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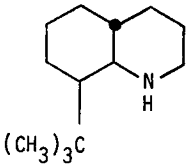
CRYSTAL STRUCTURE OF A FUSED CYCLOHEXANE WITH AN AXIAL *t*-BUTYL GROUP: 8β-*t*-BUTYL-*trans*-DECAHYDROQUINOLINE

Karl D. Hargrave and Ernest L. Eliel*
William R. Kenan, Jr. Laboratories of Chemistry
University of North Carolina, Chapel Hill, N.C. 27514 USA

Summary: 8β-*t*-Butyl-*trans*-decahydroquinoline picrate crystallizes as a double chair with an axial *t*-butyl group. Except for a 16.2° torsion of the *t*-butyl group away from the staggered conformation, the molecule displays only minor conformational deformations.

A *t*-butyl group substituted on a cyclohexane ring tends to avoid the axial position and thus serves as a "holding group" for the cyclohexane chair, preventing ring reversal.[1] The first cyclohexane with a potentially axial *t*-butyl group - *trans*-1,3-di-*t*-butylcyclohexane - was synthesized in 1960,[2] but this species,[3] as well as the corresponding *cis*-1,4-di-*t*-butyl[3,4] and *cis,trans*-1,3,5-tri-*t*-butyl[5] analogs appear to exist predominantly in the twist-boat form. A twist-boat was also originally assumed for the *cis*-1,2-di-*t*-butylcyclohexane,[6] but later work[7] suggests that this compound in fact exists as a chair with one axial *t*-butyl. The first reported axial *t*-butyl group is the one in *cis*-2-alkyl-5-*t*-butyl-1,3-dioxane (2 alkyl group Me, Et, *i*-Pr or *t*-Bu),[8] but this case is anomalous in that the *t*-butyl group is *syn*-axial with two lone pairs of electrons rather than with two axial hydrogen atoms. *trans*-1,2-Di-*t*-butylcyclohexane and the corresponding $C(CH_3)_2CH_2OH$ and $C(CH_3)_2CO_2Me$ substituted compounds in solution appear to be mixtures of diaxially substituted chairs and twist-boats;[7] the compound with two CMe_2CO_2Me groups exists as a diaxially substituted flattened chair in the crystalline state.[9] A crystal structure determination has also been carried out of a 2-*t*-butyl-1-alkylidenecyclohexane,[10] in which the *t*-butyl group is axial because of $A^{(1,3)}$ strain.

To the best of our knowledge, no structure determination has yet been performed on a fully saturated cyclohexane with an axial *t*-butyl group. Recently we have synthesized[11] such a structure in 8β-*t*-butyl-*trans*-decahydroquinoline (**1**). In relation to the argument concerning the position of the lone pair in this compound,[11] it was important to be sure that **1** in fact exists in a chair form. This appeared plausible from the ^{13}C NMR data obtained;[11] it has now been confirmed by X-ray structure analysis of the corresponding picrate (**1**.HPic). (Since - *vide infra* - the salt exists as an only slightly distorted chair, the chair conformation may, *a fortiori*, be assumed for the free base.)



1

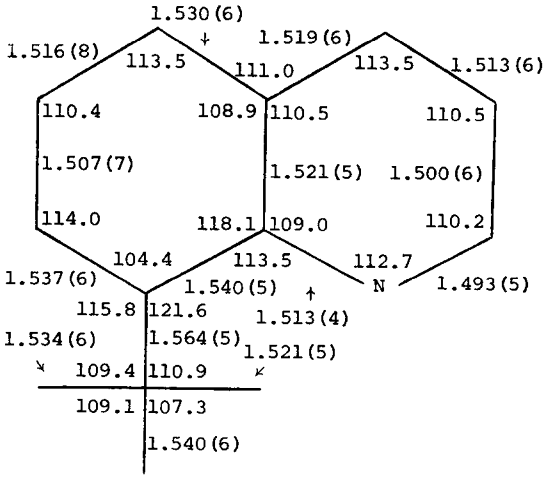
Crystal Data: $C_{19}H_{28}N_4O_7$, M=424.45, Monoclinic, a=9.241(4), b=10.484(6), c=22.584(9) Å, β=107.67(2)°, U=2084.8 Å^3, D_c=1.352 gcm^{-3}, Z=4, D_m(flotation)=1.34, F(000)=904, Mo-K_α radiation (λ=0.7093 Å), μ(Mo-K)=1.12 cm^{-1}. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $h0\ell$ when $\ell \neq 2n$, $0k0$ when $k \neq 2n$.

Crystallographic Measurements: A single crystal of dimensions *ca.* 0.16 x 0.21 x 0.88 mm was oriented on a Picker four-circle diffractometer equipped with graphite monochromater (Mo-K_α radiation; 1° take-off angle). Refined unit-cell parameters were obtained by least-squares treatment of the 2θ, χ and φ angles for 12 accurately centered high order reflections widely separated in reciprocal space. Intensities for 4692 unique reflections having 3°<2θ<55° were collected by the θ-2θ scanning technique. The data reduction procedure of Corfield *et al.*[12] was followed, yielding 2122 reflections used in the structure analysis.

Structure Analysis: The structure was solved by direct phase-determining methods with the MULTAN 76 series of programs[13] and 350 reflections. The *E*-map based on that set of phases having the lowest *R* and one of the highest absolute figures of merit revealed the positions of all the non-hydrogen atoms. Atomic positions[14] and non-hydrogen-atom anisotropic thermal parameters[14] were refined by full-matrix least-square calculations to convergence at *R*0.057 ($R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$). Bond lengths (Å) and valency angles (°) and torsional angles (°) for 1.HPic are shown in Figs. 1 and 2, respectively; e.s.d.'s for the bond lengths are shown in parentheses, those for the valency and torsional angles are in the range 0.3 - 0.4°.

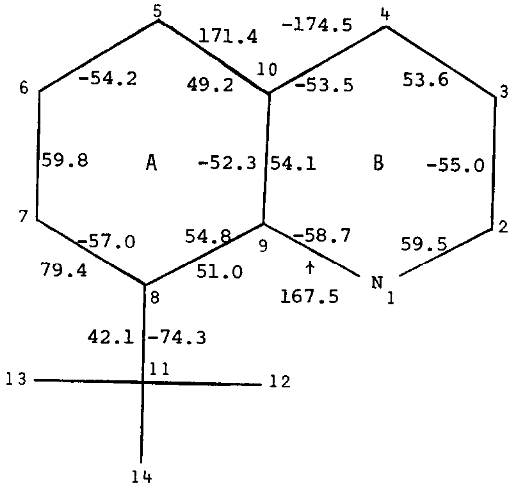
Discussion: The A ring of 1.HPic is clearly in the chair form with axial *t*-butyl; the overall distortion of this ring is surprisingly small. The mean endocyclic torsion angle in the A ring, 54.6° is intermediate between that (53.0°) of the more flattened chair predicted by empirical force field calculation (SFF) for axial *t*-butylcyclohexane[15] and the more normal value of 55.9° for cyclohexane.[16] Flattening may be restrained by the adjacent *trans*-fused B ring.

In order to minimize severe non-bonded interactions between the *t*-butyl group and the axial hydrogens on N(1), C(6) and C(10), the *t*-butyl substituent deviates from a perfectly staggered arrangement relative to the ring (Fig. 3) exhibiting a twist of 16.2°. This value agrees perfectly with the corresponding twist of 16.3° calculated (SFF)[15] for the diaxial chair conformer of *trans*-1,2-di-*t*-butylcyclohexane and closely with the value of 17.4° found in the crystal structure[9] of the diaxial *trans*-1,2-bis[(2-methoxycarbonyl)-2-propyl]cyclohexane (CMe_2CO_2Me analog), but is somewhat smaller than the 20.9° calculated (SFF)[15] for axial *t*-butylcyclohexane and a value of 24.2° recently calculated (SFF) for 1-α(axial)-*t*-butyl-*trans*-decalin.[24]



C(8)-C(11)-C(14)	114.7
C(12)-C(11)-C(13)	104.9

Figure 1



C(7)-C(8)-C(9)-N(1)	-175.9
C(11)-C(8)-C(9)-C(10)	-78.4
C(7)-C(8)-C(11)-C(12)	157.4
C(7)-C(8)-C(11)-C(14)	-81.0
C(9)-C(8)-C(11)-C(13)	170.4
C(9)-C(8)-C(11)-C(14)	47.4
N(1)-C(9)-C(10)-C(5)	176.3
C(8)-C(9)-C(10)-C(4)	-174.5

Figure 2

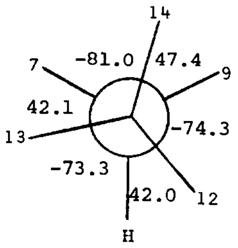


Figure 3

Further relief from steric crowding is accomplished by opening of the exocyclic valency angles at C(8) to 121.6° and 115.8°, with concomitant diminution of the endocyclic valency angle [at C(8)] to 104.4°, and by enlargement of the C(14)-C(quaternary)-C(ring) valency angle[17] to 115.7° with corresponding reduction of the C(12)-C(quaternary)-C(13) valency angle to 104.9°. Such large valency angle deformations are normally not found in cases[18-22] where the *t*-butyl group is equatorial. However, the C(ring)-C(quaternary) bond length of 1.564 Å, while longer than the normal C(sp^3)-C(sp^3) distance[23] of 1.537 Å, is comparable to values predicted (SFF)[15] and observed[18-22] for rings bearing equatorial *t*-butyl groups. Of note also is the large endocyclic valency angle at C(9) (118.1°); the mean carbon-carbon bond length (1.526 Å) and the mean endocyclic valency angle at carbon (111.2°) are normal.

Interestingly, the deformation in 1 appears to be substantially different from that in the previously studied[10] 2-*t*-butylalkylidenecyclohexane in which strain is mainly relieved by flattening of the ring and outward bending of the *t*-butyl group plus lengthening of the C_{ring}-C_{quat} and shortening of the C_{quat}-C_{Me} bonds. This may in part be a reflection of the much greater deformability of the alkylidenecyclohexane structure as compared to 1 plus a low stretching force constant in the allylic bond.

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