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DISTINCT OBSERVATION OF TWO CONFORMERS OF 7-CYANOCYCLOHEPTATRIENES CONTAINING A t-BUTYL GROUP AT 2- OR 3-POSITION: AN APPROACH TO VALID INTERPRETATION OF NMR SPECTRA OF CYCLOHEPTATRIENE DERIVATIVES

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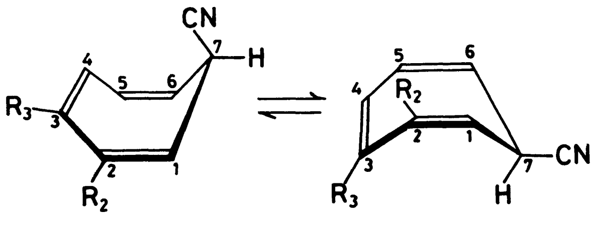
Introduction of a t-butyl group to the 2- or 3-position of 7-cyanocycloheptatriene facilitates the observation of the two conformers by ^1H and ^{13}C NMR at low temperatures. The chemical shift of *equatorial* H(7) and the equilibrium constant for the ring inversion with respect to 7-cyanocycloheptatriene have been reexamined and corrected.

The ring inversion process of cycloheptatriene derivatives is generally so rapid that considerably low temperatures as low as -150°C and the use of low-melting solvents such as vinyl chloride or ethyl chloride are usually required in NMR studies.[1] In such cases, especially in ^1H NMR studies, complication of the spectra due to solvent signals is inevitable, and this might lead to misinterpretation of the spectra. In order to avoid such complication the use of ordinary solvents such as CS_2-CD_2Cl_2 mixtures at as low as -120°C is often desired.[2] Unfortunately, however, the ring inversion of many simple cycloheptatriene derivatives can not be frozen out at this temperature.[1,3,4]

We now wish to report that the structural modification of 7-cyanocycloheptatriene (**1**) by introducing a t-butyl group to the 2- or 3-position decelerates the ring inversion process, probably due to increased torsional strain in the transition state. This technique permitted the observation of the signals ascribed to the two cycloheptatriene forms by use of a 100 MHz ^1H or 25 MHz ^{13}C NMR instrument at -125°C, and gave a clue to correction of the chemical shift of H(7) in **1a** and the equilibrium constant ([**1e**]/[**1a**]) which had been reported previously.[1c]



1: R_2=R_3=H	**1a**	**1e**
2: R_2=t-Bu, R_3=H	**2a**	**2e**
3: R_2=H, R_3=t-Bu	**3a**	**3e**

The compounds 2- and 3-t-butyl-7-cyanocycloheptatrienes (**2** and **3**, respectively) were obtained as liquids by the reaction of t-butyltropylium perchlorate with sodium cyanide in acetonitrile followed by separation by HPLC, and their ^{1}H (99.55 MHz) and ^{13}C (25.00 MHz) NMR spectra measured in CS_2-CD_2Cl_2 (3:1 by vol.). The ^{1}H signals of H(7) and the ^{13}C signals of C(1) ∿ C(6) and the cyano carbon are shown in the Figure for the three equilibrating systems **1**, **2**, and **3**. As the temperature is lowered the H(7) signal of each system shows line broadening, and after passing a coalescence point it splits into an intense signal at δ ca. 2.6 and a weak one at δ ca. 4.2. The former signal is assigned to *axial* H(7) and the latter one to *equatorial* H(7).[7] At -125°C **2** and **3** show a distinct triplet of *equatorial* H(7) at δ 4.22 (J = 8.4 Hz) and 4.20 (J = 8.4 Hz), respectively, whereas **1** shows a broadened signal centered at δ 4.19.

In 1970, Bushweller et al. examined the ^{1}H NMR spectra (60 MHz) of **1** in vinyl chloride solvent at -155°C and assigned the two signals appearing at δ 2.58 (strong triplet) and at δ 3.21 (weak triplet) to *axial* and *equatorial* H(7), respectively.[1c] From integration of the two signals they obtained an equilibrium constant ([**1e**]/[**1a**]) of 28 ± 2 at -155°C.[1c] In 1975, Wehner and Günther reexamined this system by ^{13}C NMR (22.6 MHz) in ethyl chloride solvent at -132.5°C and reported an equilibrium constant of 3.9.[1d] Although the two values were interpreted to be "in fair agreement",[1d] the present result suggests that the weak triplet at δ 3.21 observed in the ^{1}H NMR spectra by Bushweller et al.[1c] was most probably a spinning side band signal and was erroneously assigned to *equatorial* H(7). In the present study, the equilibrium constant calculated by use of the two H(7) signals at δ 2.54 and 4.19 exhibited by **1** (Figure) is 4.9 ± 0.3 at -128°C, which agrees well with Günther's result.[8] It is presumed that in Bushweller's measurement the real *equatorial*-H(7) signal at δ 4.19 was overlooked, being masked by the ^{13}C-H satellite signals of vinyl chloride which are expected to appear at δ 4.05 and 4.13 in a measurement at 60 MHz.[9]

The ^{13}C NMR spectra also showed a characteristic dependence of line-shape on the temperature, which is expected in the systems undergoing ring inversion (Figure).[10] In both of **2** and **3** the olefinic carbons — except C(3) and C(4) — and the cyano carbon exhibit splitting at -125°C. In contrast, the signals of **1** merely undergo line broadening at -125°C in harmony with Wehner and Günther's observation.[1d] The downfield shifts of the C(1) and C(6) signals of **2** and **3** by 3 ∿ 6 ppm on lowering the temperature from 25°C to -125°C suggest that the cycloheptatriene forms are in equilibrium with small amounts of the norcaradiene forms, although we were unable to obtain any other supporting evidence.

In conclusion, the introduction of a t-butyl group to the 2- or 3-position of a cycloheptatriene derivative presents a promising approach to obtaining reliable evidence and information on the ring inversion equilibrium. On the other hand, the introduction of two[11,12] or more[13] t-butyl groups often transform a cycloheptatriene structure to a norcaradiene structure. Application of these techniques to other cycloheptatriene derivatives is in progress.

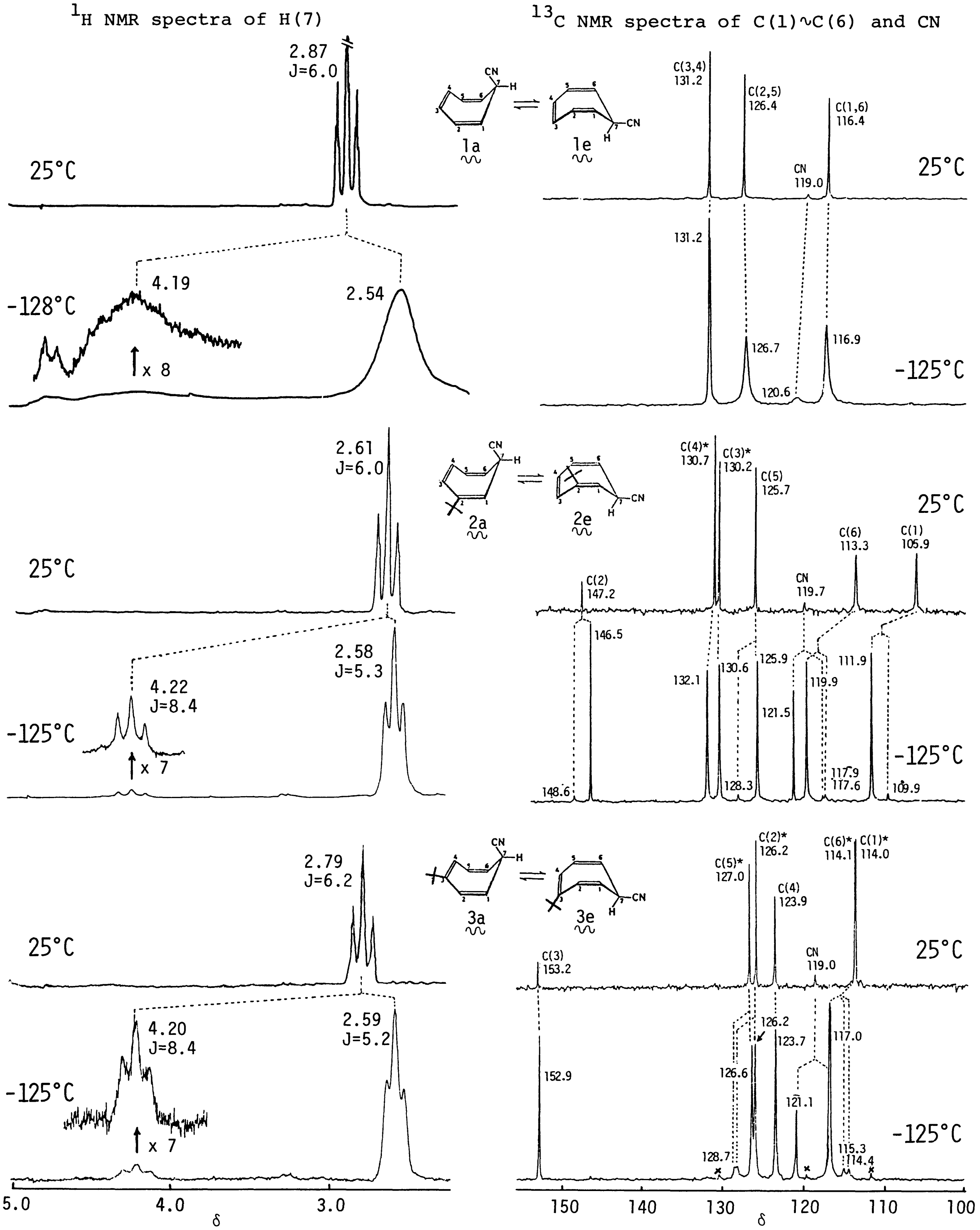


Figure. ^{1}H (99.55 MHz) and ^{13}C (25.00 MHz) NMR spectra of 7-cyanocycloheptatriene (**1**), 2-t-butyl-7-cyanocycloheptatriene (**2**), and 3-t-butyl-7-cyanocycloheptatriene (**3**) in CS_2-CD_2Cl_2 (3:1 by vol.). x; signals due to **2** as contamination. *; interchangeable.

References

1) For leading references, see; a) F. A. L. Anet, J. Am. Chem. Soc., 86, 458 (1964); b) F. R. Jensen and L. A. Smith, ibid., 86, 956 (1964); c) C. H. Bushweller, M. Sharpe, and S. J. Weininger, Tetrahedron Lett., 453 (1970); d) R. Wehner and H. Günther, J. Am. Chem. Soc., 97, 923 (1975); e) M. Balci, H. Fischer, and H. Günther, Angew. Chem., 92, 316 (1980).

2) The lowest temperature which is attainable with ease by a commercial instrument is generally in the range -100°C ∿ -130°C. In order to obtain the temperatures as low as -150°C, special precautions and some modifications of the instrument are required.

3) a) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, J. Am. Chem. Soc., 87, 3896 (1965); b) H. Günther, M. Görlitz, and H.-H. Hinrichs, Tetrahedron, 24, 5665 (1968); c) F.-G. Klärner, Tetrahedron Lett., 19 (1974).

4) It is known that 2-t-butyl-3,7,7-trimethylcycloheptatriene5) and 7-t-butyl-1-methylcycloheptatriene6) undergo relatively slow ring inversion, and the two conformers have been distinctly observed in each case at about -100°C by ^{1}H NMR at 60 or 100 MHz.

5) K. Conrow, M. E. H. Howden, and D. Davis, J. Am. Chem. Soc., 85, 1929 (1963).

6) W. E. Heyd and C. A. Cupas, J. Am. Chem. Soc., 91, 1559 (1969) and 93, 6086 (1971).

7) The difference between the chemical shifts of the *equatorial* and *axial* hydrogens [$\Delta\delta_{H(7)}$] appears to be sensibly constant irrespective of the substituent at C(7); e.g., 1.3 ∿ 1.5 ppm for cycloheptatriene1a,1b) and 1.32 ppm for 7-formylcycloheptatriene1e). See also ref. 3b for the estimated chemical shifts of H(7) for 7-alkyl- and 7-phenyl-cycloheptatrienes, which afford a constant $\Delta\delta_{H(7)}$ value of 1.45 ppm.

8) Integrations of the ^{1}H NMR spectra at -125°C for **2a** $\rightleftarrows$ **2e** and **3a** $\rightleftarrows$ **3e** yield the equilibrium constants 16 ± 1 and 7.5 ± 0.2, respectively.

9) For NMR parameters of vinyl chloride, see; E. B. Whipple and Y. Chiang, J. Chem. Phys., 40, 713 (1964) and R. E. Mayo and J. H. Goldstein, J. Mol. Spectroscopy, 14, 173 (1964).

10) For assignments of the signals of **1**, see ref. 1d. The discussion on the assignments of the signals of **2** and **3** will be described in the full paper.

11) K. Takeuchi, T. Kitagawa, Y. Senzaki, H. Fujimoto, and K. Okamoto, Chem. Lett., 1983, 69.

12) a) K. Takeuchi, M. Arima, and K. Okamoto, Tetrahedron Lett., 22, 3081 (1981); b) K. Takeuchi, H. Fujimoto, and K. Okamoto, ibid., 22, 4981 (1981).

13) K. Takeuchi, T. Kitagawa, T. Toyama, and K. Okamoto, J. C. S. Chem. Commun., 1982, 313.

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