

The Molecular Structures of Dibut-3-enylzinc and Dipent-4-enylzinc by Gas Electron Diffraction. Evidence for Weak Intramolecular Metal/CC Double-bond Interactions

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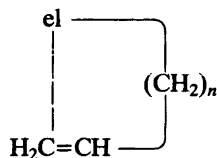
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The gas electron diffraction data of dibut-3-enylzinc and dipent-4-enylzinc have been recorded with nozzle temperatures of about 25 and 45 °C respectively. About 80 % of the hydrocarbon chains in gaseous dibut-3-enylzinc are found to be in the coiled back *gauche*, *syn* conformation, which brings the CC double bond into the vicinity of the Zn atom; $Zn \cdots C(4) = 315(6)$ pm. We assume that the preponderance of the coiled back conformation is due to metal/CC double-bond interactions and estimate the interaction energy to be about $-\Delta G^\circ = 4.5$ kJ mol⁻¹. In gaseous dipent-4-enylzinc at least 80 % of the hydrocarbon chains are found in one of the two coiled back conformations (*gauche*₊, *gauche*₋, *antichinal*₊ or *gauche*₊, *gauche*₋, *syn*). The distance from Zn to the nearest of the two unsaturated C atoms is $Zn \cdots C(4) = 300(8)$ pm. The estimated interaction energy is $-\Delta G^\circ = 6$ kJ mol⁻¹ or greater.

It is generally believed that complexes between derivatives of main group metals and alkenes are formed as intermediates when alkenes are inserted into metal-hydrogen or metal-carbon bonds.¹ Such complexes appear to be very unstable with respect to dissociation and/or rearrangement; no stable complex has been isolated and structural information is lacking.

Evidence for intramolecular metal/CC double-bond interactions has, however, been obtained

by spectroscopic (¹H NMR and IR) and molecular weight studies on compounds in which a vinyl group is attached to the metal atom through a polymethylene chain:



$el = Li, \frac{2}{3} Zn, \frac{1}{3} Al,^{4,5}$ and $n = 2, 3$ or 4 .

In this article we describe the results of gas electron diffraction studies of dibut-3-enylzinc and dipent-4-enylzinc. For both molecules the predominant, if not exclusive, conformation of the hydrocarbon chains is one which brings the double bond into contact with the metal atom.

EXPERIMENTAL

Dibut-3-enylzinc(I)⁶ and dipent-4-enylzinc(II)⁷ were synthesized by published procedures.

The electron scattering patterns were recorded on Balzers Eldigraph KDG-2. In order to keep the temperature at a minimum we used a convergent beam geometry with a nozzle with a wide opening.⁸ With this arrangement we are able to record the scattering pattern with reservoir pressures as low as 1 mm Hg.⁸ The data for I

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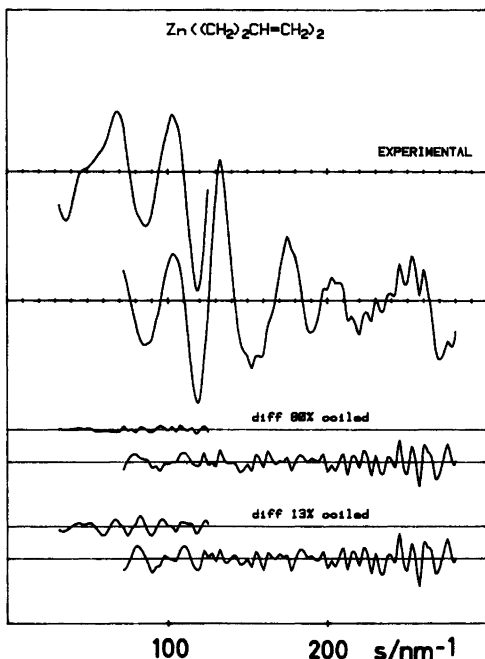


Fig. 1. Dibutenylzinc. Above: Average experimental intensity curves, $sI_m(s)$, for camera distances equal to 50 cm ($s=32.5$ to 125 nm $^{-1}$, four plates) and 25 cm ($s=72.5$ to 280 nm $^{-1}$, four plates). Below: Difference curves (experimental-theoretical).

were recorded with a nozzle temperature of about 25 °C, the data for II with a nozzle temperature of about 45 °C. Exposures were made with nozzle-to-plate distances of 50 and 25 cm. The plates were photometered and the data reduced by standard procedures at the University of Oslo. Scattering factors were taken from Ref. 9.

STRUCTURE REFINEMENTS

Structure refinements were carried out at Oregon State University using the program library developed by Ken and Lise Hedberg.

Dibut-3-enylzinc(I). A model of a molecular fragment containing the metal atom and one hydrocarbon chain is shown in Fig. 3. A recent GED study of 1-butene at room temperature¹⁰ found the gas to be a mixture of planar *syn* conformers with dihedral angle $\tau(C(1)C(2)C(3)C(4))=0^\circ$ and *anticlinal* (*skew*) conformers with $\tau=\pm 120^\circ$. Similarly a GED

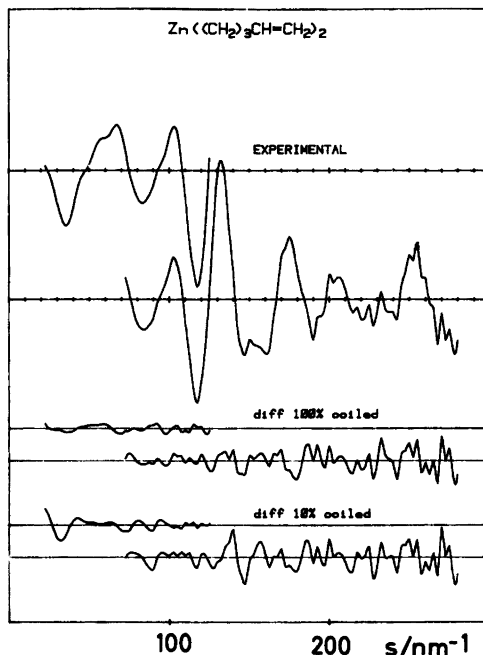


Fig. 2. Dipentylzinc. Above: Average experimental intensity curves, $sI_m(s)$, for camera distances equal to 50 cm ($s=22.5$ to 125 nm $^{-1}$, four plates) and 25 cm ($s=72.5$ to 280 nm $^{-1}$, three plates). Below: Difference curves (experimental-theoretical).

study of dipropylzinc¹¹ found the gas to consist of conformers with the hydrocarbon chains in the planar *anti* conformation $\tau(ZnC(1)C(2)C(3))=180^\circ$ or in the *gauche* conformation, $\tau=\pm 60^\circ$.

Depending on the dihedral angles around the C(1)–C(2) and C(2)–C(3) bonds the molecular fragment shown in Fig. 3 may adapt 3·3=9 different conformations. One of these is the all-planar *anti, syn* conformation, the remaining eight form mirror image pairs that cannot be distinguished by GED. Of the five distinct conformations, the *gauche, syn* conformation shown in the Figure provides the shortest distance between the metal atom and the olefinic carbon atoms. We shall refer to this as the “coiled back” conformation.

We first assumed that all hydrocarbon chains in gaseous dibut-3-enylzinc are in the coiled back, *g, s*, conformation, presumably stabilized through metal/double bond interactions.

The structure of the CZnC₄ backbone shown in Fig. 3 is determined by the four bond distances

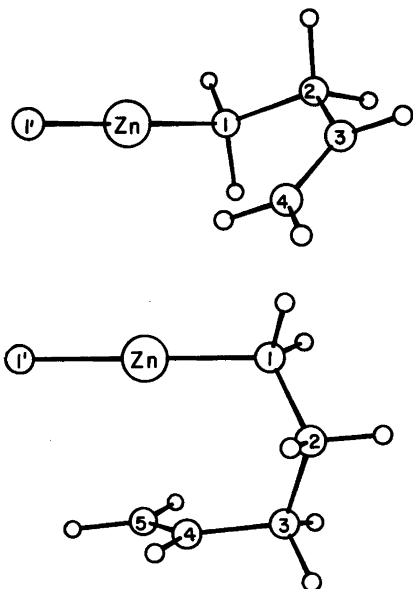


Fig. 3. Above: Molecular fragment of dibutenylzinc showing the predominant, coiled back (*gauche*, *syn*) conformation of the hydrocarbon chain. Below: Molecular fragment of dipentenylzinc showing the predominant, coiled back (*gauche*₊, *gauche*₋, *anticlinal*₊) conformation of the hydrocarbon chain.

Zn-C, C(1)-C(2), C(2)-C(3) and C(3)=C(4), the valence angles $\angle\text{CZnC}$, $\angle\text{ZnCC}$, $\angle\text{C(1)C(2)C(3)}$, $\angle\text{C(2)C(3)C(4)}$, and the dihedral angles $\tau(\text{C(1)-C(2)})$ and $\tau(\text{C(2)-C(3)})$. Initial structure refinements were carried out on models with $\angle\text{CZnC}$ less than 180° . Such models, however, failed to reproduce a small but distinct shoulder at 3.9 Å in the experimental radial distribution curve (Fig. 4). This shoulder was therefore assigned to the C(1)⋯C(1') distance in a linear CZnC fragment, and in subsequent refinements $\angle\text{CZnC}$ was fixed at 180° .

In their study of the long chain alkane C₁₆H₃₂, Fitzwater and Bartell¹² found that nonbonded CC distances beyond 1,6 and nonbonded CH distances beyond 1,5 could be neglected when theoretical intensity curves were calculated. When calculating theoretical intensity curves for the various models of I we included all ZnC and ZnH distances and all CC and CH distances between atoms in the same chain. Of the large number of distances between atoms in different chains we included only C(1)⋯C(1'), C(1)⋯C(2'), C(2)⋯C(2') and C(1)⋯H(1'). The C(2)⋯C(2') was calculated under the assumption that the dihedral angle $\tau[\text{C(2)C(1)C(1')C(2')}]$ is 120° and assigned an amplitude of $I=0.30$ Å. This means that no further assumptions regarding the relative positions of the two chains need to be made; each of the two chains may be regarded as

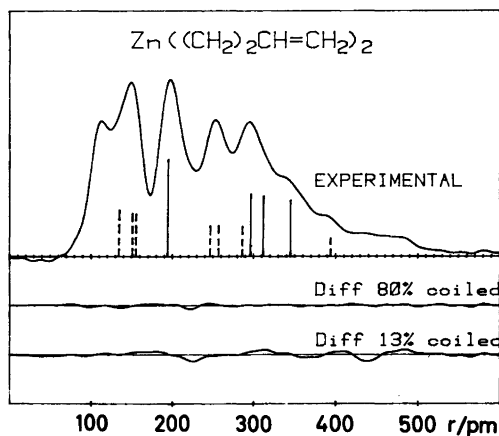


Fig. 4. Above: Experimental radial distribution curve for dibutenylzinc. Artificial damping constant $k=0.25$ pm². ZnC distances are indicated by bars, major CC distances by stippled bars. Below: Difference curves.

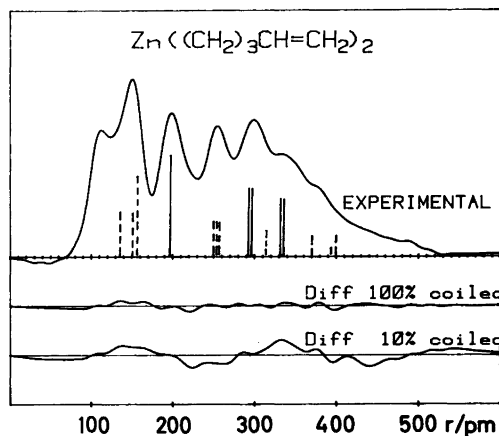


Fig. 5. Above: Experimental radial distribution curve for dipentenylzinc. $k=0.25$ pm². ZnC distances are indicated by bars, major CC distances by stippled bars. Below: Difference curves.

Table 1. Quality-of-fit factors, $R = \text{SQRT}[\Sigma(I_{\text{obs}} - I_{\text{calc}})^2 / \Sigma I_{\text{obs}}^2]$, obtained by refinement on model gases of different conformational composition.

	R(50 cm)	R(25 cm)
Dibut-3-enylzinc		
Coiled back conformer		
100 %	0.051	0.150
80 % (best model)	0.041	0.154
60 %	0.049	0.155
12.6 % ($\Delta G^\circ=0$)	0.101	0.163
Dipent-4-enylzinc		
Coiled back conformers		
100 % (best model)	0.076	0.199
80 %	0.092	0.206
7.0 % ($\Delta G^\circ=0$)	0.135	0.214

Table 2. Structure parameters of dibut-3-enylzinc (A) and dipent-4-enylzinc (B).

	A	B
Bond distances/pm		
Zn-C	195.7(4)	195.8(6)
C(sp^3)-C(sp^3)	154.7(4)	154.0(4)
C(sp^3)-C(sp^2)	151.7(4)	151.0(4)
C=C	136.3(6)	135.3(9)
C(sp^3)-H	111.9(5)	111.1(7)
C(sp^2)-H	110.9(5)	110.1(7)
Valence angles/deg		
\angle C-Zn-C	180	180
\angle Zn-C-C	115.5(7)	116(1)
\angle C-C-C	116.3(10)	(113)
\angle C-C=C	119(1)	(124)
Torsional angles/deg		
τ (C(1)-C(2))	58(3)	57(4)
τ (C(2)-C(3))	(0.0)	-67(6)
τ (C(3)-C(4))	—	133(9)
Nonbonded distances/pm		
Zn...C(2)	297(1)	297(2)
Zn...C(3)	344(3)	336(4)
Zn...C(4)	315(6)	300(8)
Zn...C(5)	—	341(18)
Vibrational amplitudes/pm		
Zn-C	7.1(6)	7.1(9)
C-C	4.1(6)	5.3(7)
C=C	3.4(6)	4.6(7)
C-H	7.9(6)	8.4(10)
Zn...C(2)	12.5(12)	9.5(15)
Zn...C(3)	(20.5)	(20.5)
Zn...C(4)	(30.0)	(30.0)
Zn...C(5)	—	(30.0)

independent. (Model calculations on both I and II make it clear that both chains may be coiled back without creating congestion).

Like the investigators of 1-butene¹⁰ we assumed that $C(sp^3)-C(sp^3)$ and $C(sp^2)-C(sp^2)$ bond distances differ by 0.030 Å and $C(sp^3)-H$ and $C(sp^2)-H$ bond distances by 0.010 Å; only average C-C and C-H bond distances were refined. H atoms were attached to the $CZnC_4$ backbone by transferring valence angles from dipropylzinc¹¹ and 1-butene.¹⁰ Root-mean-square vibrational amplitudes were transferred from the same molecules.

Average vibrational amplitudes of CH and CC bond distances, of 1,3 C...C nonbonded distances, of the Zn-C bond distance and of the Zn...C(2) distance were refined by least-squares calculations on the intensity data [$sI_m[s]$] along with nine structure parameters. The refinement converged to yield parameter values similar to those listed in Table 2. The quality-of-fit factor R defined in Table 1 was 5.1 % for the 50 cm data, 15.0 % for the 25 cm data, and 9.55 % over all. Comparison between experimental and calculated RD-curves showed that the agreement was satisfactory, but as we shall see below, better agreement was obtained with another model.

We now turn our attention to the conformer mixture expected in the absence of metal/double bond interactions. The amount of each of the five distinct conformers was assessed on the basis of the conformer distributions in 1-butene and dipropylzinc: in 1-butene $X_s=0.17(10)$ of the molecules are found in the *syn* conformation, in dipropylzinc $X_g=0.74$ chains are found in a *gauche* conformation. The amount of chains in I in the *gauche*, *syn* conformation was estimated as $X_{g,s}=X_g \cdot X_s=0.74 \cdot 0.17=0.126$. The amounts of other conformers were estimated in the same way.

It was assumed that *anti* conformers were characterized by $\tau[C(1)-C(2)]=180^\circ$ and *syn* conformers by $\tau[C(2)-C(3)]=0^\circ$. The conformer composition was fixed and the same structure parameters and vibrational amplitudes as for the coiled back model plus the torsional angle of *anticlinal* fragments were refined. The resulting R-factors (Table 1) were so much higher than for a coiled-back model that we feel that this model may be discarded.

Finally refinements were carried out on conformer mixtures when the amount of coiled-back

chains were increased to 60 and 80 % while the relative amounts of the other conformers remained unchanged. The best agreement was obtained for the model gas with $X_{g,s}=0.80$ and this constitutes our final model.

Dipent-4-enylzinc (II). A model of a molecular fragment containing the metal atom and one hydrocarbon chain is shown in Fig. 3. The conformation of the hydrocarbon chain may be described as *gauche+*, *gauche-*, *anticlinal+* since the dihedral angles $\angle[C(1)-C(2)]=+60^\circ$, $\angle[C(2)-C(3)]=-60^\circ$ and $\angle[C(3)-C(4)]=+120^\circ$. The total number of possible conformations is $3^3=27$. One of these is the all-planar *anti*, *anti*, *syn* conformation, the remaining 26 form thirteen indistinguishable (by GED) pairs. Two of the fourteen distinct conformations bring the olefinic carbon atoms into the vicinity of the Zn atom, the g_+ , g_- , ac_+ conformation shown in Fig. 3 and the g_+ , g_- , *syn* conformation obtained from it by rotating the vinyl group 120° about the C(3)-C(4) bond.

We first assumed that all chains is gaseous dipentenylzinc were in the g_+ , g_- , ac_+ conformation and refined the structure by least-squares calculations on the intensity data in the same manner as for dibutenylzinc. The large number of unknown structure parameters was, however, reduced by assuming the bond distances C(1)-C(2) and C(2)-C(3) to be equal, and by fixing the valence angles $\angle C(1)C(2)C(3)=\angle C(2)C(3)C(4)=113^\circ$ and $\angle C(3)C(4)C(5)=124^\circ$.¹⁰ Refinement of eight structure parameters and five vibrational amplitudes converged to the best values listed in Table 2.

Refinements with a starting model in the g_+ , g_- , *syn* conformation gave large shifts for the dihedral angle about the C(3)-C(4) bond and converged to the g_+ , g_- , ac_+ conformation. However, the possibility that the gas contains chains in *both* conformations has not been ruled out.

We assumed that the *gauche/anti* distribution about the C(2)-C(3) bond can be modeled by gaseous *n*-butane which contains $X_a=0.54$ molecules in the *anti*, and 0.23 molecules in each of the two *gauche* conformations.¹³ In the absence of metal/double bond interaction we expect the gas to contain $X_g \cdot 0.23 \cdot X_{ac}/2=0.070$ chains in the g_+ , g_- , ac_+ conformation and $X_g \cdot 0.23 \cdot X_s=0.031$ chains in the g_+ , g_- , *syn* conformation. The amounts of the twelve remaining conformers

were calculated in the same manner. The conformer composition was fixed and the structure parameters and vibrational amplitudes refined as for the coiled back model. The resulting *R*-factors (Table 1) were so much higher than for the coiled-back model, that we feel this model can be ruled out.

Refinement on a model gas in which 80 % of the chains were in the coiled-back conformation while the relative amounts of the other conformers remained unchanged, yielded *R*-factors so much higher than the coiled-back model that we feel that 80 % is a lower limit for the concentration of this conformer.

RESULTS AND DISCUSSION

For dipent-4-enylzinc the best agreement between observed and calculated intensities is obtained with a model gas in which *all* hydrocarbon chains are in the coiled back (*gauche*₊, *gauche*₋, *anticlinal*₊) conformation shown in Fig. 3. For dibut-3-enylzinc the best agreement is obtained for a model gas in which 80 % of the chains are on the coiled back (*gauche*, *syn*) conformation shown in Fig. 3, while 20 % of the chains are distributed among the four other possible conformations.

Consultation with Table 1 and Figs. 1 and 2 show that the agreement between experimental and calculated intensities is good for the 50 cm plates and poor for the 25 cm plates. As described under Experimental the data were recorded with an unusual scattering geometry in order to keep the temperature at a minimum and thus avoid thermal decomposition of the sample. We have earlier found that this geometry yields poorer 25 cm plates than normally expected. This appears to be particularly true in the present case which involve relatively large molecules with low symmetry: in such cases the molecular intensity is reduced by cancellation of terms. Fortunately most of the information about the conformation of the molecules is contained in the scattering range covered by the 50 cm plates, and these appear to be of normal quality.

Refinement of the best models yield the bond distances, valence angles and torsional angles listed in Table 2. They all appear normal, except the $\angle C-C=C$ angle in dibutenylzinc, 119(1) Å, which appears to be smaller than in the *syn*

conformer of 1-butene, $\angle C-C=C=127.2(3)^\circ$. The values obtained for the shortest distance between the Zn atom and the nearest olefinic carbon atom, Zn-C(4)=315(6) pm in dibutenylzinc and Zn-C(4)=300(8) pm in dipentenylzinc, indicate that the metal/CC double bond interaction is weak. The fact that the corresponding vibrational amplitudes refined to values as high as 0.30 Å (and were then fixed), and that the CZnC fragments appear to remain linear points in the same direction.

Based on the conformer distributions of dipropylzinc and 1-butene, we estimate that in the absence of metal/double bond interactions the concentration of the coiled back conformer of butenylzinc would be 13 %. An increase to 80 % corresponds to a free energy of interaction of $\Delta G^\circ = -4.5 \text{ kJ mol}^{-1}$. The *R*-factors listed in Table 1 indicate that *at least* 80 % of the chains in dipentenylzinc are found in one of the two coiled back conformations. Based on the conformer distributions of dipropylzinc, butane and 1-butene we estimate that the concentration would be about 7 % in the absence of metal/double bond interactions. The observed increase corresponds to a free energy of interaction of *at least* $\Delta G^\circ = -6 \text{ kJ mol}^{-1}$.

The behaviour of I and II may be contrasted with the saturated analogues dibutyl- and dipentenylzinc, and with the methoxy compounds $Zn[(CH_2)_nOCH_3]_2$, $n=3$ and 4: The electron diffraction data of the dialkylzinc compounds are incompatible with the presence of a single coiled back chain conformation.¹⁴ In the absence of zinc/double bond interactions the chains are probably distributed over all possible conformations. In the methoxy compounds both ligands chelate the metal atom with Zn-O bond distances of about 240 pm and vibrational amplitudes, $l(Zn-O)$, of about 15 pm.

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REFERENCES

- O'Neill, M. E. and Wade, K. In Wilkinson, G., Stone, F. G. A. and Abel, E. W., Eds., *Comprehensive Organometallic Chemistry*, Pergamon, Oxford 1982, Vol. 1, p. 24 ff.

2. Smart, J. B., Hogan, R., Scherr, P. A., Emerson, M. T. and Oliver, J. P. *J. Organometal. Chem.* 64 (1974) 1.
3. Denis, J. St., Oliver, J. P., Dolzine, T. W. and Smart, J. B. *J. Organomet. Chem.* 71 (1974) 315.
4. Hata, G. *Chem. Commun.* (1968) 7.
5. Dolzine, T. W. and Oliver, J. P. *J. Am. Chem. Soc.* 96 (1974) 1737.
6. Lehmkuhl, H., Döring, I., McLane, R. and Nehl, H. *J. Organomet. Chem.* 221 (1981) 1.
7. Lehmkuhl, H., Döring, I. and Nehl, H. *J. Organomet. Chem.* 221 (1981) 123.
8. Ashby, E. C., Fernholt, L., Haaland, A., Seip, R. and Smith, R. S. *Acta Chem. Scand. A* 34 (1980) 213.
9. Schäfer, L., Yates, A. C. and Bonham, R. L. *J. Chem. Phys.* 55 (1971) 3056.
10. Van Hemelrijk, D., Van den Enden, L., Geise, H. J., Sellers, H. L. and Schäfer, L. *J. Am. Chem. Soc.* 102 (1980) 2189.
11. Almenningen, A., Helgaker, T. U., Haaland, A. and Samdal, S. *Acta Chem. Scand. A* 36 (1982) 159.
12. Fitzwater, S. and Bartell, L. S. *J. Am. Chem. Soc.* 98 (1976) 8330.
13. Bradford, W. F., Fitzwater, S. and Bartell, L. S. *J. Mol. Struct.* 38 (1977) 185.
14. Haaland, A., Lehmkuhl, H. and Nehl, H. *Unpublished results.*
15. Boersma, J., Fernholt, L., Haaland, A. and Seip, R. *Acta Chem. Scand.* 38 (1984) 523.

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