acid, and the resultant solution was poured into 30 ml of 12.5% fluoroboric acid. The white suspension was ether extracted. The aqueous phase was extracted with four 60-ml portions of methylene chloride. *In vacuo* evaporation of the solvent gave a white solid. Recrystallization from methylene chloride–ether afforded a white solid: 0.133 g (69%); mp 240–242°; nmr spectrum (DMSO-d_6), 7.60–8.80 ppm (13 H, including s at 7.64); uv (CH_3CN), λ_{max} (ϵ) 235 (32,700), 268 (9200), 317 nm (2100). *Anal.* Calcd for $C_{18}H_{13}SBF_4$: C, 62.10; H, 3.77; S, 9.21. Found: C, 61.87; H, 3.76; S, 9.08

Reaction of *S*-Phenyldibenzothiophenium Fluoroborate with Phenyllithium. To a slurry of 0.312 g (0.89 mmole) of *S*-phenyldibenzothiophenium fluoroborate in 32.5 ml of dry THF at −78° was added 0.49 ml (0.89 mmole) of 1.82 *M* phenyllithium. After completion and work-up of the reaction as above, the crude product was chromatographed on silica gel PF-254 (elution with 97:3 hexane–ether) to yield, after recrystallization from 95% ethanol, 125 mg (42% yield) of 2-phenyl-2′-thiophenoxybiphenyl (R_f 0.52): mp 89–90°; infrared spectrum (CCl_4), 1585, 1480, 1460, 696, 690 cm^{-1}; nmr ($COCl_3$), 6.8–7.5 ppm; mass spectrum, *m/e* (% of base peak) 338 (98), 229 (100), 228 (75); uv (C_2H_5OH), λ_{max} (ϵ) 275 sh (10,500), 256 (16,850), and 223 sh (35,900). *Anal.* Calcd for $C_{24}H_{18}S$: C, 85.24; H, 5.34; S, 9.42. Found: C, 85.17; H, 5.36; S, 9.45. Vpc analysis (5 ft × 0.25 in. 3% SE30 on Aeropak 30 column) revealed the absence of dibenzothiophene. A small amount of biphenyl (approximately 4 mg) attributable to the phenyllithium solution was detected.

Acknowledgment We wish to express our thanks to the National Institutes of Health for their generous support of our program. We also thank Henry C. Arndt of these laboratories for performing one of the experiments.

Nuclear Magnetic Resonance Studies of the Conformational Behavior of Alkylcycloheptatrienes

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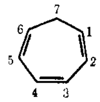
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received January 11, 1971*

Abstract: In contrast to other simple cycloheptatrienes, 7-*tert*-butyl-1-methylcycloheptatriene undergoes slow inversion at room temperature. The conformer with the "axial" 7-*tert*-butyl group, **2a**, has been found to be more stable than **2b** where the 7-butyl group is "equatorial." There is restricted rotation of the 7-*tert*-butyl group in **2b** which allows the first nmr observation of three distinct methyl resonances for this group. The ring inversion and rotational barriers for **2** have been determined. Using some rigid cycloheptatrienes as models, a conformational analysis for 7-alkylcycloheptatrienes is advanced.

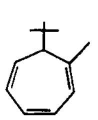
It is now well established that cycloheptatriene (**1**) exists as an interconverting pair of nonplanar conformers with an inversion barrier (**1a** ⇌ **1b**) of approximately 6 kcal/mol.[2,3] Several 7-substituted cycloheptatrienes have also been shown to exist as ring inverting conformers. Based on nuclear magnetic resonance (nmr) studies, the conformational preference of the 7-substituent has been shown to be the equatorial position in the case of deuterium,[2b] methyl[4a] (see below), isopropyl,[4a] *tert*-butyl,[4a,b] and phenyl.[4] More highly substituted derivatives of **1** have also been studied. The 7-methyl groups in 2-*tert*-butyl-3,7,7-trimethylcycloheptatriene are anisochronous at −100°, indicating a nonplanar ring.[5,6] In contrast, Roberts and coworkers[7] found that the 7-trifluoromethyl groups in 7,7-bis(trifluoromethyl)cycloheptatriene remain isochronous down to −185°. These authors argue that the observed increase in the vicinal coupling constant, $J_{2,3}$, is due to a more planar ring, which thus has a lower barrier to inversion.[8]



1

1a 1b

We reported[9] recently a preliminary account of our studies concerned with a simple derivative of **1**, namely, 7-*tert*-butyl-1-methylcycloheptatriene (**2**). The conformational and spectral behavior of **2**, as studied by nmr, proved to be quite interesting: (1) this tropilidene undergoes slow ring inversion at room temperature; (2) the conformer with the "axial" 7-*tert*-butyl group is more stable; (3) in the less stable conformer, there is restricted rotation of the "equatorial" 7-*tert*-butyl group—three distinct methyl resonances for this group can be observed. We present below a more complete description and analysis of the conformational be-



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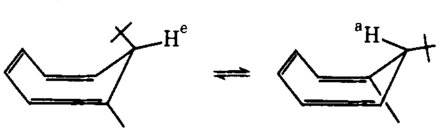

2a 2b

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(1) National Science Foundation Trainee, 1968–1969.

(2) (a) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964); (b) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(3) For an electron diffraction study of **1** and other leading references see M. Traetteberg, *ibid.*, **86**, 4265 (1964).

(4) (a) H. Gunther, M. Gorlitz, and H. H. Hinrichs, *Tetrahedron*, 24, 5665 (1968); (b) H. Kessler and E. Muller, *Z. Naturforsch.*, **22b**, 283 (1967); (c) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 3527 (1966); (d) A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 741 (1963).

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

(6) $\Delta F^{\ddagger}$ for ring inversion of this derivative has been estimated by Anet[2a] to be 9 kcal/mol.

(7) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3896 (1965).

(8) For a somewhat related example see, H. J. Reich, E. Ciganek, and J. D. Roberts, *ibid.*, **92**, 5166 (1970). $\Delta F^{\ddagger}$ for ring inversion in 7,7-dicyano-2,5-bis(difluoromethyl)cycloheptatriene is estimated to be 7 kcal/mole.

(9) W. E. Heyd and C. A. Cupas, *ibid.*, **91**, 1559 (1969).

Table I. Nmr Data for Compounds **2**, **3**, **4**, and **6**[a]

Compd	Temp, °C	H_7	H_1	H_6	H_2	H_5	H_3	H_4	*tert*-Butyl	Vinyl methyl
		Nmr chemical shift								
2	75	*b*		4.84	4.02		3.90		9.11 s	8.05
	30	7.43 br		4.81		4.02			9.16 br	8.06
2a	−24	7.36		4.85		4.03			9.23 s	8.07
	−105	7.40		4.88		4.05			9.25 s	8.07
2b	−24	9.08		~4.85	~4.04		3.56		8.94 s	8.03
	−105	*c*		~4.88	~4.11		3.60		9.11 s 8.95 s[d] 8.78 s	8.04
3	30	8.83	5.04	4.73		4.04	3.56		9.03 s	8.15
	−70	8.89	5.04	4.73		4.03	3.56		9.04 s	8.14
4	30	8.81	4.88		4.07			3.70	9.03 s	7.99
	−70	8.87	4.88		4.08			3.71	9.03 s	7.96
6	70	6.74		4.61	4.00		3.70		8.89 s	9.39[e]
	30	6.74		4.61	3.98		3.70		8.89 s	9.40[e]
	−80	6.75		4.63	3.99		3.66		8.90 s	9.47[e]

[a] Nmr spectra were taken at 100 MHz using carbon disulfide as solvent and tetramethylsilane as an internal lock and reference. With regard to the absorptions, br = broad, s = singlet. [b] H_7 of **2** at 75° is a very broad absorption and not a doublet. The chemical shift difference under conditions of no exchange (slow ring inversion) is much larger for the methine signals (172 Hz) than for the *tert*-butyl signals (29 Hz) of **2**. Consequently the temperatures for coalescence and for the appearance of sharp signals (fast ring inversion) are considerably higher for the methine signals. At 70° the *tert*-butyl resonance is a sharp singlet, whereas H_7 appears as a sharp doublet (J = 8.6 Hz, τ 7.87) at 120°. The same is true for the coalescence of the signals for H_3 and H_4 of **2a** and **2b** (separation: 47 Hz), though to a lesser extent. At 95° this resonance shows fine structure not visible in the 75° spectrum. [c] H_7 of **2b** at −105° is obscured by the three methyl signals of the *tert*-butyl group of **2b**. [d] Chemical shifts of the three anisochronous methyl groups of the *tert*-butyl group of **2b**. [e] Chemical shift of the 7-methyl group of **6**.

Table II. Nmr Coupling Constants (in Hertz)

Compd	J_{17}	J_{67}	J_{12}	J_{56}	J_{23}	J_{45}	$J_{H_7\text{-}CH_3}$
2a		8.9[a]					
2b		7.9[a]					
3	5.8	6.0		9.5		2.8[b]	
4	5.8		10.2			5.8	
6		9.3		9.5	3.0[b]		7.0

[a] Taken at −24°. [b] "Virtual coupling constant."

Table III. Uv Data of Some Cycloheptatrienes in Ethanol

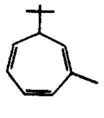
Cycloheptatriene	λ_{max}, mμ	Log ϵ
Unsubstituted, **1**	261[a,b]	
7-Methyl-	257[c]	
1-Methyl-	269[a,d]	3.53
2-Methyl-	258[a]	3.42
3-Methyl-	260[a,d]	3.58
7-*tert*-Butyl-	255[b]	3.48
7-*tert*-Butyl-1-methyl-, **2**	287[b]	3.40
7-*tert*-Butyl-2-methyl-, **3**	257[b]	3.49
7-*tert*-Butyl-3-methyl-, **4**	255[b]	3.54
1-*tert*-Butyl-7-methyl-, **6**	275[b]	3.60
1-*tert*-Butyl-	269[b,e]	3.64
3-*tert*-Butyl-	255[b]	3.53

[a] See ref 17a. [b] This work. [c] See ref 5. [d] See ref 17b. [e] λ_{max} obtained by subtracting absorption for 41% of 7-*tert*-butylcycloheptatriene contained in the sample.

havior of **2** which includes the determination of inversion and rotational barrier along with details by which **2** and related systems were prepared. Ultraviolet spectroscopic data, which provide confirmation of our earlier interpretation of the nmr behavior of **2**, are reported. Finally, using some static tropilidenes as chemical shift models, a conformational analysis for 7-alkylcycloheptatrienes is advanced.

Results and Discussion

Our interest in reacting alkyltropylium ions with organometallic reagents stemmed from some exploratory studies concerned with synthetic routes to 7,7-dialkyltropilidenes. Indeed, tropilidenes of this type were found to be completely absent in these reactions.[10] The reaction of methyltropylium tetrafluoroborate with *tert*-butyllithium in pentane gave a mixture of three isomeric products which could be separated by preparative gas chromatography and shown to be 7-*tert*-butyl-1-, -2-, and -3-methylcycloheptatriene, **2** (24%), **3** (30%), and **4** (46%), respectively.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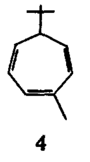
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The structures of **2**, **3**, and **4** follow from their method of preparation and their nmr and uv spectra. These data, along with relevant data from the literature, are summarized in Tables I–III. The nmr spectra of **3** and **4** exhibited the usual pattern for alkyl-substituted cycloheptatrienes in the vinyl region:[4,11,12] namely, three separate multiplets due to the pairs of protons (H_3, H_4), (H_2, H_5), and (H_1, H_6). The relative areas

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[10] C. A. Cupas and W. E. Heyd, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, ORGN 116.

[11] J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966).

[12] K. W. Egger and W. R. Moser, *J. Phys. Chem.*, **71**, 3699 (1967).

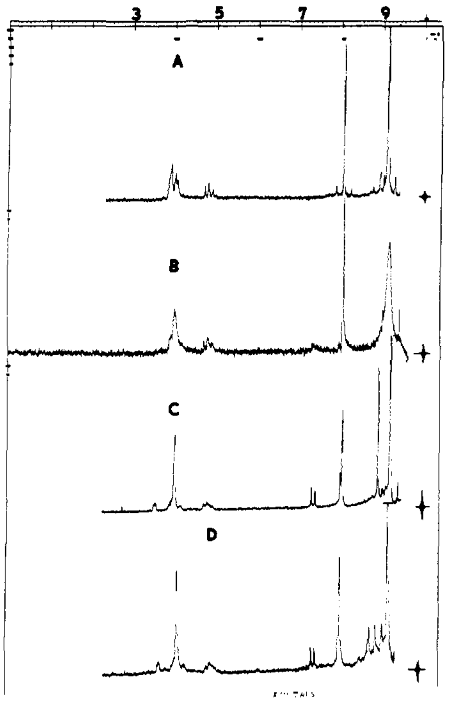

Figure 1. Spectra (100 MHz) of **2** at different temperatures: A, 75°; B, 30°; C, −24°; D, −104° (1000 sweep width).

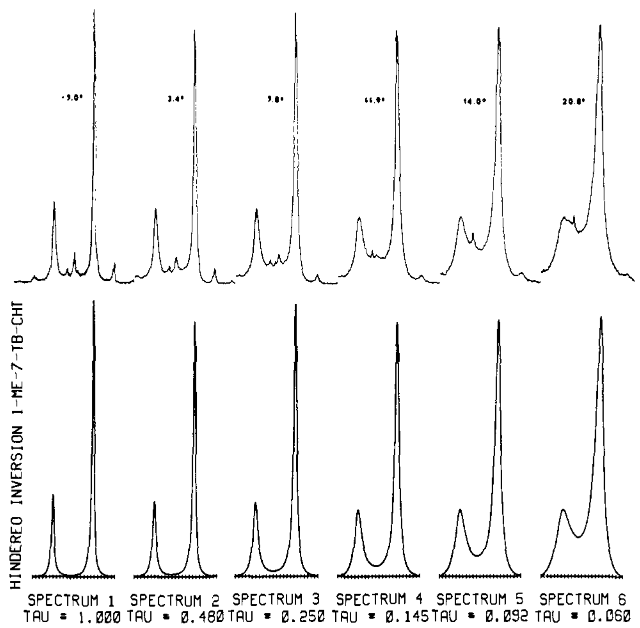

Figure 2. Calculated and experimental spectra for ring inversion of **2**.

of these three vinyl multiplets (low to high field) gave the location of the vinyl methyl group (2:1:2 for **3** and 1:2:2 for **4**). In addition, the uv data (Table III) support these structural assignments.

The room temperature nmr spectrum of **2** (Figure 1B) did not exhibit the normal pattern but showed instead a broad absorption at τ 9.17 for the *tert*-butyl group, a singlet at τ 8.06 for the 1-methyl group, and broad absorptions at 7.43 for H_7, 4.81 for H_6, and 4.02 for H_2, H_3, H_4, and H_5. However, at 75° (Figure 1A) the *tert*-butyl and methyl signals[13a] sharpen and the vinyl region shows the expected pattern.[13] Low temperature nmr studies of **2** provided an explanation for the apparently anomalous spectrum observed at room temperature. At −24° (Figure 1C) the *tert*-butyl resonance sharpens and gives rise to two singlets of unequal intensity at τ 8.94 and 9.23 (ratio of the area of low-field signal to that of the high-field signal 23:77), while the 1-methyl proton region undergoes similar changes and exhibits two signals of unequal intensity at τ 8.03 and 8.06. Furthermore, at this temperature, two new signals appear: a doublet (J = 9.1 Hz) at τ 7.37 and a less intense broader doublet (J = 7.9 Hz) at τ 9.08. These signals are assigned to 7-methine protons (see below).[14] The most reasonable interpretation of these temperature-dependent spectra is that **2** undergoes slow inversion at room temperature and exists as an equilibrating pair of nonplanar conformers **2a** and **2b**, one of which predominates. A decision concerning conformer stability from the low-temperature spectrum is, fortunately, quite unequivocal. Previous studies[2,5a] of cycloheptatriene systems have shown that for methylene protons the syn or "axial" H_7 is shielded[2b] and occurs upfield (τ 8.83–8.93) in comparison to the anti or "equatorial" H_7 (τ 6.67–6.99).[5a] From a consideration of the areas in the −24° spectrum and the relative positions of the 7-methine signals, the resonances at τ 7.37, 8.06, and 9.23 may be assigned to the 7-methine, 1-methyl, and 7-*tert*-butyl protons, respectively, of conformer **2a**, and the signals at τ 9.08, 8.03, and 8.94 to the analogous protons of **2b**. Thus **2a**, the conformer with the "axial" 7-*tert*-butyl group, is more stable than **2b**. In contrast, the "equatorial" conformer of 7-*tert*-butylcycloheptatriene has been found to be more stable.[4a] The dramatic reversal in conformational preference caused by the presence of the 1-methyl group in **2** is a particularly good example of the consequences of allylic ($A^{1,2}$) strain in nonrigid systems.[15] It should be further noted that the chemical shifts of the *tert*-butyl groups in **2a** and **2b** are also in accord with our structural assignments. For example, the same trend that is observed for the 7-methine resonances is also followed for the 7-alkyl substituent where the "axial" *tert*-butyl group in **2a** is shielded relative to the "equatorial" *tert*-butyl group in **2b**. Further confirmation concerning the above interpretation is obtained from the uv spectrum of **2** where λ_{max} is 287 mμ. In contrast, λ_{max} is 269 mμ for 1-methylcycloheptatriene. The 18-mμ bathochromic shift can only be due to a greater degree of ring planarity in **2**.[16]

In **2a** interaction of the *tert*-butyl group with the C_3–C_4 double bond is relieved by greater planarity. In **2b** minimization of the *tert*-butyl and 1-methyl group interactions can occur by greater or lesser[9] planarity, and inspection of molecular models shows that less planarity of the ring is more likely.[18] Thus severe nonbonded interactions in **2b** cause the C_1–C_7–C_6 por-

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(13) (a) The absorption for H_3 and H_4 is broader and closer than usual to that of the set H_2, H_5 (see footnote *b*, Table I); (b) disregard side bands for these signals.

(14) Changes are also observed in the olefinic region and are summarized in Table I.

(15) F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

(16) Assuming that no other unusual effects are responsible for the observed bathochromic shift, **2** is the most planar alkyl-substituted cycloheptatriene which has been reported.[4,11,17]

(17) (a) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **79**, 352 (1957); (b) N. H. Nelson, J. H. Fassnacht, and J. V. Piper, *ibid.*, **83**, 206 (1961).

(18) L. H. Knox, E. Velarde, and A. D. Cross, *ibid.*, **87**, 3727 (1965).

Table IV. Temperature Dependence of the Mean Lifetimes, the Populations, and Rates of Interconversion of **2a** and **2b**[a]

T, °K	τ_a (obsd)	P_a	P_b	τ_b	τ	$\frac{1}{\tau_a}$ ($=k_{ab}$), sec^{-1}	$\frac{1}{\tau_b}$ ($=k_{ba}$), sec^{-1}
271.2	1.000	0.725	0.275	0.379	0.275	1.00	2.64
276.6	0.480	0.705	0.295	0.201	0.142	2.08	4.98
281.0	0.250	0.697	0.303	0.109	0.0758	4.00	9.20
285.1	0.145	0.688	0.312	0.0658	0.0452	6.90	15.2
289.2	0.092	0.680	0.320	0.0433	0.0294	10.9	23.1
294.0	0.060	0.675	0.325	0.0289	0.0195	16.7	34.6

[a] The coalescence temperature, T_c (temperature of maximum broadening), is about 298°K. The forward rate at this temperature is 30 sec^{-1} and the backward rate is 49 sec^{-1}.

Table V. Arrhenius and Transition State Theory Parameters for the Interconversion, **2a** $\rightleftharpoons$ **2b**[a]

Process	E_a,[a] kcal/mol	log A[b]	$\Delta H_{298}^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}$, kcal/mol
2a → **2b**	20.6 ± 0.8	16.6 ± 1.3	20.1	17.5	14.8
2b → **2a**	19.0 ± 0.7	15.7 ± 1.3	18.4	13.2	14.4

[a] K is defined as [**2b**]/[**2a**]. Errors given for E_a are ±2 times the root-mean-square error in the slope from a linear least-squares treatment of the Arrhenius data (95% confidence level); for log A the error is estimated.

tion of this conformer to depart further than normal from the C_1–C_2–C_5–C_6 plane, and consequently results in a greater H–C_6–C_7–H_a dihedral angle.[19] An increase in the magnitude of $J_{H_6-H_7}$ is expected and is, in fact, observed: $J = 7.9$ Hz.

It seems that, due to distortion of ring geometry of **2a**, the olefinic protons H_2, H_3, H_4, and H_5 are accidently isochronous (Figure 1C). The chemical shift of H_3 and H_4 at 75° is approximately the expected weighted average[20] of the values for **2a** and **2b**. In addition, at −24° the relative areas of the three sets of vinyl resonances centered at τ 3.56 (0.54), 4.03 (3.48), and 4.85 (1.00) are consistent with our interpretation if they contain, respectively, H_3, H_4 of **2b**, H_2, H_5 of **2b** with H_2, H_3, H_4, H_5 of **2a**, and finally H_6 of both **2a** and **2b**.[21]

In contrast to the case of ring-flip in cycloheptatriene, the two conformers of **2** are not necessarily of equal energy. Thus there is no longer a unique rate of inversion for **2**, but instead the rate of inversion from **2a** → **2b** (k_{ab}) and the reverse process (k_{ba}).[22] The activation energies for these two processes were determined by comparing the line shapes of the *tert*-butyl signals in the experimental spectra (at measured temperatures) with those of theoretical spectra having various values of the mean lifetime of **2a** (τ_a) (Figure 2).[23,24a]

In comparing experimental with theoretical spectra calculated using the −24° populations (77% **2a** and 23% **2b**) it soon became apparent that the populations were changing in the temperature range studied. Thus the relative populations, as well as τ_a, were varied until a theoretical spectrum fit an experimental one, at which point the values of the populations and τ_a were those for **2a** at the particular temperature. The mean lifetime of **2b** (τ_b) and mean lifetime (τ) for the process are found from the populations P_a of **2a** and P_b of **2b** as given[22] in eq 1. The rates of interconversion are found from

$$\tau_b = \frac{\tau_a P_b}{P_a} \qquad \tau = \frac{\tau_a \tau_b}{\tau_a + \tau_b} \tag{1}$$

eq 2.[22] Their temperature dependence is shown in

$$\mathbf{2a} \longrightarrow \mathbf{2b} \quad k_{ab} = \frac{1}{\tau_a} \qquad \mathbf{2b} \longrightarrow \mathbf{2a} \quad k_{ba} = \frac{1}{\tau_b} \tag{2}$$

Table IV, along with the data from which they were derived. The Arrhenius and transition state theory parameters for the interconversion of **2a** and **2b** are given in Table V. Due to the limited temperature range over which this nmr study was possible, the difference between the forward and reverse processes is not experimentally significant, thus rendering ground state thermodynamic parameters meaningless, regardless of whether or not they satisfy intuition.[24b]

Indeed, while the ground state free energy difference between **2a** and **2b** is nonzero as evidenced by unequal populations, it is small as shown by the significant population of each conformer over a wide temperature range. It is rather surprising that the severe interaction between the *tert*-butyl and 1-methyl group of **2b** is almost totally balanced by the *tert*-butyl-C_3-C_4 π-bond interaction (see below). As would be anticipated $\Delta F^{\ddagger}$

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(19) The dihedral angle in cycloheptatriene (**1**) has been estimated to be 124 ± 3°.[2b,4b] Here $J_{vic} = 4.0$ Hz, as defined above.

(20) Compare the observed τ 3.90 with 3.82 calculated using 57:34 conformer population at 75°. This value was extrapolated from a least-squares plot of ln K *vs.* $1/T$ from populations determined in the temperature range −1.0 to 20.8° (see below).

(21) Values calculated using relative areas 0.46, 3.54, and 1.00, respectively.

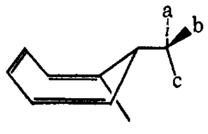
(22) (a) F. Kaplan and K. Meloy, *J. Amer. Chem. Soc.*, **88**, 950 (1966); (b) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 21, 1688 (1953).

(23) The theoretical spectra were calculated using a FORTRAN IV coded program based on the equations of Gutowsky and Holm: H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25, 1228 (1956); for these calculations T_2 was determined from the widths at half-height ($W_{1/2h}$) of each *t*-butyl peak under conditions of no exchange, using $T_2 = (\pi W_{1/2h})^{-1}$.

(24) (a) C. A. Cupas, J. M. Bollinger, and M. Haslanger, *J. Amer. Chem. Soc.*, **90**, 5502 (1968), and references cited therein. (b) The authors acknowledge the comments of the referees on this point. It would be most desirable to study the temperature variation of the line shapes of the methine proton signals, which could be studied over a much wider range of temperature (−24 to +120°), but this is not experimentally feasible. Study of the *tert*-butyl signals at 220 MHz would also increase the temperature range of observation possible.

for the interconversion of **2a** and **2b** is much larger than the $\Delta F^{\ddagger}$ of 6 kcal/mole for the parent cycloheptatriene.

As the temperature is lowered below −24°, **2** shows yet another marked change in its nmr spectrum. Between −45 and −80°, the *tert*-butyl resonance at τ 8.94 for the less stable conformer **2b** gradually broadens and then finally sharpens (at −104°) to three singlets of equal intensity at τ 8.78, 8.95, and 9.11 (Figure 1D). We ascribe these resonances to the three anisochronous methyl groups of **2b** as depicted in **5**. Restricted rotation of *tert*-butyl groups has recently been observed in a variety of substrates.[25] However, by virtue of the symmetrical nature of the compounds studied and/or the symmetry of the energy minimum conformation, only two *tert*-butyl methyl signals (in a ratio of 2:1) have been observed.[26] The energy barrier to rotation of the *tert*-butyl group in **2b** was determined by comparing experimental with theoretical[27] spectra as described above. The relation of τ, the mean lifetime for the three-site exchange process, and k, the rate of rotation, is given in eq 3.[22b,27a] The kinetic data are given in



5

$$k = \frac{2}{3\tau} \qquad (3)$$

Table VI and the Arrhenius and transition state theory parameters in Table VII. The rotational process has a low enthalpy of activation but the large opposing entropy term produces a surprisingly large free energy of activation: 10.3 kcal/mole. Consideration of the effect of a 1-methyl group on the rotational energy minima and maxima of 7-*tert*-butylcycloheptatriene leaves no doubt that the latter is more destabilized, thus leading to the observed higher rotational barrier in **2** than that (unknown) for 7-*tert*-butylcycloheptatriene. The higher barrier is due mainly to the large negative entropy term,[27c] which speaks for a highly unfavorable process, such as a cogwheel effect of the *tert*-butyl with the 1-methyl group as they rotate. Thus the barrier to rotation in **2b** is 2.5–4 kcal/mole higher than that observed by Anet[25a] for the *tert*-butylcycloalkanes (6.0–7.8 kcal/mole for five- through ten-membered rings).[28,29]

Table VI. Temperature Dependence of the Mean Lifetime for the Exchange Process for Rotation of the *tert*-Butyl Group in **2b**[a]

T, °K	τ	$3\tau\,(=k)$
167.2	0.105	6.35
170.7	0.0850	7.84
174.8	0.0450	14.8
178.2	0.0300	22.2

[a] The coalescence temperature, T^c (temperature of maximum broadening), is about 183°K and the rate of rotation at this temperature is 29 sec^{-1}.

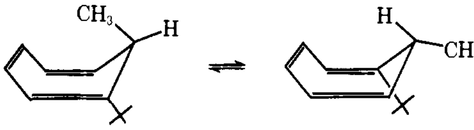
Table VII. Arrhenius and Transition State Theory Parameters for Rotation of the *tert*-Butyl Group in **2b**[a]

E_a	7.0 ± 0.7 kcal/mol
log A	9.9 ± 1.0
$\Delta H_{298}^{\ddagger}$	6.4 kcal/mol
$\Delta S^{\ddagger}$	−13.1 eu
$\Delta F_{298}^{\ddagger}$	10.3 kcal/mol

[a] See footnote *a*, Table V.

Some previous endeavors to calculate chemical shifts from C–C and C–H bond anisotropies have not proved successful.[4a,25a] Since distortions are difficult to take into account in such calculations, we sought an alternative way to assign the chemical shifts of the three anisochronous methyl groups of **5**. In principle a nuclear Overhauser effect (NOE)[30] can distinguish methyl groups b and c from a. Irradiation of either b or c should produce an increase in integrated area of H_6, while irradiation of a should have no effect on it. In practice the proximity of the methyl signals (Table I) and the low concentration of **5** made the experiment difficult and inconclusive.[31]

The conformational populations of **2** depend on a delicate balance of nonbonded interactions between the *tert*-butyl group and either the C_3–C_4 double bond (in **2a**) or the 1-methyl group (in **2b**). Removal of one of these interactions, while leaving the other essentially the same, should produce a marked change in conformational distribution. For example, if the *tert*-butyl-C_3–C_4 bond interaction is relieved while the *tert*-butyl-1-methyl interaction remains, the conformer with the "axial" 7-substituent should be of yet lower energy and therefore of higher population. This reasoning is dramatically supported by the variable temperature nmr behavior of 1-*tert*-butyl-7-methylcycloheptatriene (**6**), the compound obtained formally by the interchange of the *tert*-butyl and 1-methyl groups of **2**. **6** is obtained as the minor product from the reaction of *tert*-



6a **6b**

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[25] (a) F. A. L. Anet, M. St. Jacques, and G. N. Chmurny, *J. Amer. Chem. Soc.*, **90**, 5243 (1968); (b) A. Rieker, N. Zeller, and H. Kessler, *ibid.*, **90**, 6566 (1968); (c) H. Kessler, V. Gusowski, and M. Hanack, *Tetrahedron Lett.*, 4665 (1968); (d) J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967).

[26] Professor H. Kessler, University of Tuebingen, has observed three signals (at 220 MHz) for a *tert*-butyl group in an unsymmetrically substituted cyclohexadienone. Personal communication, 1969. See also H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

[27] (a) The authors are grateful to Dr. H. H. Freedman and Miss Sue McKinley of the Dow Chemical Company's Eastern Research Laboratory for the FORTRAN coded computer program used in this work and concurrence on the expression relating k and τ for a three-site exchange. Originally written by C. S. Johnson,[27b] the program was modified by Miss McKinley and further modified by us. Because the signals of the three anisochronous methyl groups still show some exchange broadening at −106°, the value of T_2 used was calculated from the measured line width at half height of the *tert*-butyl signal of **2a** (at −105°) by the equation in footnote 23. (b) C. S. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965). (c) As suggested by the referees, the exact magnitude of $S^{\ddagger}$ is perhaps not significant, but the qualitative indication is undoubtedly significant.

[28] *A priori*, in comparison to the *tert*-butylcycloalkanes, a lower rotational barrier in **2b** could have resulted if the energy minimum conformation **5** were destabilized to a greater extent (by the vinyl methyl group) than the energy maximum conformer.

[29] No nmr evidence could be obtained for restricted rotation of the "axial" *tert*-butyl group in **2a** at −135°.

[30] (a) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965); (b) J. G. Colson, P. T. Lansbury, and F. D. Saeva, *ibid.*, **89**, 4987 (1967).

[31] Other NOE studies of **2** at higher temperatures were successful (see below).

butyltropylium tetrafluoroborate with methyllithium in ether and is isolated as is **2**. Proof of structure of **6** is by method of preparation and by nmr and uv spectroscopy. The pertinent data for **6** are summarized in Tables I–III. In the nmr spectrum of **6**, the 7-methyl group appears as a doublet ($J_{H_7-CH_3} = 7.2$ Hz) at τ 9.40 while the 7-methine proton is a quintet at τ 6.74, arising from vicinal coupling to both the methyl and H_6 ($J_{6,7} = 9.2$ Hz). Both observed chemical shifts are in accord with strong axial preference for the 7-methyl group. This is further confirmed by the constant value of the 7-proton chemical shift (which is expected to be a sensitive probe of conformation), over the temperature range +70° to −80° (Table I). Thus, due to a large conformational free energy difference between **6a** and **6b**, this cycloheptatriene is essentially conformationally homogeneous.[32a] This stereochemical assignment was further confirmed by an NOE experiment. Irradiation of the 1-*tert*-butyl protons of **6a** at 25° produced an NOE at the H_7 methine proton (23% intensity increase).[32b] With regard to confirming our previous assignments in **2**, irradiation of the 7-*tert*-butyl protons in conformer **2b** at −30° gave an NOE at H_6 (18%[32b]) while irradiation of the 1-methyl protons in **2b** produced an NOE at the 7-methine proton (7%[32b]).

It was mentioned above that nmr parameters have been used to show the equatorial preference for 7-substituted cycloheptatrienes. The chemical shift of the 7 proton,[4] the magnitude of the vicinal coupling constant, $J_{1,7} = J_{6,7}$,[4b,7] and the sign and magnitude[3d] of the allylic coupling constant, $J_{2,7} = J_{5,7}$, have all been used to support the preferred equatorial postion of a 7 substituent. The conformational energy difference has recently been determined[4a] for phenyl (1101 cal/mol) and *tert*-butyl (1115 cal/mol) by studying the change of the 7-proton chemical shift with temperature. Similar studies were not reported for the lower 7-alkyl homologs. The availability of chemical shift models from our work allows a semiquantitative assessment of conformational free energy differences for these compounds despite possible pitfalls.[33,35] At this time the only chemical shift model for an "axial" methine H_7 proton is H_7 (τ 9.08) of **2b**, whereas for an "equatorial" methine proton there are two choices: H_e (τ 7.37) of **2a** or H_7 (τ 6.74) of **6a**. Obviously neither of these models is without its difficulties,[33] but they each can provide a first estimate of energy differences not easily accessible experimentally. Table VIII shows the equilibrium constants (defined as P_e/P_a = equatorial configurational population/axial configurational population) and resulting free energy differences, calculated using the two possible sets of chemical shift models. Both calculations show the same trend, namely, a steady increase in $\Delta F°$ with increasing size of the 7-alkyl group. However, the magnitude of these changes bears little resemblance to those analogous values found for the corresponding alkylcyclohexanes[38] and must (in the cycloheptatriene series) be associated with energetically less demanding ring distortions when the substituent is axial.

Table VIII. Results of Conformational Analysis Using Available Chemical Shift Models

R	$\nu_7(\tau)$	Using τ 7.37 and 9.08 as model chemical shifts		Using τ 6.74 and 9.08 as model chemical shifts	
		K	$\Delta F°_{298}$, cal/mol	K	$\Delta F°_{298}$ cal/mol
CH_3	8.40[a]	1.51	244	2.44	528
CH_3CH_2	8.51[b]	2.00	410	3.11	672
$(CH_3)_2CH$	8.82[a]	5.58	1020	8.0	1230
$(CH_3)_3C$	8.86[a]	6.77	1130	9.63	1340

[a] Solvent CS_2. [b] Solvent $CDCl_3$; ν_7 is difficult to determine because of partial overlap of H_7 with the methylene protons.

Experimental Section

Nmr spectra were measured on a Varian HA-100 spectrometer equipped with a variable temperature probe. Carbon disulfide was used as solvent and tetramethylsilane as internal reference and lock. Probe temperatures were measured using a thermometer placed in an nmr tube, which was placed in the probe such that the bulb of the thermometer was at the depth of the receiver coil. Temperatures reported in Table IV are corrected for calibration of the thermometer with an Anschutz thermometer. Ir spectra were recorded (neat) on a Beckman IR-8 and uv spectra (ethanol solvent) on a Cary 15 spectrophotometer. Gas chromatographic separations and preparative work were performed on an Aerograph A-90-P with a 6.1 m × 6.4 mm (o.d.) column packed with 18% 4-methyl-4-nitropimelonitrile[39] on 30–60 Chromosorb P and operated at the temperatures and flow rates of helium indicated. NOE experiments were performed on samples degassed and flushed with helium by integrating the appropriate area first with the irradiating frequency off, then on, and *vice versa*. The effects reported are averaged for 18 determinations for **6** and 13 determinations for **2b**. For the latter, the entire H_6-proton region was integrated and the observed 4.13 effect was divided by 0.23, the fractional population of **2b**.

The 7-methyl-[40] and 7-*tert*-butylcycloheptatrienes[4a] were prepared in a manner analogous to literature procedures by reacting tropylium fluoroborate[41] with the appropriate alkyllithium reagent.

Methyltropylium Fluoroborate. This compound was prepared by a procedure analogous to the preparation of the perchlorate salt.[42] To 10.0 g (0.0303 mol) of triphenylmethyl fluoroborate[43] partially dissolved in 50 ml of dry acetonitrile was added 4.20 g (0.0395 mol) of 7-methylcycloheptatriene. After stirring the mixture for 10 min, the solvent was evaporated and 50 ml of ethyl acetate was added and then evaporated. The solid residue was triturated with three 25-ml portions of anhydrous ether and dried *in vacuo* over P_2O_5 to give 5.70 g (98%) of dark blue-green solid, which was used in reactions below without further purification.

Reaction of Methyltropylium Fluoroborate with *tert*-Butyllithium. To 17.8 ml of a 1.24 *M* pentane solution of *tert*-butyllithium (1.41 g, 0.022 mol; Foote Mineral Co.) further diluted with 50 ml of pentane was added at 25° 2.50 g (0.0183 mol) of methyltropylium

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[32] (a) The situation is analogous to that in *tert*-butylcyclohexane: E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformation Analysis," Wiley, New York, N. Y., 1967, p 50; (b) a referee has correctly pointed out that the accuracy of the NOE's suffers because the experiments were not conducted with the decoupling oscillator on continuously (being moved on and off the desired frequency). While the exact magnitude of the observed effects is questionable, this does not jeopardize our conclusions.

[33] Geometrical distortions and effects of different alkyl groups on the chemical shift[34] of the methine proton are certainly important here, but are difficult to evaluate quantitatively.

[34] F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 77–78.

[35] The same type of conformational analysis[36] has been done for cyclohexanes and has received criticism[37] as well.

[36] E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, **90**, 682 (1968), and references therein.

[37] F. R. Jensen and B. H. Beck, *ibid.*, **90**, 3251 (1968).

[38] J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

[39] (a) N. A. Nelson, J. H. Fassnacht, and J. V. Piper, *J. Amer. Chem. Soc.*, **81**, 5009 (1959); (b) the nitrile was prepared analogous to reactions reported by H. A. Bruson and T. W. Riener, *ibid.*, **65**, 23 (1943).

[40] A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, **82**, 5593 (1960).

[41] K. Conrow, *Org. Syn.*, **43**, 101 (1963).

[42] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957); K. Conrow, *ibid.*, **83**, 2343 (1961).

[43] H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

fluoroborate. The reaction mixture was stirred for 30 min and then refluxed briefly (10 min). Water (100 ml) was added and the aqueous layer was washed with two 25-ml portions of pentane. The combined pentane extracts were washed with water (2 × 20 ml) and dried ($MgSO_4$), and the solvent was removed on a rotary evaporator without external heating to give 2.11 g (71%) of a light red liquid. Gc analysis (98°; 67 ml/min) of this material showed three components which were collected and shown to be (in order of elution) **3** (30%), **4** (46%), and **2** (24%), as described in the text. A glc sample of **2** gave a satisfactory analysis. *Anal.* Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.97; H, 10.94. The ir spectra on the neat liquids showed: **2**, 3040, 2980 (s), 2940, 2900, 1480, 1390, 1360, 790, 770, 710 (s), 690 (s); **3**, 3055, 3045, 2995 (s), 2900, 1470 (s), 1395, 1385, 1365, 790 (s), 755 (s), 715 (s); **4**, 3050, 2980 (s), 2900, 1460 (s), 1390, 1360, 745 (s), 725 (s), 695 (s) cm^{-1}.

***tert*-Butyltropylium Fluoroborate.** This ion could not be prepared directly from 7-*tert*-butylcycloheptatriene by hydride exchange with triphenylmethyl fluoroborate. However if 7-*tert*-butylcyclohepatriene is heated at 170° for 4.5 hr, the resulting mixture of isomers, containing only 14% of the 7 isomer, does undergo hydride exchange.[44] Thus to 4.0 g (0.012 mol) of triphenylmethyl fluoroborate, in 20 ml of methylene chloride, was added 2.42 g (0.0163 mol) of the *tert*-butylcycloheptatriene isomer mixture. The solution was allowed to stand for 3.5 hr. The solvent was then evaporated and the solid residue was washed thoroughly with ether. Three recrystallizations from ethanol gave 2.55 g (90%) of white solid, mp 146.5–148.4. This material was used directly in the reaction below.

Reaction of *tert*-Butyltropylium Tetrafluoroborate with Methyllithium. To 4.8 ml of a 1.67 *M* ether solution of methyllithium (0.176 g, 8.01 mmol) further diluted with 20 ml of ether was added 1.50 g (6.42 mmol) of *tert*-butyltropylium fluoroborate. The reaction mixture was stirred for 15 min, and 100 ml of water was added. The ether layer was separated, dried ($MgSO_4$), and concentrated to give 0.87 g (84%) of crude product. This material was distilled to give 0.40 g of colorless liquid, bp 64° at 6.7 mm. Gc analysis (90°, 60 ml/min) showed three components which were collected and shown to be (in order of elution) the 2- (40%), 3- (42%), and 1- (18%) *tert*-butyl-7-methylcycloheptatriene isomers as described in the text. The ir spectrum of **6** showed: 3060, 3000 (s), 2910, 1525, 1460, 1390, 1370, 1260, 760, 705 (s) cm^{-1}.

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[44] This technique of using isomerized cycloheptatriene isomers to prepare substituted tropylium ion, discovered independently in this laboratory, has been used to prepare phenyltropylium fluoroborate[45] although this salt can be prepared directly from 7-phenylcycloheptatriene.

[45] K. Shen, W. E. McEwen, and A. P. Wolf, *Tetrahedron Lett.*, 827 (1969).

Valence Bond Isomers of Aromatic Systems. Bicyclo[2.2.0]hexa-2,5-dienes (Dewar Benzenes)[1]

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Abstract: The first synthesis and identification of the benzene valence bond isomers, Dewar benzenes, are described in detail. In one case 1,2,4-tri-*tert*-butylbenzene is converted by ultraviolet irradiation into 1,2,5-tri-*tert*-butylbicyclo[2.2.0]hexa-2,5-diene (**28**). In the second, parent bicyclo[2.2.0]hexa-2,5-diene (**4**) was obtained by oxidative decarboxylation of bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic acid, the anhydride of which is prepared by photolysis of 1,2-dihydrophthalic acid anhydride. Related chemistry is described, including: proof of structure of Dewar benzenes **4** and **28**; the ultraviolet-induced conversion of *o*-di-*tert*-butylbenzene to *m*-di-*tert*-butylbenzene and interconversion of *m*- and *p*-di-*tert*-butylbenzenes; photolysis of [2.2]paracyclophane and certain substituted 1,2-dihydrophthalic anhydrides. Theoretical aspects of the photochemical formation and properties of Dewar benzenes are discussed.

Firmly based within the broad and intricate framework of organic chemistry, the benzene ring has served as a stable platform upon which have been performed during the last century a great variety of interesting and important chemical exercises. Until recent years, no serious question about the prevailing integrity of this structural unit had been raised, although it is of historical interest that, as concepts, certain valence bond isomer representations had appeared in the earlier literature. For reasons stated below, we started during the early 1960's to give consideration to the prospect of preparing and isolating bicyclo[2.2.0]hexadienes (Dewar benzenes), and in the ensuing few years, two examples of such benzene valence bond isomers resulted from our laboratory efforts.[1] In related programs, there were synthesized or detected valence bond isomers of other aromatic systems: *cis*- and *trans*-9,10-dihydronaphthalenes,[3,4] Dewar tropylium ion,[5] and Δ^2-cyclopropenyl ketones[6], the aromatic counterparts being 1,3,5,7,9-cyclodecapentaene, tropylium ion, and substituted furans, respectively. In addition to biscyclopropenyls,[7]

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[1] The synthesis of bicyclo[2.2.0]hexadienes was first announced in two Communications to the Editor (E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962); **85**, 3297 (1963)) and was presented as part of a lecture, "Valence Bond Isomers of Aromatic Systems," by E. E. van Tamelen: Abstracts, American Chemical Society 18th National Organic Symposium, Columbus, Ohio, June 1963.

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[3] E. E. van Tamalene and B. Pappas, *J. Amer. Chem. Soc.*, **85**, 3296 (1963).

[4] E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967).

[5] E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *ibid.*, **90**, 1372 (1968).

[6] E. E. van Tamelen and T. H. Whitesides, *ibid.*, **90**, 3894 (1968).

[7] Bistriphenylcyclopropenyl, the first formal benzene valence bond isomer to have been observed, was prepared by R. Breslow and P. Gal, *ibid.*, **81**, 4747 (1959). Since the appearance of this and our original work, a variety of other benzene valence bond isomers have been reported. No specific attempt will be made in this paper to refer to these cases, although a partial list appears in ref 11.