Tetrahedron Letters, Vol.22, No.32, pp 3081 - 3084, 1981
Printed in Great Britain

0040-4039/81/323081-04$02.00/0

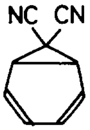
EFFECTS OF t-BUTYL SUBSTITUENTS ON VALENCE TAUTOMERISM OF 7-t-BUTYL-7-CYANO-1,3,5-CYCLOHEPTATRIENES TO THE NORCARADIENE FORM

Ken'ichi TAKEUCHI, Makoto ARIMA, and Kunio OKAMOTO*

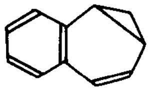
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan

Abstract. Introduction of t-butyl groups to the 2-, 3-, 2,4-, or 2,5-positions of 7-t-butyl-7-cyano-1,3,5-cycloheptatriene dramatically shifts the cycloheptatriene - norcaradiene equilibrium to the norcaradiene form. The nonbonded interaction is an important factor.

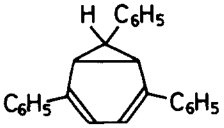
Cycloheptatriene - norcaradiene valence tautomerism is a long-standing subject which still arouses interest of organic chemists.[1,2] Several structural factors have been found to drive a cycloheptatriene (CHT) form to a norcaradiene (NCD) form, which are represented by the following examples.



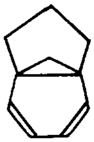
I



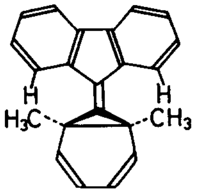
II



III



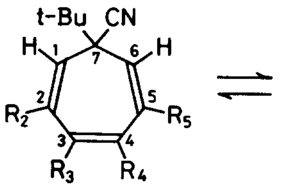
IV



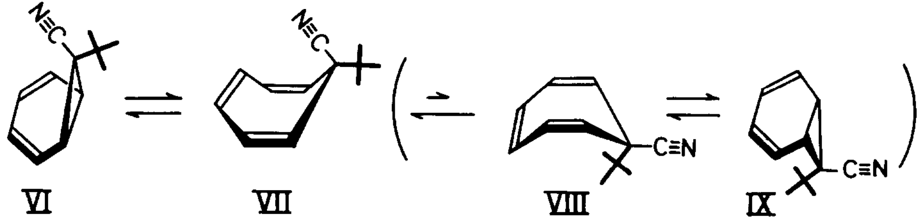
V

The factors can be classified into four categories: (a) placement of a π-acceptor group at the 7-position (I),[3] (b) extension of conjugation in the NCD form (II, III),[4,5] (c) forced shortening of C(1)-C(6) distance (IV),[6] and (d) steric destabilization of the CHT form (V).[7] Among these four factors, (a), (b), and (c) are well recognized in many examples. On the other hand, the steric factor (d) has been demonstrated only in V, and more examples are required for fundamental understanding of various CHT - NCD equilibria. In this communication we wish to describe a typical example in which the steric effect of substituents plays an important role in driving the equilibrium to the NCD form.

As model system, 7-t-butyl-7-cyano-1,3,5-cycloheptatriene has been selected, and the effect of t-butyl substituents at the 2-, 3-, 2,4-, or 2,5-positions on the CHT - NCD equilibrium examined by means of ^{1}H and ^{13}C NMR. In this system the 7-t-butyl group was expected to assume an equatorial conformation in the CHT form VII, on the one hand, and an *exo* position in the NCD form VI, on the other, for steric reasons, thereby complication caused by the incursion of different conformations, VIII and IX, being prevented.[8] Actually, this was substantiated by low temperature NMR studies (*vide infra*).



1 : $R_2=R_3=R_4=R_5=H$
2 : R_2=t-Bu; $R_3=R_4=R_5=H$
3 : R_3=t-Bu; $R_2=R_4=R_5=H$
4 : $R_2=R_4$=t-Bu; $R_3=R_5=H$
5 : $R_2=R_5$=t-Bu; $R_3=R_4=H$



All the compounds (1 - 5) were prepared by the cation - anion combination reaction of corresponding mono-, di-, or tri-t-butyltropylium perchlorates with cyanide ion (NaCN) in acetonitrile, followed by separation with HPLC. The ^1H and ^{13}C NMR chemical shift data are summariz in Table 1.

Table 1. The ^1H (99.55 MHz, CS_2-CD_2Cl_2 3:1 in vol.) and ^{13}C (25.00 MHz, $CDCl_3$) NMR chemical shifts (δ from internal TMS) and coupling patterns (J in Hz) of H(1), H(6), CH_3, C(1), and C(6) for 1 - 5.[a]

Temp. °C	^1H or ^{13}C	Compound 1[b]	 2[c]	 3[d]	 4[e]	 5[f]
25	$^1H(1)$	4.72(d) J=7.9	2.72(d) J=7.8	3.82-4.00[g]	2.43(d) J=8.4	2.36
	$^1H(6)$	4.72(d) J=7.9	2.59(dd) J=7.8,5.4	3.82-4.00[g]	2.31(dd) J=8.4,5.1	2.36
	^1H_3C	1.20	1.11 1.15	1.13 1.15	1.09 1.09 1.17	1.12 1.14 1.14
-110	$^1H(1)$	4.98(d) J=8.7	2.46(d)[h] J=8.5	—[i]	2.34(d) J=8.7	2.37
	$^1H(6)$	4.98(d) J=8.7	2.32(dd)[h] J=8.5,4.8	—[i]	2.24(dd) J=8.7,4.9	2.37
	^1H_3C	1.20	1.11[h] 1.15[h]	1.13(s)	1.05 1.09 1.16	1.14(s)
25	$^{13}C(1)$	99.5	38.4[j]	75.1[j]	30.9[j]	29.5
	$^{13}C(6)$	99.5	37.7[j]	75.3[j]	30.5[j]	29.5

(a) All new compounds gave spectral data consistent with the proposed structure. The NMR spectra were recorded on a JEOL JNM FX100. (b) Mp 86.5-88.0 °C. (c) Liquid. (d) Mp 95.0-96.2 °C. (e) Mp 62.0-63.0 °C. (f) A solid mixture of 5 (70%) and 4 (30%): difficult to separate with HPLC. (g) Complex multiplets. (h) The data at -125 °C; line broadening occured at -110 °C. (i) Line broadening occured without separation. (j) Interchangeable.

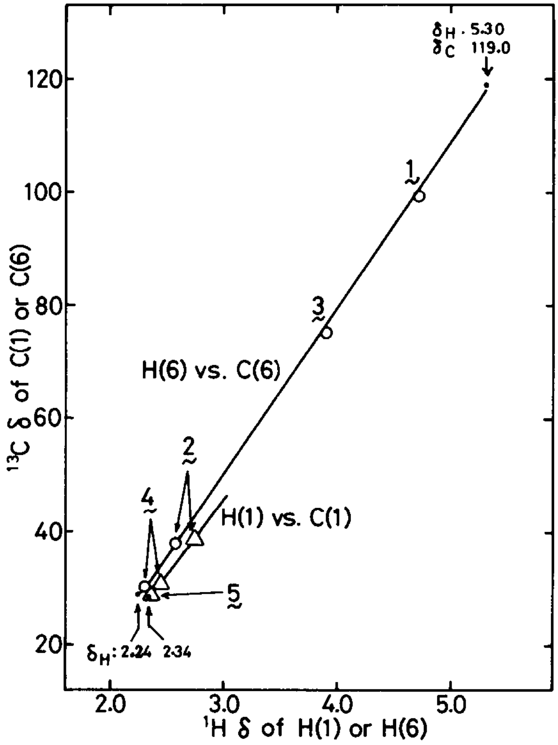


Figure. Plot of ^{13}C δ-value *vs.* ^1H δ-value for **1** - **5**. Open circle: H(6) *vs.* C(6) without t-Bu on C(5). Open triangle: H(1) *vs.* C(1) with t-Bu on C(2). Dot: estimated limiting value.

It is noted that a linear correlation holds between the time-averaged ^1H and ^{13}C NMR chemical shifts at 25 °C for each of the 1- and 6-positions (Fig.). This indicates that both the ^1H and the ^{13}C shifts can be utilized for calculating the populations of the tautomers at 25 °C, if the corresponding chemical shift data for the pure CHT and NCD forms become available.

Unfortunately, neither the ^1H nor the ^{13}C chemical shifts for the 1- and 6-positions of the pure CHT forms could not be determined by low temperature (-110 °C) NMR studies. Therefore, these values have been estimated by postulating additivity of the substituent-induced chemical shifts of the t-butyl and cyano group at the 7-position. Thus the ^1H δ-value for H(1,6) of VII is estimated to be 5.30 [= 5.18 + (5.40 - 5.28)] from the corresponding δ-values of cycloheptatriene (5.28), 7-cyanocycloheptatriene (5.40), and 7-t-butylcycloheptatriene (5.18), all of which are known to exist in the CHT form.[2d,8,10] This δ-value (5.30) was assumed to be applicable to H(6) of the CHT form of **2**, **3**, or **4**. When a t-butyl substituent is present at the 2-position as in **2**, **4**, or **5**, the ^1H δ-value for H(1) of the CHT form is estimated to be 5.42 by referring to the fact that H(1) is more deshielded than H(6) in **4** by 0.12 ppm. Similarly, the ^{13}C δ-value for C(1,6) of VII is estimated to be 119.0 [= 123.5 + (115.9 - 120.4)] from those of cycloheptatriene (120.4), 7-cyanocycloheptatriene (115.9), and 7-t-butylcycloheptatriene (123.5). The validity of these limiting δ-values [5.30 for $^1H(6)$ and 119.0 for $^{13}C(6)$] for the CHT form is supported by the finding that the values can be accomodated in the plot of the Figure.

A low temperature ^1H NMR spectrum of **4** in CS_2 - CD_2Cl_2 at -110 °C gave the δ-values of 2.34 and 2.24 for H(1) and H(6), respectively. A similar study on **5** afforded the δ-value of 2.37 for H(1,6), which is essentially invariant at 25 °C, suggesting that **5** exists virtually in the NCD form at 25 °C. The marked coincidence of the δ-values for H(1) of **4** and **5** (2.34 *vs.* 2.37) at -110 °C indicates that the above mentioned δ-values, 2.34 and 2.24, can be taken as those for H(1) and H(6), respectively, of the pure NCD form of **4**. In the following calculations of NCD %, it was postulated that the limiting values (2.34 and 2.24) can be applied to all of **1** - **5**. Furthermore, no indication for splitting of 7-t-butyl signals has been obtained at -110 °C for all the compounds (**1** - **5**), indicating that the 7-t-butyl group is fixed at the *exo* position in the NCD form.

By using these ^1H δ-values assigned to H(1) and H(6) of the CHT and NCD forms, the compositions (NCD %) and ΔG (= G_{CHT} - G_{NCD}) values have been calculated (Table 2). Notably, the

Table 2. NCD % and ΔG values for 1 - 5 at 25 °C.

	Compound				
	1	2	3	4	5
NCD %	19.0[a]	88.6[a],87.7[b]	46±3[a]	97.7[a],97.1[b]	99.4[b],100[c]
ΔG/kcal mol^{-1} [d]	-0.9	+1.2	-0.1	+2.1	+3.4

(a) NCD % = 100 x [5.30 - δH(6)]/(5.30 - 2.24). (b) NCD % = 100 x [5.42 - δH(1)]/(5.42 - 2.34). (c) NCD % = 100 x [5.42 - δH(1)]/(5.42 - 2.37). (d) ΔG = G_{CHT} - G_{NCD}; calculated by use of averaged NCD %.

substitution of a t-butyl group for H(2) of 1 increases the population of the NCD form from 19% to 88%. Further substitution for H(4) or H(5) affords essentially pure NCD forms 4 and 5. A comparison of the ΔG values indicates that the introduction of a t-butyl group to the 2- or 3-position shifts the equilibrium to the NCD form by 2.1 or 0.8 kcal mol^{-1}, respectively.

Klärner examined the effect of a methyl substituent at the 1-, 2-, or 3-position on the CHT - NCD equilibrium of the 7-carbomethoxy-7-methylcycloheptatriene system, and concluded that the NCD form is stabilized in the order 1-CH_3 < H < 3-CH_3 < 2-CH_3.[11] It has also been shown that 2,7-dimethyl-7-cyanocycloheptatriene is composed of 80% CHT and 20% NCD forms at -120 °C.[11] The enormous effect of the 2-t-butyl substituent of 2,7-di-t-butyl-7-cyanocycloheptatriene 2 to shift the equilibrium to the NCD form, as compared with the case of 2,7-dimethyl-7-cyanocycloheptatriene, is best explained by postulating destabilization of the CHT form due to nonbonded interaction between the 2-t-butyl group and H(1), which is relieved in the NCD form. Similarly, the effect of the 3-t-butyl group in 3 would be explicable by postulating the relief of the nonbonded interaction between the 3-t-butyl and H(4) due to bond alternation on structural change from the CHT to the NCD form. Inspection of molecular models supports the interpretations.

References and notes

1. For reviews, see; a) G. Mair, Angew. Chem., 79, 446 (1967); b) W. J. le Noble, "Highlights of Organic Chemistry", Marcel Decker, Inc., New York, 1974, p. 402.
2. For recent papers in this field, see for example; a) S. W. Staley, M. A. Fox, and A. Cairncross, J. Amer. Chem. Soc., 99, 4524 (1977); b) P. M. Warner and S.-L. Lu, ibid., 102, 331 (1980); c) D. M. Hayes, S. D. Nelson, W. A. Garland, and P. A. Kollman, ibid., 102, 1255 (1980); d) M. Balci, H. Fischer, and H. Günther, Angew. Chem., 92, 316 (1980).
3. E. Ciganek, J. Amer. Chem. Soc., 87, 652, 1149 (1965) and 89, 1454 (1967).
4. W. von E. Doering and M. J. Goldstein, Tetrahedron, 5, 53 (1959).
5. T. Mukai, H. Kubota, and T. Toda, Tetrahedron Lett., 3581 (1967).
6. E. Vogel, W. Wiedemann, H. Kiefer, and V. F. Harrison, ibid., 673 (1963).
7. a) H. Prinzbach, U. Fischer, and R. Cruse, Angew. Chem., 78, 268 (1966); b) H. Prinzbach and U. Fischer, Helv. Chim. Acta, 50, 1692 (1967).
8. The t-butyl group of 7-t-butylcycloheptatriene is known to assume equatorial conformation: see; a) H. Günther, M. Görlitz, and H.-H. Hinrichs, Tetrahedron, 24, 5665 (1968); b) H. Kessler and E. Müller, Z. Naturforsch., 22b, 283 (1967); c) W. E. Heyd and C. A. Cupas, J. Amer. Chem. Soc., 93, 6086 (1971).
9. The new perchlorates, 1,3-di-t-butyltropylium [mp 204.0 °C (dec.)], 1,4-di-t-butyltropylium (mp 172.0-173.0 °C), and 1,3,5-tri-t-butyltropylium (mp 195.5-196.0 °C) perchlorates were prepared by treating corresponding t-butylated tropilidenes with trityl perchlorate. The tropilidenes were obtained by ring-enlargement of corresponding t-butylated benzenes with diazomethane.
10. F. R. Jensen and L. A. Smith, J. Amer. Chem. Soc., 86, 956 (1964).
11. F.-G. Klärner, Tetrahedron Lett., 19 (1974).

(Received in Japan 2 May 1981)