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THE CONFORMATION OF 4-t-BUTYLCYCLOHEPTANONE

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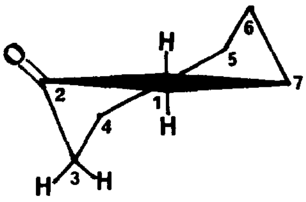
Summary: *The 400 MHz ^1H NMR spectra of two deuterated derivatives of 4-t-butylcycloheptanone (2 and 3) provided $^2J_{HH}$ values for the α-methylene protons on each side of the carbonyl group. The interpretation of their magnitude shows clearly that the carbonyl group is located at position 1 of the twist-chair conformation while the t-butyl group is located at position 4e.*

Compared to cyclohexanone and cyclooctanone, very little experimental information is available concerning the conformational properties of cycloheptanone and its derivatives[1-4]. Recently[1] we reported 100 MHz ^1H NMR results showing that the ring conformation of *gem*-dimethyl derivatives of cycloheptanone has the twist-chair geometry with the carbonyl group location at position 2(*i.e.* TC-2) (1). A similar conclusion was reached for cycloheptanone itself from the analysis of its vibrational spectra[2]. We now wish to report ^1H NMR results for 2 and 3 at 400 MHz which reveal that the stable ring conformation of 4-t-butylcycloheptanone has the TC-1 form in which the carbonyl group is located at position 1 instead of at position 2.



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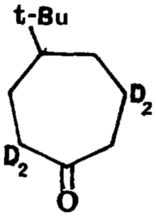

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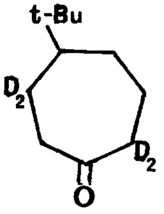

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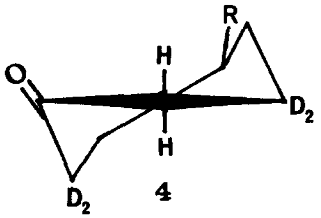
Geminal coupling constants ($^2J_{HH}$) for α-methylene groups were selected as the conformational probe[1,5] for the carbonyl group environment and the t-butyl substituent was chosen because it is the one most likely to lead to a single conformation for a monosubstituted cycloheptanone.

The 100 MHz deuterium decoupled ^1H NMR spectra of CHF_2Cl solutions of 2 and 3 showed all the expected signals compatible with their structure; it was also observed that the α-methylene protons gave singlets instead of AB patterns because of unfavorable $\Delta\nu/J$ ratios. On the other hand, the spectra recorded at 400 MHz with deuterium decoupling revealed well resolved AB patterns for each compound from which the following parameters were obtained: $^2J_{HH} = -15.5 \pm 0.1$ Hz and $\Delta\nu = 22.5$ Hz for 2; $^2J_{HH} = -15.6 \pm 0.1$ Hz and $\Delta\nu = 30.7$ Hz for 3. In addition, the upfield half of the AB pattern of 2 showed a long range coupling constant of 0.9 Hz. Surprisingly, the 400 MHz spectrum of a $CDCl_3$ solution of 2 gave a collapsed AB pattern (singlet) for the α-CH_2 signal.

Reference parameters characterizing the protons at position 1 of the TC-2 conformation (*i.e.* 1-α-CH_2) and the 3-α-CH_2 protons are $^2J_{HH}$ = 15-16 Hz and $^2J_{HH}$ = 11-12 Hz respectively[1,6]. (The absolute values of $^2J_{HH}$ are used here and in the following part of the text).

If the 4-t-butylcycloheptanone ring adopted the TC-2 form of cycloheptanone as would be expected if the conformational preference of the carbonyl group determined the nature of the most stable conformation, then two forms with the t-butyl group in equatorial-like positions are possible for compound 2 (*i.e.* TC-2,5e (4) and TC-2,6e (5) where the first number indicate the location of the carbonyl group and the second that of the substituent). The expected $^2J_{HH}$ values for 4 and 5 are then about 15.5 and 11.0 Hz respectively[1,6]. *Consequently only the* TC-2,5e form is compatible with the experimental value of 15.5 Hz.



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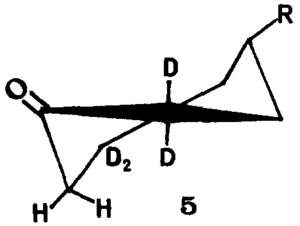

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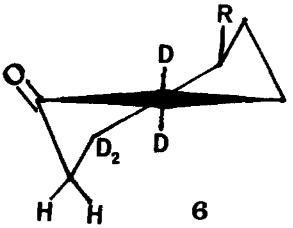
The possible forms for compound 3, obtained by an exchange of the isotope positions in 2, are TC'-2,5e (6) and TC'-2,6e (7). We now see that if TC-2,5e was the conformation of 4-t-butylcycloheptanone, then the α-methylene protons of 3 would be located at position 3 as in 6 and should show a $^2J_{HH} \approx 11.0$ Hz instead of the 15.6 Hz observed. Clearly the TC'-2,5e (or TC-2,5e) *conformation must be ruled out and similar arguments rule out TC-2,6e as the sole conformation.*



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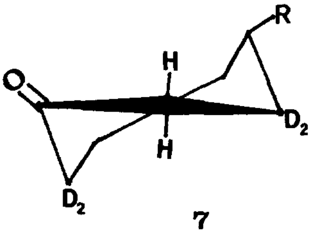

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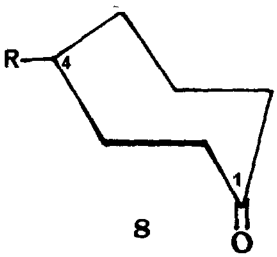
The existence of a rapidly equilibrating mixture of TC-2,5e and TC-2,6e (or more precisely its mirror image TC^*-2,6e) forms is also incompatible with the results for 2 and 3. If this were the case, the average $^2J_{HH}$ values would depend on the proportion of each conformer. Therefore the high predominance of one form must be rejected from the previous arguments and an essentially equivalent amount of each form in equilibrium would lead to an averaged $^2J_{HH}$ of about 13.5 ± 1 Hz which again is incompatible with our experimental values for 2 and 3.

As alternative we can consider conformations 8 (C-1, 4e)and 9 (TC-1,4e) each of which has both α-CH_2 groups in very similar relationships with respect to the carbonyl group. Of these possible conformations, 8 is expected to be most unfavorable because the t-butyl group is eclipsed by an adjacent proton at position 5. On the other hand, conformation 9 allows the bulky substituent to take an equatorial-like position and furthermore allows the carbonyl group to adopt position 1 of the twist-chair form which was calculated[7] to be only slightly more energetic than position 2. The dihedral angles (Θ) between each α-CH_2 group of 9 should be essentially equal and were calculated[1] to be about -5° for which a $^2J_{HH}$ value of about 15-16 Hz is expected[5] in excellent agreement with our observations for 2 and 3. On the other hand, the dihedral angle estimated for 8 from molecular models suggests that $^2J_{HH}$ ought to be less than 15 Hz. It therefore appears that 8 can be rejected and that 9 is the most stable conformation of 4-t-butylcycloheptanone. However, small amounts of TC-2,5e and/or TC-2,6e forms cannot be excluded by the present data.



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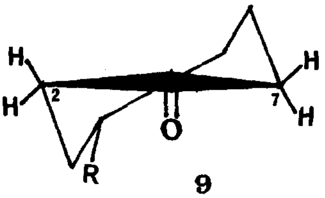

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It is also pertinent to point out that the TC-1,4e form is the twist-chair form intermediate between TC-2,5e and TC*-2,6e on the pseudorotation itinerary[2,8] for the interconversion of these two latter forms. Consequently, the TC-1,4e form would represent the minimum on the interconversion energy profile. But because the local environment of the t-butyl group is similar in both TC-1,4e and TC-2,5e, it is difficult to explain or rationalize at this time the subtle conformational change detected in the cycloheptanone ring.

Further work on compounds 2 and 3 is planned and NMR investigations of other cycloheptanone derivatives are in progress.

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