X-Ray Crystal Structures of 2,2'-Bridged Biphenyls with Heterocyclic Bridging Rings: Contraction in Ring Size on Reduction

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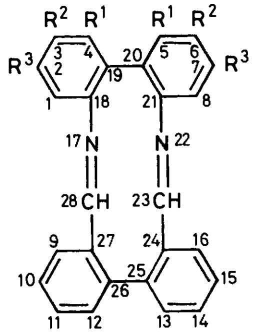
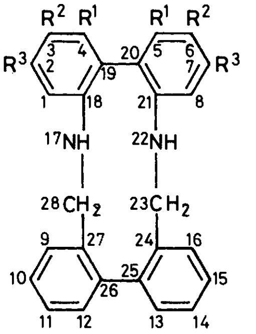
X-Ray crystal structure analysis confirms that two of the four tetrabenzo[*b,d,h,j*][1,6]diazacyclododecines previously investigated have 12-membered rings; there is a strong presumption that the other two have a similar structure. Three of the four compounds undergo (dimethylamino)borane reduction to the tetrahydro derivatives in a process shown by *X*-ray analysis and/or n.m.r. spectroscopy to involve C–N bond breaking and ring contraction from 12- to seven-membered rings. The fourth compound is shown by *X*-ray analysis to retain its (presumed) 12-membered ring structure when the tetrahydro derivative is produced by catalytic hydrogenation.

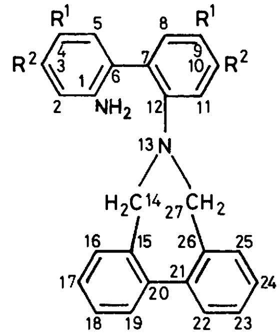
In an earlier paper[1] we discussed the geometry of four tetrabenzodiazacyclododecines (**1**)—(**4**) obtained by the interaction of biphenyl-2,2'-dicarbaldehyde and some 2,2'-diaminobiphenyls. Spectroscopic data (^1H n.m.r. and u.v.) supported the twelve-membered ring structure and chirality was demonstrated for compounds (**2**) and (**4**) by the use of a chiral lanthanide shift reagent.



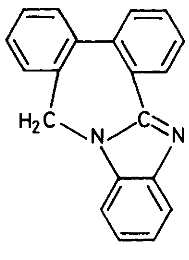
(**1**) $R^1 = R^2 = R^3 = H$
(**2**) $R^1 = R^2 = H$, $R^3 = CO_2Me$
(**3**) $R^1 = R^3 = H$, $R^2 = OMe$
(**4**) $R^1 = CO_2Me$, $R^2 = R^3 = H$



(**5**) $R^1 = R^2 = R^3 = H$
(**6**) $R^1 = R^2 = H$, $R^3 = CO_2Me$
(**7**) $R^1 = R^3 = H$, $R^2 = OMe$
(**8**) $R^1 = CO_2Me$, $R^2 = R^3 = H$



(**9**) $R^1 = R^2 = H$
(**10**) $R^1 = H$, $R^2 = CO_2Me$
(**11**) $R^1 = OMe$, $R^2 = H$



(**12**)

X-Ray crystal structure analysis confirms that compounds (**2**) and (**3**) have 12-membered rings. Reduction [(dimethylamino)borane] of compounds (**1**) (which can also be assumed to have a 12-membered ring) and (**2**) gives the corresponding tetrahydrotetrabenzo compounds shown by *X*-ray crystal structure analysis to have undergone C–N bond breaking and ring contraction to form the seven-membered ring compounds (**9**) and (**10**) (Scheme). It is reasonable to assume that compound (**3**) behaves similarly and this is confirmed by the spectroscopic data reported later in the paper. No crystals suitable for *X*-ray analysis could be obtained for compounds (**1**) and (**4**). Compound (**4**) fails to give a satisfactory product with (dimethylamino)borane but undergoes catalytic hydrogenation and is shown by *X*-ray analysis to have retained its presumed 12-membered ring structure in the process.

Collection and Processing of X-*Ray Data from Compounds* (**3**), (**8**), (**9**), *and* (**10**).—Apart from compound (**8**) *X*-ray reflection data were collected on an automated Picker four-circle diffractometer in θ—2θ scan mode with profile analysis[2] using Zr-filtered Mo-K_α radiation (λ = 0.7107 Å). Data from (**8**) were collected on a CAD-4 diffractometer using Ni-filtered Cu-K_α radiation (λ = 1.5418 Å) in θ—2θ scan mode. Except for compound (**8**), the NRC PDP-8e package of programmes was used for all calculations.[3] For compound (**8**) the XSTAL package was used.[4] All five crystals were weakly diffracting. All structures were solved by direct methods using either MULTAN[5] or XTAL[4] and refined by block-diagonal least-squares with weights $1/\sigma^2(F)$ based on counting statistics. Scattering factors were taken from International Tables.[6]

The numbering of the atoms in structures (**2**), (**3**), and (**8**)—(**10**) is given in the structural formulae and in the ORTEP[7] plots (Figures 1—5). Fractional atomic co-ordinates for (**2**) and the other four compounds are given in Tables 2—6, bond lengths

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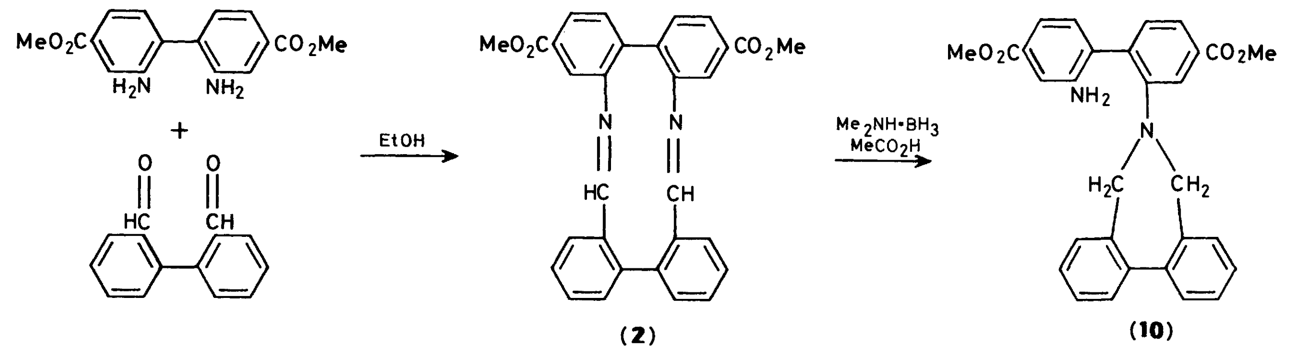
Table 1. Crystallographic details for compounds (**2**), (**3**), (**8**), (**9**), and (**10**)

	(**2**)	(**3**)	(**8**)	(**9**)	(**10**)
Formula	$C_{30}H_{22}N_2O_4$	$C_{28}H_{22}N_2O_2$	$C_{30}H_{26}N_2O_4$	$C_{26}H_{22}N_2$	$C_{30}H_{26}N_2O_4$
M	474.52	418.50	478.55	362.47	478.55
Crystal system	Tetragonal	Monoclinic	Triclinic	Monoclinic	Monoclinic
Unit cell a/Å	11.454(1)	11.243(2)	8.944(2)	10.431(4)	9.477(2)
b/Å	—	11.471(3)	9.294(1)	17.286(5)	15.599(3)
c/Å	36.196(6)	16.981(4)	16.846(2)	11.339(4)	16.528(4)
α/°	—	—	79.60(1)	—	—
β/°	—	106.04(2)	88.07(2)	109.04(1)	96.59(2)
γ/°	—	—	62.78(2)	—	—
Space group	$P4_12_12$	$I2/c$	$P\bar{1}$	$A2/m$	$P2_1/n$
Z	8	4	2	4	4
D_x/g cm^{-3}	1.33	1.32	1.30	1.25	1.30
Crystal size/mm	0.25 × 0.2 × 0.3	0.15 × 0.2 × 0.3	0.25 × 0.3 × 0.4	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.4
$2\theta_{max.}$/°	50	45	148	50	50
Total reflections measured	6 016	2 195	5 168	5 068	4 677
Significant	1 254	572	4 273	793	918
$[I > s\sigma(I)]$, s =	2.5	2.0	2.0	2.5	2.0
R_F	0.110	0.077	0.053	0.097	0.076
R_w	0.070	0.062	0.066	0.036	0.051



Scheme.

are given in Tables 7 and 8, bond angles in Tables 9 and 10, and torsion angles of interest in Tables 11 and 12.*

Compound (**2**). The large c unit-cell dimension caused rather poor resolution for many adjacent Bragg reflections. This could account for the rather high R_F value of 0.110.

Compound (**3**). The space group required molecular symmetry is a diad axis. This cuts the mid-points of bonds C(19)–C(20) and C(25)–C(26). Thus not all the atoms are given independent numbers.

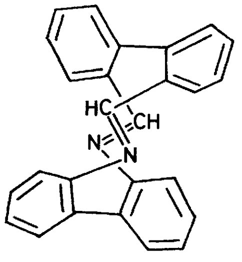
Compound (**8**). The crystal belongs to the triclinic space group $P\bar{1}$ with two molecules, one of each chirality, per unit cell.

Compound (**9**). This structure is disordered. Each molecule is mirrored with half weight about the space group mirror planes at $y = 0, \frac{1}{2}$. Atom C(17) lies too close to $y = \frac{1}{2}$ for its images to be resolvable. Certain other atoms are rather poorly resolved due to disorder and all their positions were calculated using the best molecular fitting program BMFIT.[8]

Compound (**10**). This structure shows disorder of the benzene ring C(1)—C(6) which occupies two positions related by 180° rotation about the bond C(6)—C(7). Hence the attached atoms N(1) and C(29) of the methyl group also have two half-occupied positions each. The two methoxycarbonyl oxygen atoms O(1) and O(2) and their images almost exactly coincide.

Results and Discussion

The diazacyclododecine systems of compounds (**2**) and (**3**) have closely similar structures. In both, the –CH=N– bonding is *trans* and the molecules can be depicted as in (**I**). In this they closely



(I)

resemble the homocyclic analogue of known crystal structure[9] which has symmetry D_2 (222). As noted above, compound (**3**) is required crystallographically to have at least one diad axis. Neither molecule (**2**) or (**3**) can have exact D_2 symmetry because the N–C and corresponding C–C bonds have different lengths and there are differences in the bond angles subtended at these atoms. Nevertheless the molecules approximate D_2 symmetry quite closely.

The saturated compound (**8**) has, of course, greater conformational flexibility than its unsaturated counterparts. However, its overall conformation is very similar having the

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* *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Hydrogen-atom co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Table 2. Fractional atomic co-ordinates, with e.s.d.s in parentheses, for the non-hydrogen atoms of compound (**2**)

	x	*y*	*z*
C(1)	−0.053 4(17)	0.141 6(18)	0.311 3(6)
C(2)	0.019 4(14)	0.044 9(14)	0.303 5(5)
C(3)	0.141 5(17)	0.057 7(16)	0.306 7(5)
C(4)	0.184 6(17)	0.172 3(19)	0.312 5(5)
C(5)	0.243 2(14)	0.399 8(16)	0.350 3(4)
C(6)	0.294 7(15)	0.508 5(17)	0.358 0(5)
C(7)	0.270 9(17)	0.602 1(16)	0.338 4(5)
C(8)	0.194 6(15)	0.592 6(17)	0.306 1(5)
C(9)	−0.298 4(16)	0.481 8(21)	0.336 3(7)
C(10)	−0.381 6(17)	0.570 1(17)	0.338 9(5)
C(11)	−0.416 5(17)	0.632 1(17)	0.305 8(7)
C(12)	−0.367 9(16)	0.606 5(17)	0.271 9(6)
C(13)	−0.282 9(15)	0.500 6(17)	0.203 2(5)
C(14)	−0.230 0(19)	0.484 8(19)	0.166 8(5)
C(15)	−0.109 6(17)	0.479 6(21)	0.165 5(4)
C(16)	−0.041 0(17)	0.499 0(17)	0.196 6(6)
N(17)	−0.080 5(12)	0.346 6(13)	0.323 5(3)
C(18)	−0.005 6(17)	0.252 9(14)	0.313 5(5)
C(19)	0.116 3(14)	0.270 7(15)	0.314 5(5)
C(20)	0.170 0(15)	0.382 6(13)	0.319 8(4)
C(21)	0.141 1(15)	0.483 3(14)	0.298 4(4)
N(22)	0.075 2(13)	0.462 9(13)	0.266 2(4)
C(23)	−0.019 7(14)	0.526 2(16)	0.262 3(4)
C(24)	−0.097 4(16)	0.511 4(16)	0.231 4(5)
C(25)	−0.215 2(16)	0.511 1(14)	0.230 8(5)
C(26)	−0.277 7(15)	0.526 8(15)	0.271 3(4)
C(27)	−0.244 9(13)	0.464 6(16)	0.301 2(4)
C(28)	−0.160 7(17)	0.363 3(13)	0.299 6(5)
C(29)	−0.030 4(17)	−0.069 4(16)	0.296 7(5)
C(30)	−0.212 8(20)	−0.171 1(21)	0.289 2(7)
C(31)	0.316 3(16)	0.717 2(19)	0.343 0(5)
C(32)	0.448 4(21)	0.831 5(21)	0.382 1(6)
O(1)	0.023 6(13)	−0.161 8(12)	0.296 2(4)
O(2)	−0.146 7(13)	−0.064 5(12)	0.291 2(4)
O(3)	0.316 6(15)	0.800 2(13)	0.321 8(4)
O(4)	0.384 7(12)	0.722 1(12)	0.373 9(3)

–C–NH–CH_2–C– groups approximately *trans* with torsion angles 140.2° and 141.0° (Table 11). Like the unsaturated counterparts the symmetry is close to D_2.

Two forms of the corresponding saturated homocyclic ring compounds are known. They have been shown[10] by *X*-ray analysis to be configurational isomers. The *meso*-form has centrosymmetric molecules with *cis* –C–CH_2–CH_2–C– groups (torsion angles 54.2° and 53.2°* for the two independent molecules). It is thus quite different from the molecule of compound (**8**). The racemic homocyclic form resembles the molecule of compound (**8**) much more closely. The –C–CH_2–CH_2–C– groups are *trans* and almost planar (torsion angles 175.8° and 173.1°) and the symmetry is closely D_2. It is not known whether the *meso* analogue of compound (**8**) exists.

The two seven-membered ring compounds (**9**) and (**10**) have closely similar configurations, as evidenced by the correspondence in bond and dihedral angles. In both, the seven-membered heterocyclic ring has a virtual diad axis of symmetry passing through N(13) and the mid-point of bond C(20)–C(21). This can be seen most clearly in Figure 5 where the diad axis lies almost in the plane of the Figure.

Table 3. Fractional atomic co-ordinates, with e.s.d.s in parentheses, for the non-hydrogen atoms of compound (**3**)

	x	*y*	*z*
C(1)	0.734 2(10)	0.865 6(10)	0.158 3(7)
C(2)	0.706 3(10)	0.770 5(10)	0.106 9(7)
C(3)	0.789 2(11)	0.684 5(10)	0.109 8(7)
C(4)	0.907 0(9)	0.690 7(9)	0.166 1(6)
C(9)	0.854 2(12)	1.171 9(11)	0.370 0(7)
C(10)	0.881 6(14)	1.267 2(13)	0.421 4(8)
C(11)	0.953 5(12)	1.356 0(11)	0.406 9(8)
C(12)	1.000 7(12)	1.355 2(10)	0.342 0(7)
N(17)	0.880 1(8)	0.966 5(7)	0.273 0(5)
C(18)	0.852 0(11)	0.874 3(9)	0.214 2(7)
C(19)	0.937 2(9)	0.784 1(8)	0.220 1(6)
C(26)	0.974 6(11)	1.260 7(9)	0.286 0(7)
C(27)	0.900 0(10)	1.171 8(9)	0.302 0(6)
C(28)	0.872 4(11)	1.071 0(10)	0.244 9(7)
C(29)	0.650 5(11)	0.575 0(11)	0.004 8(7)
O	0.770 8(7)	0.586 0(7)	0.062 2(5)

Table 4. Fractional atomic co-ordinates, with e.s.d.s in parentheses, for the non-hydrogen atoms of compound (**8**). (No e.s.d.s are given where the atomic positions were not allowed to vary)

	x	*y*	*z*
C(1)	0.305 8(3)	1.011 6(2)	0.128 5(1)
C(2)	0.155 4(3)	1.125 0(2)	0.150 1(1)
C(3)	0.120 7(2)	1.127 6(2)	0.230 7(1)
C(4)	0.239 6(2)	1.010 1(2)	0.290 1(1)
C(5)	0.533 4(2)	0.611 9(2)	0.366 3(1)
C(6)	0.676 3(3)	0.489 7(3)	0.412 5(1)
C(7)	0.814 0(3)	0.515 3(3)	0.421 8(1)
C(8)	0.813 5(2)	0.662 4(3)	0.387 5(1)
C(9)	0.947 3(3)	0.588 5(3)	0.097 8(2)
C(10)	1.118 2(3)	0.516 2(3)	0.117 3(2)
C(11)	1.186 6(3)	0.604 9(3)	0.145 9(2)
C(12)	1.085 2(3)	0.766 3(2)	0.152 0(1)
C(13)	0.773 6(3)	1.136 4(3)	0.062 0(1)
C(14)	0.693 5(3)	1.303 6(3)	0.062 2(2)
C(15)	0.654 1(3)	1.359 1(3)	0.133 9(2)
C(16)	0.694 3(3)	1.247 3(3)	0.206 2(1)
N(17)	0.581 6(2)	0.779 0(2)	0.164 6(1)
C(18)	0.428 3(2)	0.892 6(2)	0.187 0(1)
C(19)	0.393 4(2)	0.889 0(2)	0.269 9(1)
C(20)	0.530 3(2)	0.761 3(2)	0.329 4(1)
C(21)	0.671 4(2)	0.787 2(2)	0.341 1(1)
N(22)	0.665 3(2)	0.935 9(2)	0.306 5(1)
C(23)	0.813 5(2)	0.960 1(3)	0.286 4(1)
C(24)	0.775 5(2)	1.077 7(2)	0.207 4(1)
C(25)	0.815 1(2)	1.021 6(2)	0.134 1(1)
C(26)	0.913 8(2)	0.842 6(2)	0.130 7(1)
C(27)	0.842 4(3)	0.751 4(2)	0.104 9(1)
C(28)	0.655 6(3)	0.820 5(3)	0.090 2(1)
C(29)	0.190 6(2)	1.025 4(2)	0.374 6(1)
C(30)	0.282 8(3)	0.974 8(3)	0.510 8(2)
C(31)	0.383 2(3)	0.584 8(2)	0.360 0(1)
C(32)	0.292 8(3)	0.381 5(3)	0.359 8(2)
O(1)	0.046 8(2)	1.094 5(2)	0.392 5(1)
O(2)	0.321 1(2)	0.962 8(2)	0.427 3(1)
O(3)	0.238 8(2)	0.687 1(2)	0.357 9(1)
O(4)	0.427 7(2)	0.426 0(2)	0.360 3(1)

Spectroscopic Data.—Reduction of compounds (**1**)—(**4**) resulted in the addition of 4 H and it was assumed[1,11] that the reduction products had 12-membered ring structures (**5**)—(**8**). Spectroscopic data were not unambiguous but it was assumed that the more flexible reduced ring increased conformational possibilities and thus led to more than the expected number of signals in some of the n.m.r. spectra. However, the ^1H n.m.r. spectrum of the dimethyl 2,7-dicarboxylate [assumed to be compound (**6**)] showed two methyl group signals which failed to coalesce on heating a [$^2H_6$]dimethyl sulphoxide (DMSO)

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* Calculated from the published data.

Table 5. Fractional atomic co-ordinates, with e.s.d.s in parentheses, for the non-hydrogen atoms of compound (**9**). (No e.s.d.s are given where the atomic positions were not allowed to vary)

	x	*y*	*z*
C(1)	0.179 4(12)	0.260 9(7)	0.158 7(10)
N(1)	0.2535	0.2123	0.1061
C(2)	0.111 2(13)	0.236 1(7)	0.240 5(11)
C(3)	0.038 5(19)	0.284 0(8)	0.293 5(12)
C(4)	0.030 8(11)	0.361 3(8)	0.268 5(11)
C(5)	0.095 0(11)	0.392 6(6)	0.193 3(10)
C(6)	0.170 2(10)	0.342 4(7)	0.138 4(9)
C(7)	0.2377	0.3821	0.0531
C(8)	0.153 3(10)	0.424 4(6)	−0.047 5(10)
C(9)	0.208 3(13)	0.456 0(6)	−0.133 7(10)
C(10)	0.339 3(13)	0.444 8(6)	−0.123 4(11)
C(11)	0.424 2(9)	0.403 9(6)	−0.023 9(9)
C(12)	0.373 4(10)	0.373 0(6)	0.064 4(9)
N(13)	0.460 4(8)	0.328 7(5)	0.167 7(8)
C(14)	0.465 5(12)	0.348 8(6)	0.294 4(8)
C(15)	0.603 3(12)	0.384 2(6)	0.369 4(9)
C(16)	0.602 9(10)	0.461 8(7)	0.407 7(9)
C(17)	0.723 0(13)	0.5	0.483 6(8)
C(18)	0.842 3(12)	0.449 9(8)	0.522 4(11)
C(19)	0.836 3(12)	0.373 8(7)	0.487 5(11)
C(20)	0.722 3(12)	0.339 2(8)	0.407 7(9)
C(21)	0.7200	0.2629	0.3748
C(22)	0.785 3(9)	0.207 8(7)	0.462 7(9)
C(23)	0.7850	0.1297	0.4298
C(24)	0.718 6(13)	0.108 0(7)	0.310 6(13)
C(25)	0.652 8(12)	0.162 9(8)	0.219 5(11)
C(26)	0.653 3(10)	0.241 7(7)	0.253 8(10)
C(27)	0.587 3(11)	0.301 0(6)	0.154 8(9)

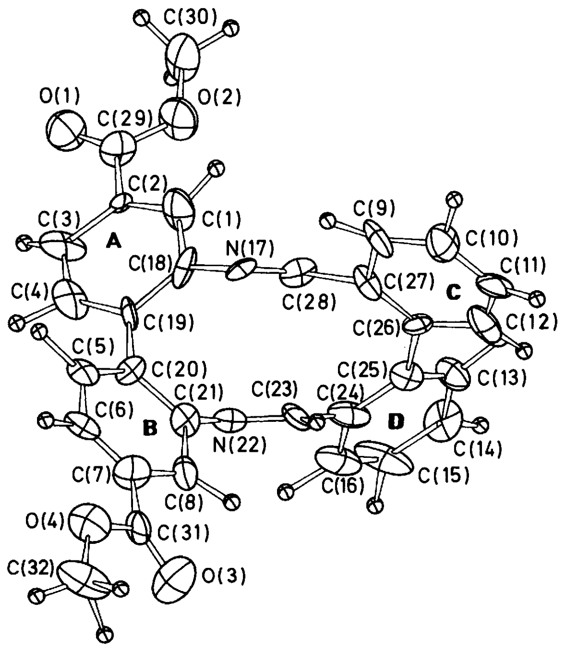


Figure 1. ORTEP[7] plot with 50% probability ellipsoids for compound (**2**)

solution to 117 °C and hence the *X*-ray crystal structure analysis reported above was undertaken. As seen, this shows that the compound has a seven-membered ring and a free amino group and is structure (**10**) in which the two methyl groups are clearly not equivalent.

As seen above, of the other reduced compounds, that which is

Table 6. Fractional atomic co-ordinates, with e.s.d.s in parentheses, for the non-hydrogen atoms of compound (**10**)

	x	*y*	*z*
C(1)	−0.001 9(19)	0.235 6(10)	−0.174 6(9)
N(1)	0.115 7(20)	0.258 3(13)	−0.207 2(12)
N(1′)	−0.127(5)	0.160(3)	0.039(3)
C(2)	−0.142 7(19)	0.250 7(11)	−0.212 7(10)
C(3)	−0.267 2(18)	0.233 3(10)	−0.181 6(11)
C(4)	−0.264 0(18)	0.198 3(11)	−0.104 6(11)
C(5)	−0.135 7(16)	0.179 6(11)	−0.054 1(12)
C(6)	−0.015 3(16)	0.199 3(8)	−0.094 7(10)
C(7)	0.124 2(19)	0.179 9(8)	−0.042 5(10)
C(8)	0.140 4(17)	0.095 4(11)	−0.016 4(10)
C(9)	0.257 7(18)	0.063 9(10)	0.380 8(11)
C(10)	0.370 8(16)	0.120 1(11)	0.047 9(9)
C(11)	0.359 7(18)	0.206 2(9)	0.025 1(10)
C(12)	0.237 0(18)	0.234 3(8)	−0.020 3(9)
N(13)	0.229 6(12)	0.319 6(7)	−0.048 4(8)
C(14)	0.361 4(16)	0.370 0(8)	−0.039 3(9)
C(15)	0.341 6(14)	0.462 7(10)	−0.073 6(8)
C(16)	0.396 5(16)	0.481 9(11)	−0.142 9(9)
C(17)	0.393 6(19)	0.567 5(11)	−0.171 8(11)
C(18)	0.334 2(18)	0.630 5(11)	−0.126 2(11)
C(19)	0.276 2(18)	0.611 0(8)	−0.055 2(9)
C(20)	0.282 1(15)	0.524 6(10)	−0.026 6(8)
C(21)	0.220 5(15)	0.502 8(9)	0.048 6(9)
C(22)	0.245 4(17)	0.551 5(11)	0.118 2(10)
C(23)	0.201 6(20)	0.524 7(11)	0.190 7(11)
C(24)	0.123 2(20)	0.450 4(12)	0.194 0(11)
C(25)	0.091 0(18)	0.400 0(10)	0.124 8(11)
C(26)	0.143 2(16)	0.425 1(9)	0.053 2(10)
C(27)	0.107 9(14)	0.371 4(8)	−0.022 4(9)
C(28)	−0.413 3(19)	0.261 2(12)	−0.230 2(11)
C(29)	−0.548 5(23)	0.331 0(18)	−0.331 9(14)
C(29′)	−0.637(5)	0.285(5)	−0.267(3)
C(30)	0.503 3(21)	0.094 9(9)	0.095 7(11)
C(31)	0.636 8(18)	−0.017 8(11)	0.165 9(12)
O(1)	−0.522 5(14)	0.239 0(9)	−0.199 4(9)
O(2)	−0.404 9(15)	0.305 3(8)	−0.293 5(8)
O(3)	0.606 6(13)	0.140 8(7)	0.118 3(8)
O(4)	0.512 5(11)	0.012 9(7)	0.118 0(7)

Table 7. Bond lengths (Å) for the 12-membered ring compounds (**2**), (**3**), and (**8**) (benzene rings excluded), with e.s.d.s in parentheses

	(**2**)	(**3**)	(**8**)
N(17)–C(18)	1.42(2)	1.43(1)	1.386(2)
N(22)–C(21)	1.41(2)	—	1.377(3)
N(17)–C(28)	1.27(2)	1.28(1)	1.407(3)
N(22)–C(23)	1.31(2)	—	1.462(3)
C(18)–C(19)	1.41(2)	1.29(1)	1.418(2)
C(21)–C(20)	1.43(2)	—	1.415(3)
C(19)–C(20)	1.43(2)	1.49(2)	1.496(2)
C(25)–C(26)	1.64(2)	1.48(2)	1.496(3)
C(26)–C(27)	1.35(2)	1.39(1)	1.401(4)
C(25)–C(24)	1.35(2)	—	1.399(3)
C(27)–C(28)	1.51(2)	1.49(1)	1.501(3)
C(23)–C(24)	1.44(2)	—	1.498(3)
C(3)–O	—	1.37(1)	—
C(2)–C(29)	1.45(2)	—	—
C(7)–C(31)	1.43(2)	—	—
C(4)–C(29)	—	—	1.488(3)
C(5)–C(31)	—	—	1.486(3)
C(29)–O	—	1.44(1)	—
C(29)–O(1)	1.23(2)	—	1.202(2)
C(31)–O(3)	1.22(2)	—	1.200(2)
C(29)–O(2)	1.35(2)	—	1.323(3)
C(31)–O(4)	1.37(2)	—	1.340(3)
C(30)–O(2)	1.44(2)	—	1.448(3)
C(32)–O(4)	1.48(2)	—	1.444(4)

Table 8. Bond lengths (Å) for seven-membered ring compounds (**9**) and (**10**) (benzene rings excluded), with e.s.d.s in parentheses

	(9)	**(10)**
C(1)–N(1)	1.40	1.34(2)
C(12)–N(13)	1.45(1)	1.41(2)
N(13)–C(14)	1.46(1)	1.47(2)
N(13)–C(27)	1.46(1)	1.51(2)
C(14)–C(15)	1.54(2)	1.56(2)
C(15)–C(20)	1.41(2)	1.40(2)
C(20)–C(21)	1.37	1.47(2)
C(21)–C(26)	1.37	1.42(2)
C(26)–C(27)	1.51(1)	1.51(2)
C(3)–C(28)	—	1.58(2)
C(28)–O(1)	—	1.25(2)
C(28)–O(2)	—	1.26(2)
C(29)–O(2)	—	1.49(2)
C(10)–C(30)	—	1.46(2)
C(30)–O(3)	—	1.23(2)
C(30)–O(4)	—	1.33(2)
C(31)–O(4)	—	1.42(2)

Table 9. Bond angles (°) for the 12-membered ring compounds (**2**), (**3**), and (**8**) (benzene rings excluded), with e.s.d.s in parentheses

	(2)	**(3)**	**(8)**
C(18)–N(17)–C(28)	112(1)	117(1)	120.7(1)
C(21)–N(22)–C(23)	116(1)	—	124.3(1)
C(1)–C(18)–N(17)	118(2)	121(1)	120.8(2)
C(8)–C(21)–N(22)	116(1)	—	121.4(2)
N(17)–C(18)–C(19)	119(1)	119(1)	120.0(1)
N(22)–C(21)–C(20)	116(1)	—	118.8(1)
C(4)–C(19)–C(20)	120(2)	117(1)	125.0(2)
C(5)–C(20)–C(19)	119(1)	—	123.4(2)
C(18)–C(19)–C(20)	124(2)	123(1)	116.6(1)
C(21)–C(20)–C(19)	123(1)	—	117.0(2)
N(17)–C(28)–C(27)	123(1)	120(1)	109.8(1)
N(22)–C(23)–C(24)	122(2)	—	108.5(2)
C(9)–C(27)–C(28)	114(2)	119(1)	119.4(3)
C(16)–C(24)–C(23)	115(2)	—	119.7(2)
C(26)–C(27)–C(28)	124(1)	118(1)	121.8(2)
C(25)–C(24)–C(23)	129(2)	—	121.4(2)
C(13)–C(25)–C(24)	129(2)	—	119.2(2)
C(12)–C(26)–C(27)	123(2)	117(1)	119.2(2)
C(24)–C(25)–C(26)	115(1)	—	122.0(2)
C(27)–C(26)–C(25)	122(1)	123(1)	123.0(2)
C(2)–C(3)–O	—	126(1)	—
C(4)–C(3)–O	—	114(1)	—
C(1)–C(2)–C(29)	121(2)	—	—
C(8)–C(7)–C(31)	112(2)	—	—
C(3)–C(2)–C(29)	120(2)	—	—
C(6)–C(7)–C(31)	128(2)	—	—
C(3)–C(4)–C(29)	—	—	114.9(1)
C(6)–C(5)–C(31)	—	—	119.3(2)
C(19)–C(4)–C(29)	—	—	123.8(1)
C(20)–C(5)–C(31)	—	—	120.8(1)
C(2)–C(29)–O(1)	126(2)	—	—
C(7)–C(31)–O(3)	130(2)	—	—
C(2)–C(29)–O(2)	112(1)	—	—
C(7)–C(31)–O(4)	110(2)	—	—
C(4)–C(29)–O(1)	—	—	123.1(2)
C(5)–C(31)–O(3)	—	—	126.2(2)
C(4)–C(29)–O(2)	—	—	113.3(2)
C(5)–C(31)–O(4)	—	—	111.4(2)
O(1)–C(29)–O(2)	122(2)	—	123.4(2)
O(3)–C(31)–O(4)	119(2)	—	122.4(2)
C(29)–O(2)–C(30)	119(2)	—	116.3(2)
C(31)–O(4)–C(32)	119(2)	—	116.7(2)

Table 10. Bond angles (°) for the seven-membered ring compounds (**9**) and (**10**) (benzene rings excluded), with e.s.d.s in parentheses

	(9)	**(10)**
C(12)–N(13)–C(14)	118.8(8)	118(1)
C(12)–N(13)–C(27)	116.3(8)	115(1)
C(14)–N(13)–C(27)	115.7(8)	111(1)
N(13)–C(14)–C(15)	111.4(9)	113(1)
C(14)–C(15)–C(20)	121.4(10)	119(1)
C(15)–C(20)–C(21)	120.9	122(1)
C(20)–C(21)–C(26)	119.3	120(1)
C(21)–C(26)–C(27)	121.4	120(1)
C(26)–C(27)–N(13)	110.9(8)	115(1)
C(3)–C(28)–O(1)	—	116(2)
C(3)–C(28)–O(2)	—	116(2)
O(1)–C(28)–O(2)	—	128(2)
C(28)–O(2)–C(29)	—	111(2)
C(10)–C(30)–O(3)	—	128(1)
C(10)–C(30)–O(4)	—	116(2)
O(3)–C(30)–O(4)	—	117(1)
C(30)–O(4)–C(31)	—	120(1)

Table 11. (a) Dihedral angles (°), and (b) torsion angles (°) in the 12-membered ring compounds (**2**), (**3**), and (**8**)

		(2)	**(3)**	**(8)**
(a)	Ring **A**, Ring **B**	55.6	57.5	77.8
	Ring **C**, Ring **D**	−48.5	56.4	104.7
	Ring **A** [C(18)–N(17)–C(28)]	54.8	57.2	29.9
	Ring **B** [C(21)–N(22)–C(23)]	56.9	—	24.4
	Ring **C** [C(27)–C(28)–N(17)]	−44.5	44.6	87.0
	Ring **D** [C(24)–C(23)–N(22)]	41.7	—	86.4
(b)	C(27)–C(28)–N(17)–C(18)	−173.5	179.9	140.2
	C(21)–N(22)–C(23)–C(24)	−177.7	—	141.0

Table 12. Dihedral angles in the seven-membered ring compounds (**9**) and (**10**)

	(9)	**(10)**
Ring **A**, Ring **B**	43.9	42.7
Ring **C**, Ring **D**	54.5	55.6

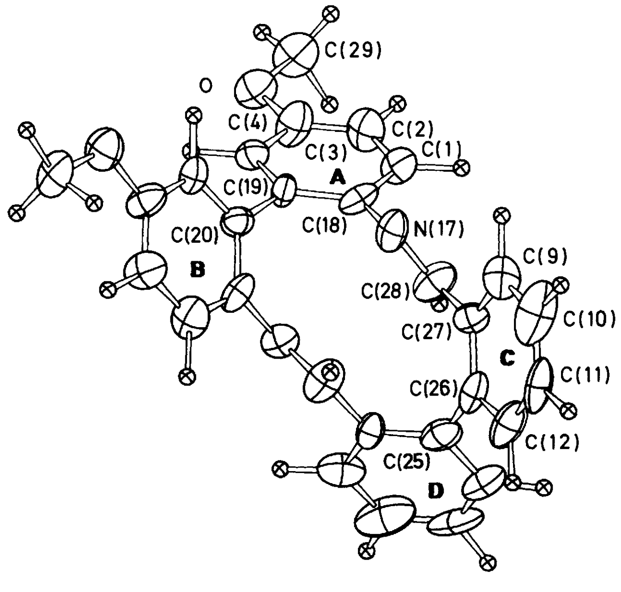


Figure 2. ORTEP[7] plot with 50% probability ellipsoids for compound (**3**)

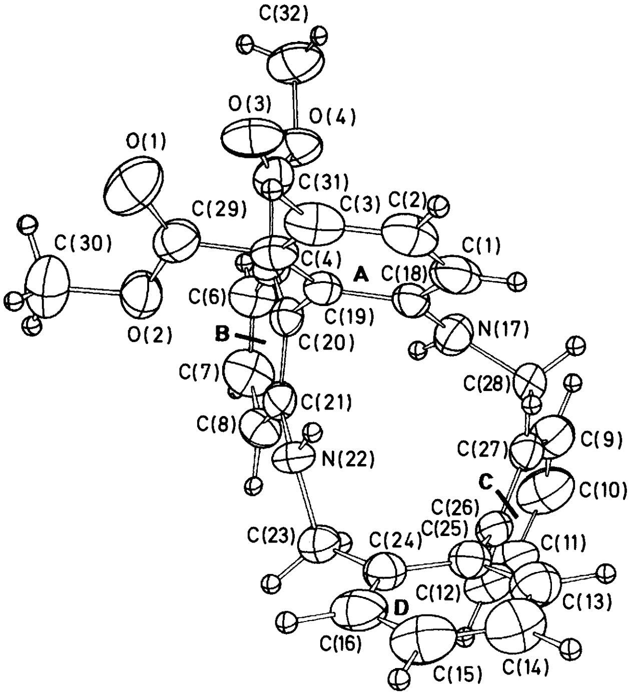


Figure 3. ORTEP[7] plot with 50% probability ellipsoids for compound (**8**)

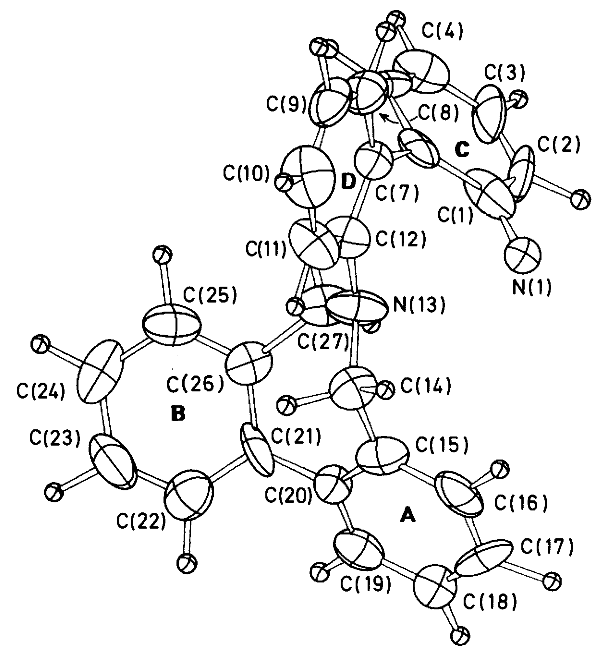


Figure 4. ORTEP[7] plot with 50% probability ellipsoids. for compound (**9**). Only one molecule resolved from its mirror image is represented

unsubstituted (**9**) has also a seven-membered ring, but that compound which has methoxycarbonyl groups *ortho* to the biphenyl link has the 12-membered ring structure (**8**) originally assigned to it.

Preparation.—The reduction of compounds (**1**)—(**4**) has already been described[1] but it is noteworthy that compounds (**1**)—(**3**) were readily reduced by (dimethylamino)borane in glacial acetic acid, giving compounds (**9**), (**10**), and (**11**) respectively, in good yield, the reduction being accompanied by contraction in ring size from 12 to seven. The substrates showed no change on suspension in the acid but exothermic reaction started when (dimethylamino)borane was added. Compound (**4**) was changed by (dimethylamino)borane in glacial acetic acid but the product, of a wide melting point range, did not contain hydrogen exchangeable with D_2O. Compound (**4**) was however readily hydrogenated in tetrahydrofuran over Adams' platinum oxide catalyst without any change in ring size. [2 H exchangeable with D_2O shows it to be different from the product obtained by hydrogenation with (dimethylamino)-borane.] Since the site of the attack by the borane is the CH=N part of the ring, it is not apparent why the di-*ortho*-substituted compound should behave differently to this reagent but perhaps steric factors prevent full co-ordination to the borane.

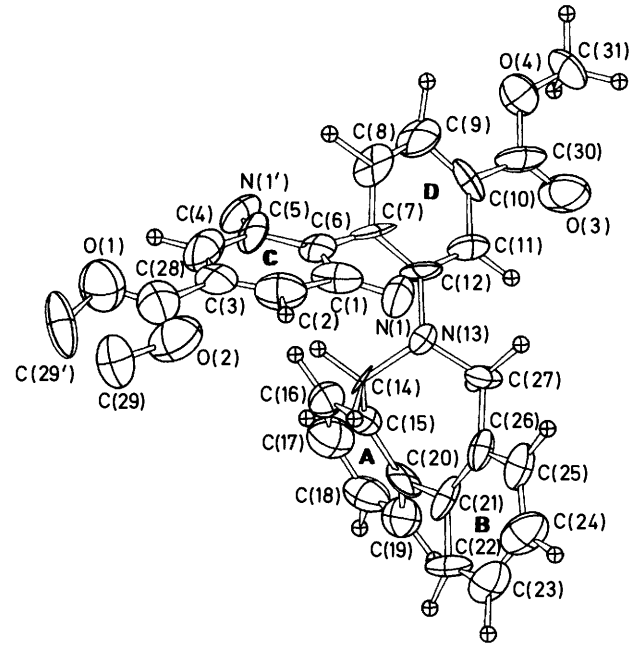
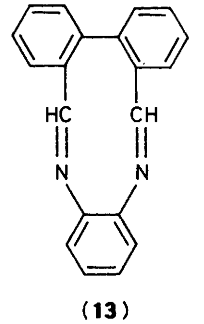


Figure 5. ORTEP[7] plot with 50% probability ellipsoids for compound (**10**). Disordered atoms have both positions given

The formation of a seven-membered ring bridging the 2,2′-positions of a biphenyl is particularly favoured, *e.g.* biphenyl-2,2′-dicarbaldehyde condenses with *o*-phenylene diamine to give (**12**) and not (**13**).[12–15] However, the 12-membered unsaturated ring has a more favourable geometry than that expected for the 10-membered ring and the ring contraction process in our compounds must occur during the reduction process.



(**13**)

Table 13. ^1H N.m.r. data (p.p.m. from $SiMe_4$ for $CDCl_3$ solutions)

Compound	Me	CH_2	NH_2	NH
(8)	3.57 (s)	4.00 (q)[a]	—	3.17 (s,b)
(9)	—	3.78 (q)	4.22 (s,b)	—
(10)	3.86 (s) 3.89 (s)	3.79 (q)	4.34 (s,b)	—
(11)	3.75 (s) 3.78 (s)	3.74 (q)	4.11 (s,b)	—

[a] A doubled quartet at room temperature.

Table 14. ^{13}C N.m.r. data (for $CDCl_3$ solutions)

Compound	Me	C=O
(8)	51.7	167.9
(10)	52.0, 52.1	167.0 (166.2, 166.4 in [$^2H_6$]DMSO)
(11)	55.6, 55.8	

^1H *N.m.r. Spectra.*—The 220 MHz spectra (Table 13) of compounds (**8**)—(**11**) show that (**8**) is clearly different from the other three. The two methyl groups of (**8**) are equivalent whereas in the seven-membered ring compounds (**10**) and (**11**) the methyl groups are structurally and magnetically non-equivalent. In the dimethoxy compound (**11**) the shift difference between the methyl resonances increases markedly on heating to 63 °C. The secondary NH protons of (**8**) resonate at higher field than the primary NH_2 protons of (**9**)—(**11**) and the ring methylene groups behave differently in the two types of structure. In both ring types the protons of each methylene group are diastereotopic and appear as an AB quartet. In the seven-membered ring conformational inversion occurs sufficiently rapidly for the quartet to collapse to a singlet on raising the temperature to about 63 °C. The 12-membered ring is also expected to be flexible but the *ortho*-methoxycarbonyl groups confer configurational stability on the biphenyl moiety in which they occur so that complete inversion of the structure is not possible. As expected therefore, the AB quartet in (**8**) does not show coalescence on heating. However, at room temperature the methylene groups appear as a *doubled* quartet which changes to a single quartet by about 64 °C. This must mean that the two methylene groups are themselves diastereotopic but that there is sufficient flexibility in the 12-membered ring for them to exchange situations on heating, even though one biphenyl moiety retains its configuration.

^{13}C *N.m.r. Spectra.*—These spectra (in $CDCl_3$) also show two distinct methyl carbons in the seven-membered ring compounds (**10**) and (**11**) but only one in the 12-membered ring compound (**8**) (Table 14). The carbons of the ester groups in (**10**) give the same signal in $CDCl_3$ but are slightly separated in [$^2H_6$]DMSO.

U.v. and I.r. Spectra.—These support the difference in structure between compounds (**8**) and (**9**)—(**11**) although, initially, the differences had been attributed to strong steric hindrance from the *ortho*-methoxycarbonyl groups in (**8**).

A biphenyl bridged in the 2,2′-positions by a saturated seven-membered ring is expected[16] to show a conjugation band at *ca.* 245—250 nm; this is apparent as an inflection at *ca.* 245 nm in compounds (**9**) and (**11**). The other biphenyl unit is di-*ortho*-substituted and its conjugation band is therefore bathochromically shifted to the low wavelength side of the 245 nm band and there is no distinct maximum; the absorption is enhanced but not doubled. In compound (**10**) however the *para*-methoxycarbonyl groups exert a counterbalancing hypsochromic effect so that the two conjugation bands overlap to give a high-intensity band at 241 nm (Table 15). If compound (**8**) also had a seven-membered ring, it could be expected to show a very strong bathochromic shift for the tetra-*ortho*-substituted biphenyl unit and thus probably leave the other conjugation band isolated. However, the spectrum shows reduced conjugation generally and no distinct band, consistent with substantial reduction in conjugation in both biphenyl units of the 12-membered ring structure.

Table 15. U.v. spectra in 95% ethanol. Wavelengths in parentheses denote inflections

	Conjugation band		Long-wave band	
Compound	$\lambda_{max.}$/nm.	$\varepsilon_{max.}$	$\lambda_{max.}$/nm.	$\varepsilon_{max.}$
(9)	(245)	28 100	290	7 830
(11)	(245)	28 100	308	8 010
(10)	241	50 250	(280) 340	12 600 7 610
(12)	(250)	18 400	(273) 334	8 770 4 890

All four compounds show two N–H stretching bands in the i.r. spectrum. In compounds (**9**)—(**11**) these are well separated with a sharp band at >3 400 cm^{-1} and a broader band at 3 275—3 350 cm^{-1}. Compound (**8**) shows two sharp bands of equal intensity, only 20 cm^{-1} apart (3 415 and 3 395 cm^{-1}).

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