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Conformational Changes in Two Modifications of 2,4-Dibromoestradiol

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Significant conformational differences in three molecules of 2,4-dibromoestradiol are seen to occur as a result of intramolecular forces involving angle strain and eclipsing strain as well as intermolecular forces of hydrogen bonding and van der Waals contacts in two crystalline modifications. Crystal A (orthorhombic, $P2_{12}_{12}_{12}$; Z=4, $\alpha=11.942$, b=13.197, c=10.639 Å, R=4.8%) has short bromine-bromine contacts of 3.63 Å, has a half-chair conformation of the B ring and has an O(3)-H(03)...O(17) hydrogen bond of 2.84 Å. Crystal B (monoclinic, $P2_{12}$; Z=4, a=13.081, b=16.995, c=8.074 Å, $\beta=111.57^{\circ}$, R=5.0%) has no bromine contacts. Molecule B2 has a half-chair conformation B ring and an O(3)-H(03)...O(17) hydrogen bond of 2.77 Å. Molecule B1 has a sofa conformation B-ring and has a double hydrogen bond O(3)-H(03)...O(17) and O(17)-H(017)...O(3) of length 2.67 Å. Each of the three types of molecules form infinite chains that are packed together in parallel strands with few contacts between the chains.

Introduction

Small molecular conformational differences observed in crystal structure determinations are most often considered to be a result of packing forces. In a series of estrane structures which all have aromatic A rings (Cooper, Norton & Hauptman, 1969; Norton, Kartha & Lu, 1963; 1964, Busetta & Hospital, 1969; Tsukuda, Soto, Shiro & Kayama, 1968) the steroid B rings are observed in either a half-chair or a sofa conformation and no clear dependence of this small but significant conformational difference upon the crystalline environment has been detected. It is possible that the molecules in which the B rings are observed in half-chair and sofa conformations represent metastable states of estranes at room temperature. Because even small conformational differences can alter molecular reactivity (Hanack, 1965; Geise, Altona & Romers, 1967; Altona, Geise & Romers, 1968) the question of whether or not this recurring conformational difference is inherent to the molecule or just an artifact of crystal environment is a pertinent one. Another steroid in the estrane series, 2,4-dibromoestradiol (Fig. 1) recently was obtained in two crystalline modifications with no solvent of crystallization in either lattice, and structure solutions were undertaken in order to study the effect of alteration of crystal environment upon this steroid's conformation.

Crystal data

Two crystalline modifications of 2,4-dibromoestradiol were prepared. Modification A was recrystallized as thin plates from a benzene-methanol solution saturated with urea at 50 °C and cooled slowly to 20 °C. The crystal system was found to be orthorhombic and the systematic absences (h00, h=2n+1; 0k0, k=2n+1; 00l, l=2n+1) indicated the space group $P2_12_12_1$. Columnar crystals of modification B were obtained from an ethanol solution cooled from room temperature to 5 °C. These crystals were monoclinic and the systematic absences (0k0, k = 2n + 1) indicated the space group $P2_1$. Unit-cell dimensions were obtained from a least-squares refinement of 2θ measurements of 6 reflections per parameter having $2\theta > 45^{\circ}$. The cell dimensions indicated that there were two steroids in the asymmetric unit of the monoclinic crystals. Densities were measured by flotation in aqueous solutions of potassium iodide.

Crystals selected for data collection were approximately spherical (0.15 mm diameter) and were mounted with the *b* axes parallel to the φ axis of a General Electric XRD-5 diffractometer.

Table 1. Crystal data for 2,4-dibromoestradiol

Crystalline modification	ation A	В	
Space group	$P2_{1}2_{1}2_{1}$	$P2_1$	
a	11.942 ± 0.002 Å	13.081 ± 0.003	Å
Ь	13.197 ± 0.002	16.995 ± 0.004	
с	10.639 ± 0.001	8.074 ± 0.002	
β	90·0°	$111.57 \pm 0.02^{\circ}$	
V	1682 Å ³	1669 Å ³	
D_c	1.70 g.cm ⁻³	1.70 g.cm ⁻³	
D_m	1.37 g.cm ⁻³	1.37 g.cm ⁻³	
Ζ.	4	4	
R (observed data)	4.8 (1037)	5.0 (2207)	
R (all data*)	6.3 (1545)	6.4 (2880)	
M.W.	430.19	430.19	
Formula	C18H22O2Br2	C18H22O2Br2	
μ (cm ⁻¹)	68.19	68.72	
Total data	1769	3249	

* Not including unobserved data for which $(|F_o| - |F_c|)/|F_o| < 0.7$.

The intensities of all reflections (1769 and 3249 respectively) with 2θ values less than 135° were measured by the stationary-crystal stationary-counter method with Cu $K\alpha$ radiation monochromatized by balanced nickel and cobalt filters. The shape anisotropy of the

crystals measured at $\chi = 90^{\circ}$ indicated a less than 5% variation in intensities over the φ range of data collection. Intensities were corrected for Lorentz and polarization factors but not for absorption ($\mu R = 0.5$). The crystal data are collected in Table 1.

 Table 2. Variation in reliability index with

 application of anomalous dispersion correction

Structure		Reliability index			
	$f^{\prime\prime}=0$	f'' = 1.46	f'' = -1.46		
A	5.9 %	5.86%	6 ∙0 5 %		
В	6.0	5.76	6.12		

Structure determination

Positional parameters for all bromine atoms in both structures were found from Patterson functions of the respective space groups. The complete steroids were found from repeated application of three-dimensional Fourier synthesis. Four cycles of isotropic diagonal least-squares refinement resulted in R values ($R = \sum ||F_o| - |F_c|| / \sum F_o$) for the orthorhombic (A) and monoclinic (B) structures of 16.4% and 10.6% respectively. Four cycles of anisotropic block diagonal least-squares refinement on observed data reduced the R values to

Table 3(a). Positional and thermal parameters of the non-hydrogen atoms at the end of the least-squares refinement The first listing are those parameters for molecule A while molecules B1 and B2 are distinguished by the prefixes 1 and 2 respectively. Thermal parameters are listed in the form

$\exp\left[-2\pi^2\right]$	$(U_{11}h^2a^*)$	$^{2}+2U_{12}hka$	*b* +)]
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				· · ·	, , ,				
	X/A	Y/B	2/0	U11	U22	U33	U12	U13	U23
C(1) C(2) C(3) C(4) C(5) C(6) C(7) C(8) C(9) C(1) C(2) C(2)	x/A 0.0163 (9) 0.0417 (10) 0.1258 (10) 0.1668 (10) 0.1622 (9) 0.2277 (9) 0.2277 (9) 0.1659 (11) 0.0456 (10) 0.0754 (9) 0.0754 (9) 0.0754 (10) 0.0754 (11) 0.0754 (11) 0.0287 (10) 0.0706 (11) 0.1563 (11) 0.5563 (11) 0.563 (7) 0.0440 (1) 0.0640 (1)	Y/E 0.9826 (6) 1.0863 (6) 1.1298 (6) 1.0654 (6) 1.0654 (6) 0.9033 (6) 0.7928 (7) 0.7486 (6) 0.7928 (7) 0.7486 (7) 0.7626 (7) 0.6370 (6) 0.5936 (7) 0.6370 (6) 0.5936 (7) 0.6370 (6) 0.5936 (7) 0.6474 (8) 1.2277 (8) 1.1676 (0)	2/C 0.0191 (9) 0.0067 (9) 0.1709 (9) 0.2643 (9) 0.2643 (9) 0.2643 (9) 0.12565 (9) 0.1125 (8) 0.0984 (10) 0.011 (11) 0.0011 (11) 0.4021 (8) 0.1656 (11) 0.1656 (11) 0.0672 (10) 0.0712 (71) 0.0072 (8) 0.1005 (8) 0.1005 (1)	U11 0.0563(73) 0.0622(71) 0.036(84) 0.0734(80) 0.0597(73) 0.0649(71) 0.0697(75) 0.0714(72) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.0772(82) 0.004(84) 0.0904(94) 0.0927(65) 0.1114(72) 0.1074(10) 0.0974(69)	U22 0.0268(47) 0.0285(49) 0.0150(39) 0.0276(46) 0.0218(43) 0.0242(43) 0.0278(46) 0.0278(46) 0.0278(46) 0.0282(46) 0.0282(46) 0.0294(52) 0.0294(52) 0.0219(52) 0.0233(47) 0.0163(39) 0.0219(32) 0.0328(59) 0.0328(50) 0.0338(50) 0.0338(50) 0.0338(50) 0.0338(50) 0.0338(50) 0.0328(50) 0.0328(50) 0.0328(50) 0.0328(50) 0.0338(50) 0.0338(50) 0.0328(50) 0	U33 0.0395(56) 0.0501(59) 0.032(56) 0.034(54) 0.0376(54) 0.0376(54) 0.0422(56) 0.0422(58) 0.0422(58) 0.0422(58) 0.0422(58) 0.0328(49) 0.0403(57) 0.0505(61) 0.0347(53) 0.0472(64) 0.0472(75) 0.0	U12 -0.0067(50) -0.0028(57) -0.0030(53) -0.012(55) 0.0017(48) -0.0027(45) 0.006(62) -0.0091(50) 0.007(48) 0.0076(51) 0.001(52) -0.0169(56) 0.0014(47) 0.0025(50) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.0025(50) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.001(52) 0.002(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.0025(50) 0.00025(50) 0.0025	U13 0.0031(55) 0.0032(65) 0.0182(61) 0.0085(63) 0.0063(59) -0.0141(67) -0.0073(60) 0.0175(65) 0.0175(65) -0.012(52) 0.002(49) -0.002(49) 0.0004(78) 0.0004(78) 0.0106(74) 0.0036(67) -0.0159(50) 0.0038(9) -0.0238(9)	023 -0.0022(43) -0.0106(45) 0.0059(43) -0.0068(43) 0.0059(44) 0.0059(44) 0.0059(44) 0.0059(45) 0.0015(39) 0.004(47) 0.0085(48) 0.0085(48) 0.0097(42) -0.0096(45) 0.0097(52) -0.0096(45) 0.0057(53) 0.0057(53) 0.0025(50) 0.0057(53) 0.0025(50) 0.0027(16) 0.0007(17) 0.0007(17)
DK(4)	0.3009 (1)	1.1235 (0)	0.2463 (1)	0.09/61 9/	0.04/01 8/	0.0732(7)	-0:02041 17	0.02121 77	
IC(1) IC(2) IC(3) IC(5) IC(5) IC(6) IC(7) IC(10) IC(10) IC(11) IC(12) IC(12) IC(12) IC(13) IC(14) IC(15) IC(15) IC(15) IC(17) IBR(2) IBR(4)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1518 (7) 0.1662 (7) 0.1913 (6) 0.2046 (6) 0.2041 (8) 0.2012 (7) 0.1478 (6) 0.1639 (6) 0.1468 (7) 0.1346 (7) 0.2764 (8) 0.2336 (10) 0.2239 (12) 0.1772 (9) 0.1901 (1) 0.2236 (1) 0.2361 (1) 0.2361 (1)	$\begin{array}{c} 0.2226 & (13) \\ 0.2872 & (13) \\ 0.1338 & (14) \\ -0.0140 & (12) \\ -0.0197 & (13) \\ -0.173 & (13) \\ 0.1733 & (13) \\ 0.121 & (12) \\ 0.1410 & (12) \\ 0.322 & (13) \\ 0.322 & (13) \\ 0.322 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.2792 & (13) \\ 0.3063 & (13) \\ 0.4955 & (1) \\ -0.2245 & (1) \\ \end{array}$	$\begin{array}{c} 0.0358(54)\\ 0.0284(54)\\ 0.0326(59)\\ 0.0368(55)\\ 0.037(56)\\ 0.031(56)\\ 0.031(56)\\ 0.0387(58)\\ 0.0388(53)\\ 0.$	$\begin{array}{c} 0.0456(68)\\ 0.0572(81)\\ 0.0376(62)\\ 0.0444(66)\\ 0.034(161)\\ 0.032(161)\\ 0.0456(59)\\ 0.039(161)\\ 0.039(161)\\ 0.039(161)\\ 0.0632(85)\\ 0.0632(85)\\ 0.138(199)\\ 0.134(199)\\ 0.1676(199)\\ 0.1676(199)\\ 0.1676(199)\\ 0.1630(199)\\ 0.0850(10)\\ 0.0979(12)\\ \end{array}$	$\begin{array}{c} 0.0336(53)\\ 0.0345(56)\\ 0.042(58)\\ 0.0243(47)\\ 0.0334(52)\\ 0.0242(51)\\ 0.0235(50)\\ 0.023(50)\\ 0.023(147)\\ 0.0189(45)\\ 0.035(54)\\ 0.035(54)\\ 0.035(54)\\ 0.035(54)\\ 0.0465(69)\\ 0.0465(69)\\ 0.0465(69)\\ 0.0465(69)\\ 0.0657(152)\\ 0.0465(69)\\ 0.0651(52)\\ 0.0455(47)\\ 0.0385(46)\\ 0.0386(6)\\ 0.0396(6)\\ 0\end{array}$	$\begin{array}{c} -0.0016(57)\\ 0.0009(53)\\ 0.0011(51)\\ -0.0022(50)\\ 0.0059(62)\\ -0.0025(59)\\ -0.0016(53)\\ -0.0016(53)\\ -0.0016(53)\\ -0.0018(62)\\ 0.0014(59)\\ -0.0018(62)\\ 0.0014(59)\\ -0.0018(62)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.0018(52)\\ -0.00018(52)\\ -0.00018(52)\\ -0.00018(52)\\ -0.00018(52)\\ -0.00018(52)\\ -0.00018(52)\\ -0.00018(52)\\ -0.00018(52)\\ -0.000018(52)\\ -0.00000000\\ -0.0000000\\ -0.000000\\ -0.00000\\ -0.0000\\ -0.0000\\ -0.0000\\ -0.0000\\ -0.0000\\ -0.0000\\ -0.000\\ -0$	0.0146(44) 0.0160(45) 0.0200(48) 0.0195(45) 0.0133(44) 0.0183(47) 0.0133(44) 0.0168(42) 0.0103(41) 0.0253(51) 0.0125(45) 0.0232(56) 0.0232(56) 0.0234(61) 0.0175(48) 0.025(45) 0.025(45) 0.0232(56) 0.024(61) 0.025(45) 0.022(45)0	-0.0056(55) 0.0115(54) 0.0075(51) 0.0064(48) -0.0072(57) 0.0044(85) -0.0120(49) 0.0004(48) 0.0004(48) 0.0004(48) -0.008(58) -0.008(58) -0.008(58) -0.008(59) -0.0343(93) -0.0343(93) -0.0120(66) 0.0279(77) -0.0139(53) -0.0082(57) -0.0082(57) -0.0082(57) -0.0181(8)
2C(1) 2C(2) 2C(3) 2C(5) 2C(5) 2C(7) 2C(10) 2C(10) 2C(10) 2C(11) 2C(12) 2C($\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.5411 (13) 0.5391 (13) 0.3800 (14) 0.2307 (13) 0.2667 (13) 0.2667 (14) 0.3934 (12) 0.3934 (12) 0.5806 (13) 0.3934 (12) 0.5804 (13) 0.4366 (12) 0.2554 (13) 0.4366 (12) 0.2555 (16) 0.3942 (13) 0.407 (16) 0.5136 (11) 0.5136 (11)	0.0359(54) 0.0275(54) 0.0275(54) 0.0295(58) 0.0205(52) 0.0402(62) 0.0315(52) 0.0374(56) 0.0278(48) 0.0374(56) 0.0238(48) 0.038(63) 0.052(51) 0.052(71) 0.052(45) 0.0370(59) 0.052(45) 0.0348(63)	0.04031661 0.05661811 0.0526181 0.03281651 0.04221631 0.08091961 0.07481831 0.05091761 0.04951701 0.04951701 0.04981681 0.065381851 0.065381851 0.05391801 0.05391801 0.0821991 0.06221791 0.07851681 0.07851681 0.07851681	0.0349(53) 0.0242(50) 0.027(51) 0.027(51) 0.025(51) 0.025(51) 0.025(50) 0.0252(50) 0.0229(46) 0.0216(48) 0.0216(48) 0.0216(48) 0.028(59) 0.028(59) 0.028(59) 0.0435(65) 0.028(51) 0.0435(65) 0.0479(45) 0.0479(45) 0.0479(45)	0.0025(51) -0.0062(61) -0.0053(50) -0.0053(50) -0.0028(47) 0.0093(62) 0.0068(63) -0.0055(55) -0.0079(52) 0.0048(56) -0.0036(54) 0.0048(56) -0.0036(54) 0.0068(73) 0.0008(71) -0.0017(57) 0.0028(66) 0.0035(42) -0.0116(47) -0.0006(73) -0.0006(73)	0.0193(44) 0.0079(44) 0.017(45) 0.0127(45) 0.0127(45) 0.0128(40) 0.0161(47) 0.0128(40) 0.0128(40) 0.0128(40) 0.0125(43) 0.0165(43) 0.0121(41) 0.0121(41) 0.0121(41) 0.0105(50) 0.0150(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.0100(50) 0.000(50) 00	0.0120(50) 0.003(54) 0.0020(49) 0.0007(47) 0.0069(47) 0.0069(57) 0.0069(57) 0.0064(59) 0.0057(49) 0.0057(49) 0.0057(49) 0.0057(49) 0.0057(50) 0.0005(50) 0.0031(52) 0.0031(61) 0.0016(45) 0.001(47) 0.0011(47) 0.0011(47)

Table 3(b). Atomic positional parameters for the hydrogen atoms of the three 2,4-dibromoestradiol molecules

	Molecule A				Molecule B			Molecule C		
	X/A	Y/B	z/c	X/A	Y/B	z/c	X/A	Y/B	z/c	
(1)	-0.0457	0.9610	-0.0344	0.2035	0.1406	0.3911	0.7147	0.4159	0.6472	
(6A)	0.2325	0.9398	0.3468	0.0565	0.1582	-0.2368	0.5425	0.4506	-0.0539	
(6B)	0.3032	0.9012	0.2464	0.0354	0.2502	-0.2502	0.5129	0.5385	0.0809	
(74)	0.1194	0.7754	0.3568	-0.0662	0.1265	-0.1844	0.4144	0.3699	0.0475	
(7B)	0.2534	0.7641	0.3220	-0.1089	0.2108	-0.2392	0.3591	0.4345	-0.0114	
(8)	0.2229	0.7748	0.0982	~0.0465	0.2608	0.0434	0.4177	0.4908	0.2848	
(9)	-0.0245	0.8040	0.1734	0.0078	0.0991	0.1121	0.4942	0.3402	0.3455	
(11A)	-0.0790	0.8006	-0.0678	0.0674	0.0956	0.3876	0.5493	0.3686	0.6387	
(11B)	0.0450	0.7917	-0.0955	0.0301	0.1961	0.3524	0.5116	0.4613	0.5894	
(12A)	-0.0856	0.6337	0.0546	-0.1230	0.0743	0.2945	0.3723	0.3287	0.5639	
(12B)	-0.0196	0.6173	-0.0623	-0.1027	0.1392	0.4729	0.3712	0.4050	0.6957	
(14)	0.0907	0.6211	0.2300	-0.2005	0.1229	-0.0180	0.3052	0.3547	0.2434	
(15A)	0.2270	0.5698	0.2868	-0.3064	0.2034	-0.1790	0.1773	0.4024	0.0099	
(15B)	0.2530	0.5873	0.1649	-0.2708	0.2889	-0.1420	0.1948	0.4951	0.0679	
(16A)	0.1621	0.4158	0.2181	-0.4216	0.1776	-0.0678	0.0663	0.3661	0.1531	
(16B)	0.2215	0.4438	0.1435	-0.3875	0.2797	0.0140	0.0727	0.4553	0.1895	
(17)	-0.0074	0.4882	0.1420	-0.3379	0.1300	0.1122	0.1936	0.3180	0.4148	
(18A)	0.2431	0.5765	-0.0506	~0.2066	0.3161	0.1955	0.2304	0.5284	0.3813	
(18B)	0.1528	0.6822	-0.1181	-0.1046	0.2937	0.2874	0.3609	0.5280	0.4896	
(180)	0.1551	0.5600	-0.1386	-0.1561	0.2916	0.4243	0.2863	0.5085	0.6160	
(03)	0.1121	1.2551	0.0519	0.4985	0.1914	0.1998	0.9825	0.4686	0.4247	
(017)	-0.0510	0.4077	-0.0398	-0.4083	0.1951	0.2742	0.1655	0.3804	0.6057	

6.9% and 6.6% respectively. A three-dimensional Fourier difference synthesis calculated without the contributions of the hydrogen atoms to the structure factors, produced well defined electron densities corresponding to 18 of the 22 hydrogen atoms of molecule *A*. Electron densities corresponding to the remaining hydrogens, $H(7\alpha)$, $H(15\alpha)$, $H(11\beta)$ and H(03) had unreasonably distorted geometries and these atoms were placed at theoretically predicted positions. Similarly all hydrogens of molecules *B*1 and *B*2 were located in difference synthesis except hydrogens $H(6\alpha)$, $H(15\beta)$, and H(16 β) of molecule B1 and H(6 β), H(15 β), and H(16 α) of molecule B2. These atoms were placed in theoretically predicted positions. Introduction of the hydrogen atoms into structure factor calculations reduced the R values for observed data to 5.9% and 6.0% for structure A and B respectively.

All scattering factors were taken from *International Tables for X-ray Crystallography* (1962), and the real part of the bromine anomalous dispersion correction was applied. The brominated derivative was prepared from naturally occurring estradiol, and the absolute

 Table 4(a). Comparison of the observed structure amplitudes with those calculated from the refined atomic parameters for structure A

	H H L JD JC	H K L FD FF	N 6 1 60 FC								
		1									
	0 10 4 412 402	1 317 314	2 3 176 179	2 12 2 191 192	3 7 1 -05 -27	3 7 605 600	5 1 0 473 452	5 13 4 152 142	6 11 4 285 303	7 11 0 214 224	
0 0 8 484 502	0 10 6 164 149	1 272 252	2 2 4 508 481	2 12 3 183 165 2 12 5 208 192	3 7 2 468 501	4 3 8 255 261 4 4 0 217 245	5 1 1 101 105	5 14 0 158 163	6 11 5 192 198 6 11 7 230 229	7 11 3 287 287	9 2 3 111 116 9 2 8 187 188
0 0 12 242 240	0 10 7 834 540	L 6 7 384 378	2 2 4 101 111	2 12 6 256 246	3 7 4 149 140	1 1 1 1 1 1 1 1	1 1 171 171	5 14 2 190 194	6 12 0 200 210	7 12 1 106 140	9 3 8 314 314
0 1 2 341 354	0 11 2 222 214	1 1 1 12 111	2 3 0 546 582	2 13 2 125 129	3 7 6 367 354	* * 3 390 334	5 1 6 244 245	6 0 1 329 343	• 12 2 113 109	1 12 3 113 129	4 3 2 202 203
0 1	0 11 5 374 340	1 1 1 1 1 1	2 3 2 607 791	2 13 2 259 251	3 7 8 179 143		5 2 0 674 648	6 0 3 331 324	6 12 5 196 206	7 13 6 117 197	• 3 • 241 241
0 1 0 102 175	0 12 0 180 171	1 7 3 501 505	2 3 4 405 574	2 13 4 243 231 2 13 5 249 250	3 8 0 491 501	• • • 308 303 • • 7 130 118	5 2 1 852 854	6 0 4 237 247 6 0 5 386 406	6 13 1 163 174 6 13 4 219 239	7 13 2 139 139	4 3 4 167 14C 9 3 7 134 1C4
0 1 7 341 404	0 12 1 243 248	1 7 4 667 670	2 3 5 217 176	2 13 6 122 122	3 8 2 313 323		5 2 3 176 176	a 0 7 133 140	a 14 2 133 149 7 0 1 375 314	B D 0 705 722	• J • 150 1+5 • 0 216 220
0 1 4 242 246	0 12 3 198 174	1 7 6 333 316		2 14 0 134 134	3 8 4 409 423	* 5 1 456 450	5 2 5 507 493	6 1 1 129 147	7 0 2 573 564	• · · · • 103	* * 1 2** 226
0 2 1 444 444	0 13 1 235 220	7 # 301 241	2 3 9 247 295	2 14 3 342 364	3 8 . 128 133	750 77.	5 2 7 177 185	• 1 3 556 543	7 0 4 516 74		12- 13-
0 2 317601735	0 13 5 235 204	1 . 1 403 389	2 . 0 254 242	2 14 5 201 192	3 6 8 132 127	4 5 5 383 371	5 2 9 219 241	6 1 5 27G 298	7 0 6 140 141	0 9 162 165	• • 1 132 132
0 2 3 401 791	0 14 1 441 454	1 8 3 568 589	2 4 1 450 452 2 4 211501104	2 14 0 154 184	3 9 0 114 101	• 5 6 170 1+3 • 5 7 1+6 132	5 2 10 213 212	6 1 6 728 719 6 1 8 182 181	7 0 8 164 175	1 1 254 272 1 3 104 111	a 5 2 240 234 a 5 3 262 224
0 2 6 411 401	0 14 4 113 101	1 8 8 240 240	2 4 3 845 805	2 15 2 265 261	3 4 2 363 377	* 5 9 154 143	5 3 1 370 386	6 2 1 548 553	7 1 1 516 525	1 1 4 422 417 4 2 1 255 257	* > • 20* 148
0 1	0 15 2 303 296	1 8 9 102 164	2 . 5 154 144	3 0 213501344	3 9 4 439 468		5 3 3 232 242	• 2 3 250 204	2 1 3 1-1 131	. 2 2 11+ 10+	9 9 2 154 175
0 2 11 250 207	1 0 1 90 66	1 9 0 740 737	2 4 7 284 298	3 0 4 442 411	3 9 10 113 122	2 241 228	5 3 5 215 209	6 2 7 309 311	7 1 5 185 140	8 2 4 184 108	• 7 0 110 120
0 3 2 805 784	1 0 3 101 74	1 9 2 451 443	2 4 10 227 249	3 0 5 872 807	3 10 2 023 031	• • • 302 309	5 3 7 120 97	6 2 8 175 146 6 3 0 182 185	7 1 6 131 121	8 2 6 260 260	· · · · · · · · · · · · · · · · · · ·
0 3 5 263 266	1 0 5 318 319	1 9 3 398 410	2 5 0 776 803	3 0 7 215 214	3 10 3 2+1 25+	• • 5 204 200 • • 5 203 204	5 • 1 **•1033	a 3 1 108 111 a 3 2 542 518	7 1 10 135 114 7 2 0 287 277	8 2 9 246 250	9 7 9 151 130
0 3 6 245 283	1 1 0 030 003	1 9 5 623 605	2 5 2 414 411	3 0 9 302 305	3 10 5 273 268	* * 7 128 141 * * 9 193 202	5 4 3 472 493	6 3 3 747 725	7 2 1 393 395	8 3 1 280 248 8 3 2 130 143	• 7 • 155 13• • 7 7 127 1•)
0 1 1 194 14	1 1 214171451	1 9 7 324 315	2 5 4 280 249	3 1 1 364 374	1 11 2 133 144	4 4 10 114 107	5 . 5 .85 500	6 3 5 298 31	7 2 3 175 165	1 1 1 1 1 1 1 1 1 1	2 4 1 117 119
0 3 12 129 132	1 1	15- 150	2 5 6 362 371	3 1 3 691 672	3 11 . 162 194	• 7 1 536 564	5 . 7 2.1 2.2	6 1 7 323 155	7 2 5 311 301	1 7 244 254	9 9 1 239 225
0 0 1 541 556	1 1 6 526 536	1 10 2 193 184	2 5 6 243 244	3 1 6 390 349	3 11 0 121 143		5 5 0 274 253	6 3 9 207 199	7 2 8 192 215	1 303 286	
0 . 2 715 700	1 1 7 395 412	1 10 2 258 276	2 6 0 965 965 2 6 1 9 6 9 6 1	3 1 7 198 209 3 1 8 320 287	3 12 0 154 104	• 7 5 345 351 • 7 • 191 345	5 5 2 227 221	• 3 11 131 13• • • 0 1•1 123	7 2 11 104 125	a 2 351 309 a 3 1a1 1a8	9 4 5 114 103
0 4 6 731 729	1 1 0 172 184	1 10 4 127 152	2 6 2 276 248	3 1 9 308 324	3 12 2 277 300	• 7 7 202 212 • 7 8 298 285	5 5 3 456 476	a 1 241 233 b 4 2 413 414	7 3 2 355 339	8 4 4 284 291	• 10 3 1 . 14. • 10 5 10. 11.
0 4 7 393 384	1 1 11 141 179	1 10 6 213 209	2	3 2 1 648 647	3 12 5 1-8 132	4 7 9 139 141	5 3 6 220 213	• 3 243 236 • 3 298 306	7 3 5 183 138	8 4 6 195 174	9 11 1 125 132
0 + 11 187 180	1 2 0 845 857	1 10 8 168 140	2 6 6 432 436	3 2 3 608 592	5 15 1 239 254	· · 1 162 175	5 6 0 645 614		7 3 9 123 130	8 5 0 100 98	4 11 4 104 141
0 5 2 541 545	2 2 958 899	1 11 1 271 201	2 6 8 106 154	3 2 3 531 494	3 13 4 196 206	4 3 241 295	5 6 2 812 833		7 . 2 197 174	8 5 2 216 200	10 0 - 332 319
0 5 5 204 219	1 2 3 588 580	1 11 2 460 430	2 6 9 158 165	3 2 6 556 560	3 14 1 162 195	• • • • • • • • • • • • • • • • • • • •	3 4 4 345 340	6 5 1 431 428	7 4 5 396 356	8 5 4 246 230	10 1 - 152 150
0 3 5 504 502	L 2 5 340 320 L 2 6 L70 L60	1 11 6 243 241	2 7 1 497 511	3 2 8 440 467	3 14 2 150 150	• • • • 215 214 • • • • 223 22•	5 6 5 247 250	6 5 2 140 143 6 5 3 102 79	7 4 6 147 147	8 5 7 194 Lol 8 6 1 306 366	10 2 1 333 324
0 5 7 220 201	1 2 7 235 234	1 11 6 319 311	2 7 3 350 359	3 3 0 9651012	3 14 4 305 306	• • 0 3+9 350 • • 1 2162302	5 6 8 266 261	6 5 6 210 200 6 5 5 290 287	7 4 8 142 182	0 0 3 298 272 8 0 1 152 155	10 2 2 114 130
0 5 9 257 245	1 2 11 151 160	1 11 9 148 146	2 7 7 200 219	3 3 2 373 356	3 15 0 179 189	* * 2 282 272	5 7 0 149 178	. 5 6 408 382	7 5 0 337 333	8 6 5 286 273	10 2 5 122 107
0 6 0 181 48	1 3 111091098	1 12 1 200 214	2 7 4 155 148	3 3 4 111 74	3 15 2 159 157	* * * 278 28*	5 7 2 146 153		7 5 2 255 244	7 199 166	16 3 0 133 111
0 6 2 133 129	1 3 2 856 811	1 12 3 450 443	2 8 0 617 623	3 3 6 408 417	. 0 1 .36 .86	+ 10 1 +05 +07	5 7 . 272 287	1 530 553	7 5 6 204 186	· 7 1 1951055	10 . 3 148 159
0 6 3 545 537	1 3 4 824 807	1 13 1 213 209	2 8 1 3914171 2 8 2 362 376	3 3 8 263 259 3 3 9 178 212	• 0 2 170 178 • 0 3 516 537	4 10 2 267 263	5 7 6 220 222	6 6 3 370 371 6 6 3 208 187	7 5 8 140 125	6 7 4 188 181	10 5 5 143 164
0 6 5 427 408	1 3 6 493 468	1 13 3 239 198	2 8 3 387 374	3 4 0 492 502	· 0 · 396 388	4 10 4 584 374	5 7 7 206 266	6 6 7 301 106 6 9 162 152	7 6 0 363 332	8 7 5 175 160 8 7 6 135 120	10 • 1 117 125
0 . 7 323 303	1 1 4 211 214	1 13 6 167 166	2 . 5 276 267	3 + 2 +17 +0+	• U • 101 #0	4 10 # 123 134	5 8 2 392 395	6 7 0 199 101	7 6 2 391 391	8 7 7 169 168	10 6 5 136 140
0 7 1 451 475	1 3 10 144 153	1 14 1 113 144	2 8 7 205 234	3	. 0 10 156 144			a 7 2 340 369	7 6 6 331 331	8 8 2 297 294	10 7 5 120 115
0 7 3 326 316	1 010201087	1 1 1.3 151	2 0 0 00 77	3 4 4 241 219	1 1 729 770		5 6 6 202 215	1 1 1 1 1 1 1	2	1 1 1 1 1 1 1 1 1 1	10 6 1 113 126
0 7 6 309 323	1 4 2 349 341	1 15 1 241 225	2 9 2 526 376	3 4 8 161 141	• 1 3 495 487	4 12 0 211 219	5 0 0 190 183	8 7 7 130 165	7 7 1 1+3 1+1		10 9 2 144 124
0 7 0 354 345	1 4 3 215 213	2 0 0 516 529	2 • 3 332 326	3 4 9 244 222	4 L 412451186 4 1 5 455 446	• 12 1 149 175 • 12 2 120 109	5 9 2 133 122	6 7 10 160 145 6 6 0 259 273	7 7 3 458 448	• • 7 122 107	10 11 2 112 113
0 7 11 116 89	4 5 207 227	2 0 228+327+0	2 9 5 241 226	3 5 0 89 55	a 1 6 153 1ee a 1 7 523 489	+ 12 3 137 170 + 12 9 211 237	5 9 3 140 165	• • 1 150 158 • • 2 239 251	7 7 5 255 230	8 10 1 222 205 8 10 2 163 155	11 0 3 204 189
0 1 1 424 428	1 4 7 324 341	2 0 4 974 925	2 9 7 289 294	3 5 2 487 491	4 1 8 279 277 5 1 10 227 261	4 13 0 249 270	5 4 6 153 135	6 8 3 136 127 8 8 4 255 240	7 7 9 116 130	8 10 3 115 107 8 10 5 18e 170	11 1 4 150 130
0 0 3 729 710	1 10 195 207	2 0 0 252 247	2 10 1 157 163	3 5 507 505	• 2 • 92 •0	• 13 2 11+ 12+	5 10 1 170 173	6 8 5 170 153	7 8 1 435 447	11 3 202 184 11 1 100 111	11 2 6 132 103
0 8 6 158 144	1 5 0 533 529	2 0 9 332 341	2 10 3 603 607	3 3 6 232 274		13 5 170 166	5 10 3 123 124	6 6 7 196 74	7 8 3 212 178	1 12 2 22 21	11 5 5 155 127
0 8 8 107 102	1 5 210741088	2 0 10 483 509 2 1 011791359	2 10 5 348 348 2 10 6 157 155	3 5 8 193 203	2 3 301 575		5 10 5 273 263	0 9 0 149 110	7 8 6 138 151	. 13 0 178 203	11 + 1 12- 102
0 4 1 184 107	1 5 5 452 464	2 1 1 358 348	2 10 9 220 224	3 5 9 206 205 3 5 10 190 199	• 2 5 369 371 • 2 7 135 132	• 1• • 136 124	5 10 6 230 212	6 9 3 250 246	1 4 1 237 234	9 0 3 129 69	11 7 2 114 47
	1 5 6 527 507	2 1 311191036	2 11 2 324 312	3 . 0	4 2 8 137 158 5 2 11 118 105	5 0 1 602 630	5 11 1 207 268	6 9 4 236 252 6 10 1 265 305	7 9 2 204 175 7 9 3 162 151	9 0 7 138 112 9 1 0 182 197	11 7 5 105 63
0 0 5 441 438	1 5 8 340 305	2 1 3 673 624	2 11 4 397 395	3 6 2 603 626	3 0 793 793	5 0 3 214 232	5 12 1 106 174	10 2 339 353 10 3 152 117	7 4 6 272 256	9 1 1 111 98 9 1 2 326 326	11 4 0 41 41
0 9 5 144 123	1 5 12 110 149	2 1 8 104 220	2 11 7 157 147	3 6 4 604 629	- 2 - 32 - 35	5 0 5 446 440	11 1 23 24	6 10 4 175 183	7 10 1 21- 220	9 1 3 356 334	12 . 0 131 141
0 9 8 324 284	1 6 0 397 344	2 1 9 182 196	2 11 8 117 118	3 6 7 283 297	• 3 3 362 342	5 0 7 412 413	5 12 5 216 207	5 10 7 273 129	7 10 5 167 153	• 1 • 150 1+•	12 . 0 1.4 1.55
@ 10 1 762 757	1 0 2 341 413	2 2 113561393	2 12 0 735 784	3 6 8 399 395	3 5 250 270	5 0 8 300 305	3 13 1 109 118	0 11 1 269 292	10 6 220 213	• 2 0 100 112	13 0 1 104 117

Table 4(b). Comparison of the observed and calculated structure amplitudes for structure B

H R L FO FC	H K L FO FC	H K L FO FC	PO PC	H K L PO PC	H K L PO PC	H K L PO PC	H K L PO PC	M K L FO FC	1 -0 -0	- * L FO FC	H A L PO PC
0 0 1 110 135 0 0 2 84 96 0 0 3 163 156	1 9 -7 278 290 1 9 -1 588 175 1 9 -4 432 434	2 2 6 544 992 2 2 7 206 22A 2 3 -7 124 151	3 0 -9 794 747 3 0 -3 931 825 3 0 -2 171 150	1 11 -5 272 221 1 12 -6 112 96 1 13 -3 211 179	• 10 0 192 712 • 10 1 201 704 • 10 2 201 201	5 0 -5 440 451 5 0 -2 170 190	6 9 -6 366 357 6 9 -3 452 446 6 9 -3 159 144	7 • • 277 240 7 • • 5 175 177	0 12 -0 130 144 0 12 -9 247 240 0 12 -4 135 162	10 1 2 161 166 10 1 3 193 193 10 2 -7 190 210	11 8 -1 274 272 11 8 0 188 198 11 8 3 184 187
0 0 415241445 0 0 5 274 289 0 0 8 477 481	1 5 -3 446 420	2 3 -0 141 150 2 3 -7 543 542 2 3 -6 296 281	3 0 -114741471 3 0 0 75 31 3 0 1 610 573	3 13 -2 121 126 3 13 -1 342 341 3 13 1 269 269	• 10 3 205 907 • 10 • 121 115 • 10 \$ 109 100	5 6 -1 204 103 5 6 0 548 539 5 7 1 565 568	• • -2 •25 •2• • • -1 252 251 • • 0 120 150	7 10 -6 222 212 7 10 -7 101 165 7 10 -5 171 176	8 12 -3 158 174 8 12 -2 235 234 8 12 -1 146 164	10 2 -6 106 324 10 2 -5 376 382 10 2 -5 239 242	11 8 2 252 224 11 9 -8 141 142 11 9 -8 290 306
0 1 1 313 300 0 1 2 370 341 0 1 3 761 749	L 5 0 9201000 L 5 1 94 72 L 5 2 498 508	2 3 -5 661 647 2 3 -4 536 495 2 3 -310751004	3 0 217661644 3 0 3 630 814 3 0 4 113 135	3 13 3 309 330 3 13 5 96 131 3 14 -3 249 266	• 11 -• 1+• 1+1 • 11 -• 121 112 • 11 -• +52 +39	\$ • 2 1•3 194 5 • 3 101 203 5 • • 279 279	• • 2 39• 357 • • 3 340 344 • 10 -7 258 241	7 10 -4 210 213 7 10 -3 341 356 7 10 -2 150 149	12 0 173 177 12 1 702 186 12 2 735 240	10 2 -2 +81 +81 10 2 -1 597 563 10 2 0 235 218	11 4 -2 208 221
0 1 5 593 396	1 3 3 334 348	2 3 -2 359 348 2 3 -111401197 2 3 0 597 613	3 0 5 356 368 3 0 6 398 423 3 0 7 196 198	3 14 -4 111 44 3 14 -1 180 147	• 11 -3 114 139 • 11 -2 159 165 • 11 -1 239 257	5 0 5 270 285 5 10 -0 210 213 5 10 -7 186 175	+ 10 -+ 33+ 313 + 10 -5 205 140	7 10 -1 106 100		10 2 1 208 182	11 10 -9 139 140
0 1 7 117 138	1 5 6 102 111			1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	• 11 9 214 200	\$ 10 -+ 191 180 5 10 -3 125 157	• 10 -3 331 3+6 • 10 -2 +21 +34	7 10 + 107 120 7 11 -• 350 329	1 14 -0 101 170 1 14 -3 163 146	10 1 -1 150 100 10 1 -7 107 710	11 10 -2 154 178
0 2 7 872 829 0 2 3 767 746	1 8 -8 340 334	1 4 247 298 1 5 212 255		1 15 -1 263 245 3 15 -2 376 393	• 11 5 95 105 • 12 -5 543 304	5 10 0 193 141 5 10 1 101 115	• 10 0 313 303 • 10 1 223 229	7 11 -3 172 180	1 1 1 1 1 2 0 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -	10 3 -3 267 262	11 11 -4 199 191
0 2 6 141 139	1 6 -6 172 161	2 3 4 202 222 2 3 7 224 234 2 3 8 220 234	1 -31038 440 1 1 -314121372 3 1 -111441209	3 15 -1 204 144 3 15 1 128 123 3 15 2 148 184	+ 12 -4 327 284 + 12 -3 144 137 + 12 -1 289 295	\$ 10 2 100 122 \$ 10 4 108 141 \$ 10 5 118 130	10 2 200 200 10 4 171 157 11 -7 339 311	7 11 -1 270 297	1 1 -1 222 212 1 1 1 105 114 1 1 2 151 171	10 3 -1 332 336 10 3 0 476 460 10 3 1 192 160	11 11 -1 188 191 11 12 -3 149 134 11 12 -2 139 142
0 2 7 182 202	1 4 -2 575 554	2 • -9 200 207 2 • -8 388 398 2 • -7 383 352	3 1 0 275 296 3 1 1 819 802 3 1 2 903 880	3 15 3 209 213 3 16 -3 181 170 3 16 0 117 117	4 12 0 431 443 4 12 1 227 734 4 12 2 172 198	5 11 -7 100 170 5 11 -6 134 113 5 11 -7 202 104	• 11 -• 203 200 • 11 -3 532 5•1	7 11 3 112 117	0 11 -3 99 100 0 13 1 117 115 9 0 -9 259 265	10 3 2 227 209	11 12 0 144 147
0 3 2 120 300	1 6 1 351 352 1 6 2 470 481		3 1 3 403 592 3 1 4 163 159	1 14 1 223 234	• 12 • 1++ 1+3 • 13 -5 223 193	\$ 11 -3 337 346 \$ 11 -2 311 331	• 11 • 391 952 • 11 • 210 735	7 12 -3 200 307	• 0 -• •• •• •• •• •• •• •• •• •• •• •• ••	10 + -8 287 240	11 14 -2 199 171
0 3 5 104 114 0 3 6 404 187		* -3 7*0 *7* * -2 2*1 2*0	3 1 1 202 227	1 10 -0 103 102	• 13 -2 148 195 • 13 -1 213 206	\$ 11 0 119 133 \$ 11 1 125 132	• 12 -• 2•3 257 • 12 -3 233 230	7 12 0 199 199	• 0 -1 +03 +74 • 0 -1 +03 957	10 4 -5 153 190	12 0 -310601023
0 3 8 142 170 0 4 033153769	6 7 208 225 7 -7 175 200	• 01+301618 • 1 682 661	3 2 -7 251 200 3 2 -5 100 175	• 0 -9 274 280 • 0 -8 335 134	• 11 2 111 115	5 11 5 254 245	• 12 1 193 204 • 13 -• 328 310	7 13 -7 204 196	• 0 1 2+1 220 • 0 2 510 501	10 4 -1 230 240	12 1 -7 146 201
0 4 2 514 514	1 7 -3 563 559	2 4 3 332 31 0 2 4 3 332 31 0 2 4 4 9 7 744	3 2 -3 871 809 3 2 -2 120 112	0 -5 822 787 0 -6 727 710	• 13 • 132 137	5 12 -5 210 100 5 12 -3 277 268 5 12 -1 267 273	• 13 -9 100 e7 • 13 -2 121 129 • 13 -1 127 119	7 14 -6 133 122	• 1 -• 110 11e • 1 -• 294 297	10 + 3 127 120	
0 4 4 872 784 0 4 9 446 443 0 4 8 306 298	L 7 -3 134 127 L 7 -2 619 612 L 7 -1 744 732	2 4 5 341 382 2 4 4 124 134 2 5 4 117 47	3 2 -1 499 517 3 2 0 103 86 3 2 1 321 336	• 0 -3 •74 •50 • 0 -2 167 152 • 0 -1 795 762	<pre>4 14 -5 198 171 4 14 -4 176 152 4 14 -2 170 180</pre>	\$ 12 0 228 242 \$ 12 1 259 262 \$ 12 3 201 227	6 13 2 149 140 6 13 3 217 227 6 14 -6 164 159	7 14 -2 128 124 7 14 1 131 125 7 14 2 115 125	9 1 -7 109 124 9 1 -6 287 295 9 1 -5 569 580	10 5 -8 187 156 10 5 -7 136 164 10 5 -6 241 265	12 1 0 313 250
0 5 1 426 443	1 7 0 578 603	2 5 -7 257 252 2 5 -5 306 302 2 5 -4 376 371	1 2 2 05 04 3 2 3 347 347 3 2 4 250 249	• 0 0 997 908 • 0 1 110 117 • 0 2 158 201	4 14 -1 227 222 4 14 0 165 102 4 14 2 161 176	5 13 -7 144 143 5 13 -6 113 114 5 13 -9 473 444	6 14 -3 297 309 6 14 -2 186 183 6 14 0 236 239	7 15 -3 144 135 7 15 -2 230 224 7 15 -1 123 124	1 -3 47 485 1 -3 47 46 1 -2 421 401	10 5 -5 474 470 10 5 -1 327 345 10 5 -1 325 314	12 2 -7 175 176 12 2 -6 396 426 12 2 -5 174 196
0 5 4 130 137 0 5 5 573 542	1 7 3 522 538	2 5 -3 250 240 2 5 -2 355 352	3 2 5 316 328 3 3 -9 191 186	• • • • • • • • • • • • • • • • • • • •	4 14 3 220 209 4 15 -5 170 140	5 13 -2 100 100 5 13 -1 125 120		7 15 2 107 102	1 -1 670 626 9 1 0 649 587	10 5 0 170 200	12 2 -3 163 155
0 . 0	1 7 6 226 252	5 L 484 501 5 2 784 805	1 1 -7 125 131 1 1 -4 573 195	• 1 -• 1•• 221 • 1 -• •12 •20	• 15 -3 172 168 • 15 -2 137 168	5 13 2 97 105 5 13 4 261 260	6 15 -6 109 133 6 15 -3 188 191	7 14 -1 125 128	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	107 143 143	12 2 2 200 240
0 6 3 277 274 0 6 130 127	1 8 -0 110 128	5 5 101 132 5 6 478 510	1 1 -4 775 724 1 3 -3 177 303	* 1 -6 161 110 * 1 -7 783 756	• 15 1 1•• 15• • 10 -5 172 153	5 14 -1 247 279	• 15 0 149 157 • 13 1 102 110	7 17 0 104 113	• 1 5 110 1•)	102 .70 720	12 1 -6 141 115
0 6 7 163 LT	1 8 -3 258 246	· -7 3+5 3+0	3 3 -1 195 212 3 3 0 519 530	• 1 -3 736 685 • 1 -2 722 710	• 16 -2 111 122 • 16 -1 160 155	5 15 -6 204 148 5 15 -5 109 123	6 16 -5 110 90 6 16 -3 168 164	0 -5 687 695 8 0 -4 365 340	• 2 -5 205 220 • 2 -4 138 181	10 • 1 127 135	12 3 -5 314 32
0 7 1 723 724	L 0 279 277	2 6 -4 397 372 2 6 -3 671 634 2 6 -2 369 369	3 3 1 308 399 3 3 2 663 678 3 3 3 208 286	+ 1 -110461073 + 1 0 706 664 + 1 1 564 536	• 10 1 114 125 • 17 0 137 127 • 10 -3 141 111	5 15 -4 120 112 5 15 -3 145 125 5 15 -2 173 103	6 16 -2 133 146 6 16 0 143 145 6 16 1 94 104	8 0 -3 822 781 8 0 -1 414 389 8 0 0 204 190	• 2 -2 145 153 • 2 -1 462 442	10 7 -7 141 157	12 4 -8 258 291
0 7 4 144 201	1 8 2 486 508	2 6 -1 0771006 2 6 0 522 537 2 6 1 106 119	3 3 4 355 349 3 3 5 148 125 3 1 6 285 305	• 1 21043 978 • 1 3 515 514	5 0 -7 134 114 5 0 -8 540 543 5 0 -4 151 142	\$ 15 -1 175 172 \$ 15 0 \$ 109 \$ 15 2 121 129	6 [7 -1 96 102 7 0 -9 416 390 7 0 -7 391 394	a 0 1 517 487 a 0 2 243 216 a 0 3 165 178	• 2 0 827 743 • 2 1 540 552 • 2 3 197 184	10 7 -9 293 262	12 + -3 520 55
0 8 0 567 573	1 1 200 227	1 1 1 1 1 1 1	1 160 160 1 117 112		5 0 -3 189 186 5 0 -2 109 125	5 15 5 114 122 5 16 0 152 157	7 0 -6 364 360 7 0 -3 360 281 7 0 -8 97 108	8 0 5 205 20C 8 1 -9 399 395 8 1 -8 218 235	• 2 • 261 205 • 2 5 214 234 • 1 • 9 199 225	10 7 0 323 324	12 + 1 240 241
2 2 2 2 2 2 2 3	4 -4 104 108 9 -5 429 399	• • • • • • •	1 4 -6 498 498 1 4 -3 511 481	• 2 -9 1+5 150 • 2 -7 +12 397	5 0 0 492 445 5 0 2 502 474	5 17 -1 181 162 5 17 0 106 111	7 0 -3 863 829	- 201 193 - 5 212 242	• 1 -8 136 138 • 1 -7 164 181	10	12 + 2 40 10
0 0 1 102 402	1 4 -1 206 185 1 4 -2 238 241	7 -0 207 218 2 7 -7 300 330	1 + -3 +75 ++7 1 + -2 +25 +50	2 -5 3-3 506	5 0 • 276 222 5 0 • 286 222	• 0 -9 118 113 • 0 -8 365 354	7 0 0 141 123	-9 913 959	1 -5 466 477 9 1 -4 373 375	10 4 -5 154 172	12 5 -3 129 12
0 0 5 252 252 0 0 0 1 10 120	1 9 0 227 251	7 588 5-0	1 4 0 400 416 3 4 1 817 811	2 -2 983 990	5 1 -8 +40 +35 5 1 -7 271 259	• 0 -• 910 8+9 • 0 -3 652 650	7 0 3 224 220	1 0 111 103 1 1 159 150	* 1 -2 +0* 3*7 * 1 -1 573 552	10 4 -2 247 266	12 5 0 155 15
0 0 3 766 265 0 0 6 139 139 0 10 0 386 396	1 0 2 303 200	2 7 -1 846 850 2 7 0 377 383 2 7 1 252 248	3 • 3 606 622 3 • 213 216	• 2 0 100 117 • 2 1 206 20• • 2 2 7•3 205	5 1 -5 204 215	• 0 0 902 8+2 • 0 1 737 •96	7 1 -9 296 289	e 1 3 260 283	9 3 3 240 243	10 • -6 11• 132	12 6 -5 204 311
0 10 1 532 524 0 10 2 455 474 0 10 3 511 497	1 0 5 134 173 1 0 7 101 215 1 10 -7 315 300	2 7 2 404 418 2 7 3 482 516 2 7 4 376 402	3 • 5 269 288 3 • 6 201 198 3 • 7 2+9 286	• 2 5 903 911 • 2 • 152 159 • 2 5 251 2•3	5 1 -3 394 379 5 1 -2 392 382 5 1 -1 635 618	• 0 • ••3 •50 • 0 5 250 207 • 1 -8 229 226	7 1 -5 356 375 7 1 -5 356 375 7 1 -6 268 261	8 2 -7 773 777 8 2 -6 664 677 8 2 -5 401 388	· · · · · · · · · · · · · · · · · · ·	10 9 -1 146 150 10 9 0 158 148	12 7 -5 152 16
0 10 6 310 314	1 10 -0 291 294 1 10 -9 158 159	2 7 6 190 206	3 5 -0 305 384 3 5 -7 345 353 3 5 -6 105 176	• 2 • 130 153 • 2 7 51• 350 • 3 • 8 529 331	5 1 C15671525 5 1 2 244 240 5 1 3 397 397	a [-7 a]; a]7 a [-6 775 55] a [-7 164 133	7 1 -3 050 047 7 1 -2 553 561 7 1 -1 510 503	8 2 -4 145 171 8 2 -3 472 473 8 2 -2 957 936	• • -• 358 376 • • -3 301 387 • • -7 +37 ++5	10 10 -7 241 275 10 10 -8 285 285	12 7 -2 133 134
0 10 7 249 281	1 10 -3 380 399	2 8 -7 235 231 2 8 -6 180 194	3 5 -5 410 300 3 5 -41075 983	+ 1 -7 2+1 233 + 3 -6 +C8 +10 + 1 -5 202 210	5 1 6 622 620 5 1 6 187 210 5 1 7 215 250	b L -4 608 584 6 L -3 834 825 6 L -2 865 836	7 1 0 217 101 7 1 1 870 786 7 1 2 453 430	8 2 -1 580 571 8 2 1 397 375 8 2 2 60+ 5+7	9 6 -1 266 256 9 6 0 637 636 9 6 1 282 266	10 10 -5 165 199 10 10 -4 198 190 10 10 -3 236 246	12 8 -5 244 26
0 11 0 142 134 0 11 0 142 147	1 10 1 218 222	2 8 -3 136 153	5 -2 +25 +37 5 5 -1 761 807	• 3 -• 707 052 • 3 -3 ••3 •15 • 3 -2 508 513	5 2 -8 227 246 5 2 -7 515 504 5 2 -7 544 514	6 1 -1 675 615 6 1 0 836 798 8 1 1 851 785	7 1 5 482 498 7 2 -8 198 208 7 2 -7 187 373	8 2 3 255 254 8 3 -9 214 221 8 3 -8 249 263	· · 2 328 31+ · · 3 184 176 · · · 149 187	15 10 -2 206 214 10 10 -1 411 408 10 16 1 164 166	12 0 -2 113 114
0 12 0 522 512 0 12 1 290 271	1 10 5 154 158 1 11 -7 297 282	2 8 -1 676 685	3 5 1 623 650 3 5 7 117 104	· 3 -1 524 537	5 2 -6 563 561 5 2 -3 956 414	6 1 2 366 349 6 1 3 285 282 8 1 5 327 518	7 2 -6 216 219 7 2 -5 188 211 7 2 -9 261 278	e 3 -7 365 349 e 3 -6 167 230 a 3 -5 447 445	9 5 -8 193 199 9 5 -7 242 236 9 5 -6 455 466	10 10 2 91 92 10 11 -6 99 104 30 11 -3 101 175	12 9 -5 173 16 12 9 -4 138 15 12 9 -8 160 16
0 12 + 324 315	1 11 -9 274 249	2 4 2 106 103 2 6 3 4264476	5 5 709 754	• 1 2 616 607 • 3 3 601 606	5 2 -1 851 819 5 2 0 123 122	6 1 5 130 147 6 2 -7 666 656	7 2 -3 314 318 7 2 -2 324 331 7 2 -2 324 331	6 3 -6 204 204 8 3 -3 756 276 8 3 -2 256 251	* 5 -5 174 20C * 5 -4 51C 533	10 11 -3 211 224	12 9 -2 245 214
0 13 3 125 102	1 11 -2 587 543	2 8 5 228 227	3 6 -7 486 454	· · · · · · · · · · · · · · · · · · ·	5 2 2 116 128	6 2 -5 240 22V 6 2 -3 682 686 8 2 -2 680 623	7 2 0 588 574 7 2 2 230 203 7 2 3 205 196	8 3 -1 514 511 8 3 0 194 192 8 3 1 573 543	* 5 7 *C7 *C3 * 5 -1 144 14* * 5 6 377 3*1	10 12 -5 156 146	12 10 -1 162 11
0 14 3 137 174	1 11 1 327 324	2 4 -5 310 315 2 4 -6 190 200	3 6 -4 345 335 3 6 -1 919 886	· · · · · · · · · · · · · · · · · · ·	5 2 5 262 265	2 -1 274 291	7 2 4 162 159	a 3 2 259 256 a 3 3 301 290 a 1 5 105 195	· · · · · · · · · · · · · · · · · · ·	10 12 -2 171 147 10 12 -1 173 188	12 11 -2 135 14
0 15 1 227 205 0 15 3 173 179	1 11 5 206 217	2 9 -2 462 457	1 6 -1 557 572 3 6 0 338 355	• • -5 538 507 • • -6 736 589	5 5 6 259 268 5 5 -7 336 338	· · · · · · · · · · · · · · · · · · ·	7 5 -6 559 550 7 5 -5 266 259	1 5 154 156 8 4 -0 171 174	* 5 + 15+ 142 * 6 -7 255 2+8	10 13 -4 117 153 10 13 -7 13 15 10 14 -4 128 15	13 0 -1 126 12
0 16 1 235 222 0 16 2 188 149 0 16 3 149 119	1 12 -0 248 293 1 12 -0 191 170 1 12 -3 275 247	2 9 1 769 789 2 9 2 305 315 2 9 3 174 171	3 6 1 522 547 3 6 3 574 587 1 6 4 399 403	· · · · · · · · · · · · · · · · · · ·	5 3 -5 667 636 5 3 -5 667 636 5 3 -6 751 753	6 2 5 67 110 6 2 6 127 120	3 -3 +16 +18 3 -2 503 +98	· · · · · · · · · · · · · · · · · · ·	• • -5 102 108 • • -4 115 122	10 14 -2 90 75 10 14 -1 125 149	13 0 -2 178 16
0 14 4 104 96 0 14 5 149 137 0 17 1 143 129	1 12 -2 364 340 1 12 -1 230 223 1 12 0 243 243	2 4 4 102 43 2 4 5 208 210 2 9 6 192 212	3 6 5 182 148 3 6 7 108 143 3 7 -8 121 115	• • • • • • • • • • • • • • • • • • •	5 3 -3 664 651 5 3 -2 -53 V61 5 3 -11115:140	• 3 -0 38• 387 • 3 -7 285 253	7 3 0 481 483	• • • • • • • • • • • • • • • • • • •	• E -2 2/1 72* • • 0 •50 62*	11 U -7 164 17J	15 1 -7 151 17
0 18 0 110 110	L 12 L 239 259 L 12 2 45 103 L 12 4 354 347	2 10 -6 183 182 2 10 -7 104 84 2 10 -8 314 301	1 7 -7 425 411 1 7 -5 241 230 1 7 -4 354 338	3 /.0 /.6 765 /99	5 9 1 862 476 5 4 1 753 749 5 4 7 982 682	6 3 -6 320 291 6 3 -5 489 462 6 3 -4 556 557	7 9 3 310 321 7 9 4 129 126	a a 1 319 316 a a 2 726 714	· · · · · · · · · · · · · · · · · · ·	11 6 - 3 231 219	11 1 4 127 14
1 0 -3 855 616	1 13 -4 329 297	2 10 -5 106 109 2 10 -6 367 325 2 10 -1 173 167	3 7 -3 815 784 3 7 -2 305 100 1 7 -1 531 545	 4 7 114 126 5 -3 186 201 5 -5 129 145 	5 5 3 540 584	6 3 -3 562 571 6 3 -2 611 595 6 3 -1 549 561	7 3 6 130 144 7 3 6 130 144 7 4 -9 304 787	8 4 3 145 167 8 4 4 431 419 8 5 - V 141 140	0 2 0 120 200 0 2 -8 120 120 0 2 -6 525 533	11 2 0 264 262	13 1 -1 104 10
0 0 47 51 0 1 460 448	1 13 -1 215 192	2 10 -2 818 787	1 7 0 174 385 1 7 1 574 627	· · · · · · · · · · · · · · · · · · ·	5 5 6 170 171 5 6 7 230 228 5 5 9 218 253	6 3 0 661 663 6 3 1 509 495 6 3 2 213 211	7 4 -7 340 384 7 4 -5 430 441 7 4 -4 86 115	8 5 -8 137 113 8 5 -7 221 244 8 5 -6 170 195	9 7 -5 200 213 9 1 -6 226 241 9 7 -3 224 244	11 0 3 215 223 11 0 3 215 226 11 1 -8 256 278	13 2 -6 149 14 13 2 -6 149 14
1 0 1 447 464	1 13 4 218 297	2 10 1 85 113	3 7 3 419 423	· · · · · · · · · · · · · · · · · · ·	5 6 -7 111 133 5 6 -6 316 135	6 3 3 144 176 6 3 4 379 364 6 3 6 134 158	7 • -3 517 520 7 • -2 209 313 7 • -1 270 205	8 5 -5 401 395 8 5 -4 319 339 8 5 -3 307 320	9 1 -2 455 450 9 1 -1 141 158 9 7 0 113 99	11 1 -7 201 208 11 1 -4 419 413 11 1 -3 252 252	13 2 -7 197 14
1 1 -0 108 120	1 14 -4 152 145	2 10 4 300 325	3 7 6 170 188 3 7 7 181 207	4 5 0 184 464 4 5 116891113	53 159 166 52 81 116 51 151 191	6 4 -9 240 258 6 4 -8 328 321 8 4 -6 135 160	7 + 0 117 12+ 7 + 1 333 317 7 + 2 001 000	8 5 -2 179 204 8 5 0 211 211 8 5 2 155 170	4 7 1 230 223 4 7 2 144 148 4 7 3 101 104	11 1 -2 103 98	13 3 -6 274 27 13 3 -6 274 27
L L -6 243 241 L L -5 306 315	1 14 -1 234 207	2 10 7 132 141 2 11 -7 146 143	5 -6 334 308 5 4 -5 189 174	• • • • 122 142	0 255 255	a 5 480 480 a 4 596 589 a 3 481 460	7 + 3 173 1+4 7 + 5 199 271 7 + 6 293 318	8 5 3 237 250 8 5 4 158 148 8 6 - 6 154 161	9 8 -1 267 259 9 8 -6 280 299 9 8 -5 208 211	11 1 1 198 195 11 1 2 134 126 11 2 -0 232 252	15 3 -2 261 22
1 1 -312551106	1 14 2 237 245	2 11 -4 156 140	5 6 -3 320 305 5 6 -2 306 323	• 5 6 1•5 151 • 6 -9 15• 152	5 5 1 2#1 2#5 5 5 110 155	6 4 -7 798 309 6 4 -1 457 459 8 9 0 0 0 0 0 0 79	7 5 -9 179 171 7 5 -8 365 362 7 5 -7 559 31	8 6 -7 - 15 - 66 8 6 - 6 196 259 8 8 - 5 126 130	4 8 - 6 235 233 4 8 - 3 300 243 4 8 - 2 243 260	11 2 -7 452 456 11 2 -6 164 159 11 2 -5 184 176	13 4 -7 107 17 13 4 -6 147 18 13 4 -6 210 71
1 1 0 91+1015	1 15 -3 257 222	2 11 0 193 200	3 8 0 206 236 3 8 1 356 363	• • -6 612 561 • • -5 259 236	5 - 6 16- 170	• • 1 ••0 •60 • • 7 157 16•	7 5 -6 222 215 7 5 -5 335 338 7 5 -5 477 896	0 350 369 0 -3 -00 -19 0 -1 500 575	4 8 -1 141 127 9 8 C 243 244 9 8 1 167 159	11 2 -4 509 579 11 2 -3 514 488 11 2 -2 156 171	13 4 -3 125 14 13 4 -1 274 77 13 4 0 314 13
	1 15 1 216 200 1 15 2 150 167	2 11 - 464 485	3 1 1 1 1 1 0 C	6 -3 606 615 6 -2 9971038	5 5 -8 162 179	· · · · · · · · · · · · · · · · · · ·	7 5 -3 467 486	8 6 C 734 276 8 6 I 379 367 8 6 2 184 189	• # 1 •7 •1 • 8 • 1•8 152 • • -8 121 156	11 2 -1 148 166 11 2 C 403 367 11 2 1 269 266	11 5 -6 136 17
1 1 7 116 126	1 14 0 100 123	2 12 -5 247 248	5 9 -8 552 518 5 9 -7 202 202	• • 0 180 71• • • 1 ••0 ••7	5 5 -5 +87 +66 5 5 -4 313 309	6 5 -6 339 306 5 -6 250 231	7 5 0 806 806 7 5 1 362 320 7 5 3 218 227	8 8 3 313 310 8 8 4 156 183 8 7 -7 380 402	9 9 -7 311 308 9 9 -6 136 162 9 9 -6 227 232	11 2 2 125 104 11 3 -8 297 317 11 3 -7 189 189	
1 2 -7 261 262	1 17 -4 124 131	2 12 -2 328 510	3	104 116	5 5 -2 635 676	6 5 -4 468 465 6 5 -3 140 124	7 5 6 317 330 7 5 5 238 252 7 6 -9 95 107	7 -5 161 171 8 7 -4 196 212 8 7 -3 516 534	• • -3 195 +000 • • 1 /67 777 • • 3 • • 72	11 3 -6 302 319 11 3 -5 222 226 11 3 -4 300 313	13 5 0 325 30 13 6 -3 298 30 13 6 0 213 70
1 2 -5 240 246 1 2 -4 761 730 1 2 -312451130	1 17 -1 104 157 1 17 0 95 74 1 17 1 106 106	2 12 0 174 183	3 9 -2 45 102 3 9 -1 251 236	• • 126 153 • • 7 125 140	5 5 1 612 617	6 3 -1 641 669 6 3 0 496 503	7 6 -8 410 408	a 7 -1 186 262 a 7 0 340 343 a 7 1 515 519	9 10 -7 145 157 9 10 -8 177 185 9 10 -5 114 138	11 3 -3 259 256	13 6 1 101 17 13 7 -5 136 16 13 7 -6 127 16
1 2 -2 246 230 1 2 -1 376 371 1 2 0 315 335	1 18 -1 137 135 1 18 2 117 127 1 19 -2 141 86	2 12 5 127 153 2 12 4 133 142 2 12 5 118 139	3 0 0 687 720 3 0 1 207 318 3 0 2 357 357	· / -0 337 312	5 5 5 611 621	• • • • • • • • • • • • • • • • • • •	7 6 -5 265 266 7 6 -6 386 415	8 7 3 151 139 8 7 8 239 249	9 16 -4 217 208	11 1 0 240 271	13 7 -3 110 14
1 2 112041366	2 0 -9 360 369 2 0 -7 407 399 2 0 -5 684 676	2 12 6 149 176 2 13 -6 192 189 2 13 -5 188 180	3 0 3 175 170 3 0 0 505 519 3 0 5 103 140	· · · · · · · · · · · · · · · · · · ·	5 6 -9 149 160 5 6 -8 310 306	• • • • 117 140 • • • • 240 311	7 6 -2 229 225 7 6 -1 428 453	8 8 -7 160 168 8 8 -6 109 137	9 10 0 711 715 9 10 1 164 174	11 5 5 161 176	13 8 -4 169 17
1 2 3 757 765	2 0 810 720 2 0 110811030 2 0 2 78 12	2 13 -3 172 147 2 13 -2 334 322 2 13 -1 139 149	3 10 -8 186 185 3 10 -7 197 191 3 10 -8 147 145	 7 -1 231 239 7 0 575 620 7 1 357 383 	5 6 -5 249 236 5 6 -4 132 128 5 6 -3 409 407	• • -• •31 •12 • • -5 35• 355	7 . 1 177 185	8 8 -4 784 796 8 8 -3 261 251	• 10 3 118 129 • 11 -7 109 13•	11 4 -5 422 438	14 0 -4 224 23
1 2 8 433 440	2 0 -1 707 652	2 13 0 148 140	1 10 -5 447 407 3 10 -4 404 380 3 10 -3 285 246	• 7 2 198 197 • 7 3 180 154 • 7 • 520 53•	5 6 -2 135 157 5 6 -1 384 405 5 6 0 279 276	• • -1 ••3 ••7 • • 0 •3 72	7 7 -8 154 150	-1 235 25- 8 0 39- 580	• 11 -5 323 31+ • 11 -7 207 217	11 . 2 311 241	14 1 -2 143 20
1 3 -6 290 301 1 3 -5 368 376	2 0 2 92 98	2 13 5 114 151	1 10 -2 236 225 3 10 -1 444 458	- 7 5 157 160 - 8 -8 131 138 - 8 -5 147 120	5 6 1 290 281 5 6 2 149 163 5 8 3 92 106	• • 1 21• 210 • • 2 557 559 • • 3 •21 •27	7 7 -9 202 512	2 133 191	9 11 0 9 97 9 11 1 115 129	11 5 -7 184 142	1. 7 - 7 73. 75
1 -3 921 866 1 3 -2 588 585	2 1 -9 242 249	2 14 -2 388 351	3 10 1 329 333 3 10 2 107 103	* # -* 517 503 * # -3 506 506	5 6 6 322 333 5 8 5 270 288 5 7 -6 614 578	6 6 6 186 186 6 7 -8 432 405 6 7 -7 244 235	7 7 -2 236 245 7 7 -1 805 856 7 7 C 196 213	8 V -6 152 140 8 9 -5 252 259	• 11 5 225 231 • 12 -5 233 219	11 5 5 176 186 11 5 -2 245 259	14 1 -6 199 23
1 5 0 575 600	2 1 -5 189 304 2 1 -4 298 265	2 14 1 210 210	1 10 4 163 158 1 10 5 247 247	* 8 -1 116 13* * 8 0 597 631	5 7 -5 241 220 5 7 -210981150 5 7 -1 292 297	• 7 -5 267 257 • 7 -4 521 532 • 7 -3 350 358	7 8 -8 107 97 7 8 -7 120 133	• • • 311 310 • • -3 187 194 • • -2 201 200	• 12 -1 116 124 • 12 -1 116 124		
3 3 712 720 3 3 712 720 1 3 3 717 370	2 1 -2 350 525	2 14 5 108 107	3 11 -6 300 331 3 11 -5 130 132	· · · · · · · · · · · · · · · · · · ·	5 7 0 170 104	6 7 -2 291 300 6 7 -1 338 549 6 7 0 400 404	7 8 -6 400 380 7 8 -5 164 161 7 8 -6 249 253	8 9 -1 245 286 8 9 0 139 134 8 9 2 46 133	9 15 -2 114 102 9 15 0 98 102 9 14 -4 98 95	11 6 -6 159 158 11 6 -5 259 278	14 4 -4 182 17
1 3 5 939 983 1 3 6 111 153 1 3 7 329 353	2 1 0 620 627 2 1 1 712 693 2 1 2 525 516	2 15 -4 153 110 2 15 -3 195 186 2 15 0 95 87	5 11 -1 162 161 5 11 -2 770 776 5 11 -1 222 221	• • • 100 170 • • • 100 112	5 7 5 108 129		7 8 -3 102 87	• • 3 144 140 • • 102 7• • 10 -7 120 130	v 14 -1 v6 107 9 15 -2 92 117 9 15 -1 230 227	11 a -4 350 381 11 a -2 181 145 11 a 0 186 154	14 5 -6 135 18
1 4 -7 193 155 1 4 -6 478 460 1 4 -9 308 579	2 1 3 303 242 2 1 4 413 426 2 1 5 416 444	2 15 4 201 225 2 16 -2 349 307 2 16 0 187 181	5 11 0 160 160 5 11 1 168 151 5 11 2 500 518	• • -6 +12 30+ • • -5 376 355	5 6 -7 296 273		7 8 0 3+3 3+0	8 10 -6 184 195 8 10 -5 158 146 8 10 -6 246 255	10 0 -8 469 490 10 0 -4 872 879 10 0 -1 159 147	11 6 1 226 222 11 6 2 185 163 11 6 1 109 126	14 5 -2 120 14 14 6 -3 110 13
1 4 -4 241 255 1 4 -3 408 376 1 4 -2 744 473	2 1 6 220 253 2 1 8 259 269 2 2 -7 333 351	2 16 1 96 96 2 167 2 16 3 113 109	3 11 3 150 174 3 11 4 157 143 3 11 5 148 177	• • -3 76• 266 • • -2 •20 ••1 • • -1 353 361	5 8 -5 505 446 5 8 -3 351 351 5 8 -2 100 112	• • - • 200 176 • • - • 136 141	7 8 9 175 195	8 10 -2 5ee 3e3 8 10 0 185 171 8 10 1 118 135	10 0 0 610 597	11 7 -6 350 344	14 6 -1 102 11 14 7 -4 146 20 14 7 -3 150 15
1 + -110531758	2 2 -4 777 744	2 17 0 45 45 2 17 2 101 44 2 17 3 44 40	5 11 6 251 267 5 12 -5 177 158 5 12 -4 198 185	• • 1 5++ 55+ • • 2 425 4+1 • • 3 230 241	5 6 0 117 124 5 6 1 433 434	• • • • • • • • • • • • • • • • • • •	7 • -• 212 247	8 10 2 587 391 8 10 4 196 174	10 1 -0 145 140	11 7 -2 176 103	1
1 4 2 909 918 1 4 3 498 522 1 4 4 128 117	2 2 -21-301391 2 2 -11002 977 2 2 0 163 180	2 18 -4 141 103 2 18 -2 133 113 2 18 0 167 144	3 12 -3 113 88 3 12 -1 252 242 3 12 0 145 149	• • • 217 228 • 10 -7 269 269 • 10 -6 187 149	3 332 35	• • 0 385 400 • 1 120 122	7 9 -3 231 250 7 9 -2 180 193	11 -+ 200 199 11 -2 97 114	10 1 -3 203 209	11 7 2 246 252	0 0 0 0 0 0 0 0 0 0 0 0
1 4 5 331 325	2 2 1 338 353 2 2 216011605 2 2 3 590 589	2 18 3 121 139 2 19 -3 111 110 3 0 -9 +13 +08	3 12 1 109 514 3 12 2 219 225 3 12 3 207 189	• 10 -5 301 351 • 10 -5 393 377 • 10 -2 404 424	5 0 -0 172 183 5 0 -7 340 325		7 0 0 466 471 7 0 1 203 300	11 2 124 217 11 2 132 127 12 -7 107 14	10 1 -1 344 344 10 1 0 338 323 10 1 1 373 355	11 0 -4 164 163 11 0 -3 163 158 11 0 -7 336 359	0 0 0 0 0 0 0 0
1 5 -0 223 215	2 2 5 172 151	3 0 -6 173 175	▶ 12	- 10 -1 129 136	/, 368 385						

configurations of the molecules were known. The imaginary part of the anomalous dispersion correction was applied to test the sensitivity of the data. The comparison of the R values for calculations in which the value of $\Delta f''$ was taken as 1.46 and -1.46 is given in Table 2.

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According to Hamilton's (1965) R factor ratio test, the differences in the R values are significant with the lower values in both cases indicating the absolute configuration to be the naturally occurring one.

For both structures the last four cycles of least-

squares refinement were based upon all data, the imaginary part of the anomalous dispersion correction was included in the calculation and the weighting scheme was the following: $w^{-1} = \{1 + [(|F_o| - 43)/25]^2\}^{1/2}$. The weighting constants were evaluated to make $\langle w \Delta^2 \rangle$ invariant with changing $|F_o|$. The unobserved data were only allowed to influence the refinement if $|F_o - F_c|/F_o$ was less than 0.7. The positional parameters of the hydrogen atoms were refined with the thermal parameters held at 3.0. The refinement was terminated when all nonhydrogen parameter shifts were less than one half standard deviations. The molecular geometry indicated that the hydrogen atom positions were improved by the refinement but in some cases they were still oscillating at standard deviations when refinement was terminated, with the minimization function, $\sum w(|F_o| - |F_c|)^2/m - n$, at 2.35 and 2.39 for structures A and B respectively. The final R values were 6.3% and 6.4% for all data except unobserved reflections with $|F_{o} - F_{c}|/F_{o} < 0.7$ and 4.8 % and 5.0% for observed data only. Data were considered observed if their intensities were greater than twice their estimated standard deviation.

The final fractional coordinates and anisotropic thermal parameters for the three molecules are given in Table 3(a) while the hydrogen parameters are listed in 3(b). The observed and calculated structure factor amplitudes for all observed data are listed in Table 4.

Results

Steroid geometry

The bond lengths, valency angles and torsional angles for the three molecules are listed in Table 5. The average standard deviations for interatomic distances and angles are 0.015 Å and 1.2° respectively. Although the observed bond lengths and angles may be as much as three standard deviations from theoretical values they are all within one standard deviation of values in similar steroid determinations (Cooper, Norton & Hauptman, 1969). The primary causes of bonding distortions observed in steroid structures are strains imposed by ring junctions, crowding due to the angular methyl groups and conformational transmission effects associated with bond unsaturation or side chain substitutions. The averages of corresponding bond lengths in the three molecules are presented in 5(a). All bond lengths are within two standard deviations of the averages and no significant differences are observed.

Similarly all of the valency angles are within two standard deviations of the average of the corresponding values in the three molecules [Table 5(b), column 4] and no significance can be attached to individual differences. However, inspection of the torsional angles [Table 5(c)] indicates significant differences in the B rings of the three molecules. The magnitudes of the differences in corresponding torsional angles, Δ tor [Table 5(c)], are less than 4.0° for the torsional angles of the A-, C- and D rings. In contrast to this, the magnitude of the differences in corresponding torsional angles in the *B* ring exceeds 4° in all cases. The *B* ring conformation of no one of the three molecules is responsible for these large deviations. Each molecule has some singularity in the *B* ring torsional angles.

Table	5(a)	. Intera	itomic	distanc	es c	observed	in	three	mol-
ecules	of	2,4- <i>dib</i> i	romoes	stradiol	in	crystall	ine	mod	ifica-
			tio	ns A an	d E	3			-

C(1)—C(2)	Molecule A 1·407 Å	Molecule <i>B</i> 1 1·380 Å	Molecule <i>B</i> 2 1·387 Å	Average 1·391 Å
C(2) = C(3)	1·3/5	1·388	1·418	1·393
C(3) = C(4)	1·393	1·384	1·392	1·389
C(4) = C(5)	1·390	1·386	1·378	1·384
C(5) - C(10)	1·401	1·427	1·444	1·424
C(10) - C(1)	1·357	1·392	1·359	1·369
C(2) - Br(2)	1·871	1·900	1·877	1·882
C(4)—Br(4) C(3)—O(3) C(5)—C(6)	1·898 1·344 1·509	1·893 1·370 1·492	1.882 1.337	1·891 1·350 1·495
C(6) - C(7) C(7) - C(8) C(7) - C(8)	1·523 1·521	1·501 1·535	1·524 1·511	1.516
C(8) = C(9) C(9) = C(11) C(11) = C(12)	1·549 1·567 1·551	1·549 1·530	1.530 1.535 1.554	1.529 1.550 1.545
C(12)-C(13)	1·487	1.522	1·525	1·511
C(13)-C(14)	1·521	1.538	1·544	1·534
C(14)-C(8)	1·526	1.512	1·521	1·519
C(14)-C(15)	1.548	1·543	1·538	1·543
C(15)-C(16)	1.560	1·554	1·551	1·555
C(16)-C(17)	1.505	1·542	1·540	1·529
C(17)-C(13)	1.562	1·515	1·544	1·540
C(17)-O(17)	1.438	1·475	1·441	1·451
C(13)-C(18)	1.545	1·511	1·515	1·523

The bromine-carbon distances (average = 1.882 Å) are in good agreement with those found in tetrabromobenzene (Gafner & Herbstein, 1960) and are shorter than the C-Br distances of 1.92 Å and 1.93 Å observed in the 4-monobrominated estranes (Norton, Kartha & Lu, 1963, 1964).

The observed carbon-hydrogen distances range from 0.76 to 1.30 Å (two values exceed 1.18 Å) and



Fig.1. Schematic representation of the steroid molecule showing the numbering of atoms and rings designations.

Table 5	5(b).	Valency	angles	observed	in ti	hree	molecul	es o	f 2,	,4-dibromoestrac	tiol
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	Molecule A	Molecule B1	Molecule B2	Average
C(10)-C(1)-C(2)	121·1°	119·8°	121·1°	120·7°
C(1) - C(2) - C(3)	120.9	122.5	121.0	121.5
C(2) - C(3) - C(4)	116.6	116.6	116.5	116.6
C(3) - C(4) - C(5)	123.8	124.2	124.0	124.0
C(4) - C(5) - C(10)	117.5	117.2	117.4	117.4
C(5) = C(10) = C(1)	120.0	119.7	119.9	119.9
C(1) - C(2) - Br(2)	119.6	119.4	120.4	119.8
C(3) - C(2) - Br(2)	119.3	118.1	118.5	118.6
C(2) - C(3) - O(3)	125.3	124.7	124.4	124.8
C(4) - C(3) - O(3)	118.0	118.7	119.0	118.6
C(3) - C(4) - Br(4)	117.1	116.4	116.3	116.6
C(5) - C(4) - Br(4)	119.4	119.3	119.5	119.4
C(4) - C(5) - C(6)	120.2	121.1	122.0	121.1
C(6) - C(5) - C(10)	122.4	121.7	120.6	121.6
C(9) - C(10) - C(5)	119.1	119.1	119.6	119.3
C(1) - C(10) - C(9)	120.0	121.2	120.2	120.5
C(5) - C(6) - C(7)	115.1	115.4	116.1	115.5
C(6) - C(7) - C(8)	109.8	112.9	111.5	111.4
C(7) - C(8) - C(9)	107.0	107.3	109.2	107.8
C(8) - C(9) - C(10)	110.6	110.7	112.0	111.1
C(7) - C(8) - C(14)	112.5	111.4	112.7	112.2
C(10)-C(9)-C(11)	112.8	112.4	112.8	112.7
C(12) - C(11) - C(9)	113.0	111.2	111.7	112.0
C(11) - C(9) - C(8)	111.6	114.4	113.0	113.0
C(9) - C(8) - C(14)	108.2	109.0	107.8	108.3
C(8) - C(14) - C(13)	113.3	112.1	112.5	112.6
C(14)-C(13)-C(12)	111.3	108.2	108.4	109.3
C(13) - C(12) - C(11)	109.9	110.4	110.2	110.2
C(12) - C(13) - C(17)	117.1	115.2	114.0	115.4
C(8) - C(14) - C(15)	117.0	118.8	119.8	118.5
C(13)-C(14)-C(15)	106-1	102.6	104.3	104.3
C(14) - C(15) - C(16)	101.7	104.5	103.4	103.2
C(15) - C(16) - C(17)	107.1	103.8	106.0	105.6
C(16) - C(17) - C(13)	105.5	105.5	104.4	105-1
C(17) - C(13) - C(14)	97.8	98.7	98.3	98.3
C(12)-C(13)-C(18)	110.4	110.9	111.9	111.1
C(14)-C(13)-C(18)	112.3	114.2	113.8	113.4
C(17)-C(13)-C(18)	107-4	109.3	109.7	108.8
C(13)-C(17)-O(17)	115-0	114.3	115.4	114.9
C(16) - C(17) - O(17)	109.9	111.0	109.3	110.1

Table 5(c). Torsional angles observed in three molecules of 2,4-dibromoestradiol Torsional angles

		l'orsional a	ngles		
		A	<i>B</i> 1	B2	⊿tor
	C(1) - C(2)	-1·3°	-1·3°	-3.9°	2.6°
	C(2) - C(3)	2.9	2.6	3.7	1.1
A	C(3) - C(4)	-4.5	-4.0	-2.8	1.7
	C(4)C(5)	4.2	3.8	1.8	2.4
	C(5) - C(10)	-2.3	-2.1	-1.8	0.2
	C(10) - C(1)	0.9	1.0	2.8	1.9
	C(5)—C(6)	-5.2	-3.0	-14.7	11.7
	C(6) - C(7)	39.5	33.7	42.9	9.2
B	C(7) - C(8)	- 66.6	62.5	-62.5	4.1
	C(8) - C(9)	59.7	59.5	53.7	6.0
	C(9) - C(10)	- 26.5	-31.2	-26.7	4.7
	C(5) - C(10)	-1.2	1.8	6.9	8∙1
	C(8)—C(9)	- 52.5	-51.4	- 54.8	3.4
_	C(9) - C(11)	52.1	50∙6	53.6	3.0
С	C(11)-C(12)	- 52.9	- 53.9	- 54.3	1.4
	C(12)-C(13)	56.0	59.6	57.3	3.6
	C(13) - C(14)	-61.2	-62.8	-62.3	1.6
	C(14) - C(8)	57.7	57.8	59.6	1.9
	C(13)–C(14)	46.0	48.5	47.6	2.5
	C(14) - C(15)	-33.4	- 34.2	-33.6	0.8
D	C(15) - C(16)	6.1	6.3	5.7	0.6
	C(16) - C(17)	22.2	24.5	24.0	2.3
	C(17)–C(13)	-41.3	-45.1	-43.3	3.8

the average distances are 0.97, 0.97, and 1.00 Å for molecules A, B1, and B2 respectively. The valency angles of the type C-C-H range in magnitude from 84 to 128° and the average magnitudes are 110, 108 and 109° for molecules A, B1 and B2. Of the 16 hydrogen atoms that have the most distorted geometry (valency angles outside the range 99 \rightarrow 121°) 10 have intermolecular van der Waals contacts of less than 2.7 Å (Table 6). The conformations of the hydrogen atoms of the three molecules can be compared in Fig. 2. The major conformational differences in hydrogen positions are associated with hydrogens on carbon atoms C(12) of molecule B1 and C(6) of molecule B2. Inspection of intermolecular contacts of less than 2.8 Å (Table 6) shows these hydrogens to be involved in several hydrogen-hydrogen contacts of less than 2.7 Å in length. The conformation of the hydrogen atoms on C(6) and



Fig. 2. (a) The B- and C-rings of the three molecules of 2,4-dibromoestradiol projected parallel to a line joining the mid points of the vectors C(9)-C(6) and C(10)-C(5). The B-rings of A and B2 are in half-chair conformations and the B-ring of B1 is in a sofa conformation. (b) Perspective views of the three molecules showing 50% probability thermal vibrational ellipsoids. (c) Projections of the three molecules perpendicular to the least squares planes through atoms C(5) to C(17). Observed hydrogen positions are included for purposes of comparison.



(e)

Fig. 3. Conformation of the hydrogen atoms on C(6) and C(7) in the estriol molecules 1(a) and 2(b) and in the 2,4-dibromoestradiol molecules B1(c), B2(d) and A(e). Hydrogen atoms H(6 β) and H(7 β) are most nearly eclipsed in the sofa conformation *B*-rings of (*c*).

C(7) is shown in the Newman projections of Fig. 3. Similar projections of the two estriol molecules are included for purposes of comparison. In molecules Aand B2 and in the estriol molecules the hydrogens are in staggered conformations. Only in molecule B1 do they come close to an eclipsed conformation. This is one of the unfavorable conditions that may occur when the B ring is in the sofa conformation.

The relative thermal motion of the three molecules is shown in Fig. 2(b). The greatest motion is perpendicular to the general plane of the steroid. The larger anisotrpoic motion of the hydroxyl groups, the angular methyl group and the bromine atoms is to be expected The only significant difference among the three molecules is the high degree of thermal motion in the *D* ring of molecule *B*1.

Molecular packing and hydrogen bonding

Inspection of the packing diagrams [Fig. 4(a) and (b)] reveals that in all cases infinite chains of 2,4dibromoestradiol molecules are formed by hydrogen bonding between translationally equivalent molecules. In the monoclinic crystal molecules B1 forms chains composed entirely of B1 type molecules.

The only intermolecular contact between chains which is closer than the sum of the van der Waals radii of the atoms involved is the Br(2)-Br(4) contact of 3.62 Å observed in the lattice of structure A. This value

Table 6. Intermolecular distances less than 2.8 Å in two crystalline forms of 2,4-dibromoestradiol

Molecule A		Molecule B1		Molecule B2	
C(5)H(17)	2·74 Å	$H(6\alpha) - H(12\beta)$	2·52 Å	$H(1) - H'(15\beta)$	2·71 Å
C(15)H(18C)	2.78	$H(7\alpha) - H(12\beta)$	2.64	$H(6\beta) - H'(16\alpha)$	2.63
O(17) - H(03)	2.26	$H(7\alpha)$ — $H'(18A)$	2.72	$H(6\beta) - H'(17)$	2.73
$Br(4) H(11\beta)$	2.69	$H(7\beta) - H(12\beta)$	2.65	$H(7\beta) - H(12\beta)$	2 ·48
H(1) - H(18A)	2.73	$H(8) - H'(16\alpha)$	2.28	$H(11\alpha)-H'(15\beta)$	2.73
$H(6\alpha) - H(17)$	2.76	$H(12\alpha) - H'(18C)$	2.73	$H(15\beta) - H'(14)$	2.21
$H(7\alpha) - H(017)$	2.74	$H(14) - H'(15\beta)$	2.21	$H(16\alpha)-H'(8)$	2.28
$H(8) - H(11\alpha)$	2.59	$H(15\beta)-H'(1)$	2.71	$H(18A)-H'(7\alpha)$	2.72
$H(9) - H(16\alpha)$	2.49	$H(15\beta) - H'(11\alpha)$	2.73	$H(18C)-H'(12\alpha)$	2.73
$H(11\alpha) - H(15\beta)$	2.70	$H(16\alpha) - H'(6\beta)$	2.63		
$H(15\alpha) - H(18A)$	2.62	$H(17) - H'(6\beta)$	2.73		
$H(15\alpha) - H(18C)$	2.36				
$H(16\alpha) - H(18A)$	2.71				
$H(16\alpha) - H(18C)$	2.68				
$H(16\beta) - H(18C)$	2.75				

	Table 7. Summar	y of	the	geometr	v of	the i	hydrogen	bonding	between i	the mo	lecule	25
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		Molecule A	Molecule B1	Molecule B2
Torsional angle	H(03) - O(3) - C(3) - C(2)	26°	16°	2 4 °
Valency angles	H(03) - O(3) - C(3)	108	123	130
<i>v</i> 0	H(017) - O(17) - C(17)	105	111	99
Interatomic distance	$H(03)\cdots Br(2)$	2·73 Å	2·77 Å	2·91 Å
	H(03) - O(3)	0.67	0.86	0.76
	H(017) - O(17)	1.25	0.76	0.70
	$H(03) \cdots O(17)$	2.25	1.89	2·0 4
	$H(017) \cdots O(3)$		1.95	
Hydrogen bond distance	$O(3) \cdots O(17)$	2∙840 Å	2·671 Å	2∙768 Å
Hydrogen bond angle	$O(3) - H(03) \cdots O(17)$	146°	150°	160°
	$O(17) H(017) \cdots O(3)$		160	

CONFORMATIONAL CHANGES IN 2,4-DIBROMOESTRADIOL



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Fig. 4. (a) Projections of four unit cells of the orthorhombic structure (A) onto the (001) and the (010) planes, illustrating the infinite chain formation via hydrogen bonding and the nature of the bromine-bromine contacts between chains. (b) Projections of four unit cells of the monoclinic structure (B) onto the (100) and the (001) planes, illustrating the alternate layers of chain types B1 and B2.

is significantly shorter than the expected van der Waals contact of 3.90 Å using Pauling's (1960) radius of 1.95 Å for bromine. However, it is only slightly shorter than the van der Waals sum of 3.70 Å using Bondi's (1964) corrected radius of 1.85 Å for bromine.

Short Br-Br contacts have also been observed in other structures. Distances range from 3.30 Å in crystalline bromine (Vonnegut & Warren, 1936) and 3.58Å in di-*p*-tolyselenium dibromide (McCullough & Marsh, 1950) to 3.63 Å in PaBr₅ (Brown, Petcher & Smith, 1969) and PBr₅ (Gabes & Olie, 1970). There are no intermolecular Br-Br contacts less than 4.0 Å in the lattice of structure *B*.

A summary of the geometry of the hydrogen bonding between the molecules is presented in Table 7. The hydrogen of O(3) is involved in the hydrogen bonding in all cases. The hydrogen of O(17) may be involved in the hydrogen bonding in molecule B1 only. The fact that the shortest hydrogen bond occurs in the B1 chain is consistent with the possible additional hydrogen bonding due to H(017). However the two hydrogens H(03) and H(017) of molecule B1 have an unfavorable close interatomic distance of 1.15 Å. The H(017) atoms of molecules A and B2 are oriented away from the hydrogen bond, in a *trans* configuration with respect to the C(16)-C(17) bond. The conformation of the hydrogen bonding region is shown in the Newman projections O(17)-C(17) of Fig. 5.

A comparison of the overall geometry and packing of the molecules of 2,4-dibromoestradiol with other estradiols shows a common preference for the formation of infinite chains of molecules connected by O(3)-O(17) hydrogen bonds. In the case of estradiol (Busetta & Hospital, 1969) there are additional hydrogen bonds to water molecules which connect adjacent steroid strands. In 4-bromoestradiol (Norton, Kartha & Lu, 1964) there is no interaction between strands even though there is additional hydrogen bonding with a methanol molecule. Although the structure of estradiol 3-p-bromobenzoate (Tsukuda, Sato, Shiro & Kayama, 1968) does not allow O(3)-O(17) interactions, there is hydrogen bonding between O(17) and the



B1

Α

benzoate carbonyl, but this is across the strands rather than along them.

Steroid molecular conformation

The major conformational differences in the three molecules of 2,4-dibromoestradiol concern the steroid's B ring. The B rings of molecules B2 and A are in a half-chair and a distorted half-chair conformation. while the *B* ring of molecule *B*1 is in a sofa conformation. The difference in these conformations is best illustrated in Fig. 2(a). The observed coplanarity of atoms C(5), C(6), C(7), C(9) and C(10) is the distinguishing feature of the sofa conformation which molecule B1 has in common with one of the two molecules in the asymmetric unit of estriol (Cooper, Norton & Hauptman, 1969), with 4-bromoestrone (Norton, Kartha & Lu, 1963), and with another estradiol derivative 3-methoxy-8 β -methyl-1,3,5(10)-estra rie 1-17 β -yl bromoacetate (Tsukuda, Soto, Shiro & Kavama, 1968). The differences in the overall conformations of the three molecules of 2,4-dibromoestradiol are shown relative to the nearly identical C and D rings in Fig. 2(b) and the molecules are projected perpendicular to the leastsquares plane through atoms C(5)-C(17) in Fig. 2(c). The three diagrams show that the sofa conformation of the B ring results in a twisting of the A ring relative to the rest of the steroid, which is out of the general plane of the rest of the molecule.

Table 8. Deviations of individual atoms from the leastsquares plane through atoms C(1), C(2), C(3), C(4), C(5), and C(10) of the A ring of the three molecules of 2.4-dibromoestradiol

Positive deviation is on the β -side of the steroid.

	A	<i>B</i> 1	<i>B</i> 2
C(1)	0∙002 Å	0∙000 Å	−0·011 Å
C(2)	0.005	0.004	0.013
C(3)	- 0 · 0 16	-0.011	-0.010
C(4)	0.021	0.014	0.005
C(5)	-0.013	-0.009	-0.002
C(10)	0.002	0.002	0.005
I (1)	0.002	0.082	0.164
Br(2)	-0.038	0.011	0.012
D(3)	-0.013	0.001	0.004
Br(4)	0.061	-0.045	-0.102
C(6)	-0.068	-0.004	0.029
C(9)	-0.011	-0.015	-0.084
I(03)	-0.278	-0.141	-0.164
C(7)	-0.231	-0.043	-0.209
C(8)	0.608	0.546	0.339

The magnitudes of the A ring torsional angles [Table 5(c)] and the deviations of individual atoms from the least-squares plane through the A ring (Table 8) indicate that the carbon atoms of the A rings of all these molecules are equally planar with some puckering of the ring indicated by the alternating sign of the torsional angles. All atoms directly bonded to the A ring are also nearly coplanar with the carbons of the

(

C(18)

B2

ring. While 5 atoms of the A and B rings of molecule A and 6 atoms of A and B rings of molecule B2 deviate by more than 0.05 Å from the plane, only atoms H(1), H(03) and C(8) of molecule B2 are more than 0.05 Å from the plane. The most significant difference in the deviations from the plane of the A ring is in the position of C(7) which is observed to be nearly in the plane in molecule B2. This is a characteristic of the sofa conformation of the B ring.

The C rings of all three molecules are in normals chair conformations with some flattening of the rings due to strain at ring junctions. This flattening of the C ring is reflected in the decrease in the magnitudes of the torsional angles [Table 5(c)]. The most pronounced flattening is observed in molecule A.

The D rings of all three molecules are in β envelope conformations as reflected by the magnitudes of the parameters φ_{max} and Δ (Altona, Geise & Romers, 1968).

Molecule	φ_{\max}	Δ
A	46∙64°	19·25°
<i>B</i> 1	49.36	22.11
<i>B</i> 2	48.42	21.63
Ideal β -envelope	46.7	36.0-

Discussion

Differences observed in the molecular geometry and conformation of the three molecules of 2,4-dibromoestradiol are caused by a combination of intramolecular bonding forces and intermolecular interactions. The occurrence of the B ring in the sofa and half-chair conformations in numerous estranes having a phenolic A ring, particularly the occurrence of the 1:1 ratio of sofa to half-chair conformation in crystals of estriol and 2,4-dibromoestradiol suggests that the potential energy of the two conformations is nearly equivalent. The distinct difference between B rings which are in the half-chair and the sofa conformations, a difference involving variations in angle strains and eclipsing strains is most strongly reflected in the torsional angle differences. The absence of strong parallels between the intermolecular hydrogen contacts (Table 6) of the two molecules having the B ring in the half-chair conformation suggests that these packing forces alone are not responsible for the adoption of a particular conformation by the B ring. The intermolecular forces in the crystal, hydrogen bonding and van der Waals packing forces probably stabilize one or the other of the B ring conformations and may also distort the conformation to some extent as is the case in the differences between molecules A and B2.

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