jugative interaction between one aryl group in diazodiarylalkanes and the in-plane π_{NN}^* orbital of the diazo group in determining the unusual pattern of reactivity with triphenylphosphine.

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Synthesis and Structure of New Bronchospasmolytic Agents. II

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Abstract

The crystal structures of four phenylethanolamines showing bronchospasmolytic activity have been determined at room temperature [293 (2) K]. Crystal data are as follows: 8-morpholinotricyclo[6.5.0.0^{2,7}]trideca-2,4,6-trien-1-ol (2), $C_{17}H_{23}NO_2$, $M_r = 273.4$, monoclinic, $P2_1/n$, $a = 6.740$ (5), $b = 12.259$ (25), $c = 18.524$ (6) Å, $\beta = 90.01$ (4)°, $V = 1531$ (3) Å^3, $Z = 4$, $D_x = 1.186$ Mg m^{-3}, $\mu = 0.0719$ mm^{-1}, Mo $K\alpha_1$ radiation, $\lambda = 0.709300$ Å, $F(000) = 592$, $R = 0.0372$ for 1556 observed reflections; 8-morpholinotricyclo[6.5.0.0^{2,7}]trideca-2,4,6-triene-13-spiro-2′-(1′,3′-dioxan)-1-ol (3), $C_{20}H_{27}NO_4$, $M_r = 345.4$, triclinic, $P\bar{1}$, $a = 10.676$ (4), $b = 13.310$ (4), $c = 14.042$ (2) Å, $\alpha = 99.09$ (2), $\beta = 112.11$ (2), $\gamma = 95.03$ (3)°, $V = 1801.6$ (10) Å^3, $Z = 4$, $D_x = 1.274$ Mg m^{-3}, $\mu = 0.0823$ mm^{-1}, Mo $K\alpha_1$ radiation, $\lambda = 0.709300$ Å, $F(000) = 744$, $R = 0.0389$ for 2871 observed reflections; 3-(2-methyl-1,3-dioxolan-2-yl)-8-morpholinotricyclo[6.5.0.0^{2,7}]trideca-2,4,6-trien-1-ol (4), $C_{21}H_{29}NO_4$, $M_r = 359.5$, monoclinic, $C2/c$, $a = 30.771$ (23), $b = 6.881$ (1), $c = 17.867$ (10) Å, $\beta = 99.10$ (8)°, $V = 3735$ (4) Å^3, $Z = 8$, $D_x = 1.278$ Mg m^{-3}, $\mu = 0.0819$ mm^{-1}, Mo $K\alpha_1$ radiation, $\lambda = 0.709300$ Å, $F(000) = 1552$, $R = 0.0392$ for 1575 observed reflections; 3-diethylamino-8-morpholinotricyclo[6.5.0.0^{2,7}]trideca-2,4,6-trien-1-ol (5), $C_{21}H_{32}N_2O_2$, $M_r = 344.5$, monoclinic, $P2_1/c$, $a = 10.017$ (1), $b = 10.823$ (2), $c = 18.143$ (3) Å, $\beta = 100.81$ (2)°, $V = 1932.0$ (5) Å^3, $Z = 4$, $D_x = 1.184$ Mg m^{-3}, $\mu = 0.5603$ mm^{-1}, Cu $K\alpha_1$ radiation, $\lambda = 1.5405620$ Å, $F(000) = 752$, $R = 0.0445$ for 2276 observed reflections. The *cis* configuration at the junction of the cyclobutene/cycloheptane rings is found for all the compounds, and indicates *syn* stereochemistry for the arynic condensation of the ketone enolate used for the preparation. The conformation of these molecules is discussed in connection with the central tricyclic system and the substituents on it. In all these molecules an intramolecular ring is present, formed by an O—H···N hydrogen-bonding interaction, between the alcoholic hydroxyl and the morpholine nitrogen, which determines the orientation of the morpholine substituent.

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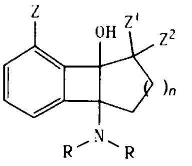
Introduction

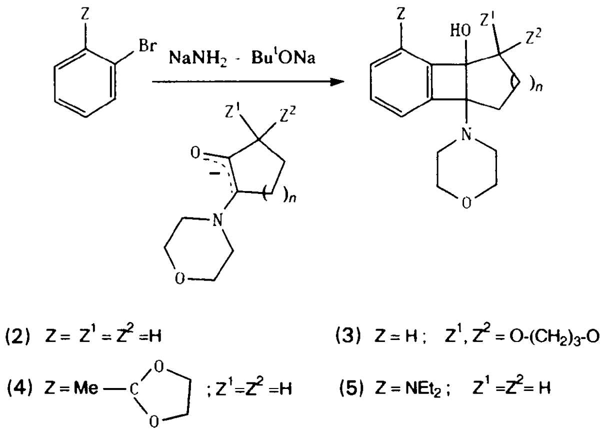
As part of our continuing work on the synthesis of new biologically active molecules, we considered the preparation of new phenylethanolamines as potential adrenergic compounds (Ianelli, Nardelli, Belletti, Jamart-Grégoire, Mouaddib & Caubère, 1992). In addition, it has been shown previously that polycyclic benzocyclobutene derivatives possess curious and interesting biological activities (Aatif, Mouaddib, Carré, Jamart-Grégoire, Geoffroy, Zouaoui, Caubère, Blanc, Gnassounou & Advenier, 1990; Carré, Youlassani, Caubère, Saint-Aubin-Floch & Advenier, 1984). Taking these observations together led us to examine the synthesis of compounds with the general structure (1).



(1)

The main point of interest concerning such molecules is that they may be considered as both phenylethanolamines and benzylamines, and it was of interest to determine the pharmacological properties of such substrates. Moreover the possibility of introducing functional groups into such amino alcohols was also of interest.

The synthesis of (1) was solved by taking into account our previous work (Grégoire, Carré & Caubère, 1986), and led to the arynic condensation of α-amino ketone enolates, shown in the scheme below, being undertaken.



(2) Z = Z¹ = Z² = H (3) Z = H ; Z¹, Z² = O-(CH₂)₃-O

(4) Z = Me—C(O—O) ; Z¹ = Z² = H (5) Z = NEt₂ ; Z¹ = Z² = H

In order to understand the stereochemistry of these condensations it was necessary to determine the structures of some of these molecules with the additional aim of seeing the influence the substituents have on their conformation. To this end the crystal structures of compounds (2), (3), (4) and (5) with n = 3 were studied.

Table 1. *Experimental data for the crystallographic analyses*

	(2)	(3)	(4)	(5)
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
Diffractometer	CAD-4	CAD-4	Siemens AED	Siemens AED
Reflections for lattice parameters				
No.	20	25	28	30
θ range (°)	15/18	12/19	10/19	18/37
Crystal size (mm)	0.26 × 0.31 × 0.59	0.33 × 0.42 × 0.46	0.29 × 0.48 × 0.52	0.12 × 0.32 × 0.41
Extinction parameter g	-	$0.25(8) \times 10^{-9}$	-	$0.19(9) \times 10^{-7}$
Scan speed (° min^{-1})	1.6/3.3	1.6/3.3	3/12	3/12
Scan width (°)	$0.8 + 0.35\tan\theta$	$1.2 + 0.35\tan\theta$	$0.8 + 0.35\tan\theta$	$1.30 + 0.35\tan\theta$
θ range for intensity collection (°)	3/25	3/25	3/25	3/70
h range	−8/8	−12/12	−36/36	−12/12
k range	0/14	−15/15	0/8	0/13
l range	0/22	0/16	0/21	0/22
Standard reflections	$\bar{3}69$	$\bar{3}96$	$\overline{10},4,8$	$\bar{9}22$
No. of measured reflections	2674	6323	3292	4099
No. of observed reflections	1556	2871	1575	2276
Condition for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.027	-	0.018	0.032
Max. LS shift to e.s.d. ratio	0.03	0.003	0.04	0.04
Min./max. height in final $\Delta\rho$ map (e Å^{-3})	−0.15/0.08	−0.17/0.19	−0.16/0.13	−0.08/0.07
No. of refined parameters	273	602	351	309
wR	0.0435	0.0433	0.0457	0.0467
k, g $\{w = k/[\sigma^2(F_o) + gF_o^2]\}$	1, 0.0005	Unit	Unit	Unit

Experimental

Table 1 summarizes the relevant data of the crystal structure analyses. For all the compounds the integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. The data were corrected for Lorentz and polarization effects, but not for absorption; extinction was considered for (3) and (5) only, according to Zachariasen (1963).

The structures were determined by direct methods: for (2), (4), and (5) using *SHELXS*86 (Sheldrick, 1986), and for (3) using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement was by anisotropic full-matrix least squares on F for all compounds except (3) for which block-matrix refinement (one block per molecule), was carried out using *SHELX*76 (Sheldrick, 1976). For (2) all H atoms were found from a $\Delta\rho$ map and refined isotropically, for the other compounds H atoms were placed in calculated positions riding on the attached C atoms, except those of the OH groups of (3) and (5) which were found from a difference Fourier synthesis, but not refined. In the case of (4) the OH hydrogen was placed in a calculated position

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

U_{eq} = 1/3(trace of the orthogonalized U_{ij} tensor).

	x	y	z	U_{eq}
Compound (2)				
N	349.9 (27)	8799.0 (14)	2047.1 (9)	344 (6)
O1	3873 (3)	8426 (2)	2621 (1)	520 (7)
O2	−593.2 (29)	8882.1 (15)	549.2 (9)	611 (7)
C1	1576 (3)	7967 (2)	3606 (1)	348 (7)
C2	1933 (4)	7217 (2)	4149 (1)	449 (9)
C3	319 (4)	6612 (2)	4374 (1)	491 (10)
C4	−1559 (4)	6749 (2)	4071 (1)	485 (9)
C5	−1909 (4)	7505 (2)	3529 (1)	429 (9)
C6	−281 (3)	8108 (2)	3304 (1)	337 (7)
C7	351 (3)	9061 (2)	2827 (1)	328 (7)
C8	2556 (3)	8848 (2)	3154 (1)	373 (8)
C9	3663 (4)	9763 (3)	3537 (2)	506 (10)
C10	2755 (5)	10196 (3)	4232 (2)	581 (11)
C11	982 (5)	10957 (3)	4138 (2)	617 (12)
C12	−853 (4)	10430 (3)	3803 (2)	523 (10)
C13	−659 (4)	10148 (2)	3005 (1)	442 (9)
C14	−1556 (4)	8390 (2)	1768 (1)	468 (9)
C15	−1298 (5)	8023 (3)	1001 (1)	579 (11)
C16	1248 (4)	9279 (3)	822 (1)	531 (10)
C17	1031 (4)	9696 (2)	1583 (1)	435 (9)
Compound (3) mol. *A*				
N1*A*	−3771 (3)	−3888 (3)	−7159 (3)	425 (16)
O1*A*	−4622 (3)	−2176 (2)	−7578 (2)	395 (12)
O2*A*	−975 (3)	−4144 (3)	−6407 (3)	651 (17)
O3*A*	−7052 (3)	−1859 (2)	−8815 (2)	445 (13)
O4*A*	−6016 (3)	−2980 (2)	−9654 (2)	468 (13)
C1*A*	−6369 (4)	−3052 (3)	−7119 (3)	426 (18)
C2*A*	−7117 (5)	−2544 (4)	−6637 (4)	620 (24)
C3*A*	−7505 (6)	−3062 (6)	−5987 (4)	901 (35)
C4*A*	−7176 (6)	−4019 (6)	−5847 (5)	1058 (43)
C5*A*	−6411 (6)	−4519 (5)	−6318 (5)	881 (35)
C6*A*	−6004 (4)	−3994 (4)	−6960 (4)	498 (21)
C7*A*	−5282 (4)	−4081 (3)	−7718 (3)	427 (19)
C8*A*	−5749 (4)	−2973 (3)	−7916 (3)	337 (17)
C9*A*	−6761 (4)	−2878 (3)	−9003 (3)	385 (18)
C10*A*	−8105 (4)	−3633 (4)	−9464 (4)	506 (20)
C11*A*	−8075 (5)	−4740 (4)	−9928 (4)	739 (26)
C12*A*	−7341 (6)	−5384 (4)	−9147 (5)	877 (31)
C13*A*	−5790 (5)	−5036 (4)	−8605 (4)	677 (25)
C14*A*	−3214 (5)	−4494 (4)	−6354 (4)	571 (24)
C15*A*	−1698 (5)	−4100 (4)	−5740 (4)	634 (26)
C16*A*	−1526 (5)	−3572 (4)	−7211 (4)	626 (26)
C17*A*	−3033 (4)	−3980 (4)	−7860 (4)	518 (22)
C18*A*	−7685 (5)	−1445 (4)	−9731 (4)	572 (23)
C19*A*	−6641 (5)	−2637 (5)	−10620 (4)	687 (27)
C20*A*	−6870 (6)	−1534 (5)	−10405 (4)	728 (29)
Compound (3) mol. *B*				
N1*B*	606 (3)	364 (2)	7981 (3)	355 (14)
O1*B*	−823 (3)	−787 (2)	8657 (2)	470 (13)
O2*B*	2326 (3)	2243 (2)	9236 (3)	578 (15)
O3*B*	−3146 (3)	−2035 (2)	7624 (3)	569 (15)
O4*B*	−3200 (3)	−356 (2)	7275 (2)	428 (13)
C1*B*	−515 (4)	−1987 (3)	7279 (3)	418 (18)
C2*B*	−407 (5)	−3015 (3)	7314 (4)	577 (22)
C3*B*	495 (5)	−3417 (4)	6909 (4)	636 (24)
C4*B*	1213 (5)	−2829 (4)	6498 (4)	642 (25)
C5*B*	1099 (4)	−1800 (4)	6465 (3)	529 (21)
C6*B*	219 (4)	−1396 (3)	6889 (3)	406 (18)
C7*B*	−369 (4)	−420 (3)	7094 (3)	365 (17)
C8*B*	−1232 (4)	−1120 (3)	7569 (3)	362 (17)
C9*B*	−2806 (4)	−1325 (3)	7061 (3)	414 (19)
C10*B*	−3455 (5)	−1836 (4)	5889 (4)	562 (21)
C11*B*	−3494 (5)	−1106 (4)	5104 (4)	618 (23)
C12*B*	−2063 (5)	−744 (4)	5105 (4)	579 (22)
C13*B*	−1091 (4)	21 (3)	6117 (3)	448 (20)
C14*B*	1932 (4)	680 (3)	7930 (3)	432 (19)
C15*B*	2890 (4)	1360 (4)	8972 (4)	523 (22)
C16*B*	1037 (4)	1925 (4)	9281 (4)	564 (23)
C17*B*	45 (4)	1292 (3)	8232 (3)	441 (19)
C18*B*	−4505 (5)	−2127 (5)	7585 (5)	810 (33)
C19*B*	−4604 (4)	−398 (4)	7150 (4)	553 (22)
C20*B*	−4880 (5)	−1082 (4)	7837 (5)	697 (28)
Compound (4)				
N	−4408 (1)	428 (5)	−1194 (2)	343 (11)
O1	−3755 (1)	2217 (4)	−1689 (2)	513 (12)
O2	−5137 (1)	2387 (5)	−719 (2)	561 (13)
C1	−3784 (1)	−1033 (6)	−2286 (2)	282 (13)
C2	−3682 (1)	−1378 (6)	−3011 (2)	310 (13)
C3	−3927 (1)	−2847 (7)	−3415 (2)	395 (15)
C4	−4246 (1)	−3902 (7)	−3116 (2)	418 (15)
C5	−4344 (1)	−3529 (7)	−2395 (2)	398 (15)
C6	−4107 (1)	−2047 (6)	−1996 (2)	303 (13)
C7	−4044 (1)	−951 (6)	−1242 (2)	312 (13)
C8	−3656 (1)	208 (6)	−1577 (2)	346 (14)
C9	−3187 (1)	31 (8)	−1162 (2)	507 (18)
C10	−2986 (1)	−1986 (10)	−1093 (3)	632 (21)
C11	−3112 (2)	−3219 (9)	−452 (3)	621 (20)
C12	−3596 (2)	−3821 (7)	−545 (2)	515 (17)
C13	−3919 (1)	−2149 (7)	−522 (2)	379 (14)
C14	−4853 (1)	−409 (7)	−1334 (2)	449 (16)
C15	−5186 (2)	1222 (8)	−1390 (3)	569 (19)
C16	−4701 (2)	3150 (7)	−555 (3)	530 (19)
C17	−4358 (1)	1542 (7)	−478 (2)	431 (16)
O3	−3272 (1)	−942 (5)	−4049 (1)	473 (11)
O4	−2928.0 (9)	−306.8 (51)	−2856.8 (16)	499 (11)
C18	−2897 (2)	−2178 (9)	−3918 (3)	681 (21)
C19	−2698 (2)	−1857 (10)	−3118 (3)	834 (26)
C20	3342 (1)	−168 (7)	−3334 (2)	386 (15)
C21	−3468 (2)	1937 (7)	−3428 (3)	524 (18)
Compound (5)				
N1	−7225 (2)	515 (2)	−8891 (1)	376 (8)
O1	−9141 (2)	−1126 (2)	−9340 (1)	437 (7)
O2	−7221 (3)	3076 (2)	−9267 (1)	633 (9)
C1	−7846 (3)	−2009 (3)	−8145 (2)	349 (9)
C2	−8340 (3)	−2763 (3)	−7623 (2)	397 (10)
C3	−7688 (3)	−2560 (3)	−6868 (2)	512 (12)
C4	−6649 (4)	−1703 (3)	−6667 (2)	557 (12)
C5	−6169 (3)	−972 (3)	−7188 (2)	481 (11)
C6	−6821 (3)	−1158 (3)	−7923 (2)	374 (9)
C7	−6720 (3)	−757 (3)	−8710 (2)	346 (9)
C8	−7925 (3)	−1728 (3)	−8985 (2)	349 (9)
C9	−7693 (3)	−2768 (3)	−9513 (2)	461 (11)
C10	−6603 (4)	−3725 (3)	−9212 (2)	569 (13)
C11	−5132 (3)	−3319 (3)	−9215 (2)	562 (13)
C12	−4651 (3)	−2237 (3)	−8690 (2)	551 (12)
C13	−5330 (3)	−991 (3)	−8930 (2)	464 (11)
C14	−6667 (3)	1446 (3)	−8331 (2)	484 (11)
C15	−7352 (4)	2680 (3)	−8534 (2)	593 (14)
C16	−7796 (4)	2171 (3)	−9807 (2)	609 (14)
C17	−7086 (3)	945 (3)	−9645 (2)	494 (11)
N2	−9353 (3)	−3633 (2)	−7798 (1)	502 (9)
C22	−9734 (3)	−4416 (3)	−7210 (2)	569 (13)
C23	−8712 (4)	−5440 (3)	−6953 (2)	673 (15)
C24	−10277 (3)	−3642 (3)	−8515 (2)	512 (11)
C25	−10290 (5)	−4848 (3)	−8942 (2)	763 (18)

assuming the same geometry for the O1—H1O···N1 system as that found for (2) (see *Discussion*).

There are differences in the environments of the two crystallographically independent molecules of (3), as found from the *PLUTO* (Motherwell & Clegg, 1976) drawing of the two independent molecules in the unit cell, shown in Fig. 2, and from the non-bonded contacts calculated by *PARST* (Nardelli, 1983*a*). The correctness of the space-group choice was checked using *TRACER* (Lawton & Jacobson, 1965), *NEWLAT* (Mugnoli, 1985), *LEPAGE* (Spek, 1988), and *MISSYM* (Le Page, 1987).

The atomic scattering factors and the anomalous-scattering coefficients are from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 102, 149). The final atomic coordinates are given in Table

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

		(3)				
	(2)	Mol. *A*	Mol. *B*	(4)	(5)	Average
N1—C7	1.480 (3)	1.481 (5)	1.465 (4)	1.480 (5)	1.482 (4)	1.478 (3)
N1—C14	1.472 (3)	1.466 (6)	1.472 (6)	1.472 (5)	1.466 (4)	1.470 (2)
N1—C17	1.469 (4)	1.472 (7)	1.470 (6)	1.479 (5)	1.476 (4)	1.473 (2)
O1—C8	1.425 (3)	1.408 (4)	1.404 (5)	1.423 (5)	1.425 (3)	1.420 (4)
O2—C15	1.427 (4)	1.419 (8)	1.426 (6)	1.430 (6)	1.426 (5)	1.426 (2)
O2—C16	1.425 (4)	1.432 (7)	1.432 (6)	1.428 (6)	1.427 (4)	1.428 (2)
C1—C2	1.384 (4)	1.382 (8)	1.390 (6)	1.400 (5)	1.409 (4)	1.395 (5)
C1—C6	1.382 (3)	1.373 (7)	1.372 (7)	1.382 (6)	1.382 (4)	1.380 (2)
C1—C8	1.518 (4)	1.512 (7)	1.524 (6)	1.527 (5)	1.541 (4)	1.527 (5)
C2—C3	1.381 (4)	1.384 (10)	1.393 (9)	1.393 (6)	1.419 (4)	1.398 (8)
C3—C4	1.395 (4)	1.375 (12)	1.380 (9)	1.395 (6)	1.391 (5)	1.392 (3)
C4—C5	1.387 (4)	1.382 (11)	1.391 (8)	1.393 (6)	1.385 (5)	1.388 (2)
C5—C6	1.388 (4)	1.388 (10)	1.391 (7)	1.383 (6)	1.385 (4)	1.387 (2)
C6—C7	1.526 (4)	1.529 (8)	1.526 (6)	1.530 (5)	1.515 (4)	1.524 (3)
C7—C8	1.626 (3)	1.629 (6)	1.634 (7)	1.627 (6)	1.608 (4)	1.623 (4)
C7—C13	1.533 (4)	1.527 (6)	1.535 (6)	1.525 (5)	1.539 (4)	1.533 (3)
C8—C9	1.522 (4)	1.535 (5)	1.538 (5)	1.521 (6)	1.524 (4)	1.527 (3)
C9—C10	1.522 (4)	1.527 (6)	1.535 (6)	1.516 (8)	1.530 (4)	1.527 (3)
C10—C11	1.526 (5)	1.522 (7)	1.571 (8)	1.523 (8)	1.539 (5)	1.534 (8)
C11—C12	1.527 (4)	1.523 (9)	1.561 (8)	1.531 (7)	1.528 (5)	1.531 (5)
C12—C13	1.523 (4)	1.530 (7)	1.543 (5)	1.526 (7)	1.536 (4)	1.532 (4)
C14—C15	1.500 (4)	1.515 (6)	1.516 (5)	1.512 (7)	1.516 (4)	1.511 (4)
C16—C17	1.507 (4)	1.518 (6)	1.509 (5)	1.521 (7)	1.508 (5)	1.511 (2)
O3—C9		1.423 (5)	1.429 (6)	–	–	1.426 (4)
O3—C18	–	1.432 (6)	1.424 (7)	1.421 (6)	–	1.426 (4)
O3—C20	–	–	–	1.431 (5)	–	–
O4—C9		1.419 (6)	1.413 (5)	–	–	1.416 (4)
O4—C19		1.436 (6)	1.438 (6)	1.401 (8)	–	1.429 (11)
O4—C20	–	–		1.419 (5)	–	
C2—C20	–	–	–	1.520 (6)	–	–
C18—C19	–	–	–	1.481 (7)	–	
C20—C21	–	–	–	1.502 (7)	–	–
N2—C2	–	–	–	–	1.377 (4)	
N2—C22				–	1.468 (5)	–
N2—C24	–	–			1.449 (4)	–
C22—C23			–		1.522 (5)	–
C24—C25	–	–	–	–	1.516 (5)	–
C18—C20		1.506 (9)	1.507 (9)	–	–	1.506 (6)
C19—C20	–	1.512 (9)	1.513 (9)	–	–	1.512 (6)
C14—N1—C17	108.8 (2)	109.0 (5)	108.9 (5)	108.4 (4)	109.7 (2)	109.1 (2)
C7—N1—C17	114.1 (2)	114.0 (4)	114.3 (4)	113.9 (3)	114.2 (2)	114.1 (1)
C7—N1—C14	114.6 (2)	115.4 (5)	116.1 (4)	115.6 (3)	114.5 (2)	114.9 (3)
C15—O2—C16	109.5 (2)	111.0 (5)	109.8 (5)	110.5 (4)	109.8 (3)	109.8 (2)
C6—C1—C8	94.7 (2)	94.8 (5)	94.7 (5)	94.5 (3)	93.1 (2)	94.1 (4)
C2—C1—C8	143.0 (3)	141.9 (6)	142.2 (5)	142.8 (4)	145.1 (3)	143.4 (6)
C2—C1—C6	122.3 (3)	123.3 (5)	123.1 (6)	122.8 (4)	121.7 (3)	122.4 (3)
C1—C2—C3	116.1 (3)	115.2 (6)	115.2 (6)	114.8 (4)	113.8 (3)	115.0 (5)
C2—C3—C4	121.9 (3)	121.8 (7)	121.8 (6)	122.4 (4)	122.8 (3)	122.3 (2)
C3—C4—C5	121.8 (3)	122.9 (8)	122.7 (6)	121.8 (4)	122.7 (3)	122.2 (2)
C4—C5—C6	116.0 (3)	115.4 (7)	115.3 (6)	116.0 (4)	114.4 (3)	115.4 (4)
C1—C6—C5	121.9 (3)	121.4 (6)	121.9 (6)	122.1 (4)	124.6 (3)	122.8 (6)
C5—C6—C7	143.4 (3)	143.6 (6)	142.9 (5)	143.1 (4)	139.8 (3)	142.2 (8)
C1—C6—C7	94.4 (2)	94.9 (5)	95.2 (5)	94.7 (3)	95.4 (2)	94.9 (2)
N1—C7—C6	113.6 (2)	112.1 (4)	113.1 (4)	112.0 (3)	113.3 (2)	113.1 (3)
C6—C7—C13	114.6 (2)	116.5 (5)	114.8 (4)	117.2 (3)	114.9 (2)	115.2 (5)
C6—C7—C8	85.2 (2)	84.5 (4)	84.8 (4)	85.2 (3)	85.7 (2)	85.3 (2)
N1—C7—C13	113.5 (2)	112.4 (5)	112.8 (5)	113.0 (3)	112.6 (2)	113.0 (2)
N1—C7—C8	109.2 (2)	106.8 (4)	106.7 (4)	108.2 (3)	109.4 (2)	108.7 (5)
C8—C7—C13	117.7 (2)	121.5 (4)	121.6 (5)	118.3 (4)	118.4 (2)	118.6 (6)
C1—C8—C7	85.5 (2)	85.8 (4)	85.3 (4)	85.6 (3)	85.8 (2)	85.6 (1)
O1—C8—C7	111.7 (2)	112.4 (4)	112.4 (4)	112.1 (4)	111.7 (2)	111.9 (1)
O1—C8—C1	113.2 (3)	114.2 (4)	113.5 (4)	113.8 (3)	114.8 (2)	114.1 (3)
C7—C8—C9	120.2 (3)	120.2 (4)	120.2 (4)	118.5 (3)	118.9 (2)	119.3 (4)
C1—C8—C9	118.7 (2)	115.0 (5)	116.2 (4)	117.4 (4)	119.4 (2)	118.4 (6)
O1—C8—C9	106.6 (2)	108.2 (4)	108.1 (4)	108.2 (4)	105.7 (2)	106.7 (5)
C8—C9—C10	117.0 (3)	115.7 (4)	115.9 (5)	117.1 (4)	117.3 (3)	116.8 (3)
C9—C10—C11	115.6 (3)	117.6 (5)	116.1 (5)	115.0 (5)	115.1 (3)	115.7 (4)
C10—C11—C12	114.9 (3)	116.3 (5)	113.9 (5)	115.3 (4)	114.0 (3)	114.7 (4)
C11—C12—C13	114.9 (3)	113.8 (6)	113.8 (5)	114.9 (4)	115.1 (3)	114.8 (2)
C7—C13—C12	116.4 (3)	116.8 (5)	117.7 (5)	117.5 (3)	116.5 (3)	116.9 (3)
N1—C14—C15	109.5 (3)	109.3 (5)	109.2 (4)	108.9 (4)	109.9 (3)	109.4 (2)
O2—C15—C14	111.9 (3)	111.5 (5)	111.7 (5)	112.3 (4)	112.0 (3)	111.9 (2)
O2—C16—C17	111.3 (3)	110.7 (5)	110.4 (5)	111.6 (4)	110.8 (3)	111.0 (2)
N1—C17—C16	108.9 (3)	108.6 (4)	108.7 (5)	108.9 (4)	109.5 (3)	109.0 (2)
C18—O3—C20	–		–	108.0 (4)	–	–
C19—O4—C20	–		–	107.7 (4)	–	–
O3—C18—C19	–	–	–	105.7 (5)	–	–
O4—C19—C18	–	–		106.3 (5)	–	–
O3—C20—O4	–		–	105.3 (3)	–	–
C2—C20—O4		–	–	109.9 (3)	–	
C2—C20—O3	–	–	–	110.2 (4)	–	–
O4—C20—C21		–	–	108.8 (4)	–	–
O3—C20—C21	–	–	–	109.4 (3)	–	–
C2—C20—C21	–	–	–	112.9 (4)	–	–
C1—C2—C20	–		–	121.8 (4)	–	–
C3—C2—C20	–	–	–	123.3 (3)	–	–
C1—C2—N2	–	–	–	–	125.2 (3)	–
C3—C2—N2	–	–	–	–	121.0 (3)	–
C2—N2—C24	–	–	–	–	122.1 (3)	–
C2—N2—C22	–	–	–	–	120.5 (3)	–
C22—N2—C24		–	–	–	116.1 (3)	–
N2—C22—C23	–	–	–	–	113.1 (3)	–
N2—C24—C25	–	–	–	–	114.1 (3)	
O3—C18—C20	–	110.5 (5)	111.0 (6)	–	–	111.7 (4)
O4—C19—C20	–	110.6 (4)	109.1 (5)	–		110.0 (7)
C18—C20—C19	–	109.1 (6)	110.0 (6)	–	–	109.6 (4)
C9—O3—C18	–	115.7 (4)	116.4 (5)	–	–	116.0 (3)
C9—O4—C19	–	113.7 (5)	114.9 (5)	–		114.3 (6)
O4—C9—C8	–	105.1 (4)	104.8 (5)	–	–	105.0 (3)
O3—C9—C8	–	102.9 (4)	102.8 (4)		–	102.8 (3)
O3—C9—O4	–	112.0 (5)	112.5 (4)	–	–	112.3 (3)
O4—C9—C10		112.2 (4)	112.8 (5)	–		112.4 (3)
O3—C9—C10	–	108.7 (5)	107.7 (5)	–	–	108.2 (5)

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 atom–atom non-bonded potential-energy calculations were carried out with the *ROTENER* (Nardelli, 1988) program which makes use of a function of the type $E_{vW} = \sum_{i<j}[B_{ij}\exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6}]$ where the *A*, *B*, *C* parameters are from Mirsky (1978), also considering the Coulombic energy: $E_C = \sum_{i<j} q_i q_j r_{ij}^{-1}$ where the atomic charges were calculated by the iterative partial equalization of orbital electronegativity method of Gasteiger & Marsili (1980) with the program *ATOMCHAR* (Nardelli, 1991).

The calculations were carried out on the ENCORE-GOULD-POWERNODE 6040 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma)'. In addition to the programs quoted, *LQPARM* (Nardelli & Mangia, 1984) and *ORTEP* (Johnson, 1965) were used.

Discussion

ORTEP drawings of the molecules of the four compounds are displayed in Fig. 1; bond distances and angles are compared in Table 3, where the weighted means are also given.

The core of all of these molecules is a system of three rings: a cyclopropene fused on opposite sides with a benzene and a cycloheptane ring. The first two

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* Lists of structure factors, anisotropic displacement parameters, H-atom parameters, and bond lengths, angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55080 (62 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0307]

rings are practically coplanar, the dihedral angle being on average only 2.9 (5)°, while the last two rings are approximately perpendicular, the dihedral angle formed by the least-squares planes through them being 94.2 (2)° on average.

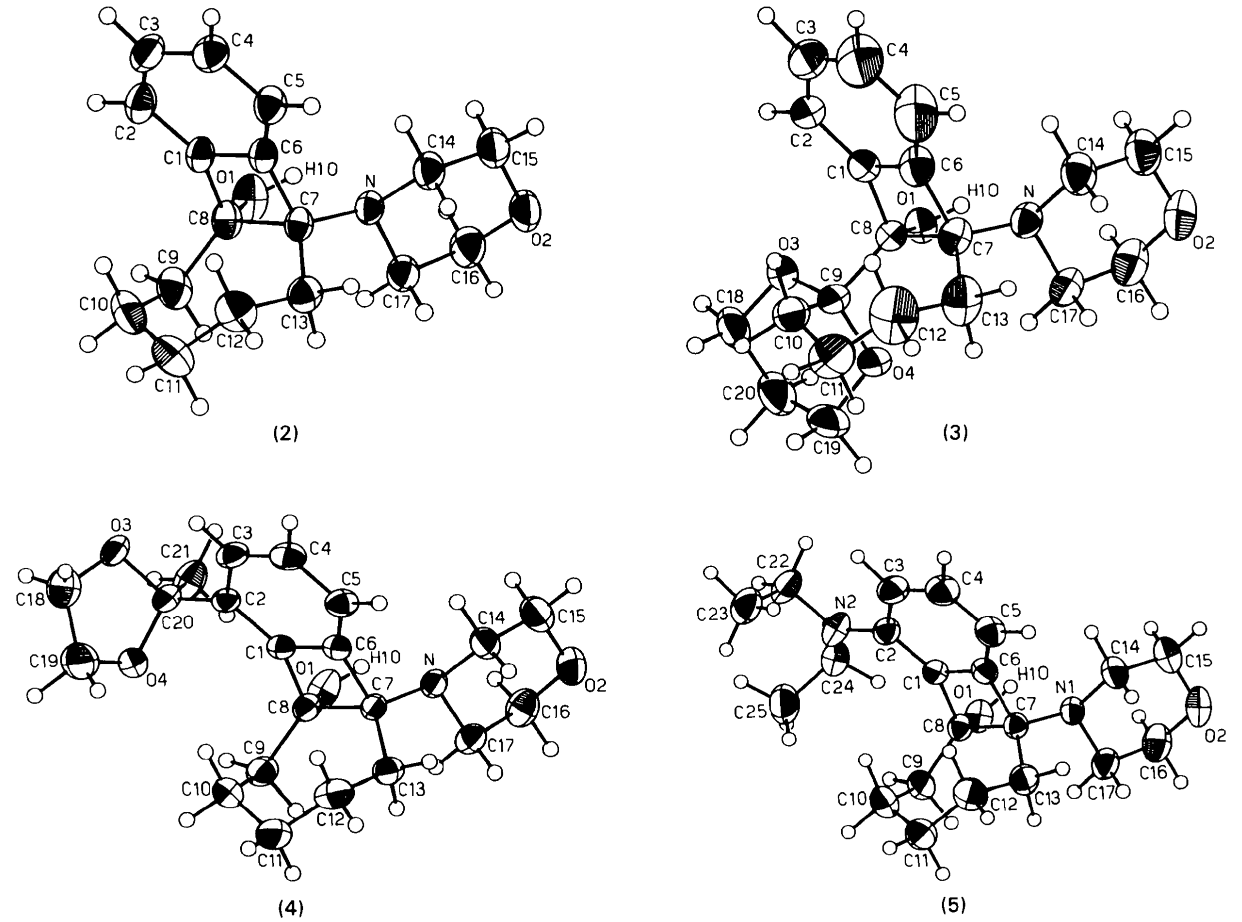
Analysis of the anisotropic atomic displacements

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

As can be seen from the U_{eq} values of Table 2 and the ellipsoids of Fig. 1, the atomic displacements and anisotropies (from the ratios of the principal axes of the displacement ellipsoids $r_{\text{max}}/r_{\text{min}}$) are more significant for molecule *A* of (3) [$(U_{\text{eq}})_{\text{max}} = 0.10$ Å^2], while (2) and (4) show the smallest averaged displacements [$(U_{\text{eq}})_{\text{max}} = 0.06$ Å^2] and (5) the smallest anisotropies [$(r_{\text{max}}/r_{\text{min}})_{\text{max}} = 2.7$]. From the data of Table 4 it appears that the best agreement for the rigid-body descriptions of the molecular displacements is observed for (2) ($R_{wU} = 0.086$) and the worst for (4) ($R_{wU} = 0.206$). No correction of bond distances for these displacements was considered for the data of Table 3, all corrections being less than 3σ.

Configurations at the junctions and reaction mechanism

From the molecular drawings of Fig. 1 it appears that in all these compounds the hydroxyl and morpholine groups at the junction of the cycloheptane and cyclobutene rings are *cis* with *S* and *R* configurations at the chiral C7 and C8 carbon atoms, respectively (of course the *R* and *S* configurations of the enantiomers are also present, the space groups all being centrosymmetric). This *cis* stereochemistry, which is in agreement with the scheme proposed by Grégoire *et al.* (1986) [see also Carré, Jamart-



(2) (3) (4) (5)

Fig. 1. *ORTEP* drawings of the molecules. Ellipsoids at 50% probability.

Grégoire, Geoffroy, Caubère, Ianelli & Nardelli (1988) and references cited therein] for the arynic condensation of 1,2-diketone monoketal enolates when the number of C atoms of the cycloalkane ring is not too large, is now favoured by the hydrogen-bonding interaction the hydroxyl group exerts on the morpholine nitrogen.

Conformation of the cyclobutene and cycloheptane rings

The cyclobutene ring does not deviate significantly from planarity, but its geometry deviates quite significantly from that of a regular square, as a consequence of the different nature of the adjacent fused rings. Indeed, the C1—C6 bond is shortened owing to the aromatic π conjugation and the C7—C8 bond is much longer [1.623 (4) Å on average] than a single C(sp^3)—C(sp^3) = 1.542 (1) Å bond, while the two C(sp^2)—C(sp^3) distances of the C1—C8 and C6—C7 bonds are practically equal. This causes a narrowing of the angles of the ring at C7 and C8 and a corresponding enlargement of the angles of the ring at C1 and C6. The same deformation has been found in a similar compound described in the previous paper of this series (Ianelli *et al.*, 1992), where a cyclobutene ring is fused to a benzene and a cyclopentane, indicating that it is peculiar to this kind of system.

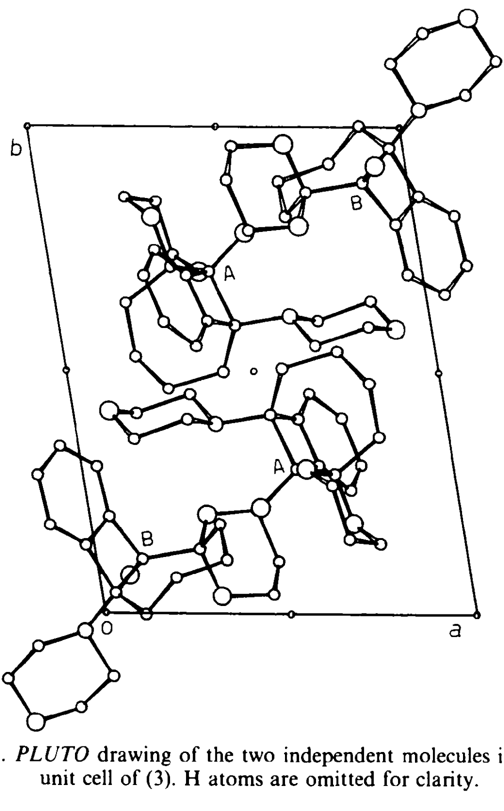


Fig. 2. *PLUTO* drawing of the two independent molecules in the unit cell of (3). H atoms are omitted for clarity.

The fusion of the cyclobutene ring with a cycloheptane has some influence on the conformation of the latter ring, as shown in Fig. 4. The averaged values for this ring are indicative of a chair conformation with a pseudomirror running through C11 and the midpoint of the junction of the two rings [minimum displacement asymmetry parameter (Nardelli, 1983*b*), DAP: $\Delta_S(\mathrm{C11}) = 0.0240(68)$ on average]. The averaged bond (116.1°) and torsion (59.9°) angles approach the theoretical average values of 115.6 and 61.0°, respectively, for the calculated chair conformation of cycloheptane which corresponds to an energy of 35.6 kJ mol^{-1} (Hendrickson, 1967). It is worth noting that the chair conformation is not that of lowest energy for the free cycloheptane molecule, while it is for cycloheptene where the local pseudomirror runs across the double bond; now this mirror runs across the abnormally long C7—C8 bond.

Deformation of the benzene ring

The fusion of a benzene with a cyclobutene ring in the central moiety causes deformation of the benzene system which is particularly relevant to the endocyclic bond angles. No significant deviations from planarity are observed, while narrowing of the angle at C2 and C5 [115.2 (4)° on average] and enlarging the angles at C1, C3, C4 and C6 [122.3 (1)° on average] are in quite good agreement with those found in a similar system recently studied by us and with the averaged values from the literature (Ianelli, Nardelli, Belletti, Geoffroy, Carré, Mouaddib & Caubère, 1990) confirming the 'push-pull' effect pivoted on the atoms of the junction, pointed out in the indane system (Ianelli, Nardelli, Geoffroy, Carré, Jamart-Grégoire & Caubère, 1989). As in the previous cases no significant trends are observed in the values of the benzene C—C bond distances.

Morpholino moiety

The average conformation of this moiety, with a total puckering amplitude (Cremer & Pople, 1975) $Q_T = 0.582$ (3) Å on average, is in quite good agreement with that found for this substituent in our previous paper in this series (Ianelli *et al.*, 1992). Its orientation, which is illustrated by the Newman projection of Fig. 3, is mainly determined by the intramolecular O—H···N hydrogen bond the alcoholic hydroxyl forms with the N atom.

Dioxane and dioxolane moieties

Dioxane is present in (3) as a spiro substituent at the cycloheptane ring; its presence produces a small narrowing of the C8—C9—C10 angle from an average of 117.1 (2)° to an average of 115.8 (4)°, with respect to the other compounds. It adopts a chair

Table 4. *Analysis of the anisotropic atomic displacements in terms of* **LST** *rigid-body motion and internal motions*

Δ = mean difference of the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms; $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$; $R_{wU} = [\sum(w\Delta U)^2/\sum(wU_o)^2]^{1/2}$; $\sigma(w\Delta U) = [\sum(w\Delta U)^2/\sum w^2]^{1/2}$; $\sigma(U_o)$ = mean e.s.d. of U_o's.

	Treatment	$\Delta \times 10^4$ Å	$\sigma(w\Delta U) \times 10^4$	$\sigma(w\Delta U) \times 10^4$	R_{wU}
Compound (2)	Rigid body	34 (45)	25	14	0.086
	Internal motions		21		0.072
Compound (3) mol. *A*	Rigid body	52 (70)	39	31	0.104
	Internal motions		32		0.085
Compound (3) mol. *B*	Rigid body	50 (70)	46	26	0.141
	Internal motions		38		0.117
Compound (4)	Rigid body	93 (133)	58	25	0.206
	Internal motions		41		0.140
Compound (5)	Rigid body	47 (65)	32	17	0.104
	Internal motions		27		0.089

Compound (2)

	Libration	
Group librating	Along	Amplitude (°)
O1	C8—C9	3.2 (8)
C2,C3,C4	C1···C5	1.1 (20)
C10,C11	C9···C12	4.0 (12)

Compound (3) mol. *A*

	Libration	
Group librating	Along	Amplitude (°)
C5,C4,C3	C6···C2	5.4 (7)
C14,C15,O2,C16,C17	N1—C7	2.2 (17)
O1	C7···C9	1.6 (9)
C11,C12,C13	C7···C10	4.2 (8)
C10	C9···C11	3.5 (38)

Compound (3) mol. *B*

	Libration	
Group librating	Along	Amplitude (°)
C5,C4,C3,C2	O1—C8	1.9 (4)
O1	C7···C9	3.1 (6)
C10,C11,C12,C13	C7···C9	4.1 (5)
O3,O4	C8—C9	1.9 (16)

Compound (4)

	Libration	
Group librating	Along	Amplitude (°)
O1	C7—C8	6.3 (9)
C8	O3—C20	5.1 (2)
C19	O4—C20	9.8 (12)
C10	C8—C9	3.3 (21)
C11	C12—C13	3.5 (17)

Compound (5)

	Libration	
Group librating	Along	Amplitude (°)
C10	C9···C11	6.9 (18)
C17	N1···C16	7.2 (16)
C25	N2—C24	5.0 (14)
C23	N2—C22	4.1 (15)

conformation with a total puckering amplitude Q_T = 0.515 (6) Å on average. Worth noticing are the non-bonded contacts the O3 and O4 oxygen atoms form with O1 [2.625 (13) and 2.716 (10) Å on average, respectively] which are a little shorter than the sum of the van der Waals radii (2.80 Å).

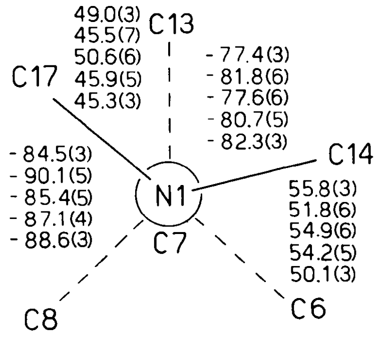


Fig. 3. Newman projection along the N1—C7 bond; data (°) refer, from the top to the bottom of each group, to the five molecules in the order: (2), (3) molecule *A*, (3) molecule *B*, (4), (5).

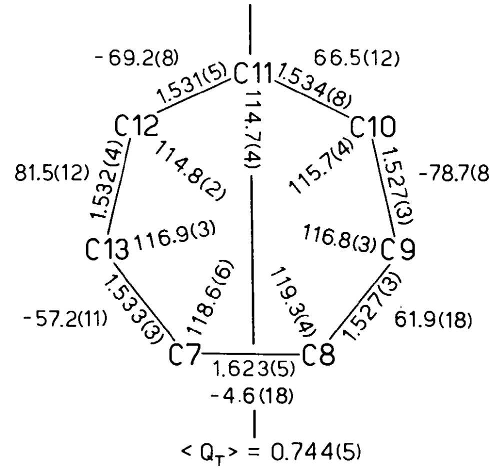
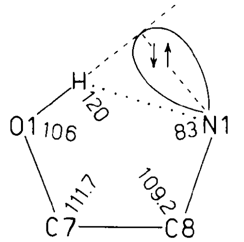


Fig. 4. Relevant parameters [bond distances *d* (Å), bond angles α (°) and torsion angles τ (°)] describing the cycloheptane ring (average values): $\langle d \rangle$ = 1.537 (10) Å, $\langle \alpha \rangle$ = 116.1 (6)°, $\langle |\tau| \rangle$ = 59.9 (12)°, $\sum\tau$ = 0.2°.

The dioxolane ring, present in (4), is puckered; its total puckering amplitude is $Q_T = 0.239\ (4)$ Å and its conformation is half-chair with a pseudo-twofold axis running along C18 and the midpoint of the C20—O4 bond [DAP: $\Delta_2(C18) = 0.0065(22)$].

Intramolecular hydrogen bonding

The *cis* stereochemistry at the C7—C8 junction allows the formation of an intramolecular O—H···N hydrogen bond which closes the N1—C7—C8—O1—H atoms in a ring whose geometrical characteristics are equal in all these molecules, as shown by the data quoted in Tables 3 and 5, according to the scheme below.



As pointed out in *Experimental*, only in the case of (2) has the hydroxyl hydrogen H1O been located and refined, while in the cases of the other compounds this atom was located from a $\Delta\rho$ map but not refined, except in the case of (4), where this atom was placed in a position calculated assuming the same geometry for the hydroxyl group as that found in (2).

From the pyramidal character of the N atom it is possible to calculate the approximate direction of the lone pair and to show that the O—H direction is approximately coplanar and perpendicular to that direction. The N1, C7, C8, O1 system is approximately planar, but the H atom is displaced out of this plane by 0.2–0.5 Å.

To check these results on the basis of the atom–atom Coulombic and van der Waals potential energy, calculations were carried out assuming both the geometry of the hydroxyl group found for (2) and that calculated on the basis of neutron crystal structures retrieved from the Cambridge Structural Database (Allen, Davies, Galloy, Johnson, Kennard, Macrae, Mitchell, Mitchell, Smith & Watson, 1991) and looking for the energy minimum obtained by rotating the OH group about the C8—O1 bond. In these calculations the whole environment of the group in the crystal was considered, as intermolecular interactions can be important. No significant differences in the position of the energy minimum were found between the calculated and observed geometry, so only the results obtained experimentally for (2) are considered.

Table 5. *Comparison of the relevant parameters describing the geometry of the intramolecular hydrogen-bonded* N1—C7—C8—O1—H10 *ring in the five molecules*

		(3)			
	(2)	Mol. *A*	Mol. *B*	(4)	(5)
O1—H1O (Å)	0.86 (3)	0.84	0.83	0.86	0.95
C8—O1—H1O (°)	106 (2)	97	108	106	108
C7—C8—O1—H1O (°)	−22 (2)	−22	−15	−23	−36
N1···(C7,C14,C17) (Å)	0.411 (2)	0.403 (5)	0.393 (4)	0.408 (3)	0.404 (2)
H1O···(N,C7,C8,O1) (Å)	0.35 (3)	0.28	0.20	0.28	0.52
(O1—H1O) (N1—⇅) (°)	89 (2)	102	96	91	83
(N1,C7,C8,O1) (C7,C14,C17) (°)	119.2 (1)	117.2 (2)	119.0 (2)	120.0 (2)	117.2 (1)
Q_T(N,C7,C8,O1,H1O) (Å)	0.25 (2)	0.21	0.14	0.20	0.36
O1···N1 (Å)	2.641 (3)	2.597 (4)	2.592 (5)	2.626 (5)	2.630 (3)
H1O···N1 (Å)	2.10 (3)	1.95	2.03	2.07	2.17
O1—H1O···N1 (°)	120 (3)	132	124	122	109

As shown by the curves of Fig. 5 which demonstrate how the energy varies with respect to that of the conformation found in the crystal as the hydroxyl group is rotated about the C8—O1 bond, the minimum is quite displaced with respect to the H position found in the crystal. This does not mean that it is necessary to assume a different orientation of the H atom, as it is possible to obtain the minimum corresponding to the orientation of the OH group in the crystal simply by increasing the atomic local charges at N and H from −0.18 and 0.16 e respectively, as found from the orbital electronegativities, to the much higher values of −0.49 and 0.47 e, respectively.

It is interesting to compare these results with those of an *ab initio* analysis of 2-aminoethanol (Vanquickenborne, Coussens, Verlinde & De Ranter, 1989), which indicates that the most stable conformation

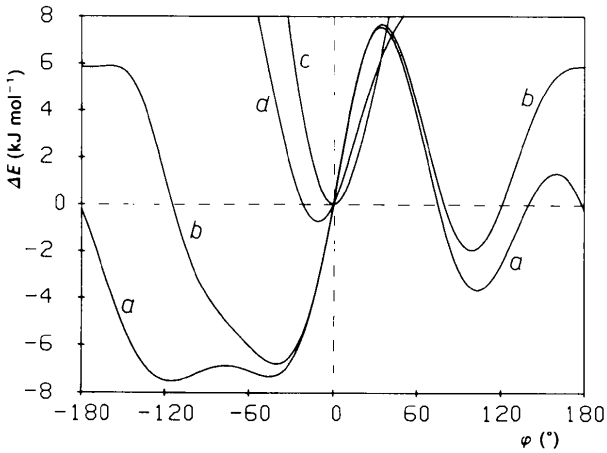


Fig. 5. Calculated energy profiles for rotation of the OH group about the C8—O1 bond for (2). The geometry of the group is that found by X-ray diffraction [O—H = 0.864 (34) Å, C—O—H = 106.4 (23)°]. Curve *a* refers to the isolated molecule, curve *b* to the molecule in the crystal, curve *c* is obtained with the charges −0.49 e at N1 and 0.47 e at H1O, curve *d* with the charges −0.53 e at N1, −0.486 e at O1 and 0.257 e at H1O. Zero corresponds to the orientation of the group observed in the crystal.

for the molecule of this amino alcohol is that involving an O—H···N intramolecular hydrogen bond producing a ring in some way similar to that found in our compounds. The Mulliken population analysis with the 6-31G* basis set gives atomic charges at the atoms involved in hydrogen bonding of 2-aminoethanol, which are much higher than those calculated from the orbital electronegatives. Assuming for (2) the values of the charges found for 2-aminoethanol, *i.e.* −0.535 e for N1, −0.486 e for O1 and 0.257 e for H1O, the curve *d* of Fig. 5 is obtained, showing the minimum much nearer to the position found in the crystals.

Packing

In all compounds the molecules are packed by van der Waals interactions and by the following weak C—H···O hydrogen bonds (*i.e.* with an H···O distance ≤ sum of the van der Waals radii, 2.63 Å).

	C—H (Å)	C···O (Å)	H···O (Å)	C—H···O (°)
Compound (2)				
C2—H···O2^{i}	0.98 (3)	3.365 (4)	2.64 (2)	132 (2)
C5—H···O1^{ii}	0.92 (2)	3.491 (4)	2.61 (2)	162 (2)
C16—H···O2^{iii}	0.97 (2)	3.425 (5)	2.55 (2)	149 (2)
Symmetry code: (i) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $x-1, y, z$; (iii) $-x, 2-y, -z$.				
Compound (3)				
C17*A*—H···O2*B*^{i}	1.08	3.442 (7)	2.60	134
C12*A*—H···O2*B*^{ii}	1.08	3.491 (7)	2.44	165
C15*B*—H···O1*A*^{i}	1.08	3.388 (7)	2.52	137
C19*B*—H···O3*A*^{iii}	1.08	3.370 (5)	2.63	125
C3*B*—H···O2*A*^{iv}	1.08	3.338 (6)	2.30	161
Symmetry code: (i) $-x, -y, -z$; (ii) $x-1, y-1, z-2$; (iii) $-x-1, -y, -z$; (iv) $-x, -y-1, -z$.				
Compound (4)				
C12—H···O1^{i}	1.08	3.396 (6)	2.49	141
C19—H···O4^{ii}	1.08	3.363 (7)	2.62	124
Symmetry code: (i) $x, y-1, z$; (ii) $-x-\frac{1}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$.				
Compound (5)				
C16—H···O1^{i}	1.08	3.363 (4)	2.52	134
Symmetry code: (i) $-x-2, -y, -z-2$.				

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

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