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2,5-DI-t-BUTYL-7-CYANONORCARADIENE IN EQUILIBRIUM WITH THE CYCLOHEPTATRIENE FORM: THE FIRST OBSERVATION OF *exo* AND *endo* ORIENTATION OF THE 7-CYANO SUBSTITUENT IN THE NORCARADIENE FORM

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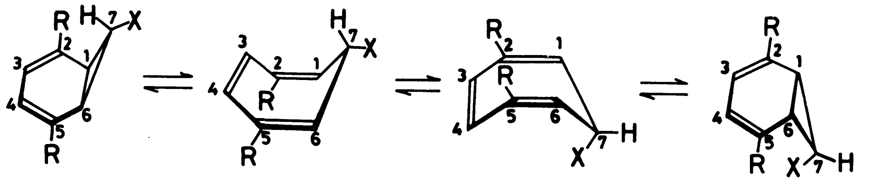
The ^{1}H NMR study showed that the *endo*-cyano isomer of the title compound is slightly more stable than the *exo*-cyano isomer with a population ratio of 22:17 at -120°C. In the cycloheptatriene form, the *axial*-cyano conformer is much less stable than the *equatorial* counterpart with a ratio of 1.7:59. The results can account for the marked stabilization in *syn*-11-cyanotricyclo[4.4.1.0]undeca-2,4-diene by the *syn*-cyano group.

The cyano, carboxyl, and formyl substituents at C(7) of 1,3,5-cycloheptatriene are typical ones which shift the equilibrium between the cycloheptatriene (CHT) and norcaradiene (NCD) forms to the NCD side, with the order of their effectiveness being CN < COOH < CHO.1,2) Previously, Günther and his coworkers reported that the COOH3) and CHO2) groups assume an *exo* position in the NCD forms (1-*exo* and 2-*exo*). The preferred *exo* orientation of these substituents has been interpreted to show that the $2p_z$ orbital of the carbonyl carbon in this orientation can overlap with the Walsh orbital of the cyclopropane ring, whereas it is difficult in the *endo* orientation (1-*endo* and 2-*endo*) for steric reasons.2,3,4) On the other hand, such a structural study has long been impossible in *exo*- and *endo*-7-cyanonorcaradienes (3-*exo* and 3-*endo*) since the equilibria among the four species of 3 lie so far to the CHT forms, and therefore, the NCD forms can not be detected by NMR.3,5,6)

Previously, we have shown that the introduction of two t-butyl groups to the 2- and 5-positions of various cycloheptatriene derivatives markedly shifts the



1: X=COOH, R=H	1-*exo*	1-*eq*	1-*ax*	1-*endo*
2: X=CHO, R=H	2-*exo*	2-*eq*	2-*ax*	2-*endo*
3: X=CN, R=H	3-*exo*	3-*eq*	3-*ax*	3-*endo*
4: X=CN, R=t-Bu	4-*exo*	4-*eq*	4-*ax*	4-*endo*

equilibrium to the NCD sides.[7,8,9] We now report that 2,5-di-t-butyl-7-cyanocycloheptatrienes (**4**-*eq* and **4**-*ax*) exist in equilibrium with the NCD forms (**4**-*exo* and **4**-*endo*) and that their populations are determined by the low temperature NMR technique. This is the first observation of the two NCD structures containing a cyano group as the sole substituent on the 7-position.

The compound **4** (liquid) was obtained in 14% yield by treatment of 1,4-di-t-butyltropylium perchlorate[7] with sodium cyanide in acetonitrile, followed by separation from other isomers by HPLC. The ^{1}H NMR (99.55 MHz) spectra at 25 and -120°C are shown in the Figure. At -120°C the existence of the two NCD forms (**4**-*exo* and **4**-*endo*) is clearly demonstrated. The triplets at δ 0.37 (J = 4.3 Hz) and 2.15 (J = 8.4 Hz) observed at -120°C are assigned to H(7) of **4**-*exo* and that of **4**-*endo*, respectively, by comparing the coupling constants with those for cyclopropanecarbonitrile.[10] Integration of the H(7) signals permits the assignment of the signals at δ 5.65 and 5.87 to H(3,4) of **4**-*exo* and that of **4**-*endo*, respectively. The strong triplet at δ ca. 2.6 (partly overlapped by the H(1,6) signals of the two NCD forms) and the strong singlet at δ 6.83 are assigned to H(7) and H(3,4) of **4**-*eq*, respectively. The weak triplet at δ 4.06 (J = 8.5 Hz) and the weak singlet at δ 6.95 are reasonably assigned to H(7) and H(3,4) of **4**-*ax*, respectively. Integration of the four H(3,4) signals which are exhibited by the four components affords the population ratio **4**-*exo* : **4**-*eq* : **4**-*ax* : **4**-*endo* = 17 : 59 : 1.7 : 22 at -120°C.

First, the most important, and rather unexpected result is that **4**-*endo* is slightly more stable than **4**-*exo*. This is in marked contrast to the case of **1** or **2**,

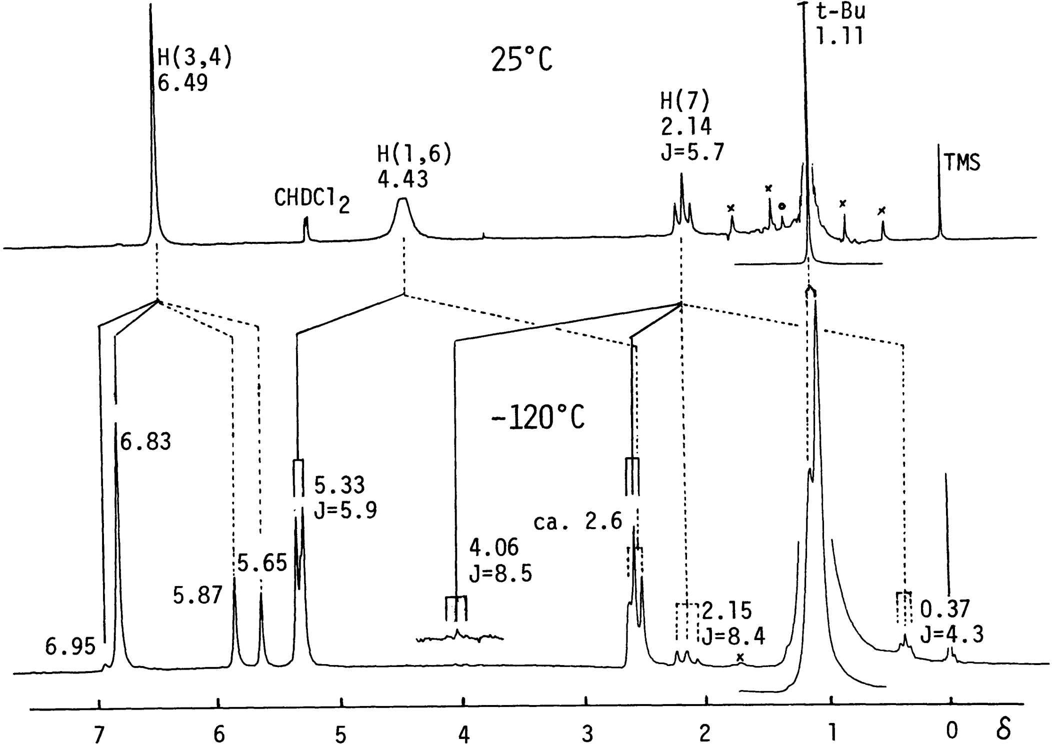


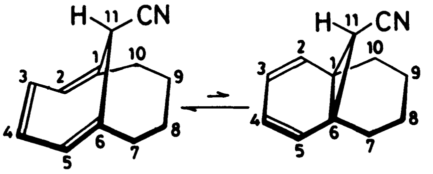
Figure. ^{1}H NMR (99.55 MHz) spectra recorded on a JEOL JNM FX100 for **4** (0.19 M) in CS_2-CD_2Cl_2 (3:1 by vol.) at 25 and -120°C. The solid and the dotted lines represent the signals assigned to the CHT and NCD forms, respectively. x; spinning side band and ^{13}C-H coupling satellite. o; unknown impurity.

where the NCD forms exist essentially with the substituent oriented *exo*. The comparable stabilities of 4-*exo* and 4-*endo* suggest that the through-space repulsion between the *endo*-CN group and the π-electrons of the C(2) and C(4) double bonds is negligibly small in 4-*endo*. However, it appears to be difficult to rationalize the slightly higher stability of 4-*endo*. A conclusion from an ab initio SCF MO (STO-3G) calculation on 3-*exo* and 3-*endo* as models was rather depressing. It showed that the total energy of 3-*endo* is higher than that of 3-*exo* by a few kJ mol^{-1}, and moreover, that the interaction between the *endo*-CN group and C(2,5) is slightly antibonding, although the interaction between the *endo*-CN group and C(3,4) is negligibly small. Thus, the subtle energy difference could not be rationalized; however, the observation that 4-*endo* is slightly more stable than 4-*exo* suggests that in the elusive norcaradienes, 3-*endo* and 3-*exo*, the former would be slightly more stable than the latter.11)

Secondly, the population ratio for 4-*eq* and 4-*ax* ([4-*eq*]/[4-*ax*] = 35 at -120 °C) is much larger than that for 3-*eq* and 3-*ax* ([3-*eq*]/[3-*ax*] = 3.9 at -132.5°C3,12) or 4.9 at -120°C13)). Possibly the t-butyl substituents at the C(2) and C(5) positions in 4 would interact with H(3) and H(4) to cause further bending of the cycloheptatriene ring, resulting in stronger through-space repulsion between the *axial*-CN group and the π-electrons of the C(3) double bond than in the absence of the two t-butyl groups.14)

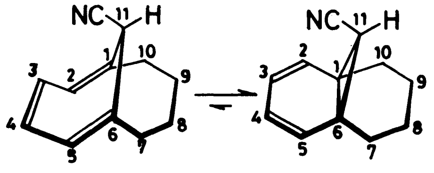
Consequently, it is suggested that (a) in various 7-cyanonorcaradienes the *endo*-cyano isomer is as stable as the *exo*-cyano isomer, or the former may be slightly more stable than the latter, and (b) in 7-cyanocycloheptatrienes the *axial*-cyano isomer is much less stable than the *equatorial*-cyano isomer, and the former is made exceedingly unstable by structural factors which cause further bending of the cycloheptatriene ring.

These simple conclusions can now account for the marked contrast in the function of the *syn* and the *anti* CN substituent on C(11) in bicyclo[4.4.1]undeca-1,3,5-triene. The parent hydrocarbon exists in the CHT form.15) Introduction of a CN group in the *anti* position as in 5 is insufficient to convert the structure to the NCD form, and 5 exists essentially as 5-CHT.15) In contrast, the introduction of a CN group in the *syn* position as in 6 markedly shifts the equilibrium to the NCD side, and 6 exists essentially as 6-NCD.15) The result of the present work suggests that the total energy of 5-NCD would be comparable to that of 6-NCD. On the other hand, 6-CHT is thought to be much more unstable than 5-CHT due to the through-space repulsion between the CN group and the π-electrons of the C(3) double bond. Inspection of molecular models suggests that this repulsion is stronger in the presence of the tetramethylene bridge than in its absence, owing to the increased



5-CHT 5-NCD

5



6-CHT 6-NCD

6

bending of the cycloheptatriene ring. Thus the equilibrium 6-CHT $\rightleftharpoons$ 6-NCD can be more shifted to the NCD side than the equilibrium 5-CHT $\rightleftharpoons$ 5-NCD. In other words, the systems 6 and 5 are analogous to the systems 4-*ax* $\rightleftharpoons$ 4-*endo* (K = 13 at -120°C) and 4-*eq* $\rightleftharpoons$ 4-*exo* (K = 0.29 at -120°C), respectively, in their equilibrium behavior.

The ^{13}C NMR spectra of 4 provided further evidence for the existence of the four components in the ratio described above. The result will be reported shortly in the full paper.

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