Fig. 3. Torsion angles (°) for the side chains.

staggered for the placing of the H atoms, except for the side chains attached to C(3) and N(6). Torsion angles for these are shown in Fig. 3; they result from electronic (conjugation) and steric effects.

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(±)-2-*exo-* and *endo*-Methylamino-l,2,3,4-tetrahydro-l,4-ethanonaphthalene Hydrochlorides

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Abstract. $C_{13}H_{18}ClN$ *(exo\ M_r* = 223-75, monoclinic, *P2/n, Z* = 4, a = 10-703 (2), *b* = 7-503 (2), c = 15-251 (2) *A,fi* = 97-78 (2)°, D_o = 1-23, D_c = 1-23 g cm~³, A(Mo *Ka*) = 0-7107 A,//(Mo *Ka*) = 2-856 cm"¹, R = 0-037 for 2142 observed reflections after anisotropic refinement of all non-hydrogen atoms and positional-parameter refinement of H atoms. $C_{13}H_{18}ClN$-*(endo),* M_r = 223-75, monoclinic, *P2jn, Z* = 4, *a* = 7-955 (4), *b* = 14-702 (5), *c* = 10-215(3) A, *p* = 93-28 (2)°, D_a = 1-25, D_c = 1-25 g cm~³, A(Mo *Ka*) = 0-7107 A, //(Mo *Ka*) = 2-905 cm"¹, *R* = 0-078 for 1175 observed reflections after anisotropic refinement of all non-hydrogen atoms.

Introduction. Single crystals of the title compounds were obtained as colorless prisms upon recrystallization from ethanol. Both compounds showed monoclinic symmetry and systematic absences consistent with the space group *P2/n*. Intensity data were collected using crystals 0-25 x 0-30 x 0-40 mm in size *(exo)* and 0-25 x 0-25 x 0-35 mm in size *(endo),* an Enraf-Nonius C A D - 4 diffractometer, a graphite mono-chromator, Mo *Ka* radiation, and the *9-28* scanning technique. Intensities were measured for 3908 indepen-

dent reflections *(exo)* with *29 < 55°* and 2339 independent reflections *(endo)* with *29 < 50°*. The intensity data were reduced to the structure factors by application of Lorentz and polarization corrections. No absorption or extinction corrections were applied. The structures were determined by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971), and were refined by a full-matrix least-squares procedure. **Anisotropic** thermal parameters were used for the non-hydrogen atoms and fixed isotropic thermal parameters (5-0 A²) for the H atoms in the *exo* case. Only the 2142 reflections *(exo)* having $F_o > 3\sigma(F^2_o)$ were used **in** the refinement *(endo,* 1175 reflections). In the last cycles of refinement, parameter shifts were less than 0-5cr, $R = I\backslash F_a\backslash - \backslash F_c\backslash J/^\wedge\backslash F_a\backslash = 0\text{-}037$ *(exo)* and 0-078 *(endo);* $R' = Q>(lF_a\backslash - \backslash F_c\backslash)^2/XwF^2_o V^{1\!\!/\!\!2}$ 0-051 *(exo)* and 0-112 *(endo* where $w = 4F^2 Jo^2(F^2_o\backslash$

The molecular structure and the atom-numbering system for the *exo* compound are shown in Fig. 1. The final atomic coordinates are given in Tables 1 and 2 for the *exo* and *endo* compounds, respectively.* Bond

* Lists of structure factors, thermal parameters, an *OR TEP* drawing of the *endo* isomer and packing diagrams of both isomers have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33770 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.
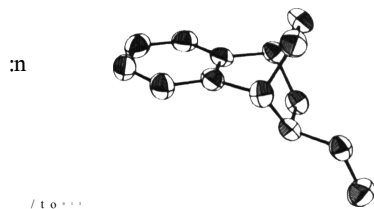

Fig. 1. exo-2-Methylamino-1,2,3,4-tetrahydro-1,4-ethanonaphthalene hydrochloride.

lengths are given in Table 3 and bond angles in Table 4. The *Enraf-Nonius Structure Determination Package (SDP)* was used for all the calculations.

Discussion. We have been interested in the benzobicyclol 2.2.2 loctene ring system as a rigid framework upon which to construct a series of conformational^ defined adrenergic phenethylamines (Grunewald, Ruth, Kroboth, Kamdar, Patil & Salman, 1976; Bartholow, Eiden, Ruth, Grunewald, Siebert & Rutledge, 1977). The title compounds are rigid analogs of meth&mphetamine; the exo-isomer corresponds to an extended conformation, and the *endo-isomer* to a *gauche*

Table 2. *Positional parameters and their estimated standard deviations for the endo isomer*

The atomic coordinates are given in the fractional crystallographic coordinate system.

		y	i
C(1)	0-1602 (8)	0-6124 (5)	0-1669 (6)
C(2)	0-1583 (8)	0-5080(5)	0-1770(6)
C(3)	0-1725 (10)	0-4786 (5)	0-3218(7)
C(4)	0-1820(10)	0-6560(5)	0-4118(7)
C(5)	0-3264 (9)	0-6211 (5)	0-3712(7)
C(6)	0-4613(11)	0-6494 (6)	0-4514(10)
C(7)	0-5859 (11)	0-7054 (6)	0-3986(11)
C(8)	0-5732 (10)	0-7304 (6)	0-2704(11)
C(9)	0-4356 (9)	0-7027 (5)	0-1856 (9)
C(OO)	0-3148 (8)	0-6477 (4)	0-2390(7)
C(11)	0-0038 (8)	0-6474 (5)	0-2342 (7)
C(12)	0-0197(10)	0-6199(6)	0-3819(7)
C(13)	0-2803 (10)	0-3668 (5)	0-0849 (8)
CI	0-1818(2)	0-0483(1) -	0-6767 (2)
N	0-2970 (6)	0-4686 (4)	0-1016(5)

Table 1. *Positional parameters and their estimated standard deviations for the exo isomer*

The atomic coordinates are given in the fractional crystallographic coordinate system.

	X	y	z		X	y	z
C(1)	0-2161 (1)	0-1820 (2)	0-0668 (1)	H(C1)	0-160 (2)	0-133(2)	0-106(1)
C(2)	0-3500(1)	0-1777(2)	0-1177(1)	H(C2)	0-372 (1)	0-063 (2)	0-133(1)
C(3)	0-4437 (1)	0-2563 (2)	0-0602(1)	H(C3)	0-509 (2)	0-167 (2)	0-054(1)
C(4)	0-3739 (2)	0-3072 (2)	-0-0309 (1)	H'(C3)	0-480(1)	0-359 (2)	0-092(1)
C(5)	0-3031 (2)	0-1469 (2)	-0-0702 (1)	H(C4)	0-432 (1)	0-353 (2)	-0-065 (1)
C(6)	0-3120 (2)	0-0717 (2)	-0-1520(1)	H(C6)	0-370 (2)	0-113(3)	-0-188(1)
C(7)	0-2355 (2)	-0-0717(3)	-0-1804 (1)	H(C7)	0-244 (2)	-0-119(3)	-0-237 (1)
C(8)	0-1536 (2)	-0-1416(3)	-0-1282(1)	H(C8)	0-100(2)	-0-237 (3)	-0-150 (2)
C(9)	0-1453 (2)	-0-0692 (2)	-0-0450(1)	H(C9)	0-091 (2)	-0-118(2)	-0-009(1)
C(OO)	0-2189 (2)	0-0778 (2)	-0-0169(1)	H(C11)	0-175 (2)	0-448 (2)	0-093 (1)
C(O1)	0-1809 (2)	0-3756 (3)	0-0397(1)	H'(CII)	0-097 (2)	0-385 (3)	0-006(1)
C(12)	0-2756 (2)	0-4504 (2)	-0-0177(1)	H(C12)	0-316(2)	0-553 (3)	0-012(1)
C(13)	0-4665 (2)	0-2350 (3)	0-2684(1)	H'(C12)	0-232 (2)	0-490 (3)	-0-078(1)
CI	0-12739 (4)	0-19740(6)	0-30068 (3)	H(C13)	0-537 (2)	0-274 (2)	0-249(1)
N	0-3555 (1)	0-2772 (2)	0-2035 (1)	H'(C13)	0-470 (2)	0-302 (3)	0-316(2)
				H"(C13)	0-469 (2)	0-111 (3)	0-278(1)
				H(N)	0-292 (2)	0-251 (3)	0-223 (1)
				H'(N)	0-356 (2)	0-393 (3)	0-200(1)

Table 3. *Bond lengths* (A) *and their standard deviations*

		endo		*exo*	*endo*			*exo*	*endo*
C(I> C<2)	1·535 (2)	538 (6)	C(4)- H(C4)	0·93 (2)		C(LL)-C(12)	1·532 (3)	1·560 (6)
C(L> C(10)	1 501 (2)	490(5)	C(5)-~C(6)	1·384 (2)	1·377 (7)	C(11)—H(C 11)	0·98 (2)	
C(\yCd i)	1·543 (2)	543 (5)	C(5)--C(10)	1·393 (2)	1·404 (6)	C(11)-H'(C11)	0·97 (2)	
C(l)~ H(C1)	0·97(2)		C(6) -C(7)	1·386 (3)	1·418(10)	C(12)-H(C12)	0·96 (2)	
C(2> C(3)	1·538 (2)	539 (6)	C(6)-~H(C6)	0·93 (2)		C(12)-H'(C12)	1·01 (2)	
C(2>-N	1·500(2)	497 (5)	C(7)--C(8)	1·366 (3)	1·358 (10)	C(13)-N	1·474 (2)	1·511 (5)
C(2> H(C2)	0·92(2)		C(7)--H(C7)	0·96 (2)		C(13)-H(C13)	0·90 (2)	
C(3)-C(4)	1·534 (2)	567 (6)	C(8)--C(9)	1·394 (3)	1·416 (9)	C(13)-H'(C13)	0·88 (3)	
C(3>-H(C3)	0·99(2)		C(8)--H(C8)	0·95 (2)		C(13)-H"(C13)	0·94 (3)	
C(3) H'(C3)	0·97(2)		C(9)-C(10)	1·389 (2)	1·392 (6)	N-H(N)	0·80 (2)	
C(4> C(5)	1·502 (2)	1492 (6)	C(9)~-H(C9)	0·92 (2)		N-H'(N)	0·87 (2)	
C(4)—C(12)	1·536 (2)	1·538 (7)						

Tabic 4. *Bond angles (°) and their standard deviations*

	exo	*endo*
C(2>—C(L)-C(10)	107·1 (1)	109·0 (3)
c(2)-c(i y-c(i\)	109·4(1)	107·0(3)
C(10)-€(1)-C(1I)	1071 (1)	109·1 (3)
C(!>—C(2)—C(3)	109·8 (1)	110·1 (3)
C(IH:(2>-N	110·8(1)	109·9(3)
C(3)—C(2)- N	110·8(1)	111·7(3)
C(3>~C(3KC<4)	109·7(1)	109·6 (4)
CQ)-C{ 4>C(5)	108·6(1)	107·3 (4)
C(3HC(4>-C(12)	108·3(1)	107·3 (4)
C(5)~~C(4}~C(12)	107·2(1)	107·8 (4)
C(4K (5 K (6)	126·4(1)	126·0(5)
C(14)—C(5)~€(10)	113·4(1)	114·3 (4)
C(6>~C(5)—C(I0)	120·2(1)	119·6(5)
C(5)—C(6>—C(7)	119·2(2)	119·1 (6)
C(6)~C(7>—C(8)	121·0(2)	120·6(6)
C(7)—C(8>—C(9)	120·4(2)	121·6(6)
C(SM9)-C(10)	119·2(2)	117·0(6)
C(1HC(10>-C(5)	113·0(1)	112·7(4)
C(1)~C(10>—C(9)	126·9(1)	125·3 (4)
C(5HC(IOH:(9)	120·0(1)	122·0(4)
C(L>—C(LL)—C(12)	110·0(1)	108·7(4)
C(4)—C(12)—C(11)	109·7(1)	110·4 (3)
C(2)~N—C(13)	114·3(1)	112·2(3)

conformation of the methamphetamine molecule. Synthesis of these compounds has been described previously (Grunewald, Ruth, Kroboth, Kamdar, Patil & Salman, 1976).

The present study was carried out to evaluate the suitability of the ring system for the preparation of conformational^ defined phenethylamines; in particular, we wished to compare bond lengths and angles of the title compounds with those of amphetamine sulfate as determined by Bergin & Carlstrom (1971).

The bond lengths observed for the bicyclic compounds arc not significantly different from those observed for amphetamine and for several other conformational^ mobile phenethylamines whose structures have been determined (phenethylamine hydrochloride, Tsoucaris, 1961; ephedrine hydrochloride, Bergin, 1971; ephedrine monohydrogen phosphate

monohydrate, Hearn, Freeman & Bugg, 1973; ephedrine dihydrogen phosphate, Hearn & Bugg, 1972; dopamine hydrochloride, Bergin & Carlstrom, 1968; 5-hydroxy-dopamine hydrochloride, Andersen, Mostad & Romming, 1972; 6-hydroxydopamine hydrochloride, Kolderup, Mostad & Romming, 1972; epinephrine hydrogen tartrate, Carlstrom, 1973; norepinephrine hydrochloride, Carlstrom & Bergin, 1967; iso-proterenol sulfate, Mathew & Palenik, 1971; 2,4,5 trimethoxyamphetamine hydrochloride. Baker, Chothia, Pauling & Weber, 1973; 4-ethyl-2,5 dimethoxyamphetamine, Kennard, Giacovazzo, Horn, Mongiorgi & Riva di Sanseverino, 1974; mescaline hydrobromide, Ernst & Cagle, 1973; mescaline hydro chloride, Tsoucaris, de Rango, Tsoucaris, Zelwer, Parthasarathy & Cole, 1973). Similarly, bond angles are within normal limits with the exception of the angles centered on C(5) and C(10). These angles are compressed about 6° by the bicyclic ring system. It would seem that this does not seriously impair the utility of the ring system as a model for /?-phenethyl-amines; for example, the distance from the N atom to the center of the aromatic ring is 5·07 A in the *exo*-isomer, compared with values of 4·98 to 5·21 A for the phenethylamines which exist in the extended conformation in the crystal structure. Three phenethylamines which exhibit the *gauche* conformation in the crystal structure, 2,4,5-trimethoxyamphetamine hydrochloride, mescaline hydrobromide and 4-ethyl-2,5-di methoxyamphetamine, show ring-to-nitrogen distances of 3·89 to 4·07 A; the *endo* bicyclic compound shows a comparable distance of 3·93 A. The C(10)-C(1)-C(2)-N dihedral angles *(exo = 179°, endo = 68°)* are in good agreement with expected values for the extended (168°) and *gauche* (60°) conformations. The C(5)-C(10)-C(1)-C(2) dihedral angles in these struc tures are 60° *(exo)* and 58° *(endo)*. It thus appears that the benzobicyclot2.2.2loctene system affords an ideal framework for the construction of conformational^ defined analogs of biologically important phenethyl amines.

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azacyclododecane

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Abstract. $C_{44}H_{60}N_4$, monoclinic, *P2ja, a* = 22-710(2), *b* = 14-639 (1), c = 11-831 (1) **A, £** = 90-5 (2)°, *U*= 3933-1 (3) **A³,** D_m = 1-08, D_c= 1-09 g cm~³, *Z = 4.* The skeleton of the molecule consists of the typical 12-membered square conformation. Compared with other related structures and the conformational-energy calculation, the molecular shape is found to be flexible, in both the N atom positions and the benzyl conformations.

Introduction. This paper is a part of a series of investigations on the cyclic tetramers of chiral aziridines. The synthesis and the identification of the title compound (Fig. 1) were described in previous papers (Tsuboyama, Tsuboyama, Uzawa & Higashi, 1974; Tsuboyama, Tsuboyama, Higashi & Yanagita, 1970). Single crystals were obtained by recrystallization from benzene solution. A clear, colorless plate crystal, 0-4 x 0-3 x 0-1 mm, was used for the study. X-ray diffraction data were measured on a Rigaku
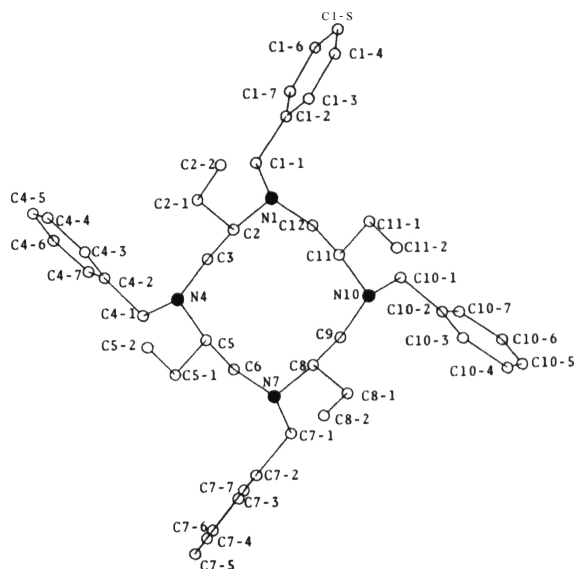

Fig. 1. The numbering of atoms in the molecule.