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STRUCTURAL EFFECTS ON VALENCE TAUTOMERISM. VII. AN NMR AND MOLECULAR MECHANICS STUDY OF THE STERIC EFFECTS OF t-BUTYL SUBSTITUENTS ON THE CYCLOHEPTATRIENE-NORCARADIENE EQUILIBRIUM OF 7-CYANO-7-METHYLCYCLOHEPTATRIENE[1]

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Abstract - 7-Cyano-7-methylcycloheptatrienes containing one t-butyl group on the 1-position (2) or two t-butyl groups on the 1- and 3-, 1- and 4-, or 1- and 5-positions (3, 4, or 5, respectively) were synthesized and their cycloheptatriene (CHT) - norcaradiene (NCD) equilibria measured by variable-temperature ^{1}H NMR for CS_2-CD_2Cl_2 solutions. The ^{1}H NMR chemical shifts of the 7-methyl group indicate that these compounds are composed of essentially one CHT and one NCD tautomer with an endo geometry of the methyl group. The introduction of a t-butyl group at the 1-position of 7-cyano-7-methylcycloheptatriene (1) markedly shifts the equilibrium to the NCD side and the addition of the second t-butyl group further favors the NCD form, with the NCD populations for 2, 3, 4, and 5 at 25 °C 70.9, 96.5, 92.3, and 99.3%, respectively. An application of molecular mechanics (MMPI) calculations to various t-butylated CHT-NCD systems suggests that the t-butyl groups sterically destabilize the CHT form more than the NCD form, bringing about increased NCD populations.

The valence tautomerism between 1,3,5-cycloheptatriene (CHT) derivatives and their bicyclo[4.1.0]-hepta-2,4-diene (norcaradiene, NCD) isomers has long attracted attention of experimental[2] and theoretical[3] chemists. This tautomerism is now regarded as a typical example of the electrocyclic rearrangement.[4] Recently, the synthesis of the parent NCD (C_7H_8) and its rapid transformation into CHT have been reported.[5] The equilibrium between these two tautomers, however, lies so far to the CHT side to such an extent as to prevent the spectroscopic detection of NCD in equilibrium with CHT.[5,6] Recent ab initio calculations on the parent system have suggested that the enthalpy of NCD be 5.5 kcal mol^{-1} greater than that of CHT.[3d,e]

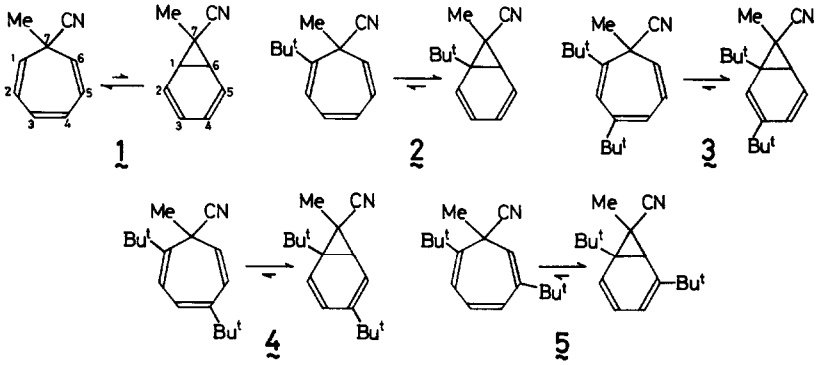
However, the equilibrium can be shifted to the NCD side by various factors.[2] The most extensively studied one is the effect of a π-acceptor substituent at the 7-position, such as cyano,[7] ethynyl,[1] formyl,[8] carboxyl,[9] alkoxycarbonyl,[10] aryls,[10c,11] phosphoryl,[12] or cationic carbon.[13] This effect has been of theoretical[3a,b] and structural[14] interests in connection with the increased stabilization of cyclopropane derivatives containing a π-acceptor substituent.[15]

The steric effect of an axially oriented methyl group at the 7-position to shift the equilibrium to the NCD side was pointed out by Tsuruta, Mori, and Mukai.[10d] They attributed the greater NCD population in 7-methyl-7-methoxycarbonylcycloheptatriene than in 7-methoxycarbonylcycloheptatriene to the through-space repulsion between the axial 7-methyl group and the C(3)-C(4) π-electrons. Takahashi, Takase, and Toda found that the NCD population in 7-alkyl-7-cyanocycloheptatrienes increases with the bulkiness of the 7-alkyl group.[7b] This was ascribed to destabilization of the CHT form due to the through-space repulsion between the equatorial 7-alkyl group and the hydrogen atoms at the 1- and 6-positions, which was supposed to cause further bending of the CHT structure.

The effects of substituents at the 2-, 3-, or 4-position have also been studied for the past decade. These include alkyls,[16] phenyl,[11a,17] chloro,[10b,12] bromo,[16a,b] and trifluoromethyl.[12b] It is known that these substituents shift the equilibrium to the NCD side, and the steric effect

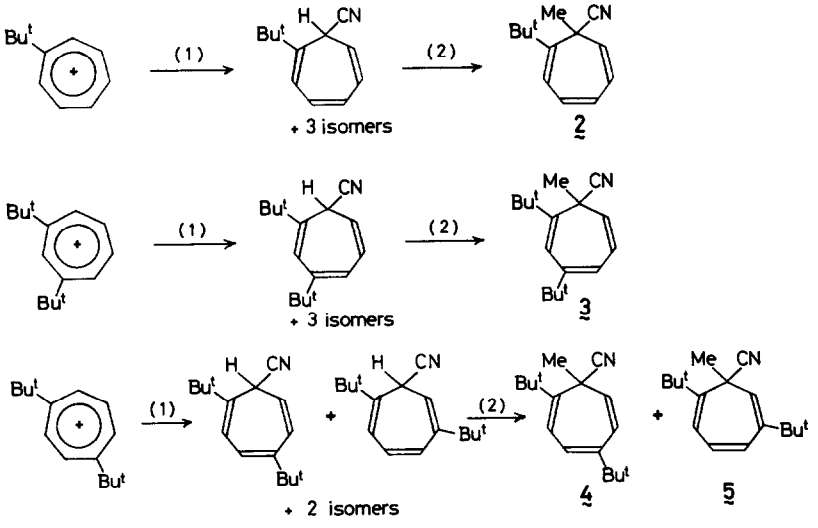
as a primary factor has been pointed out for the chloro[12b] and the methyl[16f] substituent. On the other hand, the substituent effects at the 1-position have been described in only a few papers, and moreover, the effects are complicating. Klärner showed that the introduction of a methyl group at the 1-position of 7-methyl-7-methoxycarbonylcycloheptatriene shifts the equilibrium to the CHT side.[16a] In contrast, Bedford and Smith reported that the introduction of an isopropyl or a t-butyl group at the 1-position of 4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene favors the NCD form.[16g]

Previously, we reported that the t-butyl substituents on the 3-, 2-, or 2,5-positions of 7-t-butyl-7-cyanocycloheptatriene markedly increase the amount of the NCD form in this sequence.[16c] In the present work we report that the introduction of a t-butyl group at the 1-position of 7-cyano-7-methylcycloheptatriene (1) as in 2 effects a marked shift of equilibrium to the NCD side and that the second t-butyl group at the 3-, 4-, or 5-position in 3, 4, or 5, respectively, favors the NCD form in more than 92%. Molecular mechanics (MMPI) calculations suggested that these t-butyl groups sterically destabilize the CHT form more than the NCD form shifting the equilibrium to the NCD side.



RESULTS AND DISCUSSION

Synthesis. t-Butyl, 1,3-di-t-butyl, and 1,4-di-t-butyl-tropylium perchlorates[18] were treated with sodium cyanide in acetonitrile to give mixtures containing four isomeric t-butylated 7-cyano-cycloheptatrienes. Each mixture was treated with butyllithium in THF-TMEDA and then with iodomethane following Klärner's method[16b] to give a mixture containing 2, 3, or 4 and 5 in small amounts. The desired compounds (2 - 5) were separated with HPLC.



(1); NaCN in CH_3CN. (2); BuLi in THF-TMEDA, then MeI.

^{1}H NMR Spectra of 2, 3, 4, and 5. Previously, Klärner studied the CHT-NCD tautomerism of 1 by ^{1}H NMR and reported that the equilibrium lies substantially on the CHT side.[16a,b] Therefore, we have concentrated on the tautomerism of 2, 3, 4, and 5. 99.55 MHz ^{1}H NMR spectra of the four compounds were measured for the solutions in CS_2-CD_2Cl_2 (3:1 v/v) at 25 and -107 °C. The chemical shifts and coupling constants are summarized in Table 1.

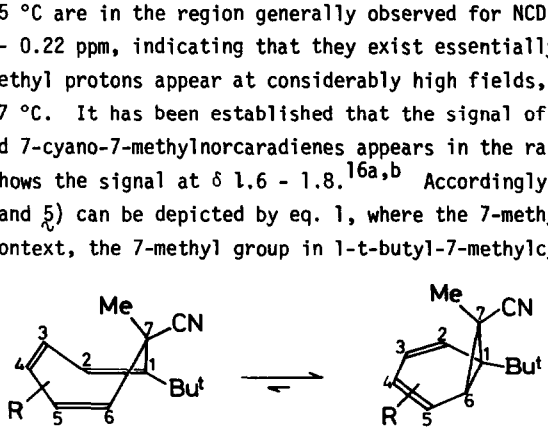
Table 1. Proton Chemical Shifts for 2, 3, 4, and 5 in CS_2-CD_2Cl_2 (3:1 v/v) at 25 and -107 °C[a,b]

compd	temp /°C	δ/ppm R^1 (=Bu^t)	R^2 (=H)	R^3	R^4	R^5	R^6 (=H)	R^7 (=Me)	coupling constant/Hz
2	25	1.16(s)	5.91-6.06(m)	H,6.12-6.29(m)	H,6.12-6.29(m)	H,5.91-6.06(m)	3.41(d)	0.96(s)	$J_{5,6}$ = 6.7
	-107	1.10(s)	5.84-5.97(br)	H,5.84-5.97(br)	H,5.84-5.97(br)	H,5.84-5.97(br)	2.68(br)	0.89(s)	——[c]
3	25	1.08(s)	5.66(s)	Bu^t,1.08(s)	H,6.23(d)	H,5.92(dd)	2.67(d)	0.84(s)	$J_{4,5}$ = 10.0 $J_{5,6}$ = 6.2
	-107	1.06(s)	5.59(s)	Bu^t,1.06(s)	H,6.23(d)	H,5.94(dd)	2.57(d)	0.78(s)	$J_{4,5}$ = 9.8 $J_{5,6}$ = 5.7
4	25	1.08(s)	5.90(d)	H,6.22(d)	Bu^t,1.09(s)	H,5.72(d)	2.81(d)	0.86(s)	$J_{2,3}$ = 10.0 $J_{5,6}$ = 6.6
	-107	1.06(s)	5.89(d)	H,6.19(d)	Bu^t,1.06(s)	H,5.65(d)	2.59(d)	0.79(s)	$J_{2,3}$ = 10.0 $J_{5,6}$ = 6.2
5	25	1.07(s)	5.70(d)	H,6.04(dd)	H,5.86(d)	Bu^t,1.14(s)	2.61(s)	0.84(s)	$J_{2,3}$ = 9.4 $J_{3,4}$ = 6.2
	-107	1.06(s)	5.72(d)	H,6.06(dd)	H,5.86(d)	Bu^t,1.13(s)	2.59(s)	0.81(s)	$J_{2,3}$ = 9.4 $J_{3,4}$ = 6.1

a) At 99.55 MHz. b) Long-range couplings with J = 1 - 2 Hz have been omitted. c) Spin-spin coupling between H(5) and H(6) could not be observed at this temperature.

Two characteristic features are seen in the chemical shift data. First, the δ values of H(6) for rapidly equilibrating 2, 3, 4, and 5 at 25 °C are 3.41, 2.67, 2.81, and 2.61, respectively. Generally, H(1,6) signals of a CHT form appear at δ 5 - 5.5 and those of a NCD form at δ ca. 2.5.[16a,b] Therefore, these compounds are highly enriched in the NCD form even at 25 °C. The H(6) signal for 2 broadened as the temperature was lowered, and essentially coalesced at -82 °C. At -107 °C, the temperature which we were able to attain, the signal shifted to δ 2.68, but with considerable broadening. This broad signal suggested that the CHT-NCD interconversion of 2 was not frozen in the NMR time scale even at -107 °C. In contrast to the behavior of 2, the H(6) shifts for 3, 4, and 5 at 25 °C are in the region generally observed for NCD forms, and undergo up-field shifts by only 0.02 - 0.22 ppm, indicating that they exist essentially in the NCD form at 25 °C.

Secondly, the 7-methyl protons appear at considerably high fields, δ 0.84 - 0.96 at 25 °C and δ 0.78 - 0.89 at -107 °C. It has been established that the signal of the endo-7-methyl group in various 2-substituted 7-cyano-7-methylnorcaradienes appears in the range δ 0.83 - 0.97, whereas the exo-7-methyl group shows the signal at δ 1.6 - 1.8.[16a,b] Accordingly, the equilibria of the four compounds (2, 3, 4, and 5) can be depicted by eq. 1, where the 7-methyl group assumes an endo geometry. In this context, the 7-methyl group in 1-t-butyl-7-methylcycloheptatriene is known to



(1)

R = H, 3-Bu^t, 4-Bu^t, or 5-Bu^t

favor the axial (endo) geometry because of its steric interaction with the 1-t-butyl group.[19] Although the signals due to the CHT form of 2 could not be observed by ^1H NMR at -107 °C, we were able to detect the CHT form by ^{13}C NMR at -142 °C (vide infra).

Variable-Temperature ^1H and ^{13}C NMR and the CHT-NCD Equilibrium of 2. The enthalpy and the entropy for equilibrating CHT-NCD systems are generally difficult to obtain, since most CHT-NCD systems are usually composed of four tautomers, making the NMR spectra difficult to analyze. However, if the equilibrating system is composed of a single CHT and a single NCD tautomer, both in observable amounts, the analysis is simplified and the equilibrium constants can be calculated easily. So far, some systems have been subjected to such a study.[20] In the present work, 2 satisfies such requirements. In Table 2 are summarized the chemical shifts of H(6), C(1), C(6), and C(7), which are pertinent to calculation of the equilibrium constants.

Table 2. H(6), C(1), C(6), and C(7) Chemical Shifts for 2 in CS_2-CD_2Cl_2 (3:1 v/v) at Various Temperatures[a]

temp /°C	δ/ppm H(6)	C(1)	C(6)	C(7)
25	3.41(d, $J_{5,6}$ = 6.7 Hz)	73.4	59.0	22.6
-4	b	c	57.3	c
-17	3.30(d, $J_{5,6}$ = 6.7 Hz)	c	55.5	c
-29	b	c	54.5	c
-43	3.20(d, $J_{5,6}$ = 6.4 Hz)	b	b	b
-68	3.13(br)	b	b	b
-92	b	45.9	c	c
-94	2.91(br)	b	b	b
-107	2.68(br)	b	b	b
-117	b	46.1[d]	34.4[d]	2.8[d]
-142	b	45.9[d] 143.5[e]	34.4[d] 118.9[e]	2.6[d] c

a) ^{13}C chemical shifts are from TMS by using δ 192.24 for CS_2. b) The measurement was not attempted. c) The signal was too broad to be observed. d) The signal assigned to NCD. e) The signal assigned to CHT.

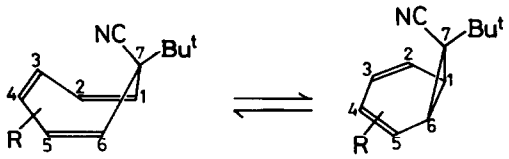
The equilibrium constants at various temperatures can be calculated by using the δ values of H(6), C(1), and C(6) from the equation $K = (\delta_{CHT} - \delta_{obs})/(\delta_{obs} - \delta_{NCD})$. The δ_{CHT} and δ_{NCD} values of C(1) and C(6) were directly obtained from the spectrum at -142 °C. From the C(6) shifts the equilibrium constant at 25 °C was calculated to be 2.436. Unfortunately, the δ_{CHT} value of H(6) could not be obtained from the low-temperature NMR. Therefore, by using this K value and by employing the δ value of 2.57 as a δ_{NCD} value for H(6), the δ_{CHT} value of H(6) was estimated to be 5.46. Table 3 summarizes the equilibrium constants calculated on the basis of the C(6) and H(6) chemical shifts. A lnK vs. 1/T plot (r = 0.9942) predicts a NCD population of 8% at -142 °C. This value is close to a population of 6% which was estimated by comparing the C(6) signal heights of the CHT and NCD forms at -142 °C. From the lnK vs. 1/T plot the ΔH° and ΔS° values are calculated to be -0.73 ± 0.07 kcal mol^{-1} and -0.7 ± 0.3 e.u., respectively. As expected from the linear shape of the cyano group, the ΔS° value is small, and the equilibrium is principally controlled by the enthalpy term.

Effects of t-Butyl Substituent at the 3-, 4-, or 5-Position. Previously, we reported that the introduction of a t-butyl group at the 2- or 3-position of 7-t-butyl-7-cyanocycloheptatriene raises

Table 3. CHT-NCD Equilibrium Constants for 2 in CS_2-CD_2Cl_2 (3:1 v/v)

temp /°C	H(6) or C(6) used	NCD : CHT	K (= [NCD]/[CHT])
25	C(6)	70.9 : 29.1	2.436
-4	C(6)	72.9 : 27.1	2.690
-17	C(6)	75.0 : 25.0	3.000
-17	H(6)	74.7 : 25.3	2.953
-29	C(6)	76.2 : 23.8	3.202
-43	H(6)	78.2 : 21.8	3.587
-68	H(6)	80.6 : 19.4	4.155

the NCD% in equilibrium at 25 °C from 19% (R = H) to 88% (R = 2-t-Bu) or 46% (R = 3-t-Bu) (eq. 2).[16c] The introduction of the two t-butyl groups at the 2- and 5-positions brings about a total transition to the NCD form.[16c] Thus, the effectiveness of the t-butyl substituent to favor the NCD form is in the order, H < 3-t-Bu < 2-t-Bu < 2,5-di-t-Bu.



(2)

R = H, 2-Bu^t, 3-Bu^t, or 2,5-di-Bu^t

In order to assess the effectiveness of the t-butyl substituents in the CHT-NCD equilibria of 2, 3, 4, and 5, the equilibrium constants and ΔG° values at 25 °C have been calculated by using their H(6) shifts and summarized in Table 4. The effectiveness of the addition of one t-butyl group to 2 in ΔG° scale at 25 °C is 1.0 or 2.4 kcal mol^{-1} for 4 or 5, respectively. These values are comparable with those obtained in the system of eq. 2, i.e., 0.8 kcal mol^{-1} for the 3-t-butyl and 2.1 kcal mol^{-1} for the 2-t-butyl group.[16c] The greater effect of the 3-t-butyl group in 3 than the 4-t-butyl group in 4 by 0.5 kcal mol^{-1} suggests a greater relief of steric strain in 3 than in 4 on conversion from the CHT into the NCD form.

Table 4. Populations of the CHT and NCD Forms, Equilibrium Constants, and ΔG° Values for 2, 3, 4, and 5 in CS_2-CD_2Cl_2 (3:1 v/v) at 25 °C

compd	NCD : CHT	K (= [NCD]/[CHT])	ΔG°[a] (= $G^\circ_{NCD} - G^\circ_{CHT}$)	ΔΔG°[a]
2	70.9 : 29.1	2.44	-0.53	0.0
3	96.5 : 3.5	28	-2.0	-1.5
4	92.3 : 7.7	12	-1.5	-1.0
5	99.3 : 0.7	1.4×10^2	-2.9	-2.4

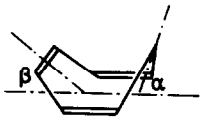
a) kcal mol^{-1}.

Molecular Mechanics Calculations. Previously, we suggested that the effect of t-butyl substituents to shift the CHT-NCD equilibrium to the NCD side should be steric in origin.[16c] However, the proposal has not been reinforced by energetics calculations. For this purpose molecular mechanics (MM) is the method of choice.

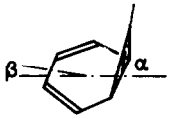
As described above, we have found three structurally interesting phenomena. First, the 7-methyl group in 2 - 5 takes on an endo geometry. Secondly, the introduction of the 1-t-butyl group to 1 to form 2 causes a marked shift of the equilibrium to the NCD side. Thirdly, the introduction of a t-butyl group at the 3-, 4-, or 5-position of 2 further favors the NCD form in the order, 4-t-butyl

< 3-t-butyl < 5-t-butyl. We wished to see if MM calculations can describe these observations.

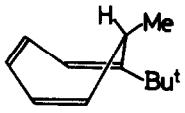
Unfortunately, however, MM has never been used to investigate CHT-NCD equilibria, although it has been applied to the parent[21] and substituted[22] CHT's. Perhaps, this is because of unsatisfactory parameterization of the cyclopropane ring and neglect of the conjugation between the double bonds and the cyclopropane ring in the NCD structure. In this sence, Allinger's MMPI program[21,23] may not be satisfactory to calculate absolute steric energies (SE's) of NCD's. However, only when a relative comparison of their SE's is questioned, this program may be used by assuming sp^3 hybridization on the cyclopropane carbons. On this assumption we used MMPI to calculate the SE's and geometries of CHT and NCD forms for the parent, 1-t-butyl-7-methyl, and related systems (6 - 11). The 7-cyano group was omitted owing to the lack of the parameter in MMPI program. Table 5 shows the SE's and the angles, α and β. The angles serve as a measure of deformation due to internal strain.



6-CHT and



6-NCD



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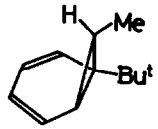
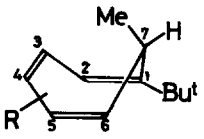
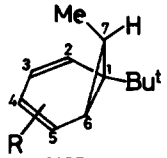


7-NCD



CHT and



NCD

8; R=H
9; R=3-Bu^t
10; R=4-Bu^t
11; R=5-Bu^t

Table 5. Steric Energies and Geometries for Various Substituted Cycloheptatrienes and Norcaradienes Calculated by MMPI

compd	SE[a]	$\Delta SE_{NCD-CHT}$	$\Delta\Delta SE_{NCD-CHT}$		α(°)	β(°)
6-CHT	16.0	79.3	0.0	—	51.1	30.1
6-NCD	95.3				72.6	0.8
7-CHT	29.0	76.7	-2.6	—	57.2	29.6
7-NCD	105.7				77.2	1.4
8-CHT	26.4	76.8	-2.5	0.0	50.4	28.3
8-NCD	103.2				71.2	2.8
9-CHT	32.4	75.7	-3.6	-1.1	49.9	31.8
9-NCD	108.1				70.8	2.9
10-CHT	32.4	76.1	-3.2	-0.7	51.1	31.7
10-NCD	108.5				71.2	2.8
11-CHT	32.8	74.4	-4.9	-2.4	51.8	33.6
11-NCD	107.2				71.7	4.0

a) kcal mol^{-1}.

As mentioned above, the calculated SE values for the NCD's cannot be used as absolute ones, although a mutual comparison between the NCD forms of 9, 10, and 11 would be sound. Therefore, the difference in SE between the NCD and the CHT form ($\Delta SE_{NCD-CHT}$) was calculated, and then this value was compared between each system. Thus, the $\Delta\Delta SE_{NCD-CHT}$ values give a measure to what extent the equilibrium be shifted to the NCD side as compared with the parent system (6) by introducing the substituents.

First, a comparison of SE between 8-CHT (SE = 26.4 kcal mol^{-1}) and 7-CHT (SE = 29.0 kcal mol^{-1}) leads that the former be more stable than the latter in accordance with the observation by Heyd and Cupas[19] and by us in the present work.† Similarly, the calculations suggest that 8-NCD (SE = 103.2 kcal mol^{-1}) be more stable than 7-NCD (SE = 105.7 kcal mol^{-1}). Secondly, a comparison of $\Delta\Delta SE_{NCD-CHT}$ for 8 with that for the parent system (6) suggests a gain of 2.5 kcal mol^{-1} in favor of the NCD form in 8 by simultaneous introduction of the 7-methyl and the 1-t-butyl group. Thirdly, a comparison of $\Delta\Delta SE_{NCD-CHT}$ among 8, 9, 10, and 11 suggests that the 3-t-butyl in 9, 4-t-butyl in 10, or 5-t-butyl in 11 favors the NCD form by 1.1, 0.7, or 2.4 kcal mol^{-1}, respectively, in comparison with 8. These values are in marked agreement with the experimental values, 1.5, 1.0, or 2.4 kcal mol^{-1} for 3, 4, or 5, respectively (Table 4). Close scrutiny of the SE values for 9 and 10 suggests that the greater effect of the 3-t-butyl in 9 than the 4-t-butyl in 10 (-1.1 vs. -0.7 kcal mol^{-1}) would be due to the higher stability (or smaller SE) of 9-NCD than 10-NCD, with the stabilities of 9-CHT and of 10-CHT comparable with each other. On the other hand, the greater effect of the 5-t-butyl in 11 (-2.4 kcal mol^{-1}) than the 4-t-butyl in 10 (-0.7 kcal mol^{-1}) would be caused by the combination of the increased SE for 11-CHT (32.8 vs. 32.4 kcal mol^{-1}) and the decreased SE for 11-NCD (107.2 vs. 108.5 kcal mol^{-1}), the latter effect being more dominant.§

An inspection of the angles (α and β) for 8, 9, 10, and 11 indicates that the t-butyl group on the 3-, 4-, or 5-position causes further bending of the cycloheptatriene ring as compared with 8 by 3 - 5° in β, while keeping α almost unchanged. On the other hand, the structural changes in the NCD's are slight. This also indicates that the t-butyl groups increase the internal strain of the CHT ring system, causing deformation of the CHT structure to a deeper boat form.

EXPERIMENTAL

Elemental analyses were performed by the Microanalytical Center, Kyoto University. NMR spectra were recorded with a JEOL FX100 (99.55 or 25.00 MHz for ^1H or ^{13}C, respectively) instrument operating in the Fourier transform mode. IR spectra were measured with a Hitachi 215 spectrophotometer. HPLC was conducted with a Waters assembly equipped with a pump 6000A, an injector U6K, a differential refractometer R401, an absorbance detector 440, and a μ-Porasil column (8 mm x 30 cm) operating at 2 - 2.5 ml min^{-1}.

Materials. t-Butyl-, 1,3-di-t-butyl-, and 1,4-di-t-butyl-tropylium perchlorates were prepared by the previously described method.[18] Acetonitrile and dichloromethane-d_2 were distilled from phosphorus pentoxide. THF was distilled from lithium aluminum hydride. Carbon disulfide was dried over calcium chloride and distilled. TMEDA was dried over sodium hydroxide. The other reagents were of reagent grade and used as purchased.

1-t-Butyl-7-cyano-7-methylcycloheptatriene (2). To a magnetically stirred suspension of pulverized sodium cyanide (0.55 g, 11 mmol) in acetonitrile (25 ml) was added t-butyltropylium perchlorate (0.668 g, 2.71 mmol) dissolved in acetonitrile (25 ml) over 15 min at room temperature and then stirring continued for 30 min. Evaporation of the acetonitrile followed by addition of water and extraction with ether afforded a mixture of four t-butyl-7-cyanocycloheptatrienes (0.435 g, 86%) as a yellow liquid. This was dissolved in THF (5 ml) containing TMEDA (0.258 g, 2.22 mmol). The resulting solution was chilled to -78 °C under nitrogen and to this was added 1.6 M butyllithium in hexane (1.32 ml, 2.11 mmol) over 4 min giving a greenish solution. After stirring for 50 min

† Introduction of a 7-cyano group in the equatorial (exo) position of 8 or the axial (endo) position of 7 would not change the conclusion of the calculations since a cyano group has much smaller steric requirement than that of a methyl as supported by the smaller conformational energy (A-value) of cyano (0.15 - 0.25 kcal mol^{-1}) than that of methyl (1.5 - 2.1 kcal mol^{-1}) in the cyclohexane system.[24]

§ An examination of the details of the SE's has revealed that the $\Delta\Delta SE_{NCD-CHT}$ values for 9, 10, and 11 are essentially controlled by a blend of the torsional and the van der Waals term. The torsional term exerts a predominant effect to increase the SE of 9-CHT, whereas the van der Waals term is a primary factor to increase that of 11-CHT. Notably, the calculations have shown that the van der Waals attractive forces contribute to reduce the SE of 11-NCD as compared with those of 9-NCD and 10-NCD by ca. 1 kcal mol^{-1}.

at -78 °C iodomethane (0.20 ml, 3.2 mmol) was added over 3 min and then the solution brought to room temperature. After stirring for 1 h the reaction mixture was poured into water and extracted with ether to give a dark brown oil (0.463 g). Chromatography of this oil over silica gel (hexane-ether 90:10) gave a yellow liquid (0.371 g). A portion (ca. 0.21 g) of this was subjected to HPLC (hexane-ether 98:2) to afford 2 (yellowish oil; 29 mg) as the first fraction of the five major components; IR (CCl_4) 3050 m, 2970 s, 2880 m, 2240 s, 1481 m, 1400 m, 1385 m, 1370 s, 1224 w, 1162 w, 978 w, 901 w, 857 w, 710 s, 672 m cm^{-1}. Found: C, 83.16; H, 9.32. Calc for $C_{13}H_{17}N$: C, 83.37; H, 9.15%.

1,3-Di-t-butyl-7-cyano-7-methylcycloheptatriene (3). The procedure is essentially the same as described for 2. The reaction of 1,3-di-t-butyltropylium perchlorate (0.654 g, 2.16 mmol) with sodium cyanide (0.50 g, 10 mmol) afforded a mixture of four di-t-butyl-7-cyanocycloheptatrienes (0.464 g, 94%) as a colorless liquid. Treatment of this with butyllithium (1.6 mmol) in THF containing TMEDA (1.63 mmol) and then with iodomethane (2.5 mmol) afforded a yellow oil (0.587 g). Chromatography of this oil over silica gel (hexane-ether 90:10) gave a yellow liquid (0.365 g), which on HPLC separation (hexane-ether 98:2) afforded 3 (yellowish oil; 23 mg) as the first fraction of the four major components; IR (CCl_4) 3050 w, 2960 s, 2870 m, 2230 m, 1640 w, 1480 m, 1400 w, 1382 w, 1370 m, 1253 w, 1221 w, 919 m, 883 m, 700 m, 660 w cm^{-1}. Found: C, 83.74; H, 10.47. Calc for $C_{17}H_{25}N$: C, 83.89; H, 10.35%.

1,4- and 1,5-Di-t-butyl-7-cyano-7-methylcycloheptatrienes (4 and 5, respectively). The procedure is essentially the same as described for 2. The reaction of 1,4-di-t-butyltropylium perchlorate (0.815 g, 2.69 mmol) with sodium cyanide (0.54 g, 11 mmol) afforded a mixture of four di-t-butyl-7-cyanocycloheptatrienes (0.611 g, 99%) as a yellowish liquid. Treatment of this with butyllithium (2.6 mmol) in THF containing TMEDA (2.36 mmol) and then with iodomethane (3.5 mmol) afforded a brown oil (0.623 g). After treated with decolorizing charcoal, a portion (ca. 0.14 g) was subjected to HPLC separation (hexane-ether 98:2) giving 4 (yellowish oil; 36 mg) and 5 (yellowish oil; 35 mg) as the second and the first fraction, respectively, of the four major components. 4; IR (CCl_4) 3055 w, 2975 s, 2920 sh, 2880 m, 2240 m, 1485 m, 1470 m, 1402 w, 1372 m, 1275 w, 1225 w, 1090 w, 965 w, 910 w, 850 m cm^{-1}. Found: C, 83.71; H, 10.57. Calc for $C_{17}H_{25}N$: C, 83.89; H, 10.35%. 5; IR (CCl_4) 3050 w, 2960 s, 2905 sh, 2875 m, 2230 m, 1480 m, 1460 sh, 1400 m, 1380 m, 1365 m, 1261 w, 1220 w, 1205 w, 870 w, 690 w cm^{-1}. Found: C, 83.99; H, 10.62. Calc for $C_{17}H_{25}N$: C, 83.89; H, 10.35%.

Variable-temperature ^{13}C NMR Spectra. The measurements were conducted on a solution (2 ml) of the compound (0.15 M) dissolved in CS_2-CD_2Cl_2 (3:1 v/v), in a 10 mm cell. Chemical shifts were determined relative to CS_2 and converted to the TMS scale using $\delta(CS_2)$ 192.24. Generally the spectra were obtained employing a 5000 Hz width in 8192 data points by use of a 45° pulse and pulse repetition of 1.5 s. The temperature indicator was calibrated to within ±1 °C by using CCl_4-$(CD_3)_2CO$ as an NMR thermometer.[25]

Variable-temperature ^1H NMR Spectra. The measurements were conducted on a solution (0.4 ml) of the compound (0.08 M) dissolved in CS_2-CD_2Cl_2 (3:1 v/v) containing TMS, in a 5 mm cell. Generally the spectra were obtained employing a 1000 Hz width in 16384 data points by use of a 50° pulse and pulse repetition of 8 s. The temperature indicator was calibrated to within ±1 °C by using methanol containing 0.03% concentrated hydrochloric acid as an NMR thermometer.[26]

Molecular Mechanics Calculations. The calculations were performed on a FACOM M382 computer at the Computer Center, Kyoto University.

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