The barrier to interconversion between the two rotamers also is extremely low (2·5 kJ mol^{-1}).

These results confirm the presence of a *cis* peptide bond geometry for the *N*-methyl peptide as suggested from solution studies. Furthermore, our observations suggest that intramolecular interactions arising from the *N*-methyl group and C-terminal esterification determine the conformational features of this blocked dipeptide. The lack of biological activity evident for this molecule, combined with the structural information, suggests that *cis* peptide bond geometry at the *N*-For-Met-*X* juncture may be unfavorable for stimulation of chemotactic responses in general. The general effect of C-terminal esterification on biological activity in these chemotactic peptides may also warrant further investigation.

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Structures of Two Products of Arynic Condensation of Ketone Enolates

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Abstract. 2,3,3a,4,5,9b-Hexahydro-1*H*-benz[*e*]indene-3-spiro-2′-(1,3-dioxolan)-5-one (1), $C_{15}H_{16}O_3$, M_r = 244·3, monoclinic, $P2_1/a$, $a = 11{\cdot}023\,(2)$, $b = 12{\cdot}020\,(1)$, $c = 9{\cdot}419\,(1)$ Å, $\beta = 100{\cdot}74\,(1)°$, $V = 1226{\cdot}1\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}323$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·540562 Å, $\mu = 0{\cdot}702$ mm^{-1}, $F(000) = 520$, $T =$

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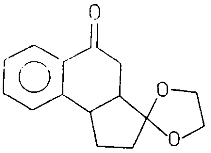
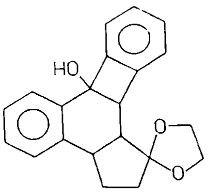
293 K, $R = 0{\cdot}0670$ for 1293 observed reflections. 2,3,3a,7b,11b,11c-Hexahydro-1*H*-benzo[*a*]cyclopenta[*c*]biphenylene-1-spiro-2′-(1,3-dioxolan)-7b-ol (2), $C_{21}H_{20}O_3$, $M_r = 320{\cdot}4$, triclinic, $P\bar{1}$, $a = 16{\cdot}921\ (4)$, $b = 10{\cdot}378\ (2)$, $c = 9{\cdot}672\ (2)$ Å, $\alpha = 77{\cdot}35\ (1)$, $\beta = 81{\cdot}03\ (1)$, $\gamma = 93{\cdot}72\ (1)°$, $V = 1628{\cdot}3\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}307$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}540562$ Å, $\mu = 0{\cdot}653$ mm^{-1}, $F(000) = 680$, $T = 293$ K, $R = 0{\cdot}0476$ for 4397 observed reflections. The stereochemistry at the junction of the pentaatomic ring with the cyclohexene ring is *trans* in both compounds, while in (2) the H atom and the OH group at the junction of the cyclobutene with the cyclohexene ring are *cis*.

Introduction. Continuing our investigations on arynic condensation of ketone enolates (Grégoire, Carré & Caubère, 1986) we have studied the reaction of bromobezene on the enolate of 2-cycloheptene-1,4-dione 1-monoethylene ketal in the presence of the $NaNH_2$–^{t}BuONa complex base. Instead of the expected products, three new compounds were isolated whose ^{1}H and ^{13}C NMR spectra could be tentatively attributed to compound (1) and to two isomers of (2) with undetermined stereochemistry.



(1)



(2)

In order to ascertain these anticipated structures and to establish their actual stereochemistry, which is necessary to interpret the reaction mechanism, the X-ray diffraction study of crystals of (1) and one isomer of (2) was performed.

In the present paper the results of this study are illustrated and, based on them, a possible mechanism is proposed for the formation of these compounds.

Experimental. Table 1 summarizes the relevant data of the crystal-structure analyses. The intensities were measured on a Siemens AED diffractometer using Cu $K\alpha$ (nickel-filtered) radiation in the $\theta/2\theta$ scan mode with a 3–12° min^{-1} scan speed and a $(1{\cdot}10 + 0{\cdot}14\tan\theta)°$ scan width. The integrated intensities were measured in the 3–70° θ range using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Correction for Lorentz and polarization effects was applied but not for absorption, while extinction was considered according to Zachariasen (1963).

Table 1. *Experimental data for the X-ray analyses*

	(1)	(2)
Reflections for lattice parameters		
No.	27	28
θ range (°)	16/39	27/34
Crystal size (mm)	0·19 × 0·48 × 0·70	0·19 × 0·28 × 0·85
Extinction parameter *g*	$0{\cdot}22\ (3) \times 10^{-7}$	$0{\cdot}37\ (9) \times 10^{-7}$
h range	−13/13	−20/20
k range	0/14	−12/12
l range	0/11	0/11
Standard reflection	$\bar{4}42$	701
No. of measured reflections	2604	6043
No. of observed reflections	1293	4397
Condition for observed reflections	$I \geq 3\sigma(I)$	$I \geq 3\sigma(I)$
R_{int}	0·084	—
Max. LS shift to e.s.d. ratio	0·08	0·15
Min./max. height in final $\Delta\rho$ map (e Å^{-3})	−0·13/0·14	−0·20/0·12
No. of refined parameters	201	594
R	0·0670	0·0476
wR	0·0676	0·0722
S	1·0124	0·5707
$k, g\ \{w = k/[\sigma^2(F_o) + gF_o^2]\}$	Unit weights	1, 0·01484

The structures were determined by direct methods with *SHELX*86 (Sheldrick, 1986) and refined by anisotropic full-matrix least squares on *F*, using *SHELX*76 (Sheldrick, 1976). The H atoms were located from difference Fourier syntheses and refined isotropically.

There are no significant differences between the two crystallographically independent molecules in compound (2). From *PLUTO* (Motherwell & Clegg, 1976) drawings of the cell content and the *SYMMOL* routine of *PARST* (Nardelli, 1983*a*), it appears that there is a pseudo twofold screw axis at about $\frac{1}{4}a$, $\frac{1}{4}b$ running along *c*. The correctness of space-group choice was checked by using *TRACER* (Lawton & Jacobson, 1965), *NEWLAT* (Mugnoli, 1985) and *MISSYM* (Le Page, 1987).

The atomic scattering factors and the anomalous-scattering coefficients are from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 2.* Throughout the paper the averaged values are means weighted according to the reciprocals of the variances, and the corresponding e.s.d.'s are the largest of the values of the 'external' and 'internal' standard deviations (Topping, 1960).

The calculations were carried out on the Gould-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma. In addition to the quoted programs, *LQPARM* (Nardelli & Mangia, 1984), *ORTEP* (Johnson, 1965)

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* Lists of structure factors, anisotropic displacement parameters, H-atom parameters, bond lengths and angles involving H, torsion angles and Cambridge Structural Database bibliographic references have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52736 (78 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^4$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Compound (1)				
O1	2515 (3)	4699 (3)	10072 (4)	831 (15)
O2	335 (3)	1550 (3)	6176 (4)	703 (15)
O3	−878 (3)	1801 (3)	7850 (4)	695 (15)
C1	−412 (5)	2325 (4)	6722 (5)	555 (18)
C2	−1516 (5)	2748 (4)	5553 (5)	654 (20)
C3	−1579 (5)	4007 (4)	5716 (5)	633 (19)
C4	−960 (5)	6326 (4)	7022 (6)	718 (22)
C5	−508 (6)	7379 (5)	7374 (6)	840 (26)
C6	642 (6)	7517 (5)	8274 (6)	828 (26)
C7	1306 (5)	6602 (4)	8831 (5)	693 (22)
C8	858 (4)	5524 (4)	8490 (5)	550 (18)
C9	1575 (4)	4552 (5)	9160 (5)	604 (19)
C10	1158 (4)	3393 (4)	8699 (5)	578 (18)
C11	268 (4)	3409 (4)	7235 (5)	495 (16)
C12	−766 (4)	4224 (4)	7223 (5)	526 (17)
C13	−295 (4)	5377 (4)	7567 (5)	522 (17)
C14	365 (7)	550 (5)	6978 (7)	894 (29)
C15	−398 (8)	738 (6)	8016 (10)	1379 (47)
Compound (2)				
O1*A*	1715·5 (7)	379·4 (13)	534·5 (14)	369 (4)
O2*A*	−846·3 (8)	−3538·9 (12)	3203·5 (14)	432 (4)
O3*A*	−776·5 (7)	−2093·9 (11)	1032·1 (13)	367 (4)
C1*A*	−856 (1)	−2180 (2)	2567 (2)	331 (5)
C2*A*	−1622 (1)	−1562 (2)	3076 (2)	423 (6)
C3*A*	−1349 (1)	−108 (2)	3029 (3)	453 (7)
C4*A*	−191 (1)	2252 (2)	3112 (2)	401 (6)
C5*A*	332 (1)	3225 (2)	3355 (2)	460 (7)
C6*A*	1151 (1)	3107 (2)	3195 (2)	439 (7)
C7*A*	1438 (1)	1999 (2)	2784 (2)	390 (6)
C8*A*	923 (1)	1020 (2)	2524 (2)	307 (5)
C9*A*	1278·1 (9)	−105·7 (16)	1957·5 (17)	293 (5)
C10*A*	672·1 (9)	−1397·7 (16)	2157·0 (18)	304 (5)
C11*A*	−180·9 (9)	−1296·2 (16)	2859·6 (18)	303 (5)
C12*A*	−449·0 (9)	86·3 (16)	2357·3 (18)	317 (5)
C13*A*	92 (1)	1144 (2)	2685 (2)	317 (5)
C14*A*	−1117 (2)	−4259 (2)	2237 (3)	517 (8)
C15*A*	−742 (2)	−3401 (2)	804 (3)	527 (8)
C16*A*	1765 (1)	−997 (2)	2902 (2)	330 (5)
C17*A*	1234 (1)	−2116 (2)	3078 (2)	341 (5)
C18*A*	1350 (1)	−3335 (2)	3905 (2)	448 (7)
C19*A*	2039 (1)	−3359 (2)	4536 (2)	505 (7)
C20*A*	2568 (1)	−2241 (2)	4348 (2)	523 (8)
C21*A*	2448 (1)	−1014 (2)	3510 (2)	445 (7)
O1*B*	−6771·2 (8)	−5277·7 (14)	−3442·1 (16)	450 (5)
O2*B*	−4080 (1)	−1672 (2)	−3640 (2)	608 (6)
O3*B*	−4153·5 (8)	−3021·1 (12)	−5192·3 (14)	434 (4)
C1*B*	−4123 (1)	−3016 (2)	−3711 (2)	421 (6)
C2*B*	−3412 (1)	−3742 (3)	−3240 (3)	541 (8)
C3*B*	−3749 (1)	−5179 (2)	−2496 (3)	529 (8)
C4*B*	−5001 (1)	−7462 (2)	−892 (2)	463 (7)
C5*B*	−5571 (2)	−8405 (2)	26 (2)	545 (8)
C6*B*	−6378 (1)	−8220 (2)	163 (2)	526 (7)
C7*B*	−6615 (1)	−7064 (2)	−602 (2)	446 (7)
C8*B*	−6043 (1)	−6094 (2)	−1532 (2)	338 (5)
C9*B*	−6336 (1)	−4896 (2)	−2424 (2)	347 (6)
C10*B*	−5682 (1)	−3653 (2)	−3096 (2)	364 (6)
C11*B*	−4854 (1)	−3854 (2)	−2729 (2)	346 (5)
C12*B*	−4628 (1)	−5262 (2)	−2734 (2)	345 (6)
C13*B*	−5223 (1)	−6295 (2)	−1687 (2)	338 (5)
C15*B*	−4140 (2)	−1689 (2)	−5977 (3)	632 (10)
C14*B*	−3840 (3)	−879 (3)	−5058 (3)	816 (14)
C16*B*	−6792 (1)	−3981 (2)	−1626 (2)	401 (6)
C17*B*	−6226 (1)	−2907 (2)	−2203 (2)	411 (6)
C18*B*	−6279 (2)	−1704 (2)	−1808 (3)	553 (8)
C19*B*	−6960 (2)	−1626 (3)	−838 (3)	657 (10)
C20*B*	−7534 (2)	−2707 (3)	−261 (3)	679 (11)
C21*B*	−7466 (1)	−3918 (3)	−628 (3)	558 (9)

and *MOLDRAW* (Ugliengo, Borzani & Viterbo, 1988) have been used.

Table 3. *Comparison of bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	(1)	(2) molecule *A*	(2) molecule *B*	Average
C1—O2	1·403 (6)	1·412 (2)	1·409 (3)	1·410 (2)
C1—O3	1·412 (6)	1·452 (2)	1·443 (2)	1·446 (6)
C14—O2	1·416 (7)	1·427 (3)	1·418 (3)	1·422 (3)
C15—O3	1·380 (8)	1·425 (3)	1·421 (3)	1·420 (8)
C14—C15	1·422 (12)	1·493 (3)	1·472 (5)	1·485 (11)
C9—O1	1·230 (6)	1·423 (2)	1·424 (3)	—
C1—C2	1·566 (6)	1·542 (3)	1·536 (3)	1·542 (6)
C2—C3	1·524 (7)	1·538 (3)	1·536 (3)	1·536 (3)
C3—C12	1·553 (6)	1·541 (2)	1·541 (3)	1·542 (2)
C1—C11	1·536 (7)	1·519 (2)	1·524 (2)	1·522 (2)
C11—C12	1·500 (6)	1·532 (2)	1·535 (3)	1·531 (6)
C11—C10	1·536 (6)	1·517 (2)	1·514 (3)	1·518 (4)
C9—C10	1·505 (7)	1·592 (2)	1·593 (2)	—
C8—C9	1·484 (7)	1·515 (2)	1·510 (2)	1·511 (4)
C12—C13	1·494 (7)	1·502 (2)	1·502 (2)	1·502 (1)
C8—C13	1·410 (6)	1·408 (2)	1·406 (2)	1·407 (1)
C4—C13	1·402 (7)	1·393 (3)	1·393 (3)	1·394 (2)
C4—C5	1·377 (8)	1·383 (3)	1·381 (3)	1·382 (2)
C5—C6	1·397 (8)	1·387 (3)	1·382 (4)	1·386 (3)
C6—C7	1·370 (8)	1·388 (3)	1·384 (3)	1·385 (3)
C7—C8	1·402 (8)	1·386 (3)	1·402 (2)	1·397 (5)
C9—C16	—	1·527 (2)	1·523 (3)	1·526 (2)
C10—C17	—	1·523 (2)	1·526 (3)	1·524 (2)
C16—C17	—	1·384 (2)	1·376 (2)	1·380 (4)
C17—C18	—	1·385 (2)	1·388 (3)	1·386 (2)
C18—C19	—	1·396 (3)	1·387 (4)	1·393 (4)
C19—C20	—	1·380 (3)	1·388 (4)	1·383 (4)
C20—C21	—	1·398 (3)	1·386 (4)	1·394 (6)
C21—C16	—	1·375 (3)	1·390 (3)	1·382 (8)
C1—O2—C14	109·0 (4)	106·5 (2)	108·2 (2)	107·5 (7)
C1—O3—C15	108·2 (5)	108·1 (2)	108·5 (2)	108·3 (2)
O2—C1—O3	107·4 (4)	105·5 (1)	106·0 (2)	105·7 (3)
O3—C1—C11	111·5 (4)	109·9 (1)	110·0 (2)	110·0 (2)
O3—C1—C2	109·2 (4)	109·2 (2)	109·8 (2)	109·5 (2)
O2—C1—C11	113·2 (4)	113·3 (2)	113·2 (2)	113·2 (1)
O2—C1—C2	113·0 (4)	115·3 (2)	114·4 (2)	114·6 (5)
C2—C1—C11	102·5 (4)	103·6 (2)	103·5 (2)	103·4 (2)
C1—C2—C3	107·2 (4)	106·1 (2)	106·8 (2)	106·5 (3)
C2—C3—C12	103·3 (4)	104·8 (2)	104·2 (2)	104·4 (3)
C5—C4—C13	121·2 (5)	121·0 (2)	121·0 (2)	121·0 (1)
C4—C5—C6	120·1 (6)	120·4 (2)	120·6 (2)	120·5 (1)
C5—C6—C7	119·8 (6)	119·1 (2)	119·6 (2)	119·4 (2)
C6—C7—C8	120·9 (5)	121·2 (2)	120·4 (2)	120·8 (3)
C7—C8—C13	119·7 (5)	119·6 (2)	119·9 (2)	119·7 (1)
C7—C8—C9	119·5 (4)	118·8 (2)	118·3 (2)	118·7 (3)
C9—C8—C13	120·7 (4)	121·4 (2)	121·6 (2)	121·4 (2)
O1—C9—C8	119·8 (5)	110·3 (1)	110·4 (2)	—
C8—C9—C10	119·8 (4)	115·5 (2)	115·8 (2)	—
O1—C9—C10	120·4 (4)	114·4 (1)	113·7 (2)	—
C9—C10—C11	110·9 (4)	114·6 (2)	114·5 (2)	—
C1—C11—C10	117·7 (4)	118·0 (2)	119·2 (2)	118·5 (4)
C10—C11—C12	111·9 (4)	112·2 (2)	112·3 (2)	112·2 (1)
C1—C11—C12	103·1 (4)	101·5 (2)	101·2 (2)	101·5 (4)
C3—C12—C11	101·9 (4)	102·6 (2)	102·6 (2)	102·5 (2)
C11—C12—C13	111·8 (4)	111·5 (2)	111·6 (2)	111·6 (1)
C3—C12—C13	118·2 (4)	119·2 (2)	117·9 (2)	118·5 (4)
C8—C13—C12	119·1 (4)	118·4 (2)	118·6 (2)	118·6 (1)
C4—C13—C12	122·6 (4)	122·9 (2)	122·9 (2)	122·9 (1)
C4—C13—C8	118·2 (5)	118·7 (2)	118·5 (2)	118·6 (1)
O2—C14—C15	105·9 (5)	102·1 (2)	104·3 (2)	103·4 (9)
O3—C15—C14	109·4 (6)	103·0 (2)	104·5 (2)	104·0 (10)
C8—C9—C16	—	117·4 (2)	117·6 (2)	117·5 (1)
O1—C9—C16	—	111·2 (2)	111·2 (2)	111·2 (1)
C10—C9—C16	—	86·4 (1)	86·2 (2)	86·4 (1)
C9—C10—C17	—	85·8 (1)	85·6 (2)	85·8 (1)
C11—C10—C17	—	118·8 (2)	117·6 (2)	118·2 (6)
C17—C16—C21	—	122·9 (2)	121·8 (2)	122·4 (6)
C9—C16—C21	—	143·7 (2)	144·2 (2)	144·0 (2)
C9—C16—C17	—	93·4 (2)	93·9 (2)	93·6 (2)
C10—C17—C16	—	94·4 (2)	94·3 (2)	94·4 (1)
C16—C17—C18	—	121·9 (2)	122·5 (2)	122·2 (3)
C10—C17—C18	—	143·6 (2)	143·0 (2)	143·3 (3)
C17—C18—C19	—	115·6 (2)	115·8 (2)	115·7 (1)
C18—C19—C20	—	122·2 (2)	121·7 (3)	122·0 (2)
C19—C20—C21	—	121·9 (2)	122·2 (3)	122·0 (2)
C16—C21—C20	—	115·5 (2)	115·8 (2)	115·6 (2)

Discussion. Bond distances and angles are compared in Table 3 and, when averaging is meaningful, the weighted means are given. The *ORTEP* (Johnson, 1965) drawings of the molecules are displayed in Fig. 1.

Analysis of the anisotropic atomic displacements

The most significant results of the analysis of the anisotropic atomic displacements are quoted in Table 4. This analysis was carried out in terms of the **LST** rigid-body model according to Schomaker & Trueblood (1968) and Trueblood (1978), considering also the internal motions according to Dunitz & White (1973) by using the *THMV* progam (Trueblood, 1984).

As can be seen from the data of Table 4 and from the ellipsoids of Fig. 1, the internal motions (or statical displacements) have some relevance particularly for some atoms of the dioxa rings. If exception is made for the O3—C15 distance in compound (1), which increases from 1·380 Å to the more reasonable value of 1·438 Å, all the other corrections are in the ranges 0·007–0·011 (av. 0·009), 0·001–0·006 (av. 0·002) and 0·002–0·004 (av. 0·003) Å in compound (1), compound (2) molecule *A* and compound (2) molecule *B*, respectively.

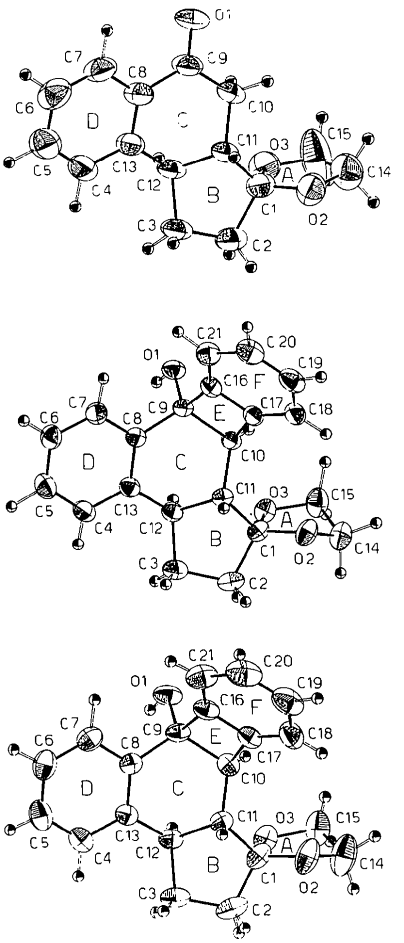


Fig. 1. *ORTEP* (Johnson, 1965) drawings of the molecules. Top: compound (1), middle: compound (2) molecule *A*, bottom: compound (2) molecule *B*. Ellipsoids are at 50% probability.

Table 4. *Results of the anisotropic atomic displacement analysis*

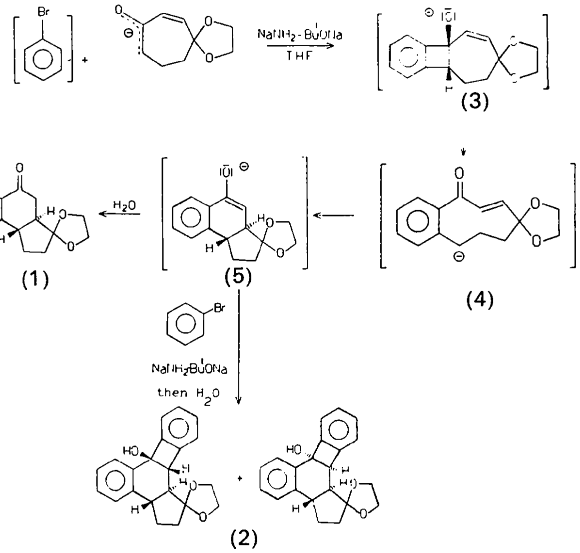
Compound	Librating group	Libration along	Group libration amplitude
(1)	C14	C1—O2	6·5 (12)°
	C15	C1—O3	17·1 (8)
(2) molecule *A*	C15	O3—C1	5·3 (12)
	O1	C9—C16	3·9 (9)
	C2, C3	C1···C12	5·1 (7)
	O2, O3	C1···*M*(C14—C15)	3·3 (10)
	C18, C19, C20, C21	*NBZF*	4·2 (5)
(2) molecule *B*	C15	O2—C1	2·3 (14)
	C14	O3—C1	5·1 (9)
	C2, C3	C1···C12	6·0 (7)
	O2, O3	C1···*M*(C14—C15)	4·0 (11)
	C18, C19, C20, C21	*NBZF*	4·2 (7)

				R_{wU}	
Compound	$\overline{\Delta} \times 10^4$	$\overline{\Delta U} \times 10^4$	$\overline{\sigma}(U_o) \times 10^4$	Rigid body	Internal motion
(1)	93 (193) Å^2	34 (41) Å^2	34 Å^2	0·163	0·081
(2) molecule *A*	34 (48)	25 (31)	9	0·134	0·102
(2) molecule *B*	48 (77)	30 (38)	11	0·121	0·098

M(C14—C15) = midpoint of the C14—C15 bond; *NBZF* = perpendicular straight line at the center of the benzene ring *F*; $\overline{\Delta}$ = mean difference of the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms; $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$; $R_{wU} = [\Sigma(w\Delta U)^2/\Sigma(wU_o)^2]^{1/2}$; $\overline{\Delta U} = [\Sigma(w\Delta U)^2/\Sigma w^2]^{1/2}$; $\overline{\sigma}(U_o)$ = mean e.s.d. of U_o's.

Configurations at the junctions and possible reaction mechanism

According to the structures of (1) and (2) a possible mechanism for the arynic condensation is proposed in the following scheme:



The stereochemistry at the *B*/*C* and *E*/*C* ring junctions of the two isomers of (2) allows us to conclude that the well known *syn* addition of arynes on ketone enolates may take place on both faces of (5).

Still more interesting, and intriguing, is the *trans* nature of the *BC* junction in compound (1). Indeed, it is well established (see, for example, Caubère, 1978) that aryne condensation of seven-membered ketone enolates leads to benzocyclobutenolates (3) with *cis* junctions. So the *trans* stereochemistry of (1) may be due either to a privileged conformation of (4) or to a *cis–trans* isomerization of its unsaturation. Moreover, the possibility of cyclization of (4), leading to (5) with a *cis* junction followed by further isomerization, cannot be discarded. Thus the present structural study leads to new questions concerning the intimate mechanism of these reactions.

As shown by the Newman projections in Fig. 2 and the drawings of the molecules in Fig. 1, the configurations at the chiral centers are *S* (C11) and *R* (C12) in compound (1) and *R* (C9), *R* (C10), *R* (C11) and *R* (C12) in compound (2). Of course the enantiomers are also present, the space groups both being centrosymmetric.

Puckering of the rings and general conformation of the molecules

It is doubtful that the small amount of puckering of the benzene and cyclobutene rings in molecule *B* of compound (2) is really significant, as the same deformations are not observed in molecule *A*. For the other three rings puckering is quite significant as expected and is comparable in the three molecules, as shown by the data of Table 5. The only exception is ring *A* in compound (1) which is much less puckered than in the two molecules of compound (2). Probably this is only an apparent effect due to the particularly high dynamical or static anisotropic displacements affecting C15 in compound (1) (see Fig. 1).

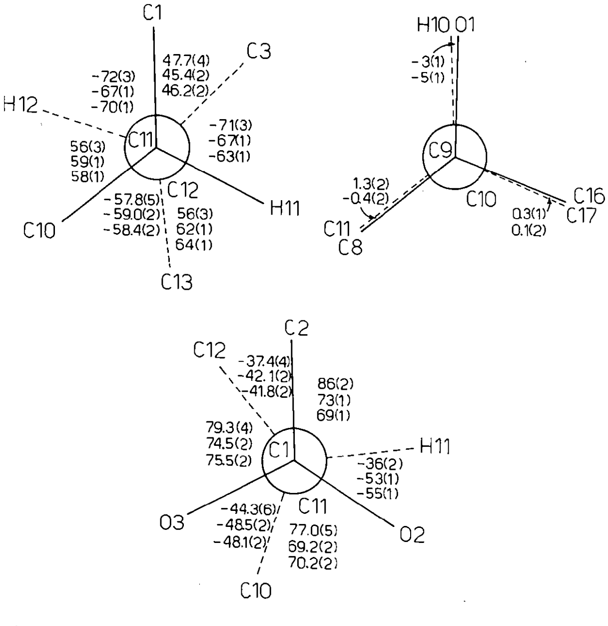


Fig. 2. Newman projections along the C11—C12, C9—C10 and C1—C11 bonds showing the configurations at the junctions and the orientation of the dioxa ring; data (°) above refer to compound (1), data in the middle to compound (2) molecule *A*, and data below to compound (2) molecule *B*.

The dioxa ring is approximately perpendicular to the flat central part of the molecule formed by the *B*, *C* and *D* fused rings, while the planar benzocyclobutene system is bent by 45° with respect to the central moiety, as shown by the values of the dihedral angles formed by the mean planes through the rings:

	(1)	(2) molecule *A*	(2) molecule *B*
A–B	95·4 (2)°	92·2 (1)°	86·8 (1)°
B–C	5·8 (2)	6·1 (1)	6·1 (1)
C–D	10·3 (2)	13·6 (1)	13·0 (1)
C–E	—	45·7 (1)	46·4 (1)
E–F	—	0·6 (1)	2·2 (1)

The abnormally high bond distance, C9—C10 = 1·592 (2) Å, at the junction of the cyclobutene with the cyclohexene ring in compound (2) is worth noticing. This value, quite significantly higher (Δ/σ = 28·4) than the expected C(sp^3)—C(sp^3) single-bond value, 1·542 (1) Å (Dewar & Schmeising, 1960), is probably due to the distorted hybridization of the C atoms involved and to some interaction between O1 and H10 which are at distances of 2·57 (2) and 2·60 (2) Å in molecules *A* and *B*, respectively.

Deformation of the benzene rings

There is a benzene fused with a cyclohexene ring in both compounds and a benzene fused with a cyclobutene ring in compound (2). The results of the analysis of the deformation of these fused benzene rings are quoted in Table 6 where the literature data refer to 23 compounds for cyclobutene and 379 for cyclohexene derivatives retrieved in the 1988 release of the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979; Allen, Kennard & Taylor, 1983). The criterion used for the search was to consider only the analyses with $R \leq$ 0·07 of compounds containing the above mono-cycloalkenobenzene moieties with no substituents at the benzene ring and no interaction with metal centers. The averaged values of Table 6 were calculated assuming a local *m* symmetry for the alkenobenzene moiety except for the angles ε and δ in the benzocyclohexene moiety of compounds (1) and (2), as the differences for them are quite significant ($\Delta/\sigma > 10·6$) and systematic.

The results obtained for the benzocyclobutene moiety agree quite well with those found by Allen (1981) in his study on the effect of small-ring fusion

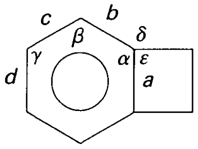
Table 5. *Ring-puckering analysis*

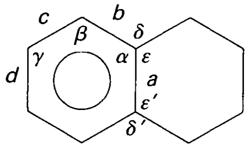
Compound	Ring *C* C13,C8,C9,C10,C11,C12 Q_T	 *DAP*	Ring *B* C11,C12,C3,C2,C1 Q_T	 *DAP*	Ring *A* C1,O2,C14,C15,O3 Q_T	 *DAP*
(1)	0·488 (4)	*D*(C8) = 0·0472 (31) (*S*)	0·458 (5)	*D*(C2) = 0·0070 (20) (*HC*)	0·014 (5)	*D*(C14) = 0·0013 (25) (*HC*)
(2) molecule *A*	0·524 (2)	*D*(C8 − C9) = 0·0033 (8) (*HC*)	0·450 (2)	*D*(C11) = 0·0398 (10) (*E*)	0·357 (3)	*D*(C15) = 0·0126 (12) (*E*)
(2) molecule *B*	0·512 (2)	*D*(C8 − C9) = 0·0047 (9) (*HC*)	0·456 (2)	*D*(C2) = 0·0444 (10) (*HC*)	0·268 (4)	*D*(C15) = 0·0046 (28) (*E*)

Q_T = total puckering amplitude (Å) (Cremer & Pople, 1975); *DAP* = minimum displacement asymmetry parameter (Nardelli, 1983*b*); *HC* = half-chair, *E* = envelope, *S* = sofa.

Table 6. *Comparison of the geometries of the fused benzene rings*

See text for the retrieval of literature data.





	C16···C21	Literature	C4···C13	Literature
a(Å)	1·380 (4)	1·383 (4)	1·404 (1)	1·399 (1)
b(Å)	1·385 (3)	1·386 (2)	1·396 (3)	1·392 (1)
c(Å)	1·393 (3)	1·396 (3)	1·383 (2)	1·390 (1)
d(Å)	1·383 (4)	1·389 (4)	1·385 (2)	1·383 (1)
α(°)	121·8 (1)	122·6 (2)	119·2 (3)	120·0 (1)
β(°)	115·7 (1)	115·2 (2)	120·9 (1)	119·6 (1)
γ(°)	122·0 (1)	122·2 (2)	119·9 (3)	120·4 (1)
ε(°)	94·0 (2)	93·4 (2)	ε 121·4 (2) ε′ 118·5 (4)	115·9 (1)
δ(°)	143·6 (2)	143·8 (1)	δ 118·7 (3) δ′ 122·9 (1)	124·0 (1)

on the geometry of benzene. In particular the narrowing of the β angle related to the narrowing of the ε angle is observed confirming the picture of a 'push–pull' effect pivoted on the atoms of the junction; this effect is of the same kind but more relevant than that observed for the indane system (Ianelli, Nardelli, Geoffroy, Carré, Jamart-Grégoire & Caubère, 1989).

The strain caused by fusion is relaxed in the benzocyclohexene moiety where the endocyclic angles at the benzene ring tend to assume the 120° value. The asymmetry observed for the δ and ε angles for this moiety in compounds (1) and (2) is systematic and probably caused by the steric interaction between the benzene and the cyclopentane ring *B*.

Crystal-packing analysis

Packing in compound (1) is essentially determined by normal van der Waals contacts, while in compound (2) the presence of the —OH group allows the formation of the following hydrogen bonds: O1*A*—HO*A*···O3*A*($\bar{x},\bar{y},\bar{z}$): O···O = 2·815 (2), H···O = 1·96 (2) Å, O—H···O = 177 (2)°; O1*B*—HO*B*···O3*B*($\bar{x}-1,\bar{y}-1,\bar{z}-1$): O···O = 2·836 (2), H···O = 1·93 (3) Å, O—H···O = 177 (2)°.

The packing analysis, carried out by using the *OPEC* program (Gavezzotti, 1983) and considering the H atoms in the positions calculated by the *PARST* program (C—H = 1·07 Å), gave the following data:

	(1)	(2)
C_K	0·705	0·678
V_M	216·2	276·2
S_M	252·6	316·5
$\sum r_i$	49·17	64·65

where C_K is the Kitaigorodskii (1973) packing coefficient, V_M is the molecular volume (Å^3), S_M is the molecular free surface (Å^2) as defined by Gavezzotti (1985), and $\sum r_i$ is the sum of the van der Waals radii of atoms in the molecule $r_H = 1·17$, $r_C = 1·75$, $r_O = 1·40$ Å).

The values of S_M are larger by 4·5% than those calculated with the linear equations derived in the previous paper (Ianelli *et al.*, 1989), probably as a consequence of less overcrowding and greater ring-strain effects. The lower value of the Kitaigorodskii coefficient, found for compound (2), can probably be related to the hydrogen bonding present in this compound.

The files of the Cambridge Crystallographic Database were accessed through 'Servizio Italiano di Diffusione Dati Cristallografici, CNR'.

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Structure of Pentacoordinated *b*-Carbonyl-*cd*-(*N*-hydroxy-*N*-nitrosobenzenaminato-*O*,*O*′)-*ae*-bis(triphenylphosphine)rhodium(I)

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Abstract. $[Rh(C_6H_5N_2O_2)(CO)\{P(C_6H_5)_3\}_2]$, M_r = 792·6, triclinic, $P\bar{1}$, a = 12·298 (9), b = 12·658 (2), c = 13·488 (3) Å, α = 90·72 (2), β = 106·38 (3), γ = 112·76 (3)°, V = 1840·1 (2) Å^3, Z = 2, D_m = 1·42 (1), D_x = 1·43 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 5·8 cm^{-1}, $F(000)$ = 812. Final R = 0·070 for 3406 observed reflections. The Rh atom has trigonal bipyramidal coordination with distortion in the trigonal plane [C—Rh—O angles of 159·6 (5) and 130·8 (5)° for amine and nitroso oxygens of the cupferron ligand respectively]. Bond distances: Rh—C = 1·77 (1), Rh—O(nitroso) = 2·339 (9), Rh—O(amine) = 2·147 (8), Rh—P = 2·323 (4) and 2·342 (4) Å.

Experimental. Yellow crystals of the title complex crystallized after 30 min from 0·6 cm^3 acetone solution containing 23 mg (0·043 mmol) $[Rh(C_6H_5N_2O_2)(CO)(PPh_3)]$ and 100 mg (0·38 mmol) PPh_3. Density determined by flotation in sodium iodide solution. Crystal size 0·09 × 0·15 × 0·2 mm, Enraf–Nonius CAD-4F diffractometer, graphite monochromator, Mo $K\alpha$ radiation, $\omega/2\theta$-scan technique, variable scan width $\Delta\omega$ = (0·77 + 0·35tanθ)°, scan speed maximum 3·3° min^{-1} in ω and minimum corresponding to 50 s per reflection, unit-cell parameters from least-squares refinement of 25 reflections with $7 < \theta < 15°$, measuring range $3 < \theta < 25°$, no absorption corrections, data corrected for Lorentz and polarization effects, mean intensity of three standard reflections measured every 3600 s of X-ray exposure varied from initial value by −0·8%, $0 < h < 14$, $-15 < k < 13$, $-16 < l < 15$. 6415 unique reflections of which 3406 observed reflections with $I > 3{\cdot}0\sigma(I)$ were used for all calculations (*XRAY72* system, Stewart, Kruger, Ammon,

0108-2701/90/071324-03$03.00