Fig. 4. Projection de la structure suivant l'axe a.

Un arrangement des atomes analogue à celui-ci a déjà été observé dans le dérivé $C_{20}H_{33}N_3$ de l'alcaloïde matrine (Chieh & Trotter, 1967) où la connectivité des atomes est identique, bien que l'atome N(4) y soit tétra-coordonné.

La cohésion du cristal est assurée par la présence d'un molécule d'eau en position particulière sur un axe d'ordre 2. Cette molécule est impliquée dans deux liaisons hydrogène de 2,830 Å avec les atomes N(4) de deux molécules différentes de la maille cristallographique comme le montre la Fig. 4.

Les auteurs remercient MM les Professeurs J. Poisson et J. Toussaint pour l'intérêt qu'ils ont porté à ce travail ainsi que M M. Vermeire pour la sélection et la préparation de l'échantillon.

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Structure of 2,5-Hexanediyl Dibenzoate*

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Abstract. $C_{20}H_{22}O_4$, orthorhombic, space group $P2_12_12_1$, $a = 16 \cdot 992$ (3), $b = 11 \cdot 666$ (3), $c = 9 \cdot 318$ (2) Å, $V = 1847 \cdot 1$ (7) Å³, $Z = 4$, $D_c = 1 \cdot 17$ Mg m⁻³. The structure was solved by direct methods and refined to $R = 0 \cdot 047$ for 1022 observed reflections. The two phenyl rings are tilted at $9 \cdot 1°$ to each other. The 'tetramethylene' part of the chain presents the usual shortening of the $-CH_2-CH_2-$ distances in two bonds only and its *gauche–trans–gauche* conformation is different from that found in the unmethylated analogous monomer and polymer.

Introduction. In the last few years an increasing number of papers have appeared dealing with crystallographic studies on small molecules which can be considered as fragments of polymers. Moreover, the comparison between geometrical parameters resulting from single-crystal X-ray analysis of these oligomers with those of related polymers, obtained by X-ray or electron diffraction methods, often leads to better understanding of the conformation and the relationships between the structure and the mechanical properties of polymers. Consequently, the X-ray study of the title oligomer reported in this paper may be considered as the first step in an explanation of polymeric structure.

Experimental. Crystals of the compound were grown by slow evaporation from a chloroform solution at room temperature as colourless prisms. The dimensions of the crystal used on the diffractometer were $0 \cdot 6 \times 0 \cdot 4 \times 0 \cdot 2$ mm. Cell parameters were obtained as part of the alignment process on the diffractometer employing the angular values of 28 reflections. These reflections were automatically centred with the program CTDIF (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) which repeatedly improves the approximate $(\theta,\chi,\varphi)_{h,k,l}$ values corresponding to the intensity barycentre until the three angles do not change by more than $0 \cdot 01°$.

The intensity data were collected at room temperature on a Siemens AED single-crystal diffractometer using nickel-monochromatized Cu $K\alpha$ radiation. The intensity of any reflection was evaluated from a profile analysis following the Lehmann & Larsen (1974) notation with a program written by Belletti et al. (1979). A monitor reflection (233) was measured every 50 reflections to check misalignment or decomposition of the specimen; the collected intensities indicate only small statistical variations ($\sim 1\%$). Of 1620 independent reflections, recorded within the θ range of 0 to 60°, 1024, for which $I > 2\sigma(I)$, were considered observed. The data were corrected for Lorentz and polarization effects but absorption was ignored.

The structure amplitudes were put on the absolute scale by Wilson's (1942) statistical method ($\bar{B} = 5 \cdot 8$ Å^2). The normalized structure factors $|E|$ were then obtained by using the overall temperature parameter. The structure was solved by direct methods with MULTAN (Germain, Main & Woolfson, 1975) using 400 $|E| > 1 \cdot 08$. An E map computed on the set of phases with the highest figure-of-merit gave the position of all non-H atoms of the molecule. The positional and isotropic thermal parameters of these atoms were refined down to $R = 0 \cdot 155$ by a few cycles of full-matrix least squares using the SHELX system (Sheldrick, 1976). After some cycles of anisotropic refinement ($R = 0 \cdot 100$) a ΔF map revealed the positions of all H atoms which were refined isotropically. The refinement was continued until the parameter shifts were insignificant compared to their e.s.d.'s. The unobserved reflections, as well as two very strong reflections (020, 002) exhibiting high discrepancy between F_o and F_c, were eliminated from the last cycles of refinement which converged to a final R value of $0 \cdot 047$ (observed reflections only).

The function minimized during the calculations was $\sum w|\Delta F|^2$; unit weights were chosen at each stage of the refinement after analysing the variation of $|\Delta F|$ with respect to $|F_o|$.

A set of local programs (Belletti et al., 1979) was used to seek reflections in a prefixed part of the reciprocal space, to assign indices to these reflections and to find.a reduced primitive cell and its parameters,

to fix an orientation for this cell on the Eulerian cradle on the diffractometer, and to collect the intensity data. DIFAU (Ugozzoli, 1981) was used to carry out the data reduction. All these programs are written in Fortran or Assembler for a General Automation Jumbo 220 computer.

PARST (Nardelli, 1979) was used for the geometrical-parameters' calculation with their standard deviations and PLUTO (Motherwell, 1976) to draw the figures on a CALCOMP 967 plotter. These programs were used on the CDC CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna, with financial support from the University of Parma.

Discussion. Positional parameters of the molecule which is depicted in Fig. 1 are reported in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters and atomic parameters and bond distances for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38028 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
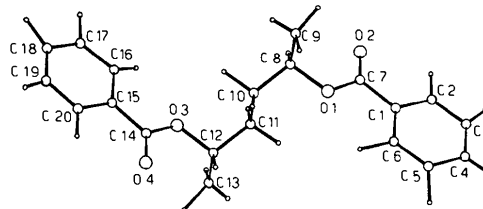

Fig. 1. Projection of the molecule.

Table 1. *Atomic coordinates* ($\times 10^4$) *and* B_{eq} (Å^2)

	x	y	z	B_{eq}*
O(1)	7721 (2)	5431 (2)	7825 (3)	6·31 (9)
O(2)	8322 (2)	6558 (3)	6226 (4)	8·42 (11)
O(3)	4870 (2)	4381 (3)	6879 (3)	6·32 (9)
O(4)	4291 (2)	3332 (3)	8586 (4)	7·20 (10)
C(1)	9020 (2)	5027 (3)	7260 (4)	5·11 (11)
C(2)	9710 (2)	5287 (4)	6556 (5)	6·19 (13)
C(3)	10381 (3)	4639 (4)	6807 (5)	7·65 (16)
C(4)	10375 (2)	3739 (4)	7724 (5)	7·37 (16)
C(5)	9677 (3)	3448 (3)	8464 (4)	7·33 (14)
C(6)	9003 (3)	4104 (4)	8218 (5)	5·64 (14)
C(7)	8336 (3)	5759 (4)	7038 (5)	5·77 (15)
C(8)	6996 (3)	6138 (4)	7843 (5)	7·06 (16)
C(9)	7083 (3)	7009 (4)	9016 (5)	8·85 (15)
C(10)	6316 (3)	5327 (4)	7964 (4)	6·54 (13)
C(11)	6265 (3)	4469 (4)	6752 (5)	6·20 (12)
C(12)	5571 (3)	3650 (4)	6892 (4)	6·48 (12)
C(13)	5497 (4)	2829 (4)	5659 (5)	8·36 (15)
C(14)	4280 (5)	4138 (4)	7778 (5)	5·61 (12)
C(15)	3612 (3)	4948 (4)	7641 (4)	5·01 (11)
C(16)	3636 (3)	5856 (4)	6689 (5)	5·91 (13)
C(17)	2985 (3)	6580 (4)	6611 (6)	6·86 (15)
C(18)	2345 (3)	6424 (5)	7457 (5)	7·60 (14)
C(19)	2343 (3)	5500 (5)	8421 (5)	8·10 (16)
C(20)	2968 (3)	4765 (4)	8506 (5)	8·42 (12)

* According to Hamilton (1959).

Table 2 reports bond distances, bond angles and selected torsion angles.

The Csp^2–Csp^2 aromatic distances average 1·388 (8) and 1·379 (7) Å for the two rings respectively, the C–H bond distances span the range 0·88 to 1·20 Å while the mean internal angles are 120·0 (4) and 120·1 (6)°. All these values are typical of those found in benzene rings.

The carboxylic parts of the molecule show a geometry similar to that already found for this type of molecular fragment (Sundararajan, Labrie & Marchessault, 1975; Pérez & Brisse, 1975, 1976a,b,c, 1977a,b; Brisse, Molhant & Pérez, 1979; Bocelli & Grenier-Loustalot, 1982).

A remarkable geometrical feature always previously observed in other oligomethylene glycol derivatives was an unusual shortening of the –CH_2–CH_2– distance [which ranges from 1·480 (7) (Pérez & Brisse, 1977b) to 1·507 (5) Å (Brisse et al., 1979)] if compared with the expected Csp^3–Csp^3 value reported by Sutton (1965) [1·537 (5) Å]. Moreover, this shortening is generally accompanied by a narrowing of the –O–CH_2–CH_2– bond angle which spans the range 104·7 (2) (Pérez & Brisse, 1976a) to 108·3 (3)° (Pérez & Brisse, 1977a)

with only one value greater [109·6 (3)°] reported by Brisse et al. (1979). In the present compound the two –O–C–C angles show the usual narrowing [106·9 (4), 105·3 (4)°] and two of the Csp^3–Csp^3 bond distances [C(8)–C(10) = 1·498 (7), C(10)–C(11) = 1·512 (6) Å] of the molecule are in the range of shortening quoted above while the third one is longer [C(11)–C(12) = 1·523 (7) Å]. It may be interesting to note as the shortening of the C(8)–C(10) distance is accompanied by a relative lengthening of the adjacent O(1)–C(8) distance [1·483 (6) Å], the relative lengthening of the C(11)–C(12) bond is coupled with a shortening of the adjacent O(3)–C(12) distance [1·465 (6) Å].

The two benzene rings are planar within experimental errors (see Table 3) and display a dihedral angle of 9·1°. The planar carboxylic groups are tilted at 2·8 and 0·3° with respect to their vicinal rings.

The chain conformation is dictated by the magnitude of the torsion angles reported in Table 2. The 'tetramethylene' part of the molecule shows a gauche–trans–gauche conformation, while the conformation of the chain starting from C(1) to C(15) is trans–trans–gauche–gauche–trans–gauche–gauche–trans–trans.

The two methyl groups as well as the two carbonyl O atoms are in trans positions; moreover, the methyls are axial with respect to the chain, the angles between the bond lines and the normals to the mean C(8)–C(10)–C(11)–C(12) plane being 89·8 and 87·7°.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

C–H bond distances are in the range 0·80–1·27 Å.

O(1)–C(7)	1·333 (6)	C(8)–C(9)	1·500 (7)
O(1)–C(8)	1·483 (6)	C(8)–C(10)	1·498 (7)
O(2)–C(7)	1·201 (6)	C(10)–C(11)	1·512 (6)
O(3)–C(12)	1·465 (6)	C(11)–C(12)	1·523 (7)
O(3)–C(14)	1·337 (8)	C(12)–C(13)	1·501 (6)
O(4)–C(14)	1·205 (6)	C(14)–C(15)	1·482 (9)
C(1)–C(2)	1·377 (5)	C(15)–C(16)	1·382 (6)
C(1)–C(6)	1·399 (6)	C(15)–C(20)	1·376 (7)
C(1)–C(7)	1·457 (6)	C(16)–C(17)	1·394 (7)
C(2)–C(3)	1·388 (6)	C(17)–C(18)	1·355 (7)
C(3)–C(4)	1·354 (7)	C(18)–C(19)	1·403 (8)
C(4)–C(5)	1·413 (6)	C(19)–C(20)	1·367 (7)
C(5)–C(6)	1·396 (7)		

C(7)–O(1)–C(8)	119·9 (3)	C(8)–C(10)–C(11)	114·0 (4)
C(12)–O(3)–C(14)	118·8 (4)	C(10)–C(11)–C(12)	113·3 (4)
C(6)–C(1)–C(7)	121·7 (4)	O(3)–C(12)–C(11)	105·3 (4)
C(2)–C(1)–C(7)	118·8 (4)	C(11)–C(12)–C(13)	113·6 (4)
C(2)–C(1)–C(6)	119·4 (4)	O(3)–C(12)–C(13)	107·3 (4)
C(1)–C(2)–C(3)	119·9 (4)	O(3)–C(14)–O(4)	123·1 (6)
C(2)–C(3)–C(4)	121·5 (4)	O(4)–C(14)–C(15)	124·3 (5)
C(3)–C(4)–C(5)	120·0 (4)	O(3)–C(14)–C(15)	112·7 (4)
C(4)–C(5)–C(6)	118·5 (4)	C(14)–C(15)–C(20)	117·4 (4)
C(1)–C(6)–C(5)	120·6 (4)	C(14)–C(15)–C(16)	121·4 (5)
O(2)–C(7)–C(1)	124·1 (4)	C(16)–C(15)–C(20)	121·2 (4)
O(1)–C(7)–C(1)	112·3 (4)	C(15)–C(16)–C(17)	118·3 (5)
O(1)–C(7)–O(2)	123·6 (5)	C(16)–C(17)–C(18)	121·7 (5)
O(1)–C(8)–C(10)	106·9 (4)	C(17)–C(18)–C(19)	118·5 (5)
O(1)–C(8)–C(9)	107·7 (4)	C(18)–C(19)–C(20)	121·1 (5)
C(9)–C(8)–C(10)	116·7 (4)	C(15)–C(20)–C(19)	119·1 (5)

C(2)–C(1)–C(7)–O(2)	3·3 (7)	C(10)–C(11)–C(12)–C(13)	177·5 (4)
C(2)–C(1)–C(7)–O(1)	–177·7 (4)	C(10) C(11)–C(12)–O(3)	60·4 (5)
C(6)–C(1)–C(7)–O(2)	–179·8 (5)	C(11)–C(12)–O(3)–C(14)	139·2 (4)
C(6)–C(1)–C(7)–O(1)	–0·8 (6)	C(13)–C(12)–O(3)–C(14)	-99·5 (5)
C(1)–C(7)–O(1)–C(8)	–174·3 (4)	C(12)–O(3)–C(14)–O(4)	–1·3 (8)
C(7)–O(1)–C(8)–C(9)	–88·5 (5)	C(12)–O(3)–C(14)–C(15)	–179·9 (4)
C(7)–O(1)–C(8)–C(10)	145·4 (4)	O(3)–C(14)–C(15)–C(16)	–1·3 (7)
O(2)–C(7)–O(1)–C(8)	6·6 (7)	O(3)–C(14)–C(15)–C(20)	179·1 (5)
O(1)–C(8)–C(10)–C(11)	–59·2 (5)	O(4)–C(14)–C(15)–C(16)	–179·9 (5)
C(9)–C(8)–C(10)–C(11)	–179·7 (4)	O(4)–C(14)–C(15)–C(20)	0·5 (8)
C(8)–C(10)–C(11)–C(12)	179·9 (4)		

Table 3. *Equations of least-squares planes with atomic deviations* (Å) *and angles between planes* (°)

E.s.d.'s are 0·003 Å and 0·2°.

Plane 1: C(1)–C(6)
$0\cdot2579X + 0\cdot6118Y + 0\cdot7478Z = 12\cdot598$
C(1) 0·000, C(2) 0·003, C(3) –0·004, C(4) 0·002,
C(5) 0·000, C(6) –0·001, C(7) –0·068, O(1) –0·113,
O(2) –0·067

Plane 2: C(15)–C(20)
$0\cdot4079X + 0\cdot5808Y + 0\cdot7045Z = 10\cdot873$
C(15) 0·001, C(16) –0·006, C(17) 0·006, C(18) 0·000,
C(19) –0·005, C(20) 0·004, C(14) –0·003, O(3) 0·014,
O(4) 0·005

Plane 3: C(1), C(7), O(1), O(2)
$0\cdot3044X + 0\cdot6007Y + 0\cdot7392Z = 13\cdot190$
C(1) 0·001, C(7) –0·005, O(1) 0·001, O(2) 0·001

Plane 4: C(15), C(14), O(3), O(4)
$0\cdot4130X + 0\cdot5805Y + 0\cdot7018Z = 10\cdot883$
C(15) 0·002, C(14) –0·008, O(3) 0·001, O(4) 0·001

Plane 5: C(8), C(10), C(11), C(12)
$-0\cdot5716X + 0\cdot6354Y - 0\cdot5193Z = -6\cdot040$
C(8) 0·000, C(10) 0·000, C(11) 0·000, C(12) 0·000,
C(9) –0·007, C(13) 0·060

1–2 = 9·1	1–3 = 2·8	2–4 = 0·3

A considerable number of papers have appeared reporting crystalline structures of poly(tetramethylene terephthalate) both in α and β forms (Mencik, 1975; Joly, Memoz, Douillard & Vallet, 1975; Desborough, 1976; Hall & Pass, 1976; Yokouchi, Sakakibara, Chatani, Tadokoro, Tanaka & Yoda, 1976) while two deal with monomers (Palmer & Brisse, 1981; Bocelli & Grenier-Loustalot, 1982). Also, a comparison between the structures of the polymer already published was examined in detail (Desborough & Hall, 1977; Hall, 1980). Though these comparisons clearly show that the geometries of the polymer, obtained through these structure determinations, are affected by sources of error which are reflected in their geometrical parameters, the molecule of the polymer nevertheless develops linearly along the c axis. This is the more important difference between the structure of the polymer and that of the monomer which develops non-linearly.

Moreover, if we compare the conformation of the title compound with that of butanediyl dibenzoate (Bocelli & Grenier-Loustalot, 1982) which differs only in the absence of the two methyls, first of all we can note a change in the chain conformation which is *trans–trans–gauche*, with the two carbonyl O atoms *cis* in the unmethylated derivative. Furthermore, the dihedral angle between the rings in the title compound is 58·5 (4)° clearly showing the steric hindrance of the two methyls which restrict rotation of the aromatic rings.
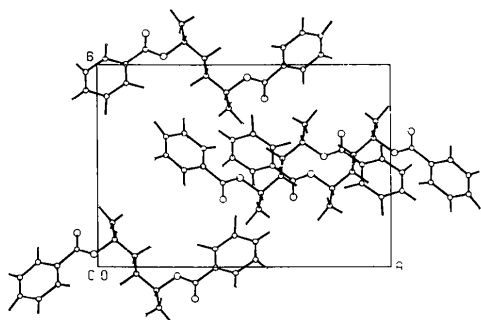

Fig. 2. Packing of the compound along the c axis.

Table 4. *Intermolecular contacts* $<3·5$ Å $(<3·0$ Å *if involving one H atom,* $<2·5$ Å *if two)*

The first atom is at x,y,z; the symmetry code for the second one is:

(i) $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$; (ii) $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (iv) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (v) $2-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (vi) $-\frac{1}{2}+x, \frac{1}{2}-y, 2-z$.

C(17)···H(22^i)	2·92 (4)	C(6)···H(20^{iv})	2·81 (4)
H(1)···O(4^{ii})	3·00 (4)	H(17)···H(11^{iv})	2·15 (6)
H(13)···C(6^{ii})	2·70 (4)	H(5)···H(20^{iv})	2·25 (5)
H(12)···H(8^{ii})	2·37 (5)	H(3)···O(2^v)	2·53 (4)
O(2)···H(10^{ii})	2·88 (4)	H(4)···C(2^v)	2·71 (6)
C(17)···O(2^{iii})	3·47 (1)	H(4)···H(1^v)	2·01 (7)
H(19)···O(2^{iii})	2·40 (4)	O(4)···H(4^{vi})	2·84 (4)

Consequently, in order to clarify the role of the attached methyl groups, which are also present in some studied polymers, in determining the conformation of this type of oligomer, the crystal analysis of some derivatives containing methyl groups will be undertaken in our laboratories.

Packing of the molecules is shown in Fig. 2. There are no intermolecular contacts less than the sum of the van der Waals radii and a list of those $<3·5$ Å is reported in Table 4.

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2α,17α-Bis(2-chloroethynyl)-A-nor-5α-œstrane-2β,17β-diol–Methanol (1/2)

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Abstract. $C_{21}H_{26}Cl_2O_2.2CH_4O$, triclinic, space group $P1$, $a = 8.438$ (15), $b = 10.339$ (17), $c = 7.155$ (15) Å, $\alpha = 98.37$ (6), $\beta = 92.83$ (4), $\gamma = 97.02$ (6)°, $Z = 1$. The structure was determined from 1896 independent intensities and refined to $R = 0.049$. Two molecules of CH_3OH (from the solvent of crystallization) are linked by hydrogen bonds to the hydroxyl groups.

Introduction. New derivatives of A-nor-5α-œstrane substituted on positions 2 and 17 (or 16) (Canceill, Gasc, Nedelec, Baert, Foulon & Jacques, 1979; Canceill & Jacques, 1980) with hydroxy, ethynyl or chloroethynyl groups have been described and their affinities for various hormonal receptors have been measured (Canceill, Azadian-Boulanger, Philibert, Raynaud & Jacques, 1977). The ability of these steroids to bind to the œstrogenic or androgenic receptors seems governed to a large extent by the 2-hydroxy group being in the α or β position. However, the establishment of the stereochemistry of these compounds by chemical methods is not simple.

In the corresponding A-norandrostane series the configuration of the 2-hydroxy group has been previously inferred from ^1H NMR and confirmed by ORD data (Jacques, Minssen, Varech & Basselier, 1965). In the A-norœstrane series, owing to the lack of the 19-methyl group, this methodology was inapplicable. This difficulty justifies the X-ray crystallographic study reported in the present paper. Moreover, our results confirm the validity of the solution of the same problem deduced from the circular dichroism properties of the 2,16 and 2,17 benzoate derivatives of

analogous steroid compounds, in the light of the exciton chirality method (Canceill, Collet & Jacques, 1981).

Experimental. The isomer studied {melting point 410 K and $[\alpha]_{578}^{25°C} = -8°$} was recrystallized from $CHCl_3$. Well shaped crystals are obtained by slow evaporation in CH_3OH. They decompose rapidly in air.

A single crystal with dimensions $0.3 \times 0.5 \times 0.4$ mm, surrounded by its mother liquor, was sealed in a glass capillary and mounted on a four-circle Philips diffractometer. Intensities for 3728 reflections were measured by the ω–2θ scan and the width of the scan was fixed at $1.6°$. The data were corrected for Lorentz–polarization, but not for absorption or extinction. 1896 reflections with $I \geq 3\sigma(I)$ were used in the determination of the structure.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) based on 200 reflections with $E \geq 1.1$. The E map corresponding to the solution with the highest combined figure of merit provided the positions of all the atoms of the molecule except those of the chloroethynyl groups. A Fourier map including all the structure factors showed the missing atoms; however, the Cl atoms appeared as rather weak peaks.

Difference Fourier syntheses clearly indicated two molecules of solvent (CH_3OH) in the vicinity of the OH groups. Subsequent difference syntheses revealed all the H atoms attached to rings A, B, C, D and some H atoms of the methyl group in the 17 position. Despite the hydrogen bond which links the methanol molecule to the hydroxyl group, it was impossible to find all the H atoms of the solvent molecules. The final R at the end of the refinement was 0.049 with unit weights.

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