

The Structures of Five Bicyclic Lactams: 2-Benzyl-3-oxo-2-azabicyclo[2.2.1]hept-6-*exo*-yl *p*-Toluenesulfonate, 2-Benzyl-6-*exo*-phenoxy-2-azabicyclo[2.2.1]heptan-3-one, 2-Benzyl-6-*exo*-(2-iodo-4-methylphenoxy)-2-azabicyclo[2.2.1]heptan-3-one, 2-Benzyl-6-*exo*-(2,6-diiodo-4-methylphenoxy)-2-azabicyclo[2.2.1]heptan-3-one and 2-Benzyl-6-*exo*-phenoxy-2-azabicyclo[2.2.2]octan-3-one

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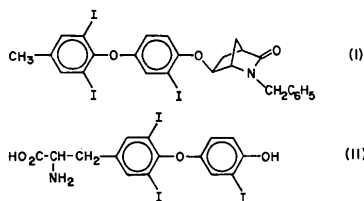
(Received 23 February 1981; accepted 27 July 1981)

Abstract

The crystal structures of the title lactams have been determined with three-dimensional, Mo $K\alpha$ diffractometer data. The structures were solved with direct methods and refined with full-matrix least-squares techniques. The total number of unique data, number of $I > 3\sigma(I)$ and final R factor, in the order of the compounds listed in the title, are: 3264, 1992, 0.037; 2158, 1444, 0.038; 1720, 1068, 0.035; 3490, 2627, 0.040; 1521, 1222, 0.031. The bicyclo[2.2.1]heptane portions are identical within experimental error. Bond lengths in the regions of the amide linkage suggest that there is more dipolar character [*viz* (+)N=C–O(–)] in the [2.2.2] lactam than in the [2.2.1] compounds. The conformations of the benzyl and phenoxy substituents relative to the bicyclic frameworks fall into two distinct patterns.

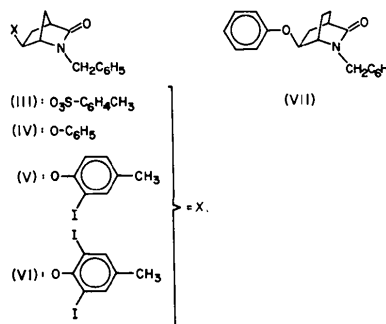
Introduction

For the past several years, we have been working with a molecular system designed to use nuclear magnetic resonance–lanthanide shift reagents (NMR–LSR) to investigate the *distal/proximal* conformation ratios of various thyroid-hormone analogs in solution. Basically, the system consists of a bicyclic lactam linked to an appropriately substituted diphenyl ether. Structure (I) illustrates one of the compounds that should mirror the conformational properties of the diphenyl ether portion of triiodothyronine (T_3 , II), the assumption being that these properties in T_3 will be unaltered by changing C–OH to C–O–C and alanyl to methyl.



0567-7408/82/020540-08\$01.00

The NMR–LSR technique consists of two parts: (1) determination of the effective location in solution of the LSR in relation to the rigid, bicyclic lactam framework [LSR complexation occurs at the amide oxygen; the position is deduced from the framework coordinates and the appropriate NMR–lanthanide induced shift (LIS) data]; (2) determination of the conformational properties of the flexible diphenyl ether fragment from the established LSR position and the fragment LIS's. The first step in the process, namely the location of the LSR, requires a knowledge of the coordinates of the bicyclic framework atoms. To this end, we have determined the crystal structures of five substituted bicyclic lactams, 2-benzyl-3-oxo-2-azabicyclo[2.2.1]hept-6-*exo*-yl *p*-toluenesulfonate (III), 2-benzyl-6-*exo*-phenoxy-2-azabicyclo[2.2.1]heptan-3-one (IV), 2-benzyl-6-*exo*-(2-iodo-4-methylphenoxy)-2-azabicyclo[2.2.1]heptan-3-one (V), 2-benzyl-6-*exo*-(2,6-diiodo-4-methylphenoxy)-2-azabicyclo[2.2.1]heptan-3-one (VI) and 2-benzyl-6-*exo*-phenoxy-2-azabicyclo[2.2.2]octan-3-one (VII), and these data are reported here.



Compounds (IV)–(VI) were prepared from the reactions of the appropriate sodium phenoxides and *p*-toluenesulfonate (III) (Liu, 1979), and (VII) was synthesized from the reaction of sodium phenoxide and 2-benzyl-3-oxo-2-azabicyclo[2.2.2]oct-6-*exo*-yl *p*-toluenesulfonate (Colicelli, 1977).

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Experimental

The specific techniques used for the measurement of X-ray diffraction data have been previously detailed (Ammon, 1973). The final cell parameter and intensity measurements were made with a Picker FACS-I automatic diffractometer, equipped with a Mo X-ray

source, and graphite-crystal monochromator (Mo $K\alpha$, $\lambda = 0.71069 \text{ \AA}$, monochromator $2\theta = 12.16^\circ$). The cell constants were refined by the method of least squares from the Bragg angles obtained from manual measurements of $\pm 2\theta$ for each of 9–12 reflections. The θ - 2θ scan method at 2° min^{-1} in 2θ was used for data collection, and 10 s background measurements were

Table 1. *Crystal, intensity and refinement data for the five lactams*

	(III) $C_{20}H_{21}NO_4S$	(IV) $C_{19}H_{19}NO_2$	(V) $C_{20}H_{20}INO_2$	(VI) $C_{20}H_{19}I_2NO_2$	(VII) $C_{20}H_{21}NO_2$
Formula	$C_{20}H_{21}NO_4S$	$C_{19}H_{19}NO_2$	$C_{20}H_{20}INO_2$	$C_{20}H_{19}I_2NO_2$	$C_{20}H_{21}NO_2$
M_r	371.4	293.4	433.3	559.2	307.4
Crystallization solvent	methanol	ether-pentane	ether-pentane	ether-pentane	acetone-nonane
Space group	monoclinic, $P2_1/n$	orthorhombic, $P2_12_12_1$	orthorhombic, $Pbca$	monoclinic, $P2_1/n$	monoclinic, $P2_1$
Unit-cell parameters (\AA , $^\circ$)	$a = 16.014 (1)$ $b = 8.736 (1)$ $c = 13.760 (2)$ $\beta = 105.88 (1)$	$a = 6.196 (1)$ $b = 19.898 (3)$ $c = 13.212 (2)$	$a = 11.673 (2)$ $b = 16.195 (6)$ $c = 19.596 (4)$	$a = 9.610 (2)$ $b = 22.495 (6)$ $c = 9.475 (2)$ $\beta = 104.19 (2)$	$a = 8.8704 (6)$ $b = 9.510 (1)$ $c = 10.4153 (7)$ $\beta = 112.41 (1)$
Z	4	4	8	4	2
Reflection width (W , $^\circ$) ⁱ	1.7	1.6	2.1	1.35	1.8
Maximum 2θ ($^\circ$)	50	50	40	50	50
Instability factor, D^{ii}	0.00018	0.000060	0.0019	0.000022	0.000064
Total data measured	3757	2283	3366	3601	1688
Total unique data ⁱⁱⁱ	3264	2158	1720	3490	1521
Data with $I > 3\sigma(I)$	1992	1444	1068	2627	1222
Final R^{iv}	0.037	0.038	0.035	0.040	0.031
Final wtd R^v	0.045	0.041	0.039	0.027	0.039

(i) 2θ scan range = $W + 0.7 \tan \theta$; all crystal dimensions were 0.2–0.5 mm. (ii) Stout & Jensen (1968); Ammon (1973). (iii) Excluding space-group-absent reflections. (iv) $R = \sum |F_o - F_c| / \sum F_o$. (v) wtd $R = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$.

Table 2. *Fractional atomic coordinates and temperature factors (\AA^2) with e.s.d's in parentheses for (III)*

Here, and in Tables 3–6, an asterisk denotes U_{eq} , the equivalent value of the anisotropic temperature factor coefficients, calculated from the expression:

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j h_i h_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U		x	y	z	U
C(1)	0.2536 (1)	0.4155 (3)	0.5427 (2)	0.056 (8)*	O(4)	0.2803 (2)	-0.0064 (3)	0.3532 (2)	0.082 (3)*
C(3)	0.1511 (2)	0.5294 (3)	0.6086 (2)	0.061 (7)*	S	0.28301 (5)	0.04351 (9)	0.45196 (6)	0.0680 (5)*
C(4)	0.1176 (2)	0.4983 (3)	0.4959 (2)	0.065 (8)*	H(1)	0.316 (1)	0.405 (3)	0.551 (2)	0.048 (6)
C(5)	0.1072 (2)	0.3226 (3)	0.4878 (2)	0.053 (7)*	H(4)	0.066 (1)	0.558 (3)	0.464 (2)	0.050 (6)
C(6)	0.2020 (2)	0.2647 (3)	0.5199 (2)	0.056 (7)*	H(5A)	0.081 (1)	0.293 (3)	0.419 (2)	0.058 (7)
C(7)	0.2002 (2)	0.5225 (3)	0.4620 (2)	0.070 (8)*	H(5B)	0.074 (1)	0.280 (3)	0.530 (2)	0.055 (7)
C(9)	0.2866 (2)	0.4460 (3)	0.7358 (2)	0.055 (9)*	H(6)	0.219 (1)	0.193 (3)	0.579 (2)	0.047 (6)
C(B1)	0.3720 (2)	0.5307 (3)	0.7652 (2)	0.055 (8)*	H(7A)	0.193 (1)	0.482 (3)	0.394 (2)	0.052 (6)
C(B2)	0.4405 (2)	0.4700 (3)	0.8397 (2)	0.069 (8)*	H(7B)	0.223 (1)	0.630 (3)	0.471 (2)	0.053 (6)
C(B3)	0.5196 (2)	0.5448 (4)	0.8691 (2)	0.066 (8)*	H(9A)	0.251 (2)	0.476 (3)	0.781 (2)	0.077 (8)
C(B4)	0.5317 (2)	0.6788 (4)	0.8243 (2)	0.055 (9)*	H(9B)	0.298 (2)	0.335 (3)	0.744 (2)	0.068 (8)
C(B5)	0.4641 (2)	0.7421 (3)	0.7514 (2)	0.071 (9)*	H(B2)	0.431 (2)	0.369 (3)	0.871 (2)	0.089 (9)
C(B6)	0.3843 (2)	0.6686 (3)	0.7224 (2)	0.064 (9)*	H(B3)	0.564 (2)	0.493 (3)	0.924 (2)	0.09 (1)
C(P1)	0.3844 (2)	0.1253 (3)	0.5101 (2)	0.075 (4)*	H(B4)	0.585 (2)	0.725 (3)	0.841 (2)	0.077 (8)
C(P2)	0.4292 (2)	0.2018 (4)	0.4528 (2)	0.089 (6)*	H(B5)	0.473 (2)	0.837 (3)	0.724 (2)	0.076 (8)
C(P3)	0.5051 (2)	0.2762 (4)	0.4999 (3)	0.099 (6)*	H(B6)	0.336 (2)	0.713 (3)	0.671 (2)	0.091 (9)
C(P4)	0.5382 (2)	0.2758 (4)	0.6038 (2)	0.075 (5)*	H(P2)	0.408 (2)	0.205 (3)	0.382 (2)	0.080 (9)
C(P5)	0.4918 (2)	0.1971 (4)	0.6591 (2)	0.086 (5)*	H(P3)	0.536 (2)	0.330 (4)	0.464 (3)	0.12 (1)
C(P6)	0.4154 (2)	0.1219 (4)	0.6134 (2)	0.088 (4)*	H(P5)	0.512 (2)	0.195 (3)	0.730 (2)	0.084 (9)
C(M)	0.6203 (2)	0.3581 (5)	0.6551 (3)	0.084 (7)*	H(P6)	0.382 (2)	0.072 (3)	0.654 (2)	0.084 (9)
N	0.2347 (1)	0.4777 (2)	0.6333 (2)	0.052 (3)*	H(M1)	0.636 (3)	0.440 (6)	0.617 (4)	0.16 (2)
O(1)	0.1127 (1)	0.5809 (2)	0.6662 (2)	0.092 (3)*	H(M2)	0.668 (3)	0.296 (6)	0.675 (4)	0.18 (2)
O(2)	0.2194 (1)	0.1863 (2)	0.4332 (1)	0.063 (3)*	H(M3)	0.620 (3)	0.398 (6)	0.709 (4)	0.19 (2)
O(3)	0.2592 (1)	-0.0583 (2)	0.5213 (2)	0.105 (2)*					

Table 3. Fractional atomic coordinates and temperature factors (\AA^2) with e.s.d.'s in parentheses for (IV)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1)	0.5066 (5)	0.3486 (1)	-0.1858 (2)	0.044 (3)*
C(3)	0.2151 (4)	0.3242 (1)	-0.0845 (2)	0.049 (3)*
C(4)	0.1783 (4)	0.3068 (2)	-0.1951 (2)	0.044 (4)*
C(5)	0.3226 (5)	0.2448 (1)	-0.2141 (2)	0.043 (4)*
C(6)	0.5537 (4)	0.2746 (1)	-0.2077 (2)	0.044 (5)*
C(7)	0.3058 (6)	0.3625 (2)	-0.2481 (2)	0.065 (5)*
C(9)	0.5478 (5)	0.3538 (1)	0.0073 (2)	0.046 (5)*
C(B1)	0.5864 (5)	0.4305 (1)	0.0375 (2)	0.047 (6)*
C(B2)	0.7697 (6)	0.4470 (2)	0.0911 (3)	0.054 (6)*
C(B3)	0.8005 (7)	0.5115 (2)	0.1274 (3)	0.047 (7)*
C(B4)	0.6519 (7)	0.5600 (2)	0.1091 (3)	0.060 (7)*
C(B5)	0.4730 (7)	0.5455 (2)	0.0530 (3)	0.080 (8)*
C(B6)	0.4395 (6)	0.4804 (2)	0.0173 (3)	0.057 (8)*
C(P1)	0.7677 (4)	0.2113 (1)	-0.3270 (2)	0.039 (8)*
C(P2)	0.7572 (6)	0.1534 (2)	-0.2692 (2)	0.06 (1)*
C(P3)	0.8746 (7)	0.0975 (2)	-0.2992 (3)	0.08 (1)*
C(P4)	0.9979 (7)	0.0990 (2)	-0.3861 (3)	0.08 (1)*
C(P5)	1.0029 (7)	0.1562 (2)	-0.4432 (3)	0.078 (9)*
C(P6)	0.8901 (6)	0.2126 (2)	-0.4147 (2)	0.059 (9)*
N	0.4164 (3)	0.3510 (1)	-0.0833 (2)	0.042 (2)*
O(1)	0.1003 (3)	0.3138 (1)	-0.0112 (2)	0.076 (2)*
O(2)	0.6673 (3)	0.2709 (1)	-0.3025 (1)	0.063 (2)*
H(1)	0.621 (4)	0.379 (1)	-0.193 (2)	0.046 (7)
H(4)	0.027 (5)	0.301 (1)	-0.211 (2)	0.075 (9)
H(5A)	0.304 (5)	0.226 (1)	-0.282 (2)	0.08 (1)
H(5B)	0.301 (5)	0.207 (1)	-0.165 (2)	0.064 (8)
H(6)	0.640 (4)	0.254 (1)	-0.155 (2)	0.046 (7)
H(7A)	0.327 (5)	0.355 (1)	-0.320 (2)	0.070 (9)
H(7B)	0.250 (5)	0.411 (1)	-0.233 (2)	0.074 (9)
H(9A)	0.466 (4)	0.334 (1)	0.065 (2)	0.053 (7)
H(9B)	0.688 (4)	0.335 (1)	-0.006 (2)	0.056 (7)
H(B2)	0.872 (5)	0.414 (1)	0.100 (2)	0.09 (1)
H(B3)	0.936 (6)	0.521 (2)	0.164 (3)	0.11 (1)
H(B4)	0.673 (5)	0.604 (1)	0.135 (2)	0.074 (9)
H(B5)	0.353 (7)	0.578 (2)	0.040 (3)	0.13 (1)
H(B6)	0.318 (7)	0.470 (2)	-0.021 (3)	0.12 (1)
H(P2)	0.673 (5)	0.155 (1)	-0.209 (2)	0.071 (9)
H(P3)	0.865 (5)	0.058 (1)	-0.258 (2)	0.09 (1)
H(P4)	1.075 (5)	0.060 (1)	-0.408 (2)	0.09 (1)
H(P5)	1.087 (7)	0.158 (2)	-0.500 (3)	0.13 (1)
H(P6)	0.905 (5)	0.254 (1)	-0.455 (2)	0.076 (9)

made at the beginning and end of each reflection scan. Three standard reflections were monitored at intervals of 50–100 reflections to correct for intensity fluctuations.

The crystal and intensity measurement data are summarized in Table 1. The data were corrected for intensity fluctuations, Lorentz and polarization factors, but not for absorption. The three structures which crystallized in centrosymmetric space groups were solved in a routine manner with the XRAY system's (Stewart, Kruger, Ammon, Dickinson & Hall, 1972; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) subprogram PHASE; the two non-centrosymmetric structures were solved with MULTAN (Main, Woolfson, Lessinger, Germain & Declercq, 1974).

Initial positions for H atoms linked to the aromatic and to the tetrahedral C atoms were calculated with a C–H distance of 1.0 Å; the methyl-group hydrogens in (III) and (VI) were located in difference maps. The least-squares structure refinement used the full matrix of the normal equations and minimized the function

$\sum w(F_o - F_c)^2$, $w = 1/\sigma^2(F)$. The calculations were carried out with anisotropic temperature factors for C, N, O, S and I and isotropic terms for H. In the case of (V), the bicyclic- and aromatic-ring-linked H atoms were placed at calculated positions and not refined; the three methyl hydrogens were not included. Only those data for which $I_c > 3\sigma(I_o)$ were used in the least-squares calculations. In the case of (III), (IV) and (VII), the F_c 's were corrected for isotropic secondary extinction [equation (22) in Larson (1970)] assuming the crystals were 0.3 mm spheres. The scattering factors for C, N, O, S and I were generated from the analytical expressions of Cromer & Mann (1968); the scattering factors for H were those of Stewart, Davidson & Simpson (1965). The final *R* factors are given in Table 1, and atomic coordinates and temperature factors are listed in Tables 2–6.*

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36369 (55 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Fractional atomic coordinates and temperature factors (\AA^2) with e.s.d.'s in parentheses for (V)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1)	0.3428 (7)	0.2936 (5)	0.7907 (5)	0.07 (2)*
C(3)	0.1515 (9)	0.3338 (6)	0.7966 (5)	0.05 (2)*
C(4)	0.1699 (7)	0.2443 (5)	0.8156 (5)	0.06 (3)*
C(5)	0.2302 (7)	0.2458 (6)	0.8862 (4)	0.06 (3)*
C(6)	0.3513 (7)	0.2827 (5)	0.8676 (5)	0.05 (3)*
C(7)	0.2669 (9)	0.2212 (6)	0.7689 (5)	0.06 (3)*
C(9)	0.2886 (8)	0.4482 (5)	0.7639 (5)	0.08 (2)*
C(B1)	0.3482 (9)	0.4908 (5)	0.8230 (6)	0.04 (3)*
C(B2)	0.458 (1)	0.5195 (6)	0.8124 (5)	0.06 (3)*
C(B2)	0.5163 (9)	0.5576 (6)	0.8663 (8)	0.07 (3)*
C(B4)	0.462 (1)	0.5653 (7)	0.9279 (8)	0.08 (3)*
C(B5)	0.352 (2)	0.5347 (7)	0.9377 (6)	0.13 (4)*
C(B6)	0.295 (1)	0.4973 (6)	0.8848 (8)	0.13 (4)*
C(P1)	0.5465 (8)	0.2430 (5)	0.8925 (4)	0.038 (9)*
C(P2)	0.5857 (8)	0.3238 (5)	0.8859 (4)	0.05 (2)*
C(P3)	0.7002 (8)	0.3415 (5)	0.8998 (4)	0.05 (2)*
C(P4)	0.7759 (7)	0.2831 (6)	0.9221 (4)	0.07 (1)*
C(P5)	0.7347 (8)	0.2040 (6)	0.9279 (4)	0.07 (1)*
C(P6)	0.6226 (8)	0.1837 (4)	0.9113 (4)	0.062 (6)*
C(M)	0.9011 (7)	0.3036 (7)	0.9382 (5)	0.06 (2)*
N	0.2584 (6)	0.3602 (5)	0.7788 (3)	0.05 (2)*
O(1)	0.0644 (6)	0.3743 (4)	0.7965 (3)	0.08 (2)*
O(2)	0.4359 (5)	0.2204 (3)	0.8824 (3)	0.06 (1)*
I	0.56905 (6)	0.06065 (3)	0.91696 (4)	0.115 (6)*
H(1)	0.4197	0.3096	0.7715	0.1
H(4)	0.0945	0.2147	0.8191	0.1
H(5A)	0.2372	0.1886	0.9056	0.1
H(5B)	0.1883	0.2817	0.9190	0.1
H(6)	0.3642	0.3365	0.8908	0.1
H(7A)	0.2452	0.2229	0.7196	0.1
H(7B)	0.3012	0.1660	0.7798	0.1
H(9A)	0.3405	0.4497	0.7234	0.1
H(9B)	0.2164	0.4789	0.7534	0.1
H(B2)	0.4941	0.5132	0.7658	0.1
H(B3)	0.5966	0.5787	0.8583	0.1
H(B4)	0.5056	0.5932	0.9658	0.1
H(B5)	0.3157	0.5406	0.9840	0.1
H(B6)	0.2151	0.4751	0.8918	0.1
H(P2)	0.5324	0.3688	0.8712	0.1
H(P3)	0.7285	0.3994	0.8928	0.1
H(P5)	0.7873	0.1595	0.9450	0.1

Table 5. Fractional atomic coordinates and temperature factors (\AA^2) with *e.s.d.*'s in parentheses for (VI)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1)	0.2258 (6)	0.1525 (3)	0.4708 (6)	0.045 (7)*
C(3)	0.4330 (7)	0.1796 (3)	0.6412 (6)	0.050 (9)*
C(4)	0.3735 (7)	0.1196 (3)	0.6703 (6)	0.06 (1)*
C(5)	0.4033 (7)	0.0770 (3)	0.5502 (7)	0.07 (1)*
C(6)	0.2975 (6)	0.1025 (3)	0.4103 (6)	0.05 (1)*
C(7)	0.2106 (7)	0.1290 (3)	0.6163 (6)	0.06 (1)*
C(9)	0.3641 (7)	0.2481 (3)	0.4303 (7)	0.06 (1)*
C(B1)	0.4258 (7)	0.2320 (3)	0.3046 (7)	0.05 (2)*
C(B2)	0.5687 (8)	0.2181 (3)	0.3235 (7)	0.06 (2)*
C(B3)	0.6247 (7)	0.2048 (3)	0.2090 (9)	0.09 (2)*
C(B4)	0.5411 (9)	0.2036 (3)	0.0707 (8)	0.10 (2)*
C(B5)	0.4003 (9)	0.2170 (4)	0.0494 (7)	0.11 (2)*
C(B6)	0.3454 (7)	0.2306 (3)	0.1639 (7)	0.10 (2)*
C(P1)	0.1177 (6)	0.0659 (2)	0.2109 (6)	0.04 (2)*
C(P2)	0.1729 (6)	0.0652 (2)	0.0892 (6)	0.05 (2)*
C(P3)	0.0903 (7)	0.0752 (3)	-0.0486 (6)	0.06 (2)*
C(P4)	-0.0561 (7)	0.0871 (3)	-0.0713 (7)	0.04 (2)*
C(P5)	-0.1138 (6)	0.0857 (3)	0.0478 (7)	0.04 (2)*
C(P6)	-0.0325 (7)	0.0750 (2)	0.1849 (6)	0.05 (2)*
C(M)	-0.1483 (7)	0.0982 (3)	-0.2240 (7)	0.06 (2)*
N	0.3383 (5)	0.1986 (2)	0.5183 (5)	0.044 (6)*
O(1)	0.5409 (5)	0.2043 (2)	0.7053 (4)	0.043 (4)*
O(2)	0.1976 (4)	0.0544 (1)	0.3489 (4)	0.040 (5)*
I(1)	0.38811 (5)	0.03957 (2)	0.10852 (5)	0.0805 (5)*
I(2)	-0.13121 (5)	0.06518 (2)	0.35693 (5)	0.0908 (4)*
H(1)	0.153 (4)	0.170 (2)	0.408 (4)	0.06 (2)
H(4)	0.415 (4)	0.112 (2)	0.763 (4)	0.05 (2)
H(5A)	0.384 (5)	0.041 (2)	0.560 (5)	0.06 (2)
H(5B)	0.501 (5)	0.077 (2)	0.539 (4)	0.05 (1)
H(6)	0.347 (4)	0.120 (2)	0.334 (4)	0.03 (1)
H(7A)	0.152 (5)	0.078 (2)	0.616 (5)	0.07 (2)
H(7B)	0.205 (5)	0.154 (2)	0.682 (5)	0.08 (2)
H(9A)	0.441 (5)	0.269 (2)	0.498 (5)	0.08 (2)
H(9B)	0.279 (4)	0.265 (2)	0.401 (4)	0.04 (1)
H(B2)	0.597 (5)	0.218 (2)	0.413 (5)	0.07 (2)
H(B3)	0.706 (7)	0.202 (3)	0.205 (7)	0.17 (3)
H(B4)	0.575 (4)	0.201 (2)	-0.010 (4)	0.04 (1)
H(B5)	0.345 (5)	0.207 (2)	-0.043 (5)	0.09 (2)
H(B6)	0.261 (5)	0.235 (2)	0.157 (5)	0.08 (2)
H(P3)	0.127 (4)	0.073 (1)	-0.130 (4)	0.02 (1)
H(P5)	-0.199 (4)	0.089 (2)	0.028 (4)	0.03 (1)
H(MA)	-0.208 (5)	0.077 (2)	-0.236 (5)	0.06 (2)
H(MB)	-0.148 (5)	0.123 (2)	-0.253 (5)	0.07 (2)
H(MC)	-0.113 (6)	0.079 (2)	-0.318 (6)	0.09 (2)

All calculations were performed at the University of Maryland Computer Science Center on a Univac 1108 computer with the XRAY system of crystallographic programs (Stewart *et al.*, 1972, 1976), the molecular drawings were made with ORTEP-II (Johnson, 1971) and the VDO2S system (Lenhert, 1975) was used for diffractometer control.

Discussion

We examined a number of rigid molecules as possible LSR complexation frameworks for the conformational analysis technique described in the *Introduction*. For several reasons, such as synthetic accessibility, ability to form a strong LSR complex, and the number of different carbon and hydrogen nuclei in the rigid framework, the [2.2.1] and [2.2.2] lactams [exempli-

fied in structures (IV) and (VII)] were selected for intensive study. These systems had a further advantage in that the LSR complexation site, the amide O atom, and the conformationally flexible substituent were on opposite ends of the molecule and, therefore, incapable of interacting or of influencing each other. Although the [2.2.2] lactam contains one more CH_2 than the [2.2.1] molecule, and initially seemed superior on this basis, the inability to assign uniquely and unambiguously all the framework protons in the [2.2.2] lactam NMR spectrum led to the concentration of the bulk of our developmental research on the [2.2.1] system. The structures of the three phenoxy-substituted lactams (IV-VI) were determined to establish the rigidity, or structural consistency, of the azabicyclo-[2.2.1]heptane framework. The structure of the *p*-toluenesulfonate (III) was determined to establish unambiguously the *exo* stereochemistry of the tosyl sub-

Table 6. Fractional atomic coordinates and temperature factors (\AA^2) with *e.s.d.*'s in parentheses for (VII)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1)	0.7197 (3)	0.2240 (4)	0.8188 (3)	0.054 (3)*
C(3)	0.8449 (3)	0.3430 (4)	1.0360 (3)	0.062 (7)*
C(4)	0.6642 (3)	0.3606 (4)	1.0043 (3)	0.064 (7)*
C(5)	0.5864 (4)	0.2146 (4)	0.9894 (3)	0.070 (4)*
C(6)	0.6333 (3)	0.1271 (4)	0.8860 (3)	0.050 (3)*
C(7)	0.6132 (4)	0.3511 (4)	0.7516 (3)	0.069 (6)*
C(8)	0.5887 (4)	0.4387 (4)	0.8658 (3)	0.086 (6)*
C(9)	1.0297 (3)	0.2410 (4)	0.9339 (3)	0.069 (4)*
C(B1)	1.0590 (3)	0.3097 (4)	0.8149 (3)	0.059 (5)*
C(B2)	1.1109 (4)	0.2293 (5)	0.7290 (3)	0.076 (5)*
C(B3)	1.1411 (5)	0.2918 (6)	0.6217 (4)	0.100 (6)*
C(B4)	1.1189 (5)	0.4332 (6)	0.5980 (4)	0.110 (8)*
C(B5)	1.0689 (5)	0.5150 (5)	0.6837 (5)	0.112 (8)*
C(B6)	1.0389 (4)	0.4534 (5)	0.7910 (4)	0.089 (7)*
C(P1)	0.4955 (3)	-0.0522 (4)	0.7159 (3)	0.06 (1)*
C(P2)	0.6373 (3)	-0.1170 (4)	0.7228 (3)	0.07 (1)*
C(P3)	0.6280 (5)	-0.2428 (5)	0.6526 (3)	0.103 (9)*
C(P4)	0.4792 (2)	-0.3018 (4)	0.5751 (3)	0.079 (9)*
C(P5)	0.3386 (4)	-0.2344 (4)	0.5656 (3)	0.059 (9)*
C(P6)	0.3452 (3)	-0.1105 (4)	0.6356 (3)	0.06 (1)*
N	0.8682 (3)	0.2729	0.9332 (2)	0.053 (1)*
O(1)	0.9552 (3)	0.3887 (4)	1.1407 (2)	0.054 (7)*
O(2)	0.4866 (2)	0.0697 (3)	0.7843 (2)	0.056 (2)*
H(1)	0.756 (3)	0.172 (3)	0.752 (2)	0.046 (6)
H(4)	0.652 (3)	0.412 (3)	1.079 (3)	0.058 (8)
H(5A)	0.473 (4)	0.222 (3)	0.953 (3)	0.068 (9)
H(5B)	0.616 (5)	0.166 (5)	1.081 (4)	0.10 (1)
H(6)	0.704 (3)	0.049 (3)	0.939 (3)	0.053 (8)
H(7A)	0.503 (3)	0.315 (3)	0.683 (3)	0.061 (8)
H(7B)	0.668 (3)	0.410 (3)	0.700 (3)	0.059 (7)
H(8A)	0.469 (4)	0.454 (4)	0.847 (3)	0.09 (1)
H(8B)	0.641 (4)	0.532 (5)	0.868 (3)	0.08 (1)
H(9A)	1.112 (4)	0.279 (3)	1.031 (3)	0.069 (8)
H(9B)	1.038 (3)	0.134 (3)	0.927 (2)	0.045 (6)
H(B2)	1.118 (4)	0.122 (4)	0.749 (3)	0.080 (9)
H(B3)	1.168 (5)	0.228 (5)	0.566 (4)	0.11 (1)
H(B4)	1.134 (4)	0.474 (4)	0.518 (4)	0.10 (1)
H(B5)	1.049 (5)	0.619 (5)	0.666 (4)	0.10 (1)
H(B6)	1.009 (4)	0.502 (4)	0.852 (3)	0.071 (9)
H(P2)	0.736 (4)	-0.078 (3)	0.771 (3)	0.067 (9)
H(P3)	0.736 (4)	-0.283 (4)	0.659 (3)	0.09 (1)
H(P4)	0.469 (4)	-0.390 (4)	0.526 (3)	0.08 (1)
H(P5)	0.226 (4)	-0.274 (4)	0.512 (3)	0.08 (1)
H(P6)	0.241 (4)	-0.064 (4)	0.628 (3)	0.070 (9)

stituent, and to help confirm an early suspicion that displacement of *p*-toluenesulfonate by phenoxide had occurred with retention.

Combined lists of bond lengths and angles are given in Tables 7 and 8, and *ORTEP* drawings are provided in Figs. 1–5. The drawings were made to show the five molecules from the same viewpoint, and to reveal all of the bicyclic ring atoms. A search of the Cambridge Crystallographic Database (current to January 1981) located only one other study of a [2.2.1] or [2.2.2] bicyclic lactam, that of 2-azabicyclo[2.2.2]octan-3-one (VIII) (Aubry, Protas, Thong, Marraud & Néel, 1973).

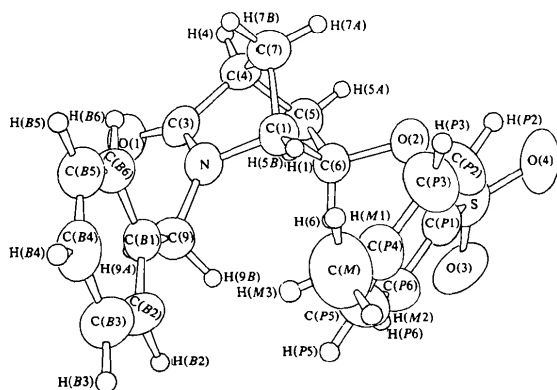


Fig. 1. *ORTEP* drawing of (III). The heavy atoms are represented as 50% ellipses, and the H atoms appear as 0.1 Å radius circles.

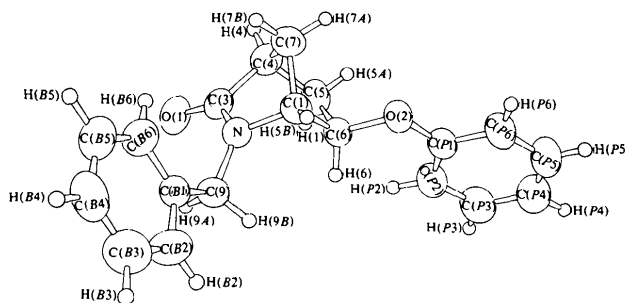


Fig. 2. *ORTEP* drawing of (IV). The heavy atoms are represented as 50% ellipses, and the H atoms appear as 0.1 Å radius circles.

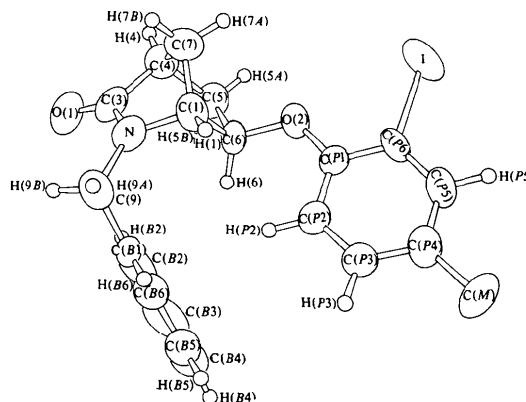


Fig. 3. *ORTEP* drawing of (V). The heavy atoms are represented as 50% ellipses, and the H atoms appear as 0.1 Å radius circles.

Table 7. Bond lengths (Å) and *e.s.d.*'s (in parentheses) for the five lactams

	(III)	(IV)	(V)	(VI)	(VII)
N—C(1)	1.465 (3)	1.467 (3)	1.48 (1)	1.486 (7)	1.475 (3)
N—C(3)	1.365 (3)	1.357 (3)	1.36 (1)	1.359 (7)	1.342 (3)
N—C(9)	1.453 (3)	1.454 (3)	1.50 (1)	1.450 (8)	1.462 (3)
C(1)—C(6)	1.542 (3)	1.528 (4)	1.52 (1)	1.502 (9)	1.528 (5)
C(1)—C(7)	1.523 (3)	1.517 (4)	1.53 (1)	1.516 (9)	1.529 (5)
C(3)—C(4)	1.520 (4)	1.520 (4)	1.52 (1)	1.52 (1)	1.518 (4)
C(3)—O(1)	1.215 (4)	1.218 (4)	1.21 (1)	1.202 (7)	1.233 (3)
C(4)—C(5)	1.545 (4)	1.545 (4)	1.55 (1)	1.567 (9)	1.532 (6)
C(4)—C(7)	1.533 (4)	1.531 (4)	1.50 (1)	1.537 (9)	—
C(4)—C(8)	—	—	—	—	1.531 (4)
C(7)—C(8)	—	—	—	—	1.534 (5)
C(5)—C(6)	1.546 (3)	1.552 (4)	1.58 (1)	1.569 (8)	1.538 (5)
C(6)—O(2)	1.466 (3)	1.439 (3)	1.44 (1)	1.469 (6)	1.436 (3)
C(9)—C(B1)	1.510 (4)	1.510 (4)	1.52 (1)	1.50 (1)	1.509 (5)
[C(B1)—C(B2), C(B1)—C(B6)]*	1.382 (4)	1.375 (5)	1.37 (2)	1.37 (1)	1.385 (5)
[C(B2)—C(B3), C(B5)—C(B6)]*	1.386 (4)	1.390 (5)	1.39 (2)	1.36 (1)	1.377 (7)
[C(B3)—C(B4), C(B4)—C(B5)]*	1.368 (5)	1.360 (6)	1.38 (2)	1.36 (1)	1.373 (8)
O(2)—C(P1)	—	1.377 (3)	1.36 (1)	1.369 (6)	1.378 (5)
[C(P1)—C(P2), C(P1)—C(P6)]*	1.373 (5)	1.384 (4)	1.38 (1)	1.400 (9)	1.384 (4)
[C(P2)—C(P3), C(P5)—C(P6)]*	1.377 (5)	1.381 (5)	1.39 (1)	1.367 (8)	1.381 (6)
[C(P3)—C(P4), C(P4)—C(P5)]*	1.382 (5)	1.373 (6)	1.37 (1)	1.39 (1)	1.374 (6)
C(P4)—C(M)	1.496 (5)	—	1.53 (1)	1.520 (8)	—
[C(P2)—I(1), C(P6)—I(2)]	—	—	2.091 (7)†	2.100 (6)*	—
S—O(2)	1.586 (2)	—	—	—	—
[S—O(3), S—O(4)]*	1.423 (3)	—	—	—	—
S—C(P1)	1.754 (3)	—	—	—	—

* Average value for the two 'equivalent' aromatic ring bonds. The *e.s.d.* reported is the larger of the two individual bond-length *e.s.d.*'s.

† Single values.

Nyburg's (1974) best molecular fit least-squares program has been used to compare the seven-atom bicyclic frameworks in the four [2.2.1] lactams, and the eight-atom frameworks in the two [2.2.2] lactams. The results of the calculations, which are summarized in Table 9, indicate that the bicyclic portions of these

molecules are identical within the associated experimental errors. The various dihedral angles in the [2.2.1] lactam frameworks fall within the ranges summarized by Altona & Sundaralingam (1970) for a number of bicyclo[2.2.1]heptanes (norbornanes) and heptenes (norbornenes).

Table 8. Bond angles ($^{\circ}$) and *e.s.d.*'s (in parentheses) for the five lactams

	(III)	(IV)	(V)	(VI)	(VII)
C(6)–C(1)–N	105.5 (2)	106.2 (2)	106.5 (7)	105.7 (5)	105.6 (3)
C(7)–C(1)–N	100.8 (2)	100.5 (2)	97.4 (7)	101.1 (4)	109.1 (3)
C(6)–C(1)–C(7)	102.3 (2)	103.3 (2)	103.0 (7)	104.0 (5)	110.9 (3)
C(1)–N–C(3)	109.1 (2)	109.1 (2)	109.9 (7)	109.0 (5)	116.1 (3)
C(1)–N–C(9)	123.9 (2)	123.4 (2)	124.6 (7)	125.2 (4)	120.7 (3)
C(3)–N–C(9)	124.5 (2)	124.3 (2)	124.3 (7)	124.1 (5)	123.2 (3)
N–C(3)–C(4)	104.1 (2)	103.8 (2)	103.5 (8)	103.4 (5)	110.6 (3)
N–C(3)–O(1)	126.6 (2)	126.4 (3)	126.7 (9)	127.0 (6)	124.7 (3)
C(4)–C(3)–O(1)	129.2 (2)	129.6 (3)	129.8 (9)	129.6 (5)	124.7 (3)
C(3)–C(4)–C(5)	104.6 (2)	104.6 (2)	105.7 (7)	105.5 (5)	108.6 (3)
C(3)–C(4)–C(7)	101.1 (2)	101.4 (2)	101.3 (7)	102.4 (5)	–
C(5)–C(4)–C(7)	101.5 (2)	101.9 (2)	101.8 (7)	101.3 (5)	–
C(3)–C(4)–C(8)	–	–	–	–	107.7 (3)
C(5)–C(4)–C(8)	–	–	–	–	109.0 (2)
C(4)–C(5)–C(6)	103.1 (2)	102.7 (2)	101.9 (7)	101.2 (5)	109.2 (3)
C(1)–C(6)–C(5)	102.0 (2)	101.7 (2)	102.4 (7)	102.4 (5)	108.2 (3)
C(1)–C(6)–O(2)	110.8 (2)	107.9 (2)	109.0 (7)	112.7 (5)	111.3 (2)
C(5)–C(6)–O(2)	108.1 (2)	112.6 (2)	107.6 (6)	106.8 (4)	108.1 (3)
C(1)–C(7)–C(4)	93.0 (2)	92.4 (2)	94.3 (7)	91.9 (5)	–
C(1)–C(7)–C(8)	–	–	–	–	108.6 (2)
C(4)–C(8)–C(7)	–	–	–	–	109.1 (3)
N–C(9)–C(B1)	113.7 (2)	113.6 (2)	113.1 (8)	115.3 (5)	112.4 (3)
C(9)–C(B1)–C(B2)	119.1 (2)	119.5 (3)	118 (1)	121.8 (5)	119.7 (3)
C(9)–C(B1)–C(B6)	122.6 (2)	122.1 (3)	120.2 (9)	122.7 (6)	121.6 (3)
C(B2)–C(B1)–C(B6)	118.3 (2)	118.3 (3)	122 (1)	115.4 (6)	118.7 (3)
[C(B1)–C(B2)–C(B3), C(B1)–C(B6)–C(B5)]*	120.7 (3)	120.7 (3)	119 (1)	122.4 (6)	120.5 (4)
[C(B2)–C(B3)–C(B4), C(B4)–C(B5)–C(B6)]*	120.3 (3)	120.2 (4)	119 (1)	120.7 (7)	120.2 (5)
C(B3)–C(B4)–C(B5)	119.7 (3)	119.9 (3)	121 (1)	118.2 (8)	119.8 (5)
C(6)–O(2)–C(P1)	–	118.0 (2)	119.6 (6)	113.4 (4)	119.1 (2)
C(6)–O(2)–S	119.4 (1)	–	–	–	–
O(2)–C(P1)–C(P2)	–	124.5 (2)	123.5 (8)	123.7 (5)	125.5 (3)
O(2)–C(P1)–C(P6)	–	115.3 (3)	118.2 (7)	120.1 (5)	114.5 (3)
C(P2)–C(P1)–C(P6)	120.5 (3)	120.2 (3)	118.3 (8)	116.0 (5)	120.0 (3)
[C(P1)–C(P2)–C(P3), C(P1)–C(P6)–C(P5)]*	119.3 (3)	119.3 (3)	120.1 (8)	121.8 (6)	119.5 (3)
[C(P2)–C(P3)–C(P4), C(P4)–C(P5)–C(P6)]*	121.8 (3)	121.0 (3)	122.4 (8)	121.3 (6)	120.6 (3)
C(P3)–C(P4)–C(P5)	117.3 (3)	119.3 (4)	116.5 (8)	117.6 (5)	119.6 (4)
C(P3)–C(P4)–C(M)	121.7 (3)	–	122.2 (9)	120.6 (6)	–
C(P5)–C(P4)–C(M)	121.0 (3)	–	121.3 (8)	121.8 (6)	–
O(2)–S–C(P1)	103.1 (1)	–	–	–	–
O(2)–S–O(3)	108.7 (1)	–	–	–	–
O(2)–S–O(4)	103.7 (1)	–	–	–	–
O(3)–S–C(P1)	109.4 (1)	–	–	–	–
O(3)–S–O(4)	120.3 (1)	–	–	–	–
O(4)–S–C(P1)	110.1 (2)	–	–	–	–
S–C(P1)–C(P2)	120.0 (2)	–	–	–	–
S–C(P1)–C(P6)	119.4 (2)	–	–	–	–
C(P1)–C(P2)–I(1)	–	–	–	119.9 (4)	–
C(P3)–C(P2)–I(1)	–	–	–	117.0 (5)	–
C(P1)–C(P6)–I(2)†	–	–	119.5 (6)	119.1 (4)	–
C(P5)–C(P6)–I(2)†	–	–	119.7 (6)	119.9 (5)	–

* Average values for 'equivalent' angles. The *e.s.d.* reported is the larger of the individual values.

† I(2) is atom I in (V).

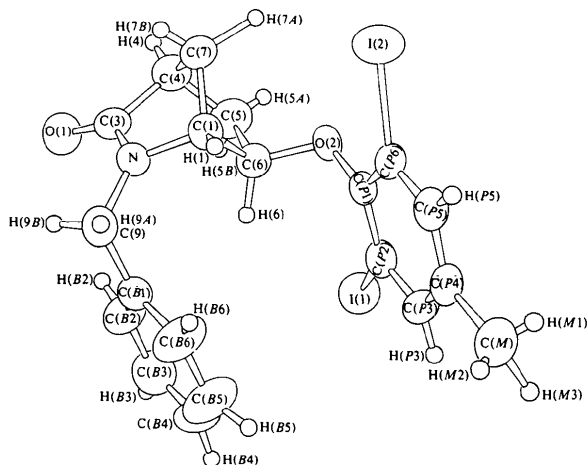


Fig. 4. ORTEP drawing of (VI). The heavy atoms are represented as 50% ellipsoids, and the H atoms appear as 0.1 Å radius circles.

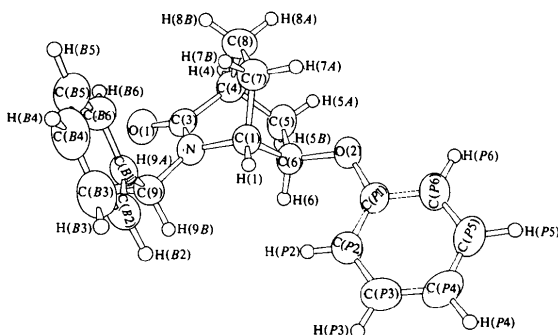


Fig. 5. ORTEP drawing of (VII). The heavy atoms are represented as 50% ellipsoids, and the H atoms appear as 0.1 Å radius circles.

Table 9. Summary of the least-squares best-molecular-fit calculations

[2.2.1] lactams*	Max diff.	R.m.s. diff.
(IV) vs (III)	0.015 Å	0.008 Å
(IV) vs (VI)	0.028	0.019
(IV) vs (V)	0.076	0.046
[2.2.2] lactams†		
(VII) vs (VIII)	0.068	0.047

* Seven atoms.

† Eight atoms.

A comparison of the analogous bond lengths and angles in these six structures reveals few significant differences. Distances associated with the N=C=O regions show a trend which could be interpreted in terms of more (+)N=C=O(-) character in the [2.2.2] lactams than in the [2.2.1] compounds (the N=C and

C=O averages are [2.2.2] 1.333, 1.238 Å, and [2.2.1] 1.360, 1.211 Å). This smaller amount of N=C character in the [2.2.1] lactams could be due to greater ring strain in these compounds, compared to the [2.2.2] lactams, which would tend to inhibit the strain-increasing N=C form in favor of N-C character. The endocyclic bond angles at N and the amide C atom are *ca* 7° larger in the [2.2.2] lactams and in accord with the ring-strain postulate.

Bond angles in the bicyclic regions clearly show the effect of the extra CH₂ bridging atoms in the [2.2.2] molecules. The endocyclic angles in the [2.2.2] lactams are several degrees larger than the corresponding [2.2.1] values at all atoms. Additionally, the internal angles at the *sp*³ carbons in the [2.2.2] lactams are within a degree or two of the ideal tetrahedral values.

Perhaps the most interesting aspects of these five structures involve the conformations of the benzyl and phenoxy substituents relative to the bicyclic frameworks. Newman-projection drawings, illustrating the phenoxy-bicyclic conformations, are shown in Fig. 6. [Aspects of the diiodophenoxy...bicyclo[2.2.1]-heptane conformation have been discussed by Ammon, Mazzocchi & Liu (1980).] In all four compounds, the C(P1)-O(2)-C(6)-H(6) unit adopts a semi-staggered arrangement with dihedral angles in the range of 34–43°, the direction of rotation being toward C(1) in three of the lactams and toward C(5) in the fourth. While the direction of rotation is probably dictated by crystal packing, the extent of rotation presumably reflects a balance of intra- and intermolecular repulsive

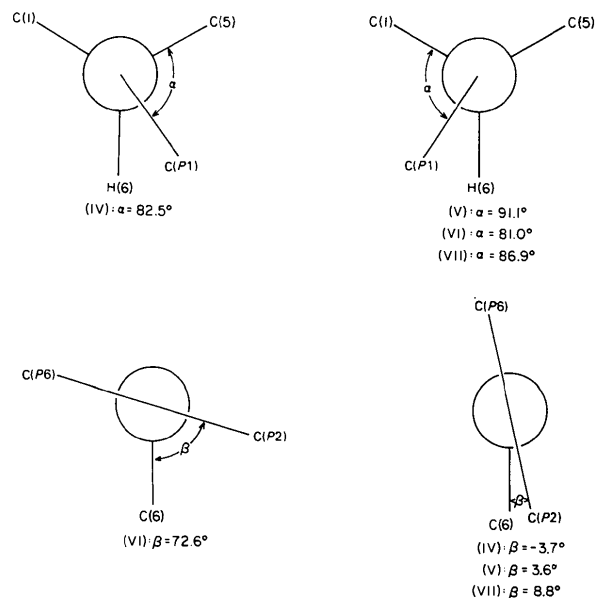


Fig. 6. Newman-projection drawings to illustrate conformations about the O(2)-C(6) bond (top) and C(P1)-C(6) bond (bottom half).

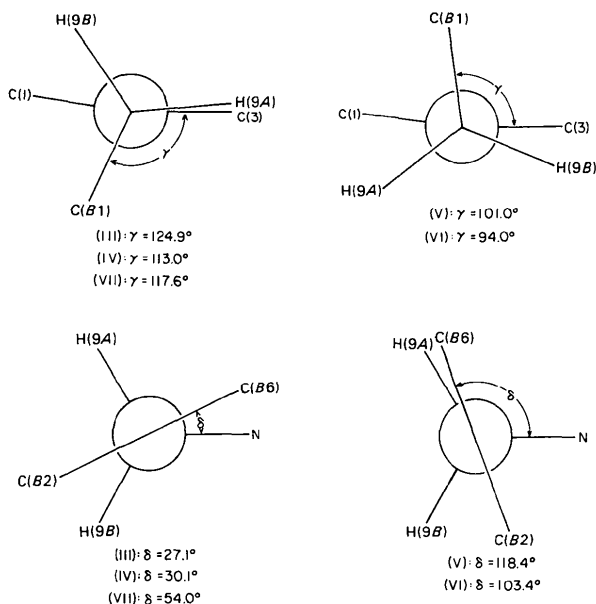


Fig. 7. Newman-projection drawings to illustrate conformations about the C(9)-N bond (top) and C(B1)-C(9) bond (bottom half).

interactions. In three of the compounds, the phenoxy aromatic ring virtually eclipses the O(2)-C(6) bond, providing an optimum arrangement for p -orbital overlap of an sp^2 -hybridized O atom with the benzene ring. The 73° dihedral angle found for (VI), the diiodo-substituted molecule, is required to reduce steric interactions between the iodines and bicyclic nucleus.

With respect to the benzyl-bicyclic conformations, the five lactams fall into two groups. The similarities are clearly visible on comparing Figs. 1-5; and summarizing Newman projections are given in Fig. 7. The two C(9)-N conformations differ mainly in the positions of the C(B1) atoms, which are found both above and below the C(1)-N-C(3) planes. The conformations within each of the two types are very similar, differing by only a few degrees in the various dihedral angles. In the case of the C(B1)-C(9) conformations, the common factor appears to be that the aromatic rings avoid close contacts with their respective nitrogens. The two ways in which this occurs are shown in Fig. 7; eclipsing of the benzylic H atoms does not appear to be important.

The crystal-packing arrangements in these five compounds are ordinary. The intermolecular contacts are characterized by the appropriate van der Waals radii.

This work was supported by the National Institutes of Health (AM-17458) and, in part, through the facilities of the University of Maryland's Computer Science Center.

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