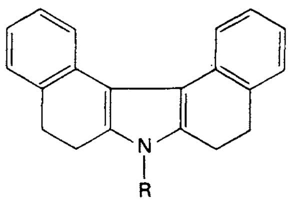


34 $R^1 = R^2 = H$

35 $R^1 = CH_2N$  ; $R^2 = H$

36 $R^1 = H; R^2 = Cl$

37 $R^1 = H; R^2 = CO_2H$



38 R = H

39 $R = CH_3$

fied as being those of the 6-isomer by chemical shift comparison with **6** and **36**. 3-Butylcarbazole (**12**), benzocarbazoles **18**, **22**, **23** and **29** and dibenzocarbazoles **27** and **34** were prepared by dehydrogenation of the analogous hydro precursors **15**, **24–26**, **32**, **28** and **38**, respectively.[8] The *N*-methyl derivatives **33** and **39** were prepared by treatment of **32** and **38**, respectively, with sodium hydride and iodomethane in THF. The syntheses of **16** and **19** have not been described elsewhere, but the procedures used were identical with those for the analogous compounds except that D_2O was used as the electrophile. The degree of deuteriation achieved was determined by ^1H NMR spectrometry as being approximately 65% for **16** and 100% for **19**.

8-Deuterio-1,2,3,4-tetrahydrocarbazole (16)

A solution of 0.51 g (2 mmol) of 9-(1-pyrrolidinomethyl)-1,2,3,4-tetrahydrocarbazole (**14**) in 60 ml of dry hexane was cooled to −78 °C under an argon atmosphere, and a solution of 1.7 M *tert*-butyllithium (1.8 ml, 1.5 equiv.) in pentane was added dropwise to the resulting white suspension. The mixture was allowed to warm to room temperature, giving a clear, colourless solution which was stirred for a further 16 h as a bright yellow precipitate was formed. The reaction mixture was then cooled to −78 °C and 20 ml of dry THF were added to dissolve the solid. D_2O (0.12 ml, 6 mmol) was added and the mixture was allowed to warm to room temperature. The solvent was removed under vacuum and the residue was treated with 60 ml of 1 M hydrochloric acid. The resulting mixture was heated on a steam-bath for 30 min to ensure complete hydrolysis of the pyrrolidinomethyl group. The product was extracted into ethyl acetate (3 x 50 ml), dried ($MgSO_4$) and the solvent was removed under vacuum to give a solid which was purified by chromatography on alumina. Elution with benzene–hexane (1 : 1) gave 0.31 g (90%) of a mixture containing approximately 65% of **16** and 35% of undeuteriated **13**. Recrystallization from benzene gave material identical with **13** by TLC and melting point (118–120 °C). ^1H NMR (DMSO-d_6), δ 1.80 (bs, 4 H, CH_2), 2.64 (d, 4 H, CH_2), 6.95 (m, 1.35 H, arom.), 7.30 (m, 2 H, arom.) and 10.60 (s, 1 H, N–H).

1-Deuteriobenzo[*a*]carbazole (19)

To a solution of 0.37 g (1.77 mmol) of benzo[*a*]carbazole (**18**) in 20 ml of dry diethyl ether at room temperature was added dropwise a solution of 1.7 ml of 2.5 M n-butyllithium (4.43 mmol) in hexane. After 28 h the colourless solution was treated with 0.1 ml (5 mmol) of D_2O and stirred for a further 15 min. The mixture was then diluted with further diethyl ether and acidified with dilute hydrochloric acid. After being washed twice with water and dried ($MgSO_4$), the solvent was removed to give 0.34 g (92%) of **19**, which was recrystallized from ethanol to give material identical with **18** by TLC and melting point (227–229 °C). ^1H NMR (DMSO-d_6), δ 7.22 (dxt, 1 H), 7.41 (dxt, 1 H), 7.52 (dxt, 1 H), 7.45–7.72 (m, 3 H), 8.01 (dxd, 1 H), 8.14 (dxd, 1 H), 8.19 (dxd, 1 H) and 12.42 (s, 1 H, N–H).

NMR spectra

The ^{13}C NMR spectra were all measured at 20 °C in DMSO-d_6 solution at 50 MHz using a Varian XL 200 NMR spectrometer. Pulse widths were optimized for estimated values of T_1 using Ernst's equation, with no delay between acquisition. Values were recorded relative to tetramethylsilane and have a reproducibility of ±0.1 ppm.

Table 1. ^{13}C NMR chemical shifts of carbazoles

Compound	C-1	C-2	C-3	C-4	C-4a	C-4b	C-5	C-6	C-7	C-8	C-8a	C-9a
1[a]	110.9	125.4	118.4	120.1	122.4	122.4	120.1	118.4	125.4	110.9	139.7	139.7
2	109.8	125.5	118.9	119.9	122.1	122.1	119.9	118.9	125.5	109.8	140.8	140.8
3	120.0	125.9	118.6[b]	117.5	122.0	122.8	120.1	118.4	125.2	111.0	139.8	139.1
4	124.8	124.9	118.5[b]	117.5	122.1	122.7	120.0	118.3	125.2	111.0	139.7	138.4
5	143.1	110.0	119.1[b]	111.2	123.9	122.8	120.1	118.2	125.1	111.0	139.5	129.4
6	115.2	126.2	119.4[b]	118.9	124.4	122.4	120.5	119.1	124.7	111.6	139.9	136.5
7	131.6	121.6	118.2[b]	127.9	121.4	127.1	120.5	120.5	127.2	112.6	140.6	132.9
8	112.6	127.5	117.9[b]	126.1	121.6	124.1	120.1	119.2	125.2	112.2	140.2	139.0
9	118.8	129.9	117.6[b]	125.8	121.5	124.5	120.2	119.5	126.2	112.3	140.5	138.7
10	119.0	129.6	117.6[b]	125.5	121.5	124.4	120.2	119.5	126.2	112.2	140.5	138.7
11	130.2	125.2	117.4[b]	118.3	121.8	123.2	119.7	119.2	125.2	111.7	139.5	137.5
12	110.5[b]	126.1	132.3	119.2	122.3	122.4	119.9	118.1	125.2	110.8	140.0	138.1
13	23.0[c]	22.8[c]	22.7[c]	20.6	108.0	127.3	117.0	117.9	119.9	110.4	135.6	134.3
14	21.7[d]	22.8[d]	22.7[d]	20.6	108.2	126.9	117.0	118.3	120.1	109.5	136.8	135.6
15	23.1[e]	23.0[e]	22.9[e]	20.7	107.6	127.5	116.2	131.6	120.7	110.1[b]	134.2[h]	134.3[h]
16	23.0[f]	22.8[f]	22.7[f]	20.6	108.0	127.3	117.0	117.9[b]	119.8	[i]	135.6	134.3
17	22.8[g]	22.8[g]	22.7[g]	20.3	108.4	128.8	122.6	117.4[b]	122.2	112.5	136.2	134.7

[a] Assignments based on Ref. 3.

[b] Unequivocal assignment due to absence of $^3J(CH)$ component.

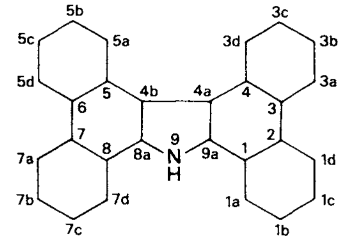
[c–h] Assignments may be interchanged.

[i] Deuteriated carbon signal not observed.

Reference Data

RESULTS AND DISCUSSION

The results obtained are given in Tables 1–6. Chemical shift assignments are based on those of carbazole[3] and were made on the basis of substituent and *N*-alkylation effects, coupling information and by comparison with model compounds. For comparative purposes the data are all tabulated using the carbazole numbering (structure A), although the correct numbering systems for the benzo and dibenzo derivatives are also given in the tables.



A

For 3–11 the spectral data are in consistent agreement with the site of substitution being at C-1. The chemical shift assignments for the C-3 carbon resonances were obtained unequivocally from the coupled spectra due to the absence of a three-bond [^{3}J(CH)] coupling component. All of the other CH carbon signals displayed this feature, with a coupling close to the benzene value of 7.63 Hz.[9]

The chemical shift assignments for 1,2,3,4-tetrahydrocarbazole (**13**) are derived from the 8-deutero derivative (**16**), which showed a small upfield shift due to deuteriation for the C-7 carbon resonance, and a disappearance of the C-8 signal. The C-6 carbon was unequivocally identified due to the absence of a ^{3}J(CH) component. The assignments obtained for C-6 and C-7 differ from those in the literature;[10] the possibility that this was a result of solvent effects was excluded by a re-run of the spectra of **13** and **16** in CDCl$_3$, the solvent used in the earlier work.[10]

The chemical shift assignments for benzo[*a*]carbazole (**18**) and dibenzo[*a*,*i*]carbazole (**27**) are based on a combination of those of carbazole, 1-aminonaphthalene and

Table 2. ^{13}C NMR chemical shifts of benzo[*a*]carbazoles

	C-1[a]	C-2	C-3	C-4	C-4a	C-4b	C-5	C-6	C-7	C-8	C-8a	C-9a	C-1a	C-1b	C-1c	C-1d
Compound	C-11b[b]	C-4a	C-5	C-6	C-6a	C-6b	C-7	C-8	C-9	C-10	C-10a	C-11a	C-1	C-2	C-3	C-4
18	121.3	131.9	119.1	119.4[c]	117.3	123.2	119.7	119.1	124.4	111.3	138.7	135.2	121.8	125.4	125.1	128.5[d]
19	121.2	131.9	119.1	119.4[c]	117.3	123.2	119.7	119.1	124.4	111.3	138.7	135.2	[f]	125.2	125.1[c]	128.5[d]
20	119.6	132.3	119.3	120.4[c]	118.9	121.8	120.0	119.5	125.0	112.5	138.6	134.1	127.6	126.8	124.9[c]	128.0[d]
21	120.2	132.9	119.4	120.1[c]	118.7	122.3	120.1	119.7	125.3	112.1	137.9	133.3	126.4	130.5	123.8[c]	134.4[d]
22	121.3	131.8	118.8[e]	119.4[c]	117.1	123.3	118.7[e]	133.0	125.2	111.0[c]	137.2	135.4	121.8	125.2	124.9	128.4[d]
23	121.5	131.8	118.9	119.4[c]	117.7	123.2	115.5	134.8	123.8	126.8	135.9	135.3	122.3	125.0	124.8	128.4[d]
24	129.3	133.2	29.1	19.4	110.8	126.9	118.4	118.8	121.6	111.4	137.2	135.8	120.9	126.6	126.4	128.2[d]
25	129.2	133.2	29.1	19.3	110.4	126.9	117.3	132.6	122.5	110.0[c]	135.7	135.7	120.7	126.5	126.2	128.1[d]
26	129.5	133.1	29.2	19.5	111.1	126.8	114.2	134.5	121.2	126.8	134.5	135.7	121.3	126.3	126.0	128.0[d]

[a] First row: carbazole numbering system (see structure A).
[b] Second row: benzo[*a*]carbazole numbering system (see structures **18–23**).
[c] Unequivocal assignment due to absence of ^{3}J(CH) component.
[d] Unequivocal assignment due to the presence of two ^{3}J(CH) components.
[e] Assignments may be interchanged.
[f] Deuteriated carbon signal not observed.

Table 3. ^{13}C NMR chemical shifts of dibenzo[*a*,*i*]carbazoles

	C-1[a]	C-2	C-3	C-4	C-4a	C-4b	C-5	C-6	C-7	C-8	C-8a	C-9a	1a/7d	1b/7c	1c/7b	1d/7a
Compound	C-13b[b]	C-4a	C-5	C-6	C-6a	C-6b	C-7	C-8	C-8a	C-12a	C-12b	C-13a	C-1/12	C-2/11	C-3/10	C-4/9
27	121.7	131.4	119.9	119.2[c]	118.4	118.4	119.2[c]	119.9	131.4	121.7	134.0	134.0	121.8	125.5	124.8	128.5[d]
28	128.2	129.6	29.2	19.6	117.7	117.7	19.6	29.2	129.6	128.2	134.1	134.1	119.4	126.4	124.5	127.9[d]

[a] First row: carbazole numbering system (see structure A).
[b] Second row: dibenzo[*a*,*i*]carbazole numbering system (see structure **27**).
[c] Unequivocal assignment due to absence of ^{3}J(CH) component.
[d] Unequivocal assignment due to presence of two ^{3}J(CH) components.

Table 4. ^{13}C NMR chemical shifts of benzo[*c*]carbazoles

	C-1[a]	C-2	C-3	C-4	C-4a	C-4b	C-5	C-6	C-7	C-8	C-8a	C-9a	C-3a	C-3b	C-3c	C-3d
Compound	C-6[b]	C-5	C-4a	C-11c	C-11b	C-11a	C-11	C-10	C-9	C-8	C-7a	C-6a	C-4	C-3	C-2	C-1
29	113.4[c]	126.8	129.4	128.4	113.9	122.9	121.5	119.5	126.8	111.6	138.6	137.4	129.1[d]	122.5	122.8	123.9
30	112.1	126.8[e]	129.0	128.4	113.8	122.6	121.5	119.9	127.0[e]	110.5	139.8	138.4	129.0[d]	122.8	122.8	124.0
31	117.5	127.1	128.8	127.5	115.9	123.0	121.8	120.1	127.0	112.2	138.9	134.2	128.4[d]	123.4	123.4	124.7
32	21.7	28.9	133.8	132.9	108.6	124.2	119.7	118.6	120.5	111.5	138.2	136.3	127.9[d]	121.4	126.7	123.7
33	19.5	28.6	133.5	132.6	108.5	123.8	120.0	118.8	120.6	109.8	139.5	137.3	127.8[d]	121.4	126.7	123.7

[a] First row: carbazole numbering system (see structure A).
[b] Second row: benzo[*c*]carbazole numbering system (see structures **29–31**).
[c] Unequivocal assignment due to absence of ^{3}J(CH) component.
[d] Unequivocal assignment due to presence of two ^{3}J(CH) components.
[e] Assignments may be interchanged.

Reference Data

Table 5. ^{13}C NMR chemical shifts of dibenzo[*c*,*g*]carbazoles

	C-1[a]	C-2	C-3	C-4	C-4a	C-4b	C-5	C-6	C-7	C-8	C-8a	C-9a	3a/5d	3b/5c	3c/5b	3d/5a
Compound	C-6[b]	C-5	C-4a	C-13d	C-13c	C-13b	C-13a	C-9a	C-9	C-8	C-7a	C-6a	C-4/10	C-3/11	C-2/12	C-1/13
34	113.6[c]	126.3	128.7	129.4	116.2	116.2	129.4	128.7	126.3	113.6[c]	136.6	136.6	129.3[d]	122.9	125.4	124.2
35	112.2	126.2	128.2	129.4	115.9	115.9	129.4	128.2	126.2	112.2	137.6	137.6	129.1[d]	123.1	125.4	124.2
													128.6[d]	123.7	124.2	124.2
36	117.6	127.2	129.6	127.3	118.2	116.5	129.6	128.5	125.7	113.8	137.2	133.2	129.3[d]	123.3	125.6	124.2
													130.7[d]	123.5	129.9	124.1
37	115.0	127.7	128.3	130.5	115.4	117.7	129.5	128.0	126.7	114.5	137.4	134.3	129.2[d]	123.0	125.3	124.1
38	21.7	29.9	133.7[e]	133.9[e]	113.5	113.5	133.7[e]	133.9[e]	29.9	21.7	131.0	131.0	127.9[d]	122.4	126.1	123.5
39	20.1	29.6	133.6[f]	133.5[f]	113.4	113.4	133.5[f]	133.6[f]	29.6	20.1	132.9	132.9	127.8[d]	122.4	126.1	123.6

[a] First row: carbazole numbering system (see structure A).

[b] Second row: dibenzo[*c*,*g*]carbazole numbering system (see structures **34**–**37**).

[c] Unequivocal assignment due to absence of ^3J(CH) component.

[d] Unequivocal assignment due to presence of two ^3J(CH) components.

[e,f] Assignments may be interchanged.

Table 6. ^{13}C NMR of substituent groups

Compound	Chemical shifts and assignments
2	23.1 (CH_2), 50.9 (CH_2N), 60.6 (NCH_2N)
3	16.9 (CH_3)
4	13.8 (CH_3), 22.1 (CH_2), 30.6 (CH_2), 31.7 (CH_2)
8	167.9 (CO_2H)
9	128.4 (C-2′, 6′), 129.1 (C-3′, 5′),[a] 131.7 (C-4′), 138.6 (C-1′), 194.2 (CO)
10	128.9 (C-2′, 6′), 129.4 (C-3′, 5′), 135.7 (C-4′), 142.1 (C-1′), 193.8 (CO)
11	81.7 (COH), 126.8 (C-4′), 127.5 (C-2′, 6′), 127.8 (C-3′, 5′),[a] 146.6 (C-1′)
12	13.8 (CH_3), 22.1 (CH_2), 30.6 (CH_2), 31.7 (CH_2)
14	23.0 (CH_2), 50.9 (CH_2N), 60.6 (NCH_2N)
15	13.8 (CH_3), 21.9 (CH_2), 34.3 (CH_2), 35.4 (CH_2)
17	168.1 (CO_2H)
21	171.7 (CO_2H)
22	13.8 (CH_3), 21.8 (CH_2), 34.1 (CH_2), 35.1 (CH_2)
23	14.7 (CH_3), 16.5 (CH_3), 23.9 (CH_2), 28.5 (CH_2)
25	13.9 (CH_3), 21.9 (CH_2), 34.1 (CH_2), 35.3 (CH_2)
26	14.8 (CH_3), 16.6 (CH_3), 23.9 (CH_2), 28.6 (CH_2)
30	23.0 (CH_2), 50.8 (CH_2N), 60.5 (NCH_2N)
33	29.1 (CH_3)
35	23.0 (CH_2), 50.7 (CH_2N), 60.4 (NCH_2N)
37	167.7 (CO_2H)
39	29.7 (CH_3)

[a] Unequivocal assignment due to absence of ^3J(CH) component.

phenanthrene,[11] and are confirmed by the predictable substituent shifts seen for the derivatives **19**–**23**. Assignments for benzo[*c*]carbazole and dibenzo[*c*,*g*]- carbazole (**29** and **34**) were similarly obtained from a combination of those of carbazole, 2-aminonaphthalene and phenanthrene.[11]

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