in Fig. 2. The intermolecular bonding arrangement in the present structure is thus similar to that in bis(p-trimethylsilyltolyl)tellurium dichloride (Chadha & Drake, 1984), phenoxatellurin 10,10-diiodide (McCullough, 1973), dibenzotellurophene diiodide (McCullough, 1975) and α-1,1-diiodo-3,4-benzo-1-telluracyclopentane (Knobler & Ziolo, 1979) in which the chains are parallel to the c, a, b, c axes respectively.

The cyclohexane ring adopts a regular chair conformation and the two substituents OCH_3 and $PhTeBr_2$, which are present at the 1,2 positions, occupy equatorial sites. This structure thus confirms the *trans* geometry of the compound as expected on the basis of bulkiness of the substituents. The average C—C distance of 1·51 Å, C—C—C bond angle of 110·8 (8)° and CCCC torsion angle of 56·1 (6)° are quite close to the cyclohexane values of 1·53 (1) Å, 111·6 (2) and 54·5 (8)° obtained from electron diffraction (Davis & Hassel, 1963).

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Formation of Diastereoisomeric Pinacols *via* Reductive Coupling of D_3-Trishomocubanone

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Abstract. Spiro[pentacyclo[7.3.0.0^{4,8}.0^{5,12}.0^{7,11}]dodecan-2-one-3,11′-pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane] (4b), $C_{22}H_{24}O$, $M_r = 303{\cdot}43$, monoclinic, $C2/c$, $a = 20{\cdot}593$ (3), $b = 6{\cdot}645$ (1), $c = 26{\cdot}061$ (4) Å, $\beta = 121{\cdot}78$ (1)°, $V = 3032{\cdot}3$ (9) Å^3, $Z = 8$, $D_x = 1{\cdot}133$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}74$ cm^{-1}, $F(000) = 1312$, $T = 298$ K, $R = 0{\cdot}0439$ for 1731 reflections. Compound (4b) consists of two spiro-fused cage systems. One cage is composed of three fused norbornane (bicyclo[2.2.1]heptane) moieties, while the other contains two norbornane and one bicyclo[2.2.2]octanone moiety. The spiro fusion involves the methano bridge of one norbornane and the ethano bridge of the bicyclo[2.2.2]octane group. The ideal envelope conformations of the five-membered rings comprising the norbornane moieties are significantly twisted by the ring fusions with the normal 0° torsion angles from 16·6 (2) to 28·5 (2)°. The bicyclooctane system also exhibits large twist distortions.

Introduction. As part of a program that is concerned with the synthesis and chemistry of novel polycyclic

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'cage compounds' (Marchand, 1989), we have undertaken a study of the reductive coupling of D_3-trishomocubanone (1) (Eaton, Hudson & Giordano, 1974). Reaction of (1) with lithium in liquid ammonia (Pradhan, Thakker & McPhail, 1987) afforded mainly D_3-trishomocubanol (Dekker & Oliver, 1979) (2) (58%) along with recovered starting material (12%). In addition, the desired pinacols [*meso* (3*a*, 3%) and D,L (3*b*, 3%)] were obtained in very low yield. Improved yields of pinacols (3*a*) and (3*b*) (*i.e.* 22% each) could be obtained when sodium in refluxing xylene was utilized (Fig. 1) (Wynberg, Boelema, Wieringa & Strating, 1970).

Of particular significance is the fact that *ca* equal amounts of (3*a*) and (3*b*) were obtained when either lithium–ammonia or sodium–xylene were utilized for reductive coupling of (1). Although enantiomeric recognition has been reported to accompany reductive coupling of a number of racemic and optically active ketones (Pradhan, Thakker & McPhail, 1987), this does not appear to be the case for the corresponding reaction of racemic (1).

Although the ^1H and ^{13}C NMR spectra were fully consistent with the assignment of the gross structures of (3*a*) and (3*b*), the absolute assignment of the *meso* and D,L structures could not be made. Single crystals of either diastereoisomer could not be obtained.

To complete the assignment of structures (3*a*) and (3*b*), the acid-promoted pinacol–pinacolone rearrangement of each isomer was studied. Treatment of pure (3*a*) and of pure (3*b*) with concentrated sulfuric acid at 273 K afforded the corresponding rearranged spiroketones [(4*a*) and (4*b*), respectively]. Careful fractional recrystallization of (4*b*) from diethyl ether afforded a useful single crystal, and X-ray analysis unequivocally provided the structure. From this information, the corresponding structures of (4*a*), (3*a*) and (3*b*) (Fig. 1) could be inferred.

Experimental. A colorless crystal of dimensions 0·40 × 0·45 × 0·50 mm was mounted on a Nicolet *R*3*m*/*μ* update of a $P2_1$ diffractometer; data collected in the ω-scan mode ($3 \leq 2\theta \leq 45°$), variable scan rate of 4–29·5° $\min^{-1}$, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($25{\cdot}92 \leq 2\theta \leq 29{\cdot}39°$); monitored reflections ($\bar{8}$,0,12) and ($8\bar{2}9$) showed variations of intensities of ±2%. Systematic absences (hkl, $h + k = 2n + 1$; $h0l$, h, $l = 2n + 1$; $00l$, $l = 2n + 1$) consistent with space group $C2/c$; 1979 unique reflections measured ($-22 \leq h \leq 18$, $0 \leq k \leq 7$, $0 \leq l \leq 26$), equivalent reflections averaged ($R_{\rm int} = 0{\cdot}025$), $1731 \geq 3\sigma(I)$; Lorentz–polarization corrections applied, ψ-scan-based empirical absorption correction applied (transmission factors 0·895 to 0·951); structure solved by direct methods and refined with anisotropic thermal parameters by a block-cascade least-squares technique, all H atoms located in a difference map and refined with isotropic thermal parameters; $R = 0{\cdot}0439$, $wR = 0{\cdot}0647$ for 304 parameters and 1731 reflections, $S = 1{\cdot}048$, $(\Delta/\sigma)_{\max} = 0{\cdot}021$, largest peaks in a final difference map of 0·14 and $-0{\cdot}24$ e Å^{-3}; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0{\cdot}00317F_o^2]^{-1}$. All computer programs supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Table 1 contains a listing of atomic positional parameters and Table 2 interatomic distances and bond angles.*

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* Lists of H-atom coordinates, anisotropic thermal parameters, NMR data and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52254 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

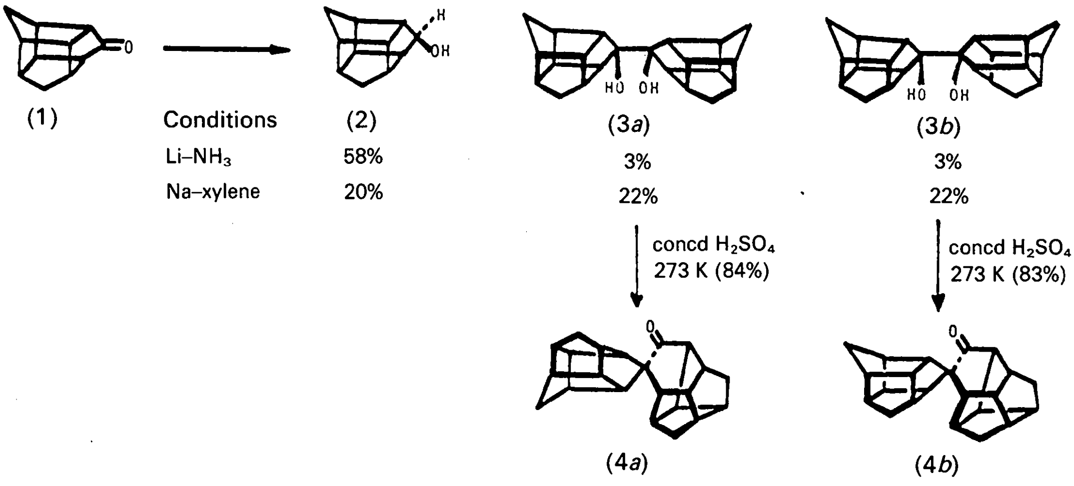

Fig. 1. Synthetic scheme.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for compound* (4*b*)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	−463 (1)	8105 (4)	922 (1)	57 (1)
C(2)	174 (1)	9540 (3)	992 (1)	48 (1)
C(3)	575 (1)	8315 (3)	716 (1)	42 (1)
C(4)	1426 (1)	8277 (2)	1204 (1)	34 (1)
C(5)	1263 (1)	7785 (3)	1705 (1)	34 (1)
C(6)	771 (1)	9530 (3)	1685 (1)	42 (1)
C(7)	356 (1)	8656 (4)	1968 (1)	53 (1)
C(8)	−7 (1)	6977 (3)	1517 (1)	51 (1)
C(9)	640 (1)	6100 (3)	1437 (1)	39 (1)
C(10)	289 (1)	6227 (3)	740 (1)	43 (1)
C(11)	−560 (1)	6530 (4)	464 (1)	62 (1)
C(12)	1902 (1)	6714 (2)	1114 (1)	34 (1)
C(13)	2710 (1)	6346 (3)	1663 (1)	36 (1)
C(14)	3170 (1)	5752 (3)	1359 (1)	42 (1)
C(15)	2583 (1)	5536 (3)	689 (1)	47 (1)
C(16)	2127 (1)	7373 (3)	662 (1)	41 (1)
C(17)	2760 (1)	9026 (3)	1005 (1)	46 (1)
C(18)	3519 (1)	7787 (3)	1391 (1)	50 (1)
C(19)	3843 (1)	8418 (3)	2040 (1)	56 (1)
C(20)	3068 (1)	8381 (3)	1984 (1)	44 (1)
C(21)	2654 (1)	9988 (3)	1499 (1)	45 (1)
C(22)	1833 (1)	10234 (3)	1292 (1)	47 (1)
O	1524 (1)	11876 (2)	1182 (1)	83 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for compound* (4*b*)

C(1)—C(2)	1·553 (3)	C(1)—C(8)	1·521 (3)
C(1)—C(11)	1·519 (4)	C(2)—C(3)	1·578 (4)
C(2)—C(6)	1·560 (2)	C(3)—C(4)	1·531 (2)
C(3)—C(10)	1·522 (3)	C(4)—C(5)	1·543 (3)
C(4)—C(12)	1·530 (3)	C(4)—C(22)	1·498 (3)
C(5)—C(6)	1·523 (3)	C(5)—C(9)	1·564 (2)
C(6)—C(7)	1·511 (4)	C(7)—C(8)	1·504 (3)
C(8)—C(9)	1·566 (4)	C(9)—C(10)	1·563 (3)
C(10)—C(11)	1·514 (3)	C(12)—C(13)	1·539 (2)
C(12)—C(16)	1·537 (3)	C(13)—C(14)	1·572 (4)
C(13)—C(20)	1·556 (2)	C(14)—C(15)	1·520 (2)
C(14)—C(18)	1·514 (3)	C(15)—C(16)	1·520 (3)
C(16)—C(17)	1·574 (3)	C(17)—C(18)	1·575 (3)
C(17)—C(21)	1·552 (4)	C(18)—C(19)	1·514 (3)
C(19)—C(20)	1·524 (3)	C(20)—C(21)	1·527 (3)
C(21)—C(22)	1·489 (3)	C(22)—O	1·219 (2)
C(2)—C(1)—C(8)	98·7 (1)	C(2)—C(1)—C(11)	105·6 (2)
C(8)—C(1)—C(11)	102·5 (2)	C(1)—C(2)—C(3)	104·0 (2)
C(1)—C(2)—C(6)	103·7 (2)	C(3)—C(2)—C(6)	104·1 (2)
C(2)—C(3)—C(4)	105·9 (1)	C(2)—C(3)—C(10)	98·3 (2)
C(4)—C(3)—C(10)	104·4 (1)	C(3)—C(4)—C(5)	92·5 (2)
C(3)—C(4)—C(12)	115·4 (1)	C(5)—C(4)—C(12)	115·4 (1)
C(3)—C(4)—C(22)	114·6 (1)	C(5)—C(4)—C(22)	114·1 (2)
C(12)—C(4)—C(22)	105·1 (2)	C(4)—C(5)—C(6)	104·3 (1)
C(4)—C(5)—C(9)	105·5 (1)	C(6)—C(5)—C(9)	98·9 (1)
C(2)—C(6)—C(5)	98·5 (2)	C(2)—C(6)—C(7)	105·3 (2)
C(5)—C(6)—C(7)	103·3 (2)	C(6)—C(7)—C(8)	94·5 (2)
C(1)—C(8)—C(7)	102·6 (2)	C(1)—C(8)—C(9)	99·2 (2)
C(7)—C(8)—C(9)	105·9 (2)	C(5)—C(9)—C(8)	103·3 (2)
C(5)—C(9)—C(10)	104·4 (2)	C(8)—C(9)—C(10)	103·3 (1)
C(3)—C(10)—C(9)	98·3 (1)	C(3)—C(10)—C(11)	103·6 (2)
C(9)—C(10)—C(11)	105·8 (2)	C(1)—C(11)—C(10)	94·4 (2)
C(4)—C(12)—C(13)	115·5 (1)	C(4)—C(12)—C(16)	113·6 (1)
C(13)—C(12)—C(16)	98·3 (2)	C(12)—C(13)—C(14)	102·3 (2)
C(12)—C(13)—C(20)	109·7 (1)	C(14)—C(13)—C(20)	104·3 (2)
C(13)—C(14)—C(15)	106·2 (2)	C(13)—C(14)—C(18)	98·3 (2)
C(15)—C(14)—C(18)	102·4 (2)	C(14)—C(15)—C(16)	94·3 (2)
C(12)—C(16)—C(15)	99·5 (2)	C(12)—C(16)—C(17)	104·9 (2)
C(15)—C(16)—C(17)	103·1 (2)	C(16)—C(17)—C(18)	104·2 (1)
C(16)—C(17)—C(21)	108·8 (2)	C(18)—C(17)—C(21)	102·2 (2)
C(14)—C(18)—C(17)	98·5 (1)	C(14)—C(18)—C(19)	103·0 (2)
C(17)—C(18)—C(19)	105·9 (2)	C(18)—C(19)—C(20)	93·8 (1)
C(13)—C(20)—C(19)	104·0 (2)	C(13)—C(20)—C(21)	105·2 (1)
C(19)—C(20)—C)21)	99·6 (2)	C(17)—C(21)—C(20)	97·9 (2)
C(17)—C(21)—C(22)	111·9 (2)	C(20)—C(21)—C(22)	114·1 (2)
C(4)—C(22)—C(21)	113·4 (2)	C(4)—C(22)—O	124·1 (2)
C(21)—C(22)—O	122·4 (2)		

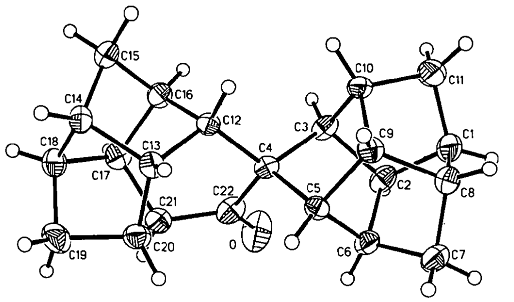

Fig. 2. Drawing of compound (4*b*). Thermal ellipsoids are drawn at the 35% probability level while H atoms are represented by spheres of arbitrary size.

Discussion. Fig. 2 is a drawing of compound (4*b*). A spiro fusion at C(4) joins two cage systems. One cage is composed of three fused norbornane rings while the second is composed of two norbornane moieties and a bicyclo[2.2.2]octanone unit. Isolated norbornane systems are composed of two fused five-membered rings which exhibit perfect envelope conformations. The bottom of the envelope has a torsion angle of 0°. In the cage system composed of the three fused norbornane moieties all rings are equally distorted as indicated by the bottom envelope torsion angles which average 18 (1)° for the six five-membered rings. In the other cage the four five-membered rings of the two norbornane moieties divide into two groups with averaged basal torsion angles of 16·7 (4) and 28·1 (4)°. The six-membered rings of bicyclo[2.2.2]octanone are normally in perfect boat conformations; however, fusion to the norbornane moieties results in a skew boat or twist conformation (Toromanoff, 1980).

In norbornane the observed and calculated (*ab initio*) methano bridge bonds are the shortest and the ethane bond is the longest (Doms, Van Hemelrijk, Van de Mieroop, Lenstra & Geise, 1985; Doms, Van den Enden, Geise & Van Alsenoy, 1983). In *MM*2 molecular-mechanics calculations the bond-length variations in these systems are not reproduced; however, the introduction of a torsion-stretch interaction (Allinger, Geise, Pyckhout, Paquette & Gallucci, 1989) now reproduces the correct bond-length patterns. In the cage with the three fused norbornane moieties four bridging methano bonds range from 1·504 (3) to 1·519 (4) Å while the two methano bonds at the spiro fusion center are 1·543 (3) and 1·531 (2) Å. Because of fusion the six ethano bonds are also connecting bonds (between ethano and methano bridges) and range from 1·553 (3) to 1·578 (4) Å. The three pure connecting bonds range from 1·521 (3) to 1·523 (3) Å. In general, this pattern is repeated in the other cage; however, the bicyclo[2.2.2]octanone moiety introduces additional variations. The carbonyl C atom is slightly pyramidalized with C(22) lying 0·021 (3) Å out of the plane of the three connecting atoms. The shortest significant contact between the two cages is 2·12 (4) Å between H(10) and H(12).

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Stereochemistry of Rings. XVII.* Norbornane Derivatives. 1. 2-(*p*-Methoxyphenyl)-3-phenylbicyclo[2.2.1]heptane (I) and 2-(*p*-Nitrophenyl)-3-phenylbicyclo[2.2.1]heptane (II)

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Abstract. (I): $C_{20}H_{22}O$, monoclinic, $P2_1/a$, $M_r = 278{\cdot}4$, $a = 22{\cdot}039$ (2), $b = 5{\cdot}910$ (2), $c = 11{\cdot}722$ (2) Å, $\beta = 92{\cdot}75$ (3)°, $V = 1525{\cdot}0$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}21$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5{\cdot}22$ cm^{-1}, $F(000) = 600$, room temperature. (II): $C_{19}H_{19}NO_2$, monoclinic, $P2_1/n$, $a = 9{\cdot}141$ (2), $b = 13{\cdot}048$ (2), $c = 13{\cdot}091$ (3) Å, $\beta = 92{\cdot}47$ (3)°, $V = 1559{\cdot}9$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}25$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 6{\cdot}06$ cm^{-1}, $F(000) = 624$, room temperature. $R = 0{\cdot}049$ for 1953 reflections above $2\sigma(I)$ for compound (I) and $R = 0{\cdot}060$ and $wR = 0{\cdot}068$ for 2169 reflections above $2\sigma(I)$ for compound (II). Only small conformational differences, due to the differently substituted benzene groups and the methylene bridge, are remarkable in the two six-membered rings of the norbornane skeletons which show boat conformations. The planar phenyl rings are all in equatorial positions and form dihedral angles of 43·4 (1) and 51·8 (1)° to each other in (I) and (II) respectively.

Introduction. Extensive structural analysis on norbornane derivatives has been carried out in recent years in view of their increasing importance in organic synthesis. In particular, in the course of studies aimed at the synthesis of rigid systems containing adjacent aromatic nuclei, two derivatives of bicyclo[2.2.1]heptane with two different aryl groups in 2,3 positions were prepared starting from bicycloheptane, aryl bromides and sodium tetraphenylborate under the catalytic action of a Pd complex (Catellani, Chiusoli, Fornasari & Concari, 1989). In view of the spectroscopic properties and reactivity of these compounds and as part of our program of investigations on ring deformations induced by substituents it has been deemed useful to determine the conformation of the two molecules by X-ray methods.

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* Part XVI: Bocelli & Rizzoli (1989).

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